Supporting Information

Three-component synthesis of 1,4-benzothiazines via iodide-catalyzed aerobic C-H sulfuration with elemental sulfur

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General information

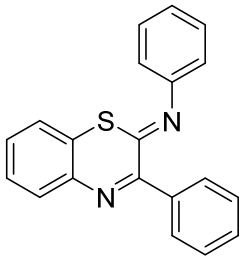
All reactions were carried out under oxygen atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded with the Thermo Scientific LTQ Orbitrap XL mass spectrometer (ESI). The structures of compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were obtained from commercial suppliers and used without further purification. The molecular weight of S is determined to be 32 g/mol unless otherwise noted.

General procedure for the synthesis of 1,4-benzothiazine

Acetophenone (**1a**, 47μL, 0.4 mmol), aniline (**2a**, 37μL, 0.4 mmol), S (25.6 mg, 0.8 mmol), KI (50 mol%), DMSO (4 equiv) and chlorobenzene (PhCl, 2.2 mL) were added successfully to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 150 °C for 16 h under oxygen atmosphere. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and filtered through a short column of silica gel with additional ethyl acetate (15 mL), the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOA: 200/1) to yield the desired product **3a** as yellow solid (44.6 mg, 71%), mp: 142-143 ^{o}C.

Characterization data of products

(Z)-N,3-Diphenyl-2H-benzo[b][1,4]thiazin-2-imine (3a)

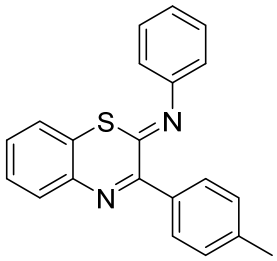


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3a** (44.6 mg, 71%) as yellow solid.

mp: 142-143 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.00 (m, 2H), 7.75 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 – 7.40 (m, 5H), 7.36 – 7.18 (m, 3H), 7.12 (dd, J = 7.8, 1.5 Hz, 1H), 7.01 – 6.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.0, 149.6, 137.8, 137.6, 131.8, 130.0, 129.8, 129.6, 128.6, 127.9, 127.1, 125.4, 125.2, 124.4, 118.8; HRMS (ESI) m/z calcd for $C_{20}H_{15}N_2S^+$ $(M+H)^+$ 315.0951, found 315.0954.

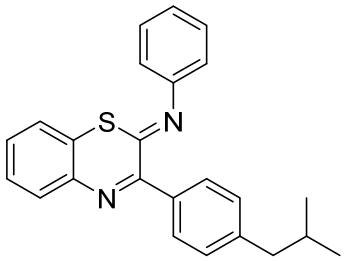
(Z)-N-Phenyl-3-(p-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (3b)



The reaction was conducted with 1-(p-tolyl)ethan-1-one (**1b**, 54 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3b** (33.5 mg, 51%) as orange solid. mp: 155-156 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.9 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.33 – 7.28 (m, 1H), 7.27 – 7.17 (m, 4H), 7.09 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.1, 149.7, 140.3, 137.9, 134.8, 131.7, 129.8, 129.6, 128.6, 128.3, 127.0, 125.3, 125.1, 124.3, 118.8, 21.4; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2S^+$ $(M+H)^+$ 329.1107, found 329.1112.

(Z)-3-(4-Isobutylphenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3c)

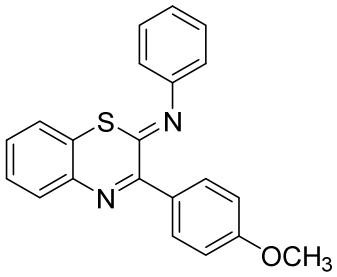


The reaction was conducted with 1-(4-isobutylphenyl)ethan-1-one (**1c**, 76 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3c** (43.7

mg, 59%) as yellow solid. mp: 94-95 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.11 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 7.7 Hz, 2H), 2.52 (d, J = 7.2 Hz, 2H), 1.96 – 1.86 (m, 1H), 0.93 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.1, 149.7, 144.2, 137.9, 135.0, 131.7, 129.7, 129.6, 128.7, 128.3, 127.0, 125.3, 125.2, 124.4, 118.8, 45.4, 30.1, 22.4; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2S^+$ $(M+H)^+$ 371.1577, found 371.1578.

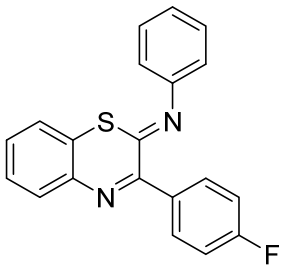
(Z)-3-(4-Methoxyphenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3d)



The reaction was conducted with 1-(4-methoxyphenyl)ethan-1-one (**1d**, 60 mg, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) to yield the desired product **3d** (31.0 mg, 45%) as yellow solid. mp: 127-128 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 7.9 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.18 (m, 2H), 7.13 – 7.07 (m, 1H), 7.01 – 6.88 (m, 4H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 154.8, 150.2, 149.6, 138.0, 131.6, 131.5, 129.9, 129.6, 128.1, 127.0, 125.3, 125.1, 124.2, 118.8, 113.3, 55.3; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2OS^+$ $(M+H)^+$ 345.1056, found 345.1057.

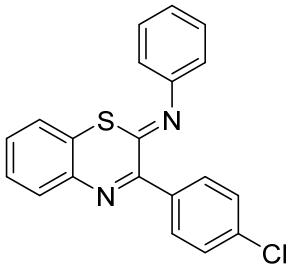
(Z)-3-(4-Fluorophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3e)



The reaction was conducted with 1-(4-fluorophenyl)ethan-1-one (**1e**, 49 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3e** (42.5 mg, 64%) as yellow solid. mp: 117-118 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.03 (m, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.36 – 7.30 (m, 1H), 7.29 – 7.19 (m, 2H), 7.17 – 7.06 (m, 3H), 6.92 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.7, 154.5, 150.1, 149.5, 137.7, 133.5 (d, J = 3.4 Hz), 132.0 (d, J = 8.4 Hz), 131.8, 129.7, 128.7, 127.2, 125.3 (d, J = 4.9 Hz), 124.4, 118.7, 114.9 (d, J = 21.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5; HRMS (ESI) m/z calcd for $C_{20}H_{14}FN_2S^+$ $(M+H)^+$ 333.0856, found 333.0858.

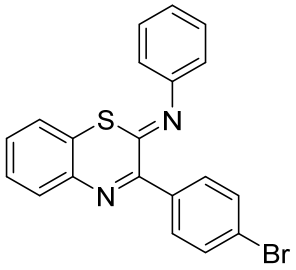
(Z)-3-(4-Chlorophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3f)



The reaction was conducted with 1-(4-chlorophenyl)ethan-1-one (**1f**, 54 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3f** (49.4 mg, 71%) as yellow solid. mp: 104-105 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.73 (dd, J = 7.9, 1.5 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 7.29 – 7.19 (m, 2H), 7.15 – 7.09 (m, 1H), 6.91 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 149.9, 149.4, 137.6, 136.2, 135.9, 131.9, 131.3, 129.7, 128.8, 128.1, 127.2, 125.4(1), 125.3 (7), 124.5, 118.8; HRMS (ESI) m/z calcd for $C_{20}H_{14}ClN_2S^+$ $(M+H)^+$ 349.0561, found 349.0560.

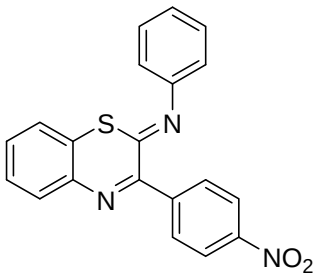
(Z)-3-(4-Bromophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3g)



The reaction was conducted with 1-(4-bromophenyl)ethan-1-one (**1g**, 82 mg, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3g** (50.9 mg, 65%) as yellow solid. mp: 116-117 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.30 – 7.19 (m, 2H), 7.12 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 149.9, 149.4, 137.6, 136.4, 131.9, 131.5, 131.1, 129.7, 128.8, 127.2, 125.4(0), 125.3 (6), 124.6, 124.4, 118.8; HRMS (ESI) m/z calcd for $C_{20}H_{14}BrN_2S^+$ $(M+H)^+$ 393.0056, found 393.0057.

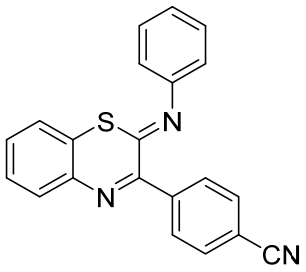
(Z)-3-(4-Nitrophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3h)



The reaction was conducted with 1-(4-nitrophenyl)ethan-1-one (**1h**, 68 mg, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) to yield the desired product **3h** (41.7 mg, 58%) as orange solid. mp: 192-193 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.16 (m, 4H), 7.81 – 7.72 (m, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.31 (m, 2H), 7.25 (d, J = 10.6 Hz, 1H), 7.19 – 7.13 (m, 1H), 6.93 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 149.6, 149.0, 148.4, 143.8, 137.4, 132.3, 130.9, 129.8, 129.6, 127.4, 125.6, 125.6, 124.7, 123.0, 118.7; HRMS (ESI) m/z calcd for $C_{20}H_{14}N_3O_2S^+$ $(M+H)^+$ 360.0801, found 360.0797.

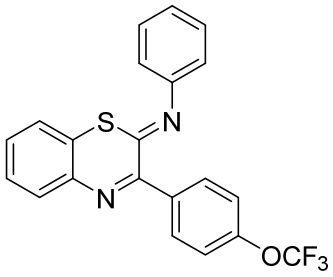
(Z)-4-(2-(Phenylimino)-2H-benzo[b][1,4]thiazin-3-yl)benzonitrile (3i)



The reaction was conducted with 4-acetylbenzonitrile (**1i**, 59 mg, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) to yield the desired product **3i** (42.7 mg, 63%) as yellow solid. mp: 147-148 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 2H), 7.77 – 7.70 (m, 3H), 7.48 – 7.42 (m, 2H), 7.38 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 7.14 (d, J = 7.7 Hz, 1H), 6.91 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 149.6, 149.1, 142.0, 137.4, 132.2, 131.6, 130.5, 129.7, 129.4, 127.4, 125.6, 125.5, 124.6, 118.7, 113.2; HRMS (ESI) m/z calcd for $C_{21}H_{14}N_3S^+$ $(M+H)^+$ 340.0902(9), found 340.0903(3).

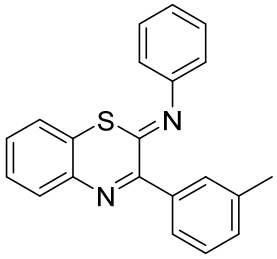
(Z)-N-Phenyl-3-(4-(trifluoromethoxy)phenyl)-2H-benzo[b][1,4]thiazin-2-imine (3j)



The reaction was conducted with 1-(4-(trifluoromethoxy)phenyl)ethan-1-one (**1j**, 65 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3j** (56.5 mg, 71%) as yellow solid. mp: 103-104 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 – 7.19 (m, 5H), 7.15 – 7.10 (m, 1H), 6.97 – 6.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.4, 150.0, 149.4, 137.6, 136.0, 131.9, 131.6, 129.7, 128.9, 127.2, 125.4, 124.5, 120.1, 118.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5; HRMS (ESI) m/z calcd for $C_{21}H_{14}F_3N_2OS^+$ $(M+H)^+$ 399.0773, found 399.0775.

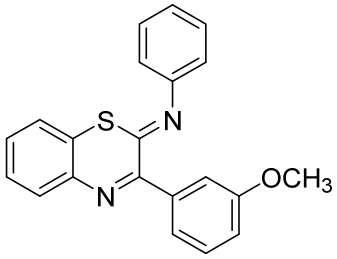
(Z)-N-Phenyl-3-(m-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (3k)



The reaction was conducted with 1-(m-tolyl)ethan-1-one (**1k**, 54 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3k** (39.4 mg, 60%) as orange solid. mp: 140-141 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.75 (dd, J = 7.9, 1.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.18 (m, 3H), 7.11 (d, J = 7.5 Hz, 1H), 6.97 – 6.88 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.1, 149.7, 137.8, 137.6, 137.6, 131.8, 130.9, 130.2, 129.6, 128.5, 127.7, 127.1, 127.0, 125.4, 125.2, 124.4, 118.8, 21.5; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2S^+$ $(M+H)^+$ 329.1107, found 329.1111.

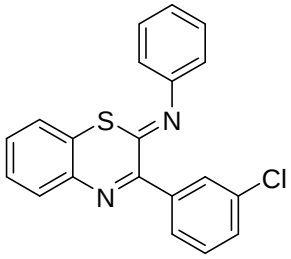
(Z)-3-(3-Methoxyphenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3l)



The reaction was conducted with 1-(3-methoxyphenyl)ethan-1-one (**1l**, 56 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) to yield the desired product **3l** (37.9 mg, 55%) as orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.9, 1.5 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.31 (m, 2H), 7.26 – 7.18 (m, 2H), 7.12 (dd, J = 7.8, 1.5 Hz, 1H), 7.01 (dd, J = 8.2, 2.4 Hz, 1H), 6.95 – 6.89 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 155.6, 150.0, 149.6, 138.9, 137.8, 131.8, 129.6, 128.9, 128.6, 127.1, 125.4, 125.2, 124.5, 122.4, 118.8, 115.9, 115.3, 55.3; HRMS (ESI) m/z calcd. for $C_{21}H_{17}N_2OS^+$ $(M+H)^+$ 345.1056, found 345.1050.

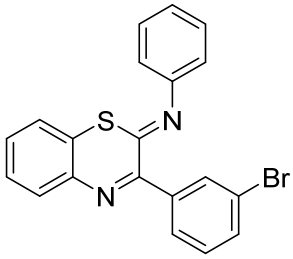
(Z)-3-(3-Chlorophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3m)



The reaction was conducted with 1-(3-chlorophenyl)ethan-1-one (**1m**, 53 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3m** (49.4 mg, 71%) as orange solid. mp: 92-93 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 1H), 7.98 – 7.93 (m, 1H), 7.75 (dd, 1H), 7.48 – 7.41 (m, 3H), 7.40 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 6.98 – 6.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.7, 149.4, 139.3, 137.6, 133.9, 132.0, 130.0, 129.9, 129.7, 129.0(3), 128.9 (7), 128.1, 127.2, 125.4 (3), 125.3 (8), 124.6, 118.8; HRMS (ESI) m/z calcd for $C_{20}H_{14}ClN_2S^+$ $(M+H)^+$ 349.0561, found 349.0564.

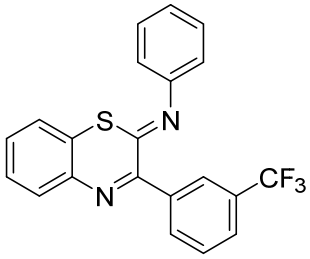
(Z)-3-(3-Bromophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3n)



The reaction was conducted with 1-(3-bromophenyl)ethan-1-one (**1n**, 54 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3n** (43.1 mg, 55%) as yellow solid. mp: 99-100 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 1H), 8.01 – 7.98 (m, 1H), 7.75 (dd, J = 7.8, 1.5 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.47 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 7.24 – 7.19 (m, 1H), 7.13 (dd, J = 7.8, 1.5 Hz, 1H), 6.95 – 6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 149.7, 149.4, 139.6, 137.5, 132.9, 132.7, 132.0, 129.7, 129.3, 129.0, 128.6, 127.2, 125.4, 125.4, 124.5, 122.0, 118.8; HRMS (ESI) m/z calcd for $C_{20}H_{14}BrN_2S^+$ $(M+H)^+$ 393.0056, found 393.0060.

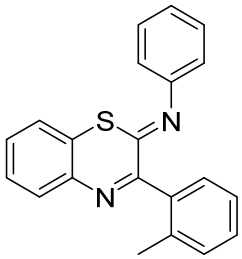
(Z)-N-Phenyl-3-(3-(trifluoromethyl)phenyl)-2H-benzo[b][1,4]thiazin-2-imine (3o)



The reaction was conducted with 1-(3-(trifluoromethyl)phenyl)ethan-1-one (**1o**, 62 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3o** (48.9 mg, 64%) as yellow solid. mp: 127-128 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.36 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 149.7, 149.3, 138.3, 137.5, 133.2, 132.1, 130.4 (q, *J* = 31.8 Hz), 129.7, 129.1, 128.2, 127.3, 126.9 (q, *J* = 7.8 Hz), 126.5 (q, *J* = 7.5 Hz), 125.5, 125.4, 124.6, 124.0 (q, *J* = 272 Hz), 118.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; HRMS (ESI) m/z calcd for $C_{21}H_{14}F_3N_2S^+$ $(M+H)^+$ 383.0824, found 383.0823.

(Z)-N-Phenyl-3-(o-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (3p)

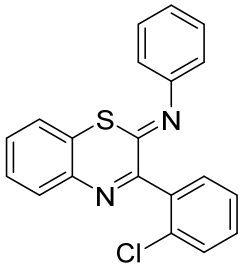


The reaction was conducted with 1-(o-tolyl)ethan-1-one (**1p**, 53 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) to yield the desired product **3p** (29.5 mg, 45%) as orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.42 – 7.25 (m, 7H), 7.19 – 7.13 (m, 2H), 6.89 – 6.80 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.5, 150.0, 138.6, 137.5, 135.8, 132.0, 130.3, 129.6, 129.0, 128.9, 128.8, 127.2, 125.8, 125.6,

125.1, 124.4, 118.5, 20.2; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2S^+$ $(M+H)^+$ 329.1107, found 329.1109.

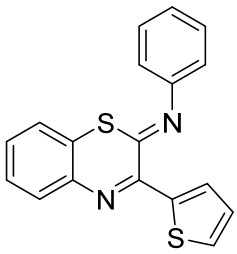
(Z)-3-(2-Chlorophenyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3q)



The reaction was conducted with 1-(2-chlorophenyl)ethan-1-one (**1q**, 53 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3q** (29.3 mg, 42%) as orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.46 – 7.24 (m, 7H), 7.20 – 7.13 (m, 2H), 6.88 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 149.8, 149.7, 138.3, 137.6, 132.5, 132.1, 130.5, 130.1, 129.6, 129.5, 129.1, 127.2, 127.0, 125.7, 125.2, 124.7, 118.6; HRMS (ESI) m/z calcd for $C_{20}H_{14}ClN_2S^+$ $(M+H)^+$ 349.0561, found 349.0563.

(Z)-N-Phenyl-3-(thiophen-2-yl)-2H-benzo[b][1,4]thiazin-2-imine (3r)

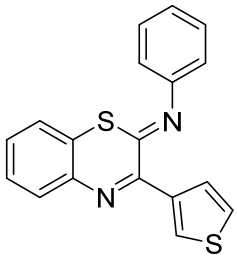


The reaction was conducted with 1-(thiophen-2-yl)ethan-1-one (**1r**, 44 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3r** (14.8 mg, 23%) as yellow solid. mp: 165-166 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 3.8 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.37 – 7.31 (m, 1H), 7.26 – 7.22 (m, 2H), 7.16 – 7.08 (m, 2H), 7.01 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.5, 147.9, 140.4, 137.5, 132.7, 132.3, 131.5,

129.7, 128.1, 127.4, 127.1, 125.3, 125.2, 123.6, 119.0; HRMS (ESI) m/z calcd for $C_{18}H_{13}N_2S_2^+$ $(M+H)^+$ 321.0515, found 321.0518.

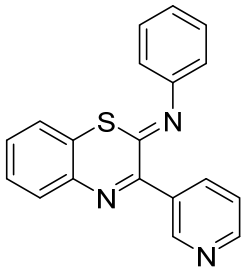
(Z)-N-Phenyl-3-(thiophen-3-yl)-2H-benzo[b][1,4]thiazin-2-imine (3s)



The reaction was conducted with 1-(thiophen-3-yl)ethan-1-one (**1s**, 52 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3s** (15.4 mg, 24%) as yellow solid. mp: 146-147 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.54 (m, 1H), 8.05 – 7.99 (m, 1H), 7.75 – 7.68 (m, 1H), 7.50 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.19 (m, 2H), 7.11 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.5, 149.0, 138.6, 137.7, 131.6, 131.1, 129.7, 129.5, 128.3, 127.0, 125.2, 125.2, 124.2, 124.1, 118.8; HRMS (ESI) m/z calcd for $C_{18}H_{13}N_2S_2^+$ $(M+H)^+$ 321.0515, found 321.0509.

(Z)-N-Phenyl-3-(pyridin-3-yl)-2H-benzo[b][1,4]thiazin-2-imine (3t)

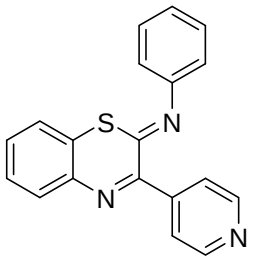


The reaction was conducted with 1-(pyridin-3-yl)ethan-1-one (**1t**, 44 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) to yield the desired product **3t** (20.8 mg, 33%) as yellow solid. mp: 107-108 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 9.37 – 9.20 (m, 1H), 8.66 (d, J = 4.6 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.19 (m, 4H), 7.13 (d, J = 7.8 Hz, 1H),

6.93 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.8, 150.4, 149.7, 149.2, 137.5, 137.3, 133.4, 132.1, 129.7, 129.1, 127.3, 125.5, 125.4, 124.4, 122.5, 118.7; HRMS (ESI) m/z calcd for $C_{19}H_{14}N_3S^+$ $(M+H)^+$ 316.0903, found 316.0905.

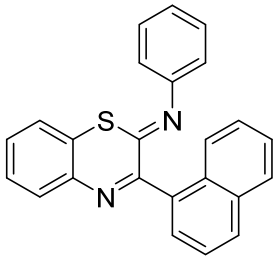
(Z)-N-Phenyl-3-(pyridin-4-yl)-2H-benzo[b][1,4]thiazin-2-imine (3u)



The reaction was conducted with 1-(pyridin-4-yl)ethan-1-one (**1u**, 45 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) to yield the desired product **3u** (18.9 mg, 30%) as yellow solid. mp: 48-49 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.8 Hz, 2H), 7.93 (d, J = 5.9 Hz, 2H), 7.77 (d, J = 7.8 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.40 – 7.29 (m, 2H), 7.27 – 7.20 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.6, 149.2, 149.1, 147.8, 145.1, 137.3, 132.3, 129.7, 129.5, 127.4, 125.6, 124.7, 123.9, 118.7; HRMS (ESI) m/z calcd for $C_{19}H_{14}N_3S^+$ $(M+H)^+$ 316.0903, found 316.0904.

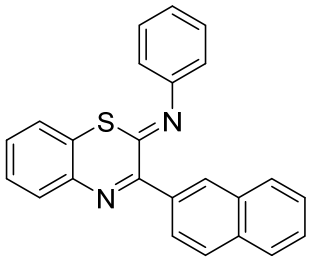
(Z)-3-(Naphthalen-1-yl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3v)



The reaction was conducted with 1-(naphthalen-1-yl)ethan-1-one (**1v**, 63 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3v** (16.0 mg, 22%) as yellow solid. mp: 154-155 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.4 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.80 – 7.72 (m, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.46 (m, 2H), 7.38 – 7.29 (m, 4H), 7.21 – 7.17 (m, 1H), 7.14 – 7.10 (m, 1H), 6.78 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 150.7, 149.8, 137.6, 136.4, 133.7, 132.1, 131.2, 129.5, 129.5, 129.0, 128.5, 127.2, 127.0, 126.2, 125.8, 125.7, 125.5, 125.2, 125.1, 124.5, 118.4; HRMS (ESI) m/z calcd for $C_{24}H_{17}N_2S^+$ $(M+H)^+$ 365.1107, found 365.1108.

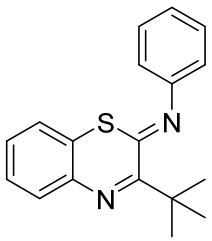
(Z)-3-(Naphthalen-2-yl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3w)



The reaction was conducted with 1-(naphthalen-2-yl)ethan-1-one (**1w**, 69 mg, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3w** (19.7 mg, 27%) as yellow solid. mp: 175-176 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.15 (dd, J = 8.6, 1.8 Hz, 1H), 7.95 – 7.78 (m, 4H), 7.55 – 7.42 (m, 4H), 7.38 – 7.32 (m, 1H), 7.29 – 7.19 (m, 2H), 7.17 – 7.11 (m, 1H), 7.01 – 6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.1, 149.6, 137.9, 135.0, 134.2, 132.9, 131.8, 130.1, 129.6, 129.0, 128.6, 127.6, 127.3, 127.1, 127.0, 126.8, 126.1, 125.4, 125.3, 124.4, 118.9; HRMS (ESI) m/z calcd for $C_{24}H_{17}N_2S^+$ $(M+H)^+$ 365.1107, found 365.1108.

(Z)-3-(tert-Butyl)-N-phenyl-2H-benzo[b][1,4]thiazin-2-imine (3x)

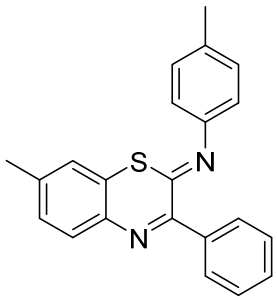


The reaction was conducted with 3,3-dimethylbutan-2-one (**1x**, 52 μL, 0.4 mmol), aniline (**2a**, 37 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **3x** (10.0 mg, 17%) as

yellow solid. mp: 116-117 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.30 – 7.23 (m, 1H), 7.23 – 7.11 (m, 2H), 7.05 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.7 Hz, 2H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.4, 147.5, 137.3, 131.2, 129.6, 127.7, 126.6, 125.0, 124.8, 124.4, 118.7, 41.8, 29.2; HRMS (ESI) m/z calcd for $C_{18}H_{19}N_2S^+$ $(M+H)^+$ 295.1264, found 295.1266.

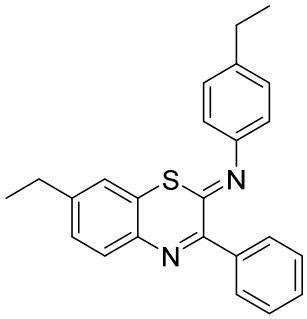
(Z)-7-Methyl-3-phenyl-N-(p-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (4a)



The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), p-toluidine (**2b**, 43 mg, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4a** (42.4 mg, 62%) as yellow solid. mp: 139-140 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.25 – 7.21 (m, 2H), 7.12 (dd, J = 8.2, 1.9 Hz, 1H), 6.91 (d, J = 1.9 Hz, 1H), 6.83 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 149.8, 147.1, 139.0, 137.9, 135.8, 134.8, 131.5, 130.1, 129.8, 129.8, 128.1, 127.8, 125.5, 124.3, 118.8, 21.3, 21.1; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2S^+$ $(M+H)^+$ 343.1264, found 343.1266.

(Z)-7-Ethyl-N-(4-ethylphenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4b)

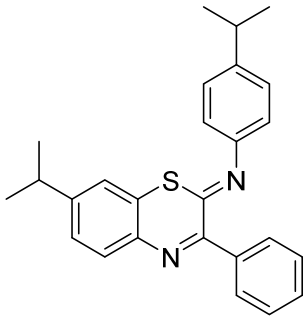


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 4-ethylaniline (**2c**, 51 μL,

0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4b** (45.9 mg, 62%) as orange solid. mp: 66-67 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.26 (d, J = 8.2 Hz, 2H), 7.14 (dd, J = 8.1, 1.9 Hz, 1H), 6.94 (d, J = 1.9 Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 2.71 – 2.59 (m, 4H), 1.29 – 1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 149.8, 147.2, 145.3, 141.3, 137.9, 136.0, 131.6, 129.8, 128.9, 127.8, 127.0, 124.4, 124.3, 118.9, 28.5, 28.4, 15.5, 15.1; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2S^+$ $(M+H)^+$ 371.1577, found 371.1580.

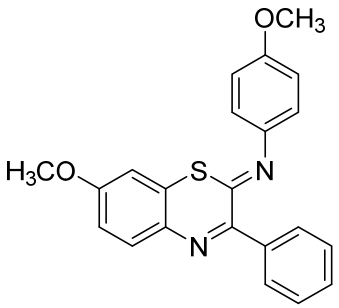
(Z)-7-Isopropyl-N-(4-isopropylphenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4c)



The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 4-isopropylaniline (**2d**, 59 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4c** (54.9 mg, 69%) as orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.28 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 8.3, 1.9 Hz, 1H), 6.98 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 8.1 Hz, 2H), 2.97 – 2.84 (m, 2H), 1.28 (d, J = 7.2 Hz, 6H), 1.22 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 149.8, 149.7, 147.3, 145.9, 137.9, 136.1, 131.6, 129.8, 129.8, 127.8, 127.4, 125.7, 124.3, 123.0, 118.9, 33.9, 33.7, 24.0, 23.7; HRMS (ESI) m/z calcd for $C_{26}H_{27}N_2S^+$ $(M+H)^+$ 399.1890, found 399.1893.

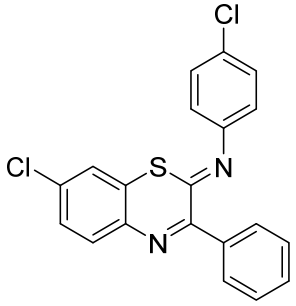
(Z)-7-Methoxy-N-(4-methoxyphenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4d)



The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 4-methoxyaniline (**2e**, 50 mg, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) to yield the desired product **4d** (29.9 mg, 40%) as yellow solid. mp: 131-132 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.45 – 7.40 (m, 3H), 6.99 – 6.94 (m, 2H), 6.93 – 6.85 (m, 3H), 6.63 (d, J = 2.7 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 157.3, 153.5, 149.2, 142.8, 138.1, 133.1, 132.1, 129.7, 129.6, 129.6, 127.8, 126.1, 120.6, 114.7, 113.9, 109.3, 55.6, 55.5; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2O_2S^+$ $(M+H)^+$ 375.1162, found 375.1167.

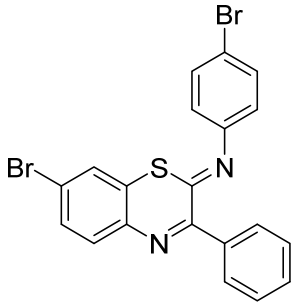
(Z)-7-Chloro-N-(4-chlorophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4e)



The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 4-chloroaniline (**2f**, 52 mg, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4e** (26.0 mg, 34%) as yellow solid. mp: 158-159 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.95 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.49 – 7.37 (m, 5H), 7.31 – 7.24 (m, 1H), 7.12 (s, 1H), 6.85 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 149.5, 147.7, 137.1, 136.3, 134.6, 132.8, 130.8, 130.3, 129.8, 129.8, 128.0, 127.6, 125.7, 124.9, 120.3; HRMS (ESI) m/z calcd for $C_{20}H_{13}Cl_2N_2S^+$ $(M+H)^+$ 383.0171, found 383.0173.

(Z)-7-Bromo-N-(4-bromophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4f)

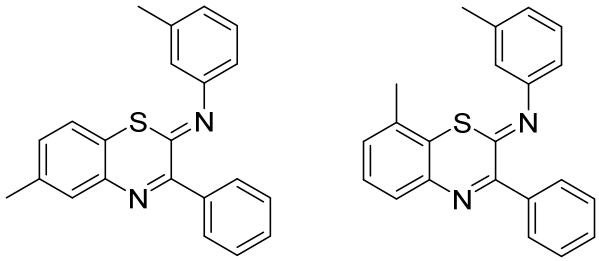


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 4-bromoaniline (**2g**, 70 mg, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4f** (32.9 mg, 35%) as yellow solid. mp: 154-155 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.95 (m, 2H), 7.64 – 7.52 (m, 3H), 7.51 – 7.40 (m, 3H), 7.31 – 7.24 (m, 2H), 6.85 – 6.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 149.5, 148.2, 137.1, 136.7, 133.0, 132.8, 130.6, 130.4, 129.8, 128.0, 127.8, 125.9, 122.6, 120.6, 118.5; HRMS (ESI) m/z calcd for $C_{20}H_{13}Br_2N_2S^+$ $(M+H)^+$ 470.9161, found 470.9163.

(Z)-6-Methyl-3-phenyl-N-(m-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (4g)

(Z)-8-Methyl-3-phenyl-N-(m-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (4g')

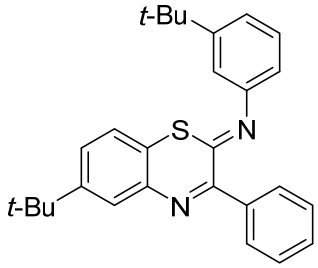


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), m-toluidine (**2h**, 44 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4g+4g'** (51.3 mg, 75%) as orange solid. mp: 79-80 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.64 – 7.56 (m, 1H), 7.47 – 7.40 (m, 3H), 7.35 – 6.97 (m, 4H), 6.85 – 6.64 (m, 2H), 2.38 (s, 5H), 2.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.3, 150.1, 149.7, 149.4, 139.6, 139.6, 137.8, 137.8, 137.7, 137.6, 137.0, 133.5, 132.1,

129.9, 129.8, 129.6, 129.4, 127.8, 126.3, 125.9, 125.8, 125.0, 123.8, 121.0, 119.4, 119.4, 115.6, 115.5, 21.5, 20.9, 18.8; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2S^+$ $(M+H)^+$ 343.1264, found 343.1265.

(Z)-6-(tert-Butyl)-N-(3-(tert-butyl)phenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4h)

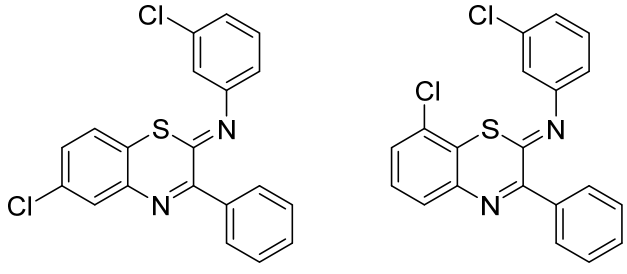


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 3-(tert-butyl)aniline (**2i**, 65 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4h** (61.3 mg, 72%) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.77 (d, J = 2.1 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.39 – 7.29 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 6.92 (s, 1H), 6.78 – 6.71 (m, 1H), 1.34 (d, J = 7.9 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 152.9, 150.6, 150.1, 149.5, 137.9, 137.5, 129.9, 129.8, 129.1, 128.7, 127.9, 126.1, 125.0, 122.1, 121.2, 116.2, 115.8, 34.9, 34.6, 31.3, 31.2; HRMS (ESI) m/z calcd for $C_{28}H_{31}N_2S^+$ $(M+H)^+$ 427.2203, found 427.2207.

(Z)-6-Chloro-N-(3-chlorophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4i)

(Z)-8-Chloro-N-(3-chlorophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4i')

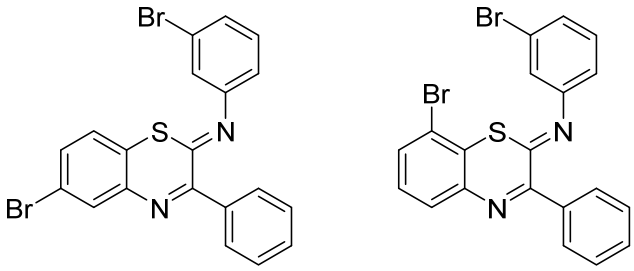


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 3-chloroaniline (**2j**, 43 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4i+4i'** (45.1 mg, 59%) as yellow solid. mp: 110-111 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 2H), 7.77 (d, J = 2.2 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.39 – 7.33 (m, 1H), 7.27 – 7.23 (m, 1H), 7.21 – 7.13 (m, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.97 – 6.87 (m, 1H), 6.84 – 6.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.4, 150.3, 138.5, 136.9, 135.3, 132.7, 131.4, 130.9, 130.5, 129.8, 128.7, 128.0, 126.2, 125.3, 122.4, 118.9, 116.9; HRMS (ESI) m/z calcd for $C_{20}H_{13}Cl_2N_2S^+$ $(M+H)^+$ 383.0171, found 383.0173.

(Z)-6-Bromo-N-(3-bromophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4j)

(Z)-8-Bromo-N-(3-bromophenyl)-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4j')

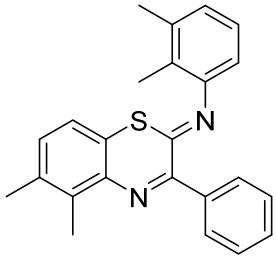


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 3-bromoaniline (**2k**, 44 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4j+4j'** (48.9 mg, 52%) as yellow solid. mp: 149-150 ^{o}C, 114-115 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.91 (m, 2H), 7.75 (dd, J = 8.0, 1.3 Hz, 1H), 7.58 – 7.42 (m, 4H), 7.35 – 7.23 (m, 3H), 7.11 (s, 1H), 6.93 – 6.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 151.6, 150.3, 139.5, 136.6, 132.3, 131.2, 131.0, 130.4, 129.9, 128.2, 128.0, 127.7, 125.6, 123.4, 121.8, 119.5, 117.1; HRMS (ESI) m/z calcd for $C_{20}H_{13}Br_2N_2S^+$ $(M+H)^+$ 470.9161, found 470.9164.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.93 (d, J = 2.1 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.35 – 7.28 (m, 2H), 7.08 (s, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.88 – 6.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.6, 150.3, 138.7, 136.9, 134.4, 131.5, 131.1, 130.5, 129.8, 128.2, 128.0, 126.4, 123.3, 123.1, 121.8, 120.2, 117.4; HRMS (ESI) m/z calcd for $C_{20}H_{13}Br_2N_2S^+$ $(M+H)^+$ 470.9161, found 470.9165.

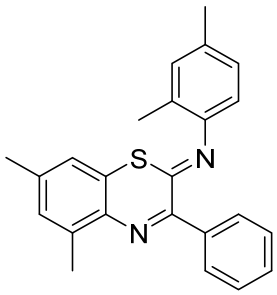
(Z)-N-(2,3-Dimethylphenyl)-5,6-dimethyl-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4k)



The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 2,3-dimethylaniline (**2l**, 50 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4k** (17.0 mg, 23%) as yellow solid. mp: 137-138 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.09 (m, 2H), 7.50 – 7.39 (m, 3H), 7.17 – 7.12 (m, 1H), 7.08 – 6.99 (m, 2H), 6.86 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 2.61 (s, 3H), 2.32 (d, J = 5.7 Hz, 6H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.9, 148.8, 138.6, 138.3, 138.2, 135.9, 135.7, 130.0, 129.8, 127.8, 126.5, 126.3, 125.7, 122.1, 115.3, 20.3 (4), 20.2 (7), 14.0, 13.8; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2S^+$ $(M+H)^+$ 371.1577, found 371.1579.

(Z)-N-(2,4-Dimethylphenyl)-5,7-dimethyl-3-phenyl-2H-benzo[b][1,4]thiazin-2-imine (4l)

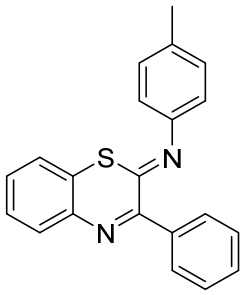


The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), 2,4-dimethylaniline (**2m**, 51 μL, 0.4 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) to yield the desired product **4l** (16.3 mg, 22%) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 6.6, 3.0 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.14 – 6.96 (m, 3H), 6.81 – 6.55 (m, 2H), 2.61 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 150.0, 146.3, 139.8, 138.7, 138.2, 134.5, 134.0, 131.8, 130.0, 129.7, 127.7,

127.4, 127.3, 124.9, 123.3, 117.4, 21.2, 21.0, 18.1, 17.7; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2S^+$ $(M+H)^+$ 371.1577, found 371.1580.

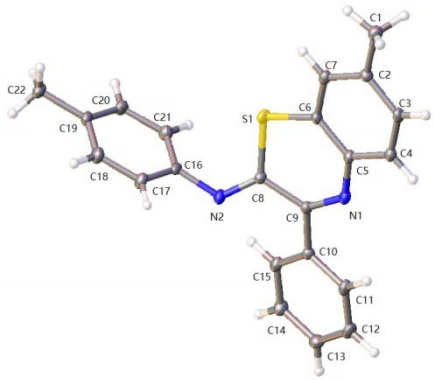
(Z)-3-phenyl-N-(p-tolyl)-2H-benzo[b][1,4]thiazin-2-imine (5a)



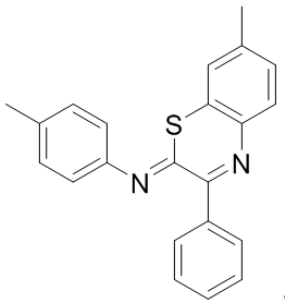
The reaction was conducted with acetophenone (**1a**, 47 μL, 0.4 mmol), *p*-toluidine (**2b**, 22 mg, 0.2 mmol), 2-aminobenzenethiol (21 μL, 0.2 mmol) and S (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) to yield the desired product **5a** (40.7 mg, 62%) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.78 – 7.73 (m, 1H), 7.48 – 7.41 (m, 3H), 7.35 – 7.31 (m, 1H), 7.29 – 7.22 (m, 3H), 7.13 (dd, J = 7.8, 1.5 Hz, 1H), 6.85 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 149.5, 147.0, 137.9, 137.7, 135.0, 131.7, 130.1, 130.0, 129.8, 128.5, 127.9, 127.0, 125.4, 124.5, 118.9, 21.1. HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2S^+$ $(M+H)^+$ 329.1104, found 329.1107.

Crystal date and structure refinement for 4a



CCDC:1946031



4a

Table 1 Crystal date and structure refinement for 4a

Crystal data	
Identification code	**4a**
Chemical formula	$C_{22}H_{18}N_2S$
M_r	342.44
Crystal system	Monoclinic,
Space group	$P2_1$
Temperature (K)	173
a, b, c (Å)	9.768 (2), 5.0226 (10), 17.193 (3)
β (°)	95.43 (3)
V (Å^3)	839.7 (3)
Z	2
F(000)	360
Density (calculated)	1.354 Mg/m^3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.46 × 0.07 × 0.03
Theta range for date collection	2.5 to 27.5^o
Data collection	
Diffractometer	Saturn724+ CCD
Absorption correction	Multi-scan *CrystalClear* (Rigaku Inc., 2007)
T_{min}, T_{max}	0.716, 1.000
No of measured reflections	6116
No of independent reflections	3658
No of observed [$I > 2\sigma(I)$] reflections	3175
Rint	0.050

$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Index range	h = -12→12, k = -6→6, l = -22→22
Refinement	
Refinement method	Full-matrix least-squares on F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.070, 0.136, 1.13
No of reflections	3658
No of parameters	228
No of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, -0.32
Absolute structure	Flack x determined using 1022 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).
Absolute structure parameter	0.02 (9)

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	*y*	*z*	*U*iso*/*U*eq
S1	0.21314 (13)	0.6567 (3)	0.22140 (7)	0.0343 (3)
N1	0.4432 (4)	0.8013 (9)	0.3543 (2)	0.0274 (9)
N2	0.4087 (4)	0.8909 (9)	0.1469 (2)	0.0304 (10)
C1	0.0753 (5)	−0.0278 (11)	0.4280 (3)	0.0321 (12)
H1A	0.1282	−0.1826	0.4443	0.048*
H1B	0.0125	−0.0713	0.3835	0.048*
H1C	0.0246	0.0314	0.4700	0.048*
C2	0.1700 (5)	0.1891 (10)	0.4067 (3)	0.0266 (10)
C3	0.2809 (5)	0.2695 (10)	0.4591 (3)	0.0294 (11)
H3	0.2959	0.1858	0.5074	0.035*
C4	0.3684 (5)	0.4707 (11)	0.4403 (3)	0.0293 (11)
H4	0.4396	0.5232	0.4768	0.035*
C5	0.3520 (5)	0.5974 (9)	0.3673 (3)	0.0257 (11)
C6	0.2425 (5)	0.5160 (10)	0.3144 (3)	0.0266 (11)
C7	0.1532 (5)	0.3148 (11)	0.3342 (3)	0.0299 (11)
H7	0.0810	0.2636	0.2982	0.036*
C8	0.3679 (5)	0.8348 (10)	0.2137 (3)	0.0254 (10)
C9	0.4526 (5)	0.9136 (10)	0.2872 (3)	0.0243 (10)
C10	0.5601 (5)	1.1257 (11)	0.2847 (2)	0.0248 (10)
C11	0.6634 (5)	1.1404 (12)	0.3469 (2)	0.0305 (11)
H11	0.6634	1.0186	0.3876	0.037*
C12	0.7653 (5)	1.3320 (11)	0.3491 (3)	0.0340 (12)
H12	0.8319	1.3396	0.3914	0.041*
C13	0.7685 (6)	1.5134 (11)	0.2881 (3)	0.0325 (12)
H13	0.8380	1.6401	0.2886	0.039*
C14	0.6663 (5)	1.5013 (11)	0.2270 (3)	0.0322 (12)
H14	0.6666	1.6232	0.1863	0.039*
C15	0.5631 (5)	1.3107 (10)	0.2250 (3)	0.0309 (11)
H15	0.4953	1.3071	0.1833	0.037*
C16	0.3295 (5)	0.8121 (10)	0.0769 (3)	0.0261 (10)

C17	0.3812 (5)	0.6133 (11)	0.0319 (3)	0.0341 (12)
H17	0.4636	0.5291	0.0486	0.041*
C18	0.3087 (6)	0.5416 (12)	−0.0381 (3)	0.0370 (13)
H18	0.3440	0.4085	−0.0680	0.044*
C19	0.1859 (5)	0.6603 (13)	−0.0649 (2)	0.0323 (11)
C20	0.1373 (5)	0.8623 (12)	−0.0205 (3)	0.0362 (13)
H20	0.0560	0.9487	−0.0380	0.043*
C21	0.2083 (5)	0.9390 (11)	0.0501 (3)	0.0341 (12)
H21	0.1742	1.0757	0.0793	0.041*
C22	0.1075 (6)	0.5730 (12)	−0.1411 (3)	0.0395 (14)
H22	0.1705	0.5511	−0.1802	0.059*
H22	0.0404	0.7058	−0.1579	0.059*
H22	0.0620	0.4070	−0.1334	0.059*

Table 3 Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0302	0.0491	0.0222 (6)	−0.0073 (7)	−0.0053	0.0075 (6)
N1	0.029 (2)	0.033	0.0198	0.0009 (19)	−0.0012	−0.0036 (18)
N2	0.034 (2)	0.038	0.019 (2)	−0.007 (2)	−0.0006	−0.0013 (18)
C1	0.033 (3)	0.033	0.029 (3)	−0.001 (2)	0.001 (2)	0.001 (2)
C2	0.028 (2)	0.026	0.026 (2)	−0.001 (2)	0.0041	0.001 (2)
C3	0.032 (3)	0.037	0.018 (2)	0.003 (2)	0.001 (2)	0.003 (2)
C4	0.032 (3)	0.033	0.022 (2)	0.002 (2)	0.001 (2)	−0.003 (2)
C5	0.027 (2)	0.029	0.021 (2)	−0.002 (2)	0.0006	−0.0025 (19)
C6	0.029 (3)	0.033	0.018 (2)	0.001 (2)	0.0020	0.000 (2)
C7	0.028 (3)	0.038	0.023 (2)	0.004 (2)	−0.001 (2)	−0.002 (2)
C8	0.024 (2)	0.029	0.023 (2)	−0.001 (2)	0.0004	0.002 (2)
C9	0.023 (2)	0.028	0.022 (2)	0.001 (2)	0.0009	−0.0001 (19)
C10	0.022 (2)	0.028	0.023 (2)	0.003 (2)	0.0020	−0.001 (2)
C11	0.034 (3)	0.035	0.021 (2)	0.002 (3)	−0.0048	0.001 (2)
C12	0.029 (3)	0.044	0.027 (3)	0.007 (3)	−0.007 (2)	−0.001 (2)
C13	0.030 (3)	0.034	0.034 (3)	−0.005 (2)	0.003 (2)	−0.002 (2)
C14	0.037 (3)	0.029	0.029 (3)	−0.003 (2)	−0.001 (2)	0.002 (2)
C15	0.032 (3)	0.035	0.024 (2)	0.001 (2)	−0.003 (2)	−0.004 (2)
C16	0.027 (2)	0.033	0.018 (2)	−0.008 (2)	−0.0011	0.005 (2)
C17	0.037 (3)	0.037	0.027 (2)	0.001 (3)	−0.003 (2)	−0.006 (2)
C18	0.039 (3)	0.043	0.029 (3)	0.001 (3)	0.000 (2)	−0.009 (2)
C19	0.034 (3)	0.044	0.018 (2)	−0.006 (3)	−0.0005	0.000 (3)
C20	0.029 (3)	0.049	0.029 (3)	0.001 (3)	−0.004 (2)	0.001 (2)
C21	0.033 (3)	0.039	0.030 (3)	0.002 (3)	0.002 (2)	−0.005 (2)
C22	0.038 (3)	0.053	0.026 (3)	−0.010 (3)	−0.003 (2)	−0.001 (2)

Table 4 Geometric parameters (Å, º)

S1—C6	1.747 (5)
S1—C8	1.772 (5)
N1—C5	1.389 (6)
N1—C9	1.294 (6)
N2—C8	1.281 (6)
N2—C16	1.424 (6)
C1—H1A	0.9600
C1—H1B	0.9600
C1—H1C	0.9600
C1—C2	1.497 (7)
C2—C3	1.401 (6)
C2—C7	1.392 (6)
C3—H3	0.9300
C3—C4	1.381 (7)
C4—H4	0.9300
C4—C5	1.403 (6)
C5—C6	1.398 (6)
C6—C7	1.398 (7)
C7—H7	0.9300
C8—C9	1.498 (6)
C9—C10	1.500 (7)
C10—C11	1.400 (6)
C10—C15	1.387 (7)
C11—H11	0.9300
C11—C12	1.382 (7)
C12—H12	0.9300
C12—C13	1.391 (7)
C13—H13	0.9300
C13—C14	1.381 (7)
C14—H14	0.9300
C14—C15	1.388 (7)
C15—H15	0.9300
C16—C17	1.387 (7)
C16—C21	1.384 (7)
C17—H17	0.9300
C17—C18	1.385 (7)

C18—H18	0.9300
C18—C19	1.379 (7)
C19—C20	1.380 (8)
C19—C22	1.519 (6)
C20—H20	0.9300
C20—C21	1.395 (7)
C21—H21	0.9300
C22—H22A	0.9600
C22—H22B	0.9600
C22—H22C	0.9600

C6—S1—C8	101.9 (2)
C9—N1—C5	124.4 (4)
C8—N2—C16	120.4 (4)
H1A—C1—H1B	109.5
H1A—C1—H1C	109.5
H1B—C1—H1C	109.5
C2—C1—H1A	109.5
C2—C1—H1B	109.5
C2—C1—H1C	109.5
C3—C2—C1	120.7 (4)
C7—C2—C1	121.8 (4)
C7—C2—C3	117.6 (5)
C2—C3—H3	119.4
C4—C3—C2	121.2 (4)
C4—C3—H3	119.4
C3—C4—H4	119.3
C3—C4—C5	121.4 (5)
C5—C4—H4	119.3
N1—C5—C4	117.3 (4)
N1—C5—C6	125.0 (4)
C6—C5—C4	117.7 (4)

C5—C6—S1	121.8 (4)
C5—C6—C7	120.6 (4)
C7—C6—S1	117.6 (4)
C2—C7—C6	121.5 (5)
C2—C7—H7	119.3
C6—C7—H7	119.3
N2—C8—S1	121.2 (4)
N2—C8—C9	120.3 (4)
C9—C8—S1	118.5 (3)
N1—C9—C8	123.8 (4)
N1—C9—C10	116.4 (4)
C8—C9—C10	119.7 (4)
C11—C10—C9	118.1 (4)
C15—C10—C9	124.1 (4)
C15—C10—C11	117.7 (5)
C10—C11—H11	119.3
C12—C11—C10	121.5 (5)
C12—C11—H11	119.3
C11—C12—H12	119.9
C11—C12—C13	120.2 (5)
C13—C12—H12	119.9
C12—C13—H13	120.7
C14—C13—C12	118.6 (5)
C14—C13—H13	120.7
C13—C14—H14	119.3
C13—C14—C15	121.3 (5)
C15—C14—H14	119.3
C10—C15—C14	120.7 (4)
C10—C15—H15	119.7
C14—C15—H15	119.7
C17—C16—N2	118.3 (4)
C21—C16—N2	122.1 (5)

C21—C16—C17	119.4 (4)
C16—C17—H17	120.4
C18—C17—C16	119.3 (5)
C18—C17—H17	120.4
C17—C18—H18	118.8
C19—C18—C17	122.4 (5)
C19—C18—H18	118.8
C18—C19—C20	117.8 (4)
C18—C19—C22	121.0 (5)
C20—C19—C22	121.1 (5)
C19—C20—H20	119.5
C19—C20—C21	121.0 (5)
C21—C20—H20	119.5
C16—C21—C20	120.1 (5)
C16—C21—H21	119.9
C20—C21—H21	119.9
C19—C22—H22A	109.5
C19—C22—H22B	109.5
C19—C22—H22C	109.5
H22A—C22—H22B	109.5
H22A—C22—H22C	109.5
H22B—C22—H22C	109.5

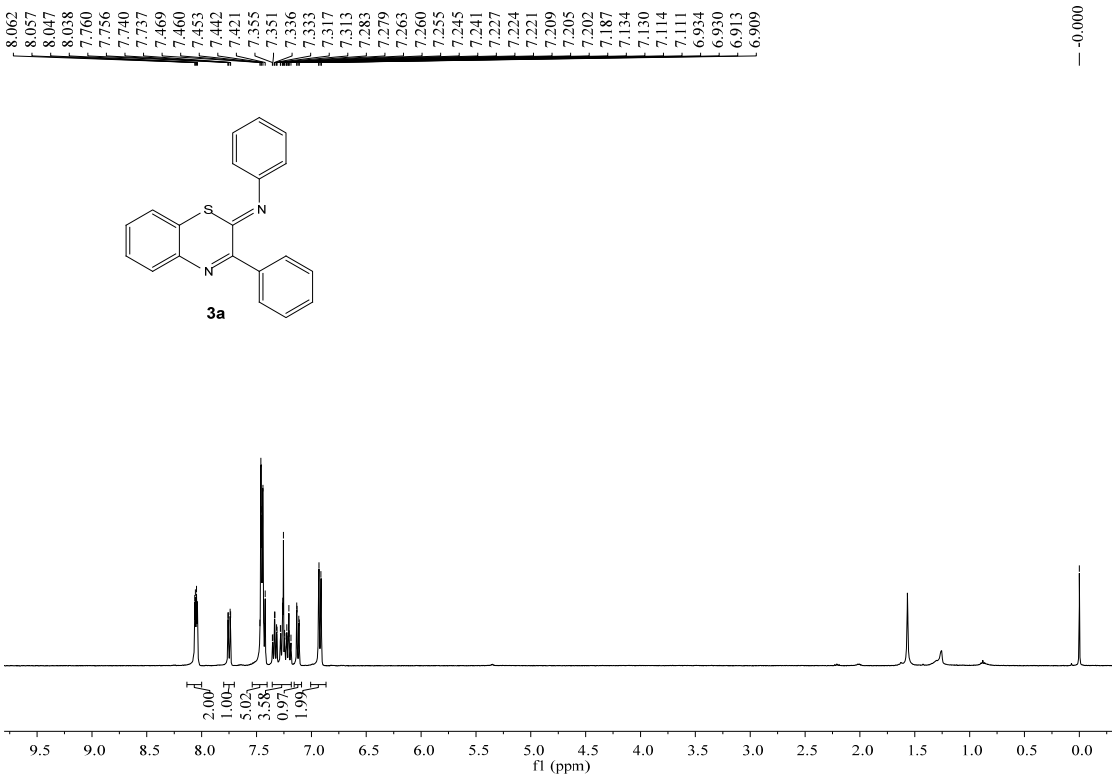
S1—C6—C7—C2	179.2 (4)
S1—C8—C9—N1	20.1 (7)
S1—C8—C9—C10	−162.8 (4)
N1—C5—C6—S1	3.2 (7)
N1—C5—C6—C7	−177.6 (5)
N1—C9—C10—C11	16.1 (7)
N1—C9—C10—C15	−163.2 (5)
N2—C8—C9—N1	−158.4 (5)
N2—C8—C9—C10	18.7 (7)

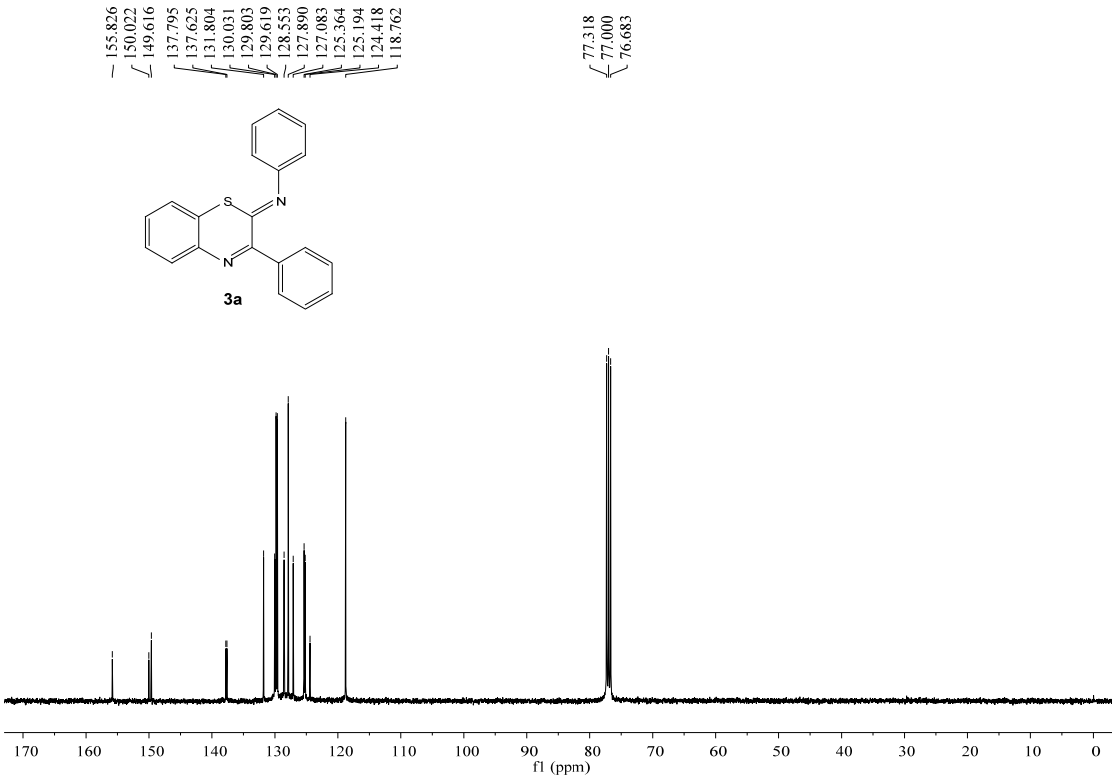
N2—C16—C7—C18	−177.3 (5)
N2—C16—C7—C20	177.3 (5)
C1—C2—C3—C4	−179.5 (5)
C1—C2—C7—C6	−179.6 (5)
C2—C3—C4—C5	−1.8 (8)
C3—C2—C7—C6	−0.7 (8)
C3—C4—C5—N1	178.7 (5)
C3—C4—C5—C6	1.0 (7)
C4—C5—C6—S1	−179.2 (4)
C4—C5—C6—C7	−0.1 (7)
C5—N1—C9—C8	−1.3 (8)
C5—N1—C9—C10	−178.5 (4)
C5—C6—C7—C2	0.0 (8)
C6—S1—C8—N2	155.9 (4)
C6—S1—C8—C9	−22.6 (4)
C7—C2—C3—C4	1.6 (8)
C8—S1—C6—C5	12.4 (5)
C8—S1—C6—C7	−166.7 (4)
C8—N2—C16—C17	−110.1 (6)
C8—N2—C16—C21	74.2 (7)
C8—C9—C10—C11	−161.3 (5)
C8—C9—C10—C15	19.4 (7)
C9—N1—C5—C4	170.8 (5)
C9—N1—C5—C6	−11.7 (8)
C9—C10—C11—C12	−179.4 (4)
C9—C10—C15—C14	180.0 (5)
C10—C11—C12—C13	−1.1 (8)
C11—C10—C15—C14	0.7 (7)
C11—C12—C13—C14	1.6 (8)
C12—C13—C14—C15	−0.9 (8)
C13—C14—C15—C10	−0.2 (8)
C15—C10—C11—C12	−0.1 (8)
C16—N2—C8—S1	0.4 (7)
C16—N2—C8—C9	178.9 (4)
C16—C17—C18—C19	−0.2 (8)
C17—C16—C21—C20	1.6 (8)
C17—C18—C19—C20	1.7 (9)
C17—C18—C19—C22	−178.7 (5)
C18—C19—C20—C21	−1.6 (8)

C19—C20—C21—C16	−0.1 (8)
C21—C16—C17—C18	−1.5 (8)
C22—C19—C20—C21	178.9 (5)

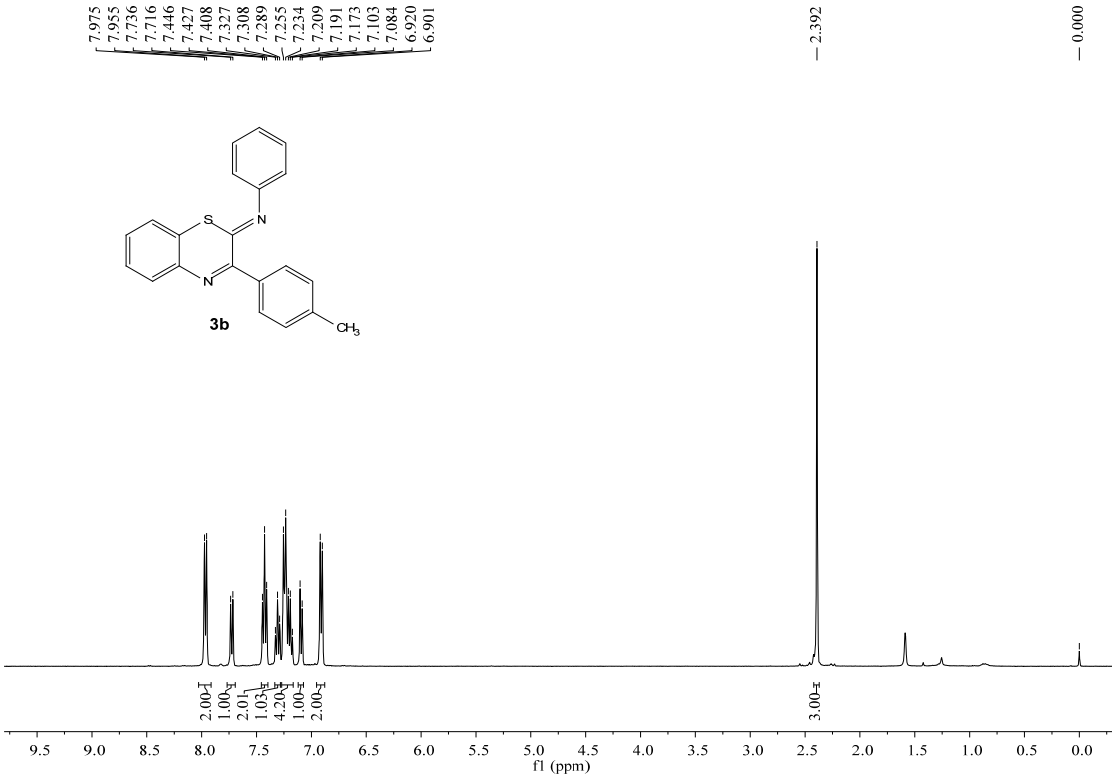
Copies of ^{1}H and ^{13}C NMR spectra of all products

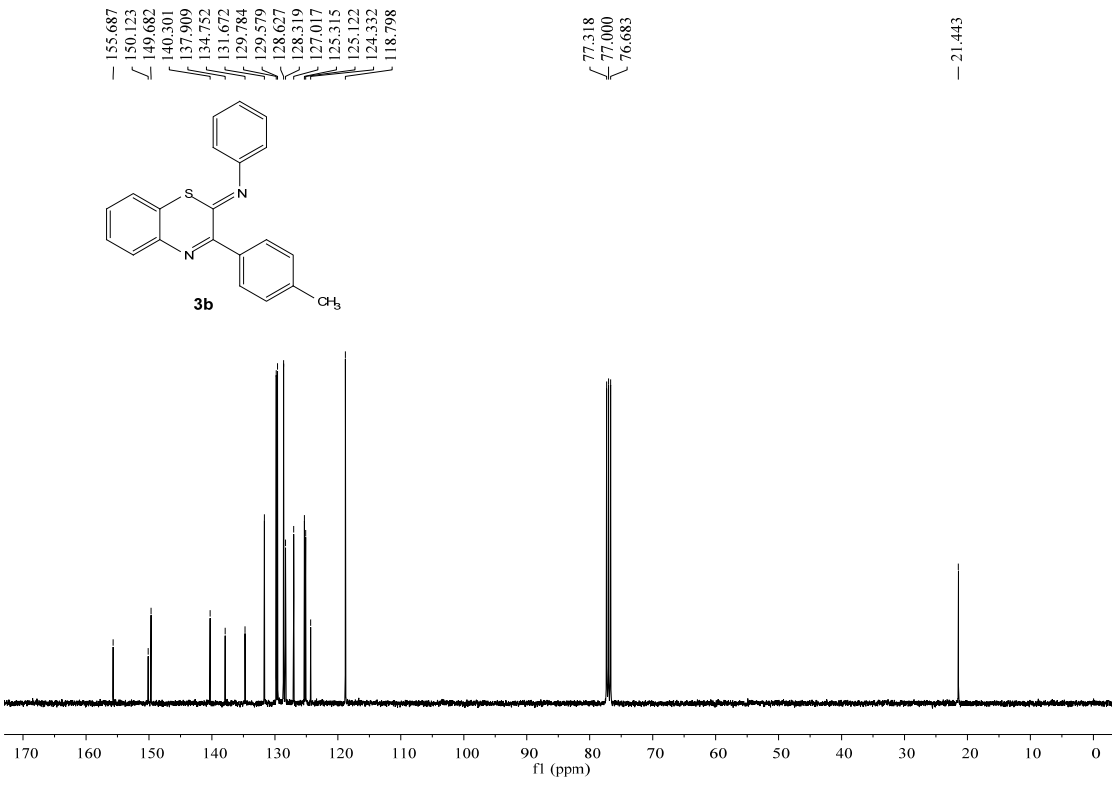
^{1}H and ^{13}C NMR spectra of 3a



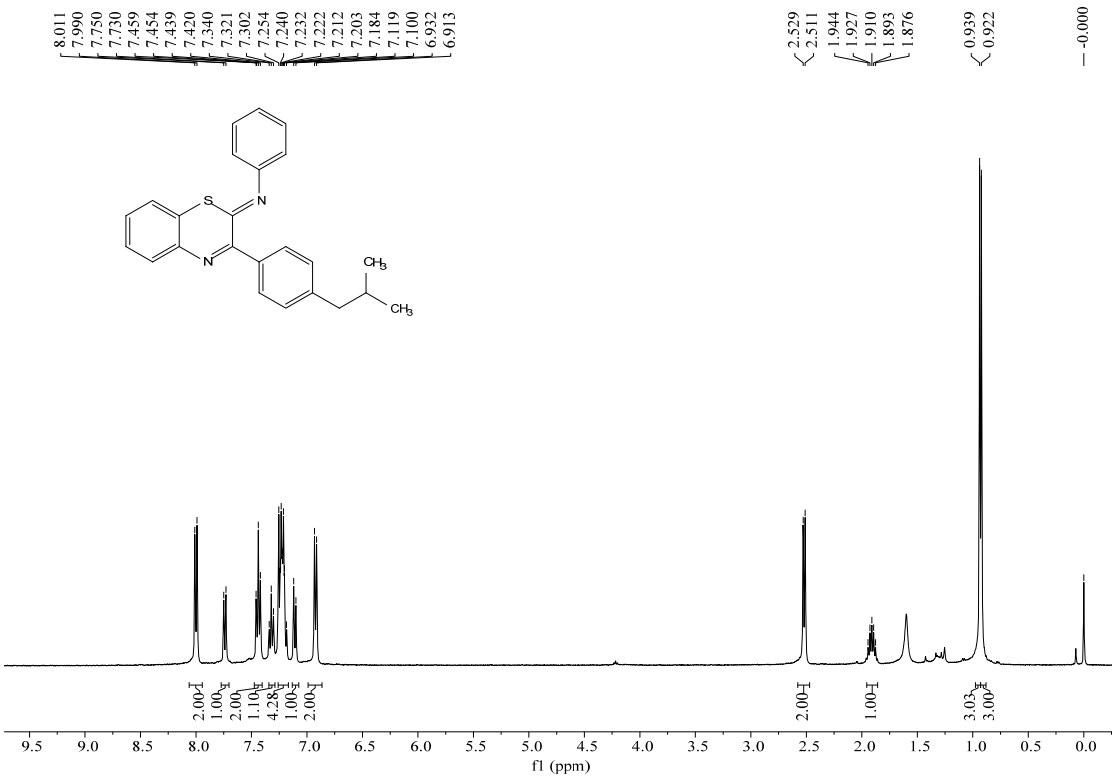


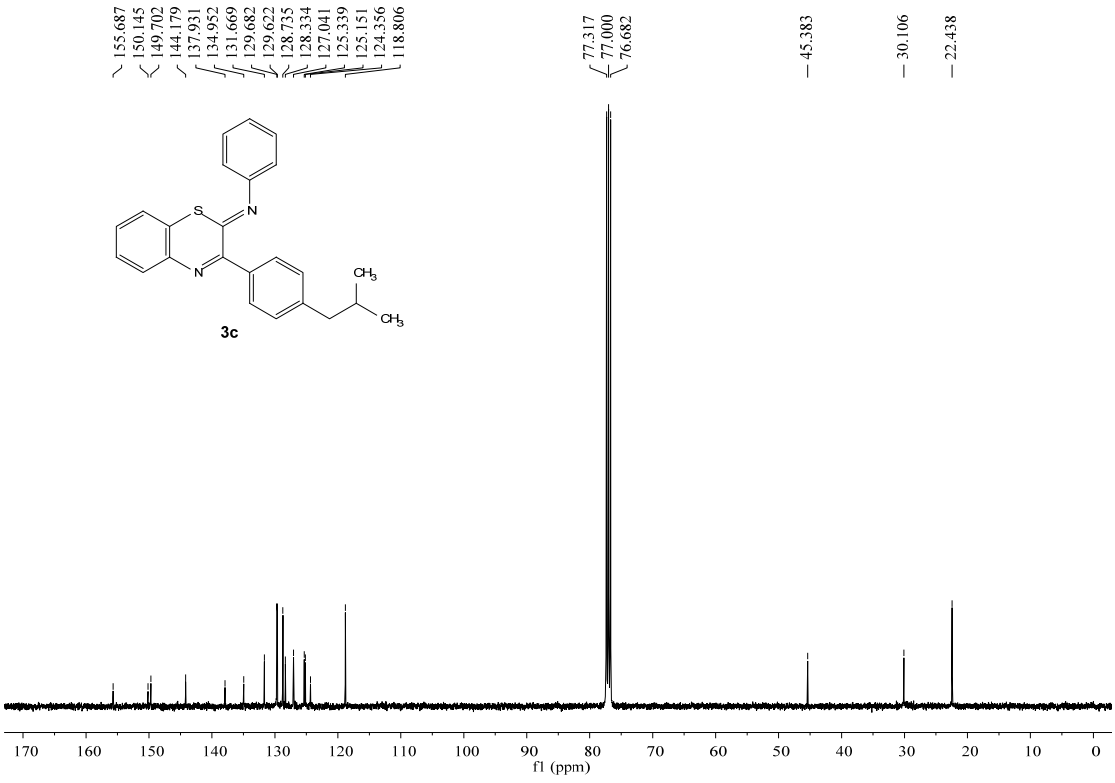
^{1}H and ^{13}C NMR spectra of 3b



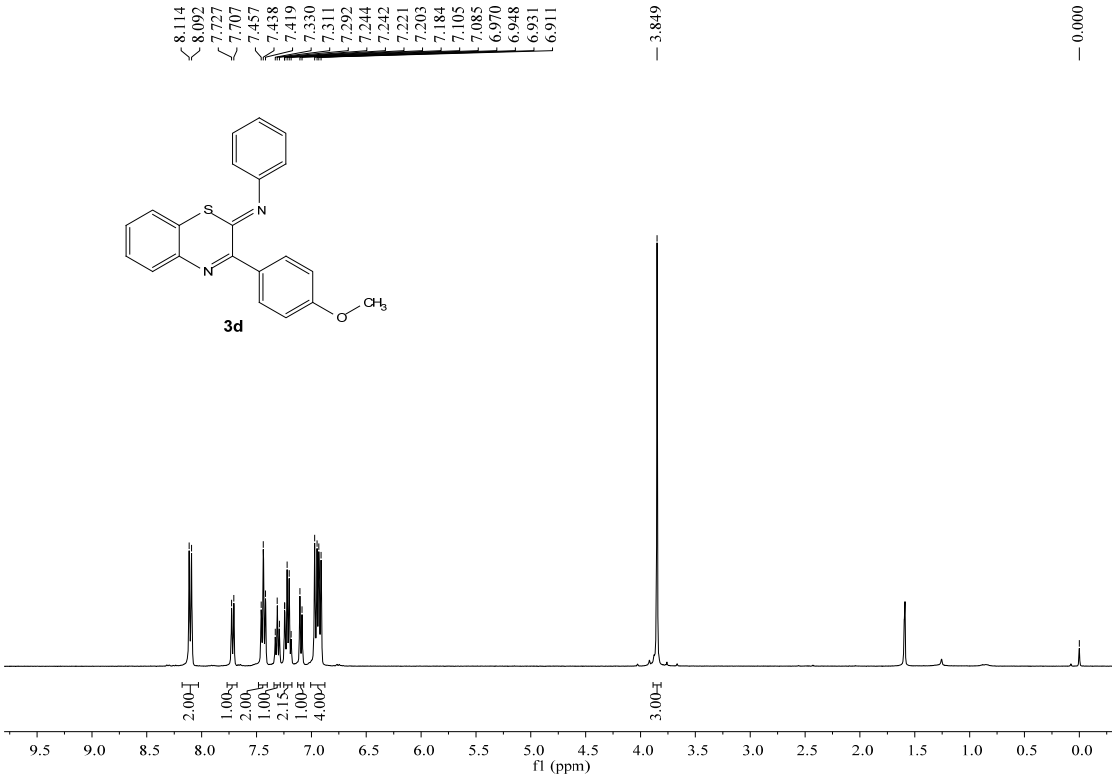


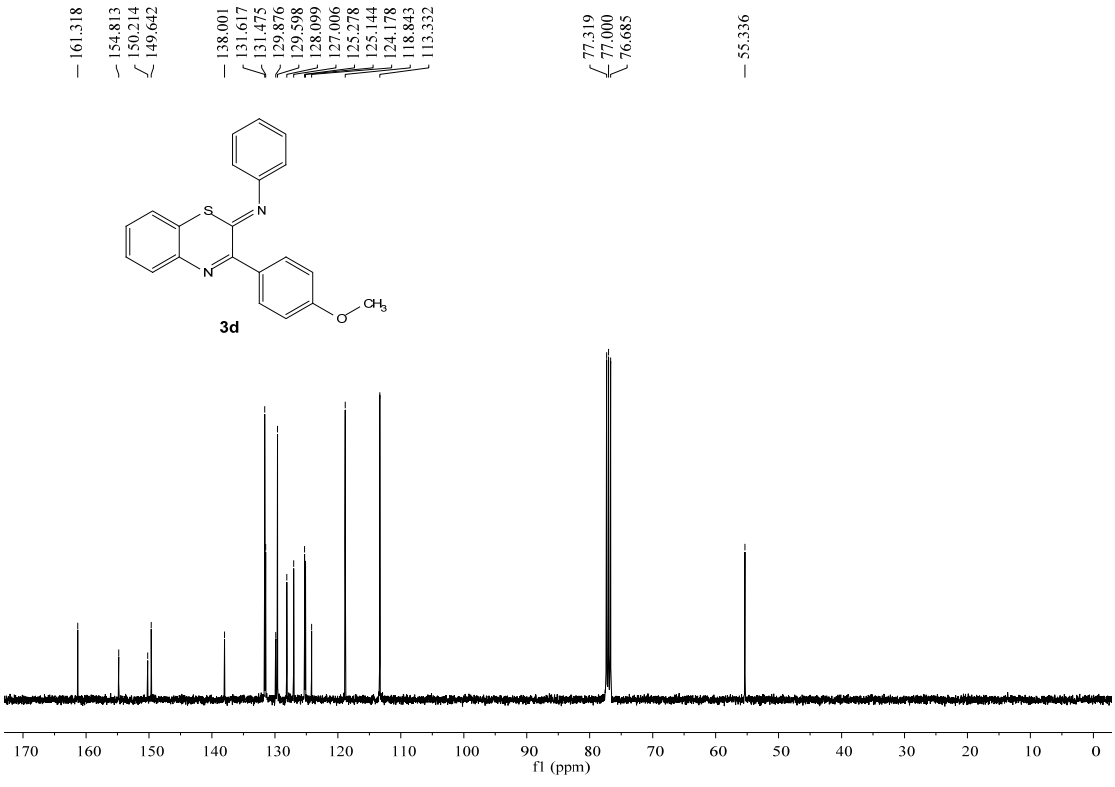
^{1}H and ^{13}C NMR spectra of 3c



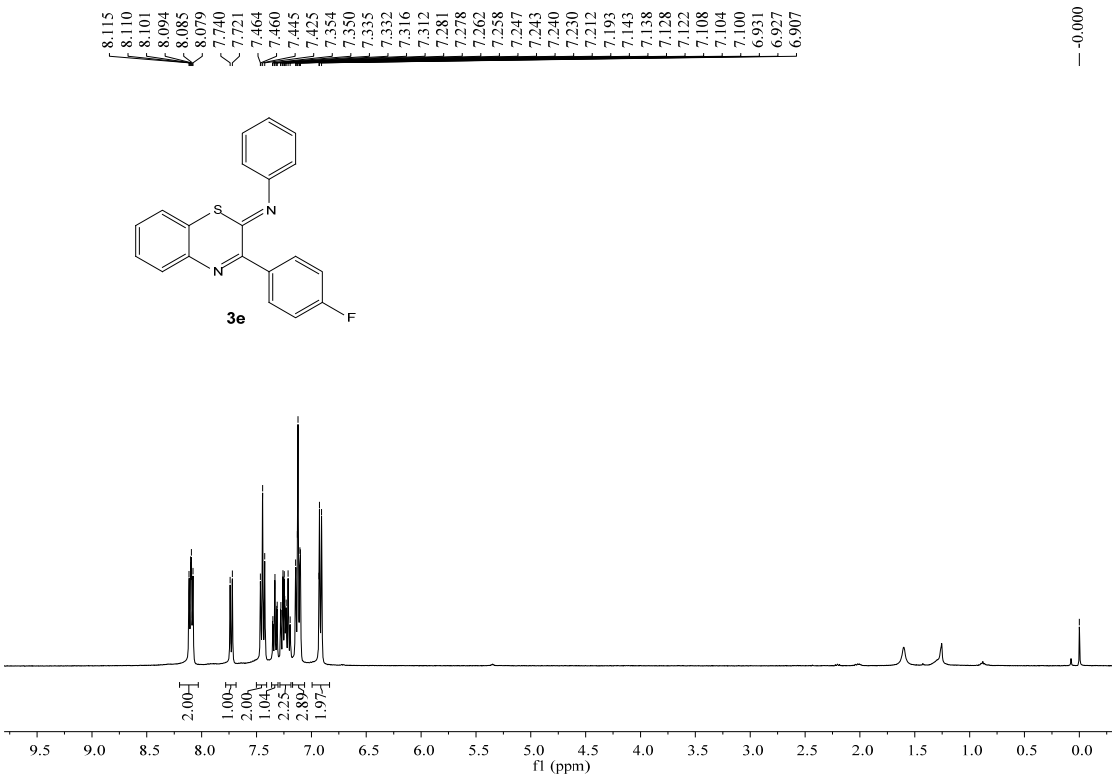


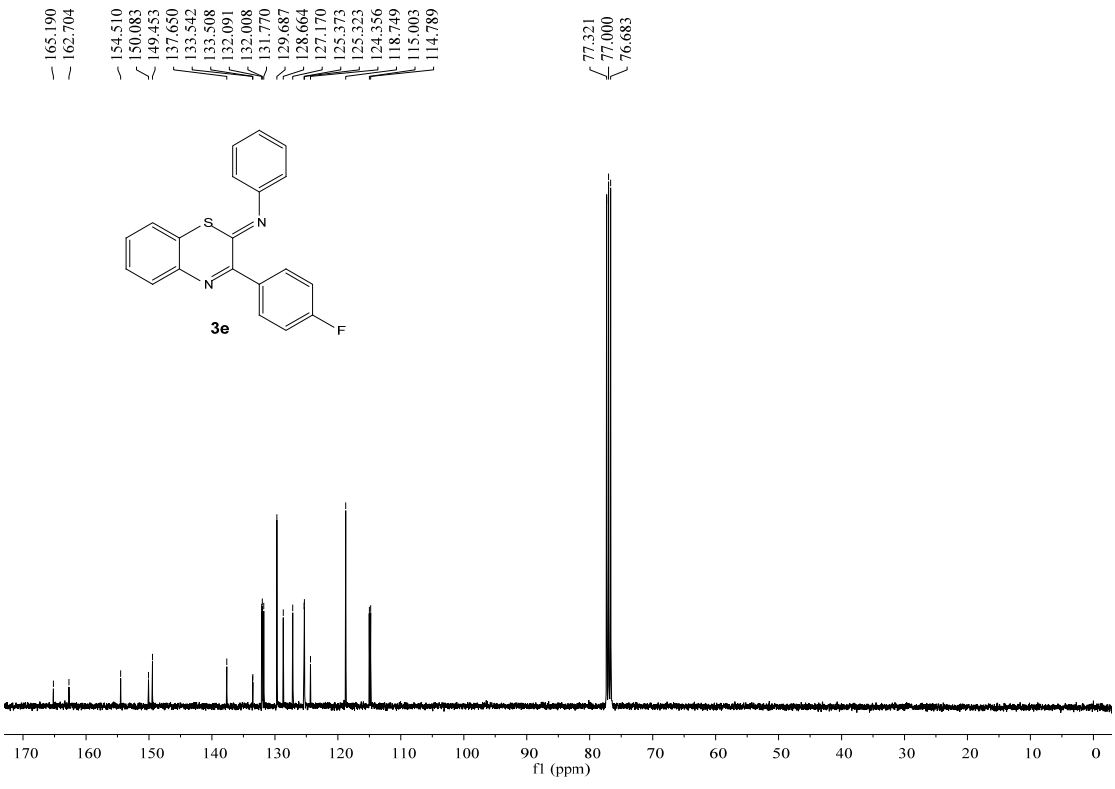
^{1}H and ^{13}C NMR spectra of 3d



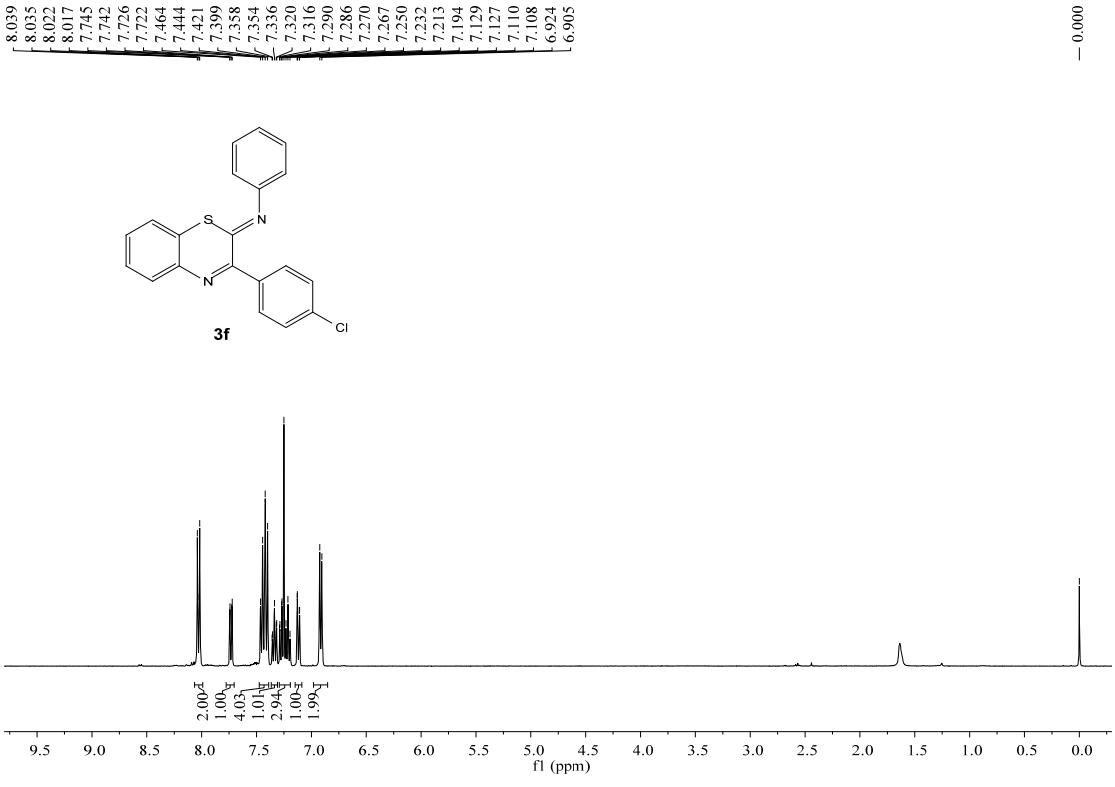


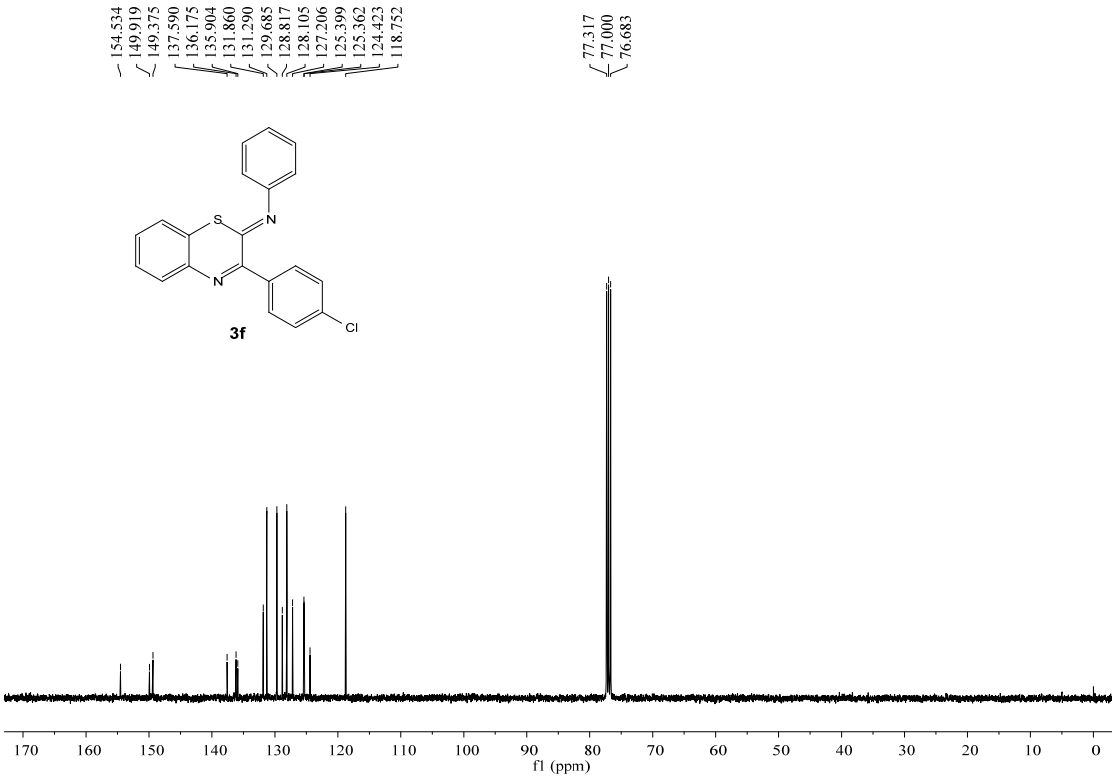
^{1}H, ^{13}C and ^{19}F NMR spectra of 3e



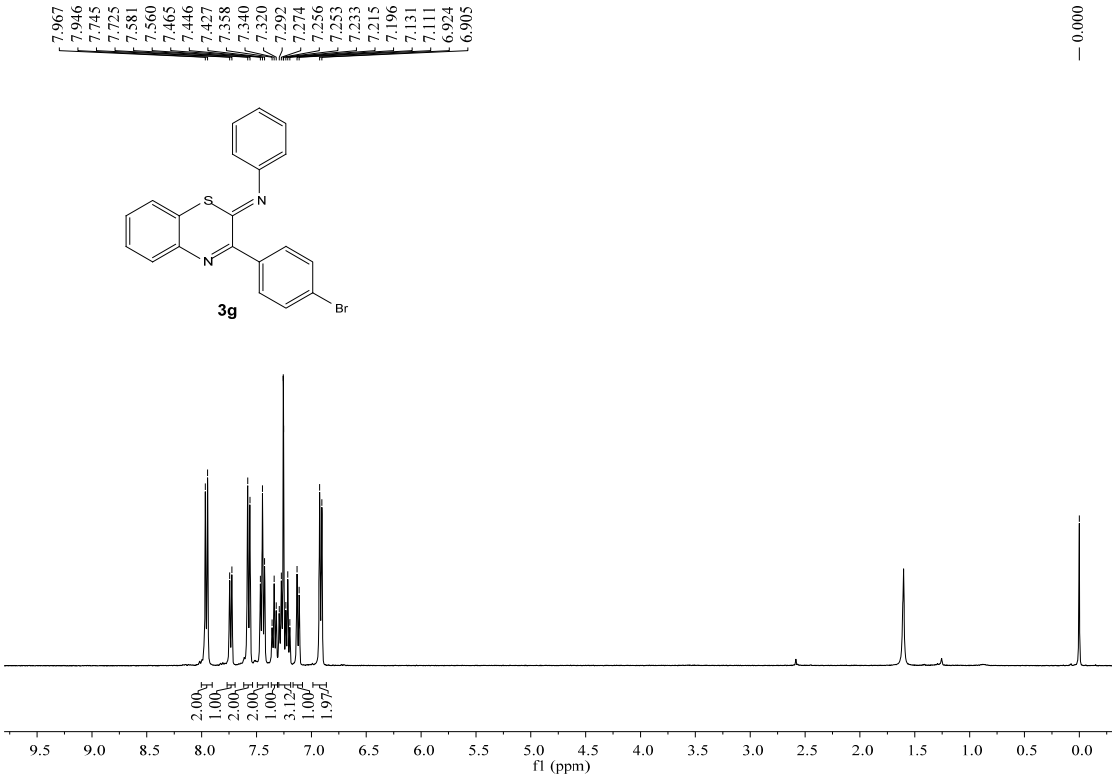


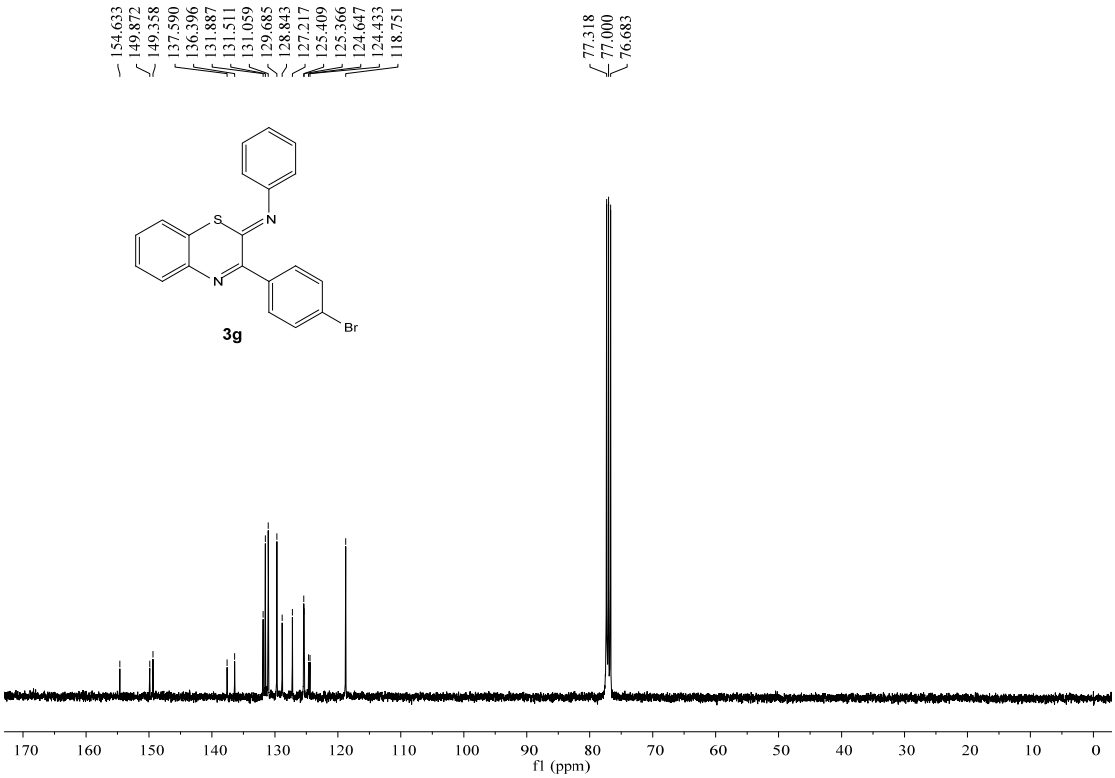
^{1}H and ^{13}C NMR spectra of 3f



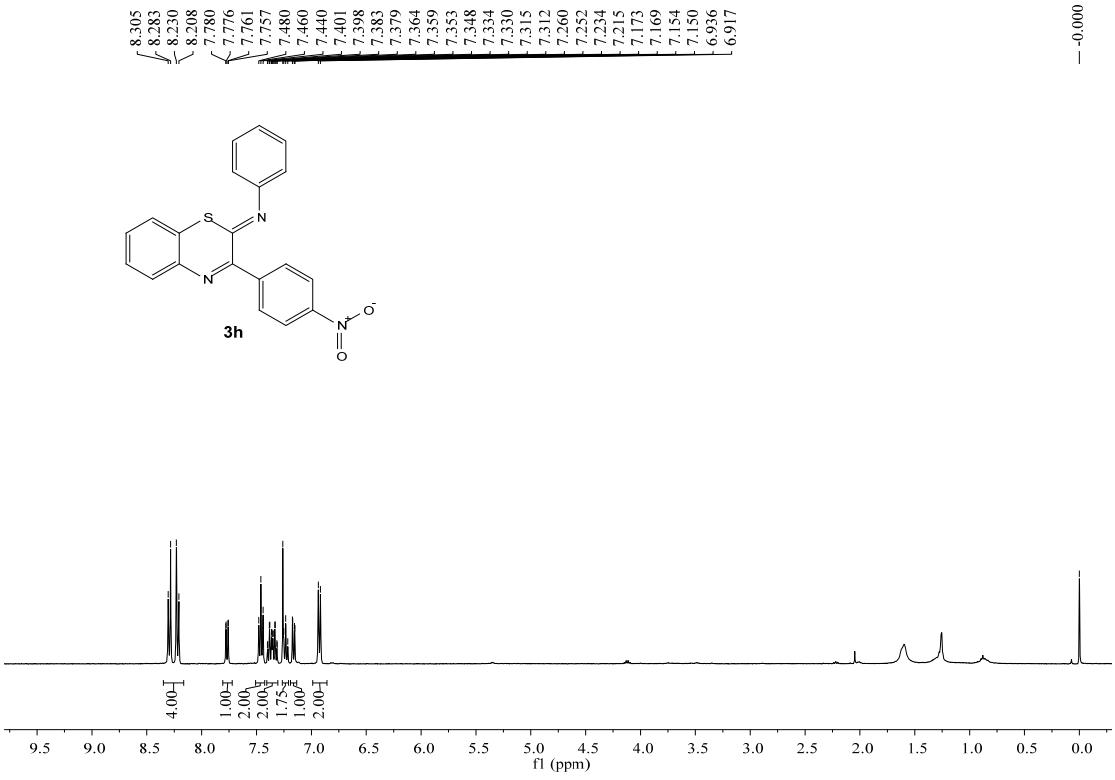


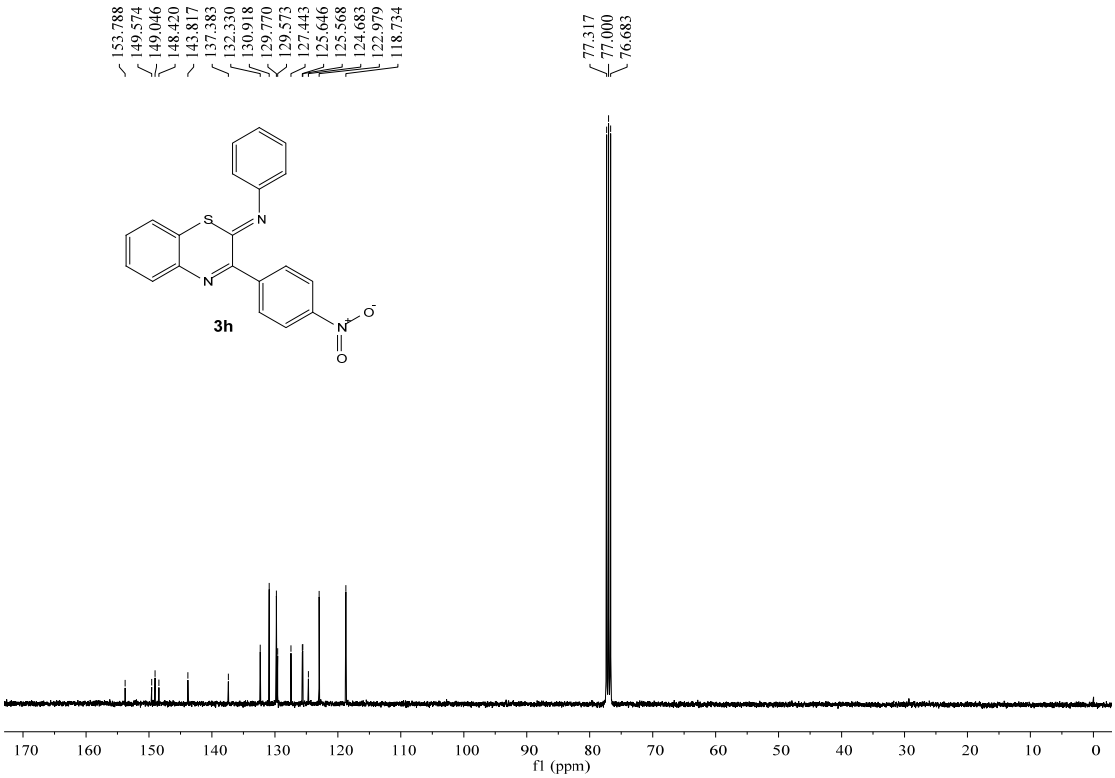
^{1}H and ^{13}C NMR spectra of 3g



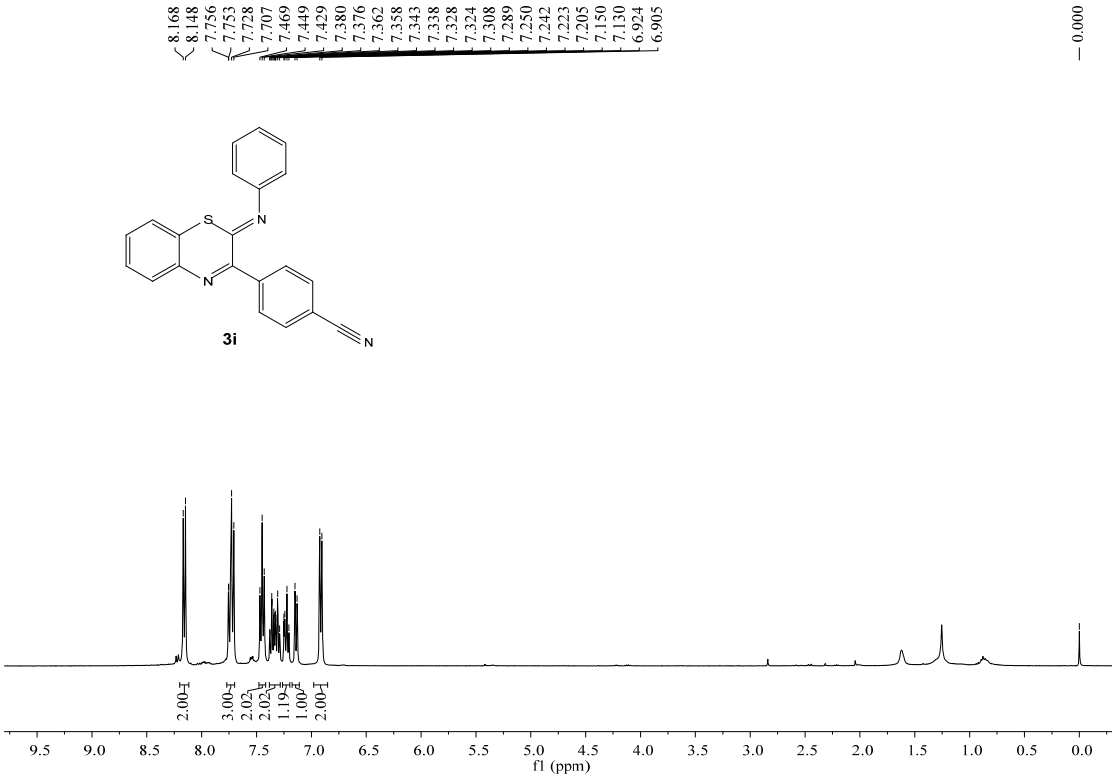


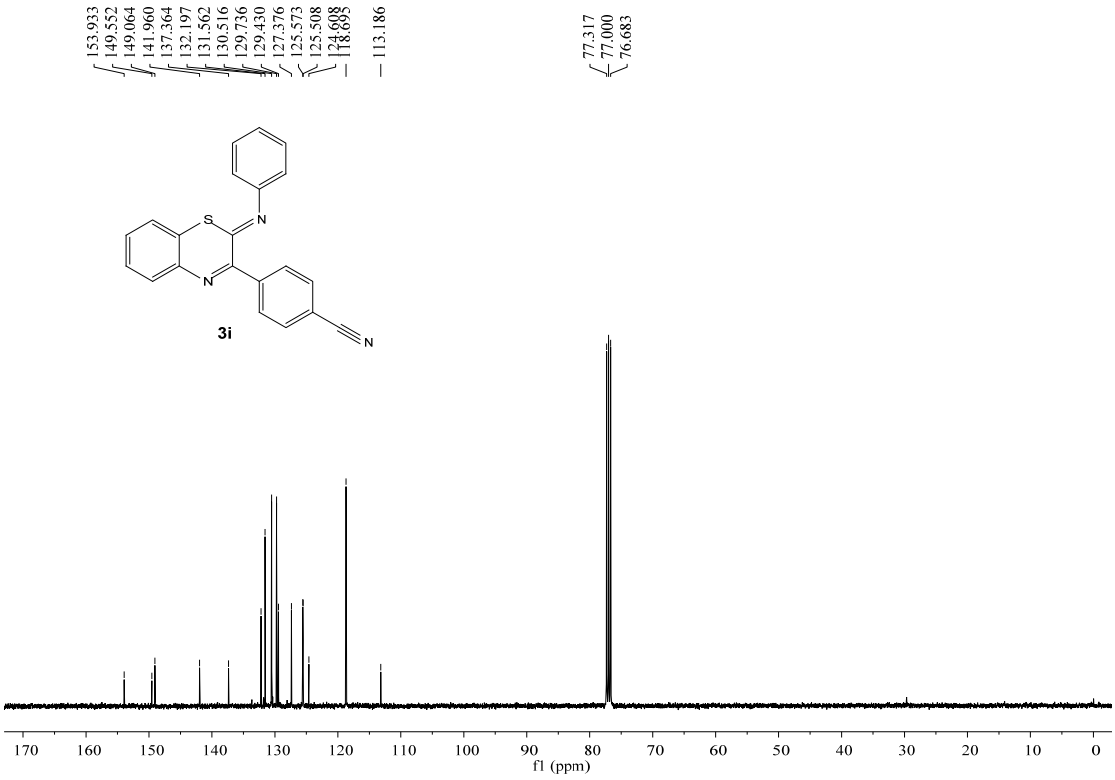
^{1}H and ^{13}C NMR spectra of 3h



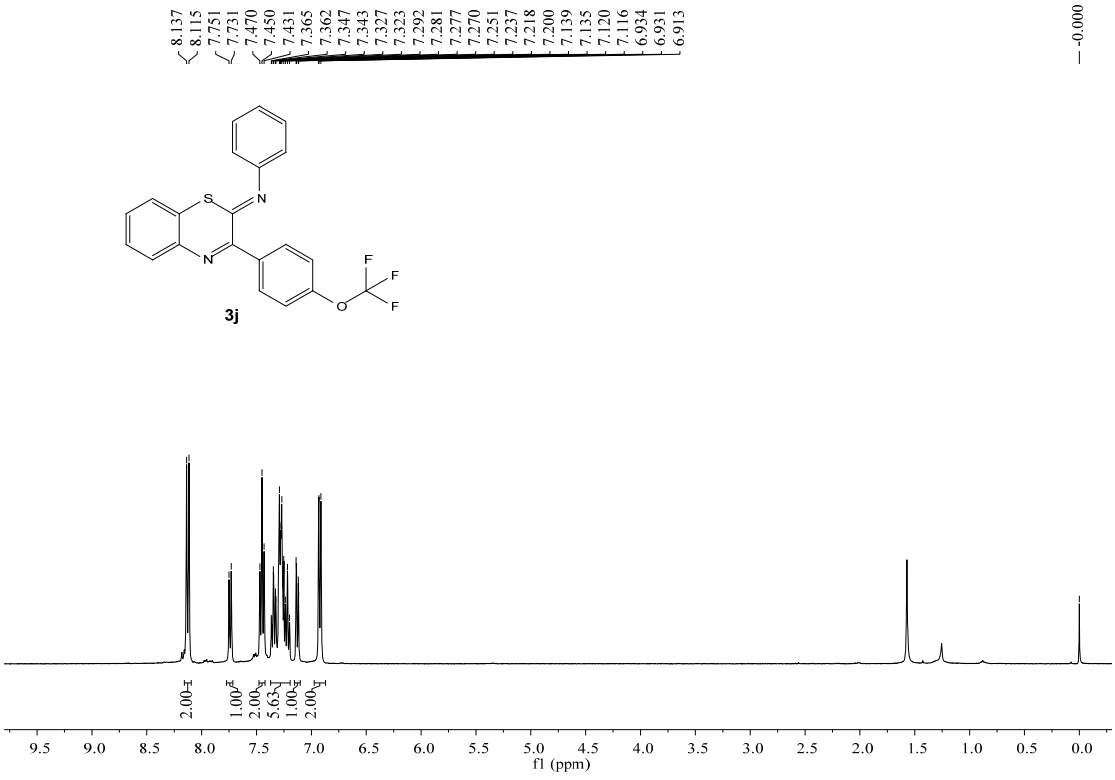


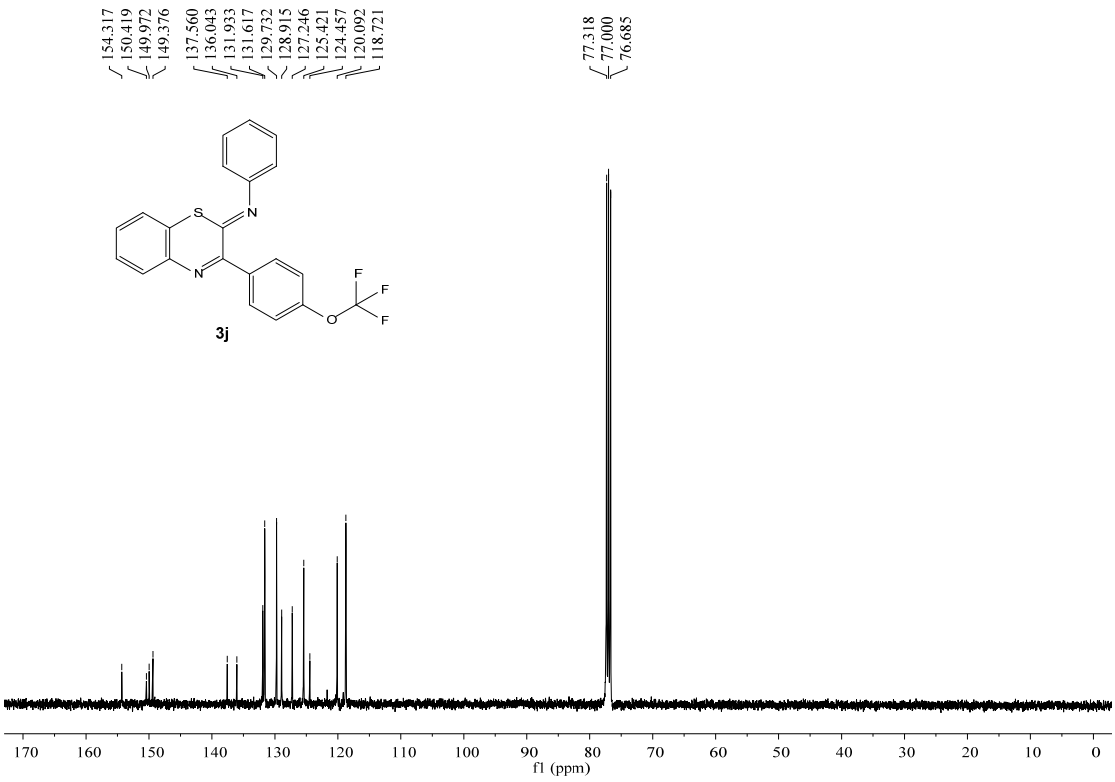
^{1}H and ^{13}C NMR spectra of 3i





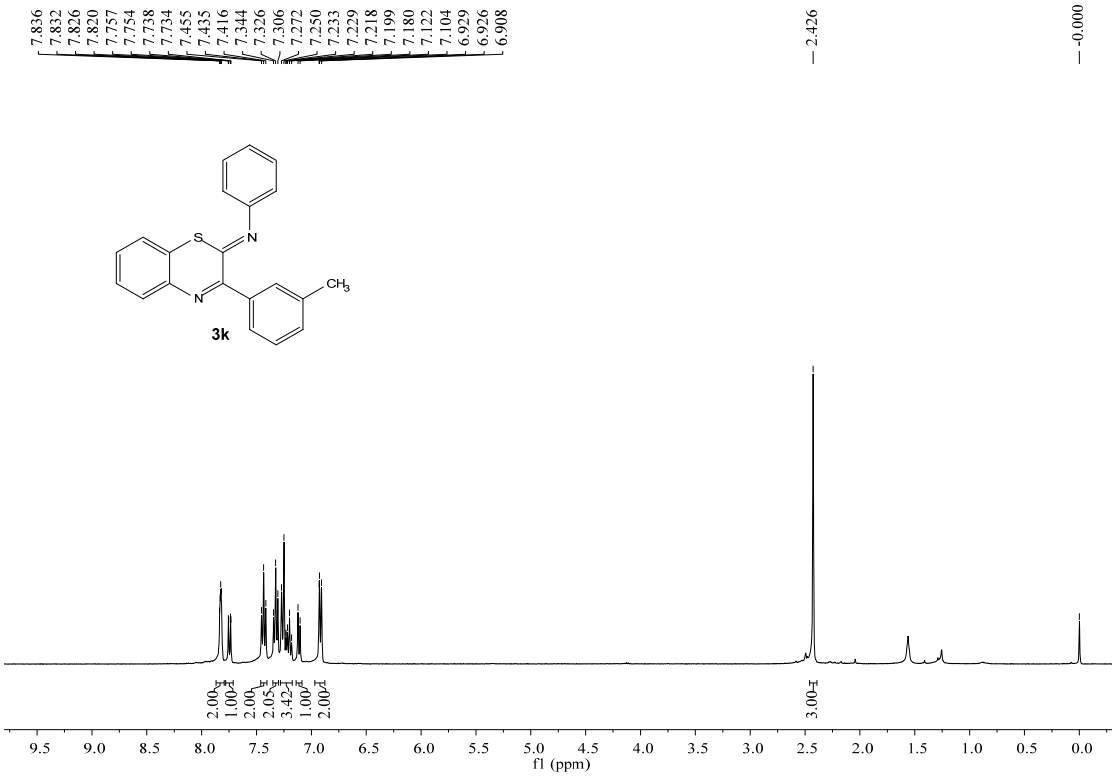
^{1}H, ^{13}C and ^{19}F NMR spectra of 3j

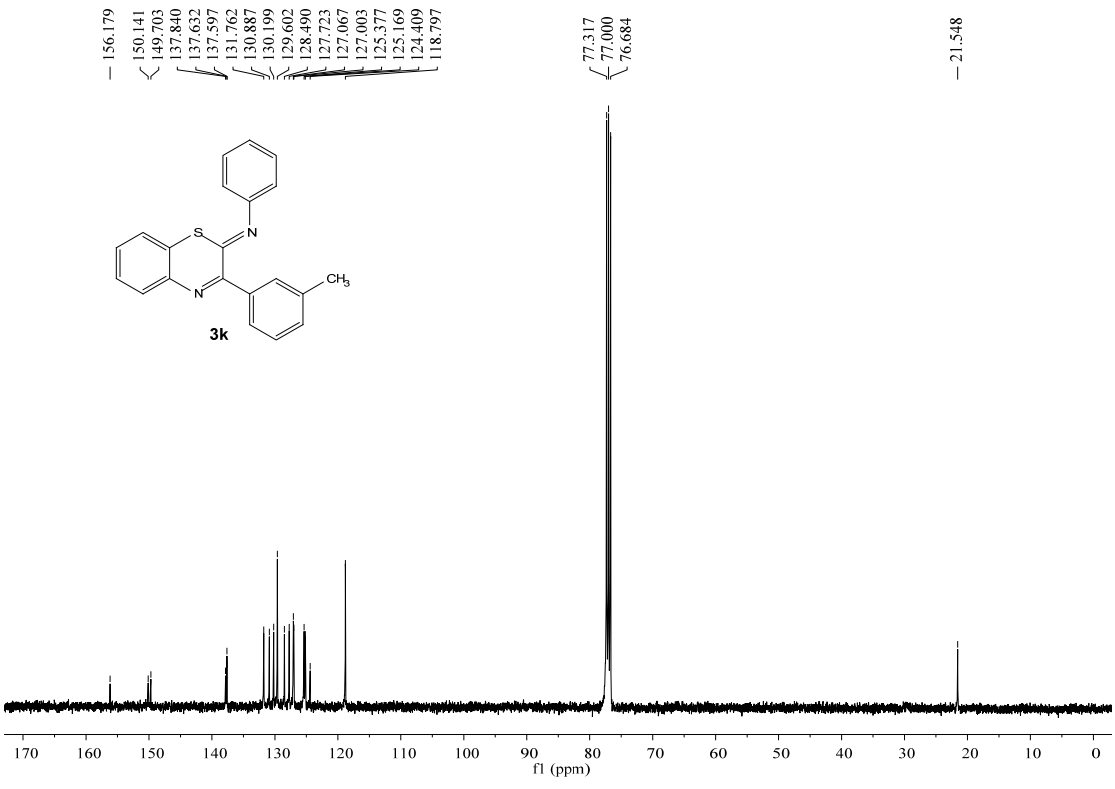



154.317
150.419
149.972
149.376
137.560
136.043
131.933
131.617
129.732
128.915
127.246
125.421
124.457
120.092
118.721
77.318
77.000
76.685
S
N
N
F
F
F
O
3j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

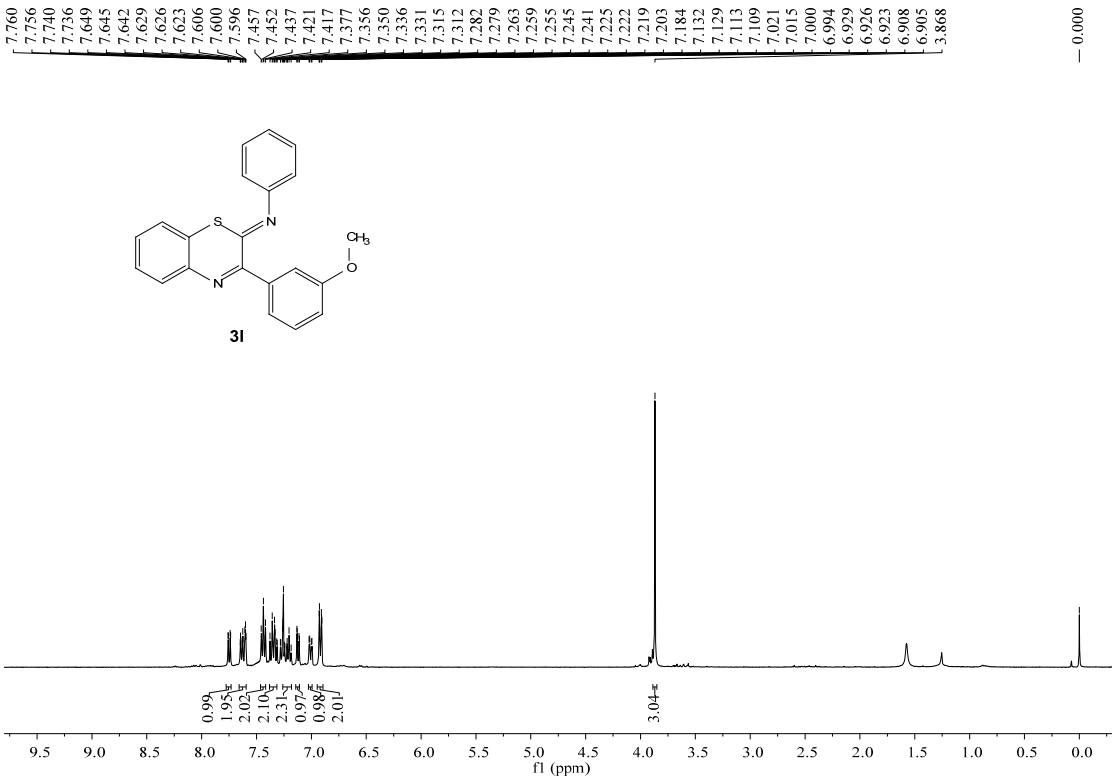

-57.549
S
N
N
F
F
F
O
3j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

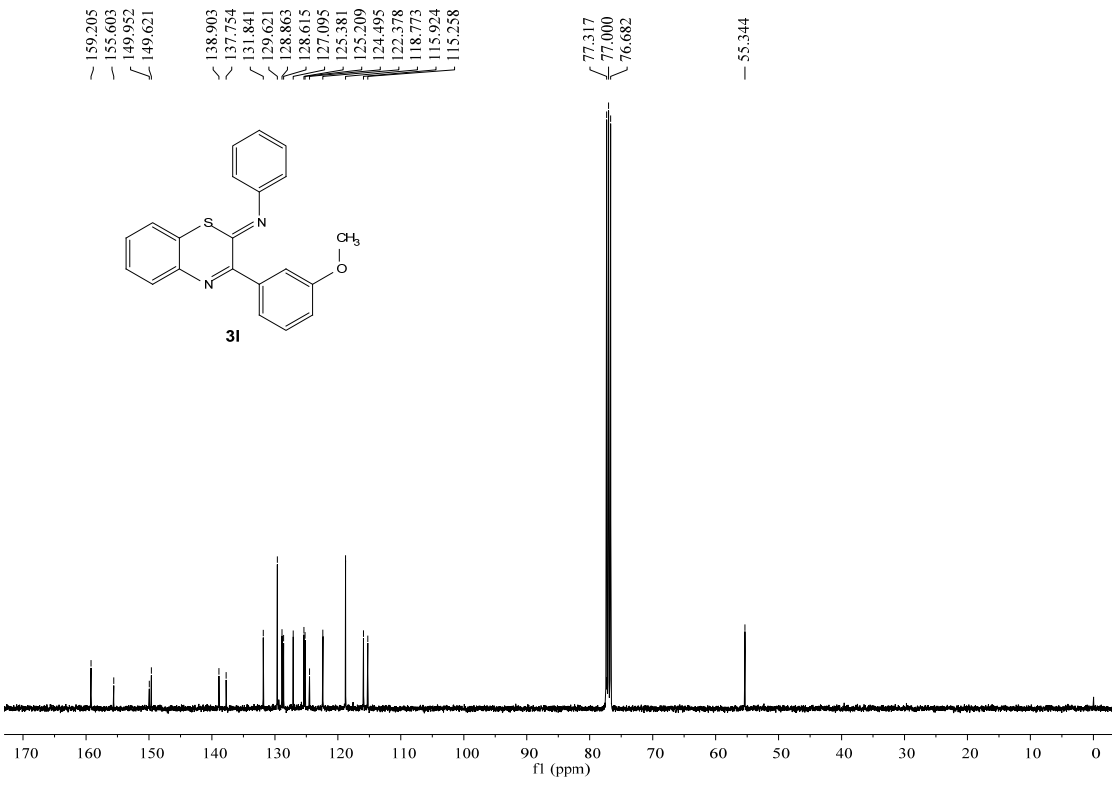
^{1}H and ^{13}C NMR spectra of 3k



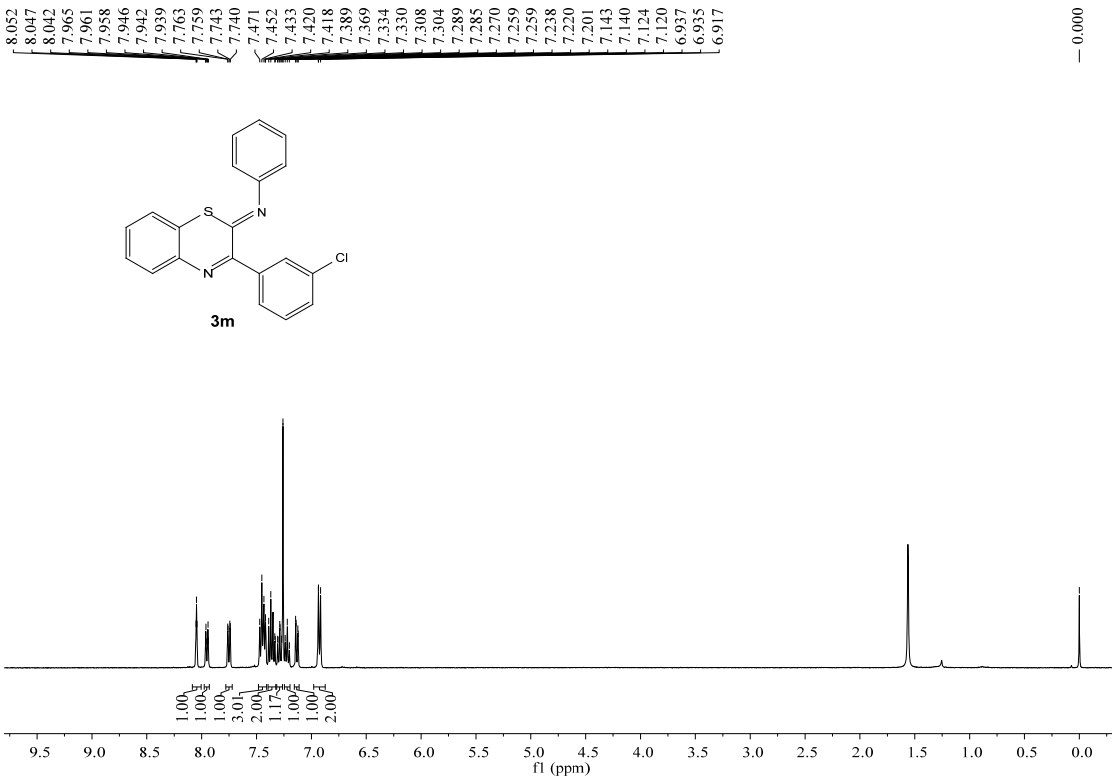


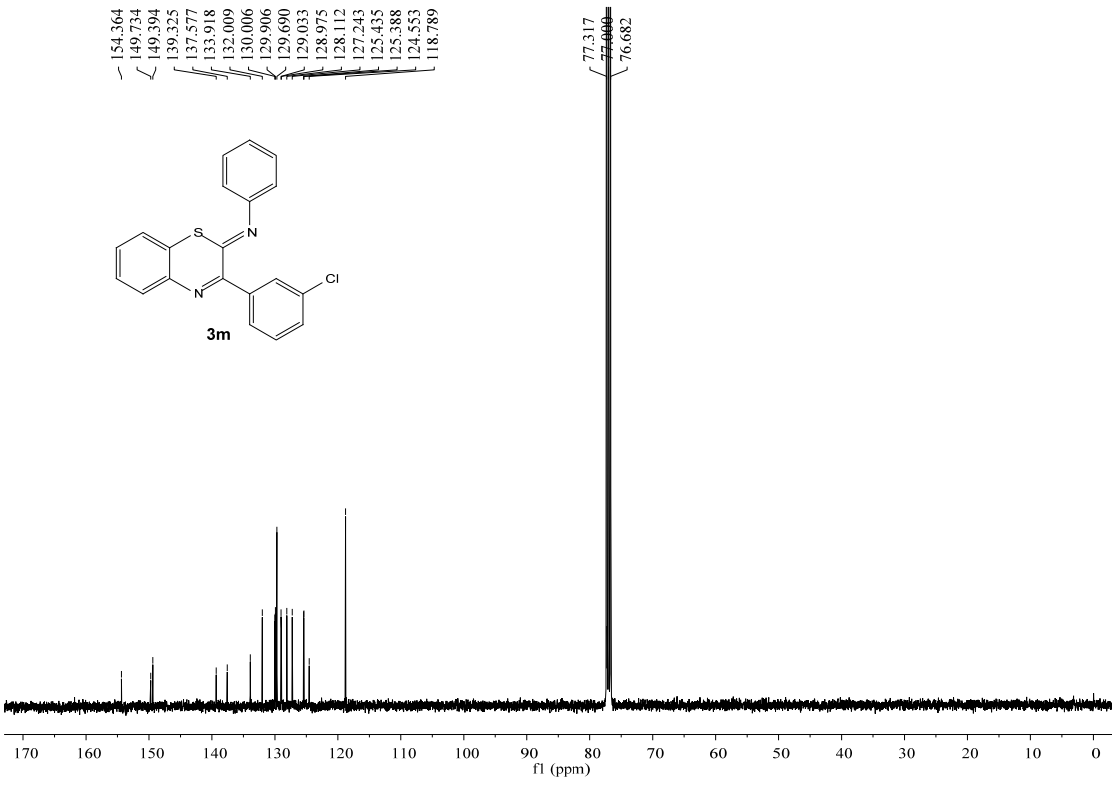
^{1}H and ^{13}C NMR spectra of 3l



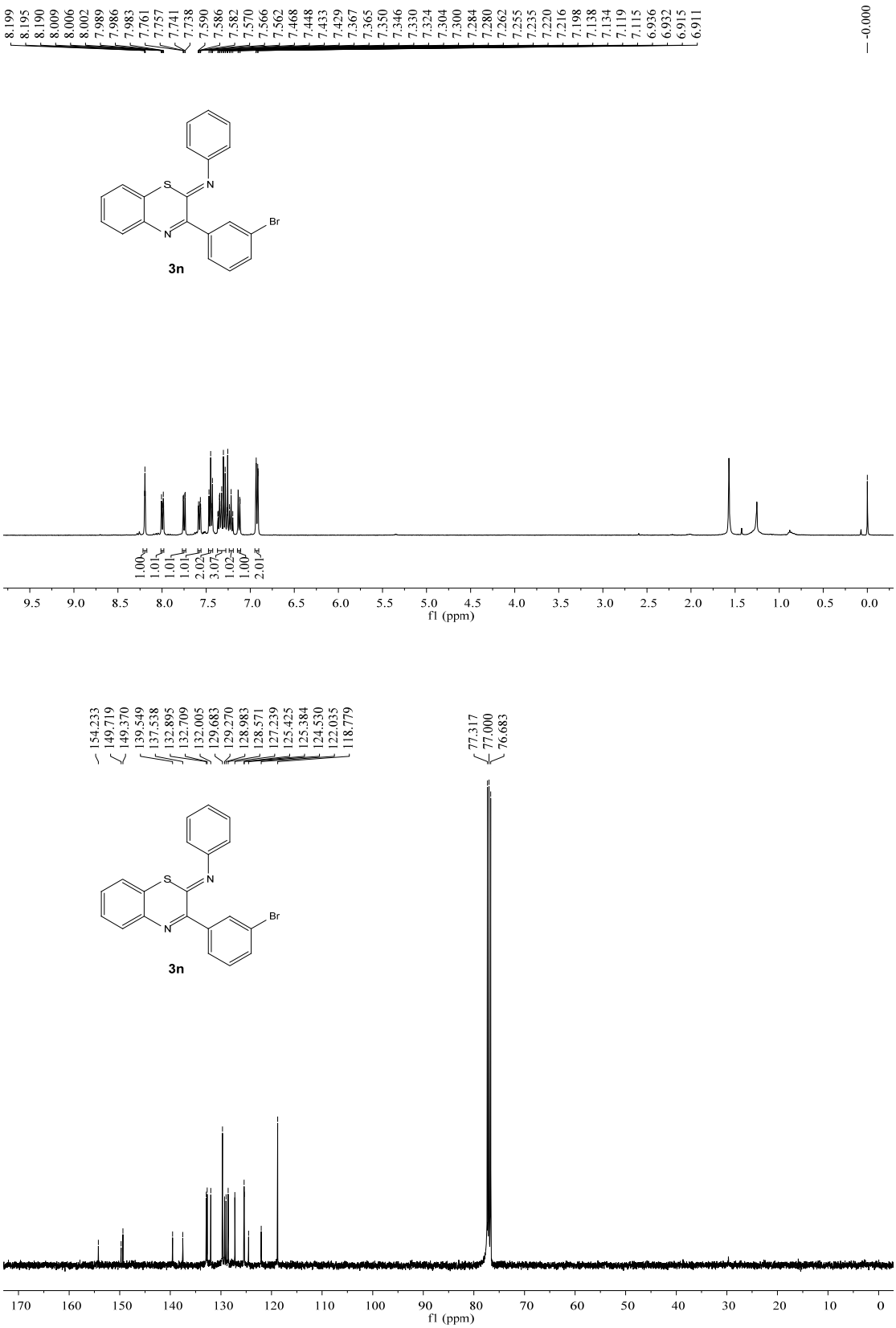


^{1}H and ^{13}C NMR spectra of 3m

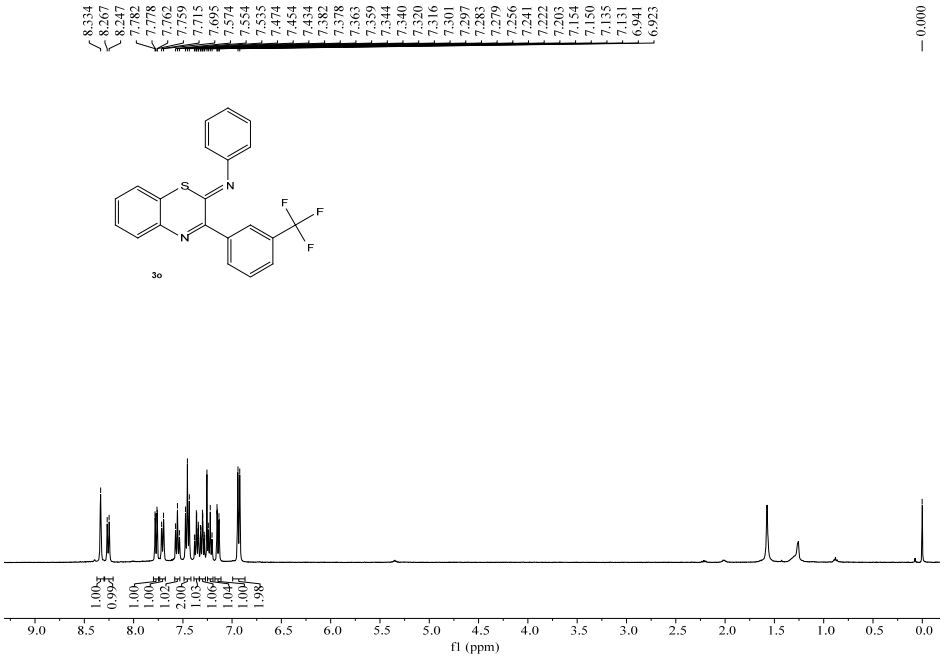


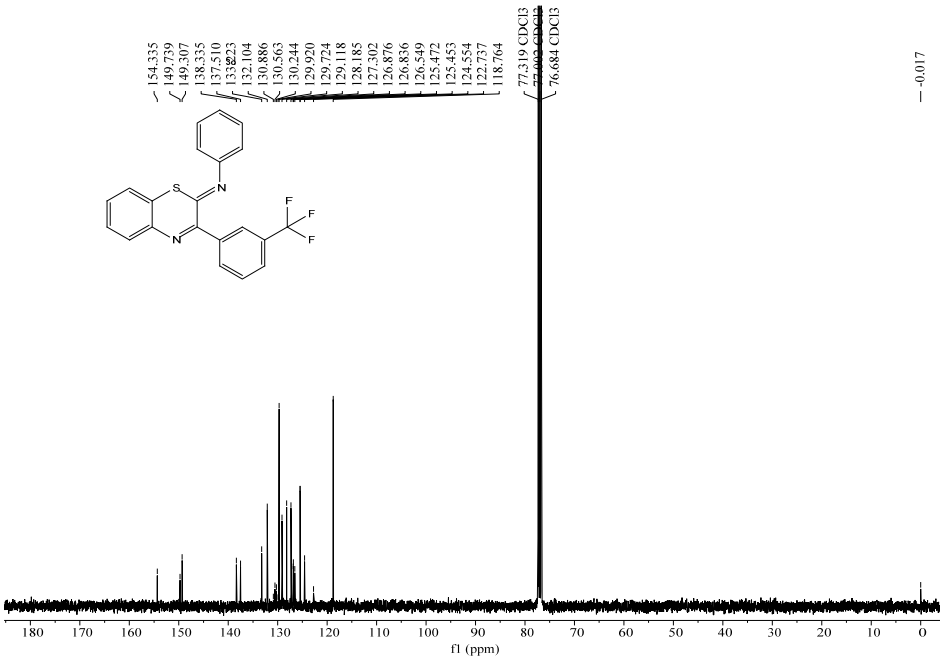


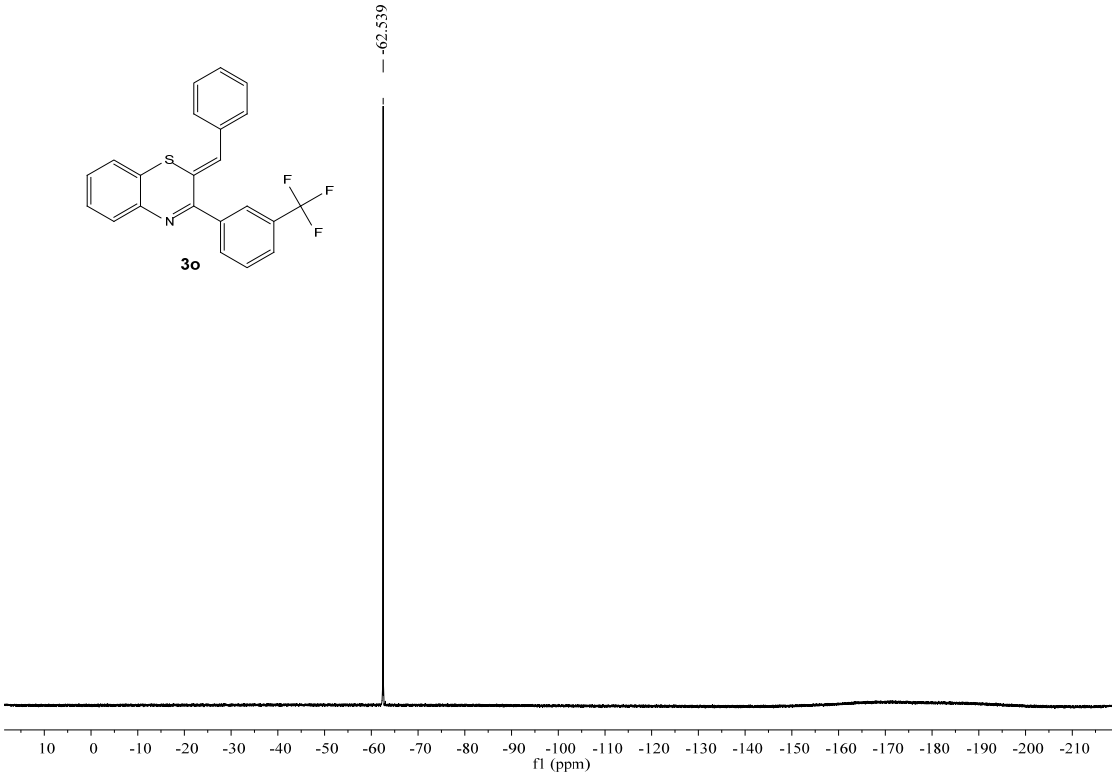
^{1}H and ^{13}C NMR spectra of 3n



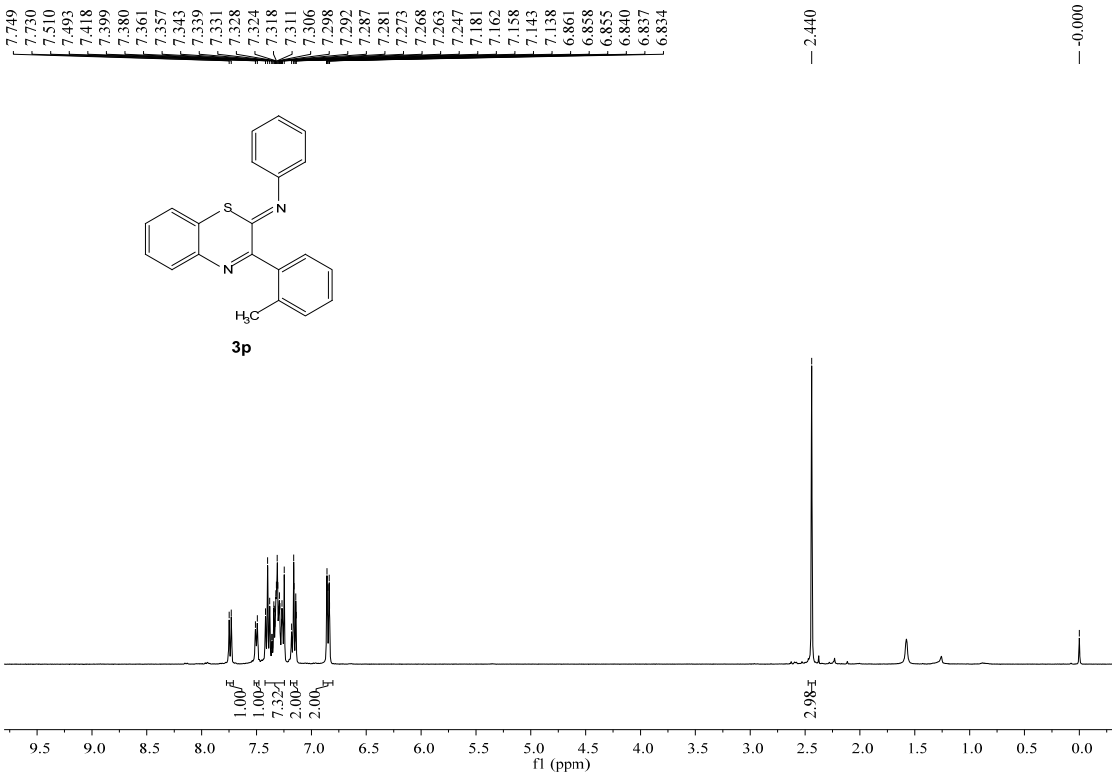
^{1}H, ^{13}C and ^{19}F NMR spectra of 3o

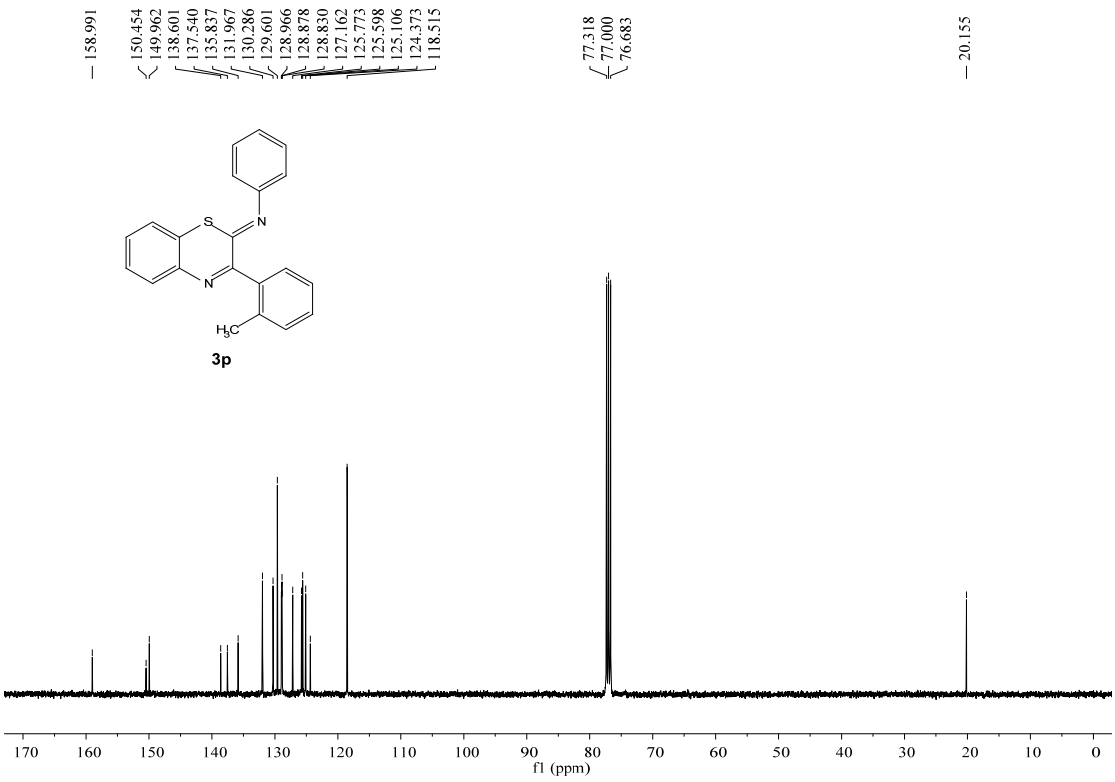




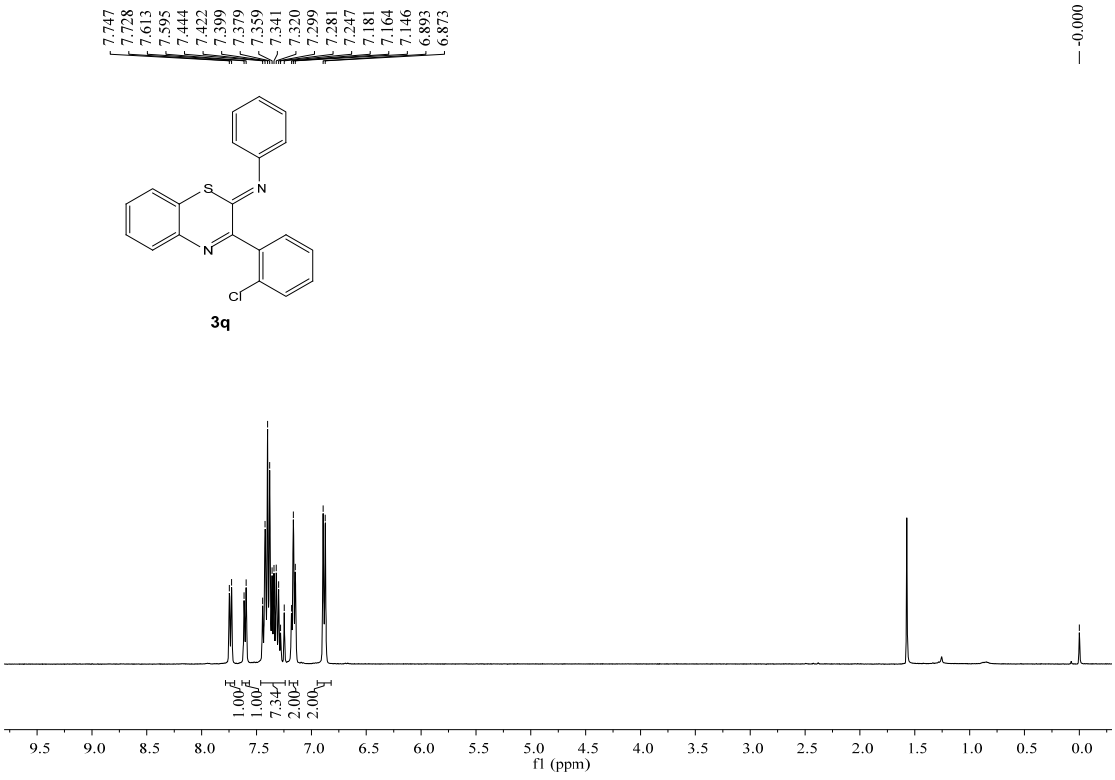


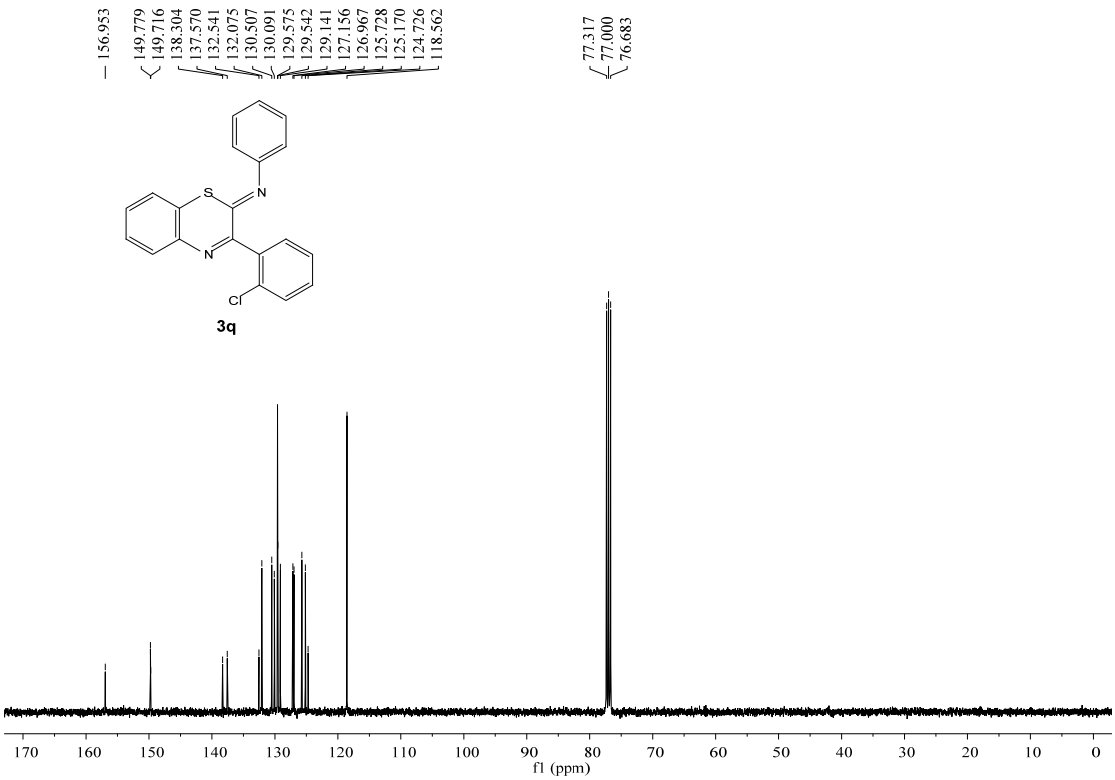
^{1}H and ^{13}C NMR spectra of 3p



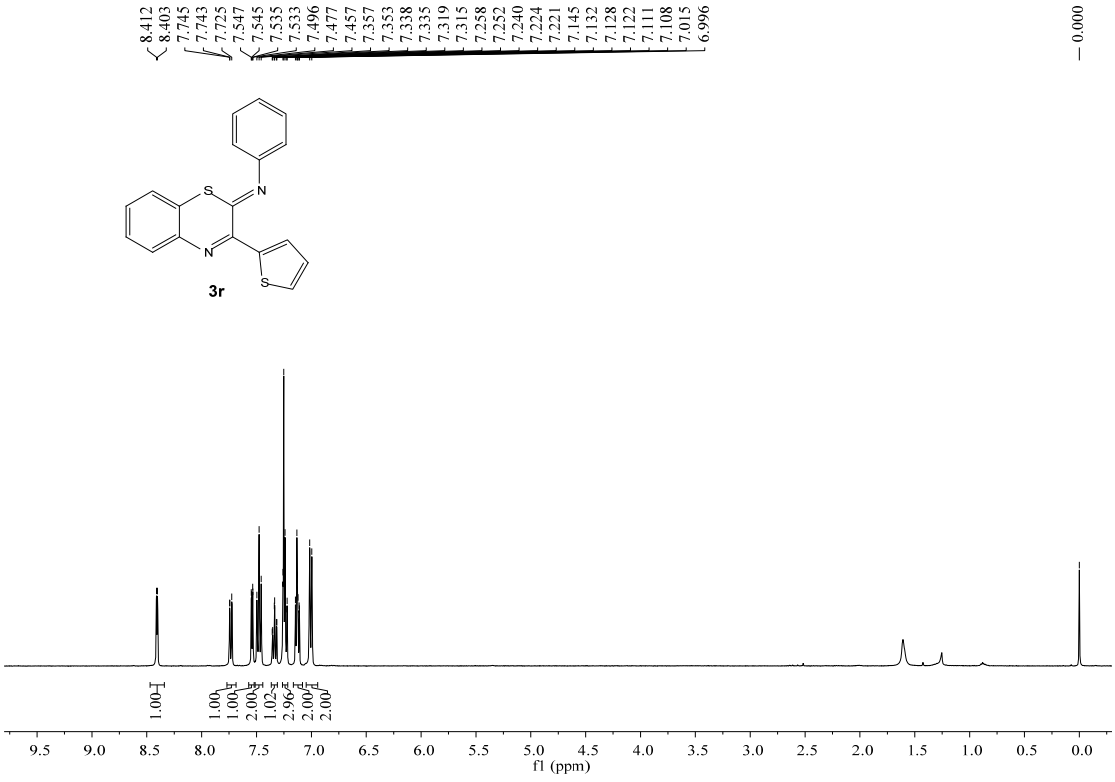


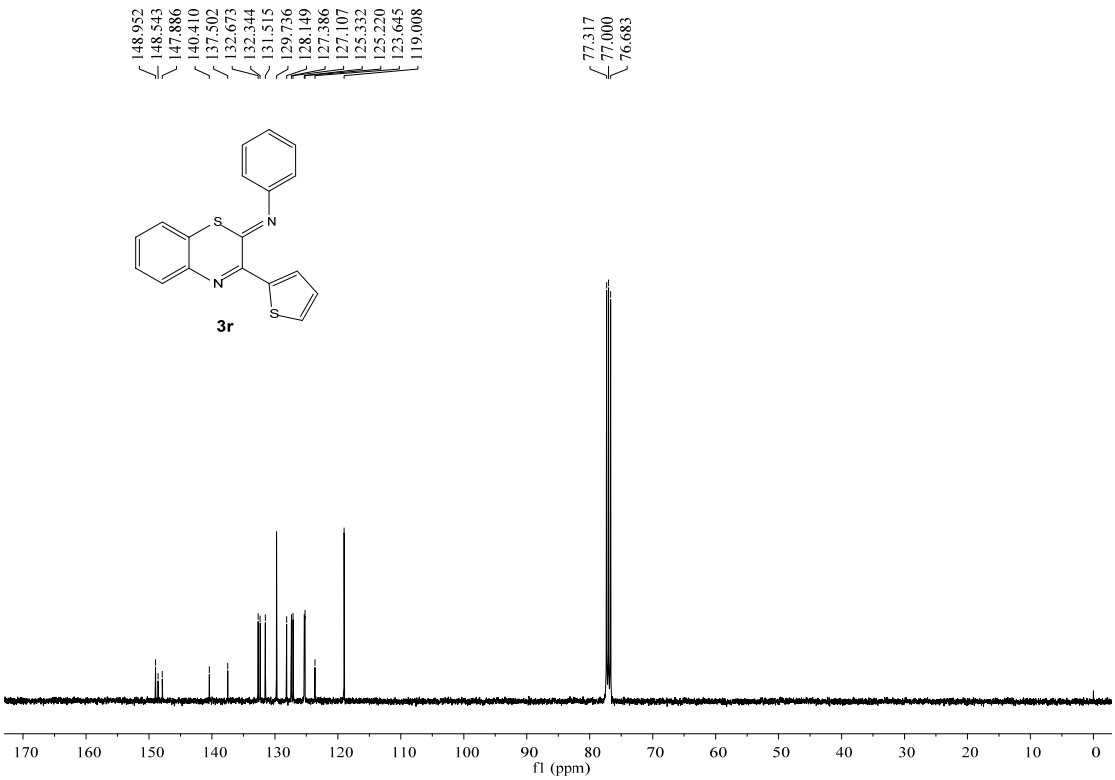
^{1}H and ^{13}C NMR spectra of 3q



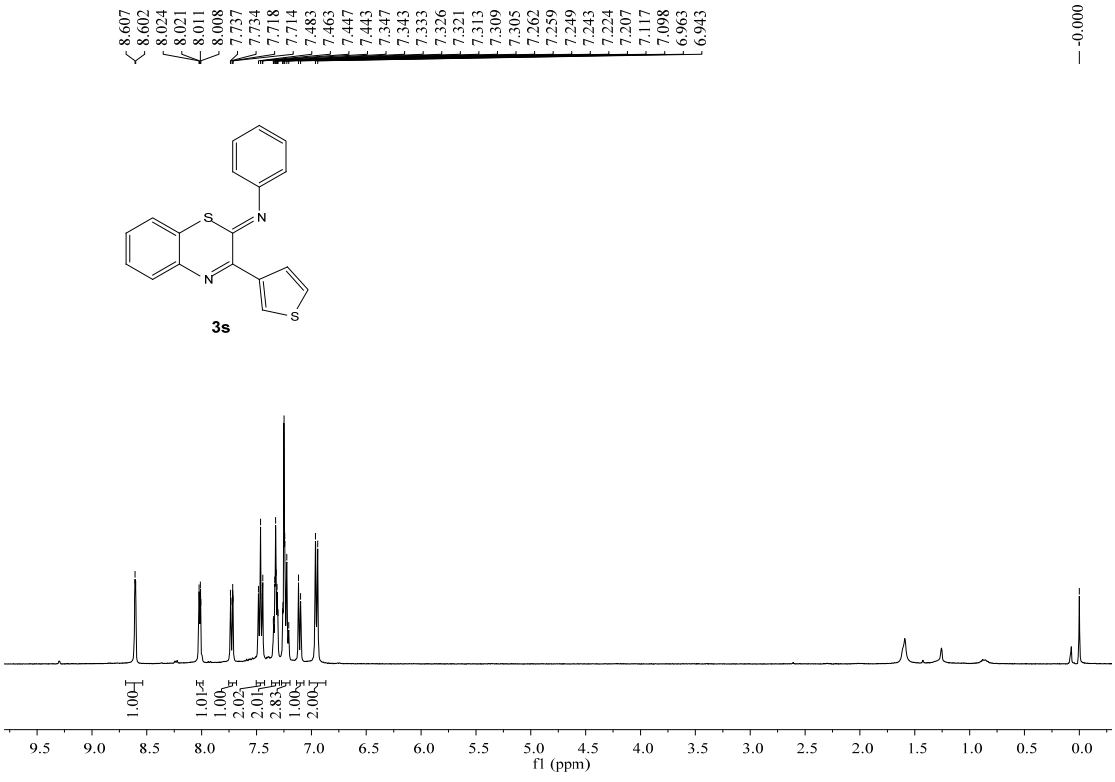


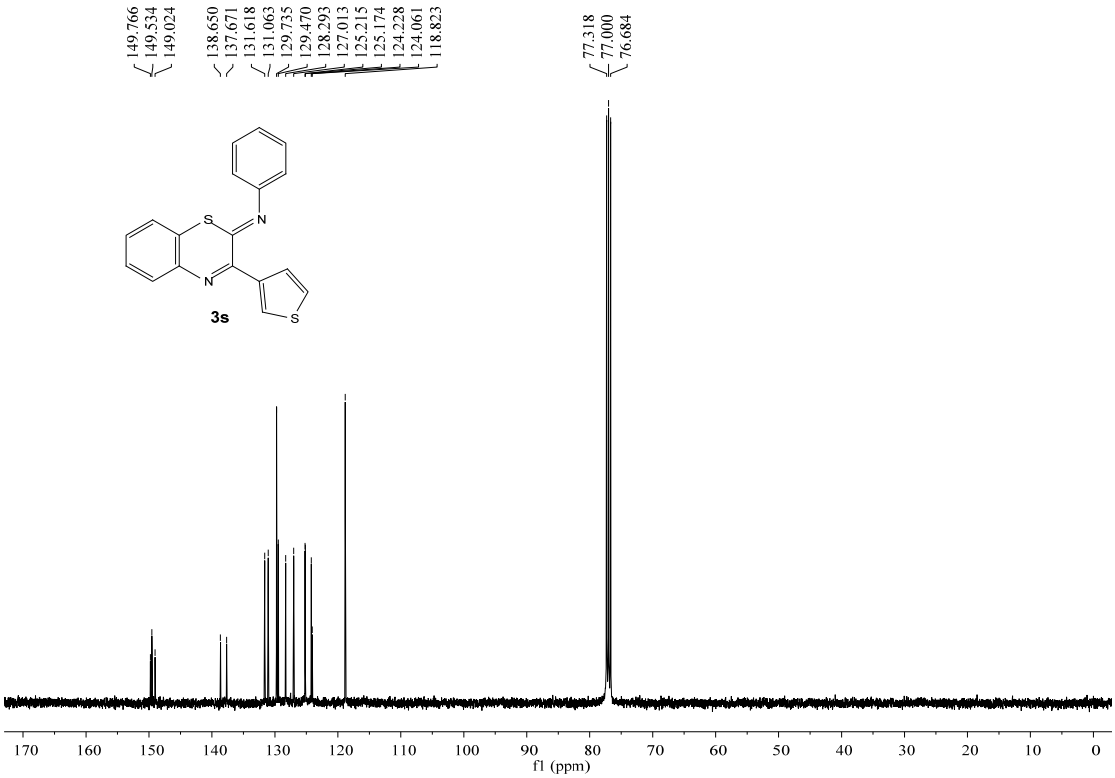
^{1}H and ^{13}C NMR spectra of 3r



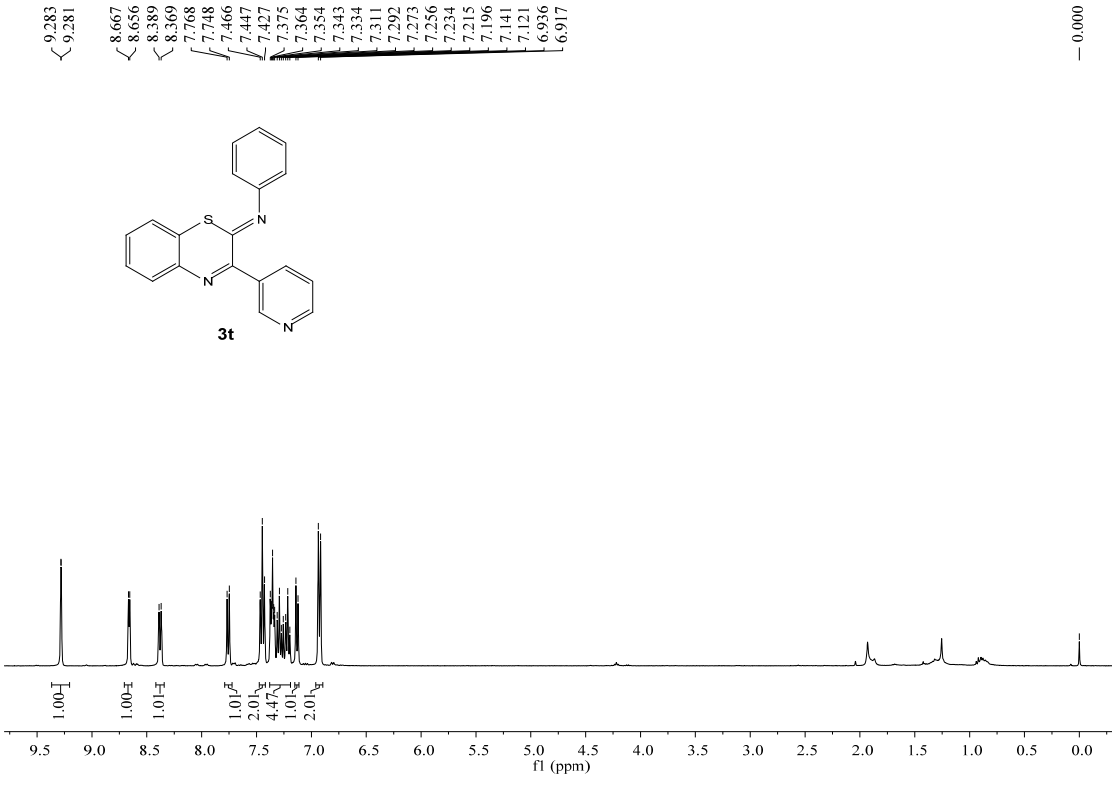


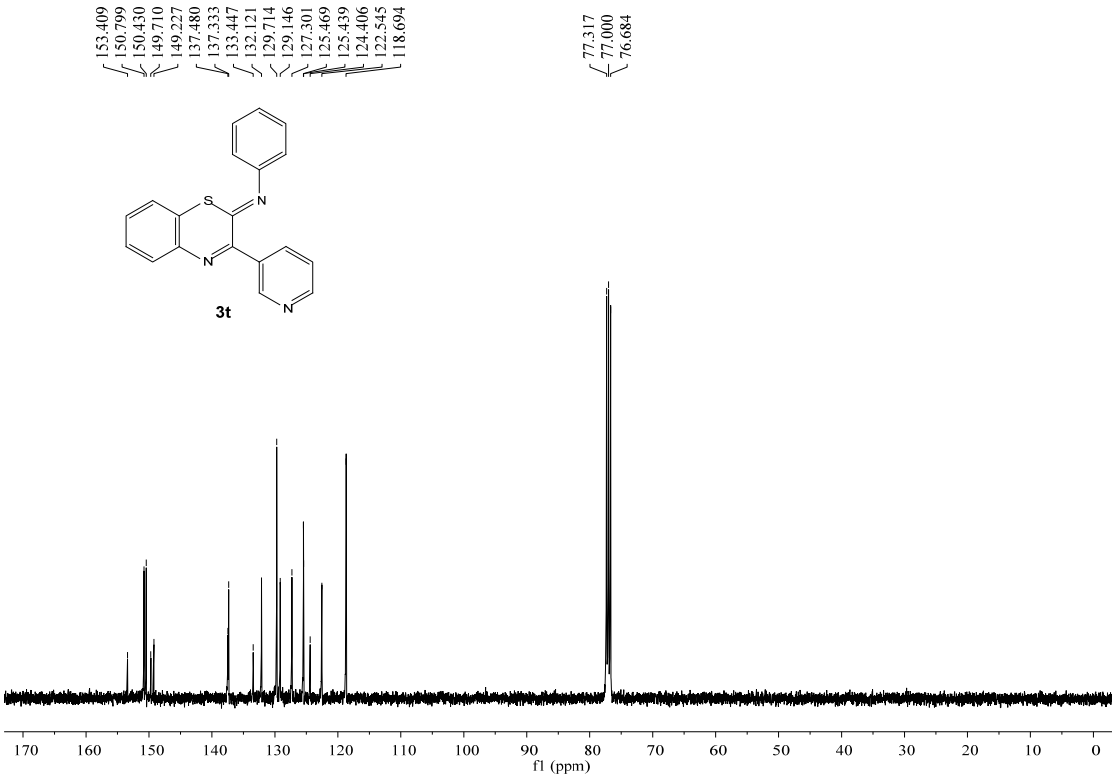
^{1}H and ^{13}C NMR spectra of 3s



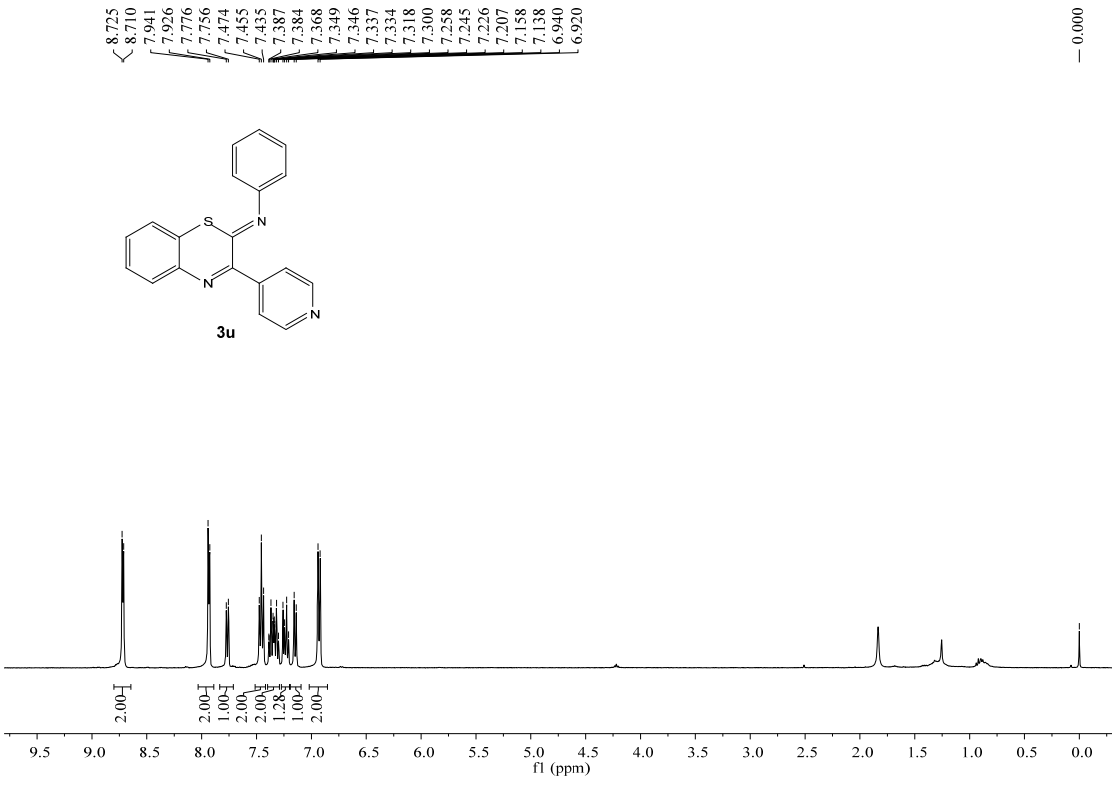


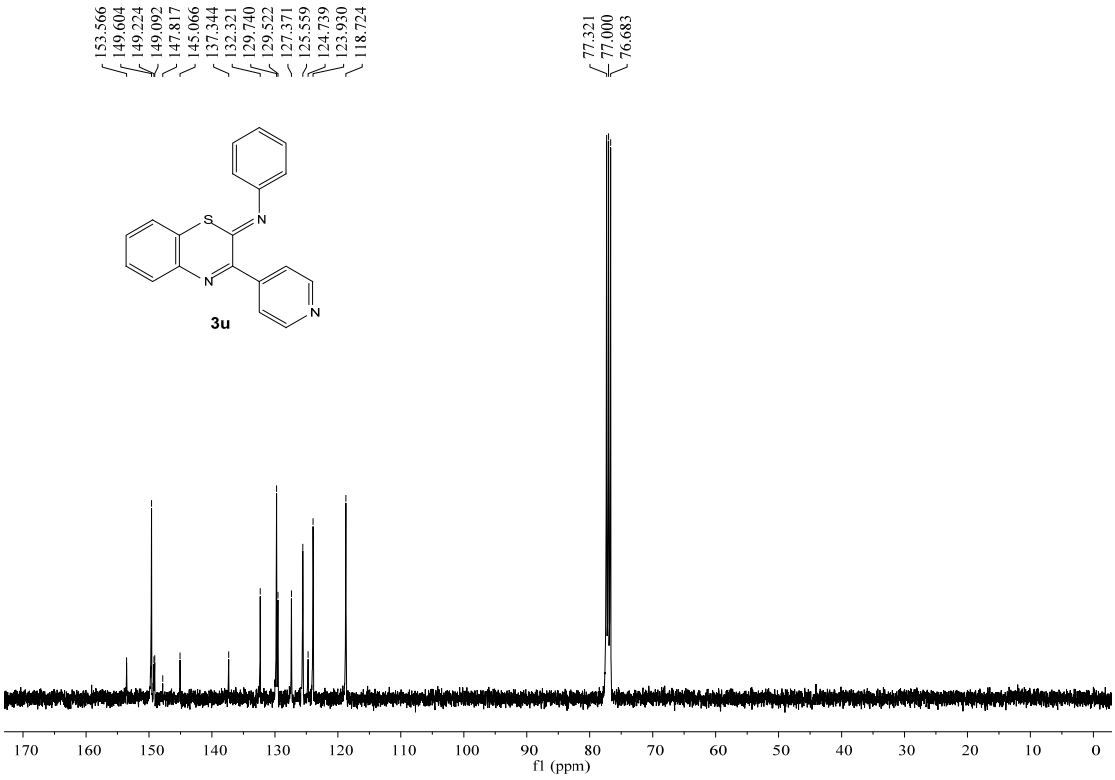
^{1}H and ^{13}C NMR spectra of 3t



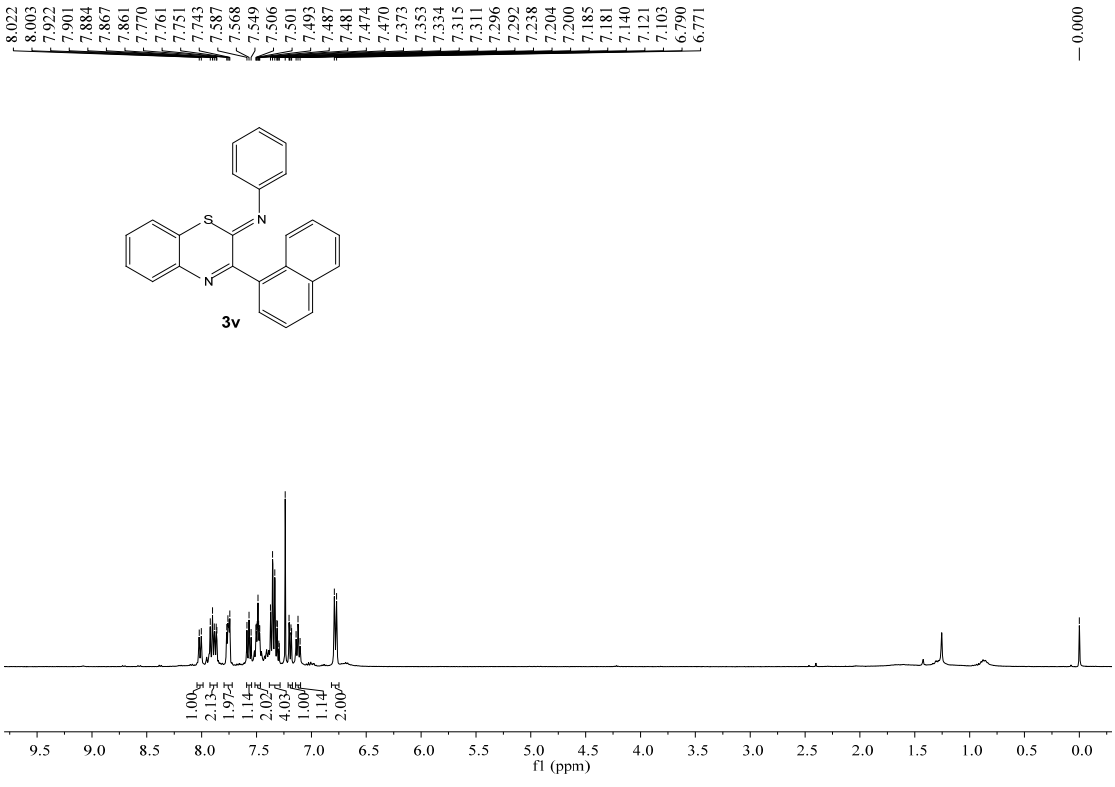


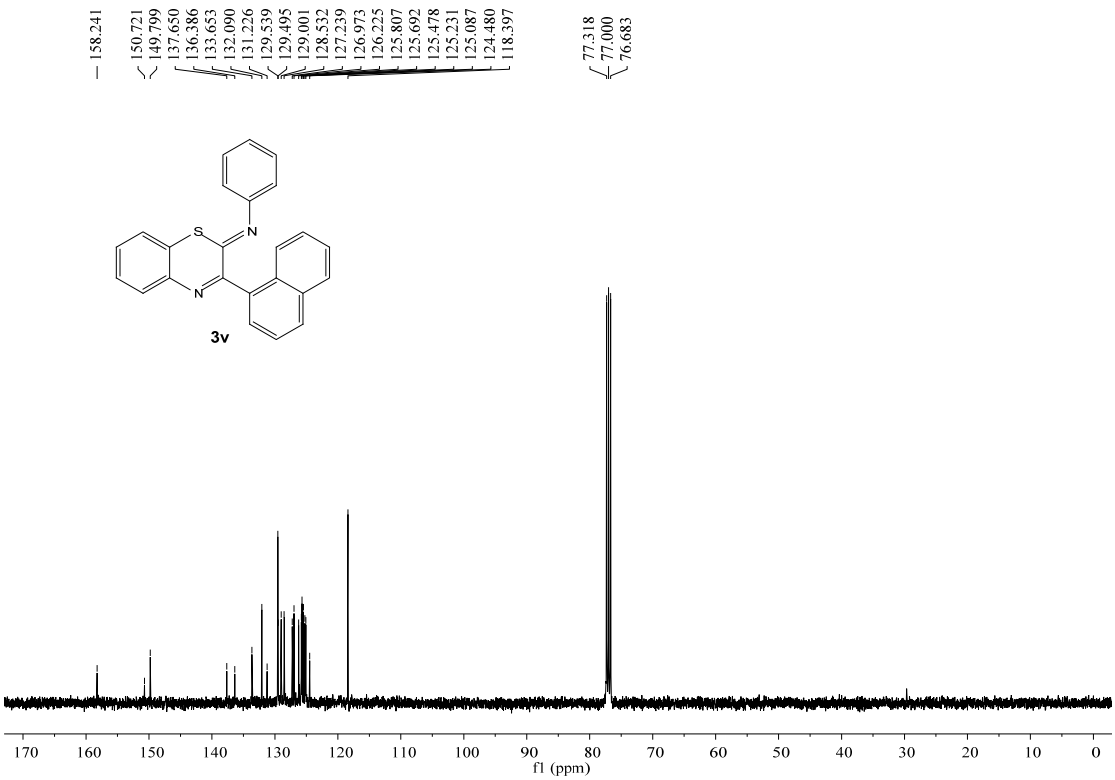
^{1}H and ^{13}C NMR spectra of 3u



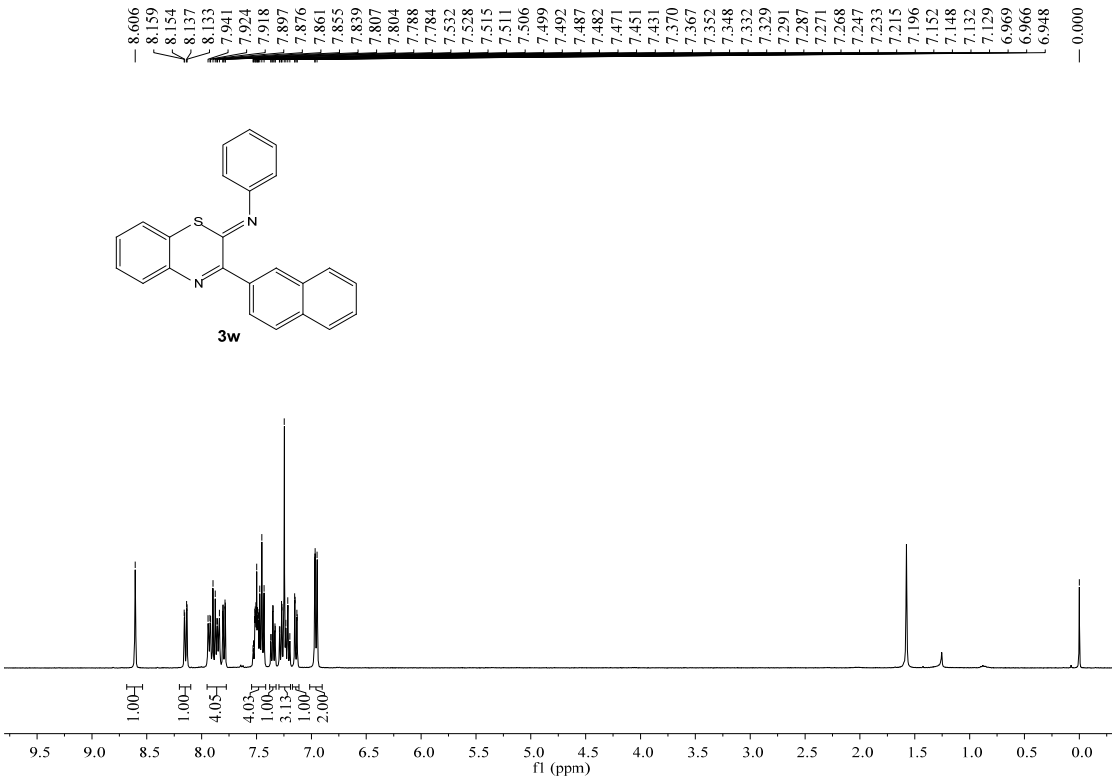


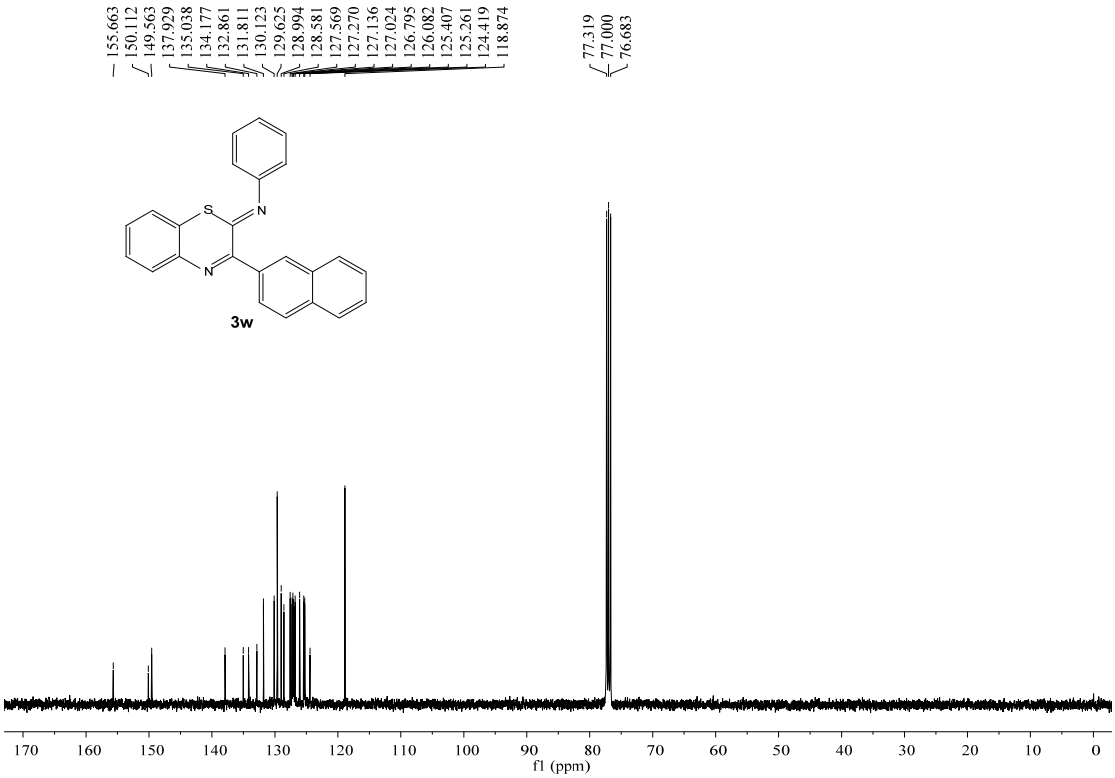
^{1}H and ^{13}C NMR spectra of 3v



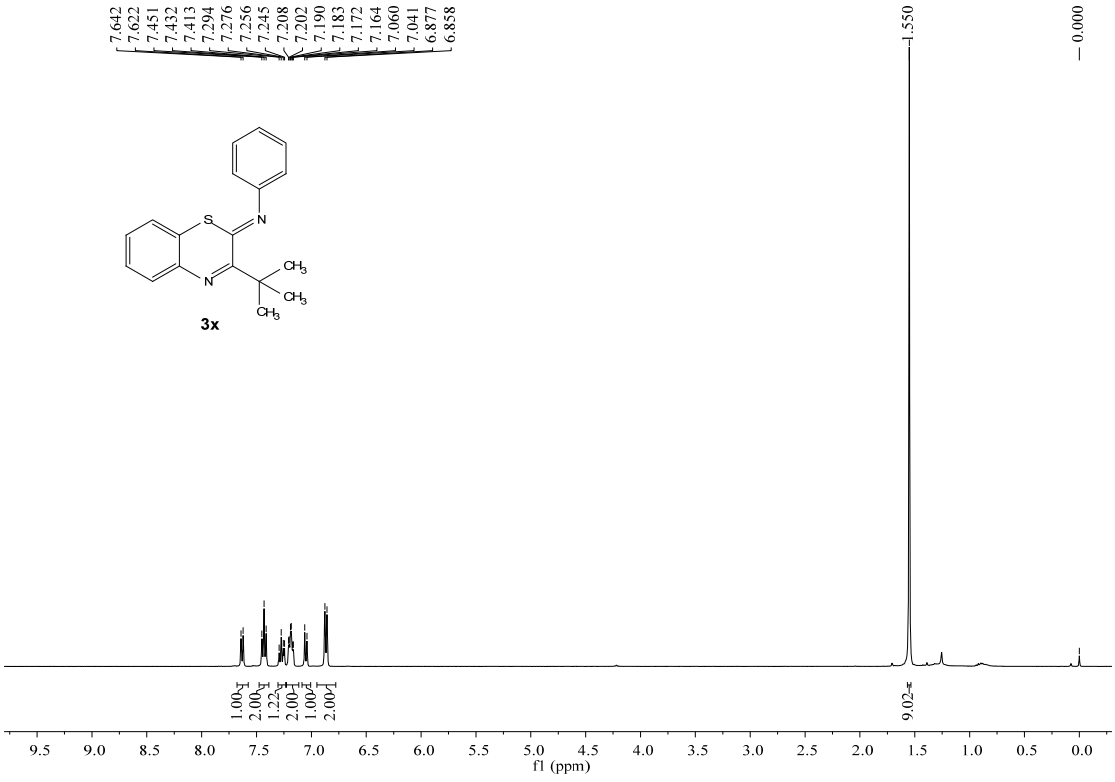


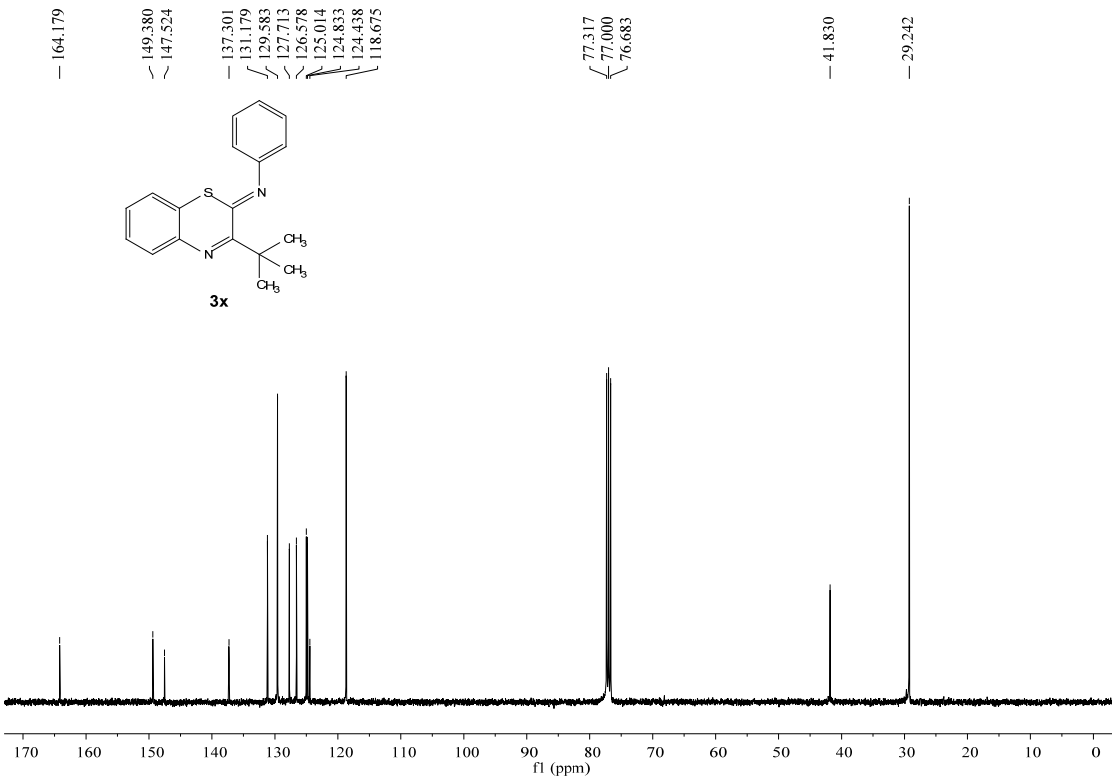
^{1}H and ^{13}C NMR spectra of 3w



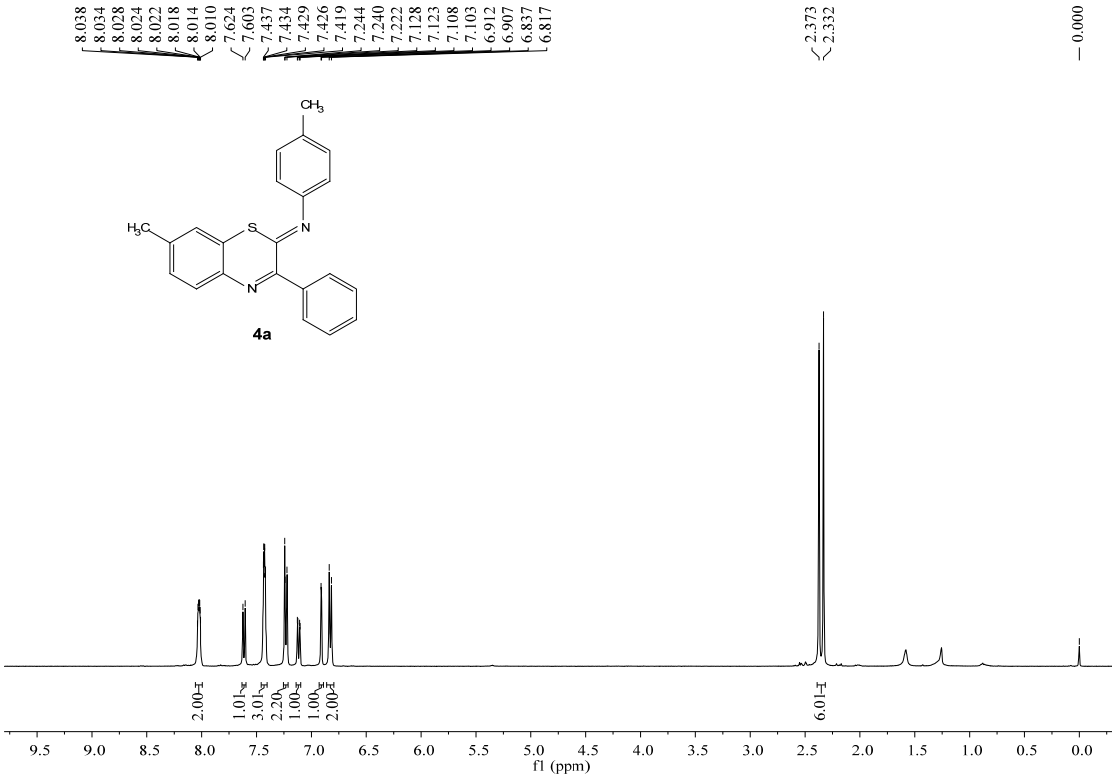


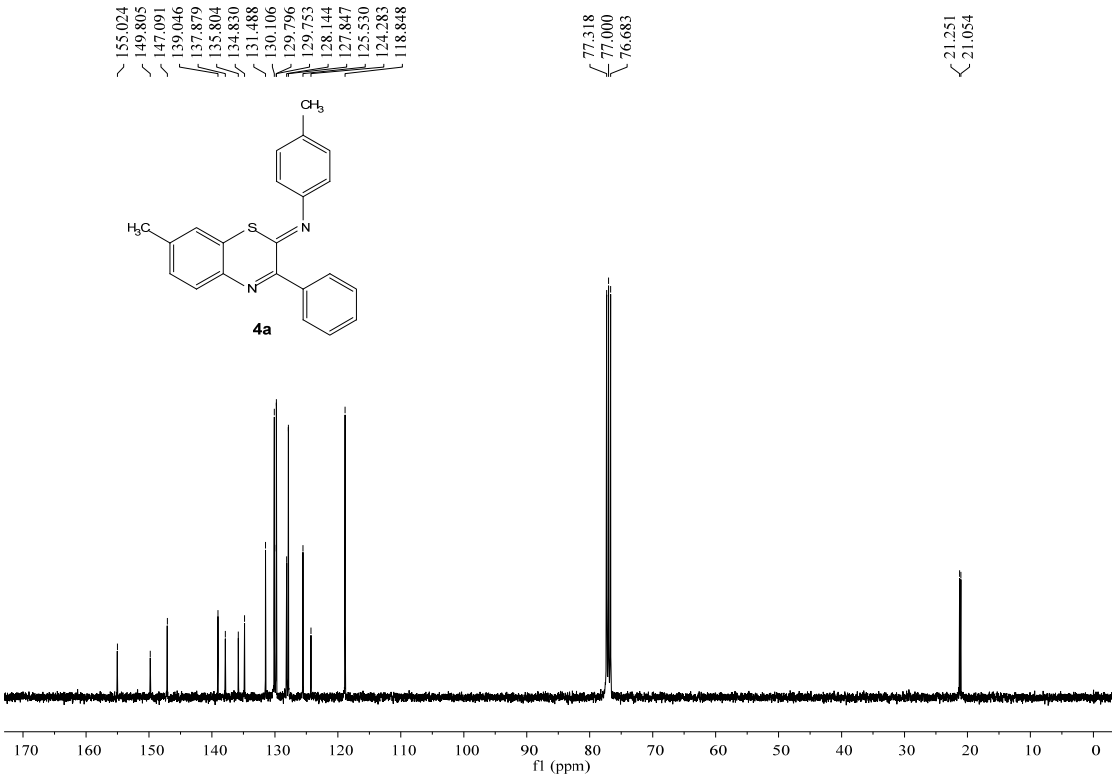
^{1}H and ^{13}C NMR spectra of 3x



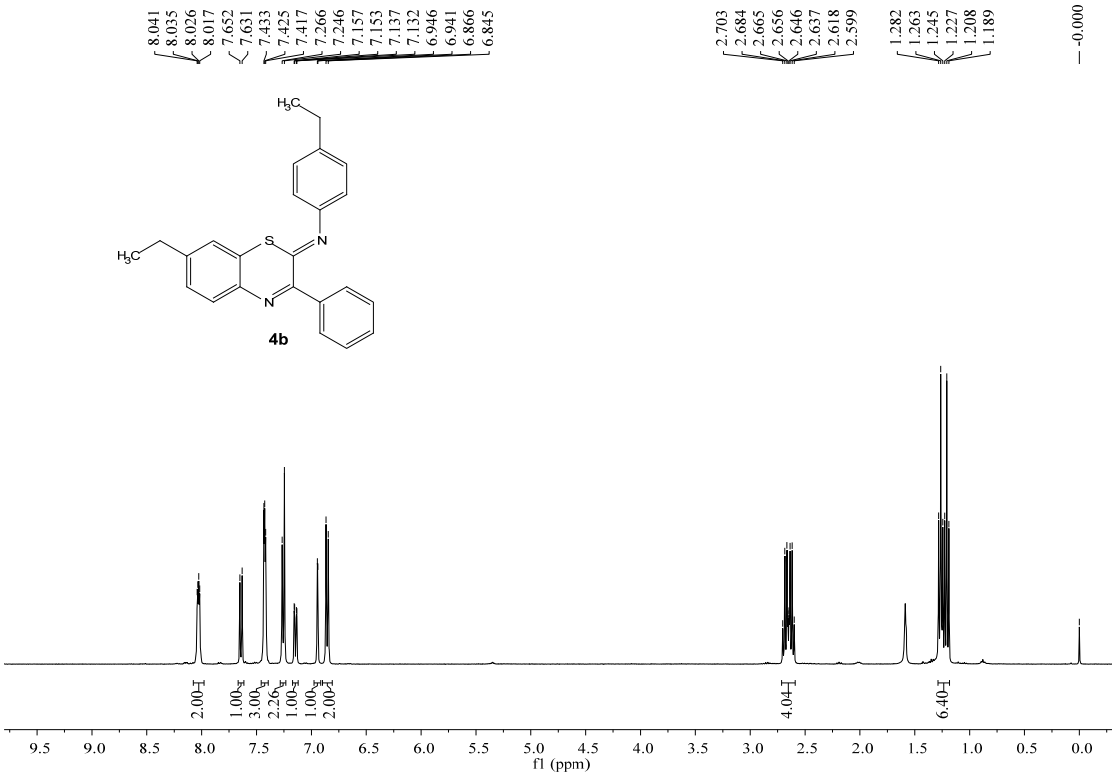


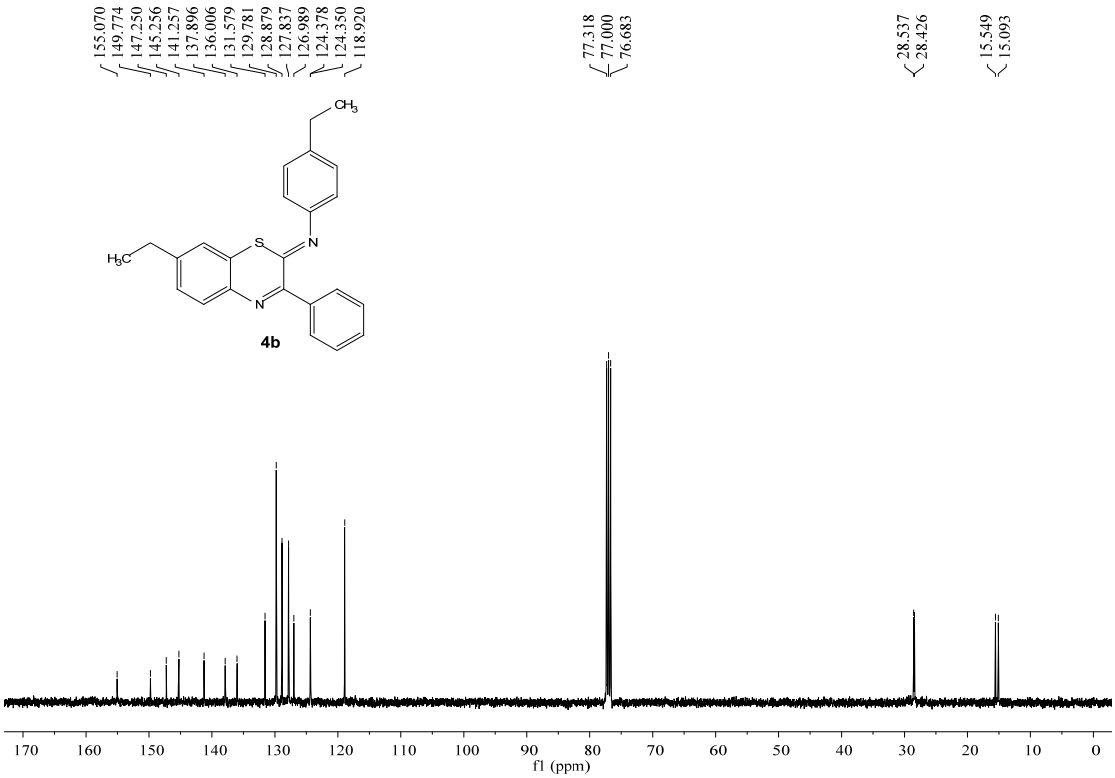
^{1}H and ^{13}C NMR spectra of 4a



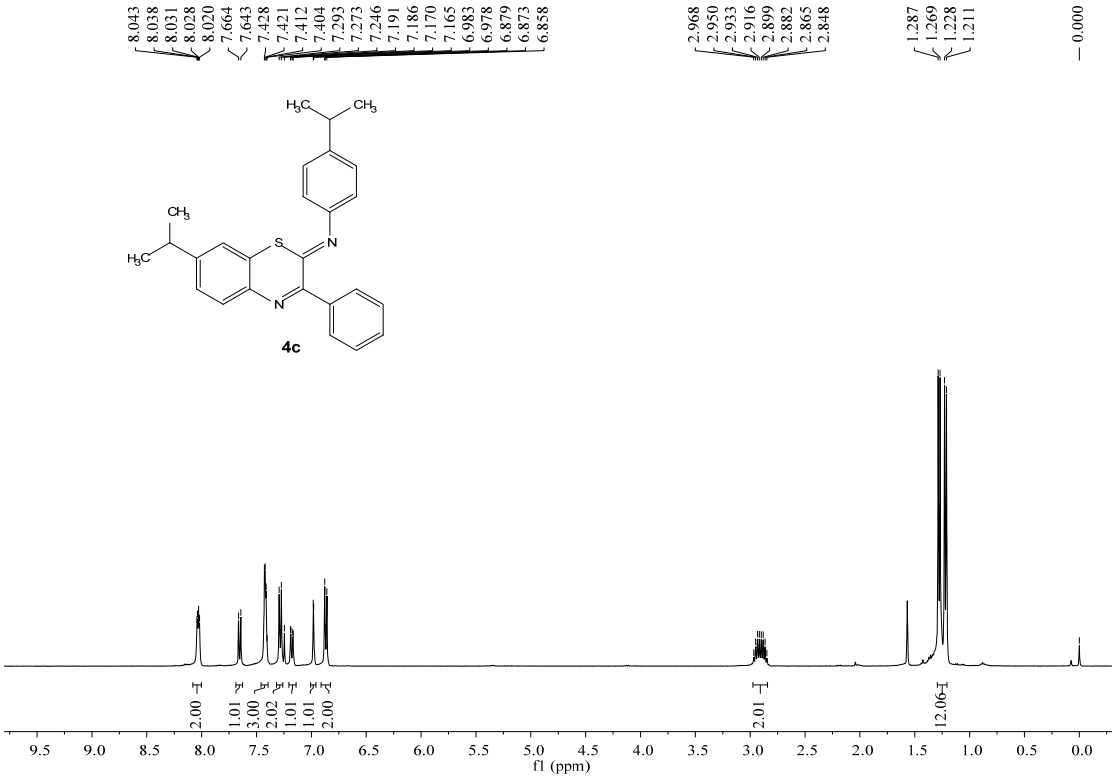


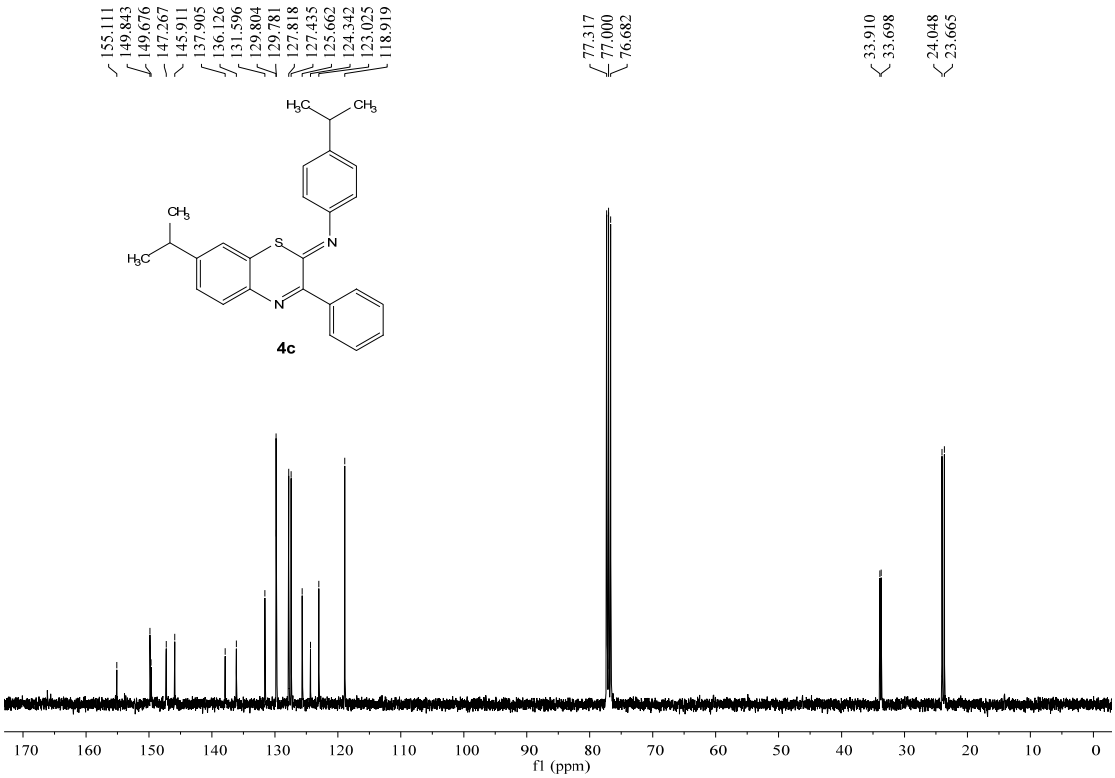
^{1}H and ^{13}C NMR spectra of 4b



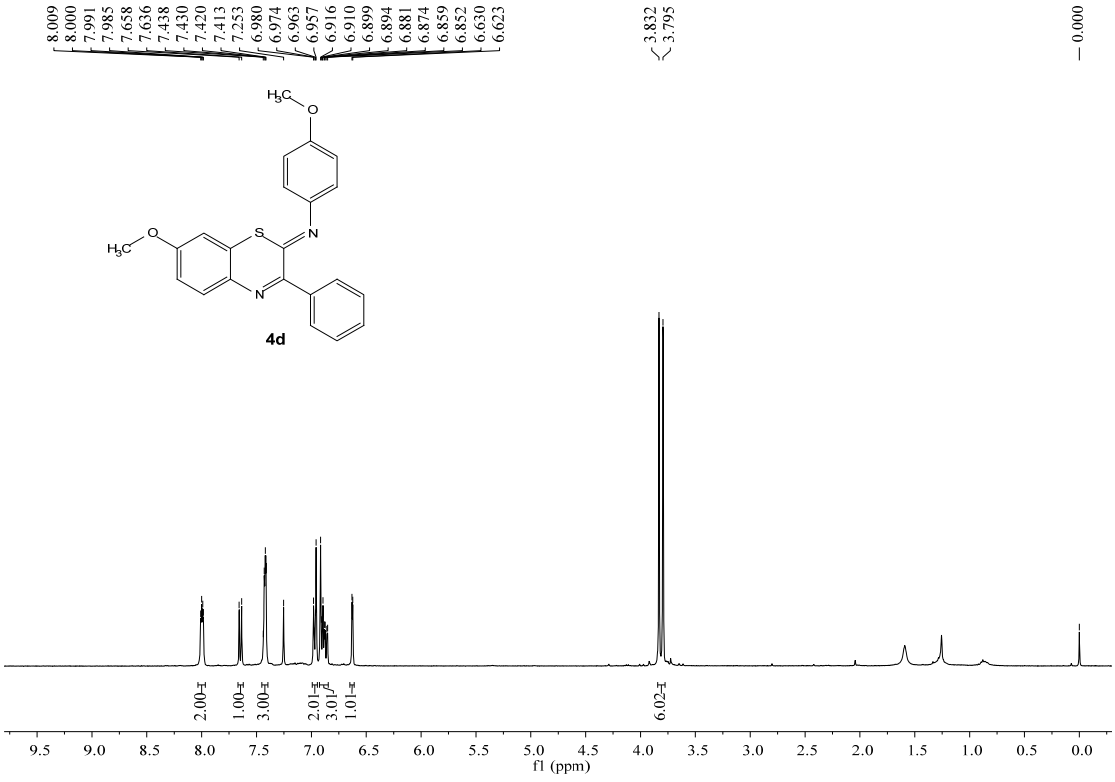


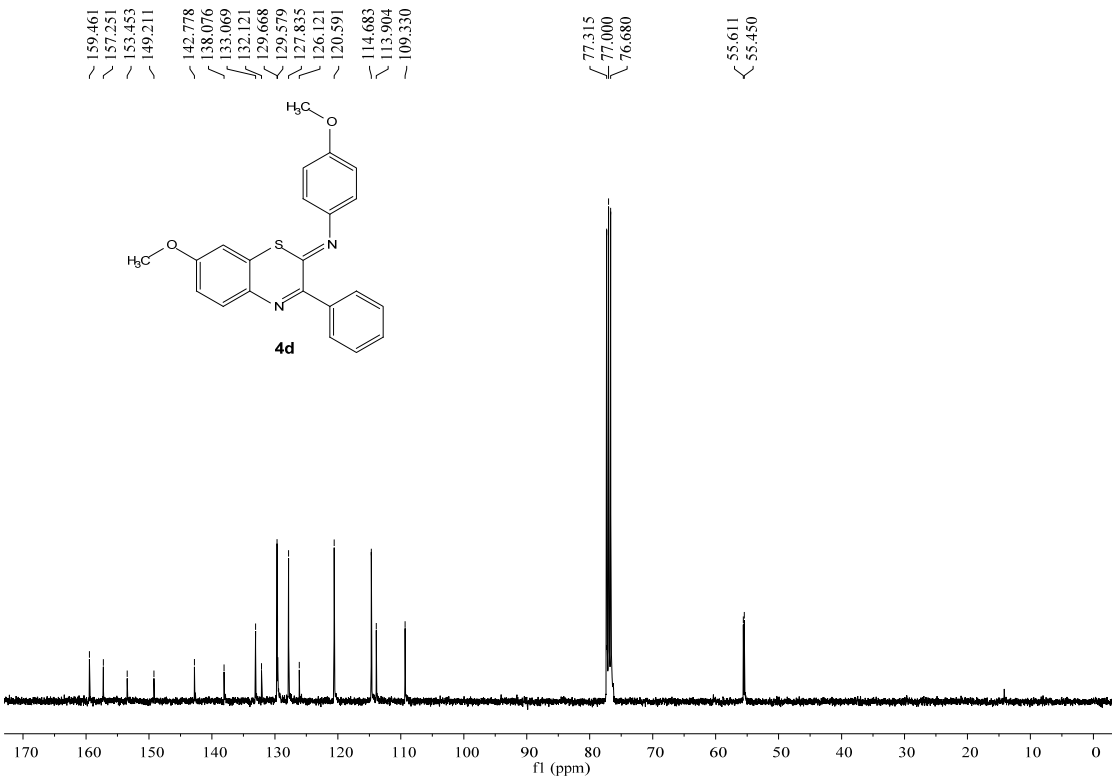
^{1}H and ^{13}C NMR spectra of 4c



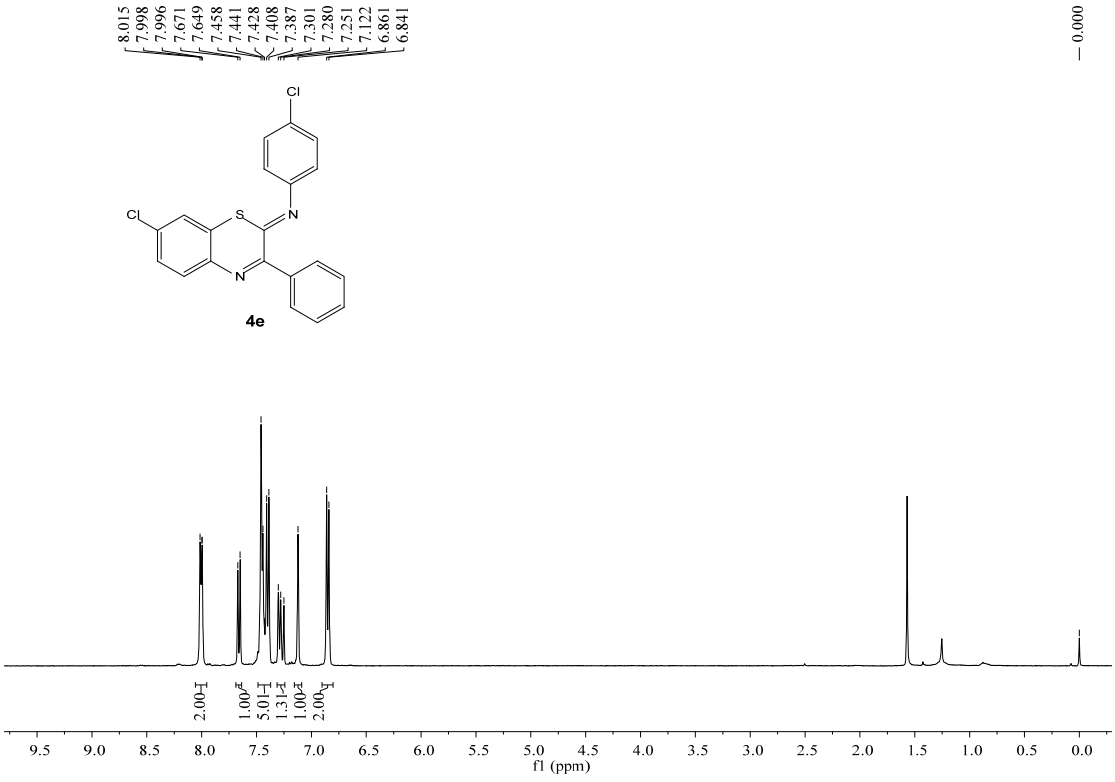


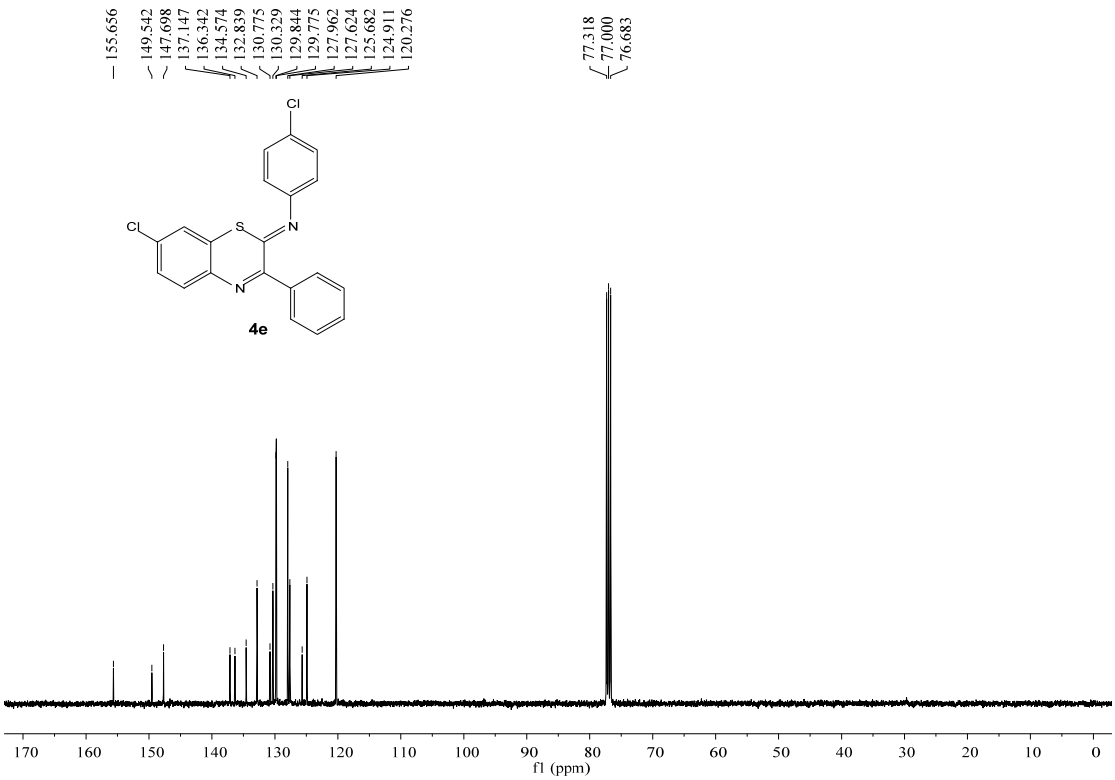
^{1}H and ^{13}C NMR spectra of 4d



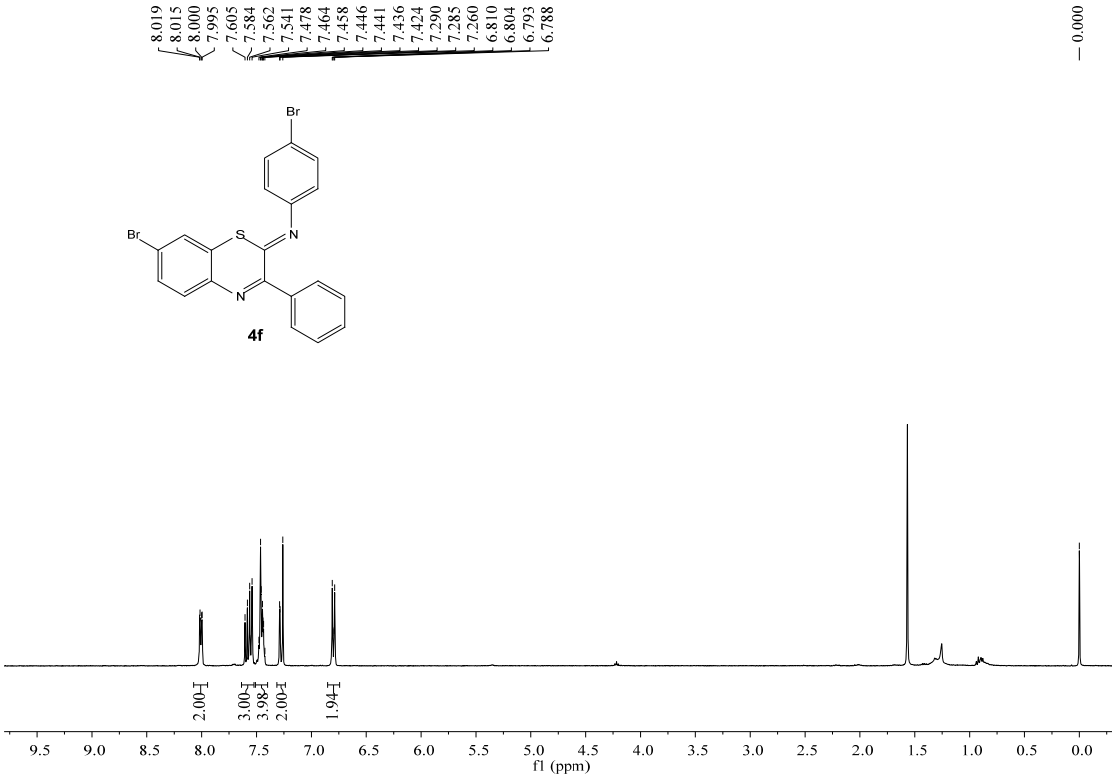


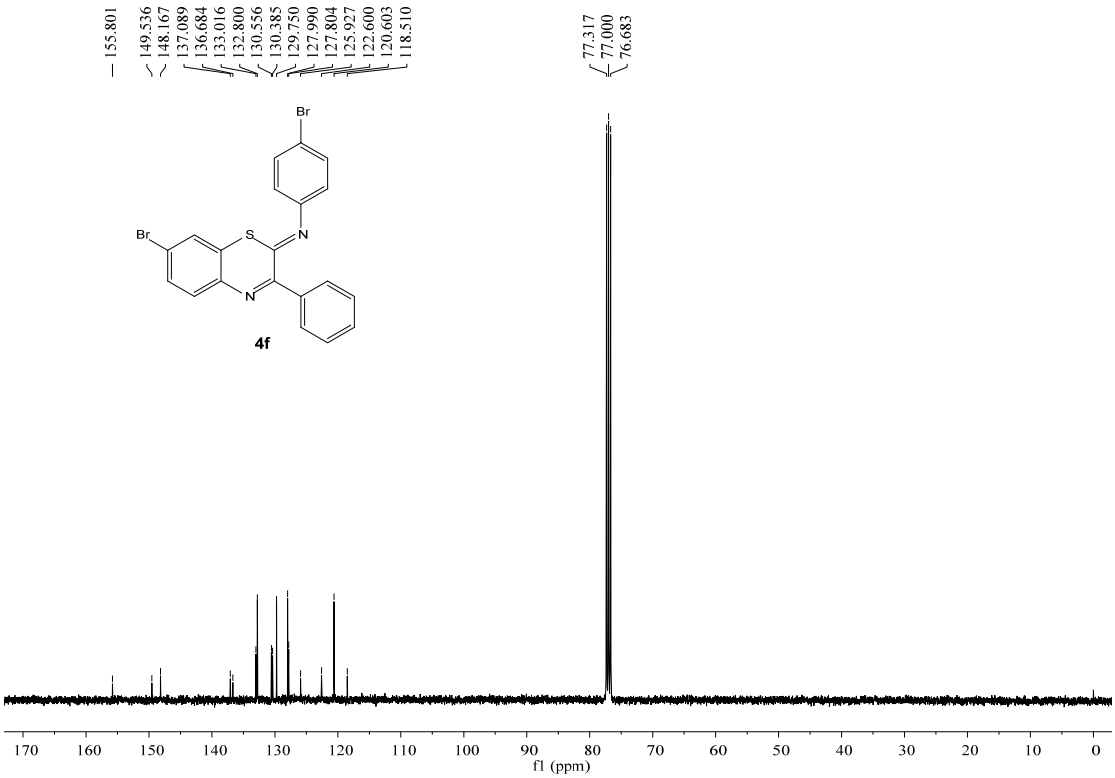
^{1}H and ^{13}C NMR spectra of 4e



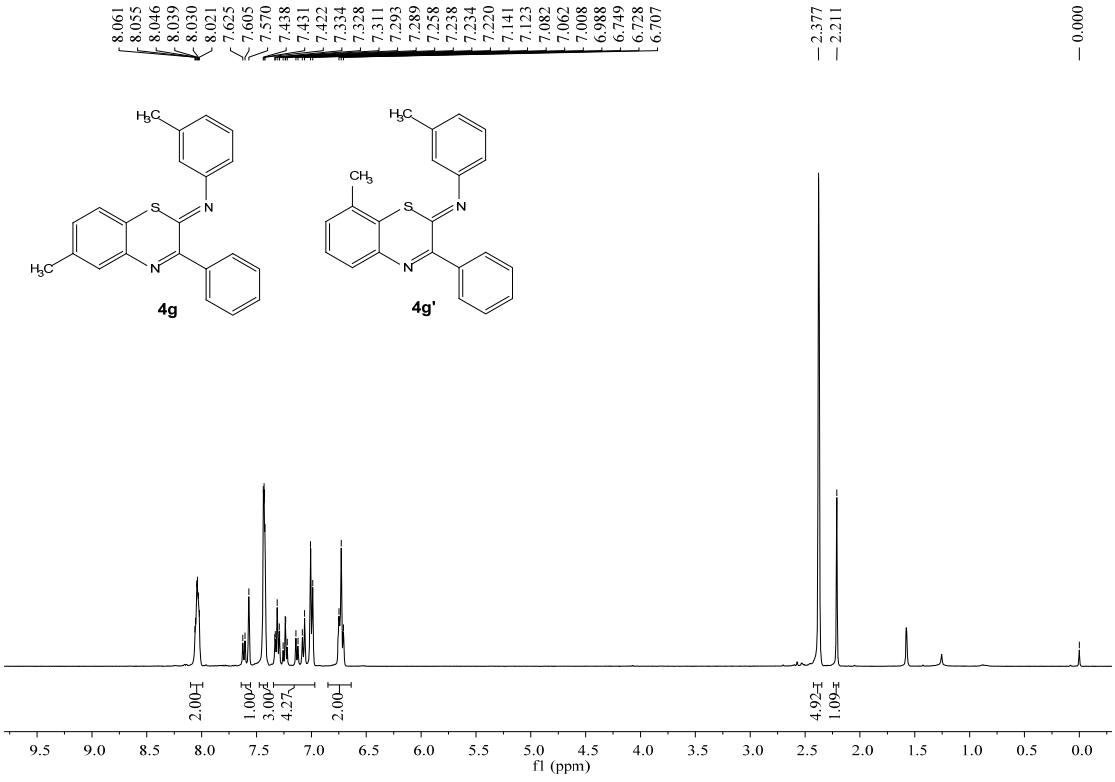


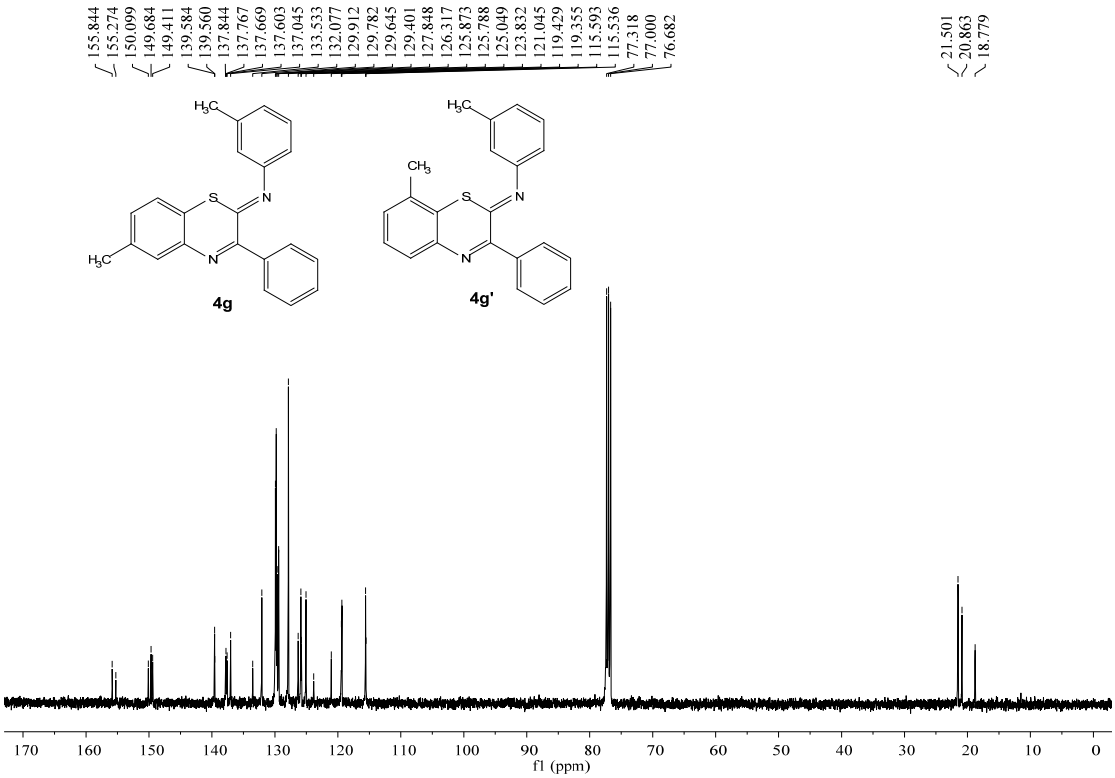
^{1}H and ^{13}C NMR spectra of 4f



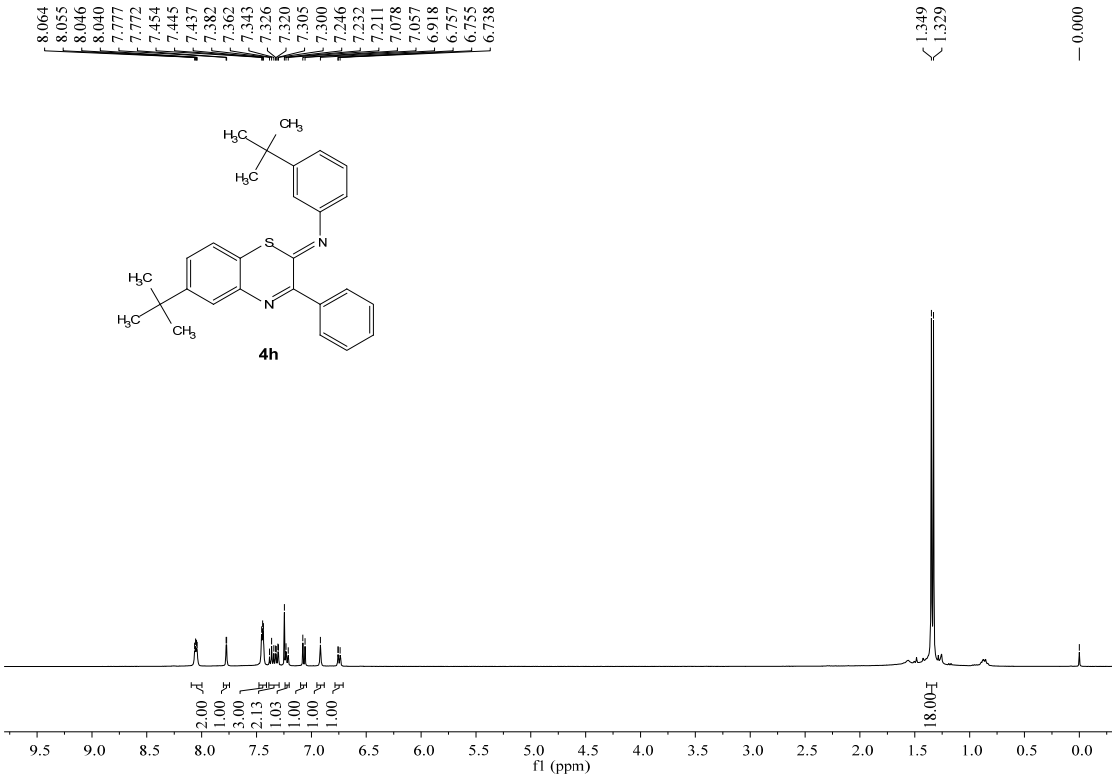


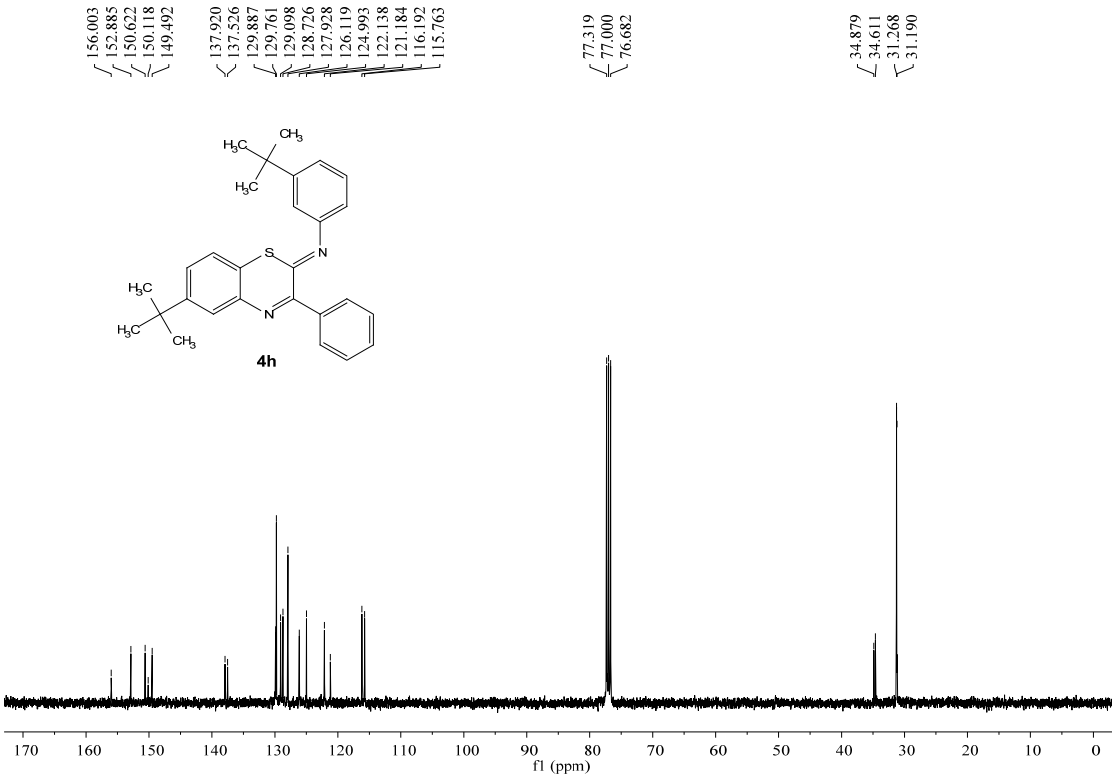
^{1}H and ^{13}C NMR spectra of 4g+4g'



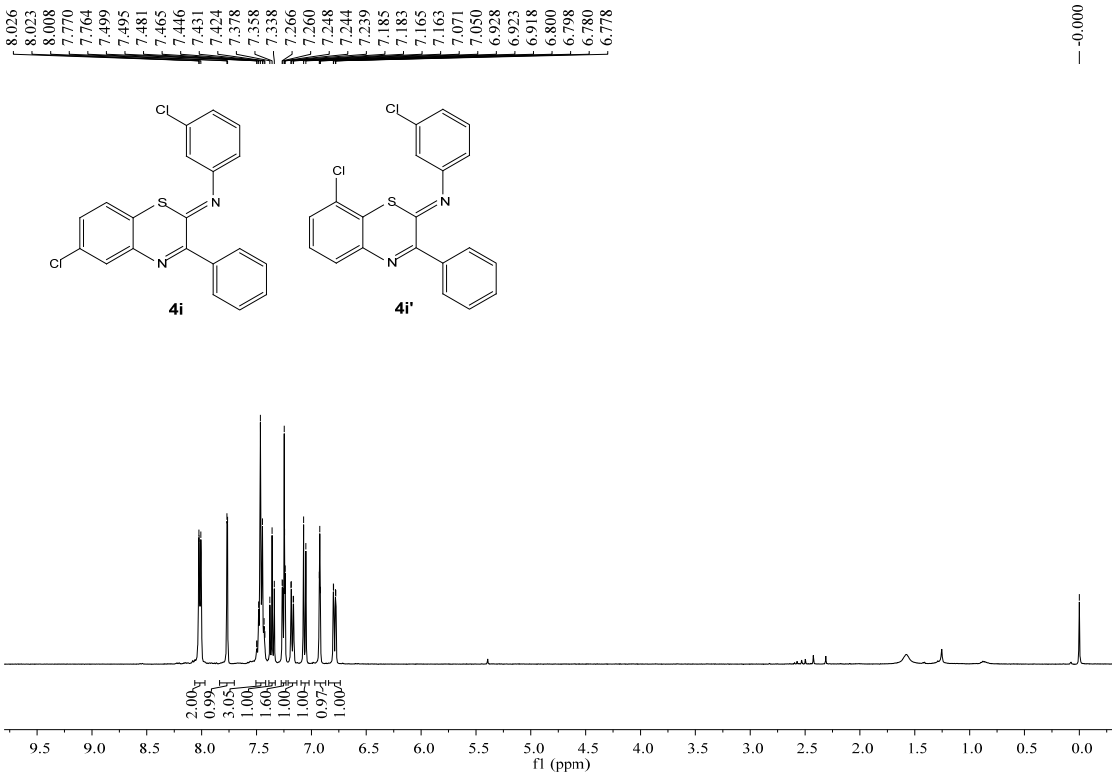


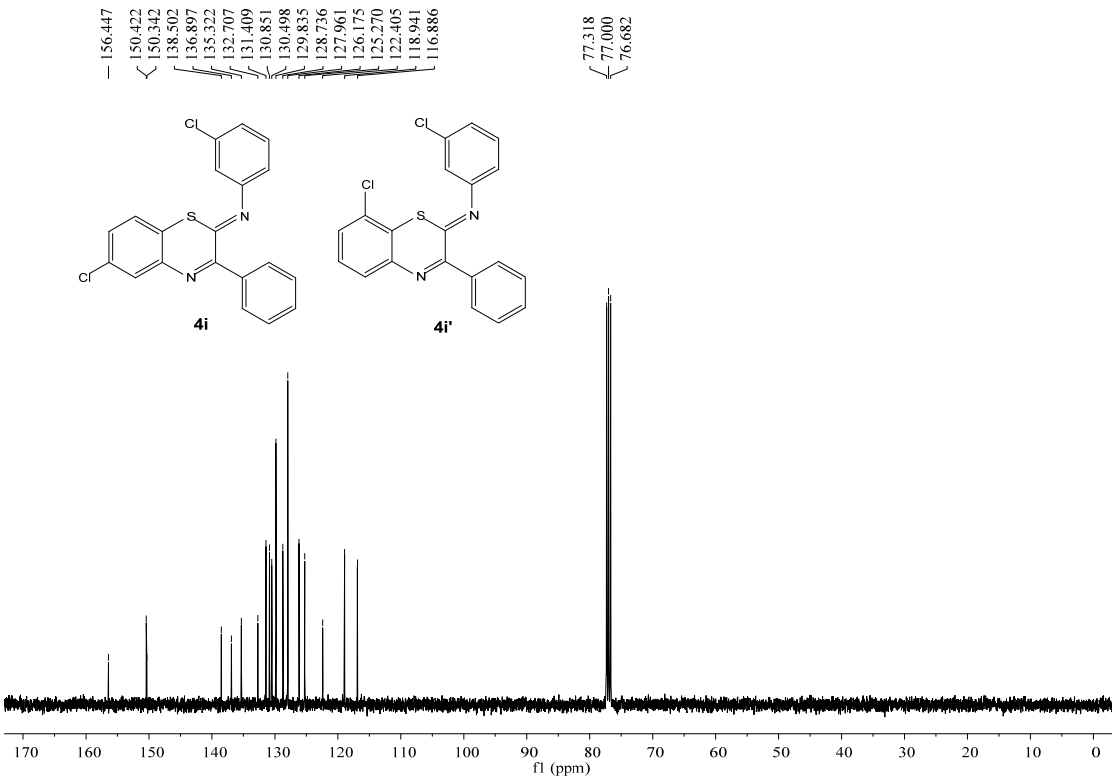
^{1}H and ^{13}C NMR spectra of 4h



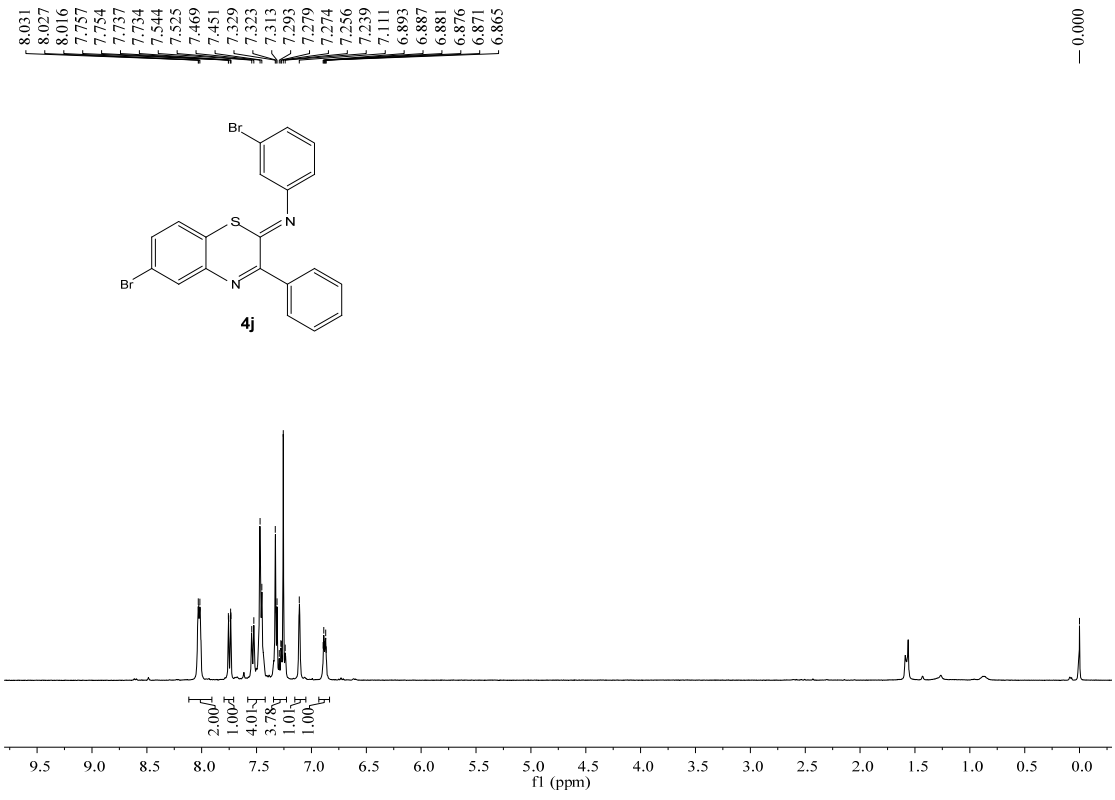


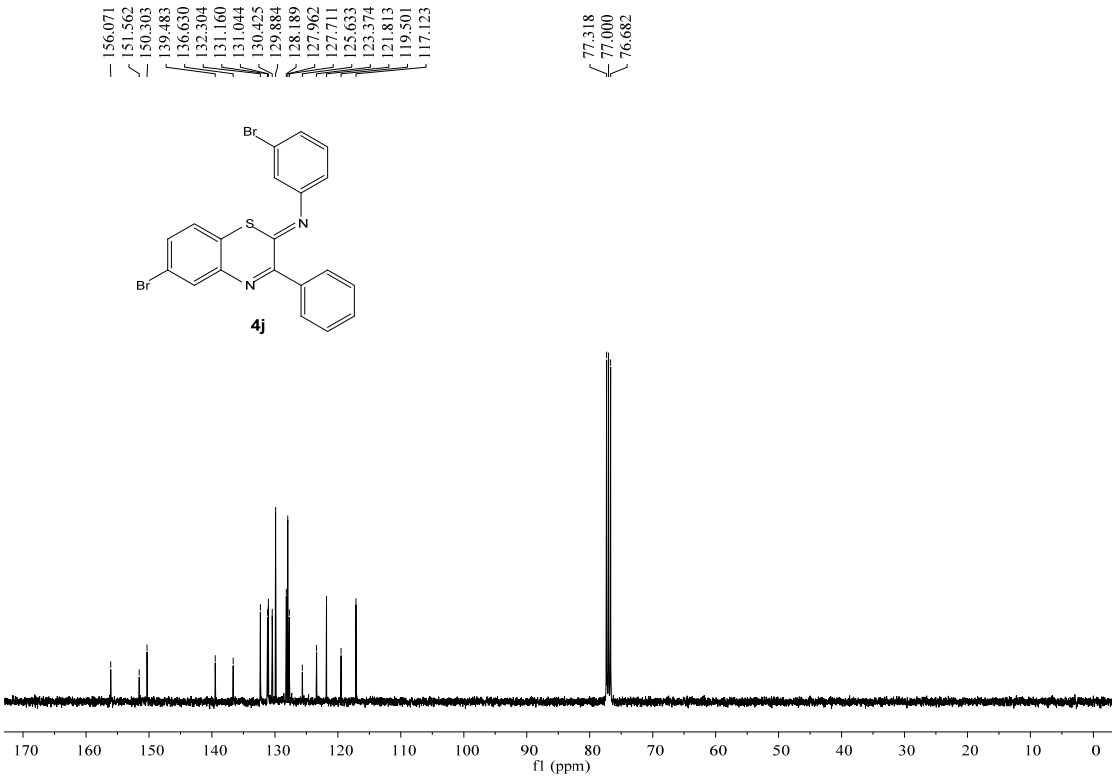
^{1}H and ^{13}C NMR spectra of 4i+4i’





^{1}H and ^{13}C NMR spectra of 4j+4j'

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125.633
123.374
121.813
119.501
117.123
77.318
77.000
76.682
Br
S
N
Br
N
4j
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160
150
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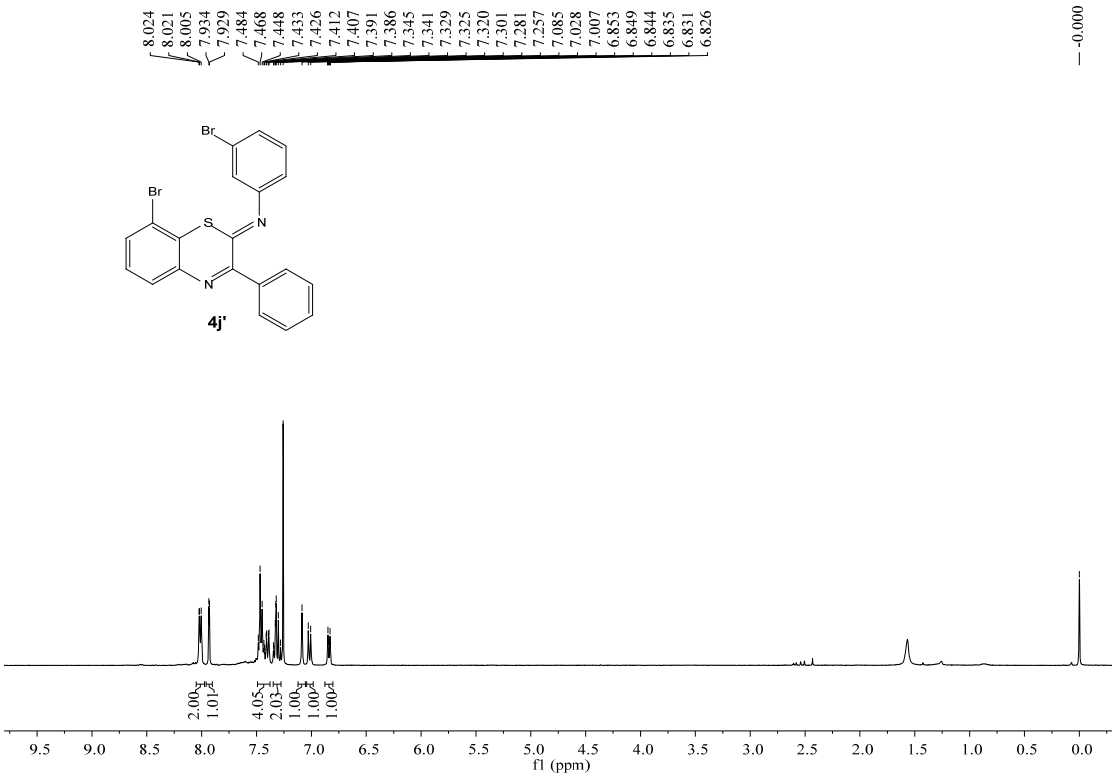
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.007
6.853
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6.844
6.835
6.831
6.826
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Br
S
N
N
4j'
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1.01
4.05
2.03
1.00
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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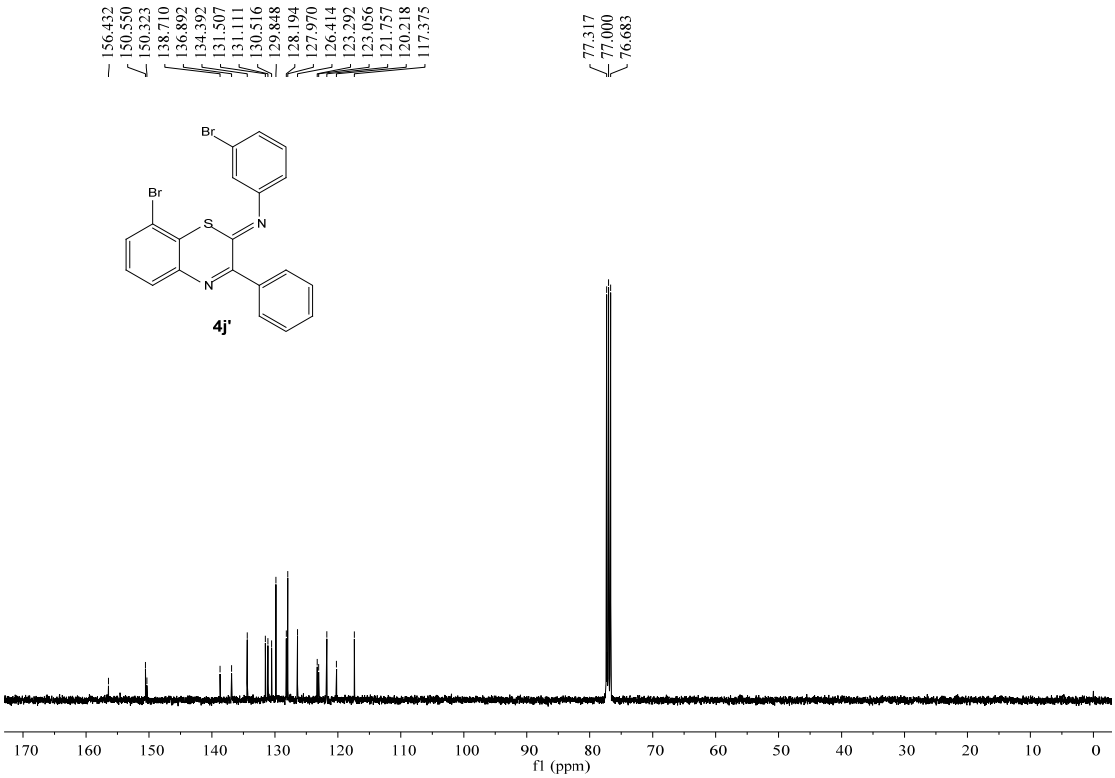
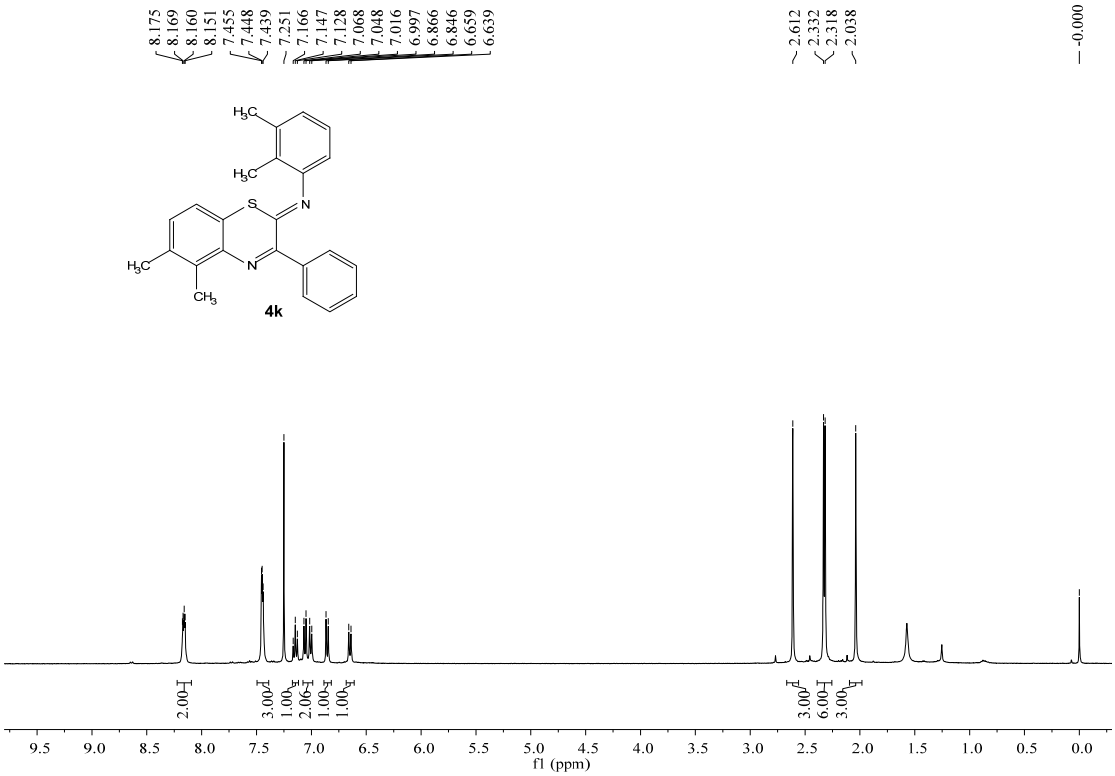
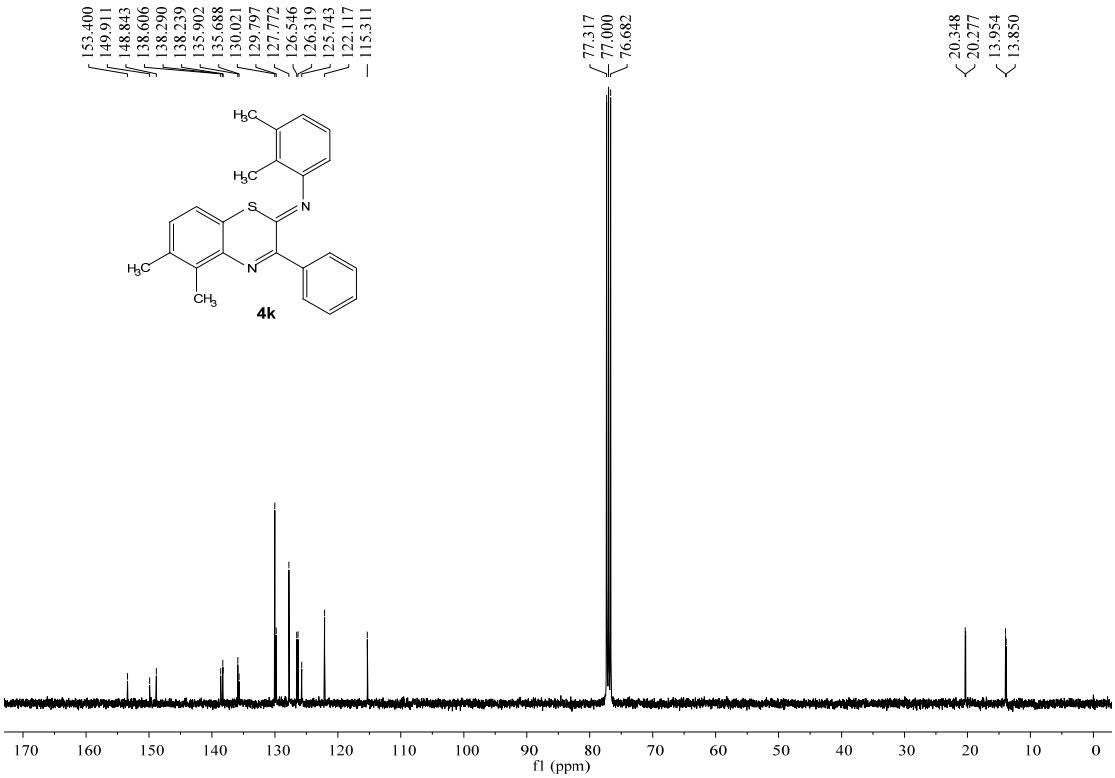
f1 (ppm)

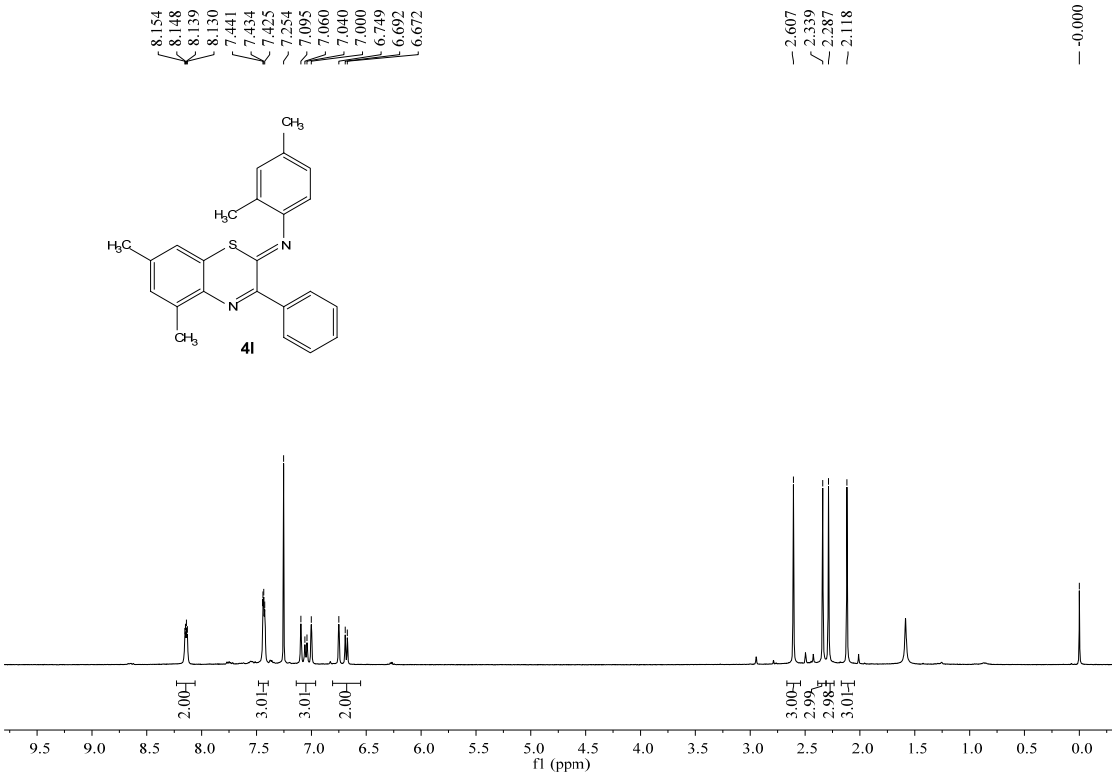


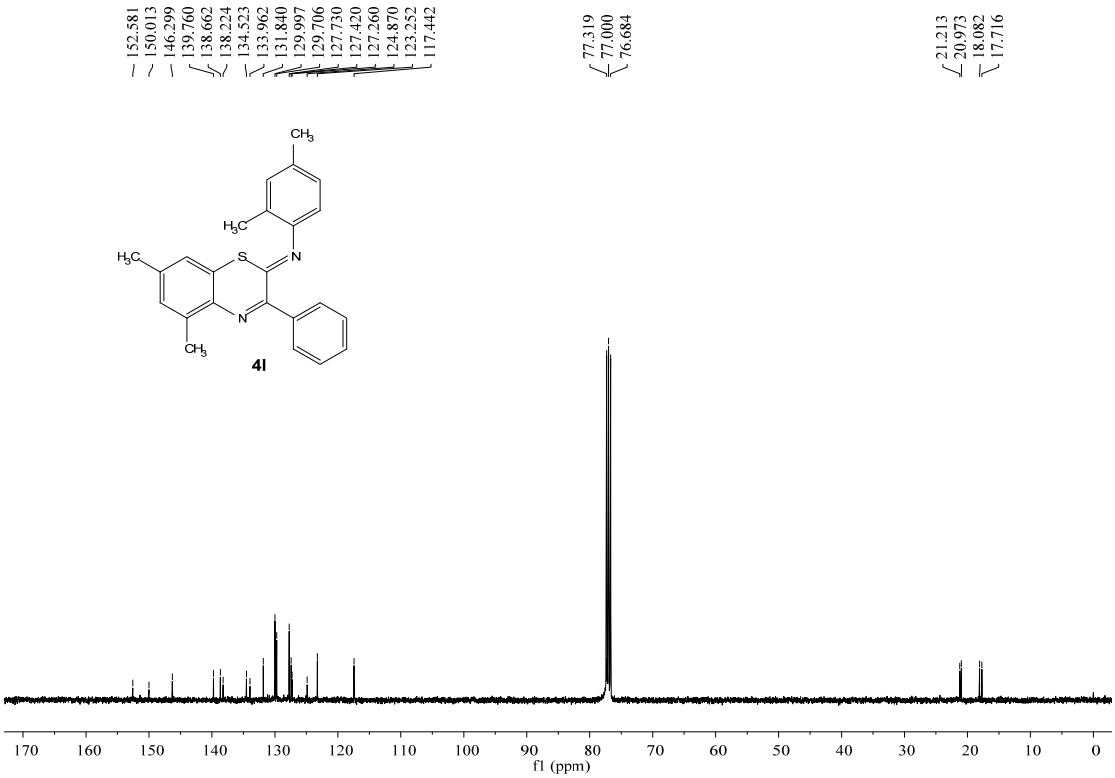
^{1}H and ^{13}C NMR spectra of 4k



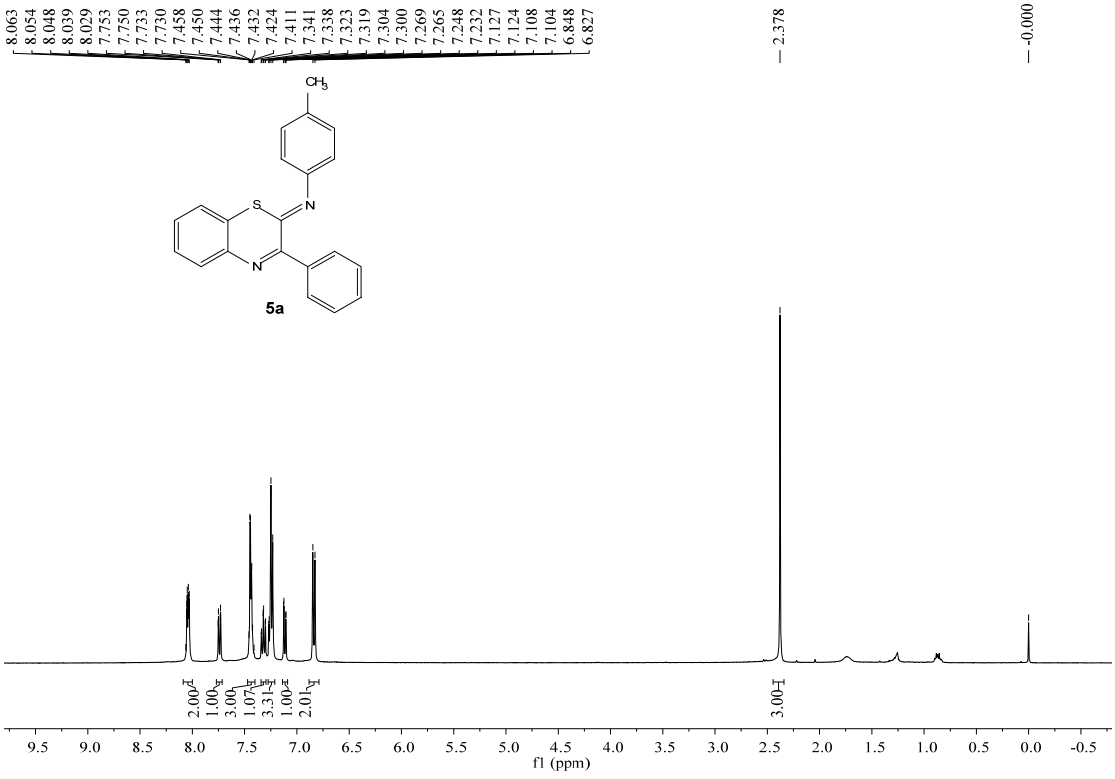


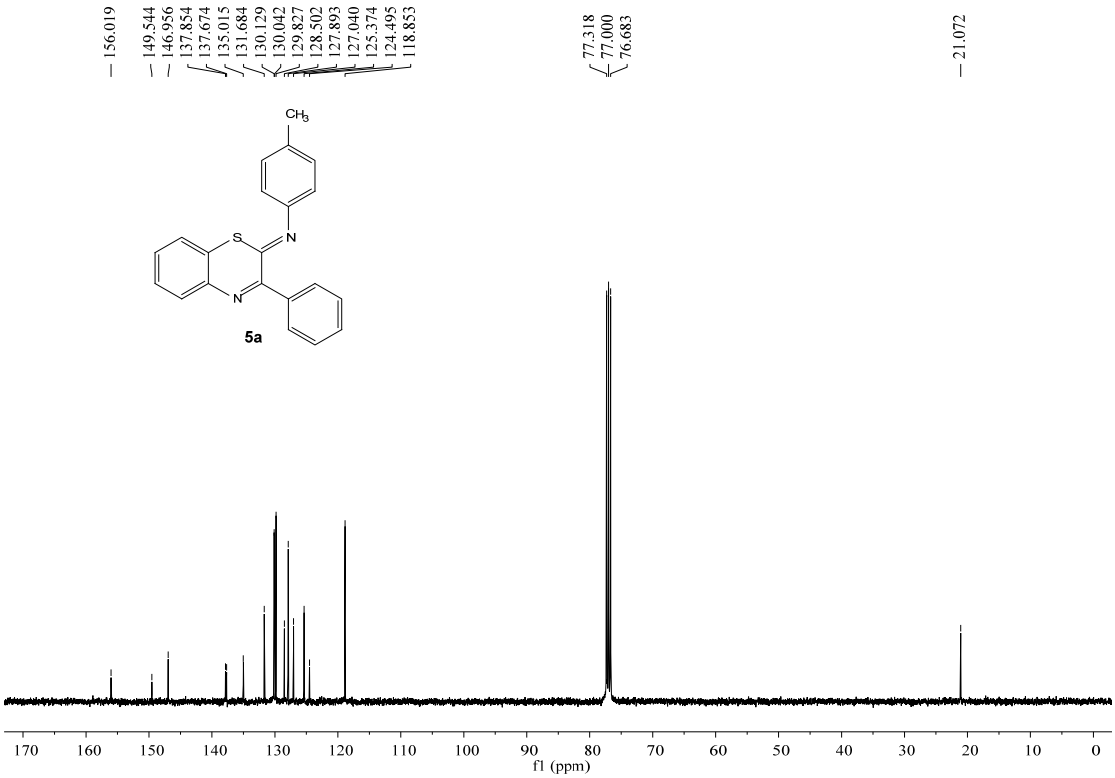
^{1}H and ^{13}C NMR spectra of 4l





^{1}H and ^{13}C NMR spectra of 5a

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5a
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90
80
70
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50
40
30
20
10
0
f1 (ppm)