Iodine-Catalyzed Direct C-H Thiolation of Imidazo[1,5-a]quinolines for the Synthesis of 3-Sulfenylimidazo[1,5-a]quinolines

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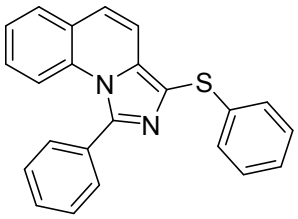
Supporting Information

General Remarks

^{1}HNMR and ^{13}CNMR spectra were recorded at 400MHz and 100MHz respectively, using tetramethylsilane (TMS) as internal reference, in $CDCl_3$. HRMS was obtained using electrospray ionization (ESI) method on a TOF mass analyzer. Melting points were determined on a melting point apparatus and are uncorrected. Unless otherwise indicated, all commercial reagents and solvents were used without further purification. All the imidazo[1,5-a]N-heterocyclics **1** were prepared by using following the reported methodology.[1-5] Products were purified by flash chromatography on 200−300 mesh silica gels using petroleum ether/ethyl acetate as eluent.

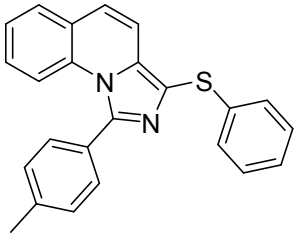
Characterization Data of the Product

1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3aa)



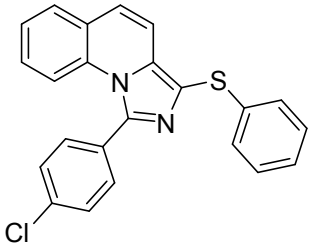
White solid (65 mg, 92%), melting point 156-159 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.65 (m, 3H), 7.56-7.51 (m, 5H), 7.37-7.33 (m, 1H), 7.26-7.15 (m, 6H), 7.11-7.07 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.1, 138.0, 136.6, 134.2, 133.0, 132.4, 129.7, 129.6, 129.4, 128.8, 128.8, 127.8, 127.2, 125.6, 125.5, 123.5, 122.5, 117.4, 116.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}N_2S$ 353.1107, found 353.1113.

3-(phenylthio)-1-(p-tolyl)imidazo[1,5-a]quinoline (3ba)



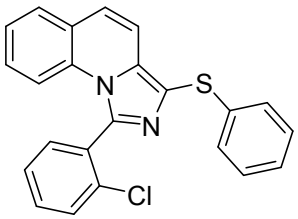
White solid (56 mg, 76%), melting point 210-212 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.62-7.52 (m, 4H), 7.38-7.32 (m, 3H), 7.27-7.14 (m, 6H), 7.11-7.09 (m, 1H), 2.47 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 143.3, 139.6, 138.1, 134.1, 132.5, 130.1, 129.6, 129.5, 128.8, 128.0, 127.7, 127.1, 125.6, 125.5, 125.5, 123.4, 122.3, 117.4, 116.5, 21.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}N_2S$ 367.1264, found 367.1269.

1-(4-chlorophenyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ca)



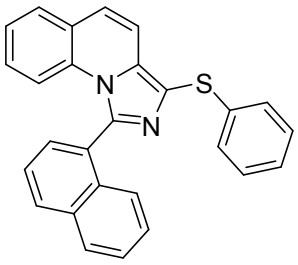
Yellow solid (58 mg, 75%), melting point 173-179 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 3H), 7.58-7.50 (m, 4H), 7.41-7.37 (m, 1H), 7.31-7.28 (m, 1H), 7.25-7.17 (m, 5H), 7.12-7.09 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.8, 137.7, 135.7, 134.4, 132.2, 131.4, 131.1, 130.9, 129.1, 129.0, 128.8, 127.9, 127.3, 125.8, 125.6, 123.7, 122.9, 117.2, 116.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2ClS$ 387.0717, found 387.0722.

1-(2-chlorophenyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3da)



White solid (55 mg, 71%), melting point 150-155 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.59-7.46 (m, 4H), 7.40-7.36 (m, 1H), 7.30-7.27 (m, 2H), 7.23-7.17 (m, 5H), 7.11-7.07 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.7, 138.1, 135.3, 133.9, 132.8, 132.5, 132.4, 131.3, 129.8, 128.8, 128.8, 128.5, 127.4, 126.9, 125.7, 125.4, 125.3, 123.7, 122.2, 116.4, 115.9; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2ClS$ 387.0717, found 387.0722.

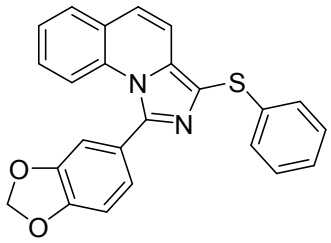
1-(naphthalen-1-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ea)



White solid (74 mg, 92%), melting point 141-145 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.77 (dd, J_1 = 7.0 Hz, J_2=1.2 Hz, 1H), 7.66-7.62 (m, 3H), 7.52-7.48 (m, 1H), 7.36-7.35 (m, 2H), 7.31-7.29 (m, 2H), 7.25 (s, 1H), 7.24-7.20 (m, 3H), 7.13-

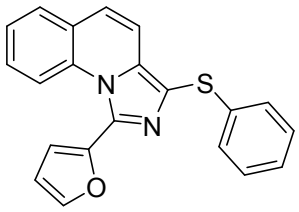
7.09 (m, 1H), 7.01-6.93 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) 141.2, 138.1, 133.9, 133.7, 132.4, 132.3, 130.7, 130.4, 129.0, 128.8, 128.7, 128.5, 128.2, 127.3, 127.2, 126.5, 125.5, 125.4, 125.4, 125.3, 123.6, 122.6, 116.9, 116.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{19}N_2S$ 403.1264, found 403.1271.

1-(benzo[d][1,3]dioxol-5-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3fa)



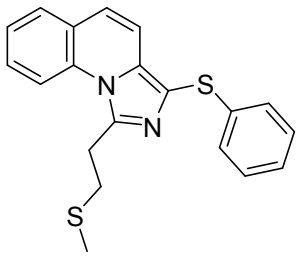
White solid (71 mg, 90%), melting point 179-181 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.52 (d, J = 9.3 Hz, 1H), 7.37 (td, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 7.31-7.28 (m, 1H), 7.25-7.08 (m, 8H), 6.96-6.94 (m, 1H), 6.08 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.8, 147.9, 142.6, 137.9, 134.0, 132.4, 128.8, 128.8, 127.9, 127.3, 126.4, 125.6, 125.6, 124.0, 123.5, 122.2, 117.4, 116.5, 110.1, 108.7, 101.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{17}O_2N_2S$ 397.1005, found 397.1014.

1-(furan-2-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ga)



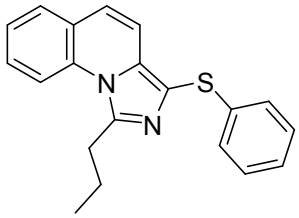
Yellow solid (56 mg, 82%), melting point 146-151 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 2H), 7.55 (d, J = 9.3 Hz, 1H), 7.44-7.37 (m, 2H), 7.25-7.18 (m, 6H), 7.12-7.08 (m, 1H), 6.95-6.94 (m, 1H), 6.68-6.67 (m, 1H), 6.67 (dd, J_1 = 3.3 Hz, J_2 = 1.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.3, 143.4, 137.6, 134.5, 133.0, 132.2, 128.8, 128.6, 127.3, 125.9, 125.7, 125.5, 124.3, 123.1, 116.8, 116.2, 113.5, 112.0; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{15}N_2OS$ 343.0899, found 343.0907.

1-(2-(methylthio)ethyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ha)



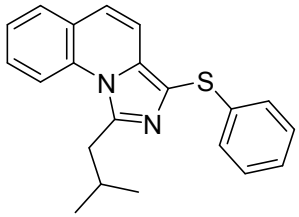
Yellow oil (56 mg, 80%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 1H), 7.70 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.48-7.44 (m, 2H), 7.20-7.06 (m, 6H), 3.73-3.69 (m, 2H), 3.22-3.18 (m, 2H), 2.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.9, 138.1, 134.3, 132.9, 129.1, 128.8, 128.5, 126.8, 125.8, 125.5, 125.4, 123.1, 120.5, 116.6, 116.4, 32.9, 31.3, 15.8; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_2S_2$ 351.0984, found 351.0989.

3-(phenylthio)-1-propylimidazo[1,5-a]quinoline (3ia)



Yellow oil (60 mg, 94%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.5 Hz, 1H), 7.60 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 7.51-7.47 (m, 1H), 7.39-7.33 (m, 2H), 7.11-7.05 (m, 4H), 7.01-6.97 (m, 2H), 3.32 (t, J = 7.7 Hz, 2H), 2.00-1.94 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.9, 137.4, 133.1, 132.1, 127.9, 127.8, 127.7, 127.2, 125.6, 124.7, 124.2, 121.7, 119.2, 115.7, 115.5, 33.3, 19.5, 12.9; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_2S$ 319.1264, found 319.1269.

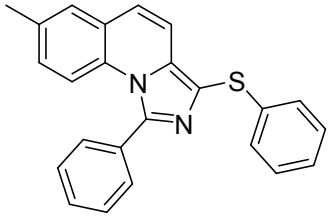
1-isobutyl-3-(phenylthio)imidazo[1,5-a]quinoline (3ja)



Yellow oil (63 mg, 95%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 1H), 7.57 (dd, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 1H), 7.50-7.45 (m, 1H), 7.37-7.31 (m, 2H), 7.09-7.03 (m, 4H), 6.99-6.95 (m, 2H), 3.22 (d, J = 7.0 Hz, 2H), 2.35-2.32 (m, 1H), 1.00 (d, J = 6.6 Hz, 6H); ^{13}C-NMR (100 MHz,

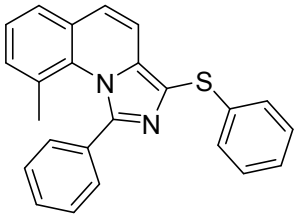
$CDCl_3$) δ 144.3, 138.5, 134.2, 133.0, 129.0, 128.7, 128.2, 126.6, 125.8, 125.3, 125.2, 122.8, 120.2, 116.7, 116.5, 41.0, 26.4, 22.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}N_2S$ 333.1420, found 333.1427.

7-methyl-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3ka)



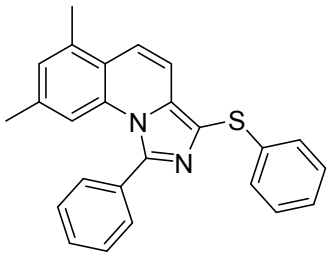
White solid (59 mg, 80%), melting point 154-157 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.54-7.52 (m, 4H), 7.47-7.42 (m, 2H), 7.31-7.29 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15-7.11 (m, 2H), 7.07-7.04 (m, 1H), 2.41 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.8, 138.1, 135.3, 134.1, 133.1, 130.4, 129.8, 129.5, 128.9, 128.8, 128.7, 128.7, 127.1, 125.6, 125.5, 123.4, 122.3, 117.2, 116.4, 20.8; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}N_2S$ 367.1264, found 367.1267.

9-methyl-1-phenyl-3-(phenylthio)imidazo[1, 5-a]quinoline (3la)



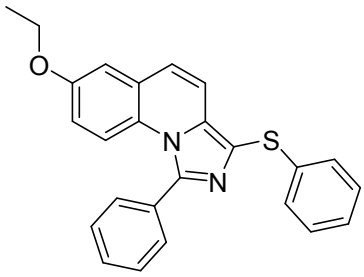
White solid (66 mg, 90%), melting point 155-159 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 9.2 Hz, 1H), 7.32-7.31 (m, 2H), 7.21-7.19 (m, 4H), 7.15-7.08 (m, 3H), 7.05-7.01 (m, 2H), 1.70 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.1, 136.7, 134.9, 132.6, 131.2, 130.3, 127.8, 127.8, 127.7, 127.6, 126.9, 126.1, 125.3, 124.9, 124.5, 124.4, 123.0, 122.7, 115.3, 20.6; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}N_2S$ 367.1264, found 367.1269.

6, 8-dimethyl-1-phenyl-3-(phenylthio)imidazo[1, 5-a]quinoline (3ma)



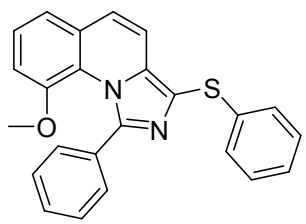
White solid (66 mg, 87%), melting point 163-166 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.54-7.49 (m, 4H), 7.35 (d, J = 9.6 Hz, 1H), 7.23-7.17 (m, 5H), 7.11-7.09 (m, 1H), 7.04 (s, 1H), 2.59 (s, 3H), 2.15 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.9, 138.2, 137.5, 135.6, 134.3, 133.3, 132.6, 129.7, 129.4, 128.8, 128.6, 128.2, 127.1, 125.4, 121.8, 121.7, 119.8, 116.1, 115.0, 21.7, 19.9. HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}N_2S$ 381.1420, found 381.1423.

7-ethoxy-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3na)



White solid (71 mg, 90%), melting point 143-147 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.54-7.50 (m, 4H), 7.46 (d, J = 9.3 Hz, 1H), 7.26-7.17 (m, 4H), 7.11-7.07 (m, 3H), 6.80 (dd, J_1 = 9.3 Hz, J_2 = 2.8 Hz, 1H), 4.07 (q, J = 6.9 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.2, 142.5, 138.1, 133.8, 132.9, 129.7, 129.6, 128.8, 127.2, 127.0, 126.5, 125.5, 123.4, 122.3, 118.6, 116.9, 116.0, 111.5, 63.8, 14.7; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}ON_2S$ 397.1369, found 397.1371.

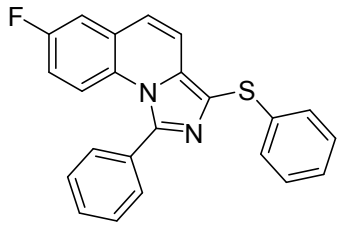
9-methoxy-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3oa)



Yellow solid (68 mg, 89%), melting point 133-137 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.48 (d, J = 9.2 Hz, 1H), 7.40-7.34 (m, 4H), 7.27 (d, J = 1.2 Hz, 1H), 7.25-7.23 (m, 2H),

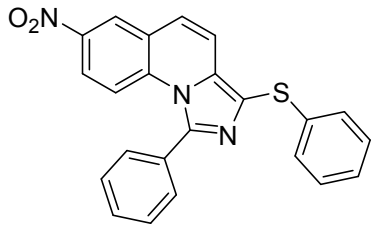
7.20-7.16 (m, 2H), 7.10-7.07 (m, 2H), 6.84 (dd, J_1=8.0 Hz, J_2=1.2 Hz, 1H), 3.05 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.1, 147.1, 138.0, 135.8, 135.2, 128.8, 128.5, 128.0, 127.9, 127.0, 126.4, 125.4, 125.3, 123.1, 123.0, 122.5, 119.7, 117.2, 110.3, 53.7; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}ON_2S$ 383.1213, found 383.1216.

7-fluoro-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3pa)



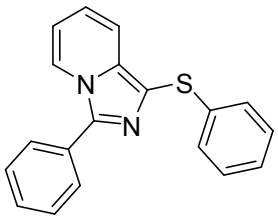
White solid (63 mg, 85%), melting point 165-169 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.60-7.51 (m, 5H), 7.33 (dd, J_1 = 8.5 Hz, J_2 = 2.9 Hz, 1H), 7.28-7.26 (m, 2H), 7.22-7.19 (m, 2H), 7.13-7.08 (m, 2H), 6.97-6.92 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.8, 158.4, 143.0, 137.7, 133.8, 132.7, 129.8, 129.7, 129.0, 128.8, 127.4, 127.3, 125.7, 123.3, 122.6, 122.6, 119.1, 119.1, 117.9, 115.4, 115.2, 113.9, 113.7; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2FS$ 371.1013, found 371.1019.

7-nitro-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3qa)



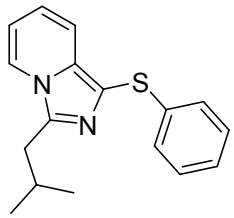
Yellow solid (58 mg, 73%), melting point 208-212 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55-8.53 (m, 1H), 8.07-8.02 (m, 1H), 7.70-7.56 (m, 7H), 7.31-7.29 (m, 2H), 7.25-7.14 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.9, 130.3, 129.6, 129.4, 129.3, 129.2, 128.9, 127.8, 126.1, 126.1, 124.1, 124.0, 122.4, 122.3, 122.2, 121.9, 119.1, 118.1, 117.9; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}O_2N_3S$ 398.0958, found 398.0963.

3-phenyl-1-(phenylthio)imidazo[1,5-a]pyridine (3ra)



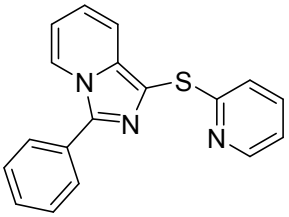
Yellow oil (57 mg, 94%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (m, 1H), 7.75-7.72 (m, 2H), 7.54 (dt, J_1 = 9.1 Hz, J_2 = 1.1 Hz, 1H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 1H), 7.13-7.06 (m, 4H), 7.00-6.96 (m, 1H), 6.78-6.74 (m, 1H), 6.57-6.54 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.2, 137.3, 134.0, 128.5, 128.0, 127.9, 127.7, 127.1, 125.9, 124.3, 120.9, 120.0, 118.9, 117.3, 112.8; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}N_2S$ 303.0951, found 303.0956.

3-isobutyl-1-(phenylthio)imidazo[1,5-a]pyridine (3sa)



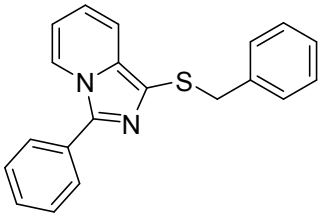
Yellow oil (42 mg, 74%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.55 (dt, J_1 = 9.1 Hz, J_2 = 1.1 Hz, 1H), 7.17-7.05 (m, 5H), 6.80-6.76 (m, 1H), 6.64-6.62 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.7, 139.0, 134.1, 128.7, 126.5, 125.1, 121.3, 120.0, 118.2, 117.3, 112.9, 35.6, 27.5, 22.6; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2S$ 283.1264, found 283.1268.

3-phenyl-1-(pyridin-2-ylthio)imidazo[1,5-a]pyridine (3rb)



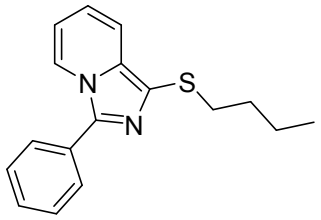
Yellow oil (51 mg, 84%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.76-7.74 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.32-7.27 (m, 1H), 6.87-6.76 (m, 3H), 6.63-6.59 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.8, 148.1, 138.7, 135.7, 134.5, 128.3, 128.2, 128.0, 127.1, 121.1, 120.5, 119.4, 118.7, 117.2, 116.7, 113.0; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}N_3S$ 304.0903, found 304.0899.

1-(benzylthio)-3-phenylimidazo[1,5-a]pyridine (3rc)



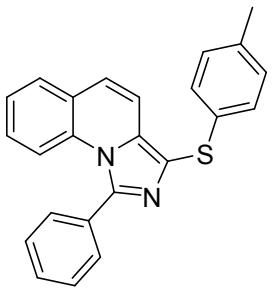
Yellow oil (52 mg, 82%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (dt, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 1H), 7.74-7.71 (m, 2H), 7.47-7.43 (m, 2H), 7.39-7.35 (m, 1H), 7.13-7.04 (m, 6H), 6.59-6.55 (m, 1H), 6.47-6.43 (m, 1H), 3.98 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.2, 133.3, 128.5, 128.1, 127.9, 127.9, 127.4, 127.3, 127.2, 126.8, 125.8, 120.5, 119.6, 117.5, 113.3, 40.1; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}N_2S$ 317.1107, found 317.1103.

1-(butylthio)-3-phenylimidazo[1,5-a]pyridine (3rd)



Yellow oil (35 mg, 62%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 6.9 Hz, 1H), 7.71-7.65 (m, 2H), 7.54 (d, J = 9.0 Hz, 1H), 7.41 (t, J = 14.6 Hz, 2H), 7.35-7.31 (m, 1H), 6.69 (t, J = 15.1 Hz, 1H), 6.49 (t, J = 6.3 Hz, 1H), 2.79 (t, J = 7.2 Hz, 2H), 1.53-1.46 (m, 2H), 1.38-1.31 (m, 2H), 0.79 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.4, 132.7, 128.7, 127.9, 127.8, 127.0, 122.3, 120.6, 118.7, 117.6, 112.4, 35.3, 31.0, 20.7, 12.6; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2S$ 283.1191, found 283.1195.

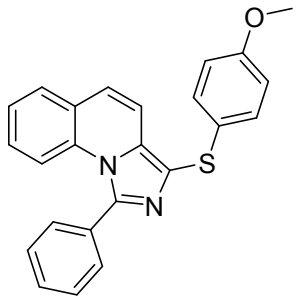
1-phenyl-3-(p-tolylthio)imidazo[1,5-a]quinoline (3ad)



White solid (66 mg, 90%), melting point 155-158 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 3H), 7.46-7.41 (m, 5H), 7.27-7.23 (m, 1H), 7.14-7.10 (m, 3H), 7.05 (d, J = 9.4 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 2.16 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.9, 135.6, 134.2, 133.9, 133.1,

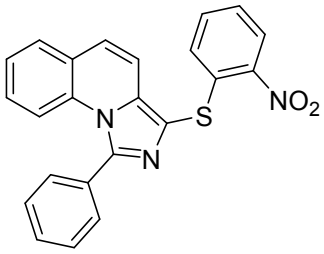
132.4, 129.8, 129.6, 129.0, 128.8, 128.8, 128.5, 127.9, 127.8, 125.6, 125.5, 123.4, 117.4, 116.6, 20.9; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}N_2S$ 367.1264, found 367.1272.

3-((4-methoxyphenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ae)



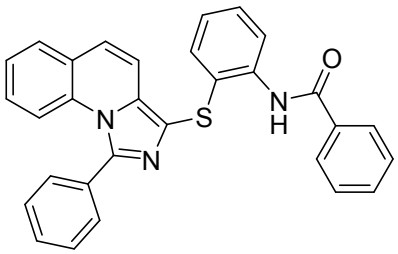
White solid (70 mg, 92%), melting point 107-113 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 3H), 7.57-7.49 (m, 5H), 7.34-7.30 (m, 3H), 7.21-7.18 (m, 1H), 7.13 (d, J = 9.3 Hz, 1H), 6.78-6.76 (m, 2H), 3.72 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.4, 142.7, 133.4, 133.1, 132.4, 130.5, 129.7, 129.6, 129.0, 128.8, 128.1, 127.7, 125.6, 125.5, 124.4, 123.2, 117.3, 116.6, 114.5, 55.3; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}ON_2S$ 383.1213, found 383.1220.

3-((2-nitrophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3af)



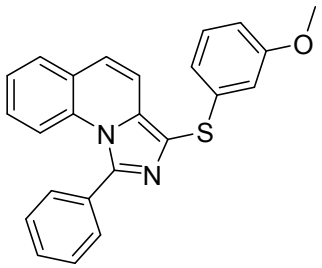
White solid (56 mg, 70%), melting point 179-183 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.63-7.61 (m, 3H), 7.54-7.41 (m, 5H), 7.31 (t, J = 7.2 Hz, 1H), 7.25-7.11 (m, 4H), 6.96 (d, J = 8.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.0, 143.0, 138.0, 134.3, 132.5, 131.6, 131.3, 128.8, 128.6, 128.0, 127.8, 127.2, 127.1, 124.8, 124.7, 124.4, 124.0, 123.5, 119.3, 116.3, 114.8; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}O_2N_3S$ 398.0958, found 398.0964.

N-(2-((1-phenylimidazo[1,5-a]quinolin-3-yl)thio)phenyl)benzamide (3ag)



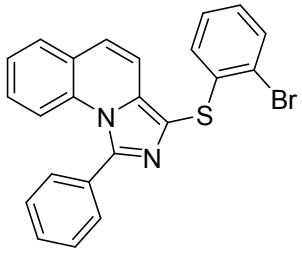
White solid (51 mg, 54%), melting point 253-257 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.15 (d, J = 7.2 Hz, 2H), 7.70 (dd, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 1H), 7.57-7.54 (m, 2H), 7.46-7.41 (m, 4H), 7.39-7.35 (m, 2H), 7.32-7.26 (m, 2H), 7.19-7.15 (m, 3H), 7.13-7.08 (m, 2H), 7.02-6.98 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.1, 141.9, 140.8, 135.1, 134.7, 132.5, 132.2, 131.5, 130.0, 129.7, 129.7, 128.9, 128.9, 128.3, 128.1, 127.9, 125.7, 125.5, 125.1, 124.4, 123.6, 117.3, 116.1; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{22}ON_3S$ 472.1478, found 472.1484.

3-((3-methoxyphenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ah)



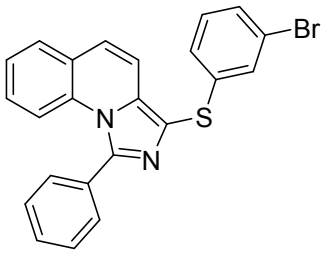
White solid (65 mg, 84%), melting point 123-126 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68-7.64 (m, 3H), 7.55-7.50 (m, 5H), 7.36-7.32 (m, 1H), 7.24-7.21 (m, 1H), 7.16-7.09 (m, 2H), 6.83-6.80 (m, 2H), 6.63 (dd, J_1 = 8.3 Hz, J_2 = 2.0 Hz, 1H), 3.71 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.8, 143.1, 139.4, 134.2, 133.0, 132.4, 129.7, 129.6, 129.6, 128.9, 128.8, 127.8, 125.6, 125.6, 123.6, 122.2, 119.5, 117.4, 116.5, 112.8, 111.1, 55.2; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{19}ON_2S$ 383.1213, found 383.1218.

3-((2-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ai)



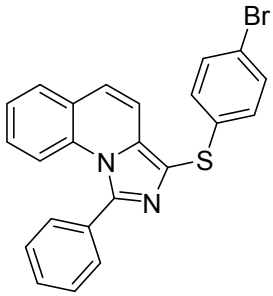
White solid (74 mg, 85%), melting point 183-185 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 3H), 7.51-7.39 (m, 6H), 7.31-7.27 (m, 1H), 7.18-7.09 (m, 2H), 6.99-6.95 (m, 1H), 6.86-6.82 (m, 1H), 6.75-6.72 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.8, 138.5, 134.1, 131.8, 131.5, 131.4, 128.7, 128.6, 127.9, 127.8, 126.9, 126.6, 126.1, 125.2, 124.7, 124.5, 123.0, 119.8, 119.2, 116.3, 115.2; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2BrS$ 431.0212, found 431.0219.

3-((3-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3aj)



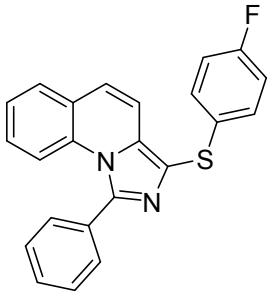
White solid (85 mg, 99%), melting point 148-152 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.48-7.41 (m, 5H), 7.29-7.25 (m, 2H), 7.16-7.05 (m, 4H), 6.98-6.94 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.3, 140.5, 134.4, 132.9, 132.4, 130.5, 130.1, 129.7, 129.4, 128.9, 128.9, 128.6, 128.0, 125.7, 125.5, 124.0, 122.8, 121.2, 117.4, 116.2; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2BrS$ 431.0212, found 431.0219.

3-((4-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ak)



White solid (83 mg, 96%), melting point 167-171 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 3H), 7.56-7.49 (m, 5H), 7.37-7.29 (m, 3H), 7.25-7.16 (m, 2H), 7.11-7.09 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.2, 137.3, 134.2, 132.9, 132.3, 131.8, 129.7, 129.7, 128.9, 128.9, 128.7, 128.0, 125.7, 125.5, 123.9, 121.8, 119.3, 117.4, 116.2; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2BrS$ 431.0212, found 431.0219.

3-((4-fluorophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3al)



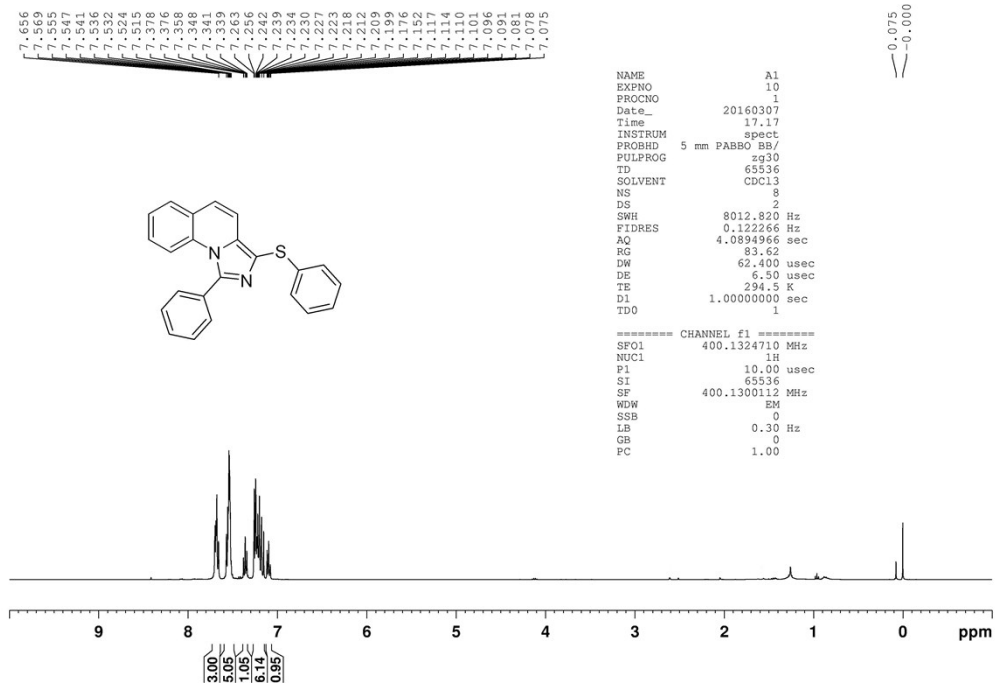
White solid (72 mg, 97%), melting point 163-166 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 3H), 7.46-7.41 (m, 5H), 7.27-7.23 (m, 1H), 7.21-7.16 (m, 2H), 7.14-7.10 (m, 1H), 7.07 (d, J = 9.3 Hz, 1H), 6.84-6.79 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 160.2, 143.0, 133.9, 133.0, 132.8, 132.4, 129.7, 129.7, 129.6, 129.6, 128.8, 128.8, 127.8, 125.6, 125.5, 123.6, 123.1, 117.4, 116.3, 115.9, 115.7; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}N_2FS$ 371.1013, found 371.1017.

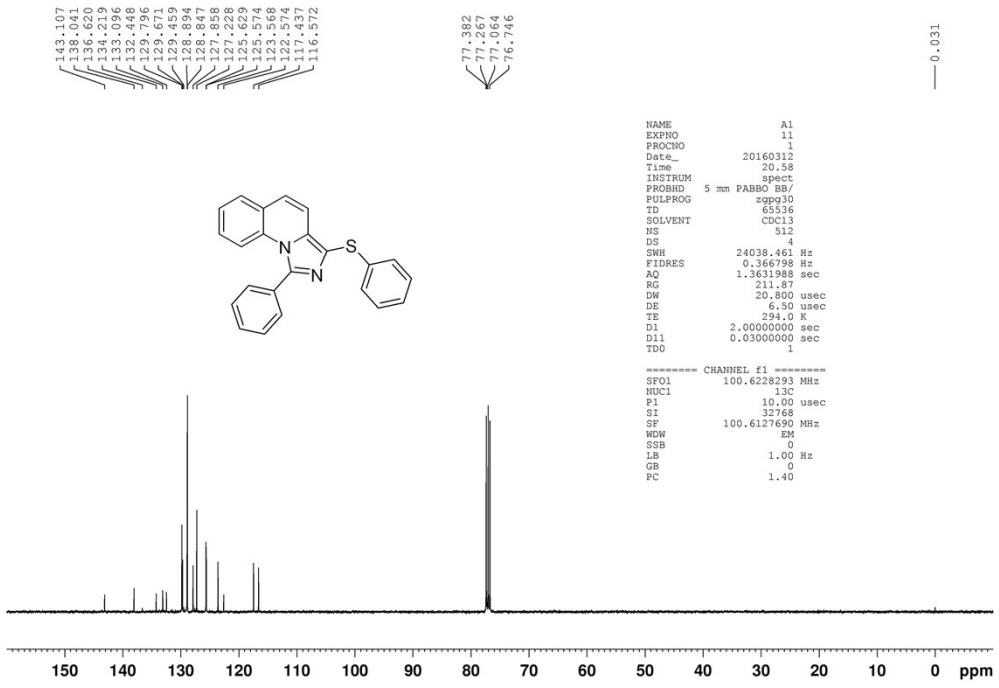
Reference

1. *Tetrahedron*., **2009,** *65,* 5062-5073.
2. *J. Org. Chem.*, **2016,** *81,* 3681-3687.
3. *J. Org. Chem.*, **2016,** *81*, 4386-4392.
4. *J. Org. Chem.*, **2012,** *77,* 11161-11166.
5. *J. Org. Chem.*, **2015,** *80,* 2431-2435.

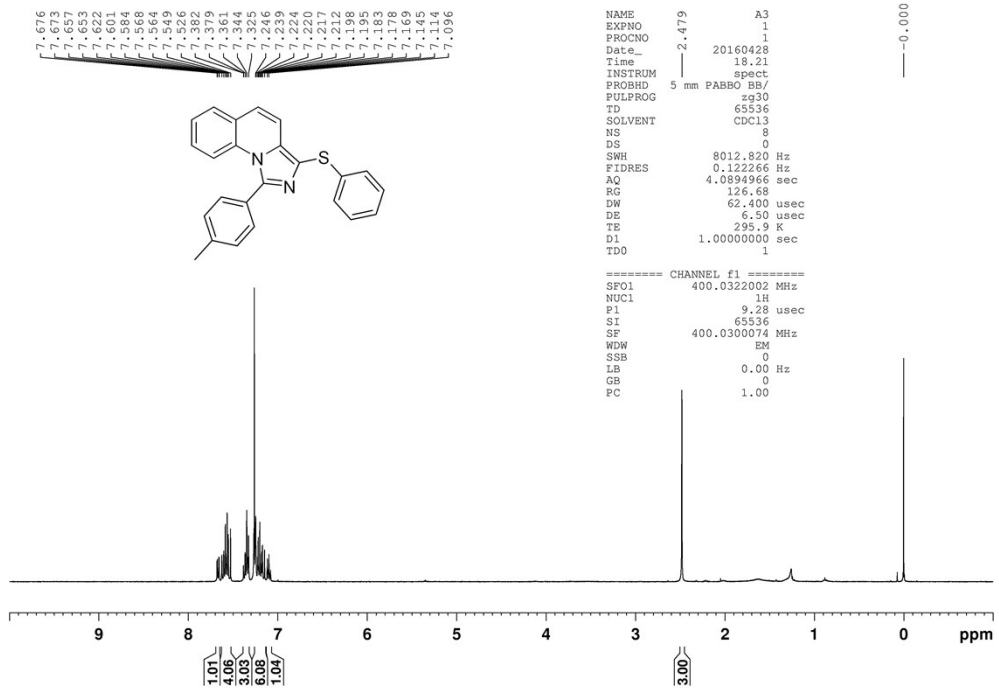
Copies of NMR Spectra of the Product

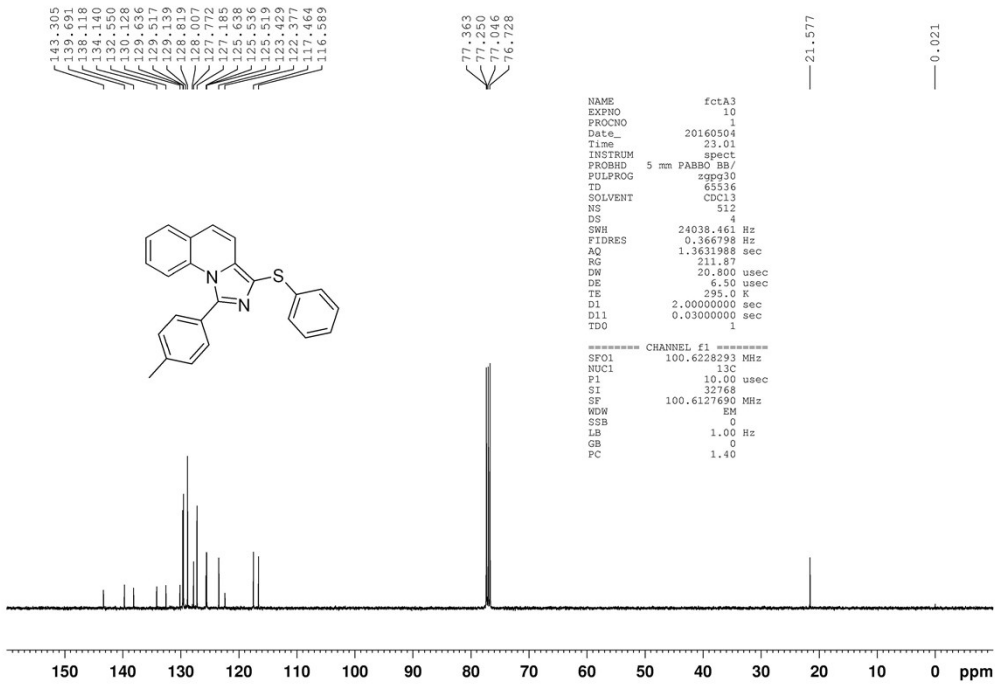
1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3aa)



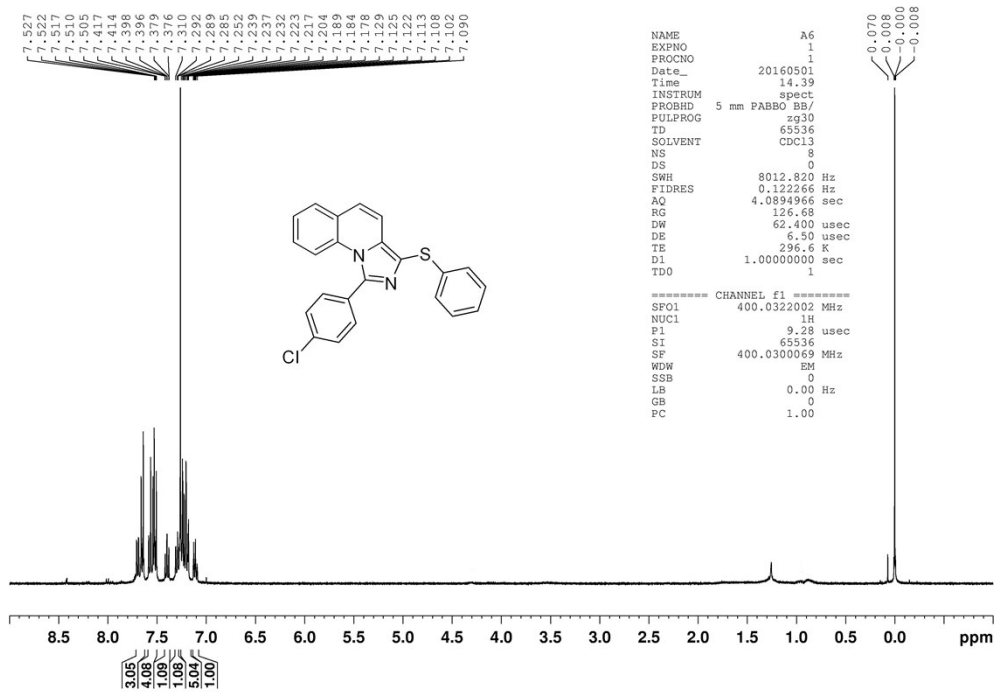


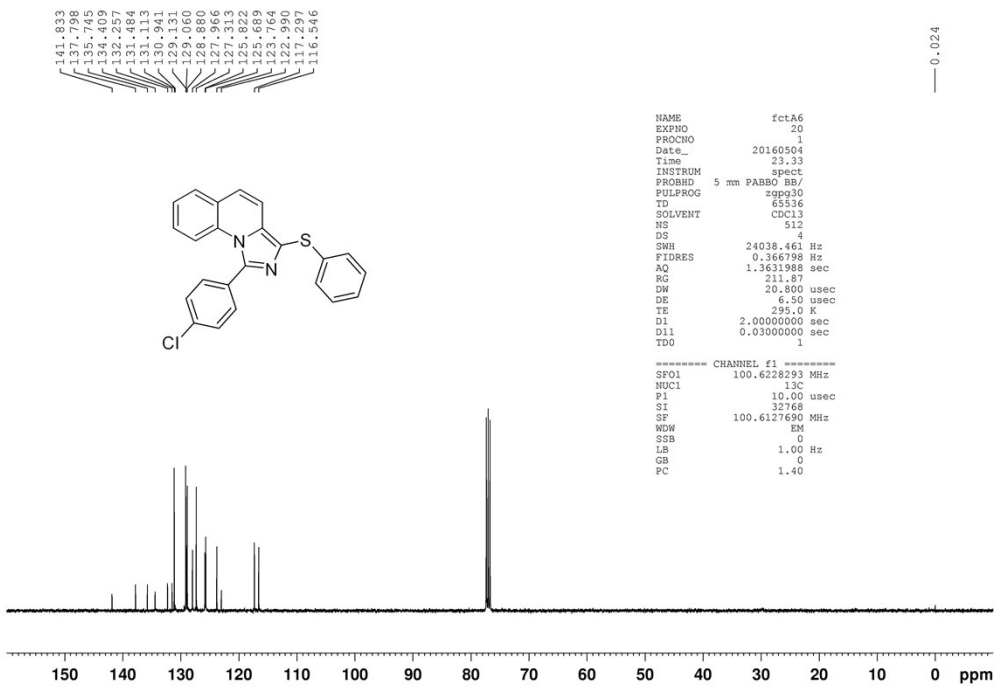
3-(phenylthio)-1-(p-tolyl)imidazo[1,5-a]quinoline (3ba)



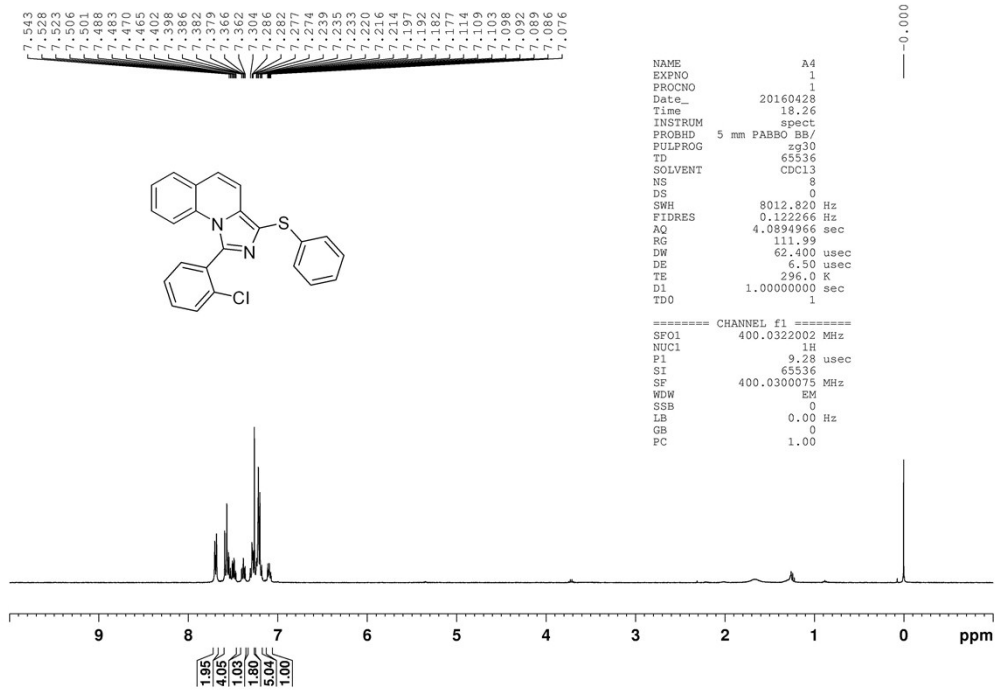


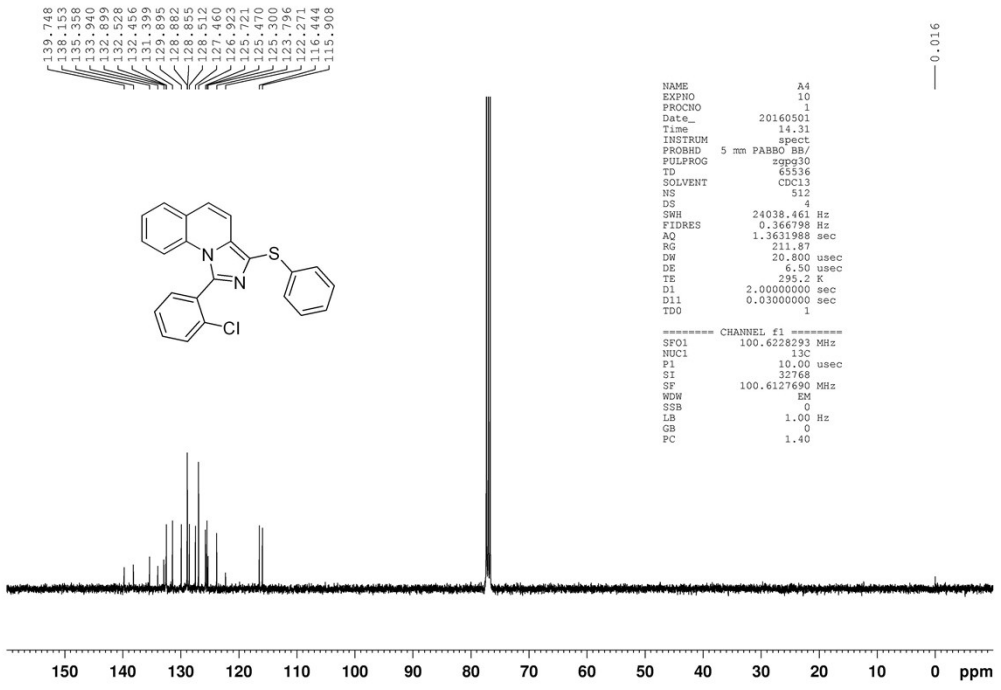
1-(4-chlorophenyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ca)



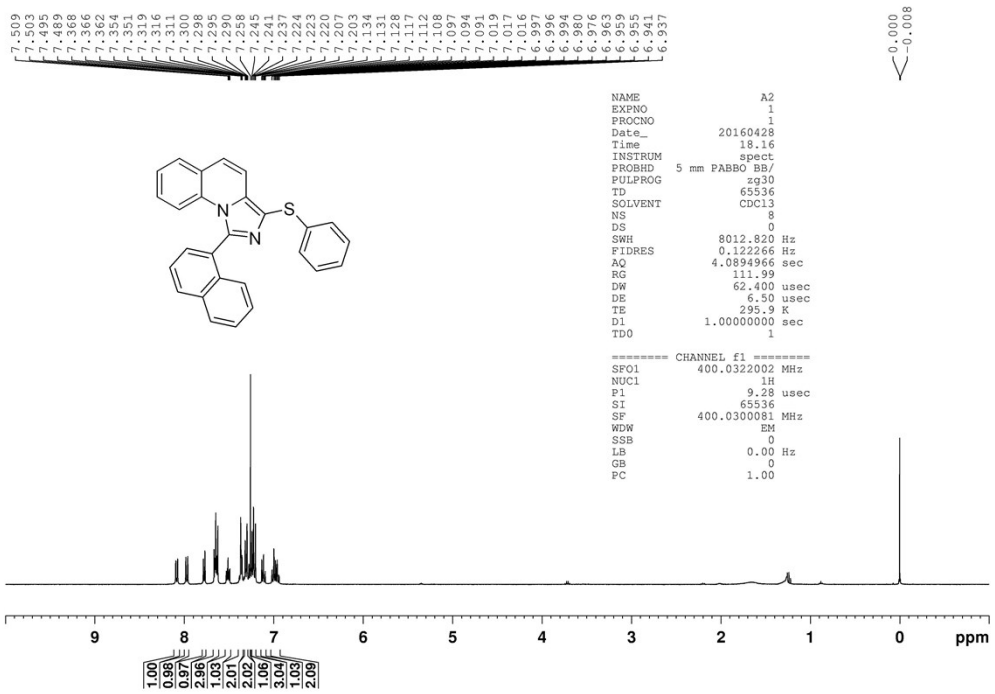


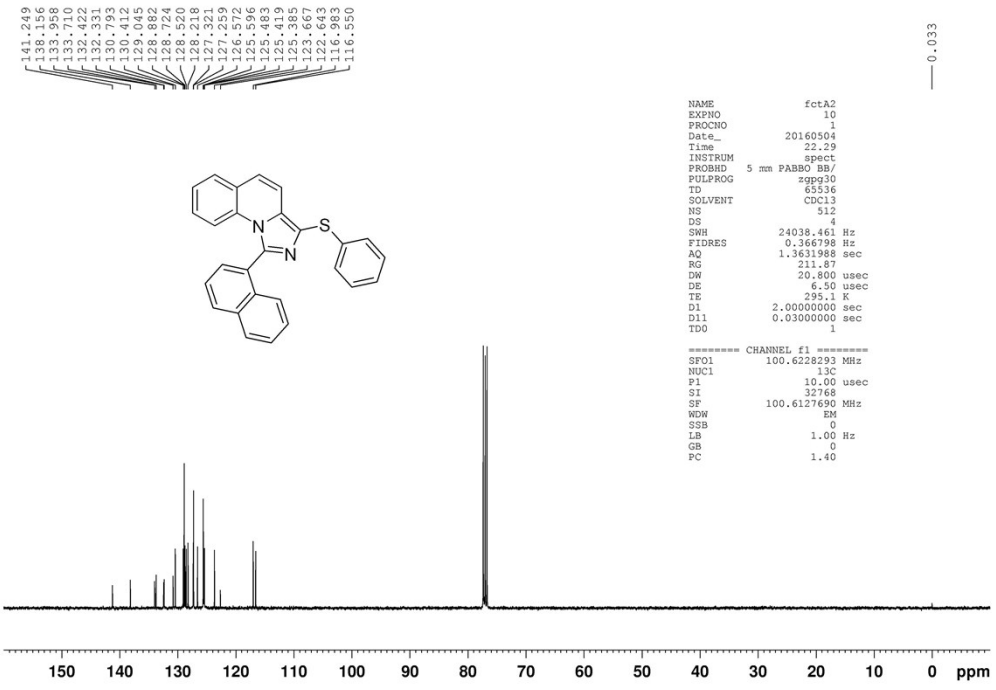
1-(2-chlorophenyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3da)



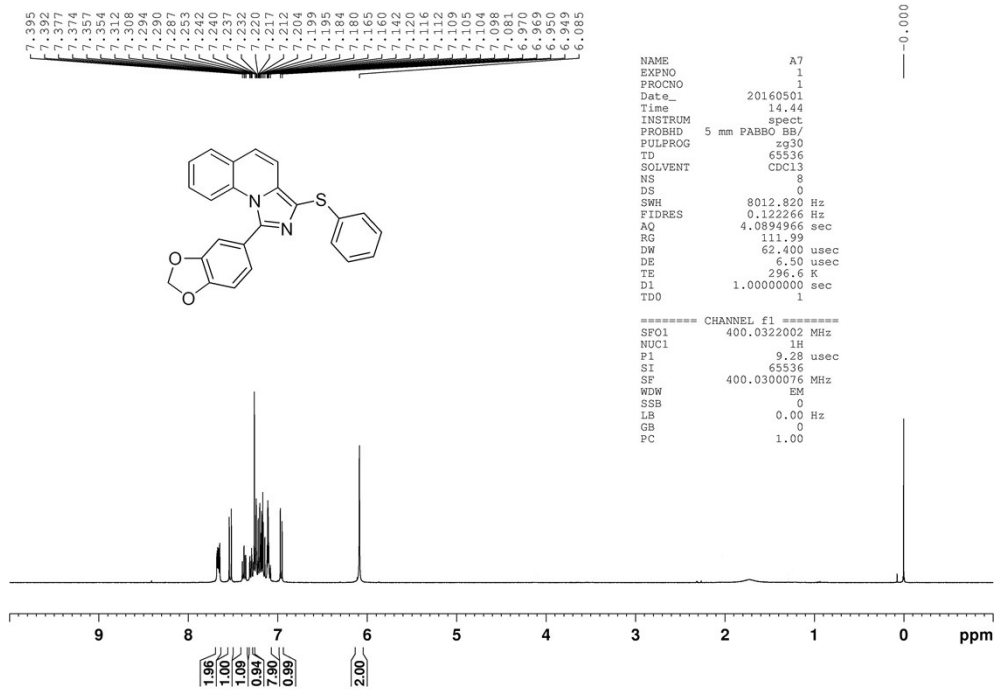


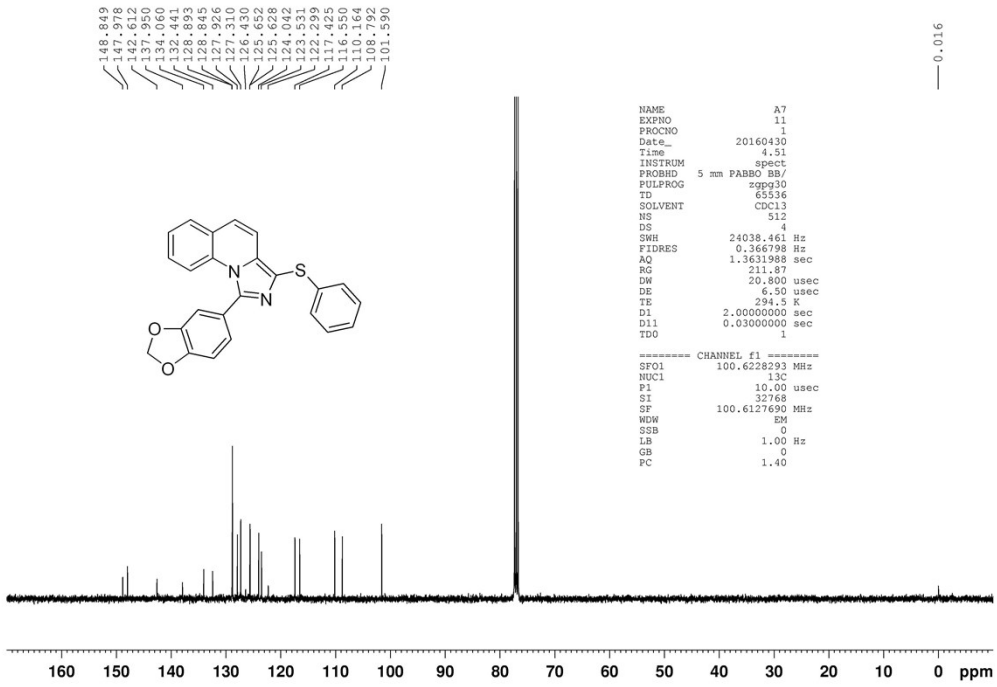
1-(naphthalen-1-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ea)



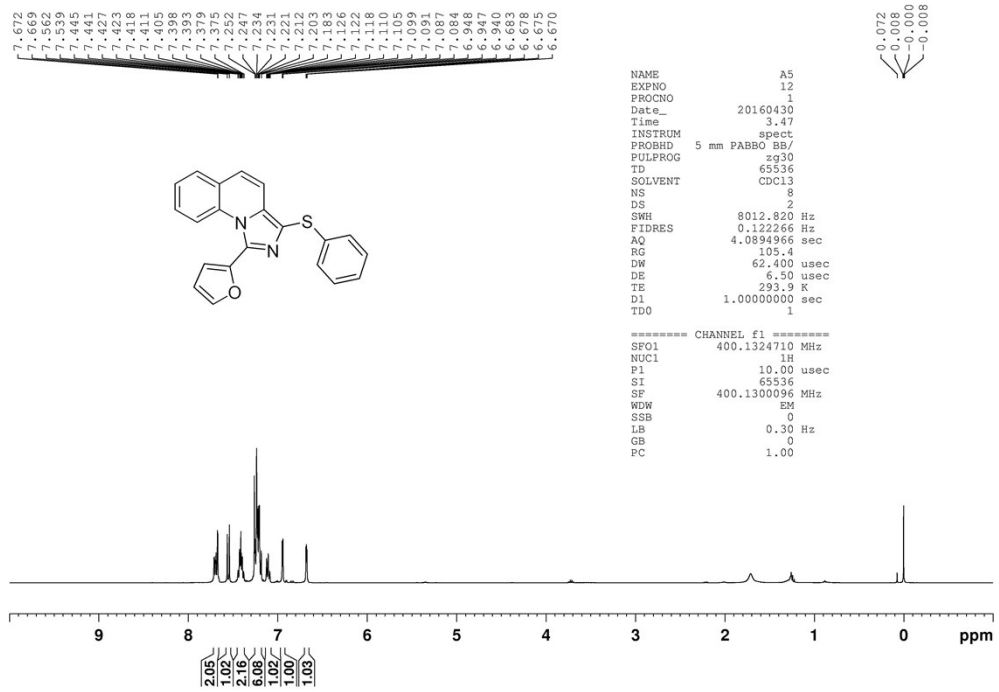


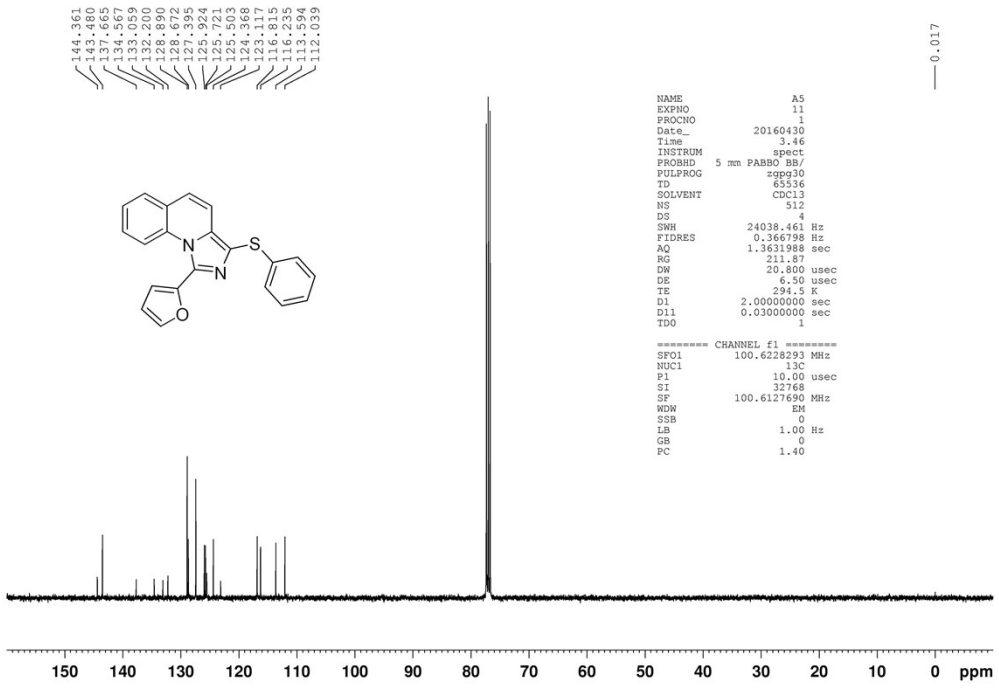
1-(benzo[d][1,3]dioxol-5-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3fa)



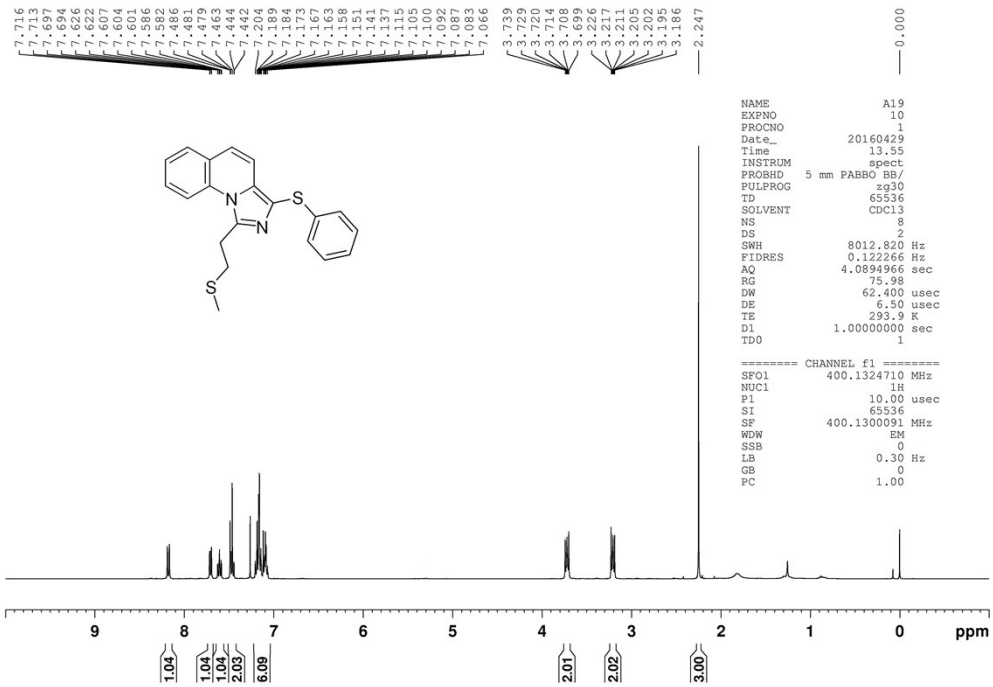


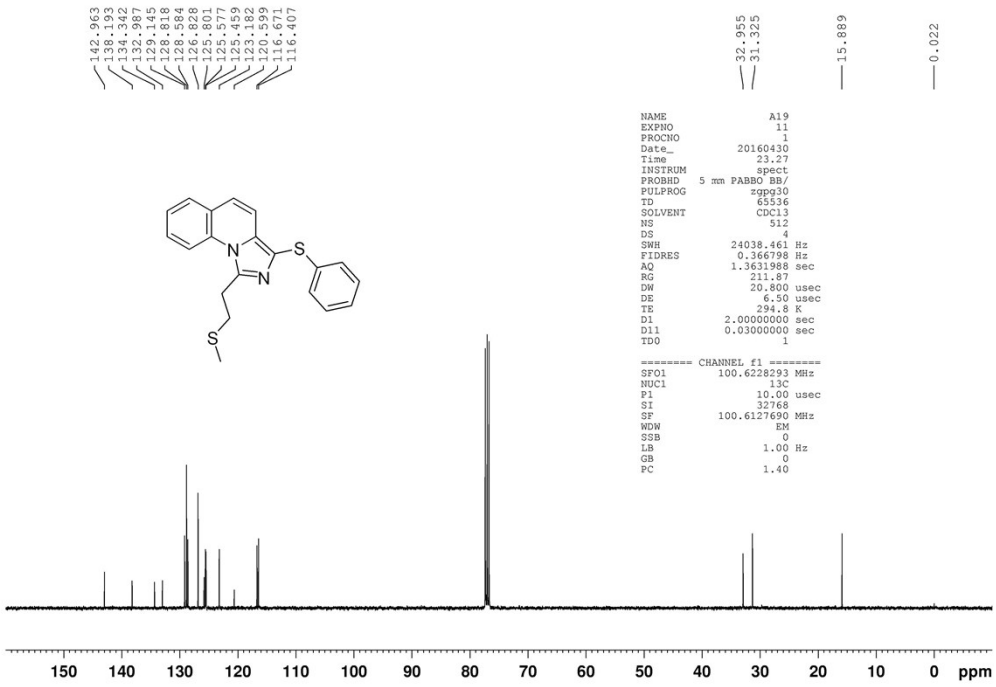
1-(furan-2-yl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ga)



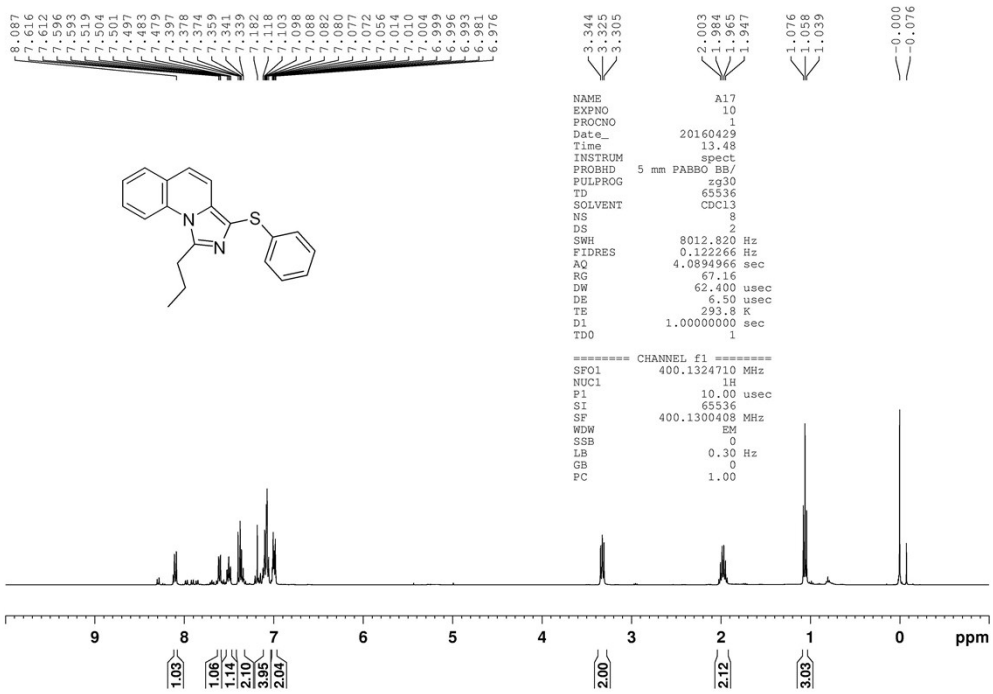


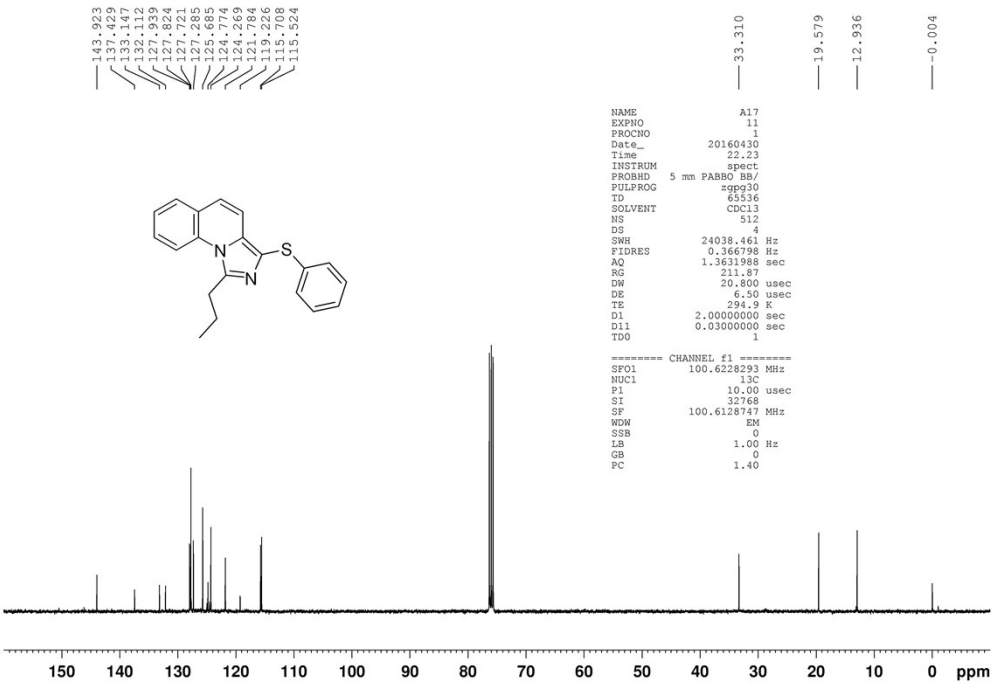
1-(2-(methylthio)ethyl)-3-(phenylthio)imidazo[1,5-a]quinoline (3ha)



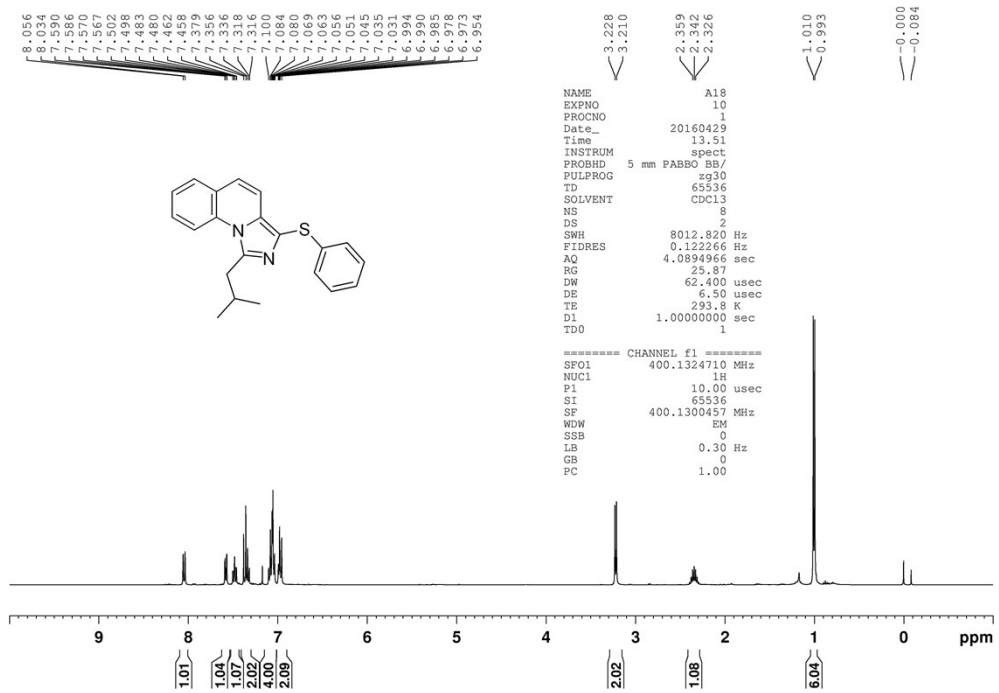


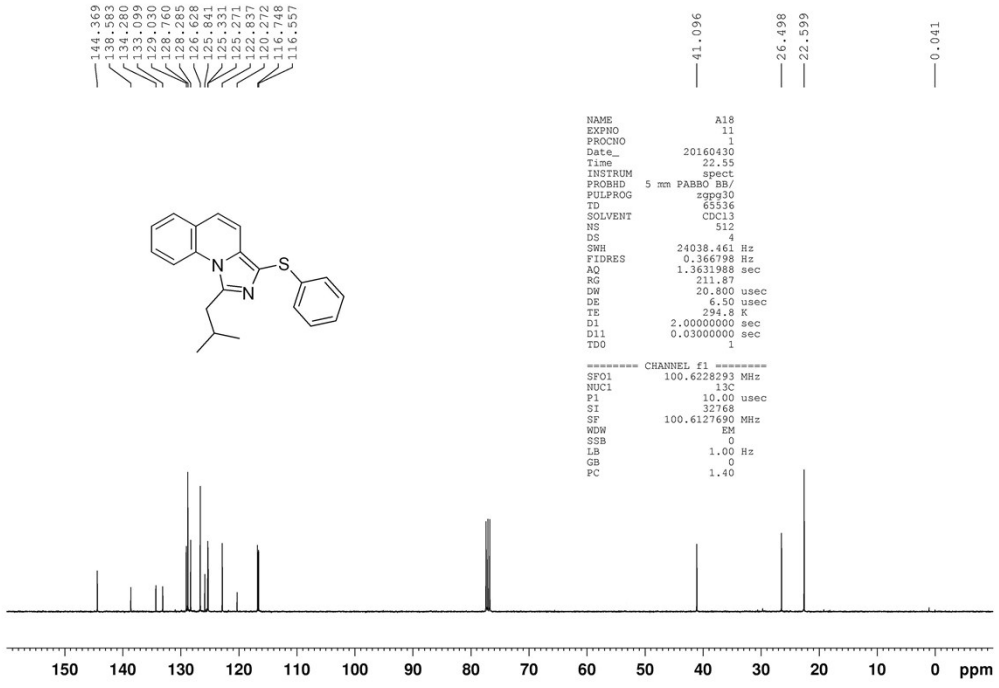
3-(phenylthio)-1-propylimidazo[1,5-a]quinoline (3ia)



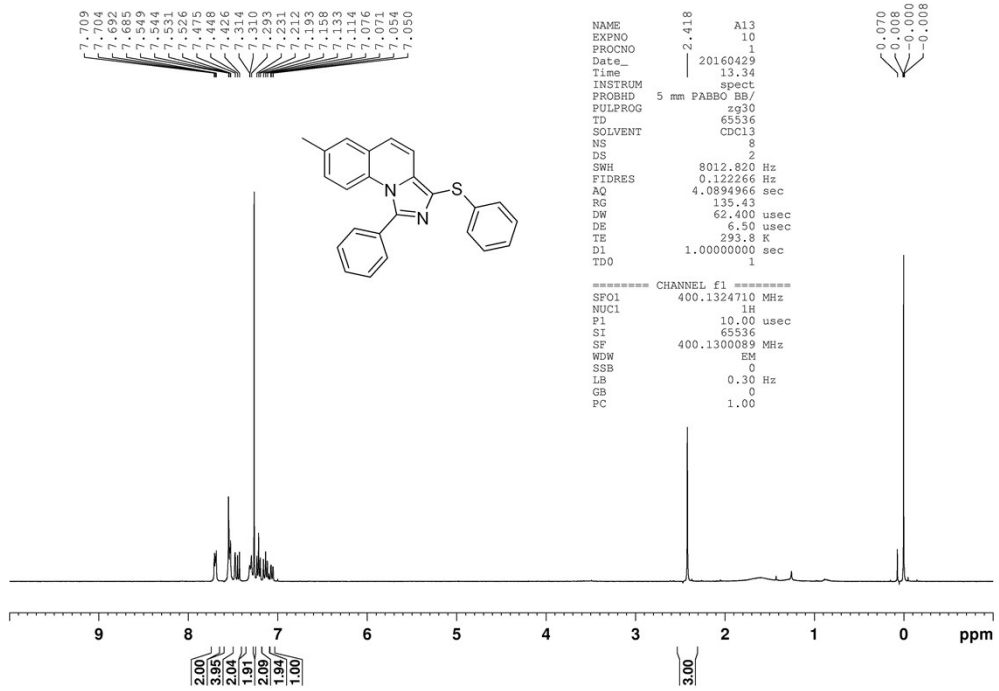


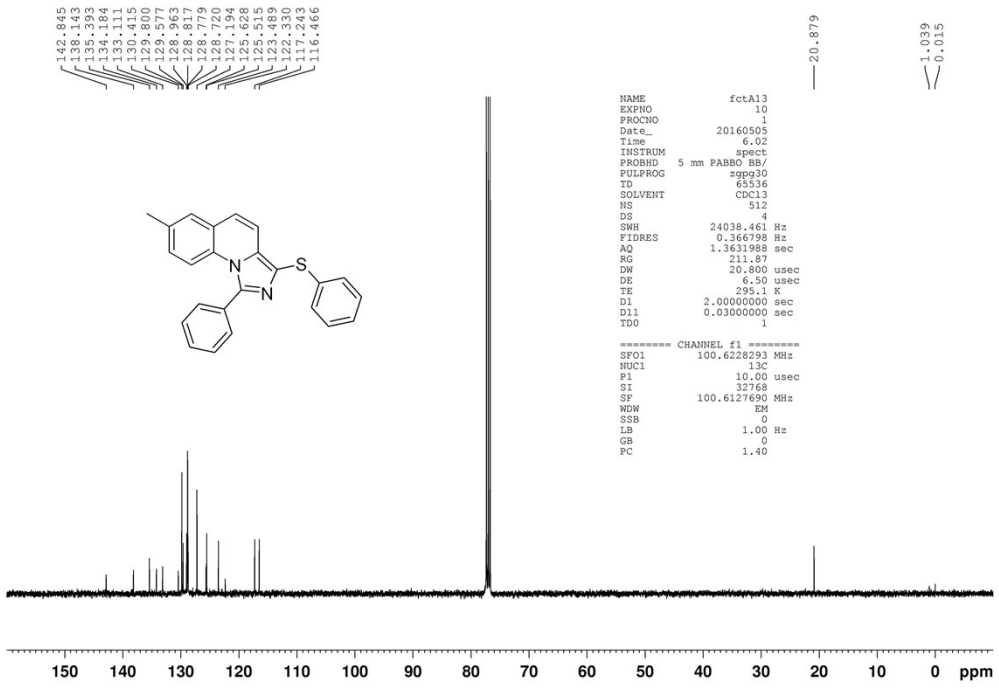
1-isobutyl-3-(phenylthio)imidazo[1,5-a]quinoline (3ja)



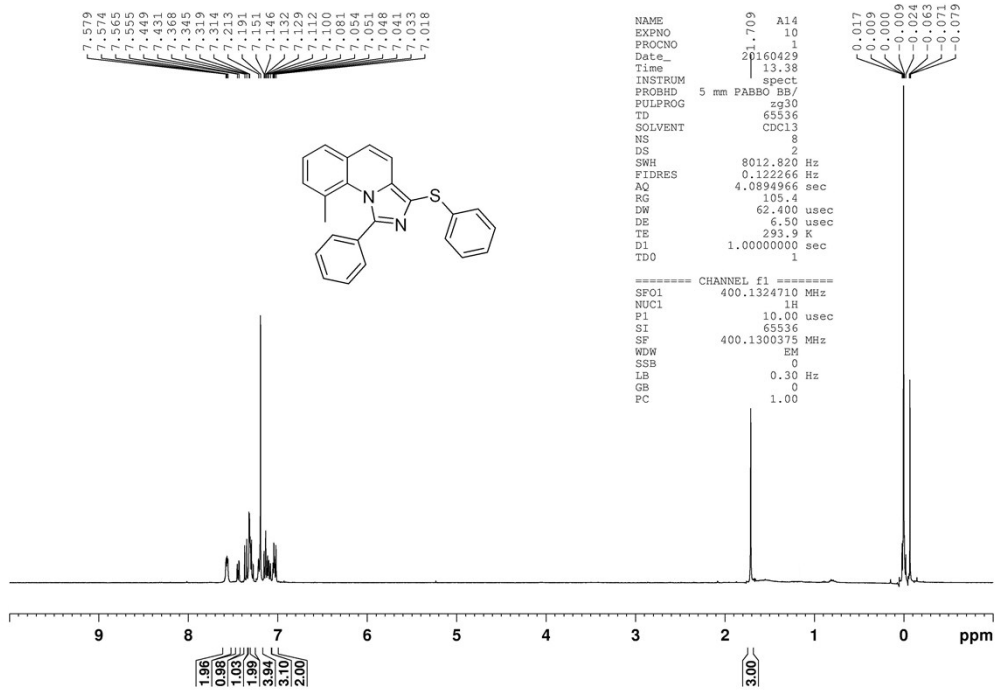


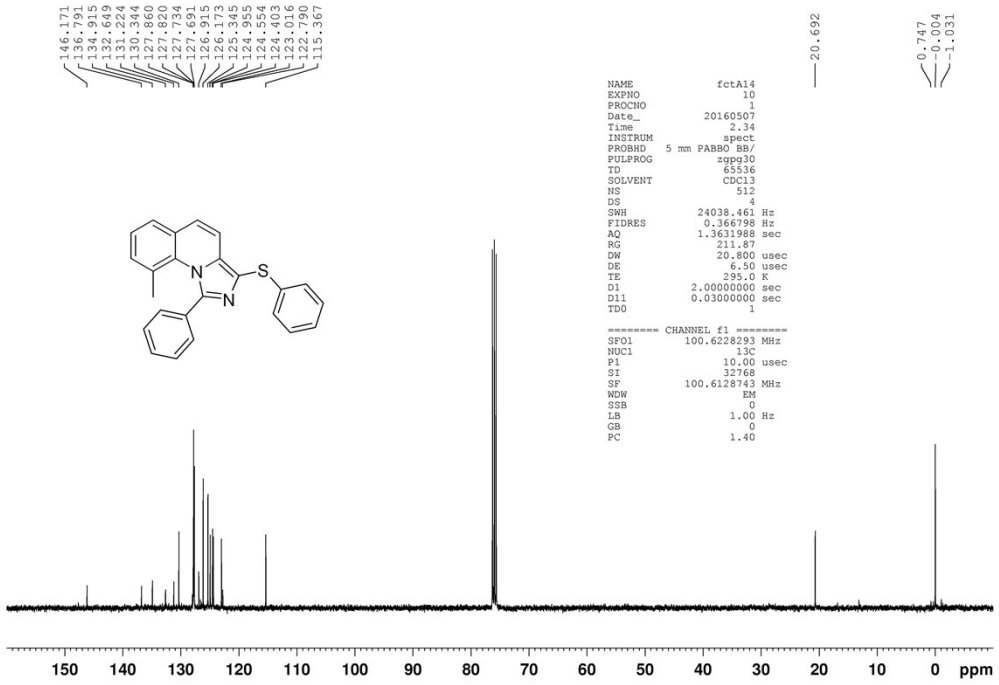
7-methyl-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3ka)



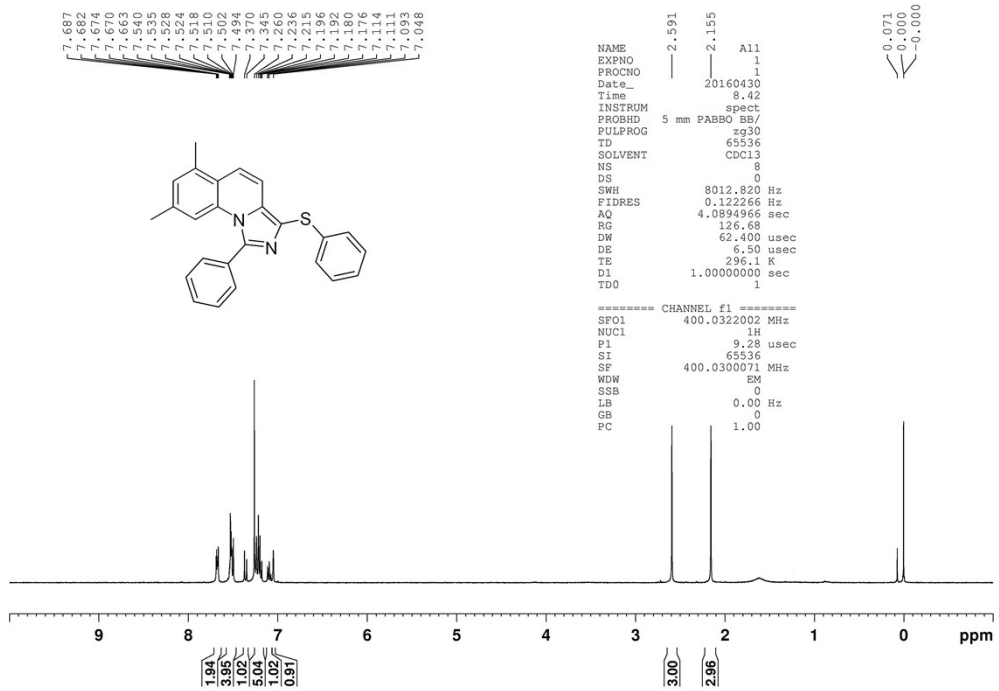


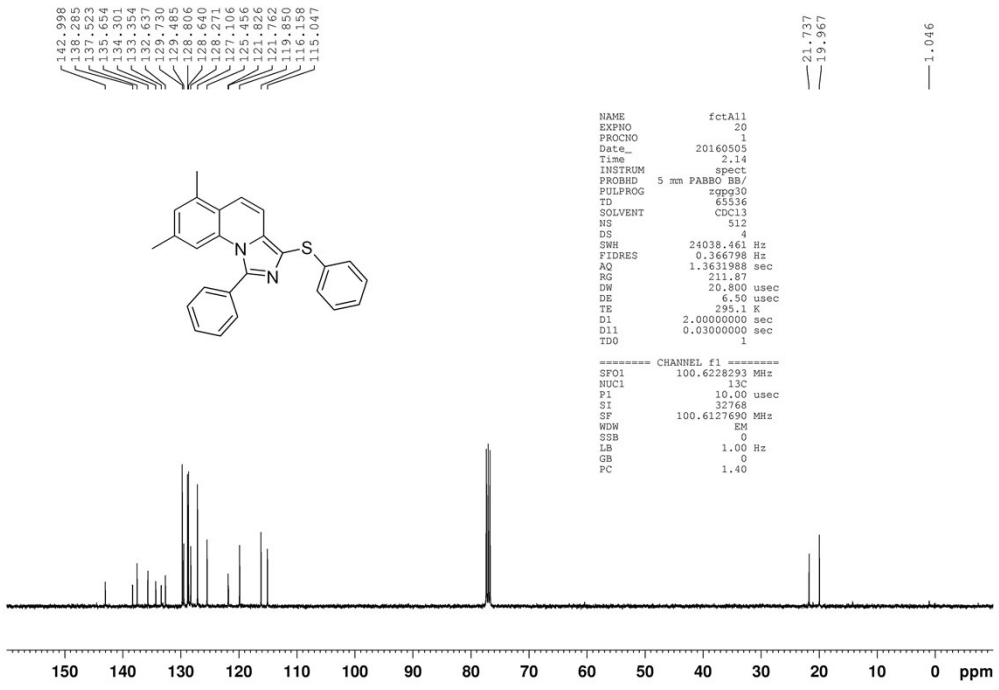
9-methyl-1-phenyl-3-(phenylthio)imidazo[1, 5-a]quinoline (3la)



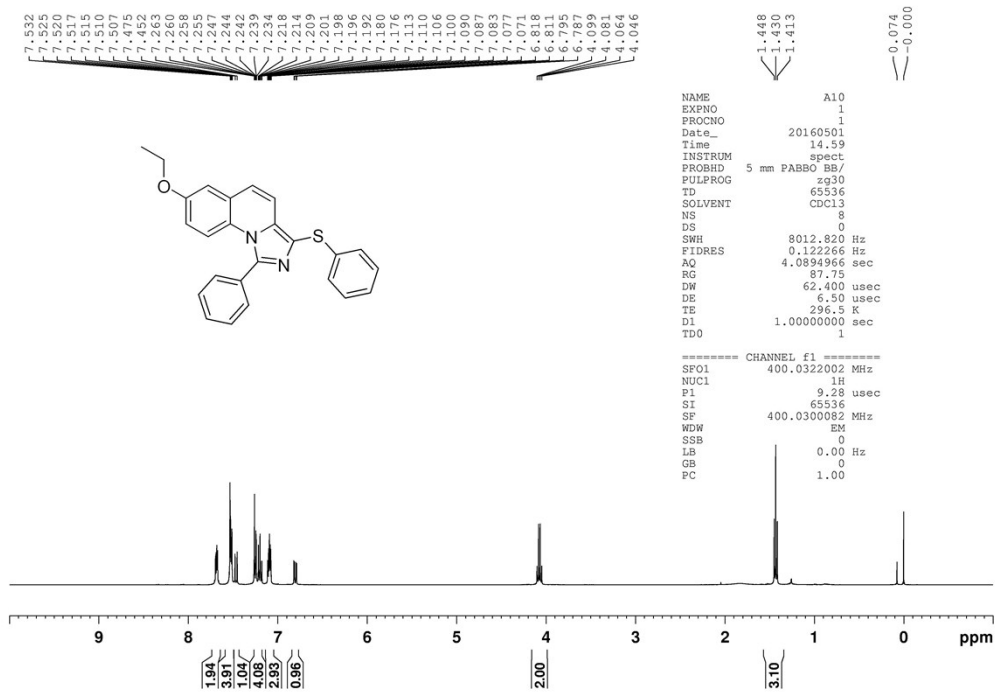


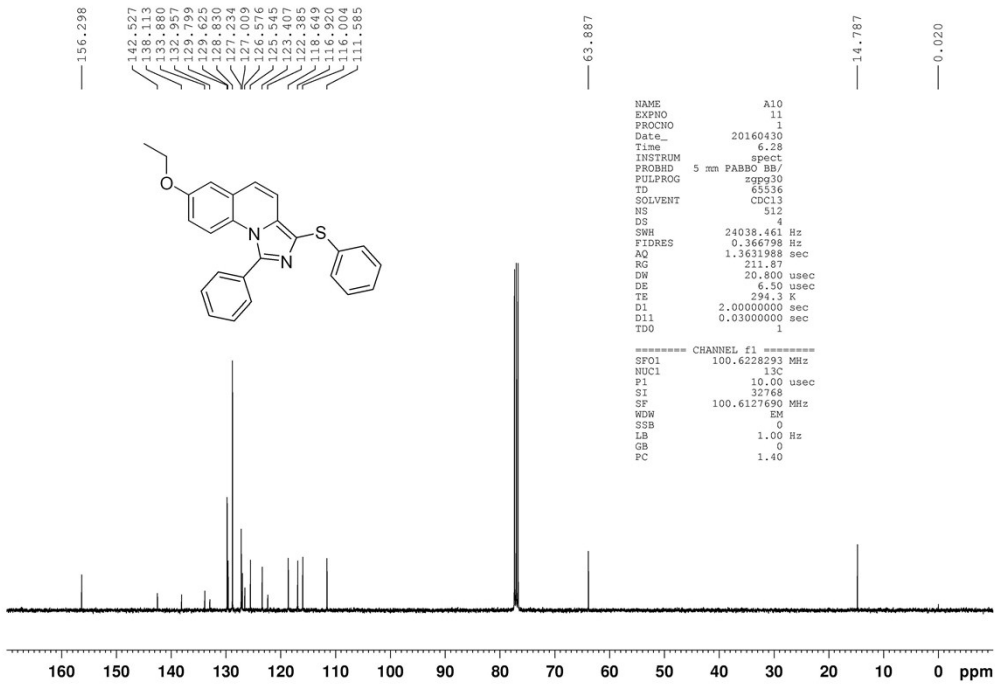
6, 8-dimethyl-1-phenyl-3-(phenylthio)imidazo[1, 5-a]quinoline (3ma)



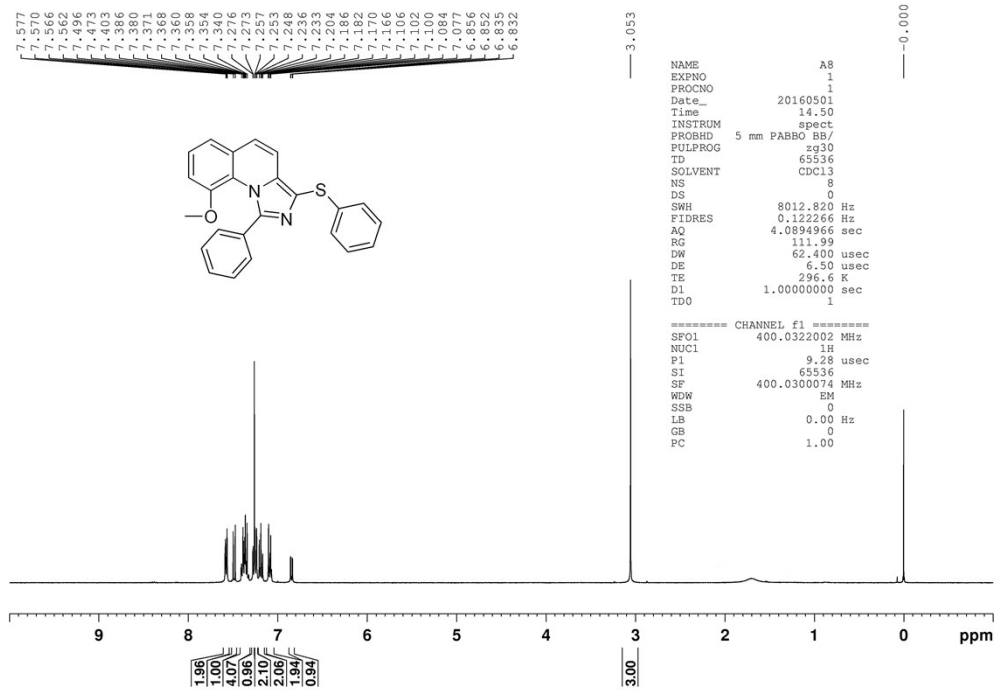


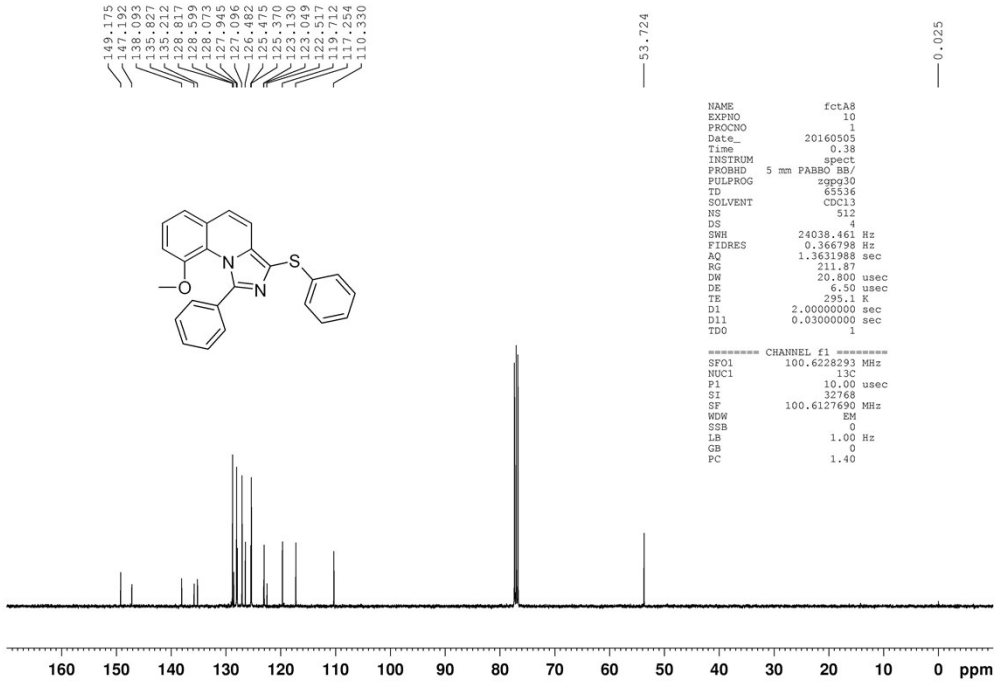
7-ethoxy-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3na)



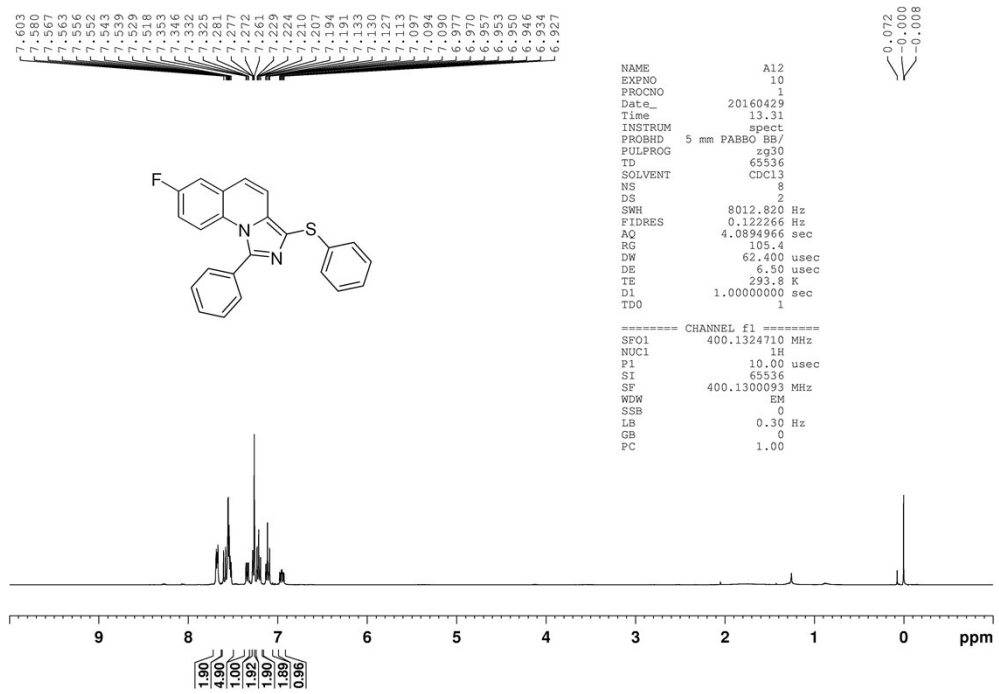


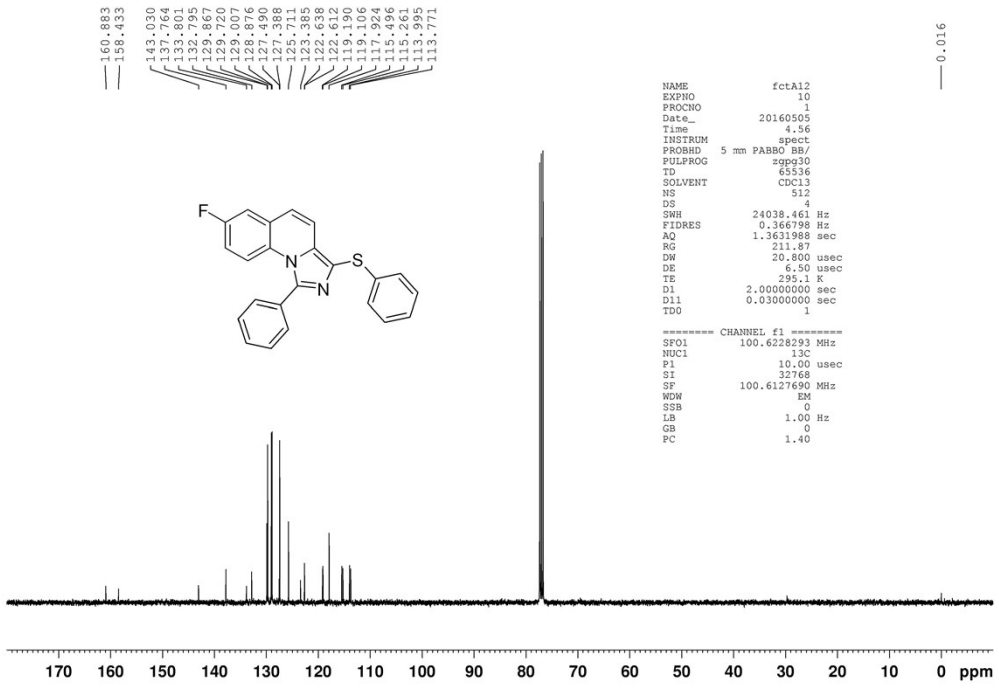
9-methoxy-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3oa)



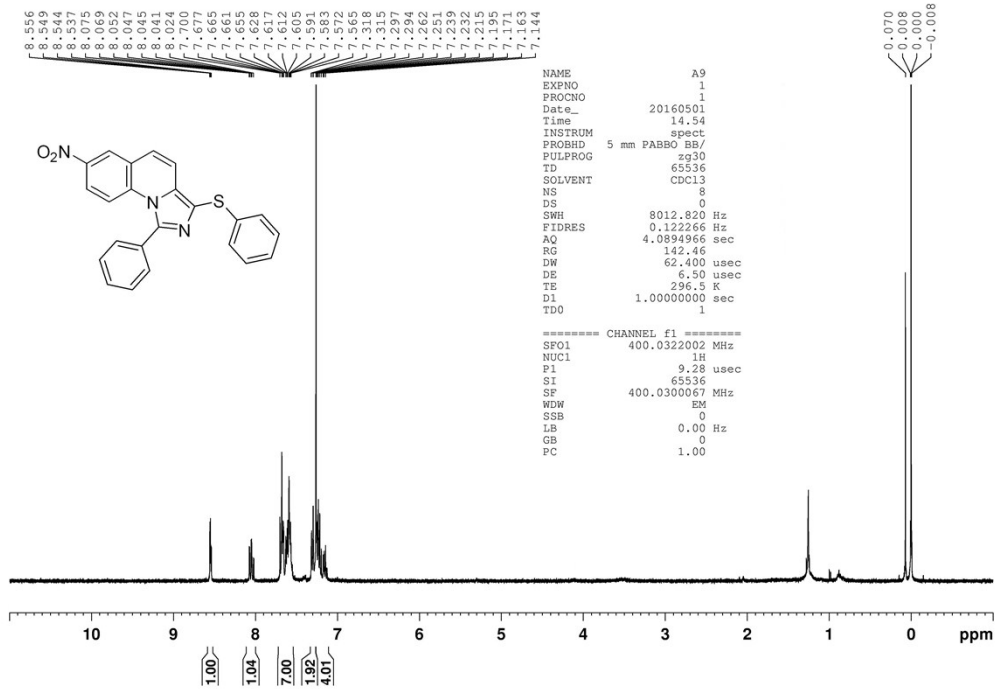


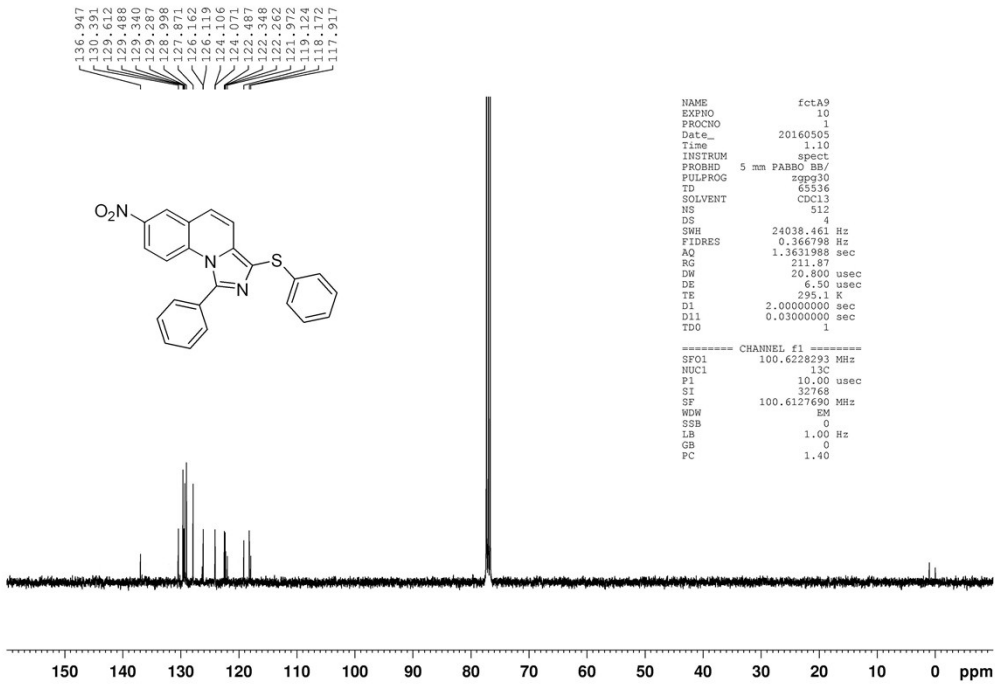
7-fluoro-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3pa)



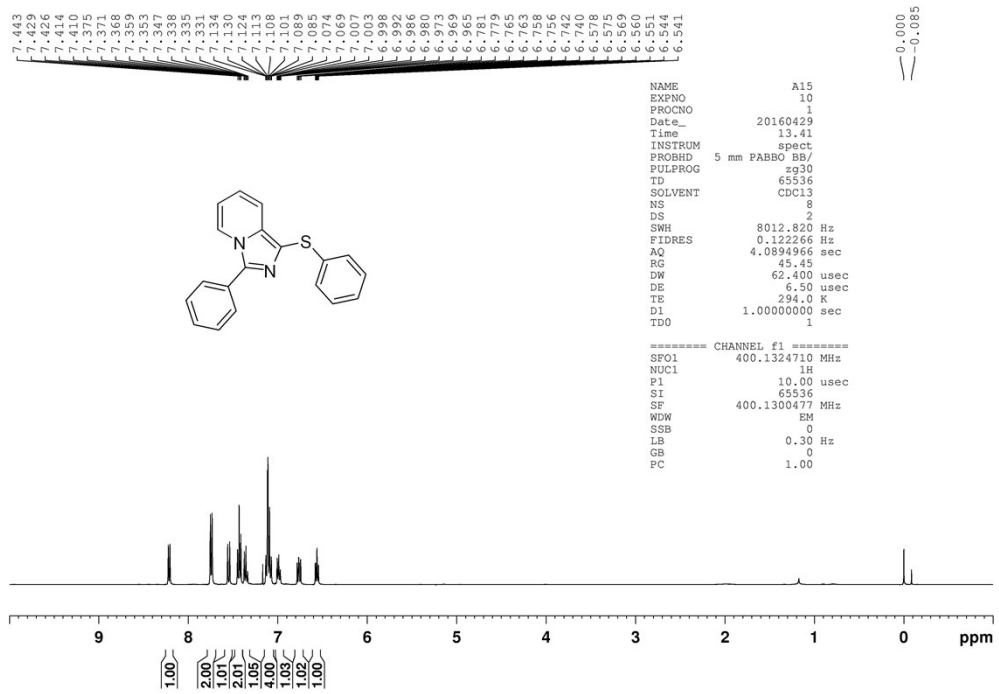


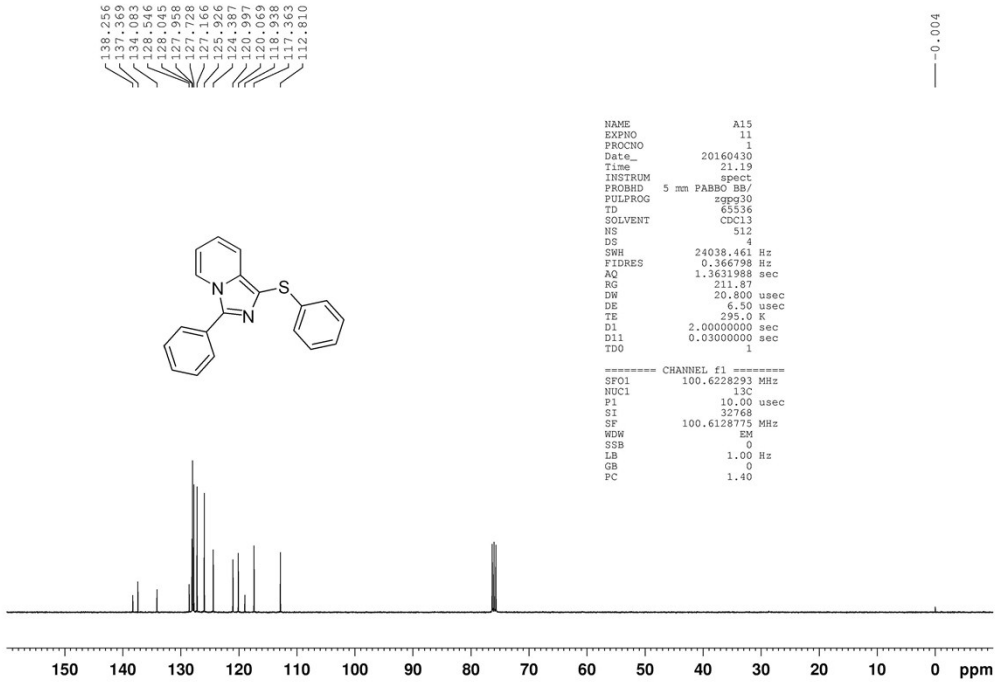
7-nitro-1-phenyl-3-(phenylthio)imidazo[1,5-a]quinoline (3qa)



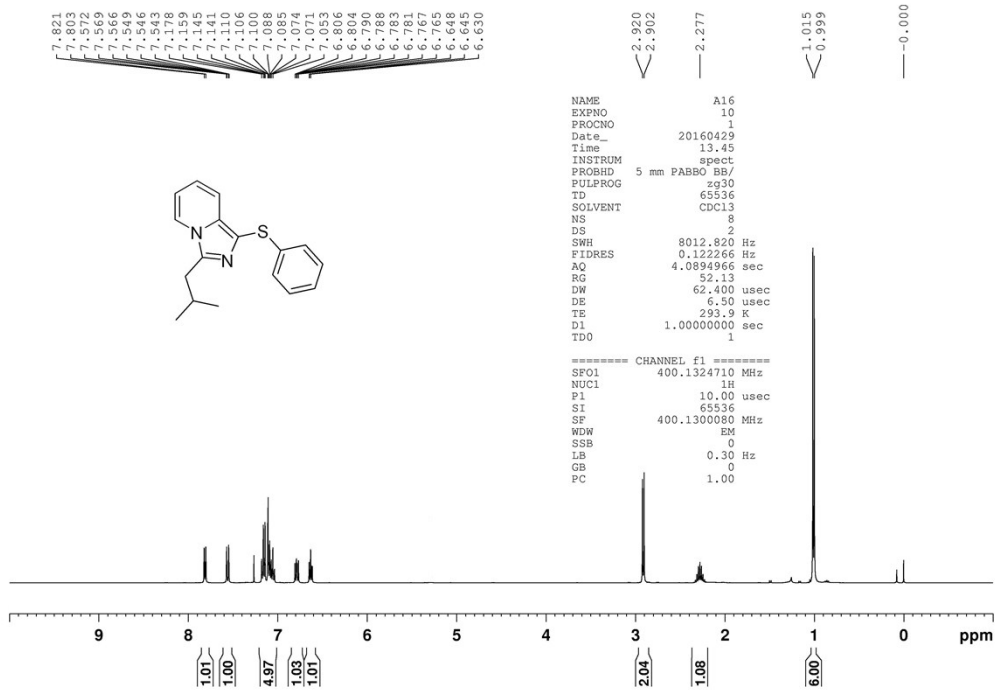


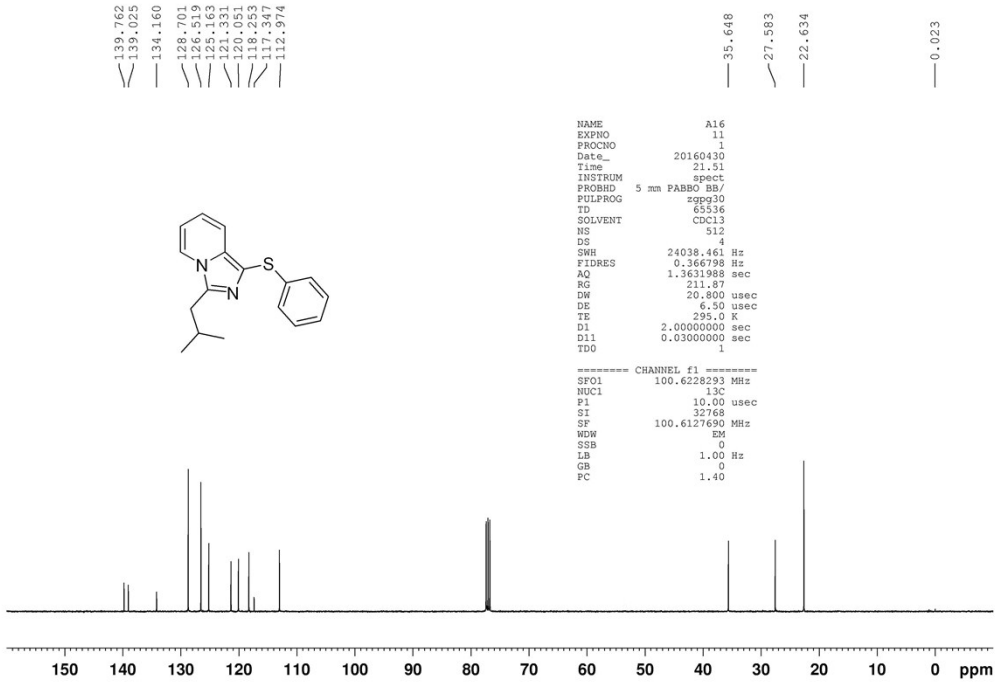
3-phenyl-1-(phenylthio)imidazo[1,5-a]pyridine (3ra)



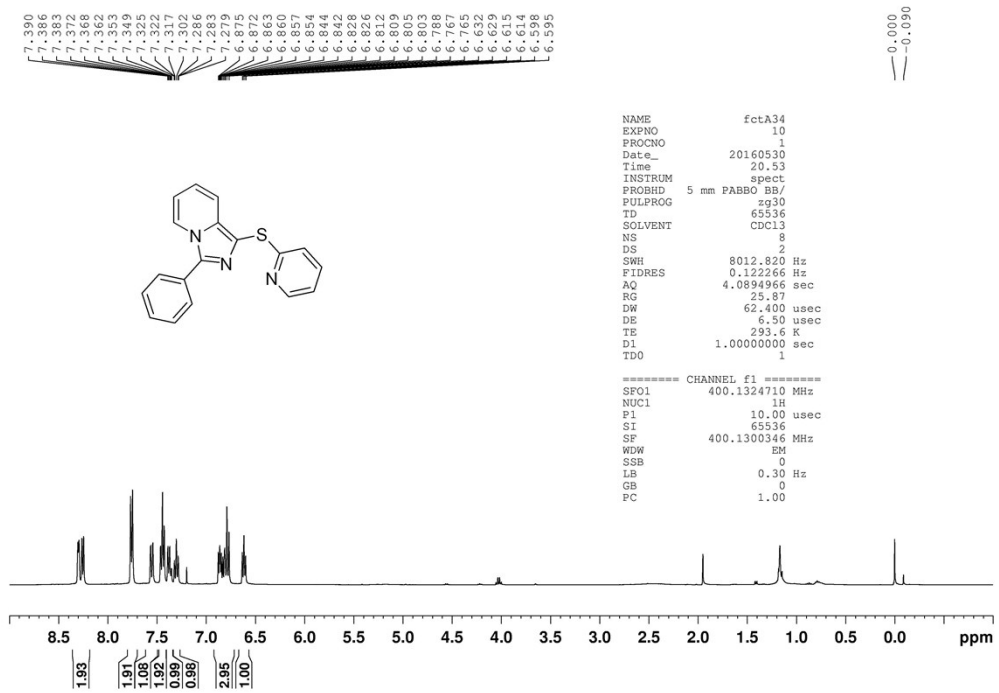


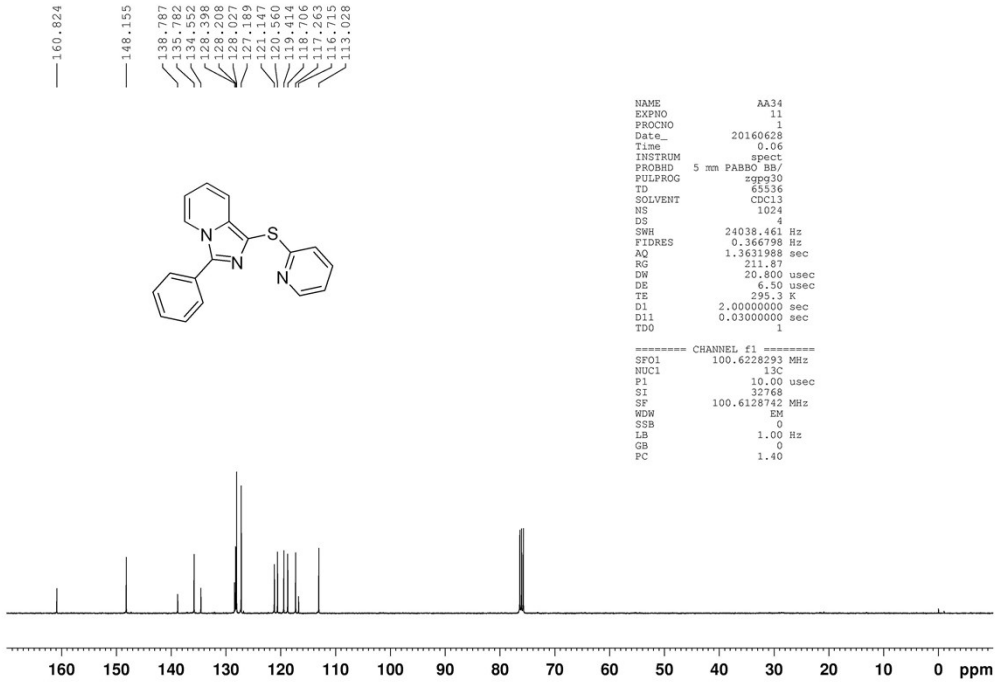
3-isobutyl-1-(phenylthio)imidazo[1,5-a]pyridine (3sa)



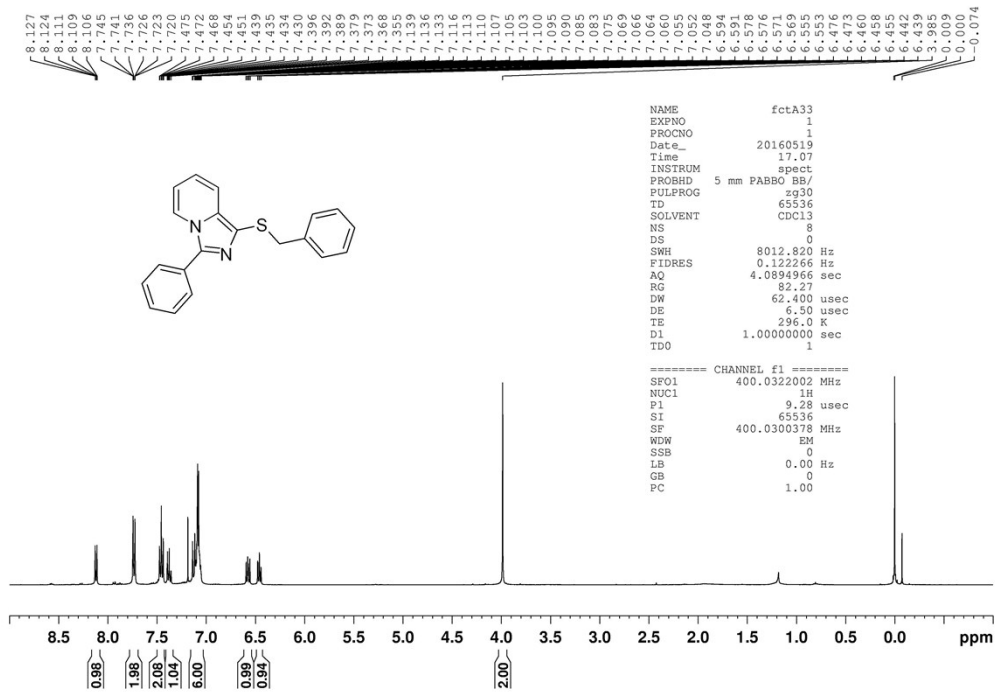


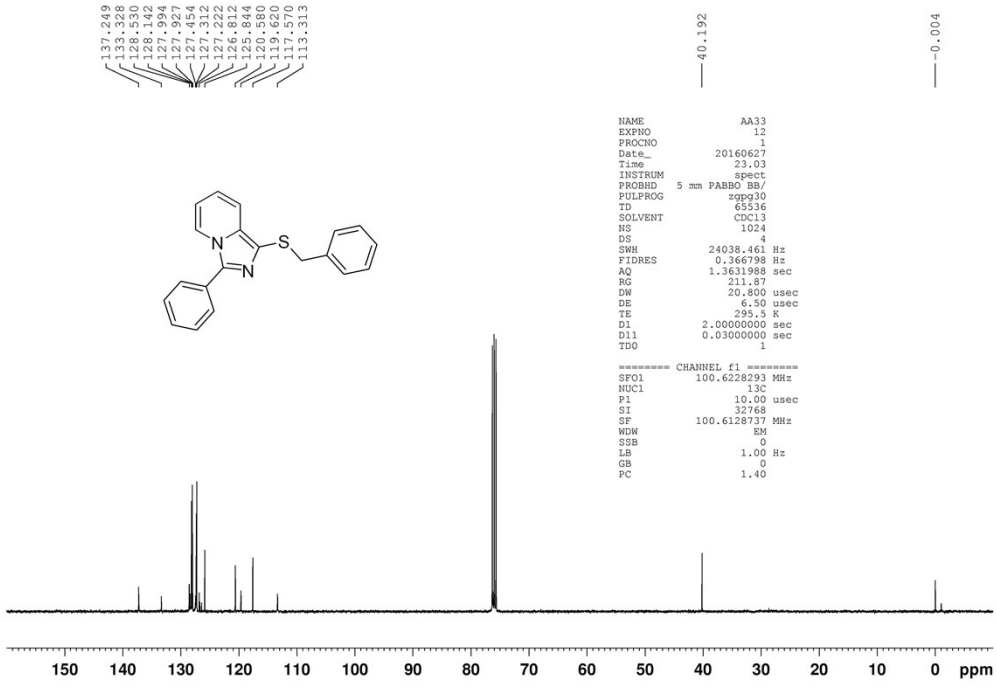
3-phenyl-1-(pyridin-2-ylthio)imidazo[1,5-a]pyridine (3rb)



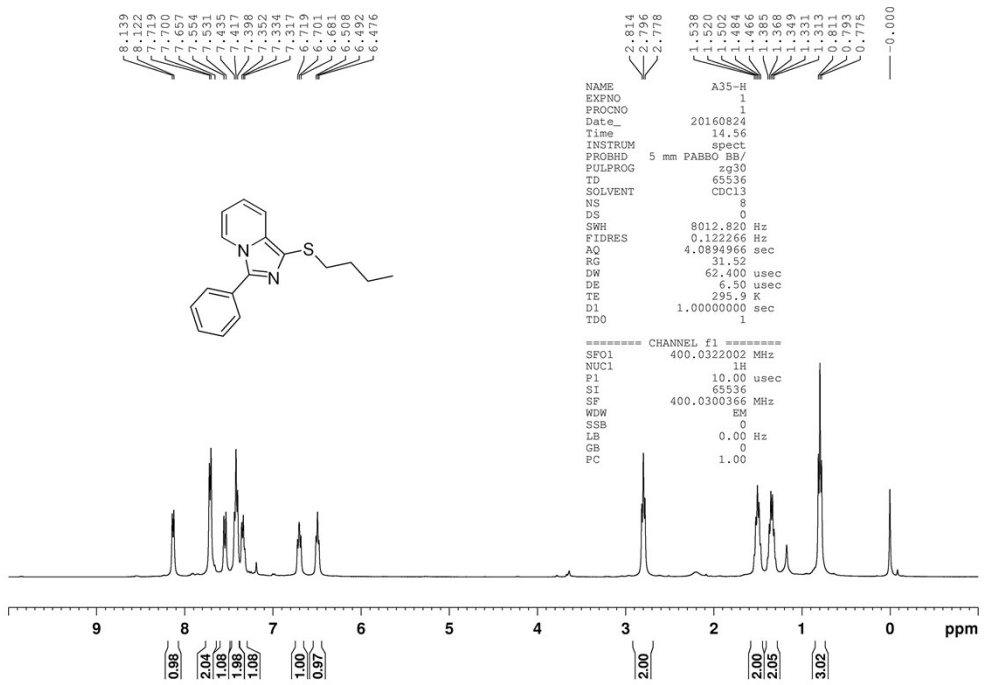


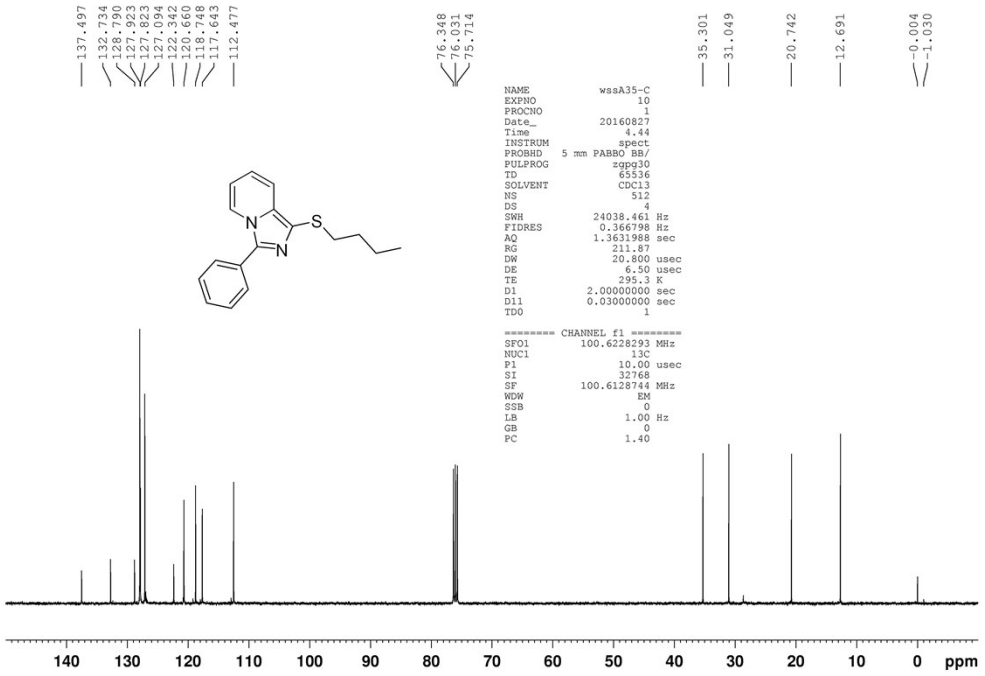
1-(benzylthio)-3-phenylimidazo[1,5-a]pyridine (3rc)



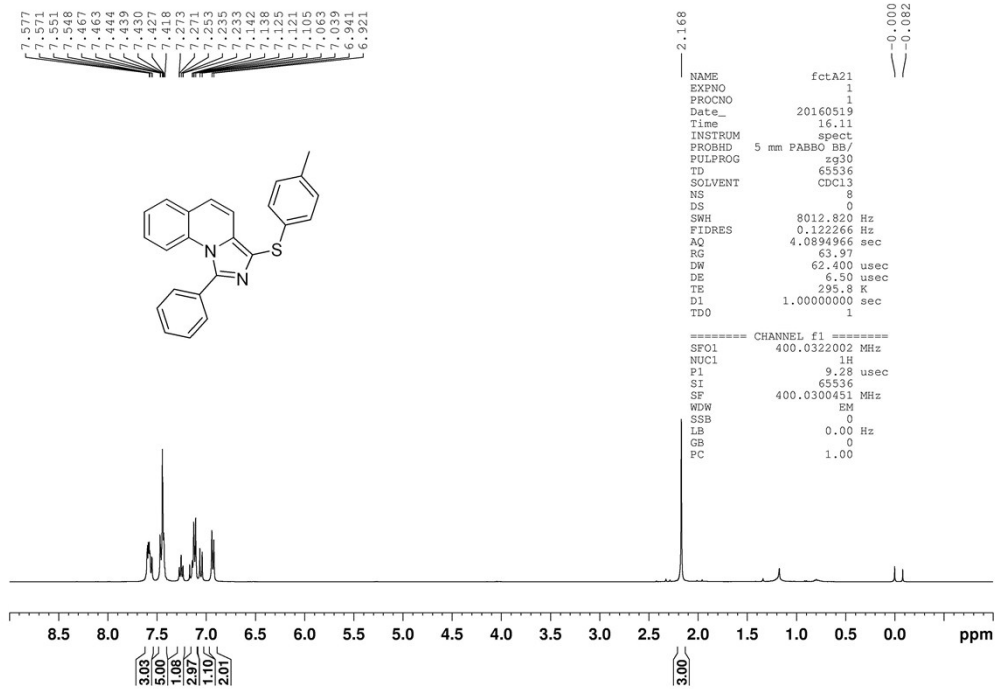


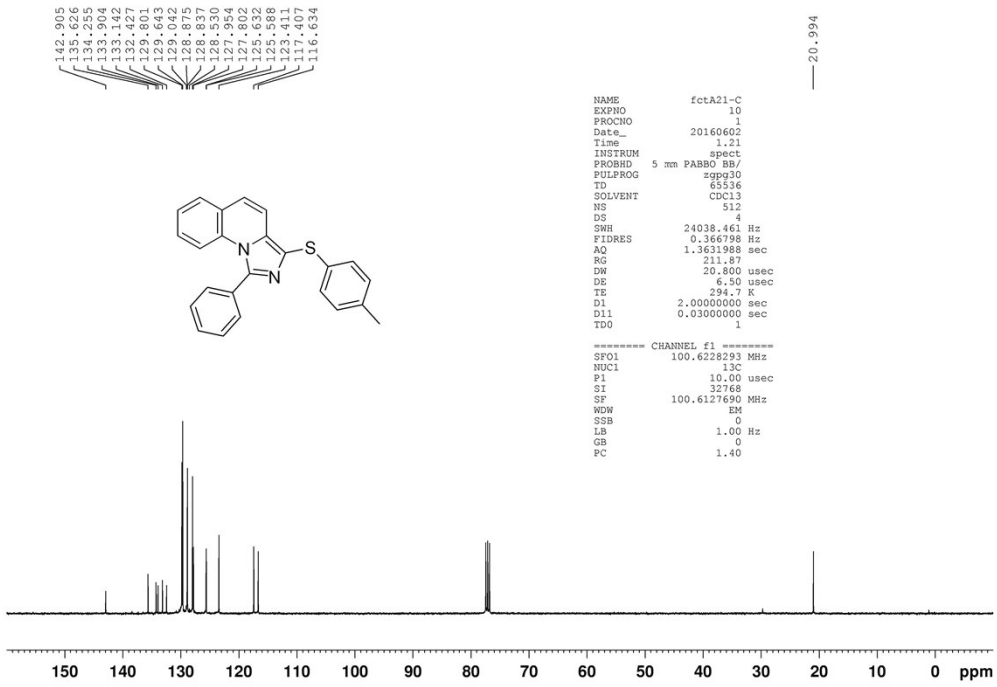
1-(butylthio)-3-phenylimidazo[1,5-a]pyridine (3rd)



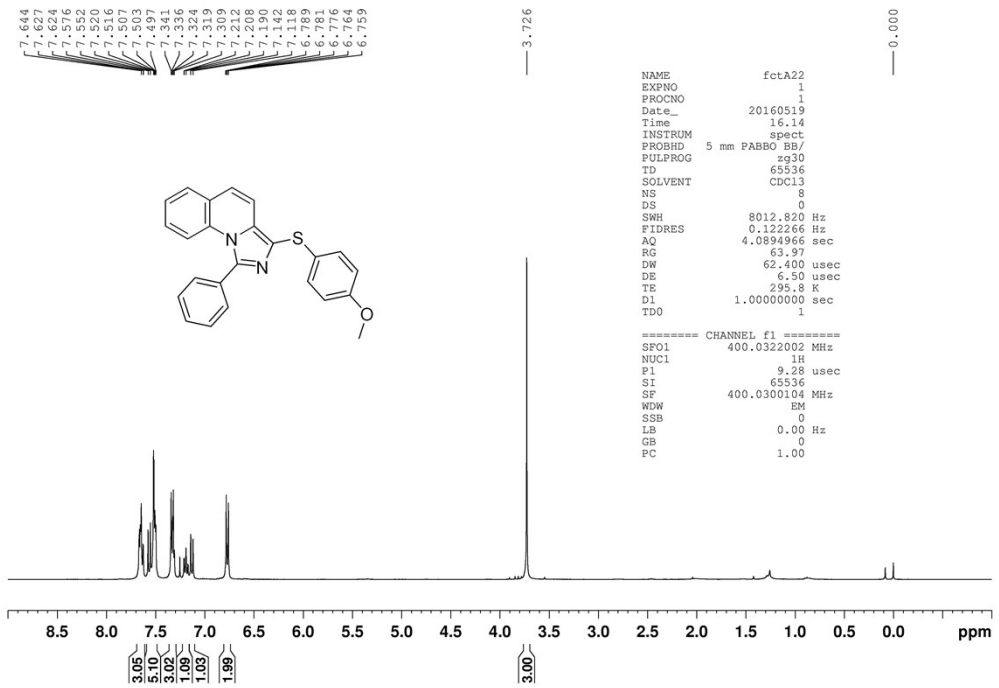


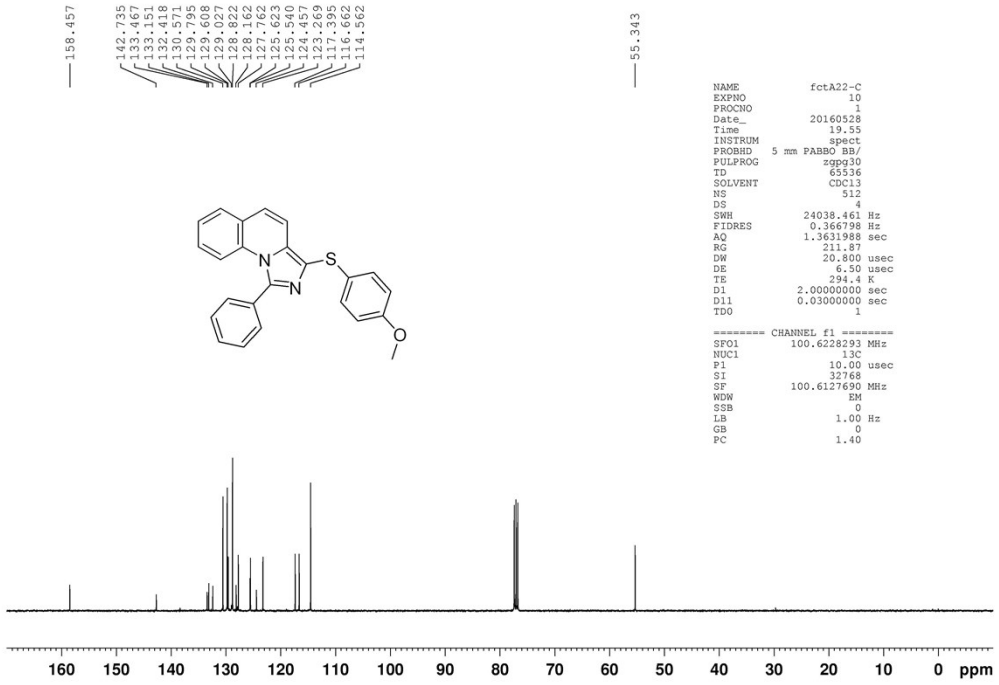
1-phenyl-3-(p-tolylthio)imidazo[1,5-a]quinoline (3ad)



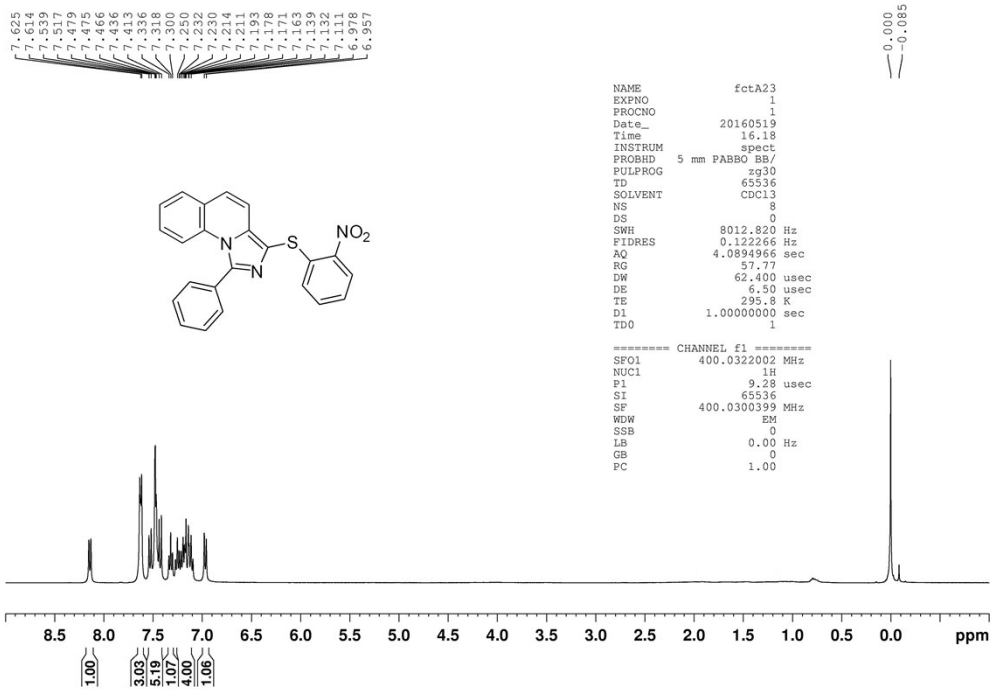


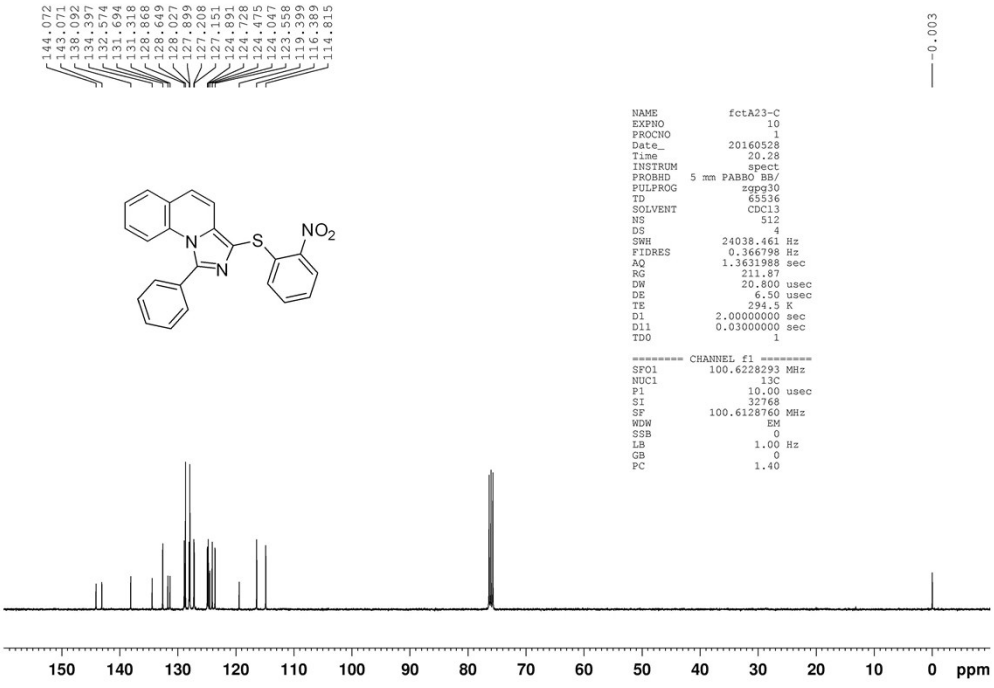
3-((4-methoxyphenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ae)



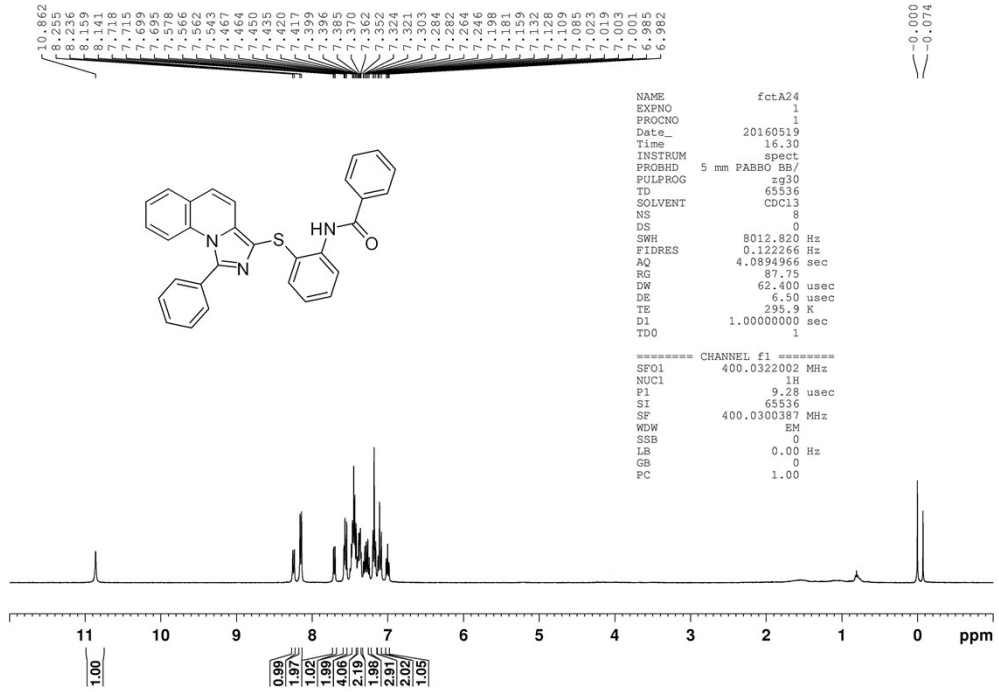


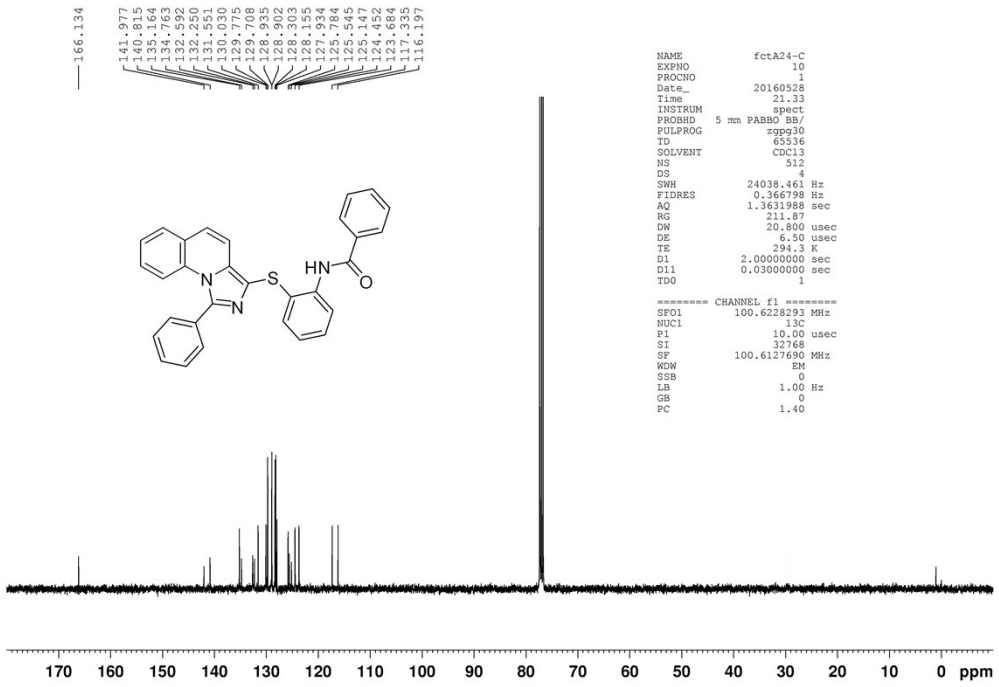
3-((2-nitrophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3af)



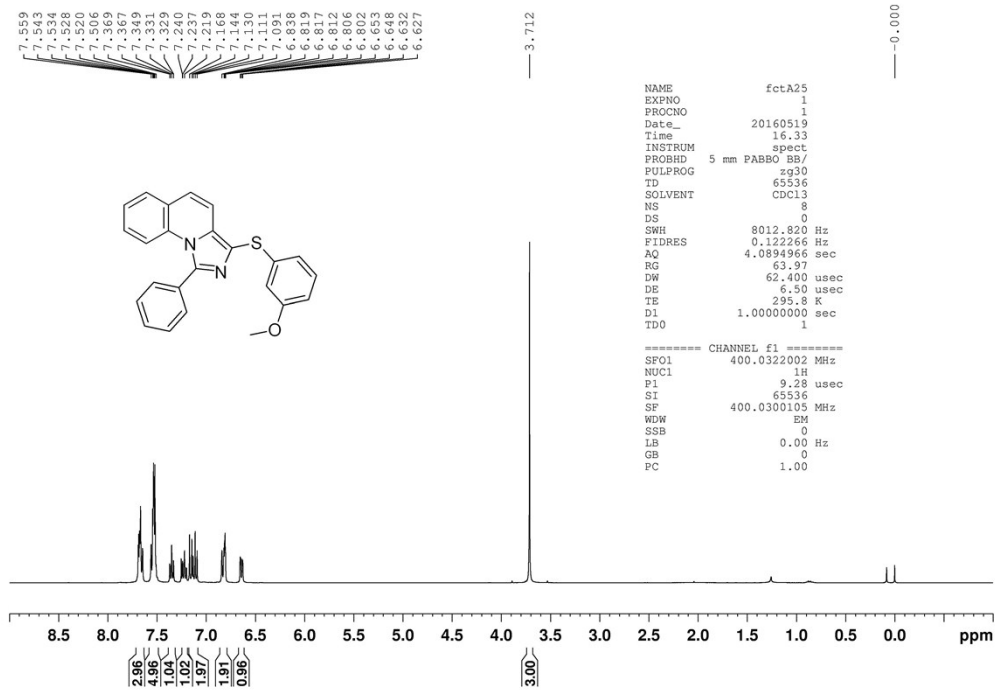


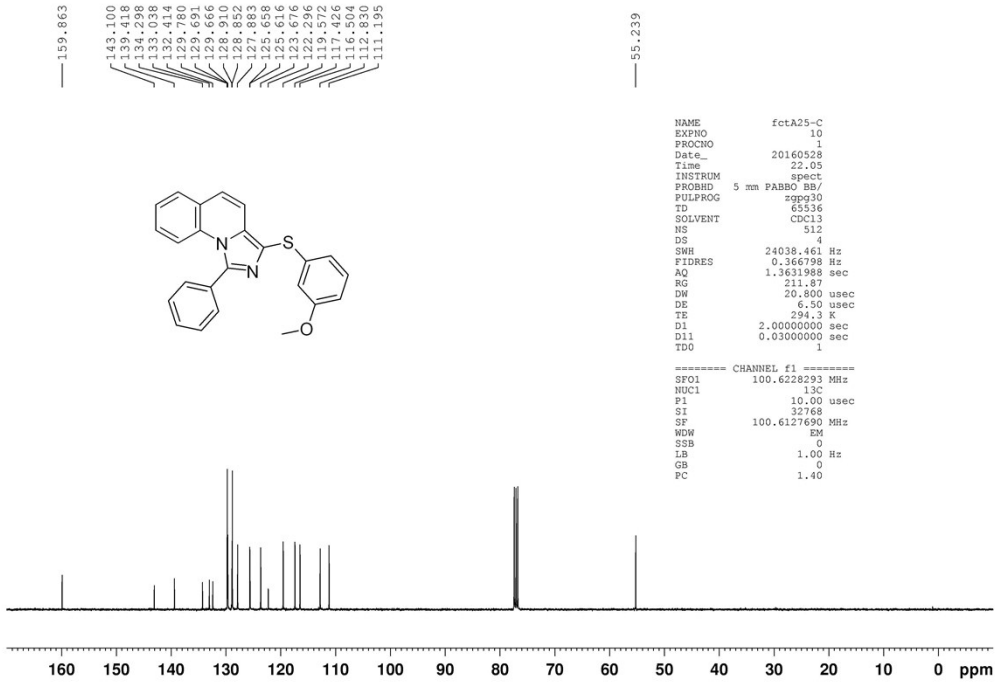
N-(2-((1-phenylimidazo[1,5-a]quinolin-3-yl)thio)phenyl)benzamide (3ag)



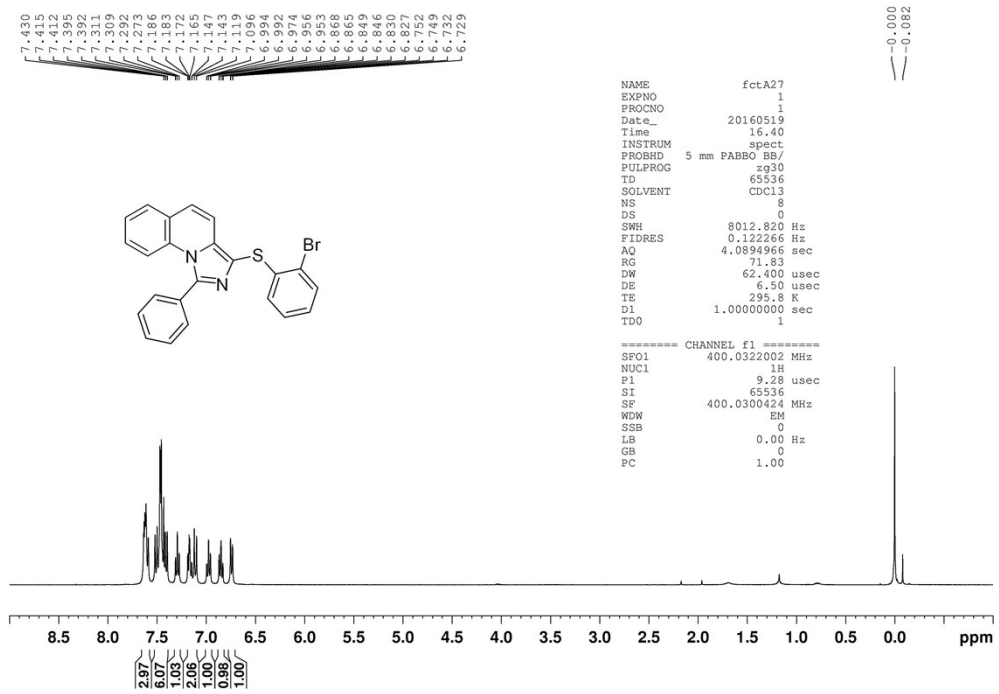


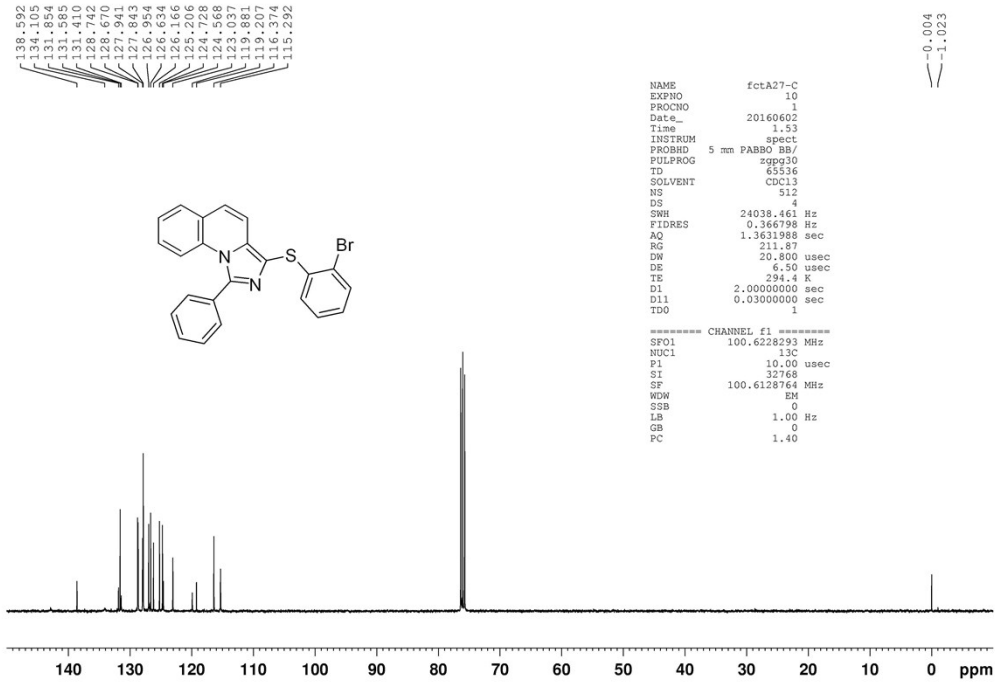
3-((3-methoxyphenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ah)



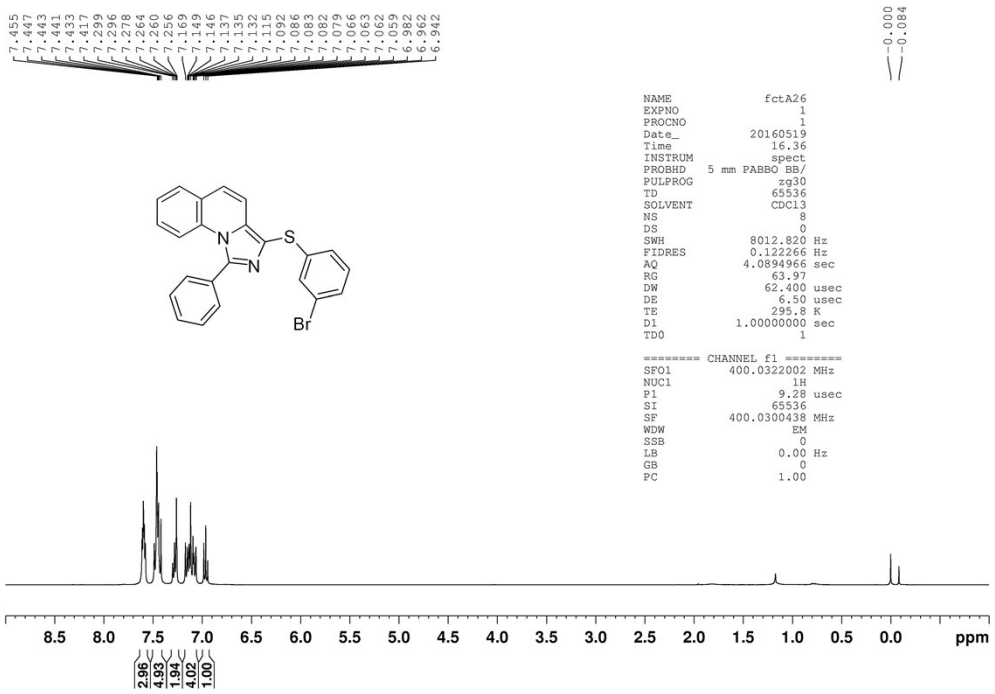


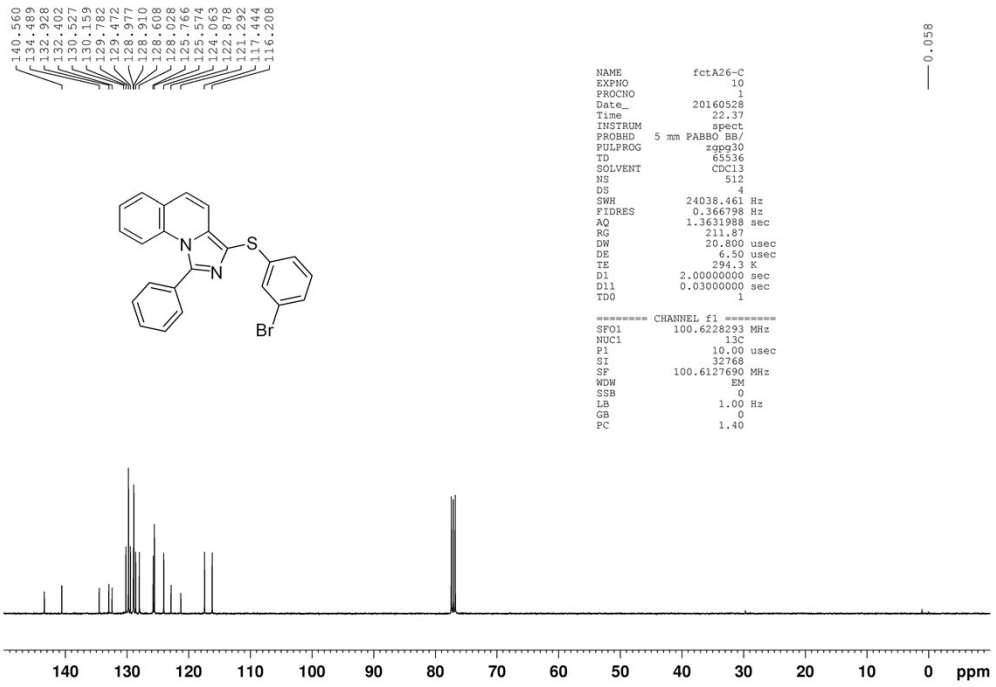
3-((2-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ai)



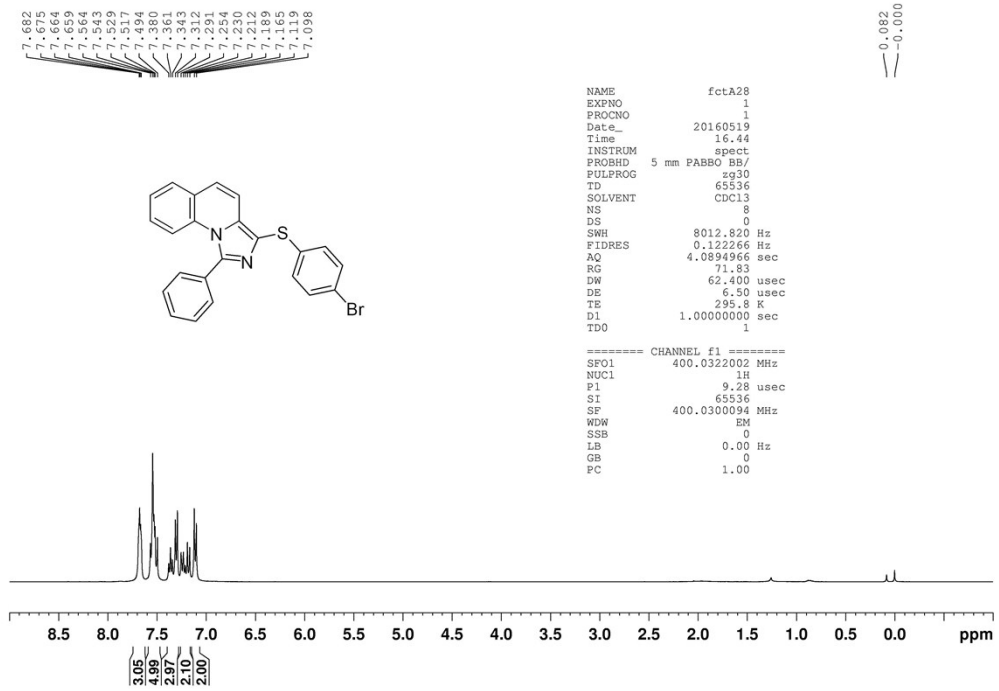


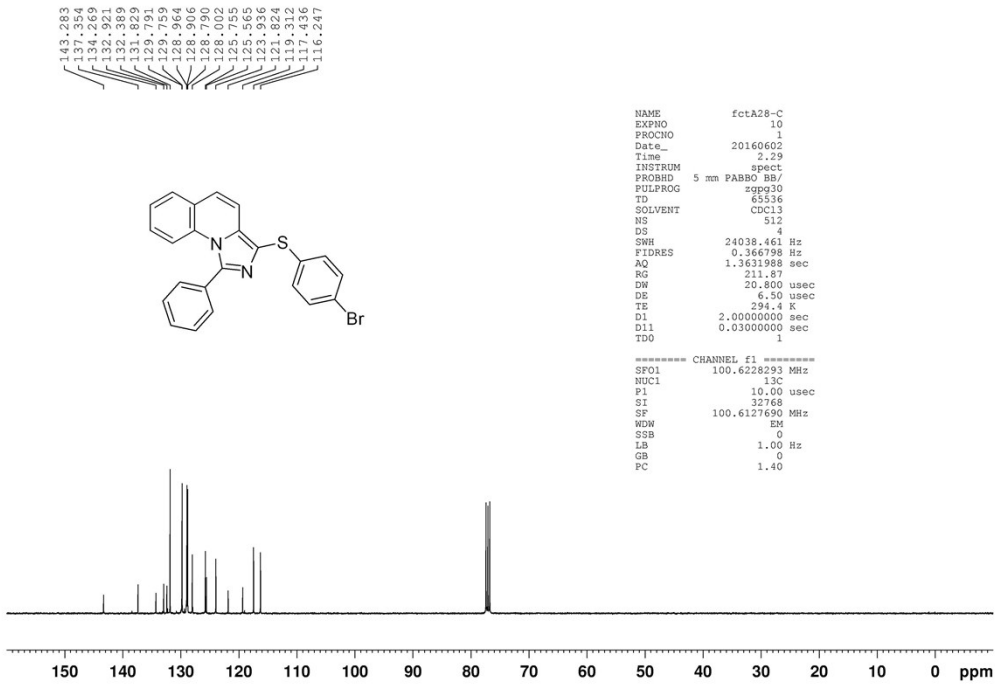
3-((3-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3aj)





3-((4-bromophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3ak)





3-((4-fluorophenyl)thio)-1-phenylimidazo[1,5-a]quinoline (3al)