Electronic Supplementary Information

Access to 2-Naphthols via Ru(II)-Catalyzed C-H Annulation of Nitrones with α-Diazo Sulfonyl Ketones

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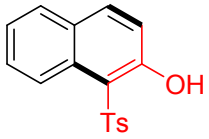
I. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on a 600 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate/hexanes. Aryl nitrones [1] and α-diazo sulfonyl ketones[2] were prepared according to literature reports.

II. Experimental Procedures and Characterizations

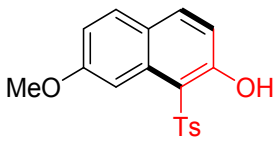
A mixture of aryl nitrone (**1**, 0.3 mmol), α-diazo sulfonyl ketone (**2**, 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol %), $AgNTf_2$ (20.0 mol %), $AgPF_6$ (20.0 mol %), PivOH (2.0 equiv), and DCE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 120 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (25:1) to afford the product **3**.



1-Tosylnaphthalen-2-ol (**3aa**)

3aa was obtained according to the general procedure in 79% yield (47.1 mg), white solid, mp = 123.6-125.3 ºC, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.14 (s, 1H), 8.34 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.34 – 7.31 (m, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 144.8, 139.4, 137.5, 130.0, 129.7, 129.2, 128.9, 128.8, 126.8, 124.5, 123.2, 120.4, 112.3, 21.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{15}O_3S^+$: 299.0736, found 299.0736.

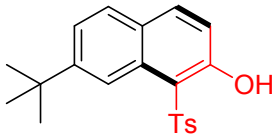


7-Methoxy-1-tosylnaphthalen-2-ol (**3ba**)

3ba was obtained according to the general procedure in 66% yield (43.1 mg), white solid, mp = 90.8-91.8 ºC, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.84 - 7.81 (m, 3H), 7.66 (d, J = 2.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 9.0 Hz, 1H), 6.94 (dd, J = 8.8, 2.4 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 159.5, 144.8, 139.2, 137.2, 131.4, 130.6, 129.9,

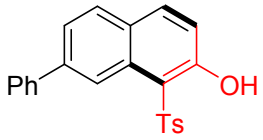
126.8, 124.0, 117.5, 116.3, 111.3, 103.3, 55.5, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_4S^+$: 351.0662, found 351.0659.



7-(*tert*-Butyl)-1-tosylnaphthalen-2-ol (**3ca**)

3ca was obtained according to the general procedure in 74% yield (52.5 mg), white solid, mp = 154.5-155.3 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

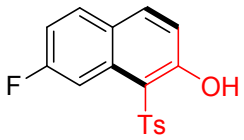
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.26 (s, 1H), 7.86 – 7.85 (m, 3H), 7.63 (d, J = 8.5 Hz, 1H), 7.39 (dd, J = 8.5, 1.8 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 9.0 Hz, 1H), 2.35 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 151.7, 144.7, 139.4, 137.0, 129.8, 129.5, 128.7, 127.0, 126.9, 123.0, 119.5, 119.1, 112.2, 35.6, 31.3, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{21}H_{22}NaO_3S^+$: 377.1182, found 377.1177.



7-Phenyl-1-tosylnaphthalen-2-ol (**3da**)

3da was obtained according to the general procedure in 67% yield (50.4 mg), yellow solid, mp = 160.0-161.5 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.18 (s, 1H), 8.54 (s, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 144.9, 141.4, 140.9, 139.4, 137.2, 130.0, 129.9, 129.6, 129.1, 128.0, 127.9, 127.7, 126.9, 124.1, 121.5, 120.3, 112.5, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{23}H_{18}NaO_3S^+$: 397.0869, found 397.0863.

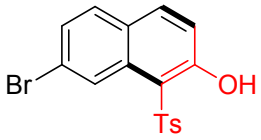


7-Fluoro-1-tosylnaphthalen-2-ol (**3ea**)

3ea was obtained according to the general procedure in 51% yield (32.3 mg), yellow solid, mp = 159.5-160.4 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.14 (s, 1H), 8.05 (dd, J = 12.2, 2.4 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.69 (dd, J = 8.9, 6.0 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 9.1 Hz, 1H), 7.09 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 248.4 Hz), 159.7, 145.1, 138.9, 137.2, 131.5 (d, J_{C-F} = 10.0 Hz), 131.1 (d, J_{C-F} = 10.6 Hz), 130.1, 126.8, 125.8, 119.6 (d, J_{C-F} =

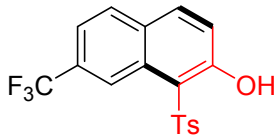
2.7 Hz), 114.3 (d, $J_{C\text{-}F}$ = 24.9 Hz), 112.3, 108.3 (d, $J_{C\text{-}F}$ = 25.8 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.2. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}FNaO_3S^+$: 339.0462, found 339.0461.



7-Bromo-1-tosylnaphthalen-2-ol (**3fa**)

3fa was obtained according to the general procedure in 60% yield (45.1 mg), yellow solid, mp = 166.7-168.6 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

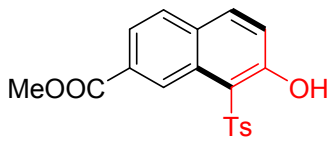
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.56 (d, J = 1.8 Hz, 1H), 7.86 – 7.83 (m, 3H), 7.54 (d, J = 8.5 Hz, 1H), 7.40 (dd, J = 8.6, 1.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 9.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 145.2, 138.8, 137.2, 130.8, 130.5, 130.1, 128.0, 127.3, 126.9, 125.7, 123.8, 120.8, 112.0, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}BrNaO_3S^+$: 398.9661, found 398.9656.



1-Tosyl-7-(trifluoromethyl)naphthalen-2-ol (**3ga**)

3ga was obtained according to the general procedure in 61% yield (45.0 mg), yellow solid, mp = 148.6-150.2 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

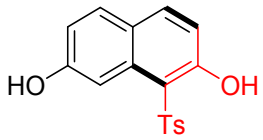
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.76 – 8.70 (m, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.82 (d, J = 8.4 Hz, 1H), 7.51 (dd, J = 8.3, 1.7 Hz, 1H), 7.33 – 7.27 (m, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 145.4, 138.8, 136.9, 130.2, 130.1, 130.0, 128.9, 127.0, 124.2 (q, $J_{C\text{-}F}$ = 272.9 Hz), 122.8, 120.9 (q, $J_{C\text{-}F}$ = 4.6 Hz), 120.4 (q, $J_{C\text{-}F}$ =3.3 Hz), 113.8, 100.2, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{13}F_3NaO_3S^+$: 389.0430, found 389.0422.



Methyl 7-hydroxy-8-tosyl-2-naphthoate (**3ha**)

3ha was obtained according to the general procedure in 69% yield (48.3 mg), white solid, mp = 169.2-170.3 °C, R_f = 0.20 (hexanes/ethyl acetate = 15/1).

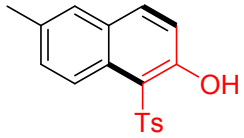
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.20 (s, 1H), 9.15 (s, 1H), 7.95 – 7.89 (m, 4H), 7.74 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.28 – 7.23 (m, 1H), 3.97 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 159.0, 145.1, 139.0, 136.9, 131.1, 130.1, 129.9, 129.3, 128.9, 127.2, 125.8, 124.3, 122.8, 113.8, 52.6, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{19}H_{16}NaO_5S^+$: 379.0611, found 379.0601.



1-Tosylnaphthalene-2,7-diol (**3ia**)

3ia was obtained according to the general procedure in 56% yield (35.4 mg), white solid, mp = 194.9-195.8 °C, R_f = 0.10 (hexanes/ethyl acetate = 15/1).

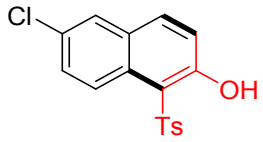
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.04 (s, 1H), 7.84 – 7.81 (m, 4H), 7.58 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.9 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.34 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 156.6, 144.9, 138.9, 137.5, 131.5, 131.3, 130.1, 126.7, 124.0, 117.4, 115.8, 110.8, 106.7, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{14}NaO_4S^+$: 337.0505, found 337.0498.



6-Methyl-1-tosylnaphthalen-2-ol (**3ja**)

3ja was obtained according to the general procedure in 64% yield (40.2 mg), yellow solid, mp = 126.0-127.7 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

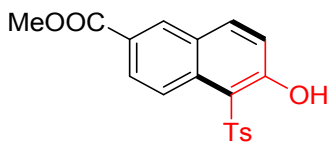
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.88 – 7.78 (m, 3H), 7.47 (s, 1H), 7.29 (dd, J = 8.9, 1.9 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.13 (d, J = 9.1 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 144.7, 139.4, 137.0, 134.1, 130.9, 130.0, 129.2, 128.4, 127.6, 126.7, 123.0, 120.2, 112.2, 21.7, 21.1. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_3S^+$: 335.0712, found 335.0705.



6-Chloro-1-tosylnaphthalen-2-ol (**3ka**)

3la was obtained according to the general procedure in 66% yield (44.1 mg), white solid, mp = 142.0-143.6 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

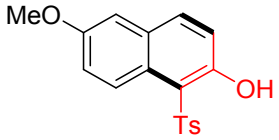
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.11 (s, 1H), 8.30 (d, J = 9.2 Hz, 1H), 7.82 – 7.80 (m, 3H), 7.67 (d, J = 2.3 Hz, 1H), 7.39 (dd, J = 9.3, 2.3 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 9.1 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 145.1, 139.0, 136.4, 130.4, 130.1, 129.8, 129.4, 127.9, 127.8, 126.7, 124.8, 121.7, 112.7, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}ClNaO_3S^+$: 355.0166, found 355.0160.



Methyl 6-hydroxy-5-tosyl-2-naphthoate (**3la**)

3ma was obtained according to the general procedure in 81% yield (71.2 mg), white solid, mp = 154.2-155.7 °C, R_f = 0.10 (hexanes/ethyl acetate = 15/1).

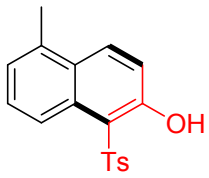
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.42 (s, 1H), 8.39 (d, J = 9.2 Hz, 1H), 8.01 (m, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.25 (m, 3H), 3.93 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 160.4, 145.1, 138.9, 138.4, 132.3, 131.7, 130.1, 128.4, 128.1, 126.8, 126.1, 123.3, 121.3, 112.8, 52.4, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{19}H_{16}NaO_5S^+$: 379.0611, found 379.0604.



6-Methoxy-1-tosylnaphthalen-2-ol (**3ma**)

3ka was obtained according to the general procedure in 80% (20:1) yield (52.6 mg), white solid, mp = 131.1-133.2 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

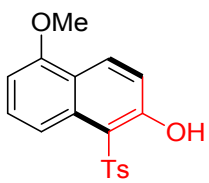
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.27 (d, J = 9.4 Hz, 1H), 7.82 – 7.79 (m, 3H), 7.25 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 9.0 Hz, 1H), 7.12 (dd, J = 9.4, 2.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 3.82 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 156.3, 144.7, 139.3, 136.3, 130.3, 130.0, 126.7, 124.6, 124.3, 120.7, 120.4, 112.5, 108.2, 55.4, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_4S^+$: 351.0662, found 351.0655.



5-Methyl-1-tosylnaphthalen-2-ol (**3na**)

3na was obtained according to the general procedure in 74% yield (46.4 mg), yellow solid, mp = 160.2-161.4 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

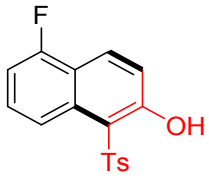
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.21 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 9.4 Hz, 1H), 7.82 – 7.80 (m, 2H), 7.34 – 7.31 (m, 1H), 7.25 – 7.23 (m, 2H), 7.20 (d, J = 9.3 Hz, 1H), 7.16 – 7.14 (m, 1H), 2.61 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 144.7, 139.4, 135.6, 133.5, 130.0, 129.9, 128.6, 127.9, 126.7, 125.7, 121.5, 119.9, 112.7, 21.7, 19.9. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_3S^+$: 335.0712, found 335.0704.



5-Methoxy-1-tosylnaphthalen-2-ol (**3oa**)

3oa was obtained according to the general procedure in 90% yield (59.0 mg), white solid, mp = 142.2-143.0 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

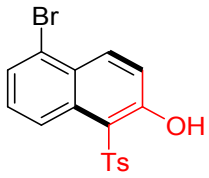
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.14 (s, 1H), 8.42 (d, J = 9.3 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.3 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.13 (d, J = 9.3 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.0, 144.5, 139.2, 131.4, 130.9, 129.8, 129.3, 126.6, 120.5, 118.9, 115.3, 111.9, 103.2, 55.6, 21.6. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_4S^+$: 351.0662, found 351.0658.



5-Fluoro-1-tosylnaphthalen-2-ol (**3pa**)

3pa was obtained according to the general procedure in 53% yield (33.4 mg), white solid, mp = 146.1-146.6 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

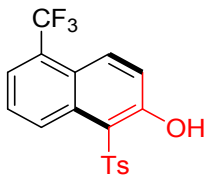
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.23 (d, J = 9.3 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.83 – 7.81 (m, 2H), 7.40 – 7.36 (m, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 9.3 Hz, 1H), 7.01 – 6.98 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 159.2 (d, $J_{C\text{-}F}$ = 253.0 Hz), 145.0, 139.1, 131.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 130.1, 129.7 (d, $J_{C\text{-}F}$ = 7.3 Hz), 129.2 (d, $J_{C\text{-}F}$ = 9.1 Hz), 126.8, 120.8 (d, $J_{C\text{-}F}$ = 2.1 Hz), 119.1 (d, $J_{C\text{-}F}$ = 16.7 Hz), 119.0 (d, $J_{C\text{-}F}$ = 4.3 Hz), 112.5, 108.7 (d, $J_{C\text{-}F}$ = 19.7 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}FNaO_3S^+$: 339.0462, found 339.0454.



5-Bromo-1-tosylnaphthalen-2-ol (**3qa**)

3qa was obtained according to the general procedure in 76% yield (57.4 mg), white solid, mp = 158.0-1158.8 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

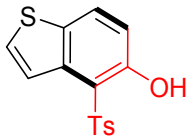
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.42 (d, J = 9.4 Hz, 1H), 8.35 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.28 – 7.25 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 145.0, 139.1, 136.4, 131.2, 130.1, 129.1, 128.8, 127.2, 126.7, 124.0, 122.9, 121.8, 112.6, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}BrNaO_3S^+$: 398.9661, found 398.9648.



1-Tosyl-5-(trifluoromethyl)naphthalen-2-ol (**3ra**)

3ra was obtained according to the general procedure in 63% yield (46.4 mg), white solid, mp = 98.0-99.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

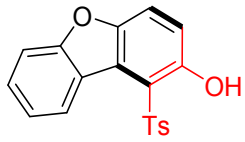
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.25 (s, 1H), 8.61 (d, J = 8.9 Hz, 1H), 8.30 (d, J = 9.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 7.4 Hz, 1H), 7.49 (t, J = 8.1 Hz, 1H), 7.33 (d, J = 9.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 145.2, 139.0, 133.0 (q, $J_{C\text{-}F}$ = 3.0 Hz), 130.8, 130.2, 127.5, 127.3, 127.2 (q, $J_{C\text{-}F}$ = 42.2 Hz), 126.8, 124.7, 124.4 (q, $J_{C\text{-}F}$ = 274.1 Hz), 123.01 (q, $J_{C\text{-}F}$ = 6.1 Hz), 122.3, 113.4, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{13}F_3NaO_3S^+$: 389.0430, found 389.0424.



4-Tosylbenzo[*b*]thiophen-5-ol (**3sa**)

3sa was obtained according to the general procedure in 22% yield (13.2 mg), yellow solid, mp = 179.3-179.9 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

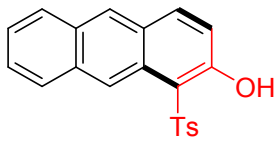
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 5.6 Hz, 1H), 7.57 (d, J = 5.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.8 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 145.0, 139.0, 136.3, 133.3, 130.8, 130.1, 129.9, 126.7, 122.8, 117.1, 115.1, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{15}H_{12}NaO_3S_2^+$: 327.0120, found 327.0116.



1-Tosyldibenzo[*b*,*d*]furan-2-ol (**3ta**)

3ta was obtained according to the general procedure in 23% yield (15.7 mg), white solid, mp = 163.5-164.0 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

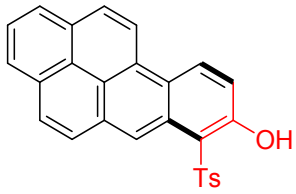
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.59 (d, J = 8.1 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.32 – 7.28 (m, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 154.8, 150.3, 145.1, 138.8, 130.1, 128.5, 126.2, 125.8, 123.2, 121.8, 121.4, 120.1, 119.1, 114.2, 111.8, 21.8. HRMS: m/z: $[M + Na]^+$ calculated for $C_{19}H_{14}NaO_4S^+$: 361.0505, found 361.0509.



1-Tosylanthracen-2-ol (**3ua**)

3ua was obtained according to the general procedure in 61% yield (42.8 mg), yellow solid, mp = 136.2-137.0 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

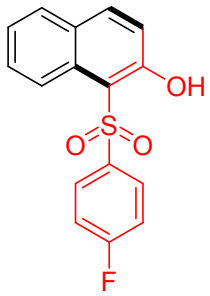
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.83 (s, 1H), 8.24 (s, 1H), 8.04 (d, J = 9.2 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.88 (t, J = 8.6 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.43 -7.40 (m, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 9.2 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 144.8, 139.2, 138.2, 133.1, 130.1, 129.9, 128.6, 128.3, 127.9, 127.7, 126.9, 126.8, 126.4, 125.8, 122.0, 120.9, 109.9, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{21}H_{16}NaO_3S^+$: 371.0712, found 371.0708.



7-Tosylbenzo[*pqr*]tetraphen-8-ol (**3va**)

3va was obtained according to the general procedure in 62% yield (52.4 mg), yellow solid, mp = 222.1-222.9 °C, R_f = 0.30 (hexanes/ethyl acetate = 5/1).

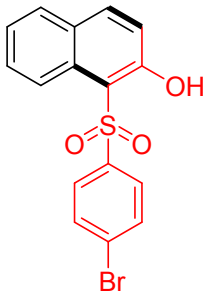
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.42 (s, 1H), 9.67 (s, 1H), 9.41 (d, J = 9.3 Hz, 1H), 9.09 (d, J = 9.1 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.24 (d, J = 7.3 Hz, 1H), 8.15 – 8.09 (m, 2H), 8.06 (t, J = 7.9 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 9.3 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.9, 144.0, 140.2, 132.2, 130.9, 130.6, 130.3, 129.6, 129.1, 128.6, 128.4, 127.7, 126.9, 126.6, 126.2, 125.8, 123.7, 122.3, 120.9, 119.3, 119.3, 115.2, 21.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{27}H_{19}O_3S^+$: 423.1049, found 423.1049.



1-((4-Fluorophenyl)sulfonyl)naphthalen-2-ol (**3ab**)

3ab was obtained according to the general procedure in 76% yield (46.0 mg), white solid, mp = 118.4-119.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

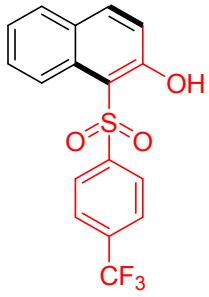
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.05 (s, 1H), 8.31 (d, J = 8.7 Hz, 1H), 7.98 – 7.95 (m, 2H), 7.94 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 9.1 Hz, 1H), 7.15 (t, J = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7 (d, $J_{C\text{-}F}$ = 256.6 Hz), 159.0, 138.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 137.9, 129.6 (d, $J_{C\text{-}F}$ = 31.4 Hz), 129.5, 129.4, 129.1, 128.9, 124.7, 122.9, 120.4, 116.8 (d, $J_{C\text{-}F}$ = 22.7 Hz), 111.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.3. HRMS: m/z: $[M + Na]^+$ calculated for $C_{16}H_{11}FNaO_3S^+$: 325.0305, found 325.0302.



1-((4-Bromophenyl)sulfonyl)naphthalen-2-ol (**3ac**)

3ac was obtained according to the general procedure in 72% yield (52.5 mg), white solid, mp = 157.0-157.6 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

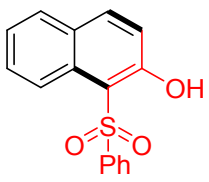
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 9.1 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.49 – 7.46 (m, 1H), 7.36 – 7.33 (m, 1H), 7.18 (d, J = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 141.2, 138.0, 132.7, 129.5, 129.4, 129.1, 128.91, 128.90, 128.2, 124.7, 122.9, 120.3, 111.4. HRMS: m/z: $[M + Na]^+$ calculated for $C_{16}H_{11}BrNaO_3S^+$: 384.9504, found 384.9506.



1-((4-(Trifluoromethyl)phenyl)sulfonyl)naphthalen-2-ol (**3ad**)

3ad was obtained according to the general procedure in 69% yield (48.5 mg), white solid, mp = 151.8-152.3 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 9.0 Hz, 1H), 7.75 – 7.72 (m, 3H), 7.50 – 7.47 (m, 1H), 7.38 – 7.35 (m, 1H), 7.20 (d, J = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 145.7, 138.4, 135.3 (q, $J_{C\text{-}F}$ = 33.1 Hz), 129.5, 129.4, 129.3, 128.9, 127.2, 126.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.8, 123.1 (q, $J_{C\text{-}F}$ = 273.1 Hz), 122.8, 120.4, 110.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{11}F_3NaO_3S^+$: 375.0273, found 375.0272.

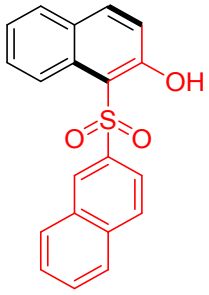


1-(Phenylsulfonyl)naphthalen-2-ol (**3ae**)

3ae was obtained according to the general procedure in 65% yield (36.8 mg), yellow solid, mp = 123.9-

125.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

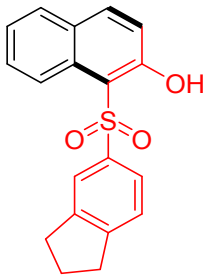
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.12 (s, 1H), 8.33 (d, J = 8.7 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.93 (d, J = 9.1 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.49 – 7.43 (m, 3H), 7.34 – 7.31 (m, 1H), 7.18 (d, J = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 142.2, 137.7, 133.7, 129.6, 129.4, 129.3, 128.9, 128.9, 126.7, 124.5, 123.1, 120.3, 111.9. HRMS: m/z: $[M + Na]^+$ calculated for $C_{16}H_{12}NaO_3S^+$: 307.0399, found 307.0397.



1-(Naphthalen-2-ylsulfonyl)naphthalen-2-ol (**3af**)

3af was obtained according to the general procedure in 76% yield (50.5 mg), white solid, mp = 164.7-165.1 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.62 (s, 1H), 8.42 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.44 – 7.40 (m, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 138.9, 137.8, 135.3, 132.1, 129.9, 129.7, 129.6, 129.5, 129.3, 129.0, 128.9, 128.1, 128.0, 127.9, 124.5, 123.1, 121.6, 120.4, 111.9. HRMS: m/z: $[M + Na]^+$ calculated for $C_{20}H_{14}NaO_3S^+$: 357.0556, found 357.0551.

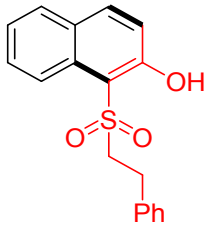


1-((2,3-Dihydro-1*H*-inden-5-yl)sulfonyl)naphthalen-2-ol (**3ag**)

3ag was obtained according to the general procedure in 74% yield (48.1 mg), white solid, mp = 143.4-144.0 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.18 (s, 1H), 8.36 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 9.1 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.33 – 7.30 (m, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 2.89 – 2.87 (m, 2H), 2.87 – 2.85 (m, 2H), 2.07 – 2.01 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 151.2, 145.9, 140.0, 137.4, 129.7, 129.2, 128.9, 128.8, 125.03, 125.00, 124.4, 123.2, 122.5, 120.3, 112.5, 33.0, 32.7, 25.4. HRMS: m/z: $[M + Na]^+$ calculated for

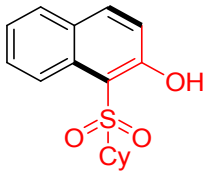
$C_{19}H_{16}NaO_3S^+$: 347.0712, found 347.0706.



1-(Phenethylsulfonyl)naphthalen-2-ol (**3ah**)

3ah was obtained according to the general procedure in 72% yield (44.9 mg), white solid, mp = 91.9-92.6 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

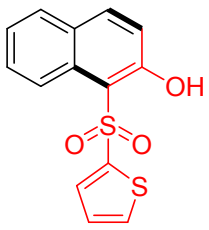
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.51 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.45 – 7.41 (m, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.13 (m, 1H), 7.12 (d, J = 9.0 Hz, 1H), 7.04 – 7.02 (m, 2H), 3.66 – 3.62 (m, 2H), 3.09 – 3.05 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 137.7, 136.9, 130.0, 129.6, 129.4, 128.9, 128.8, 128.3, 127.1, 124.7, 122.7, 120.3, 110.2, 57.5, 28.6. HRMS: m/z: $[M + Na]^+$ calculated for $C_{18}H_{16}NaO_3S^+$: 335.0712, found 335.0705.



1-(Cyclohexylsulfonyl)naphthalen-2-ol (**3ai**)

3ai was obtained according to the general procedure in 65% yield (37.9 mg), yellow solid, mp = 91.4-92.3 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.55 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.612 – 7.59 (m, 1H), 7.44 – 7.41 (m, 1H), 7.13 (d, J = 9.0 Hz, 1H), 3.27 – 3.22 (m, 1H), 2.04 – 1.86 (m, 4H), 1.67 – 1.63 (m, 3H), 1.25 – 1,18 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 137.4, 130.4, 129.5, 129.1, 129.0, 124.5, 123.2, 120.1, 109.0, 63.82, 63.80, 25.2, 25.1. HRMS: m/z: $[M + Na]^+$ calculated for $C_{16}H_{18}NaO_3S^+$: 313.0869, found 313.0864.

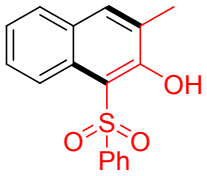


1-(Thiophen-2-ylsulfonyl)naphthalen-2-ol (**3aj**)

3aj was obtained according to the general procedure in 73% yield (42.6 mg), white solid, mp = 135.3-136.5 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.87 (s, 1H), 8.60 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.78 –

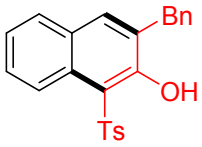
7.77 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 9.0 Hz, 1H), 7.04 (t, J = 4.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 143.6, 137.9, 133.5, 133.0, 129.5, 129.4, 129.1, 128.9, 127.7, 124.7, 123.2, 120.4, 113.4. HRMS: m/z: $[M + Na]^+$ calculated for $C_{14}H_{10}NaO_3S_2^+$: 312.9964, found 312.9958.



3-Methyl-1-(phenylsulfonyl)naphthalen-2-ol (**3ak**)

3ak was obtained according to the general procedure in 66% yield (39.2 mg), white solid, mp = 141.6-142.4 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.41 (s, 1H), 8.27 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 7.8 Hz, 2H), 7.78 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 142.4, 136.9, 133.6, 129.4, 129.0, 128.5, 128.48, 128.44, 127.9, 126.6, 124.4, 122.9, 111.2, 17.2. HRMS: m/z: $[M + Na]^+$ calculated for $C_{17}H_{14}NaO_3S^+$: 321.0556, found 321.0552.

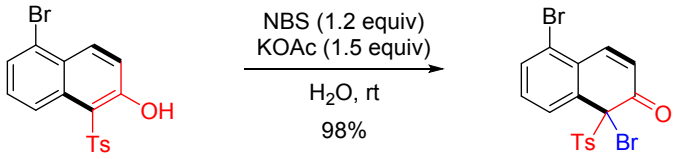


3-Benzyl-1-tosylnaphthalen-2-ol (**3al**)

3al was obtained according to the general procedure in 45% yield (34.9 mg), white solid, mp = 166.7-167.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.50 (s, 1H), 8.29 (dd, J = 8.7, 1.0 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.63 (s, 1H), 7.58 (dd, J = 8.1, 1.4 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.27 (m, 2H), 7.27 – 7.22 (m, 4H), 4.16 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7, 144.7, 139.5, 139.4, 136.8, 132.0 130.0, 129.3, 128.8, 128.7, 128.66, 128.4, 128.1, 126.7, 126.5, 124.4, 122.9, 112.0, 36.5, 21.7. HRMS: m/z: $[M + Na]^+$ calculated for $C_{24}H_{20}NaO_3S^+$: 411.1025, found 411.1034.

III. Derivatization Reaction



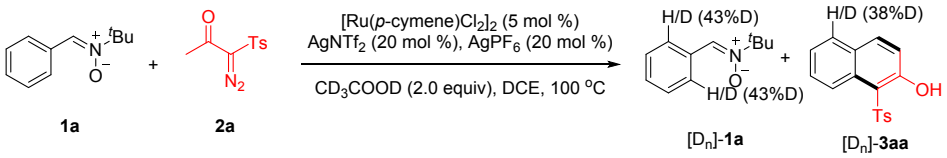
3qa **5**

To a 15 mL tube equipped with a magnetic stirrer was charged with **3qa** (37.7 mg, 0.1 mmol), NBS (21.4 mg, 0.12 mmol), and KOAc (14.7 mg, 0.15 mmol) in 1.0 mL H_2O. Then the mixture

was stirred at room temperature for the desired time (monitored by TLC). After the reaction, the resulting mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, after which the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (20:1) as the eluent to afford the desired product **5** as brown solid in 98% yield (44.5 mg), mp = 82.3-84.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 10.3 Hz, 1H), 7.72 (dd, J = 8.1, 1.2 Hz, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.38 – 7.36 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 10.2 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.6, 146.9, 143.7, 135.4, 135.0, 134.2, 132.0, 131.1 130.4, 129.2, 126.7, 125.7, 124.9, 81.1, 22.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{13}Br_2O_3S^+$: 454.8947, found 454.8947.

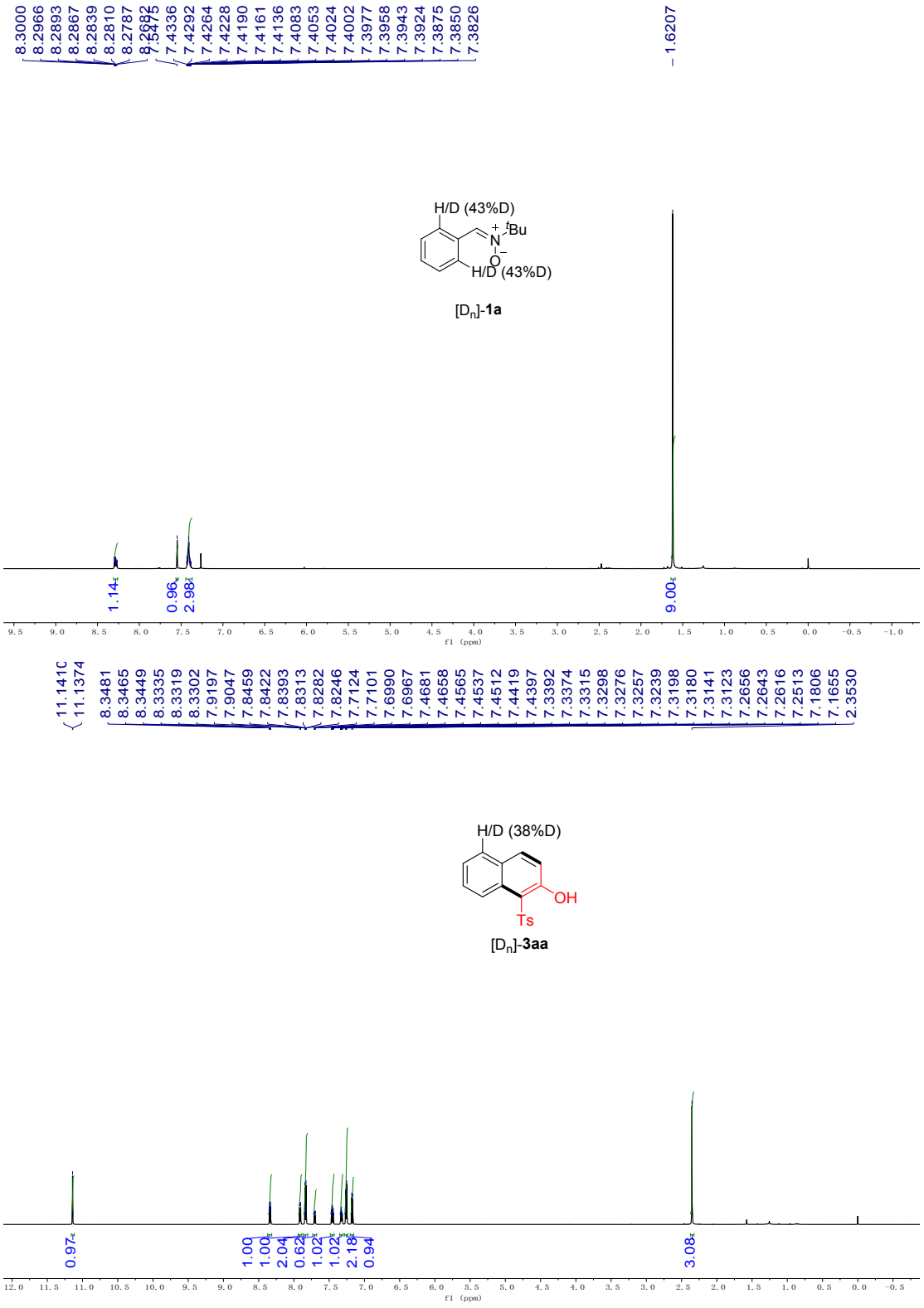
IV. Mechanistic Studies

(a) H/D Exchange Experiment

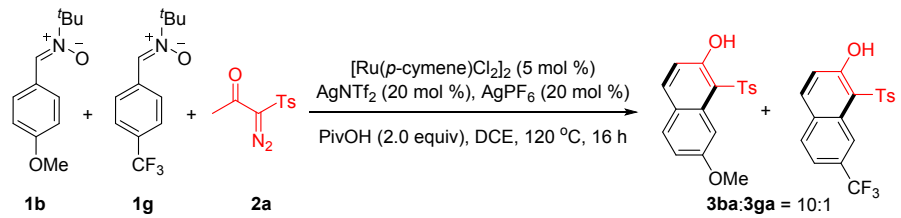


1a **2a** [D_n]-**1a** [D_n]-**3aa**

Aryl nitrone (**1**, 0.3 mmol), α-diazo sulfonyl ketone (**2**, 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), and CD_3COOD (2.0 equiv) were dissolved in DCE in a pressure tube under N_2 atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the recovered **1a** and the product **3aa**, which was characterized by ^{1}H NMR spectroscopy. The *ortho'* positions of the recovered **1a** and the product **3aa** were deuterated (43% D, and 38% D respectively).

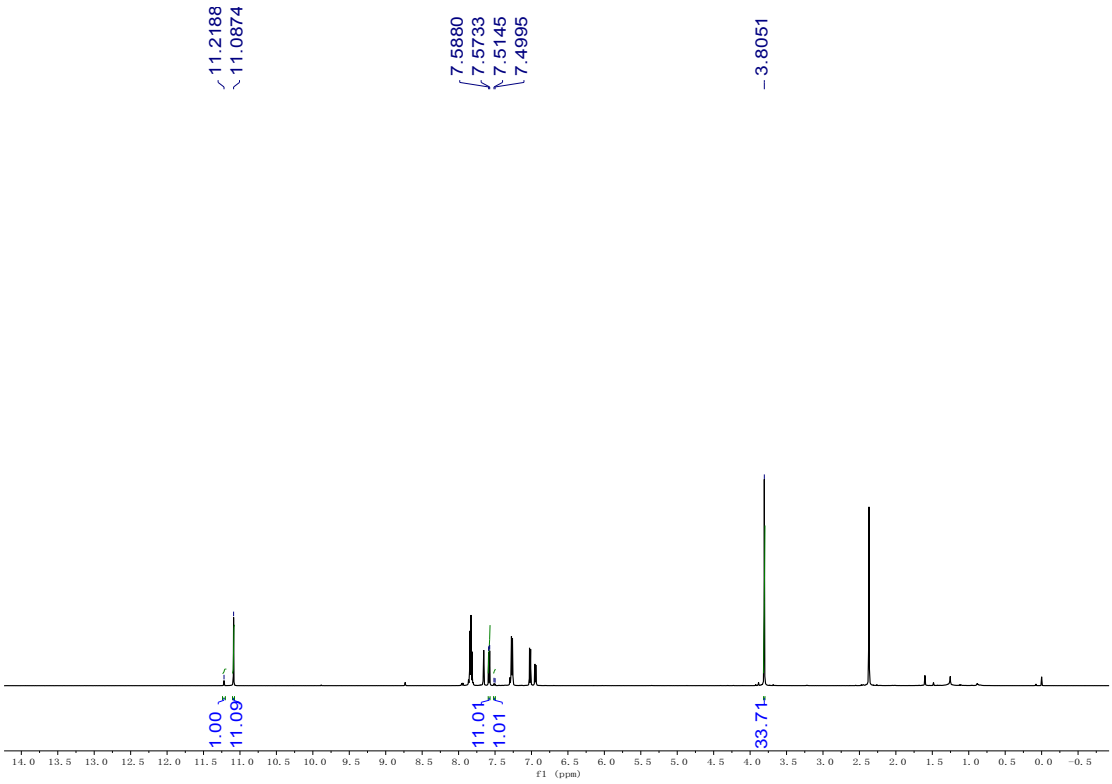


(b) The intermolecular competition experiment

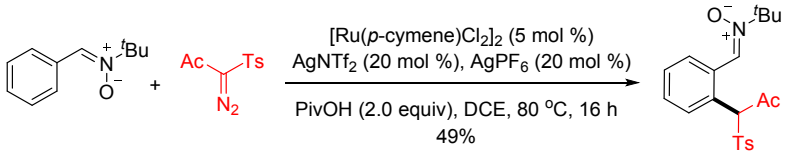


1b **1g** **2a** **3ba**:**3ga** = 10:1

An equimolar mixture of aryl nitrone **1b** (0.1 mmol) and **1g** (0.1 mmol), α-diazo sulfonyl ketone (**2,** 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), PivOH (2.0 equiv), and DCE (2 mL) were charged into a pressure tube under N_2. The reaction mixture was stirred at 120 °C for 12 h. The solvent was rapidly removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the mixed product. The yield ratio (**3ba**/**3ga** = 11:1) was determined on the basis of ^{1}H NMR analysis.

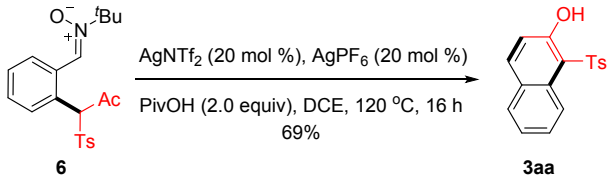


(c) Isolation of Intermediate 6 and Control Experiments



1a **2a** **6**

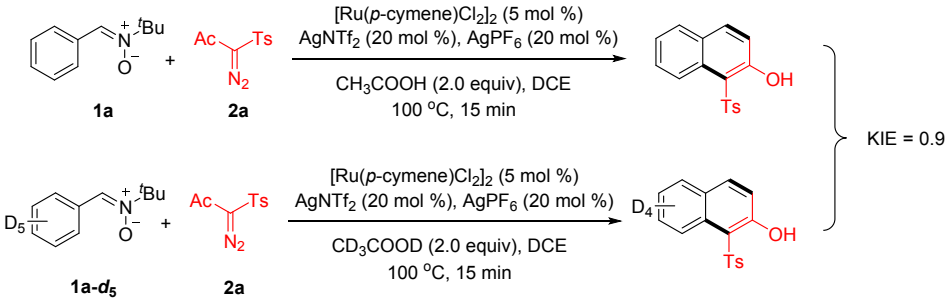
Aryl nitrone **1a** (0.3 mmol), diazo sulfonylketone **2a** (0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), PivOH (2.0 equiv), and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 80 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (2:1) to afford the product **6** in 49% yield (38.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.63 – 7.61 (m, 1H), 7.43 – 7.40 (m, 3H), 7.28 – 7.25 (m, 1H), 7.21 – 7.16 (m, 3H), 5.84 (s, 1H), 2.41 (s, 3H), 2.37 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.3, 145.0, 134.3, 132.5, 130.8, 130.2, 130.1, 129.7, 129.5, 129.4, 129.1, 127.9, 78.1, 71.2, 31.7, 28.2, 21.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{26}NO_4S^+$: 388.1577, found 388.1576.



6 3aa

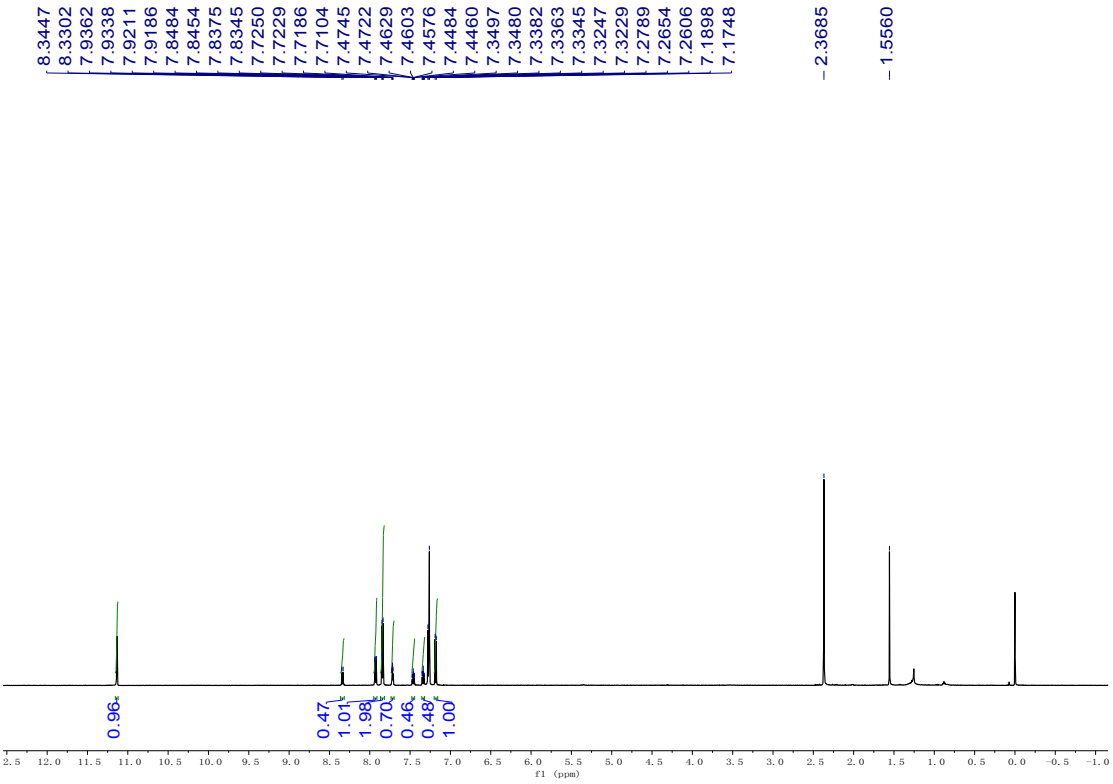
Intermediate **6** (0.14 mmol), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), PivOH (2.0 equiv), and DCE (1.4 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 120 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (2:1) to afford the product **3aa** in 69% yield (28.8 mg). What's more, the intermediate **6** could be converted to the final product **3aa** without Ru(II) catalyst.

(d) **KIE Study**

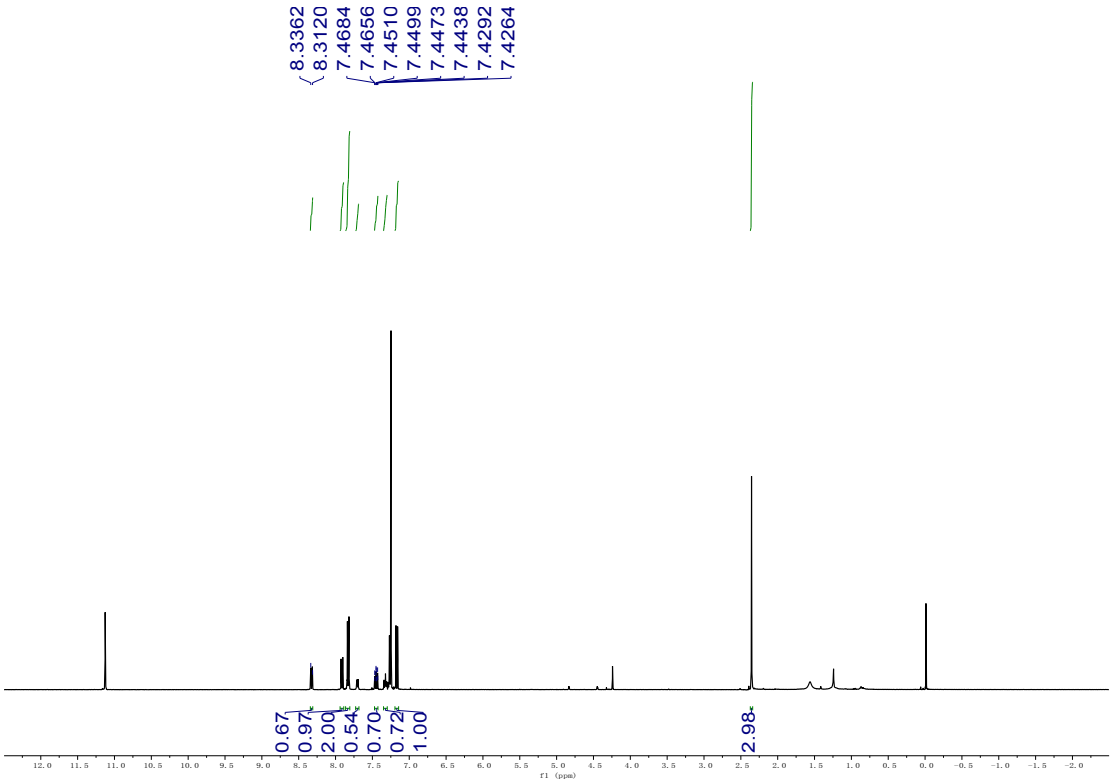


1a 2a 1a-d_5 2a

Aryl nitrone **1a** (0.15 mmol), diazo sulfonylketone **2a** (0.1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), and CH_3COOH (2.0 equiv) were dissolved in DCE (1 mL) in a pressure tube under N_2 atmosphere, while the other pressure tube was changed with **1a**-d_5 (0.1 mmol), **2a** (0.1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), and CD_3COOD (2.0 equiv) in DCE (1 mL) under N_2 atmosphere. The two reaction mixtures were stirred side by side in an oil bath preheated at 100 ºC for 15 min. The two reaction tubes were chilled in an ice bath and the resulting mixtures in the two tubes were rapidly combined. The solvent was rapidly removed under reduced pressure. The resulting residue was purified by silica gel chromatography using EA/PE to afford the rude products. The KIE value was determined to be k_H/k_D= 0.9 on the basis of ^{1}H NMR analysis.



Aryl nitrone **1a** (0.2 mmol), **1a**-d_5 (0.2 mmol), diazo sulfonylketone **2a** (0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgNTf_2$ (20 mol %), $AgPF_6$ (20 mol %), and CH_3COOH (1.0 equiv), and CD_3COOD (1.0 equiv) were dissolved in DCE (2 mL) in a pressure tube under N_2 atmosphere. The reaction mixture was stirred at 100 ºC for 15 min. After the solvent was removed under reduced pressure, the resulting residue was purified by silica gel chromatography using EA/PE to afford the rude products. The KIE value was determined to be k_H/k_D= 2.0 on the basis of ^{1}H NMR analysis.



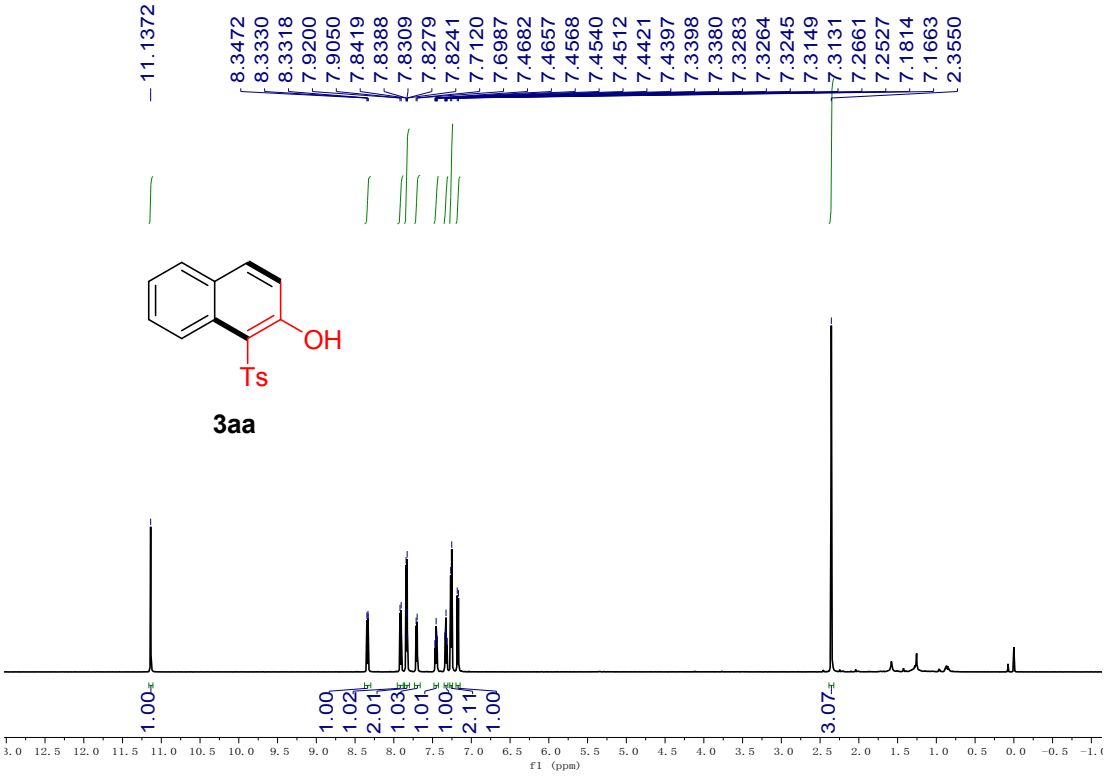
V. Reference

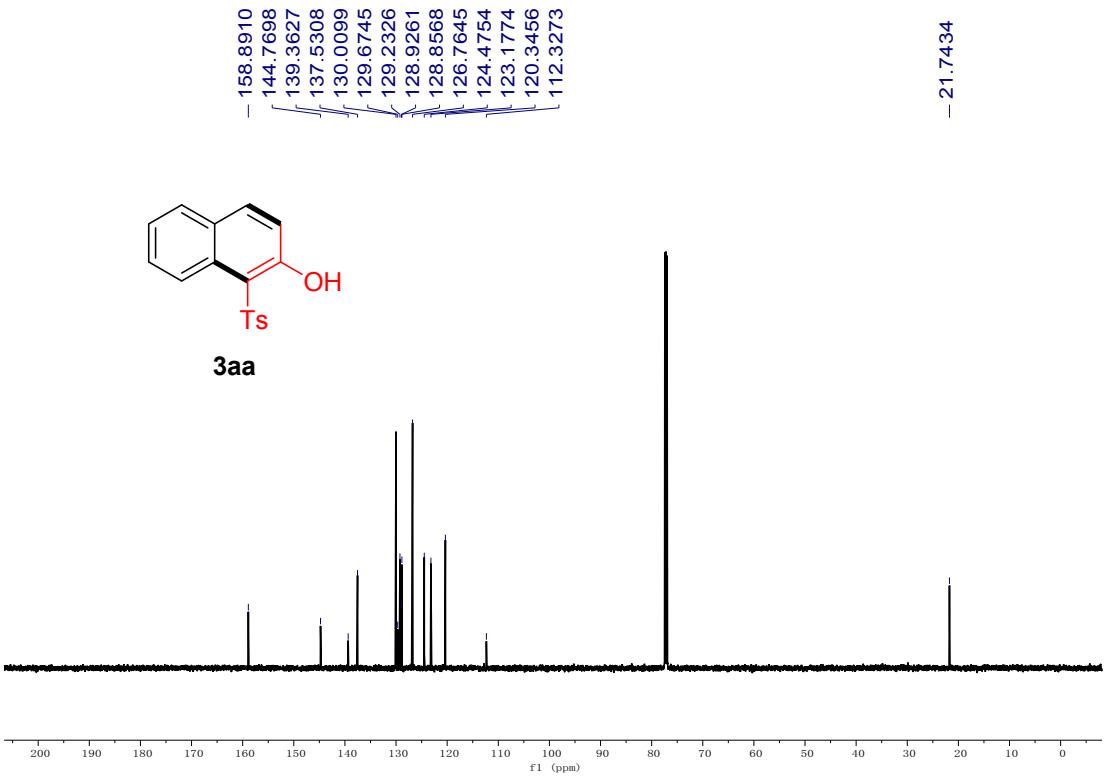
1. Morales, S.; Guijarro, F. G.; Alonso, I.; GarcíaRuano, J. L.; Belen Cid, M. *ACS Catal.* **2016**, *6*, 84.

2. Shi, B.; Blake, A. J.; Lewis, W.; Campbell, I. B.; Judkins, B. D.; Moody, C. J. *J. Org. Chem.* **2010**, *75*, 152.

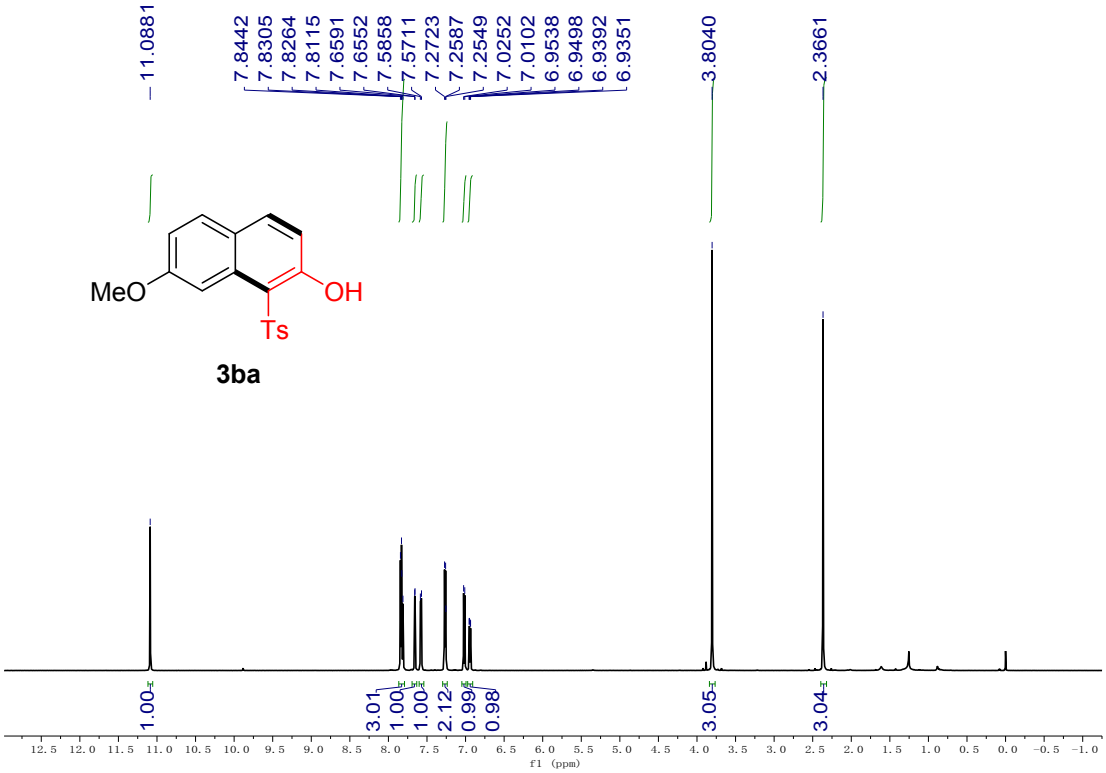
VI. NMR Spectra

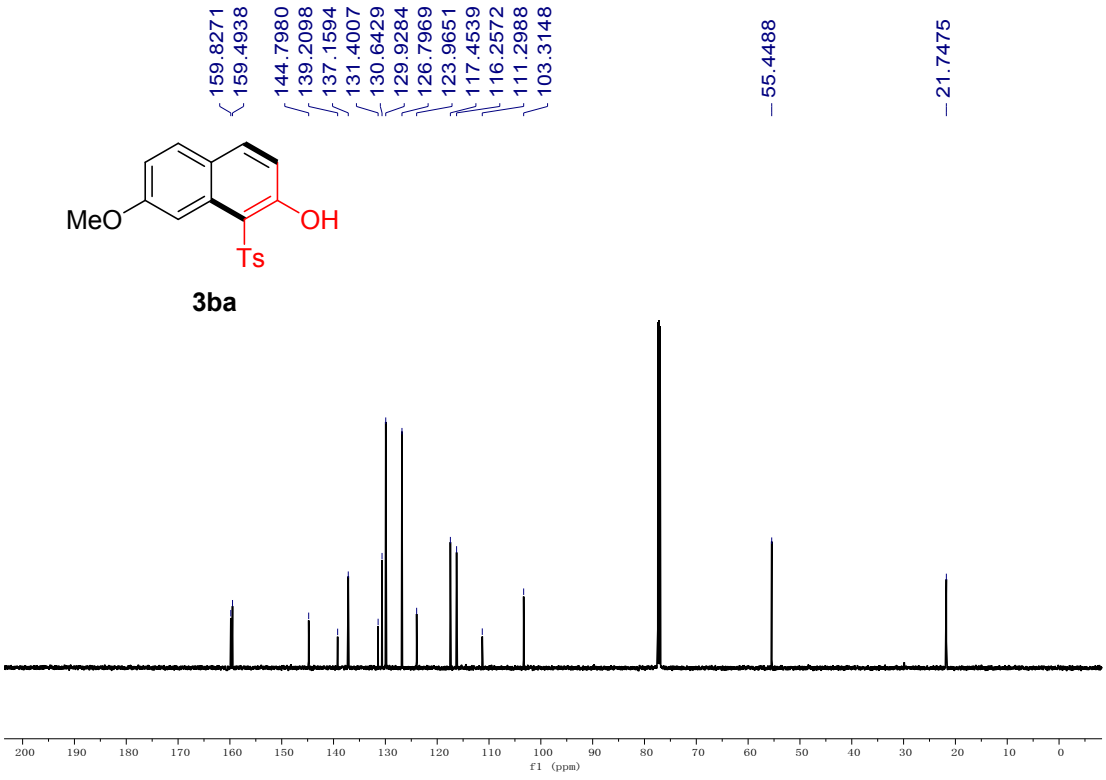
^{1}H and ^{13}C NMR spectra for compound **3aa**



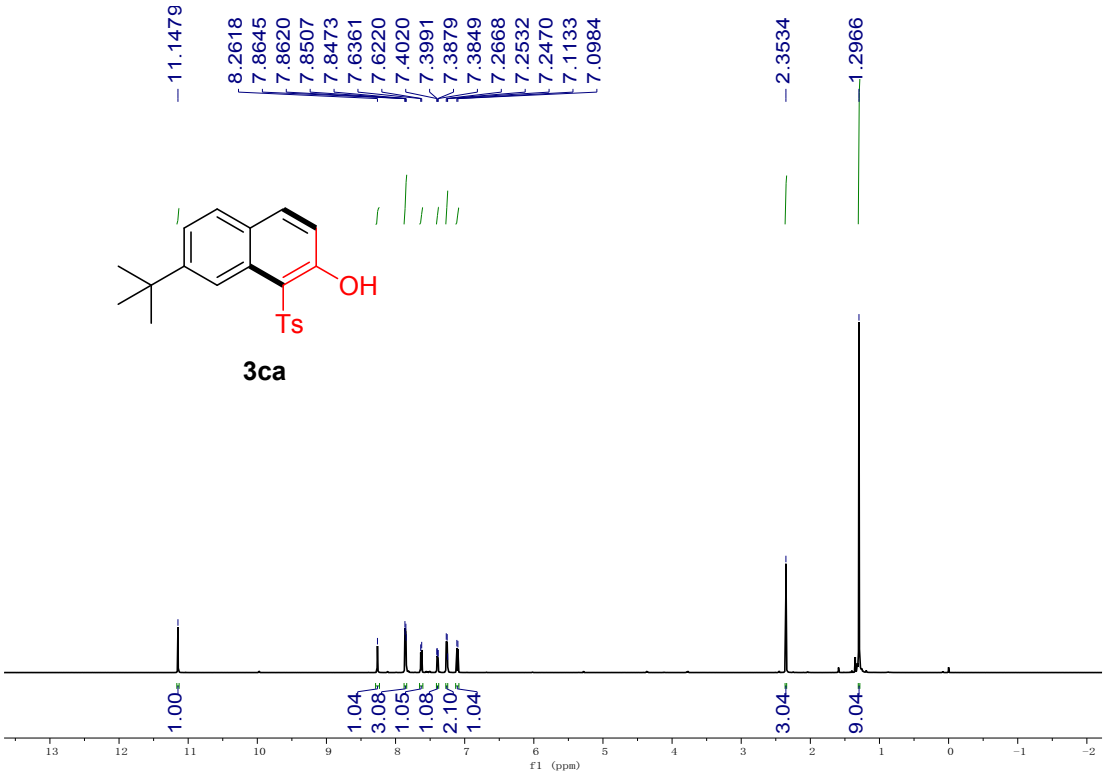


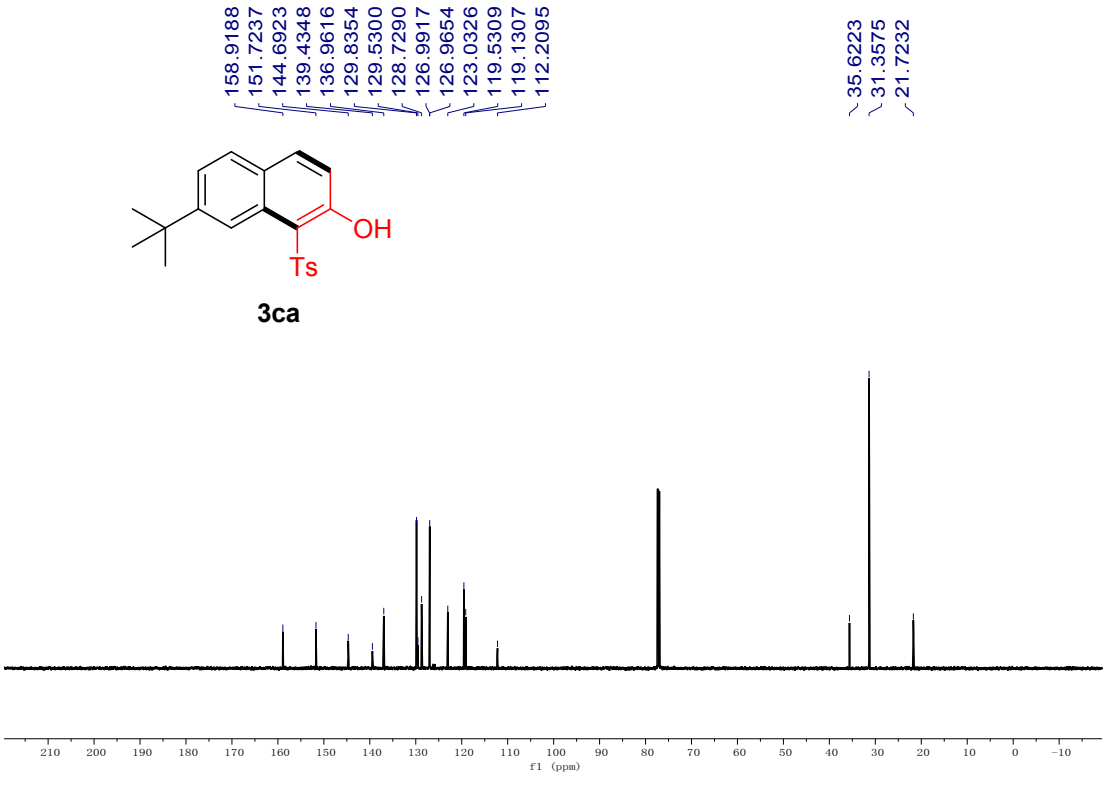
^{1}H and ^{13}C NMR spectra for compound **3ba**



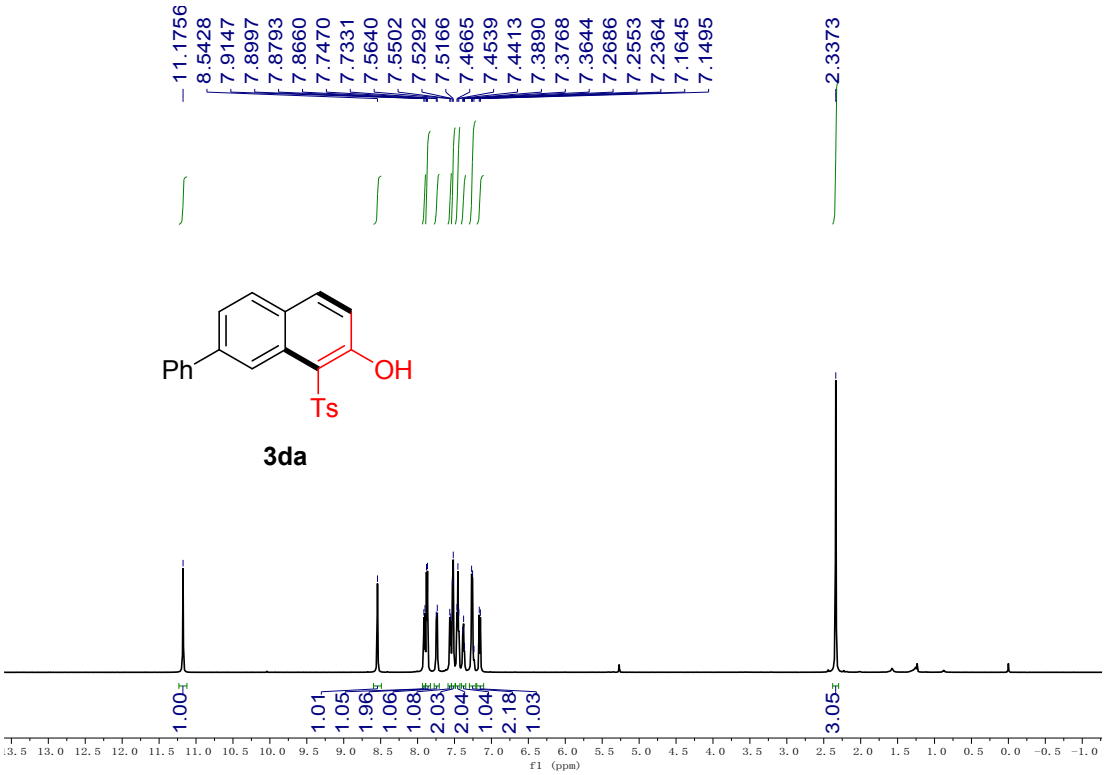


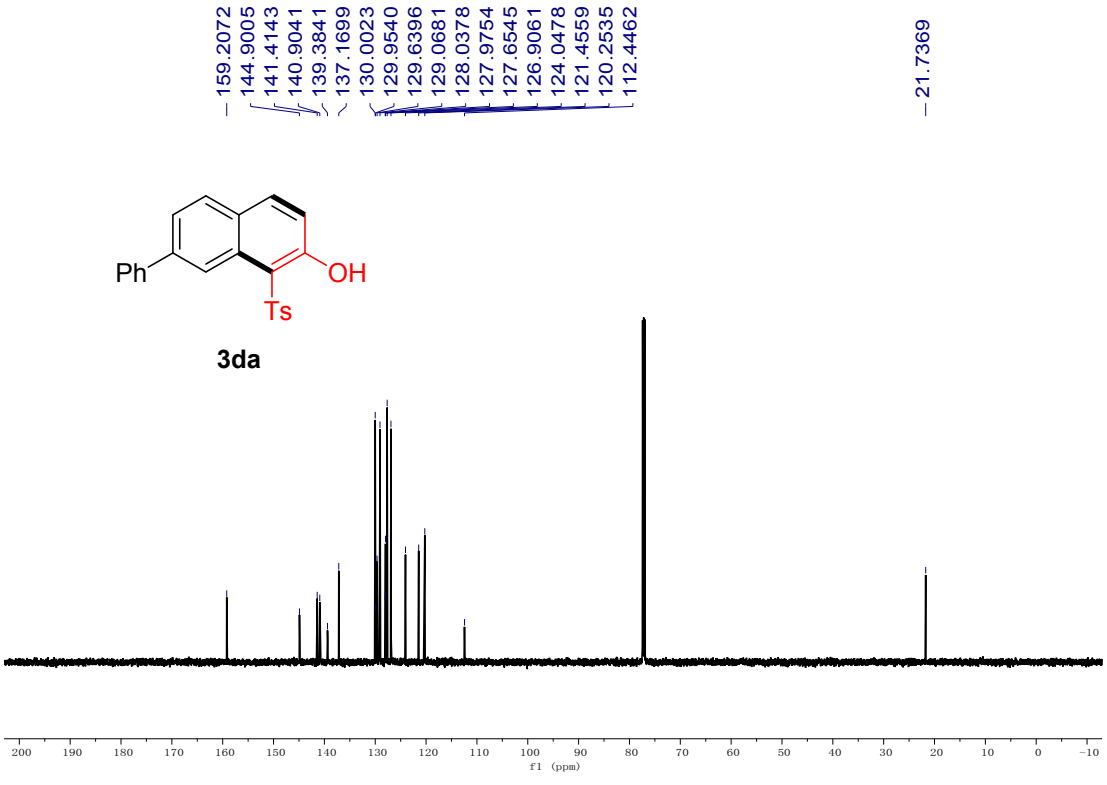
^{1}H and ^{13}C NMR spectra for compound **3ca**



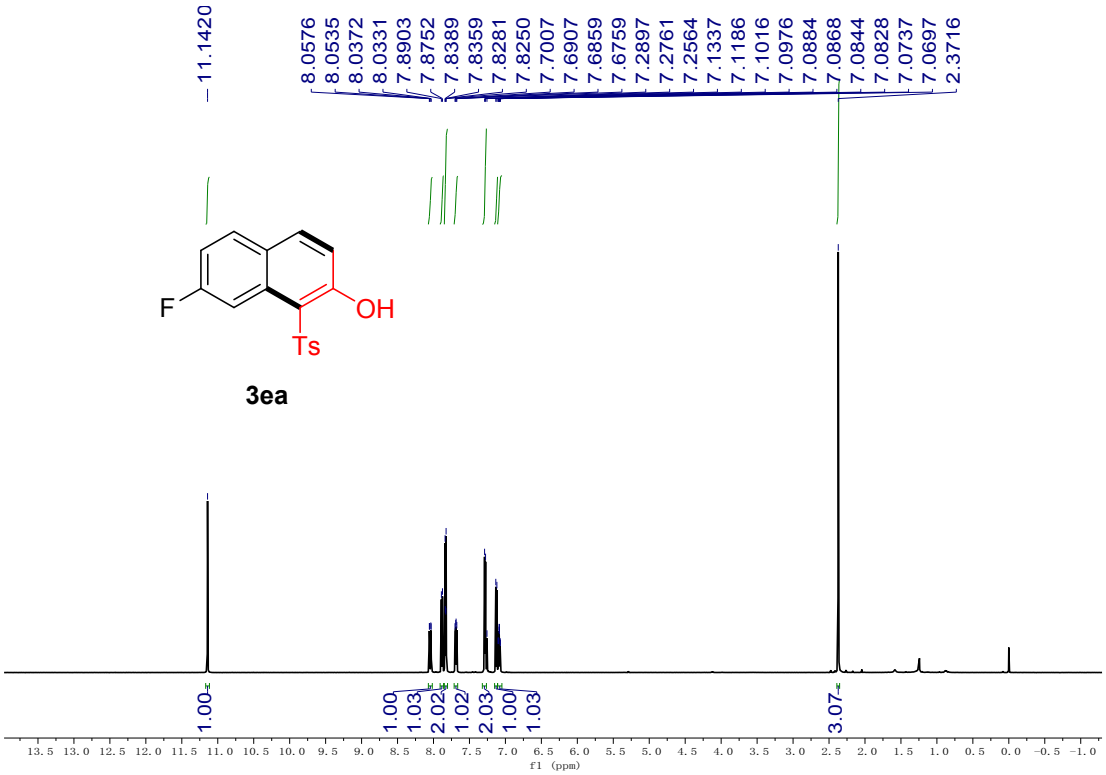


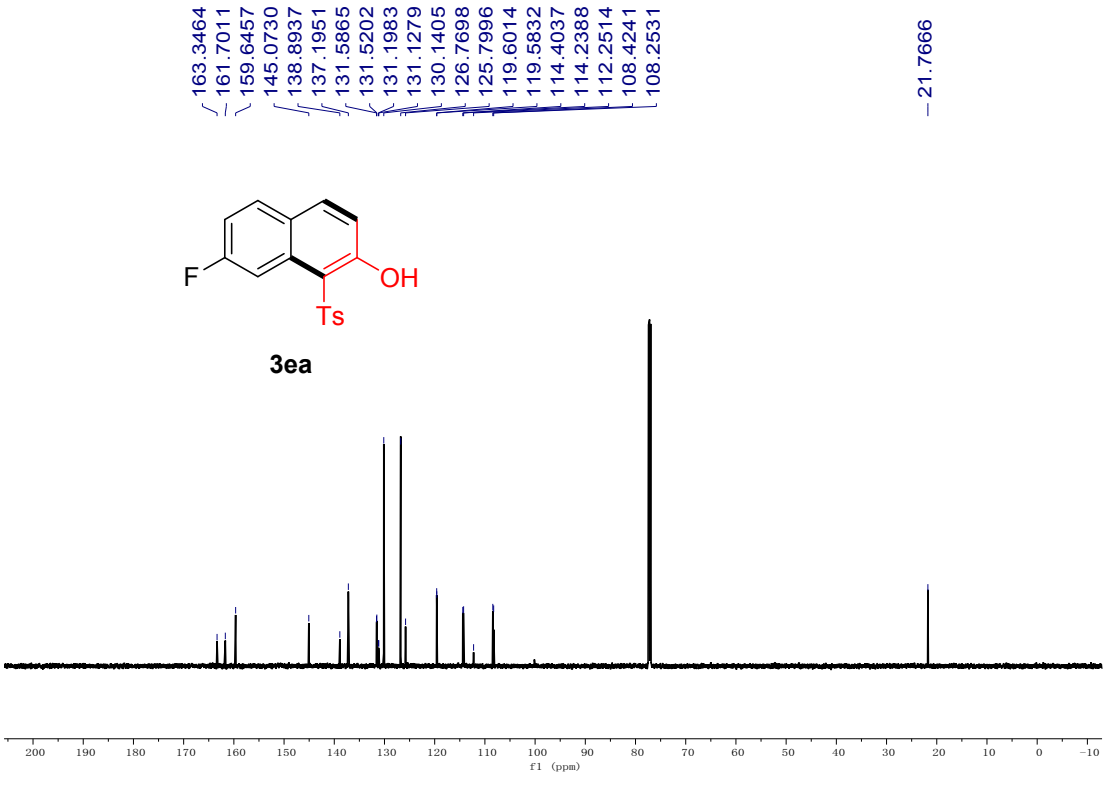
^{1}H and ^{13}C NMR spectra for compound **3da**

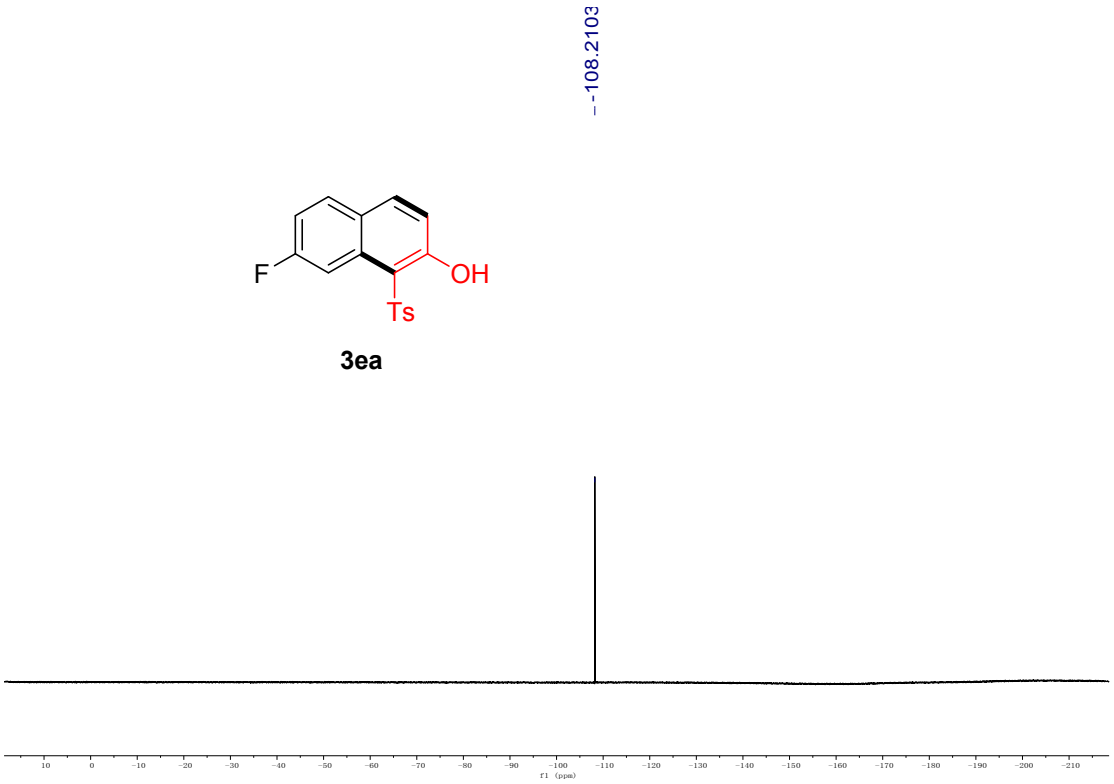




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3ea**



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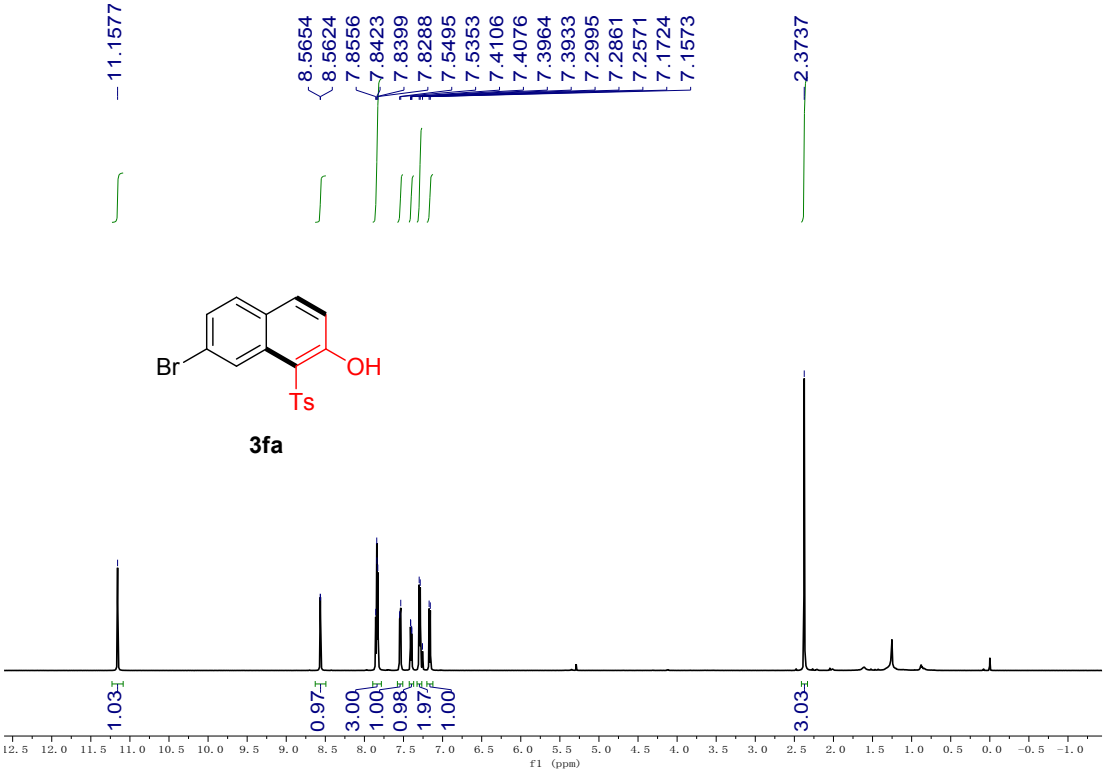
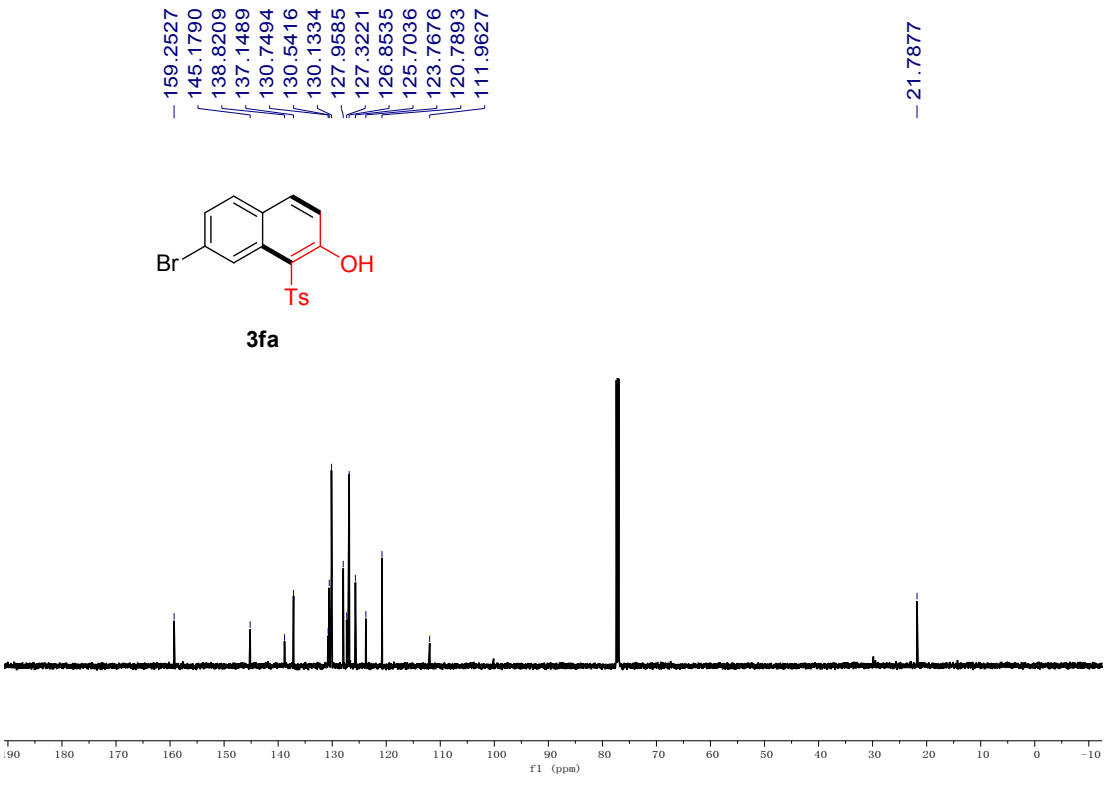
f1 (ppm)

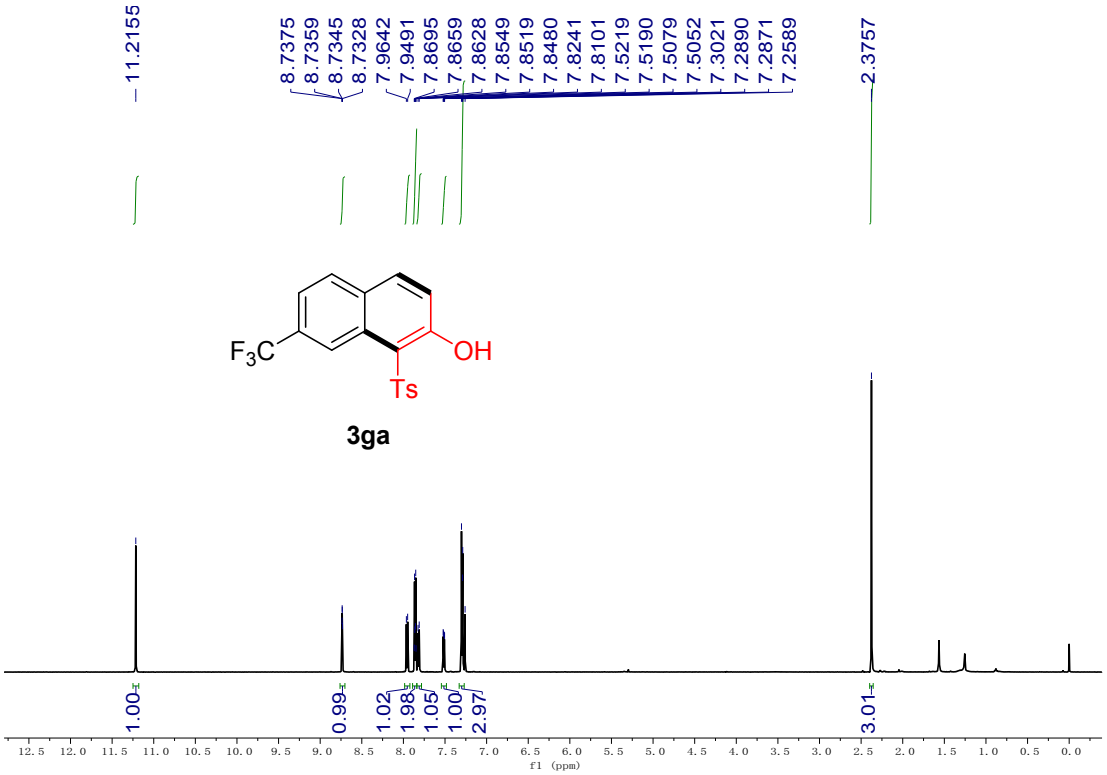
3ea

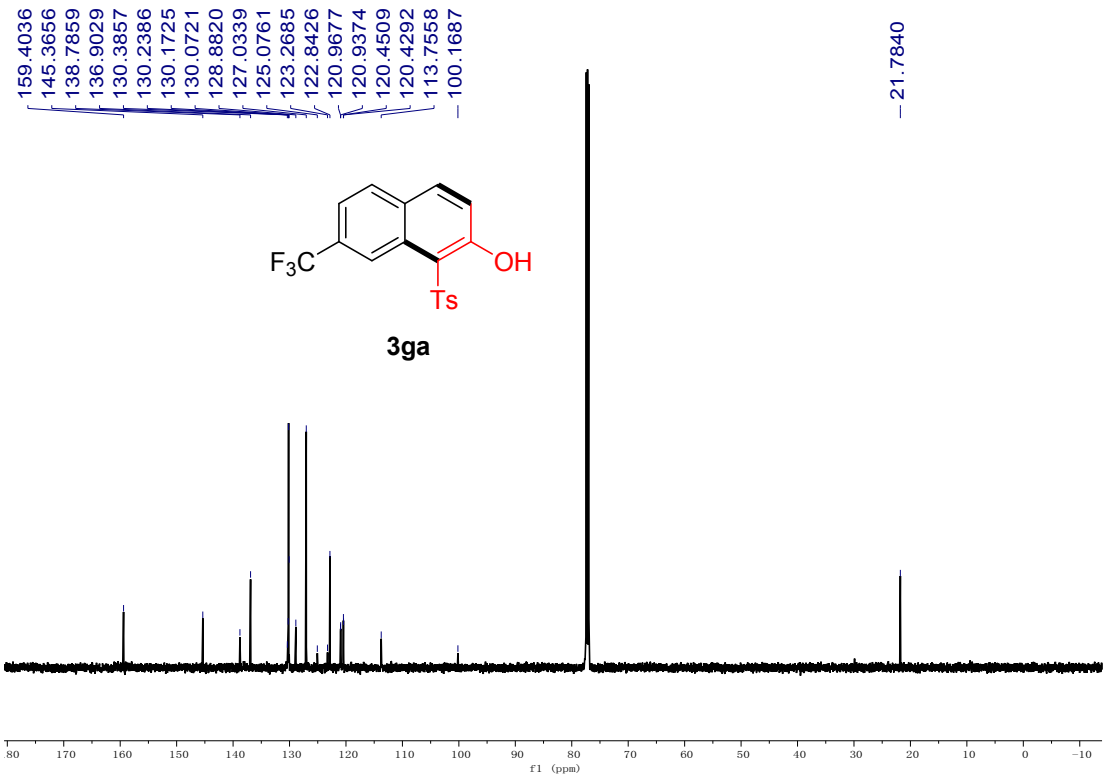
^{1}H and ^{13}C NMR spectra for compound **3fa**

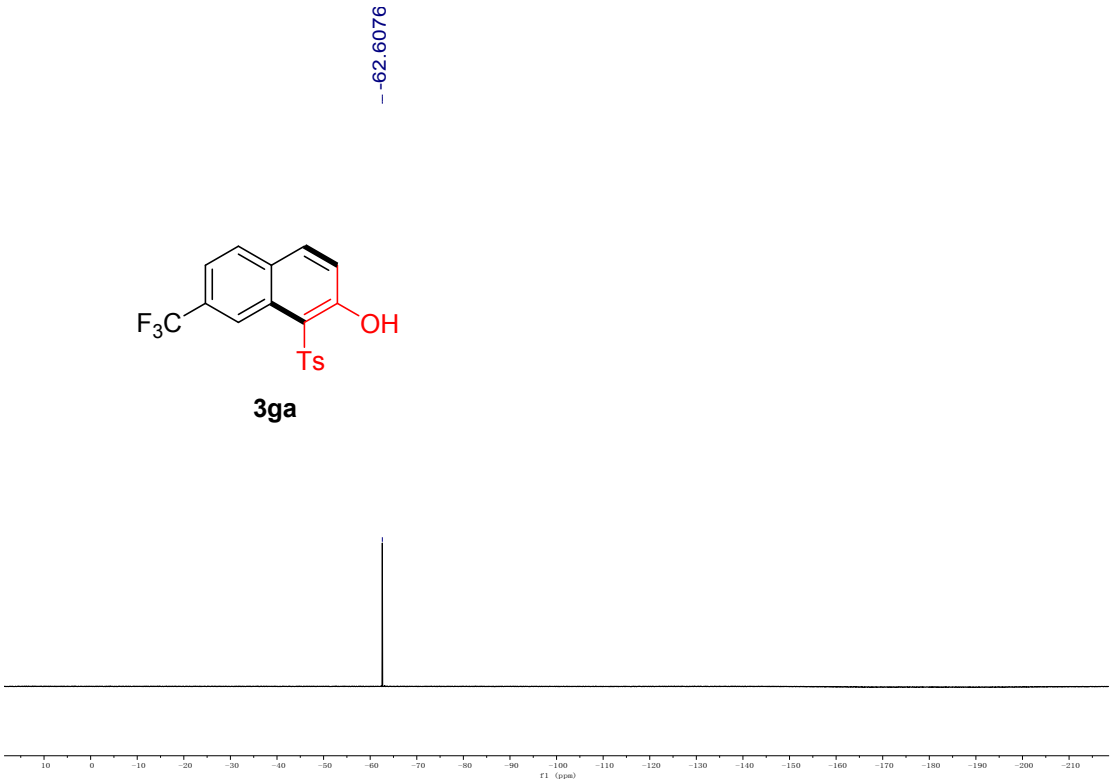




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3ga**



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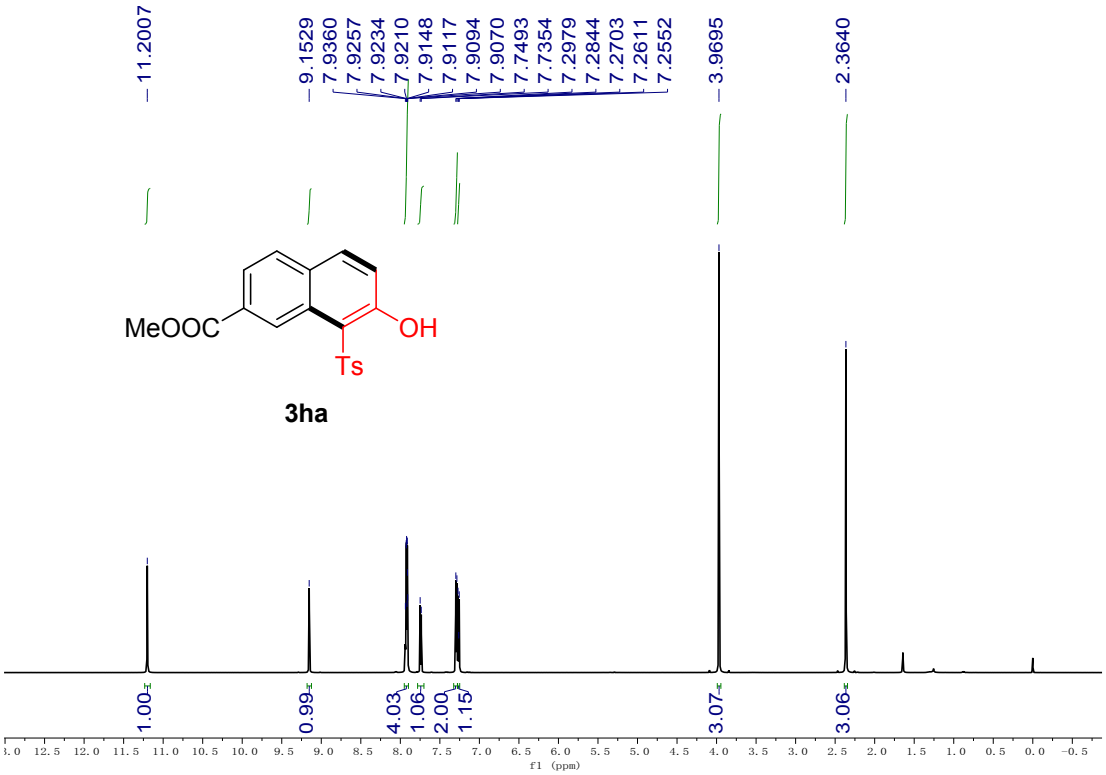
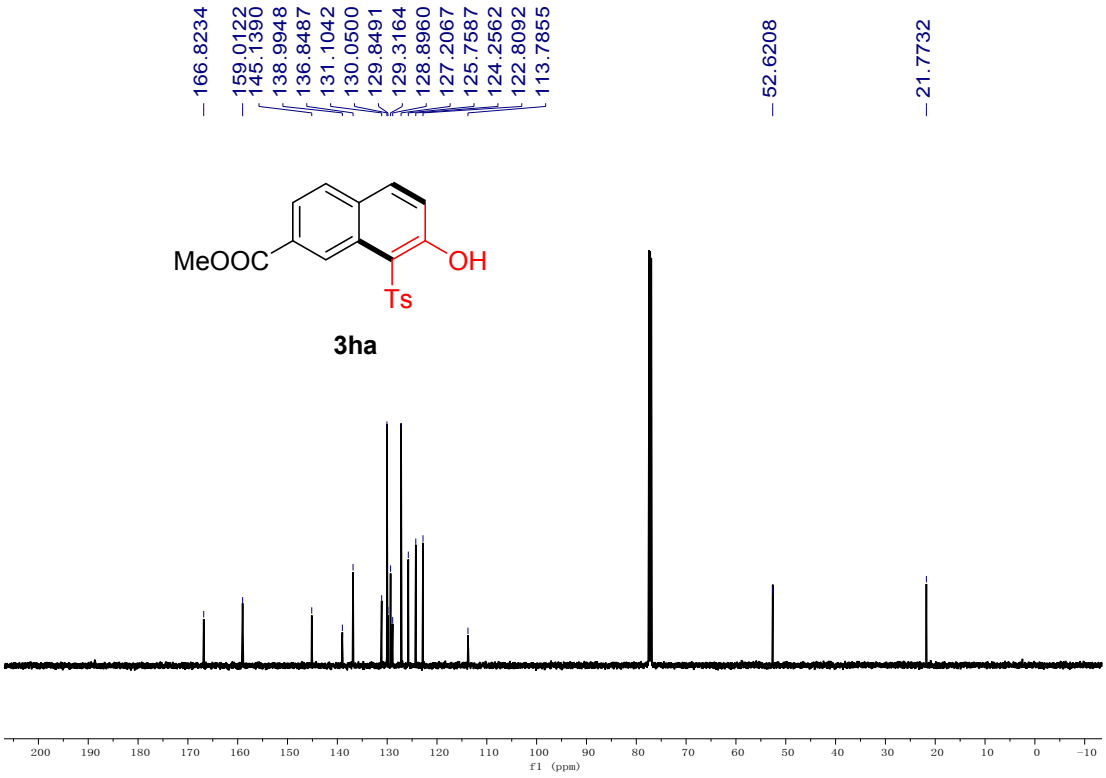
f1 (ppm)

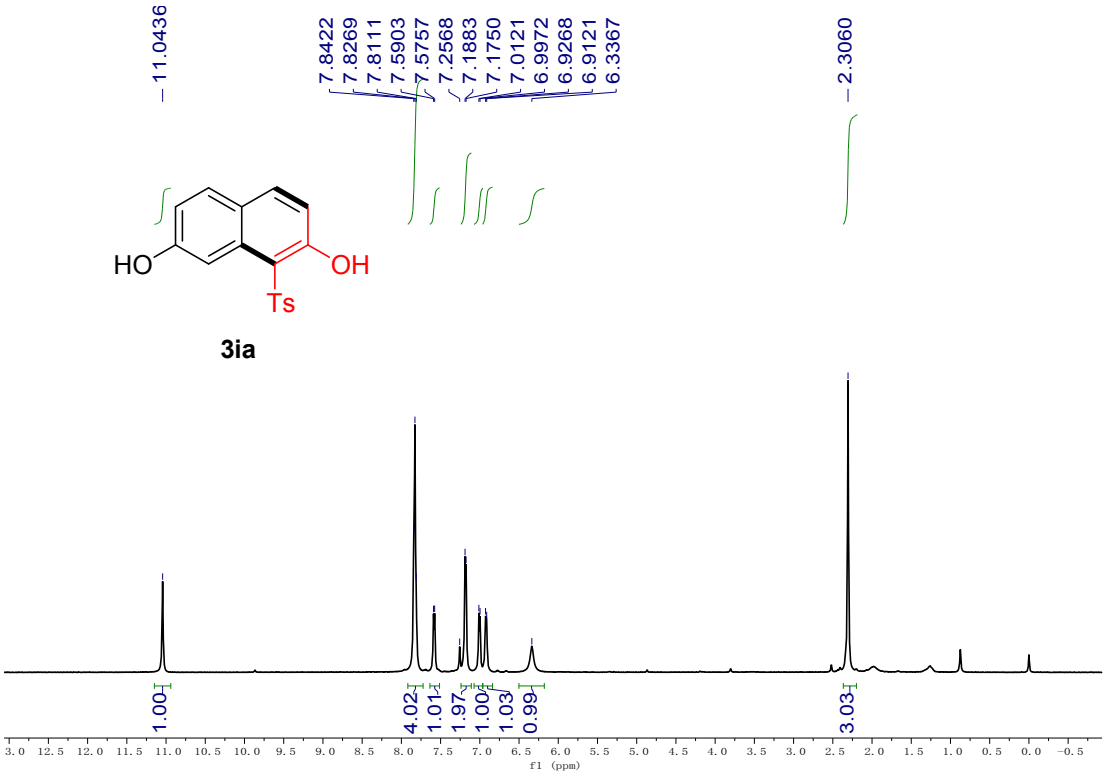
3ga

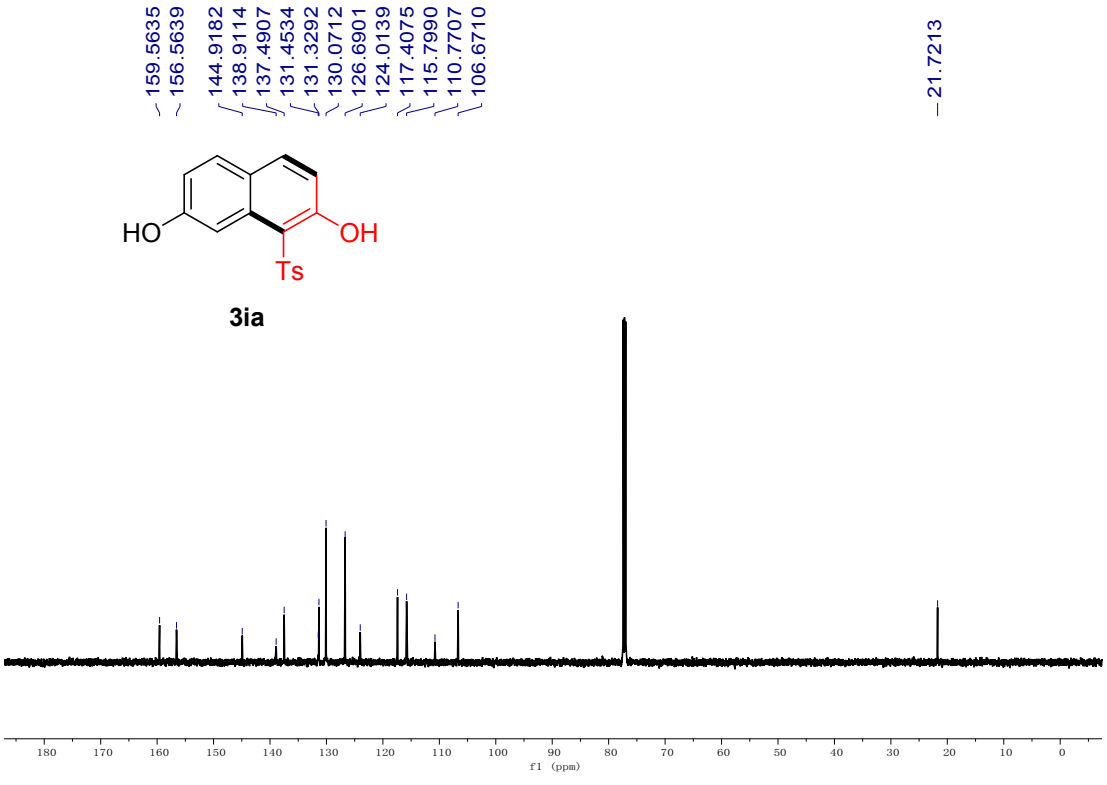
^{1}H and ^{13}C NMR spectra for compound **3ha**



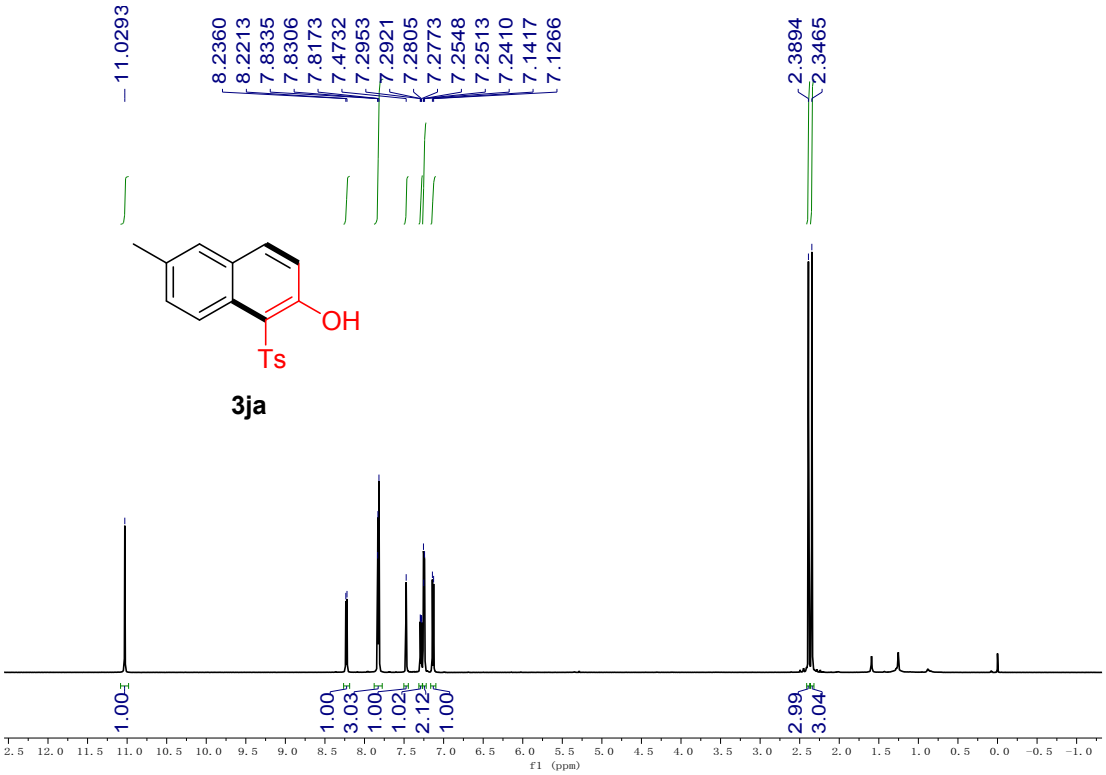


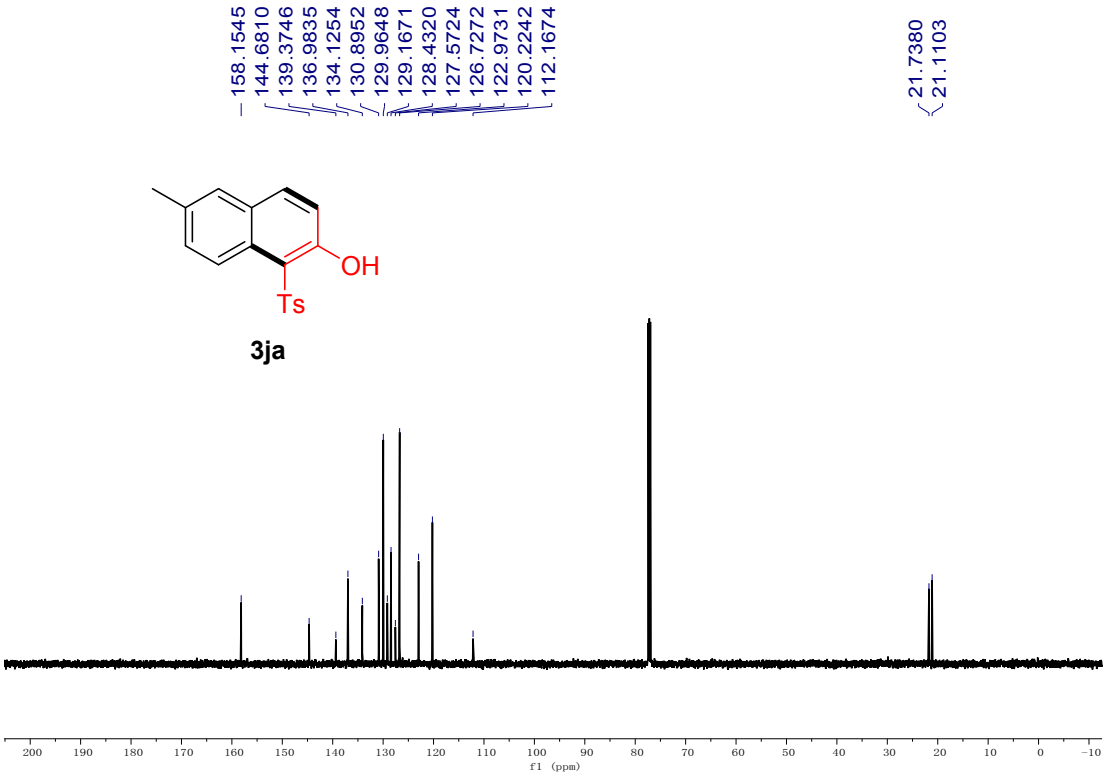
^{1}H and ^{13}C NMR spectra for compound **3ia**



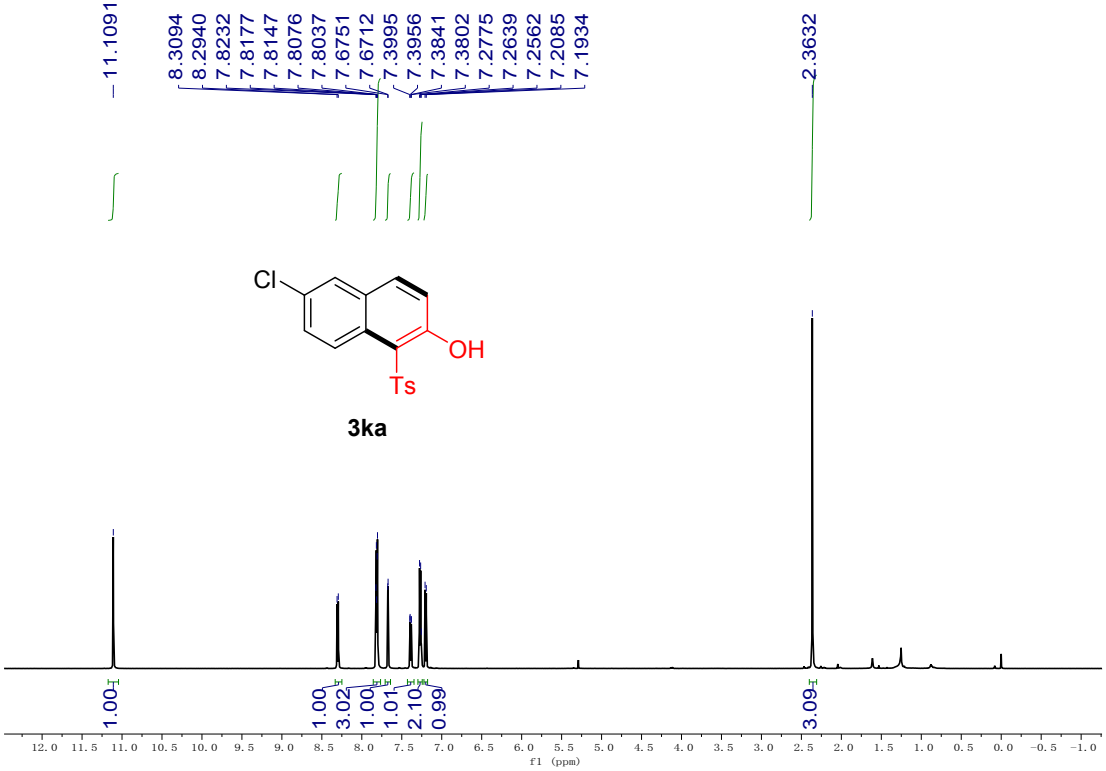


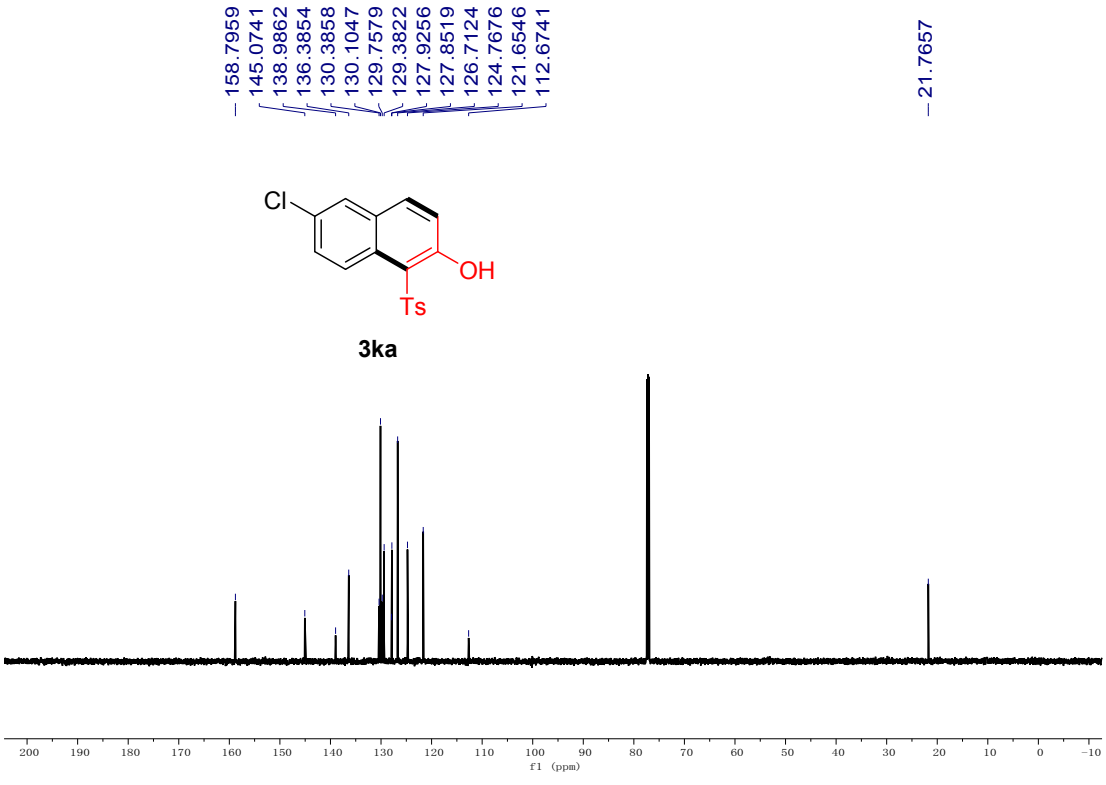
^{1}H and ^{13}C NMR spectra for compound **3ja**



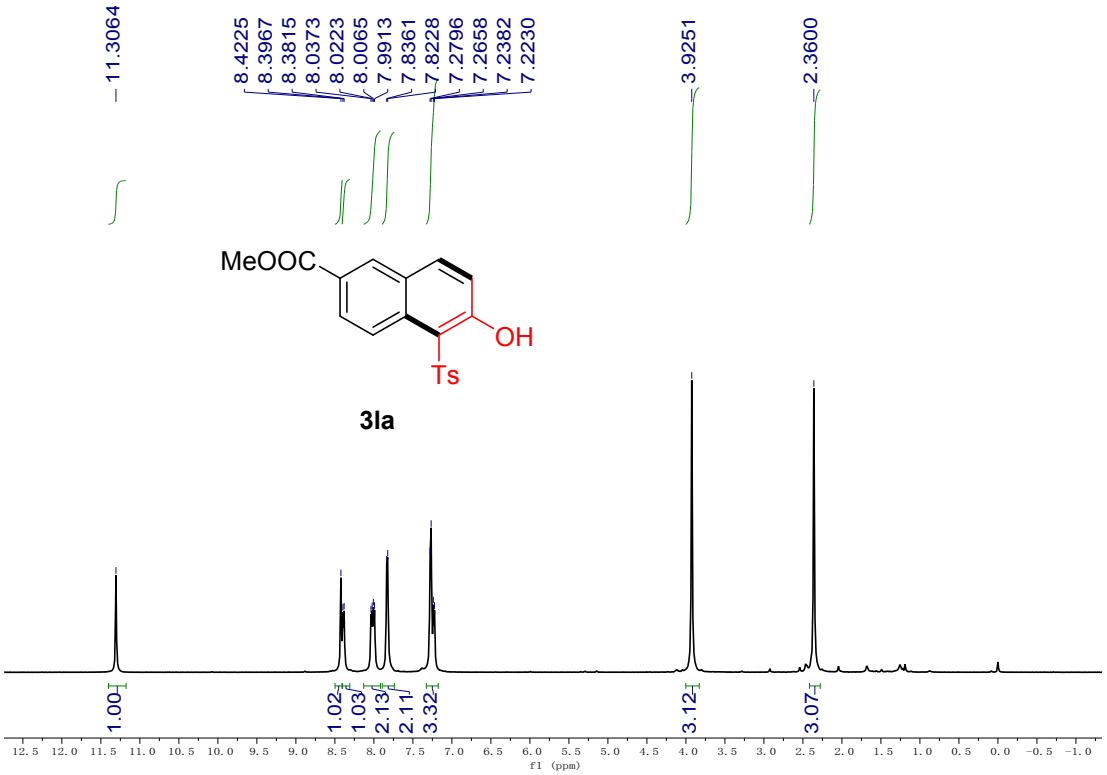


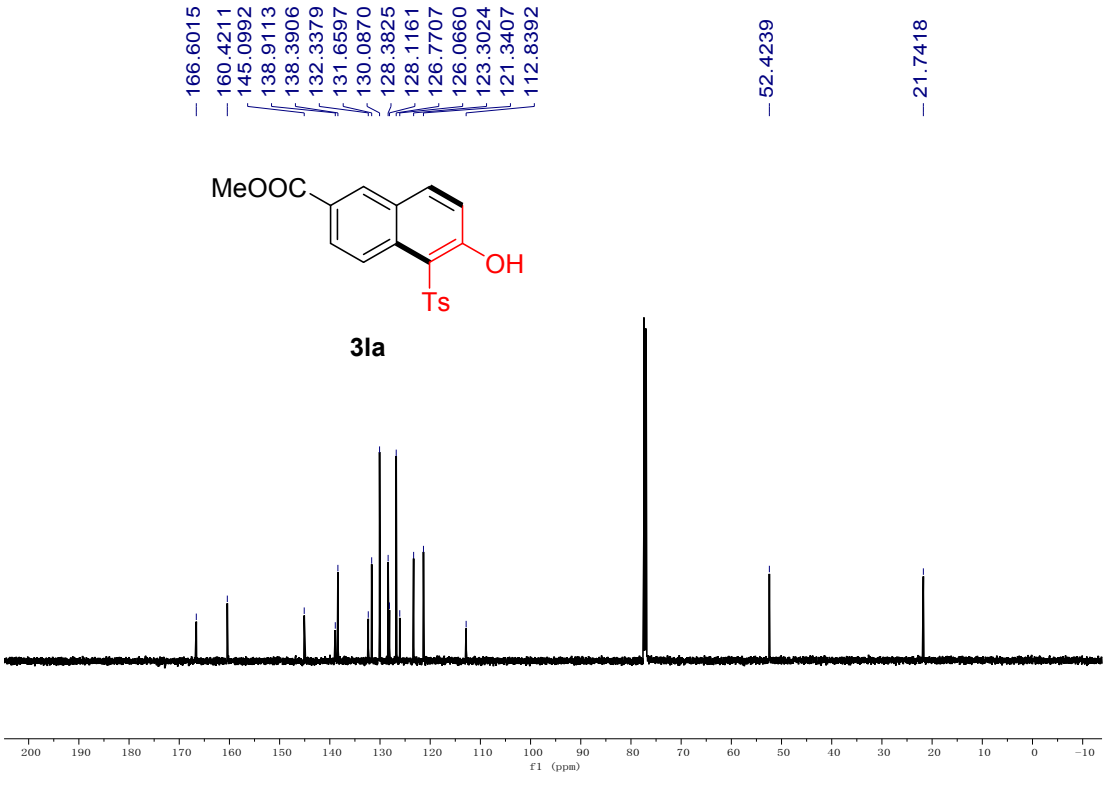
^{1}H and ^{13}C NMR spectra for compound **3ka**



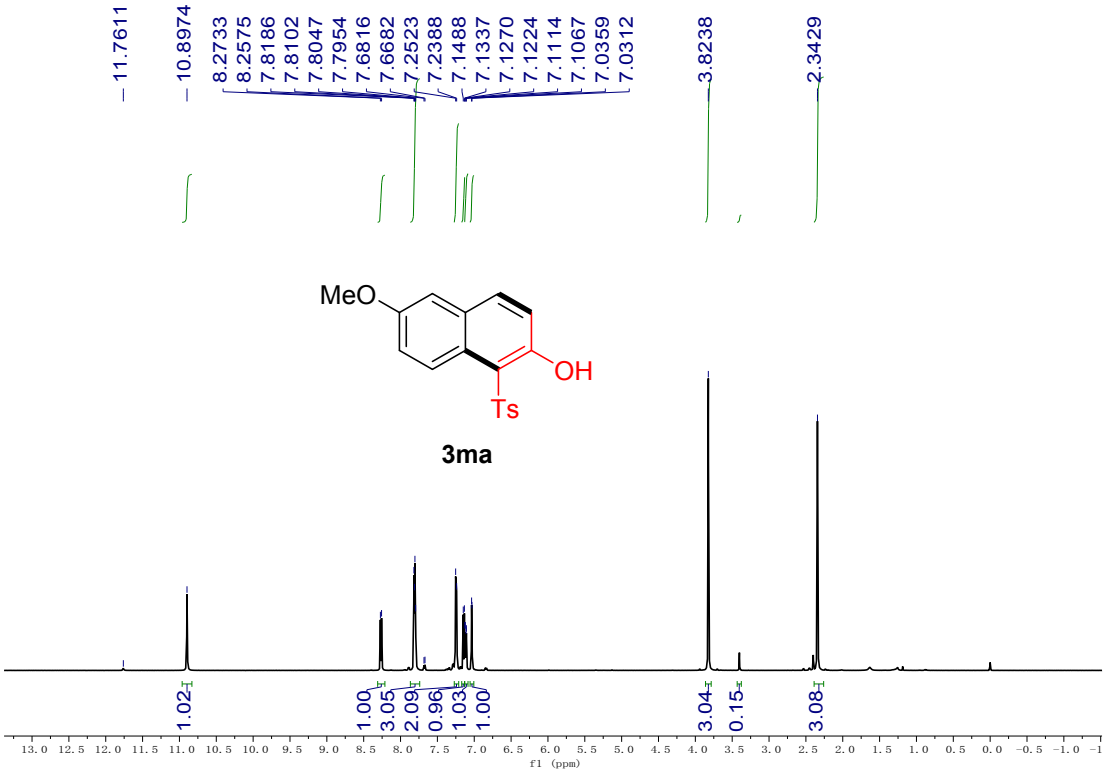


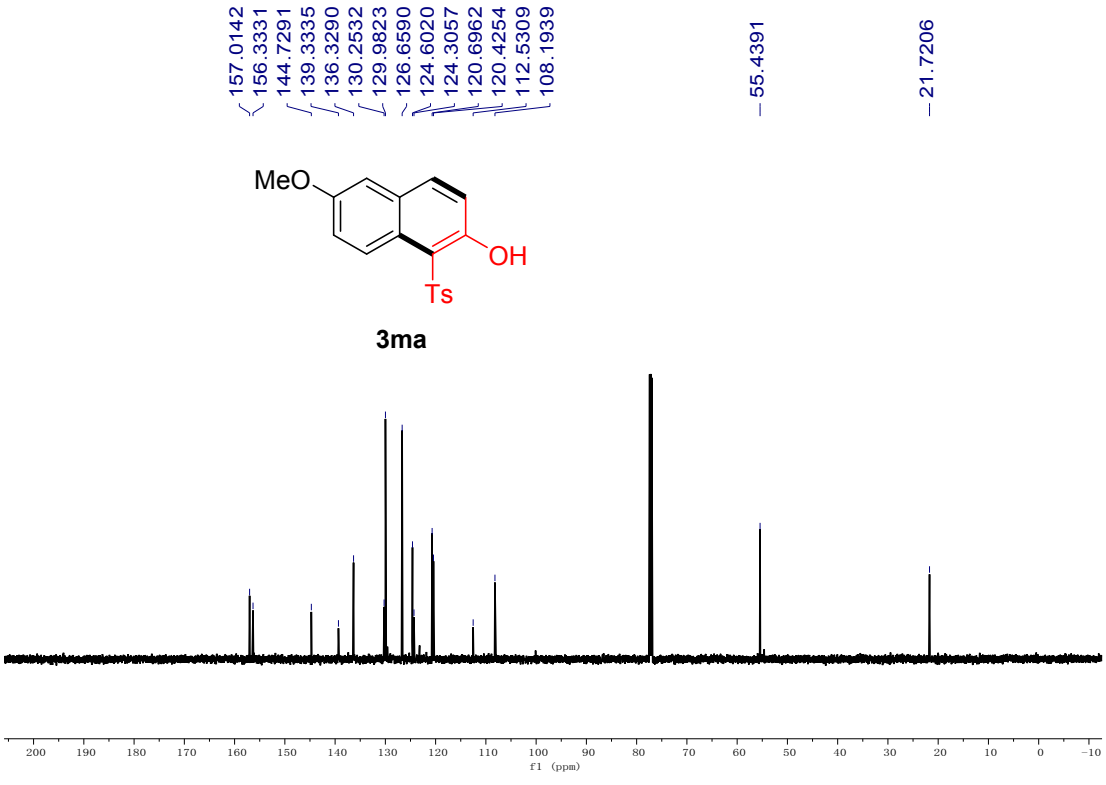
^{1}H and ^{13}C NMR spectra for compound **3la**



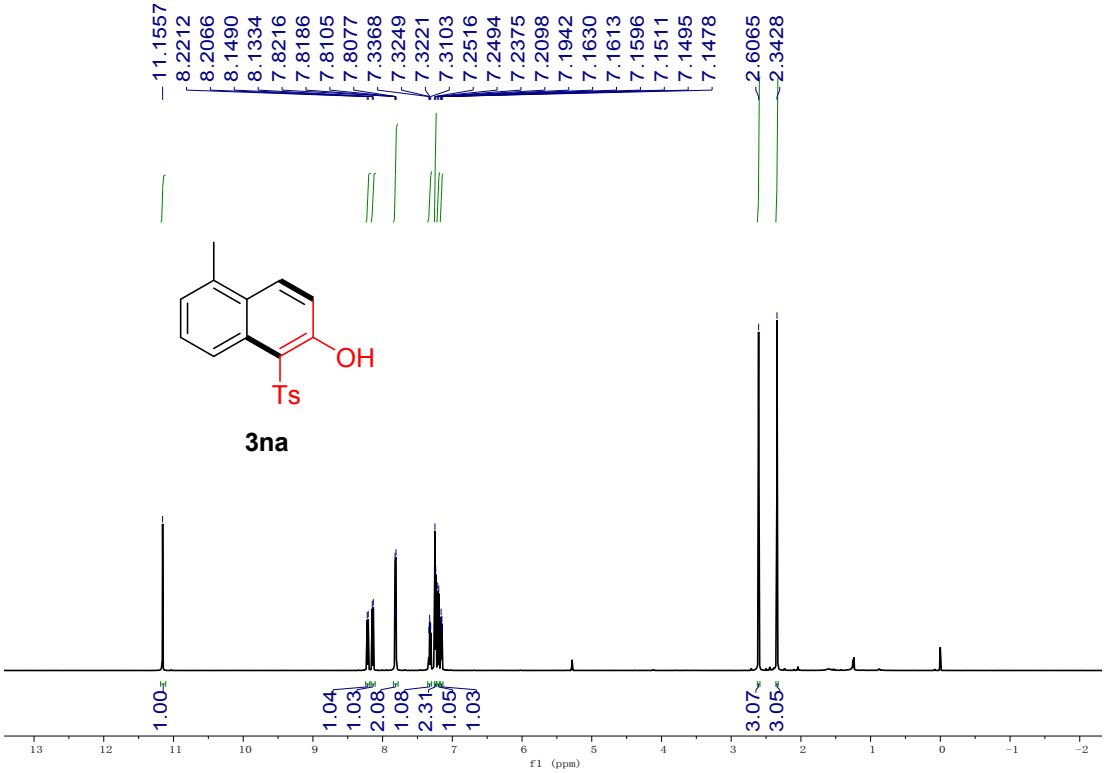


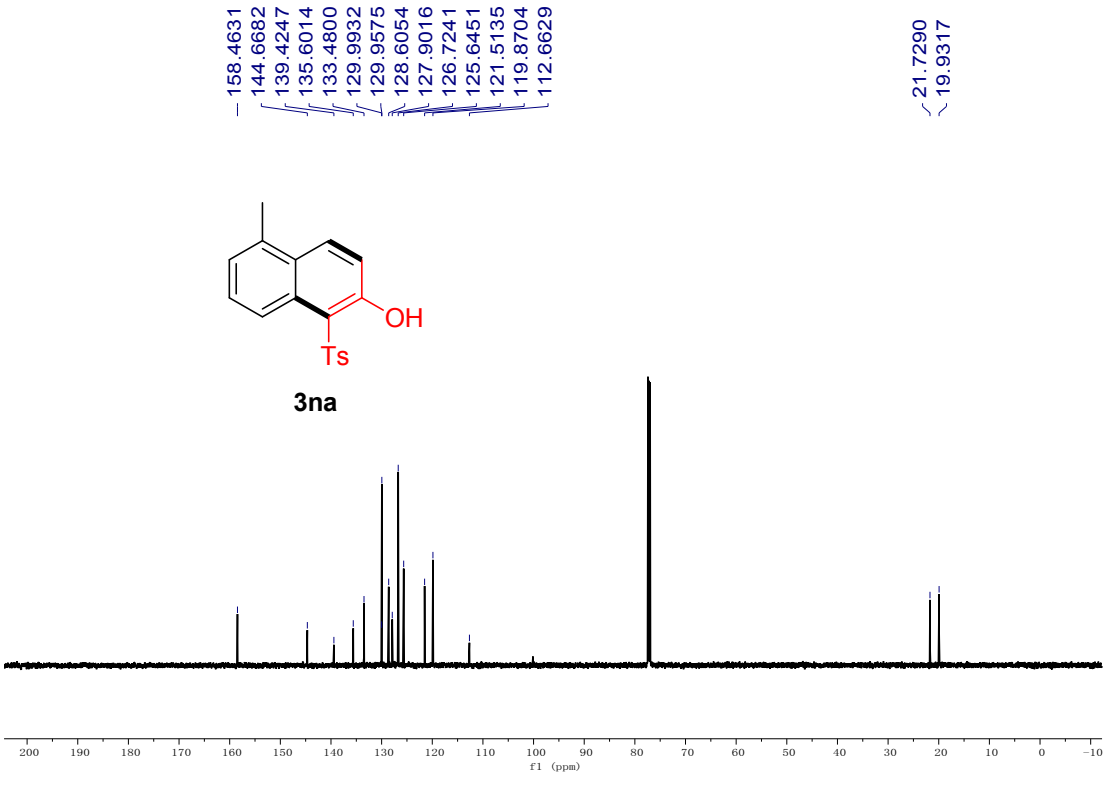
^{1}H and ^{13}C NMR spectra for compound **3ma**



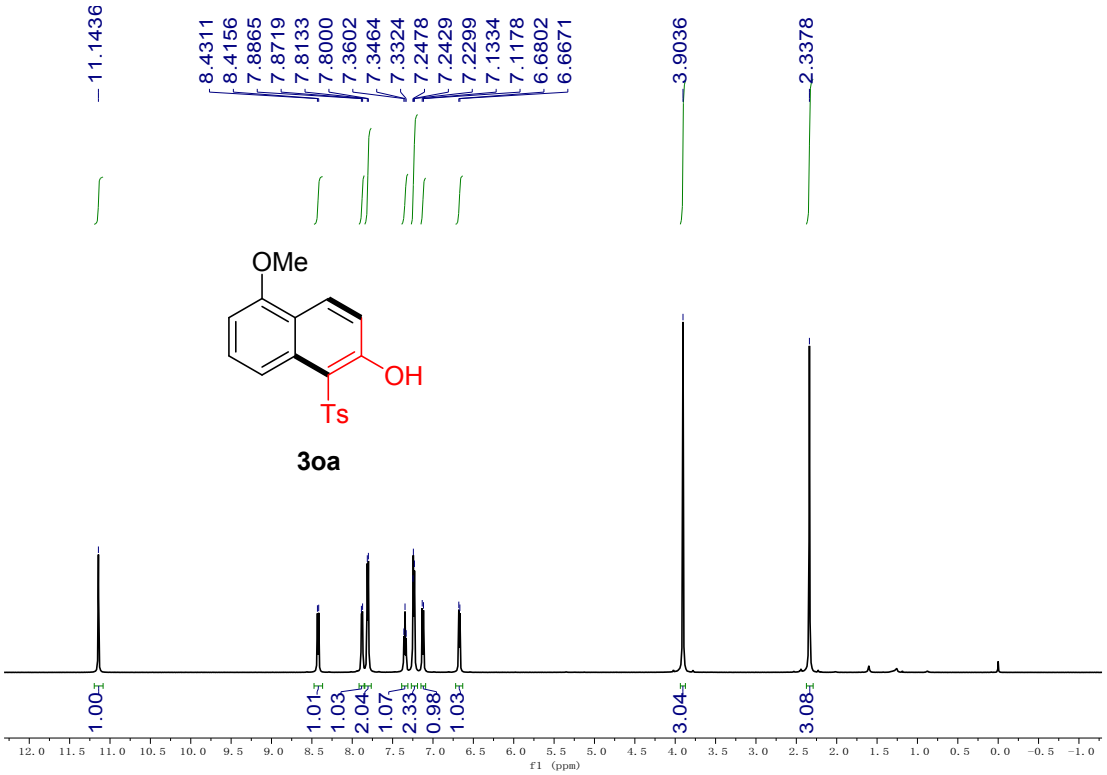


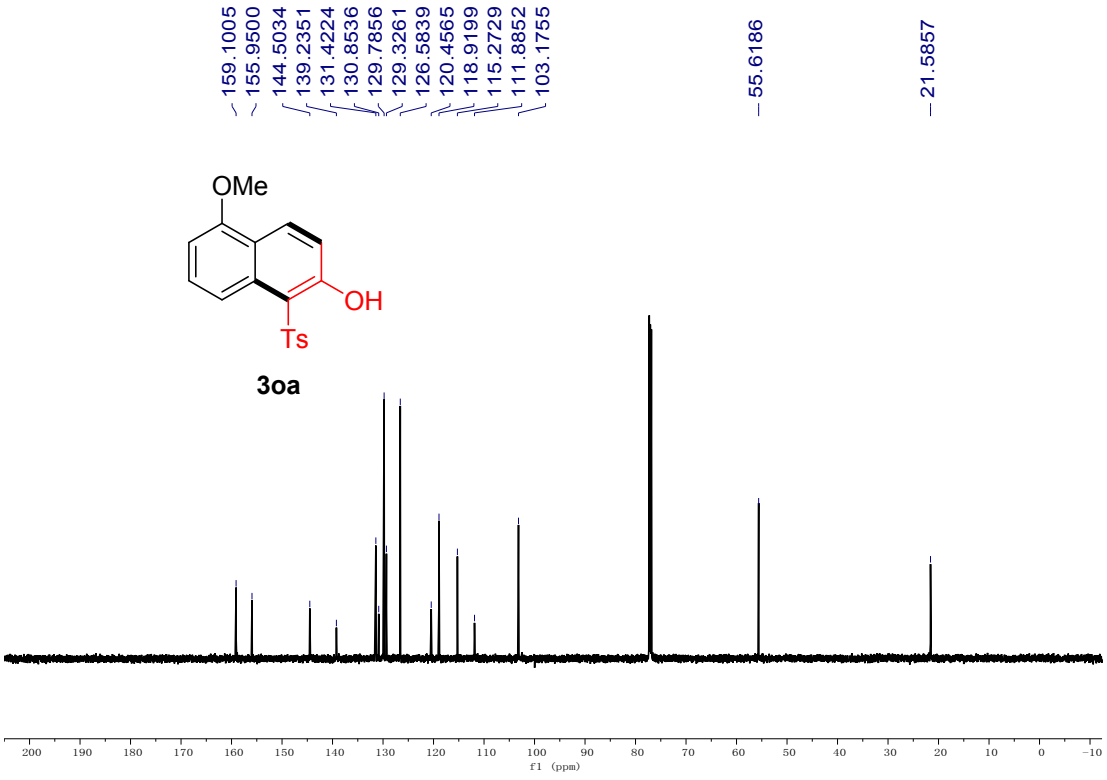
^{1}H and ^{13}C NMR spectra for compound **3na**



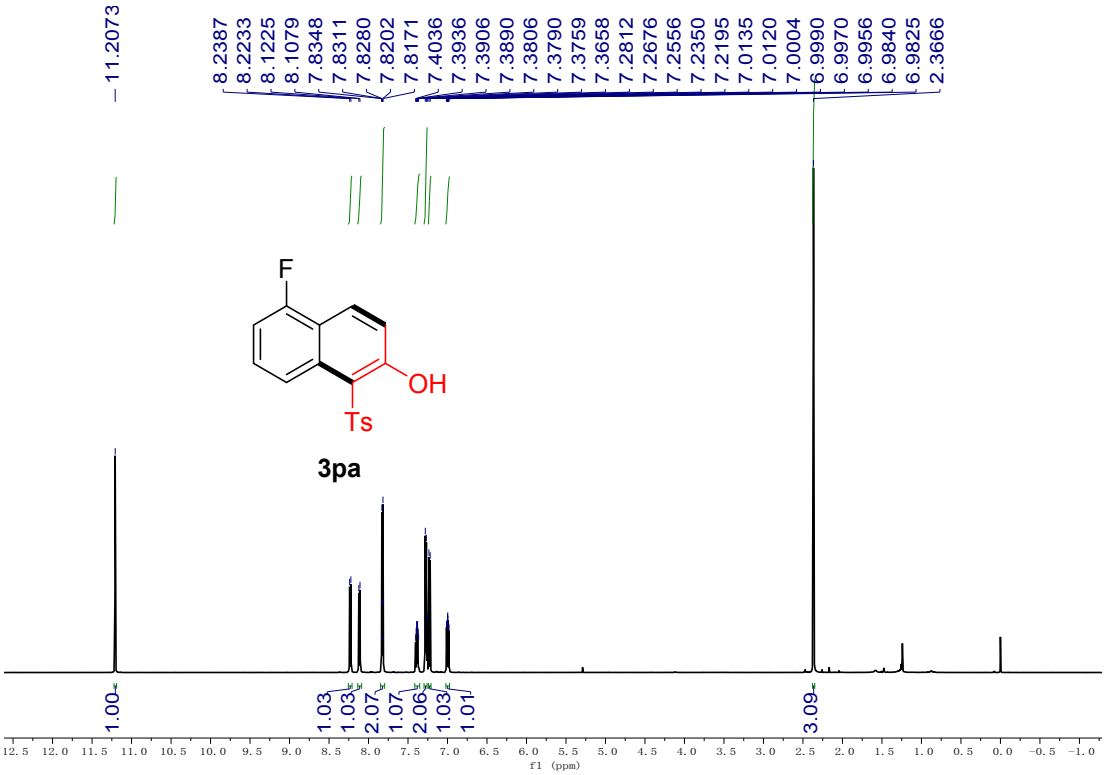


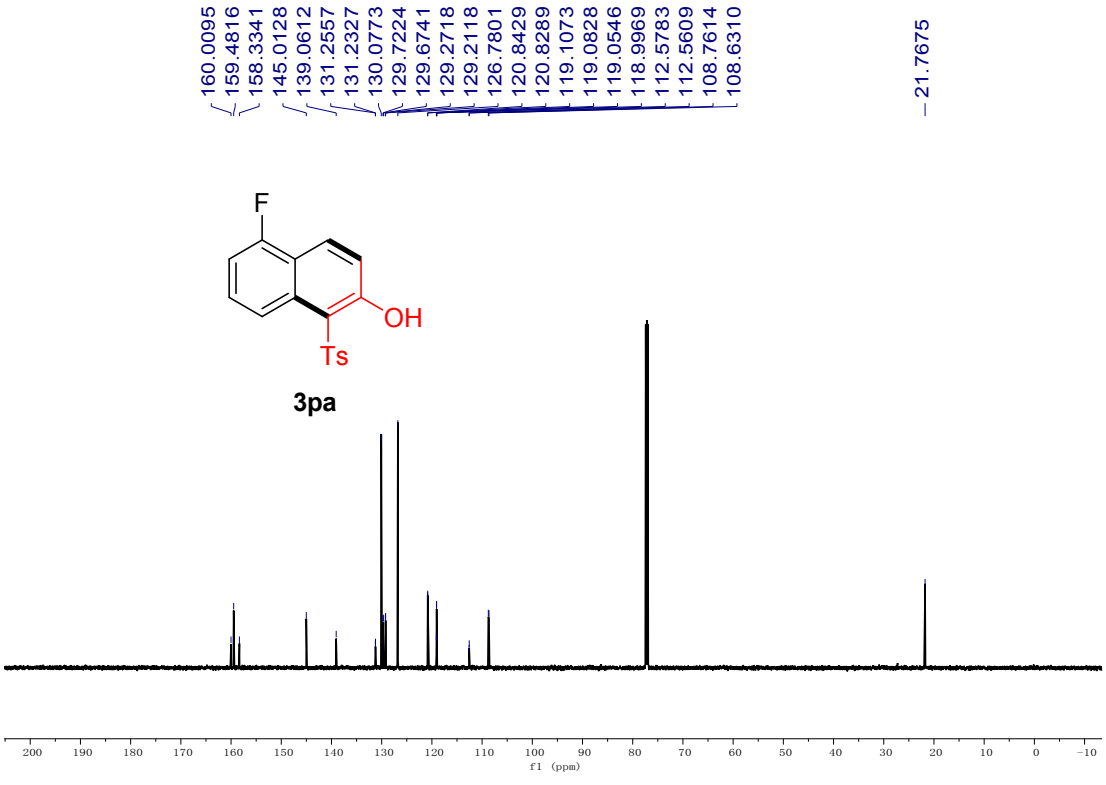
^{1}H and ^{13}C NMR spectra for compound **3oa**

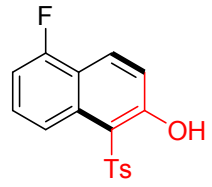




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3pa**



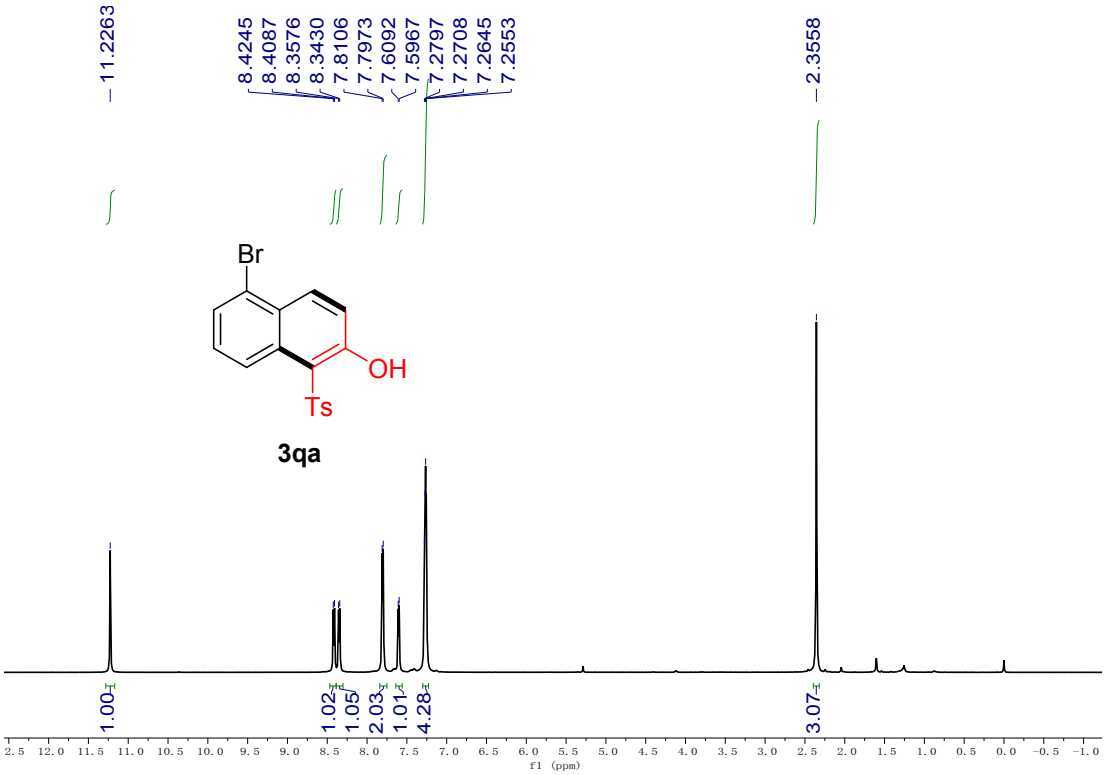


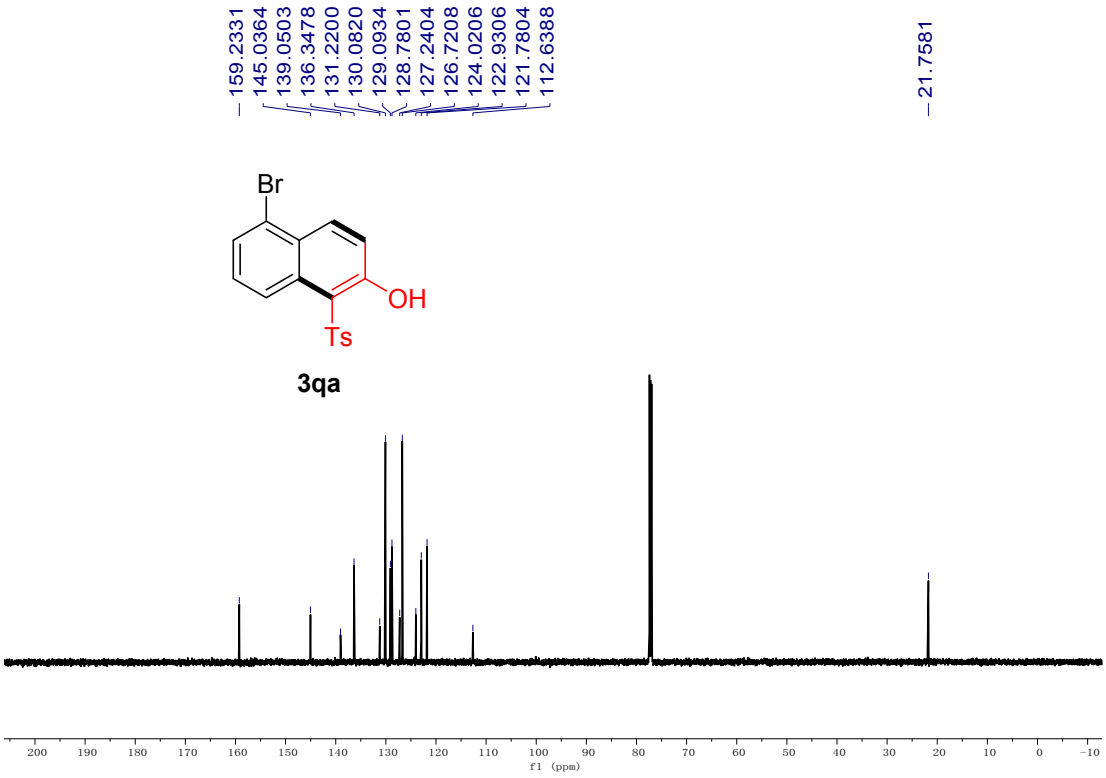

F
OH
Ts

3pa

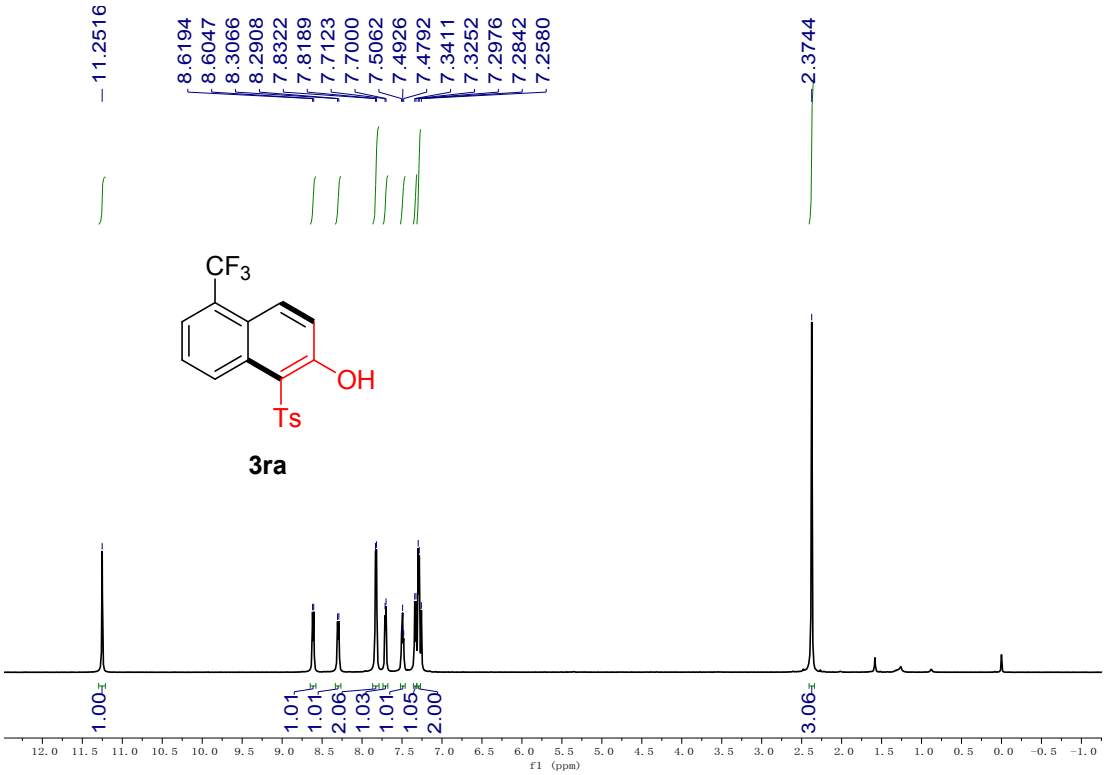
-120.7638
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

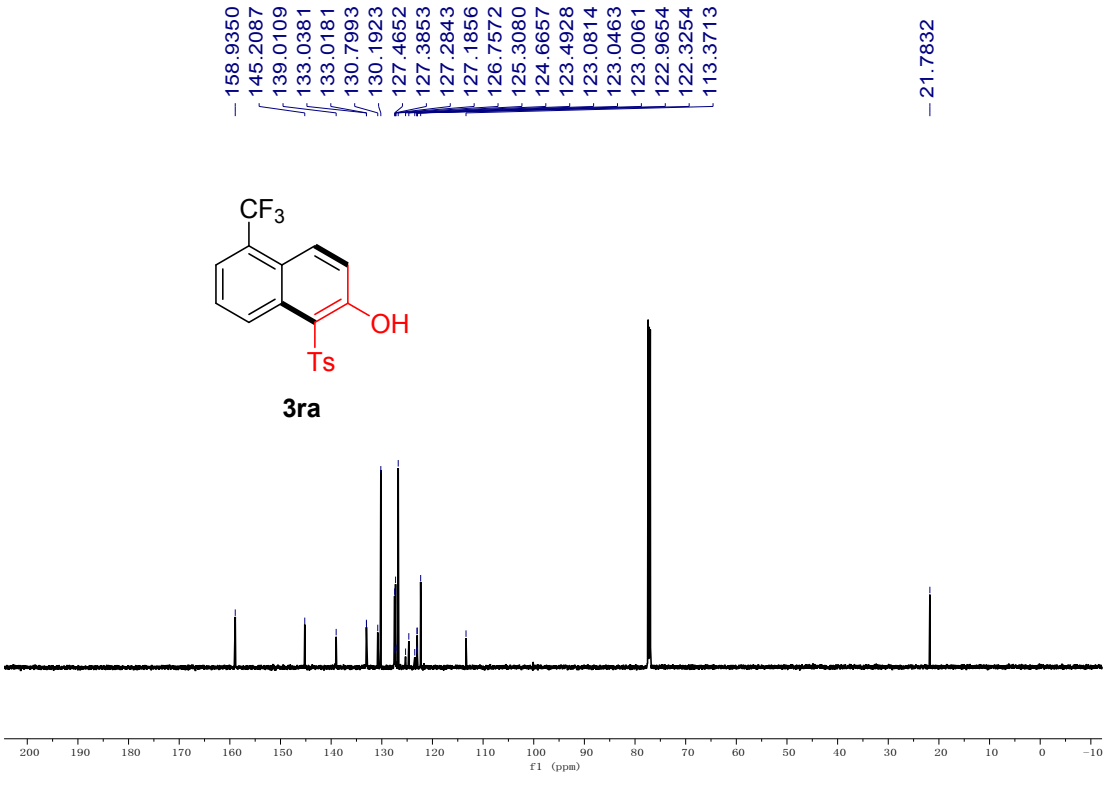
^{1}H and ^{13}C NMR spectra for compound **3qa**

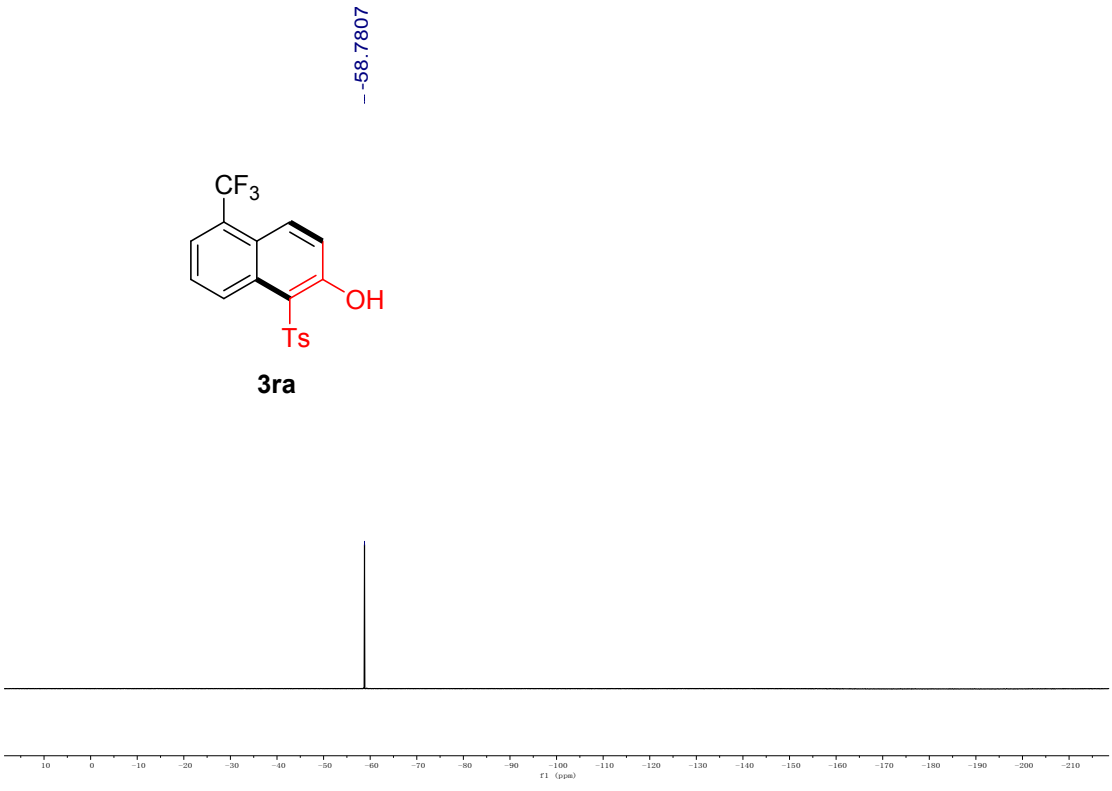




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3ra**

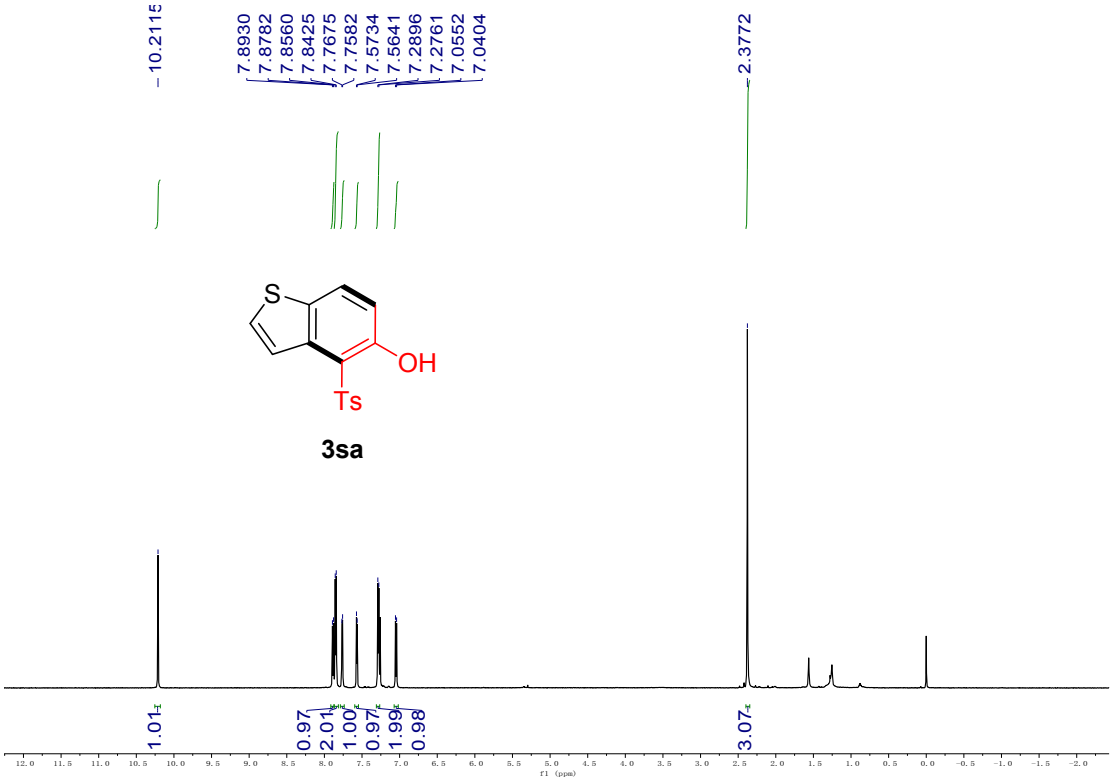


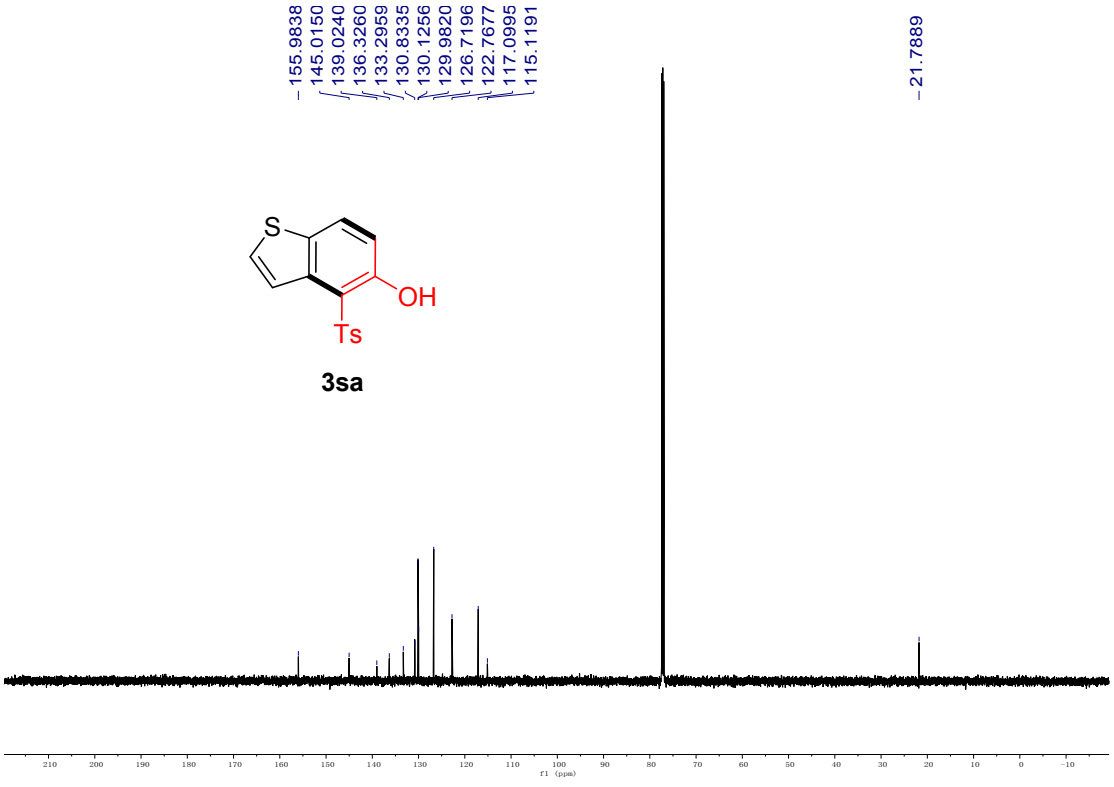



-58.7807
CF3
OH
Ts
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

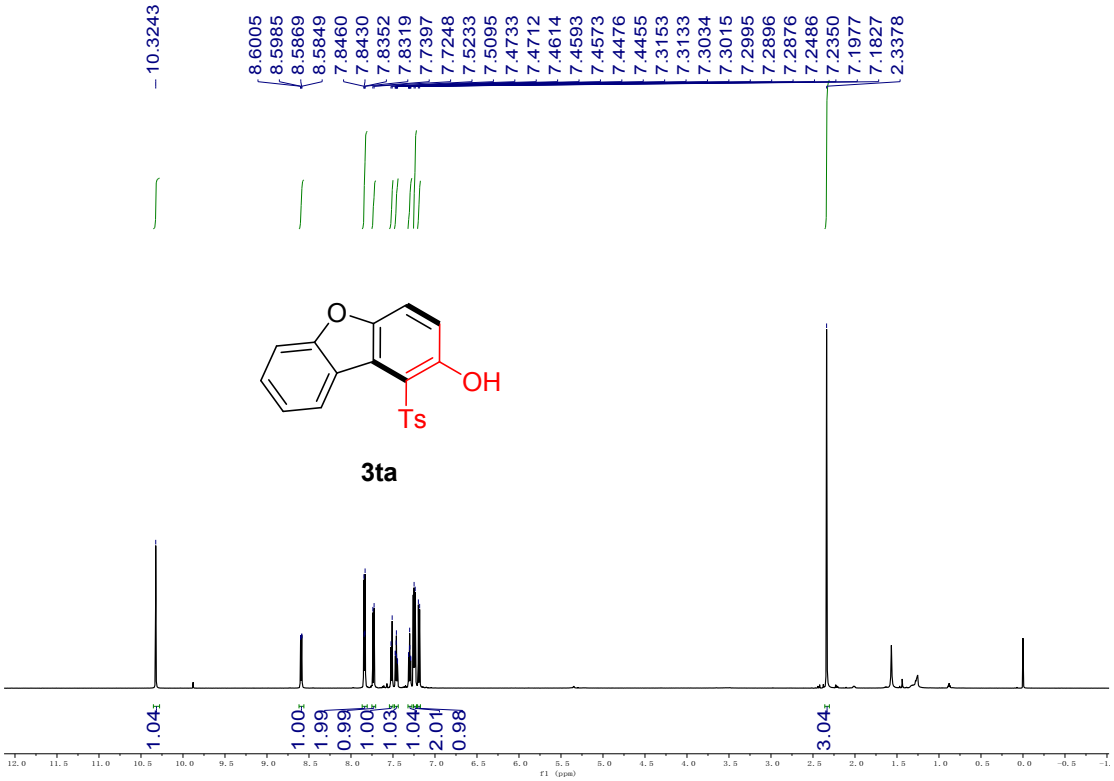
3ra

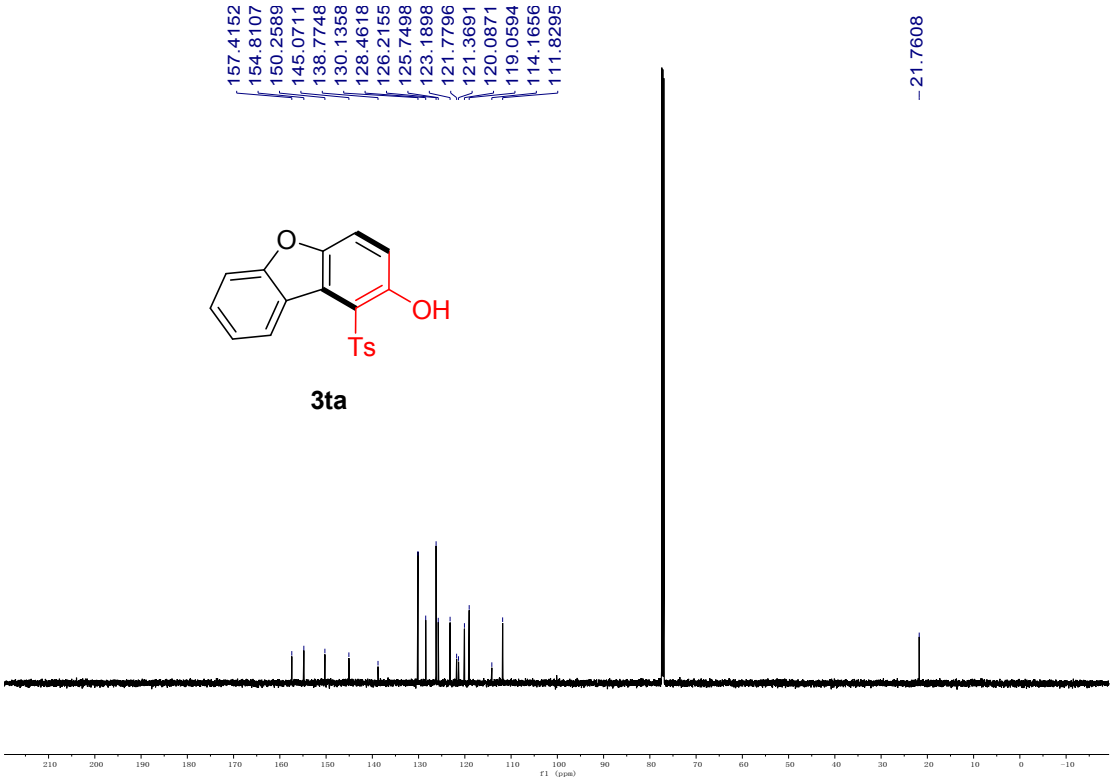
^{1}H and ^{13}C NMR spectra for compound **3sa**



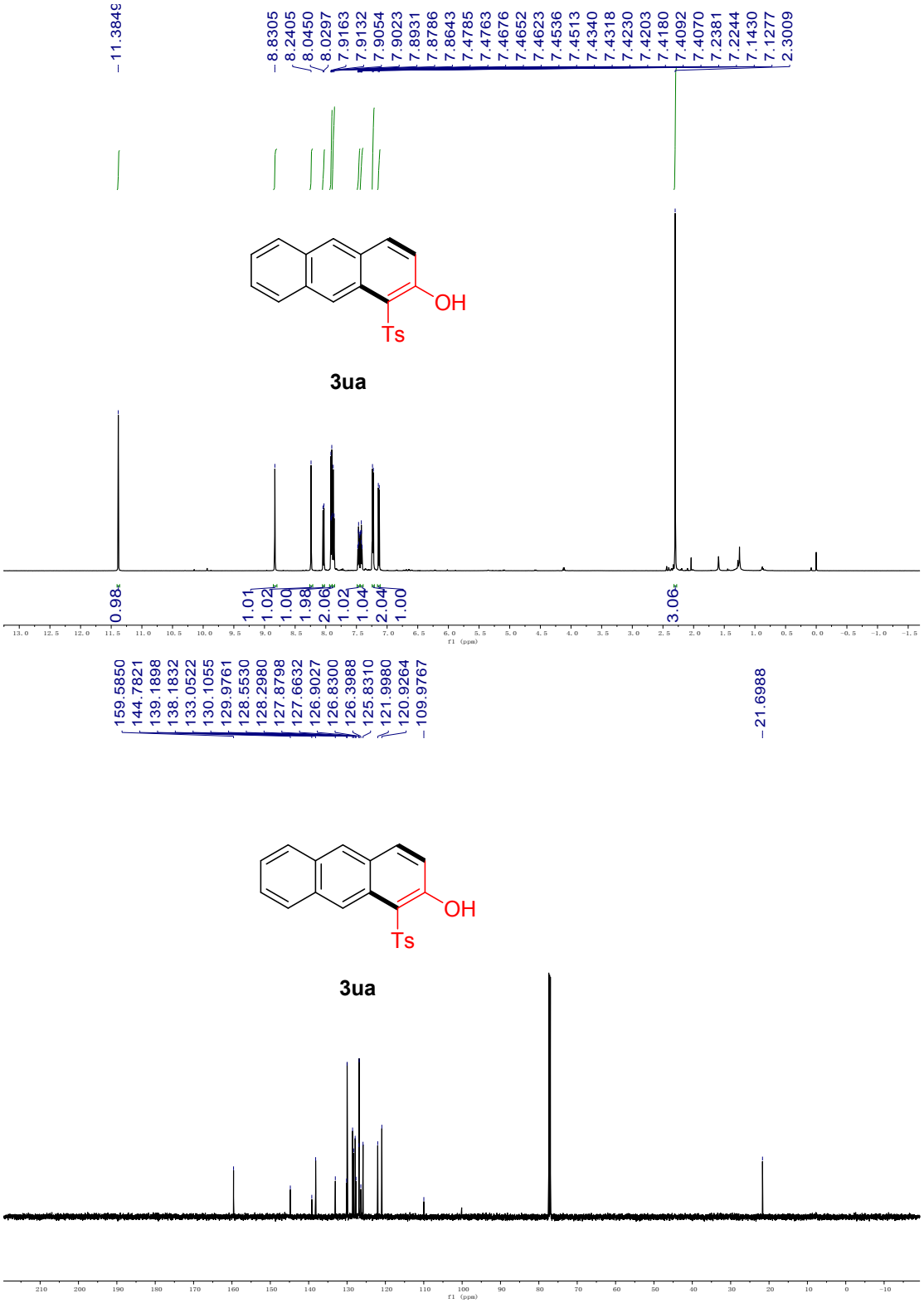


^{1}H and ^{13}C NMR spectra for compound **3ta**

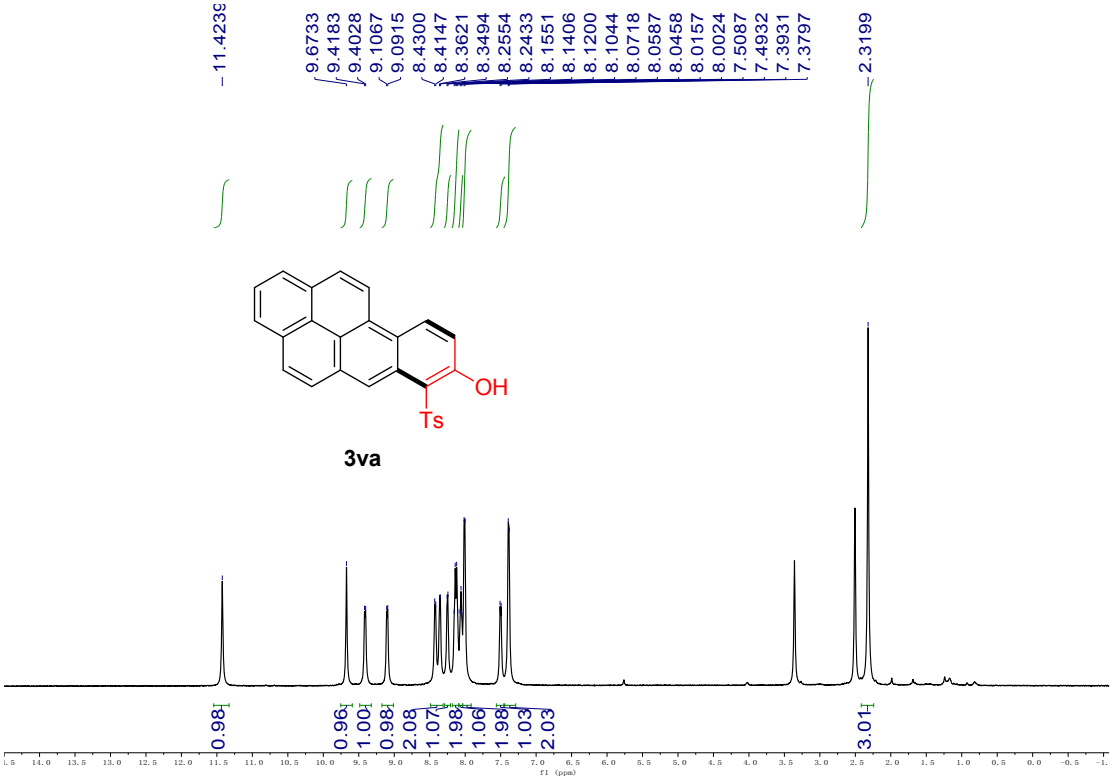


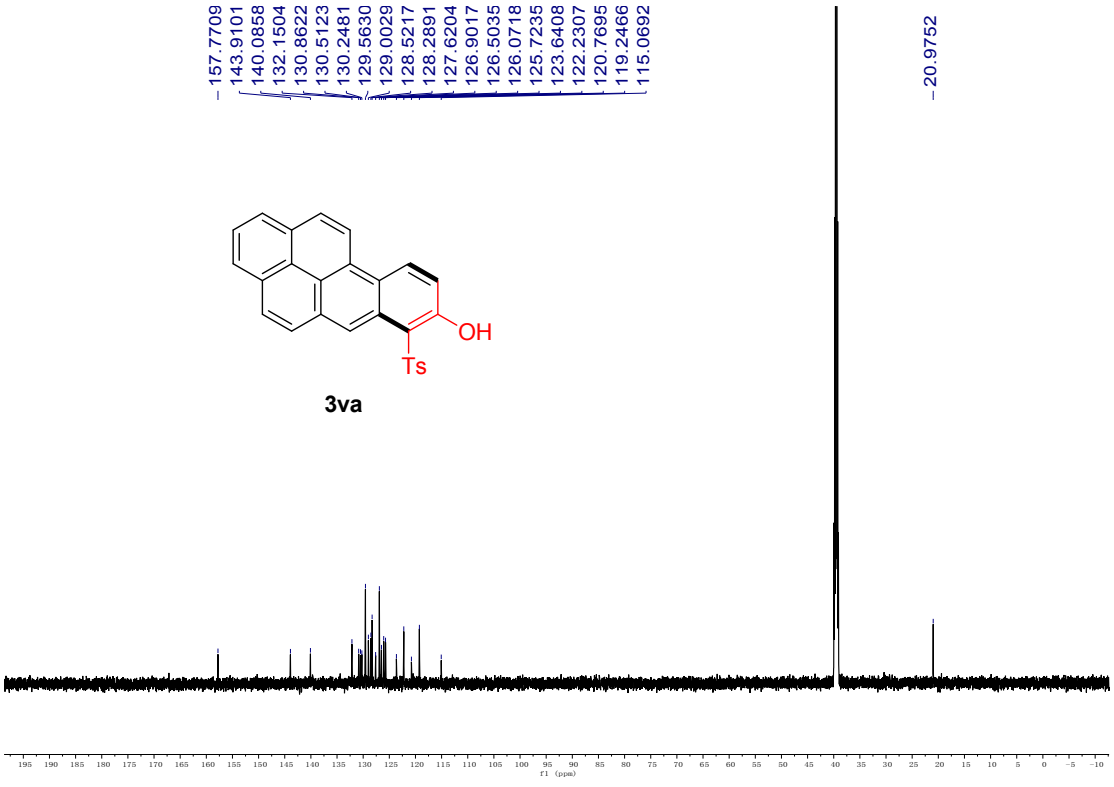


^{1}H and ^{13}C NMR spectra for compound **3ua**

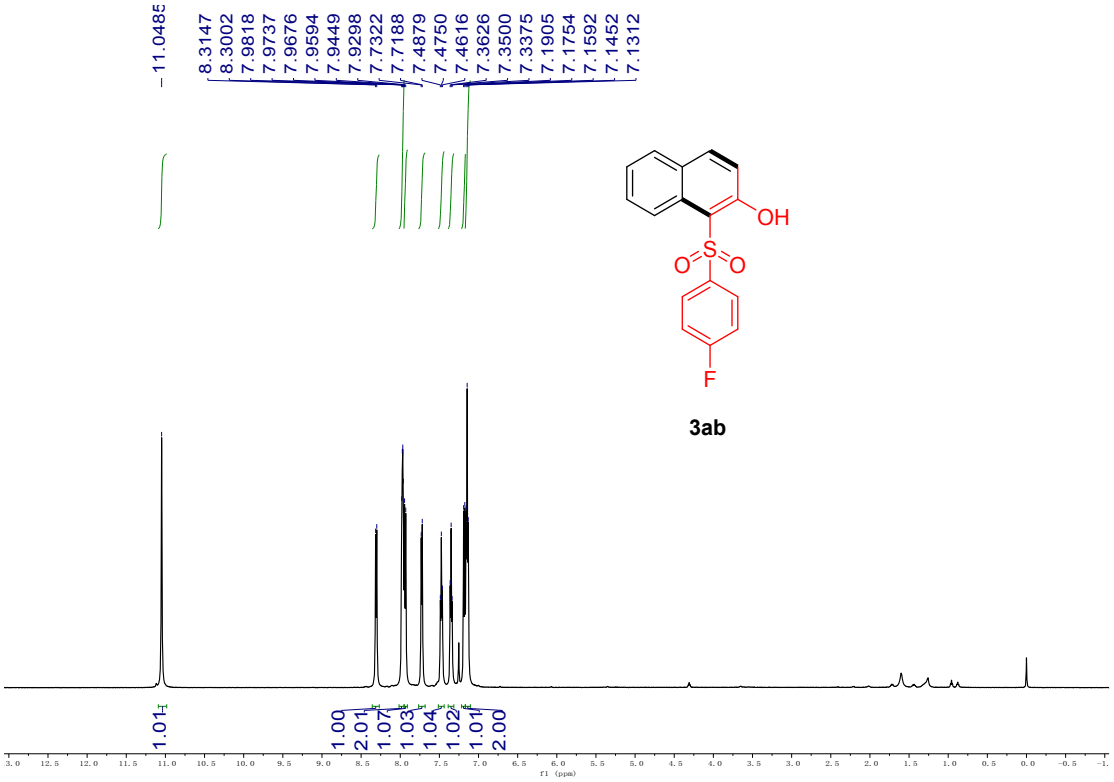


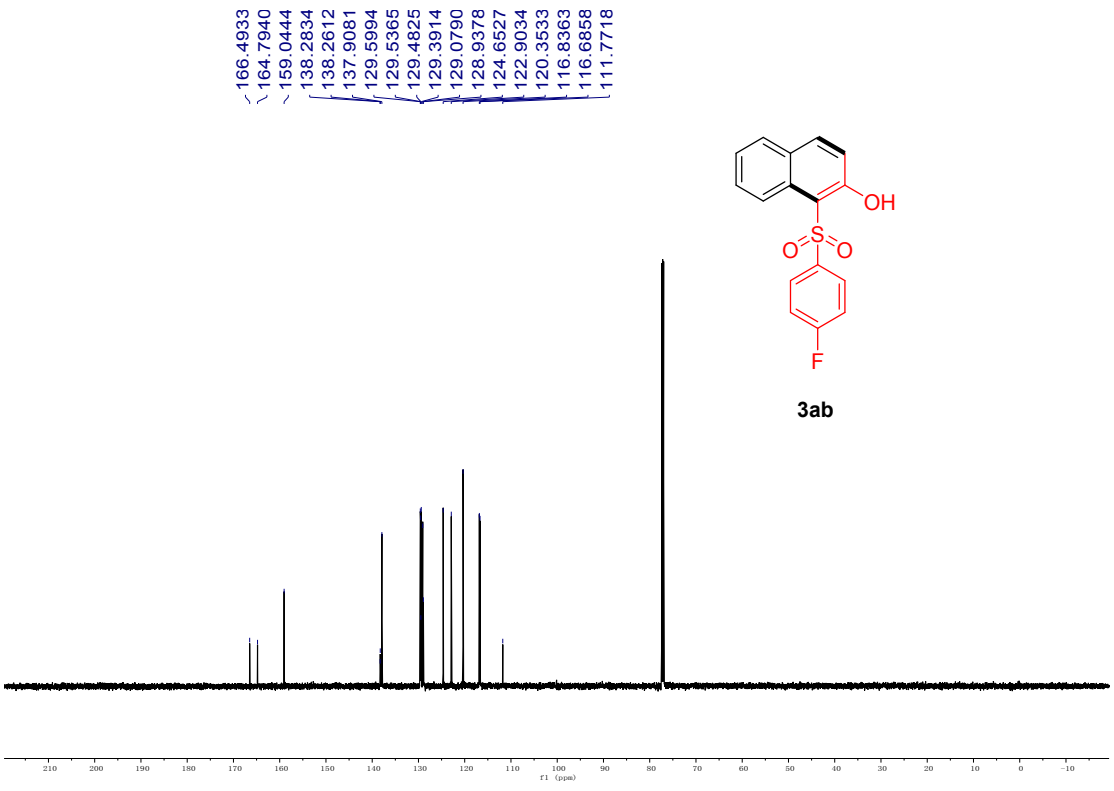
^{1}H and ^{13}C NMR spectra for compound **3va**

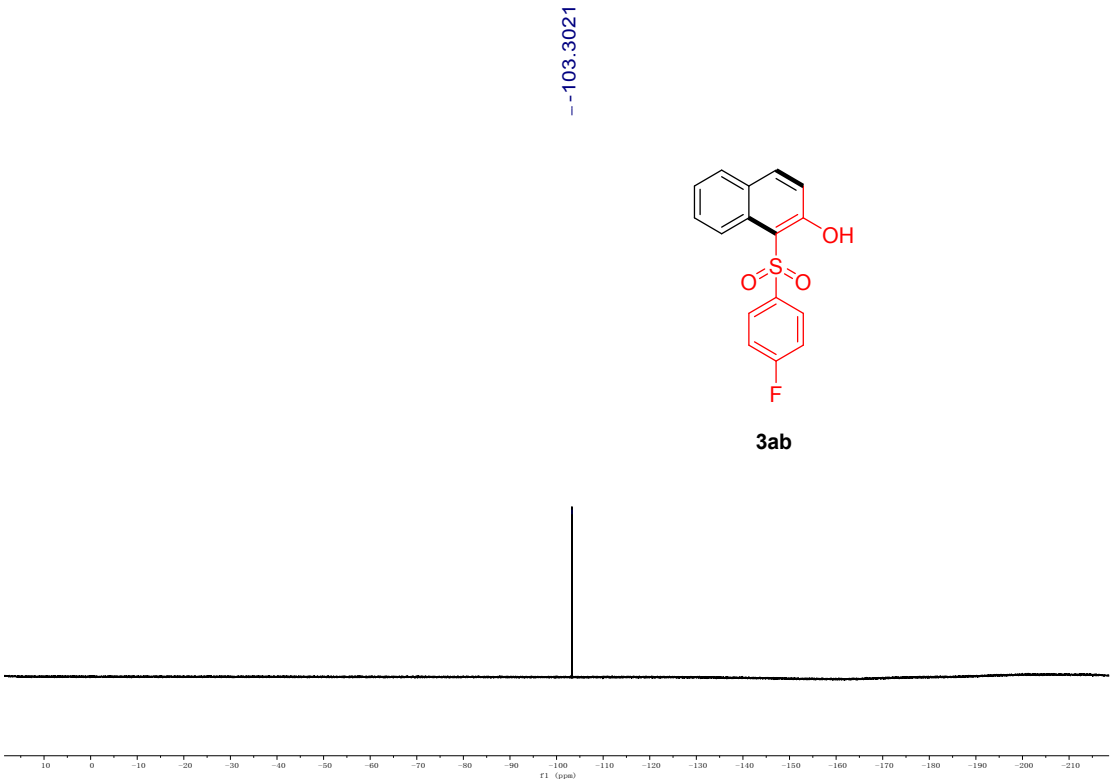




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3ab**

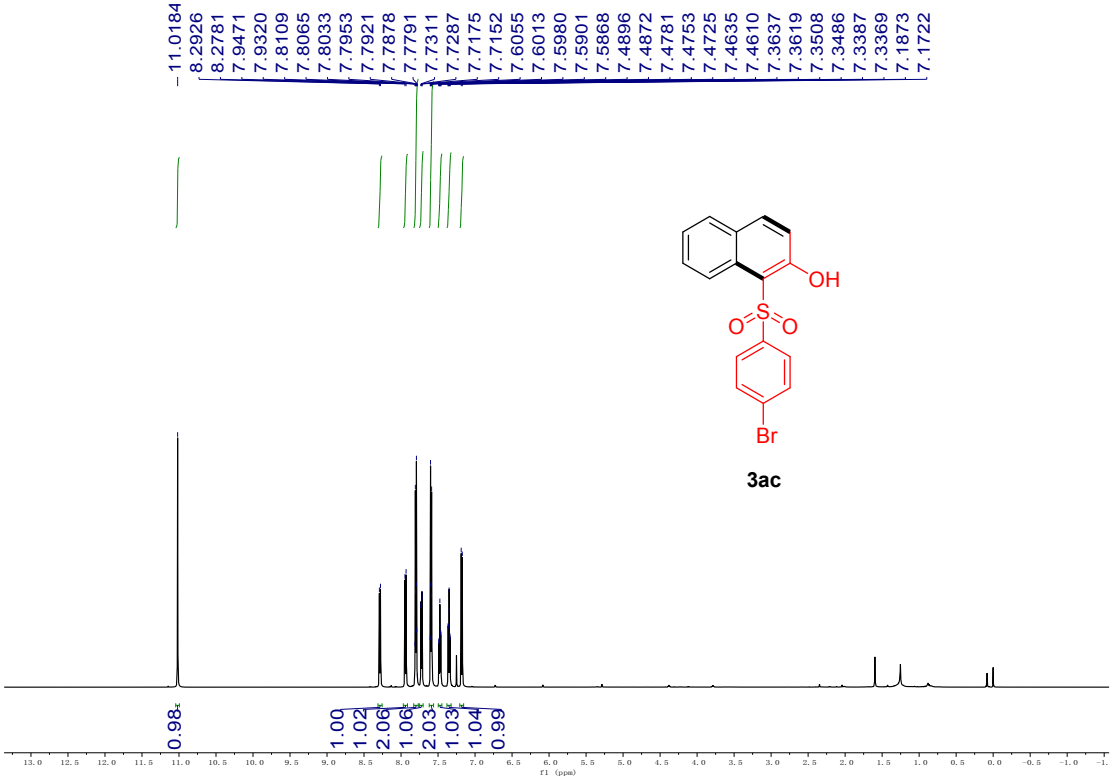


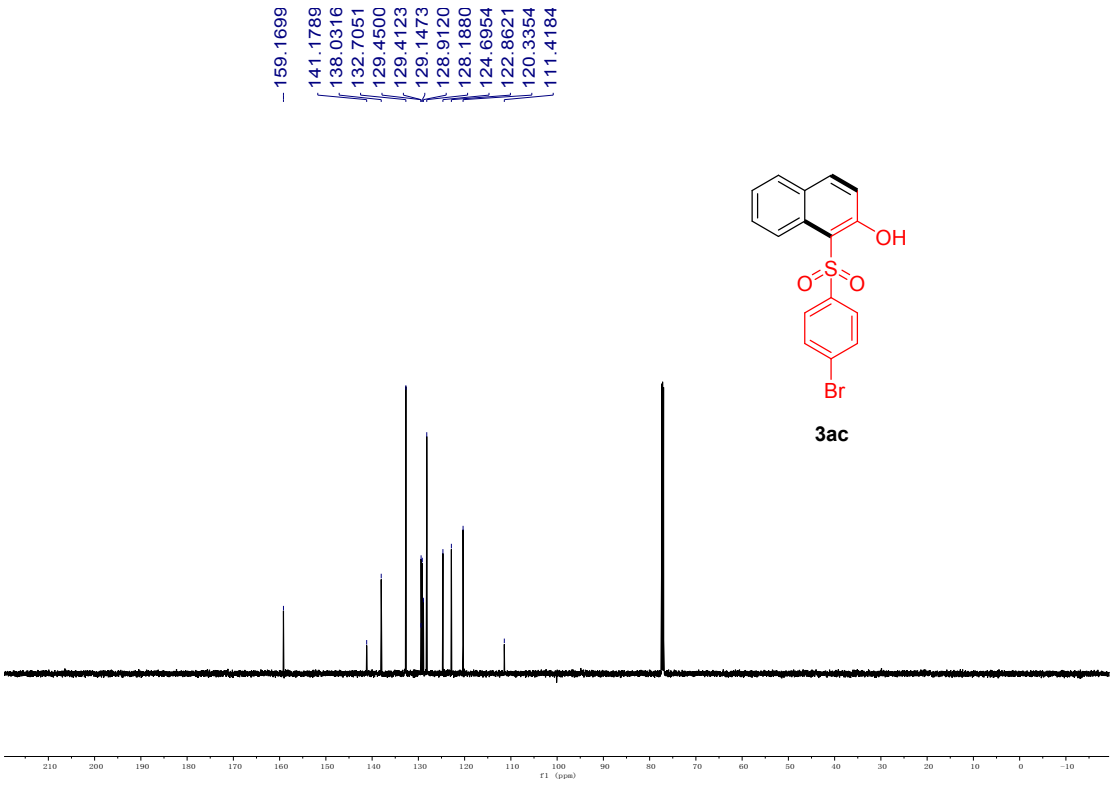



-103.3021
OH
S
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

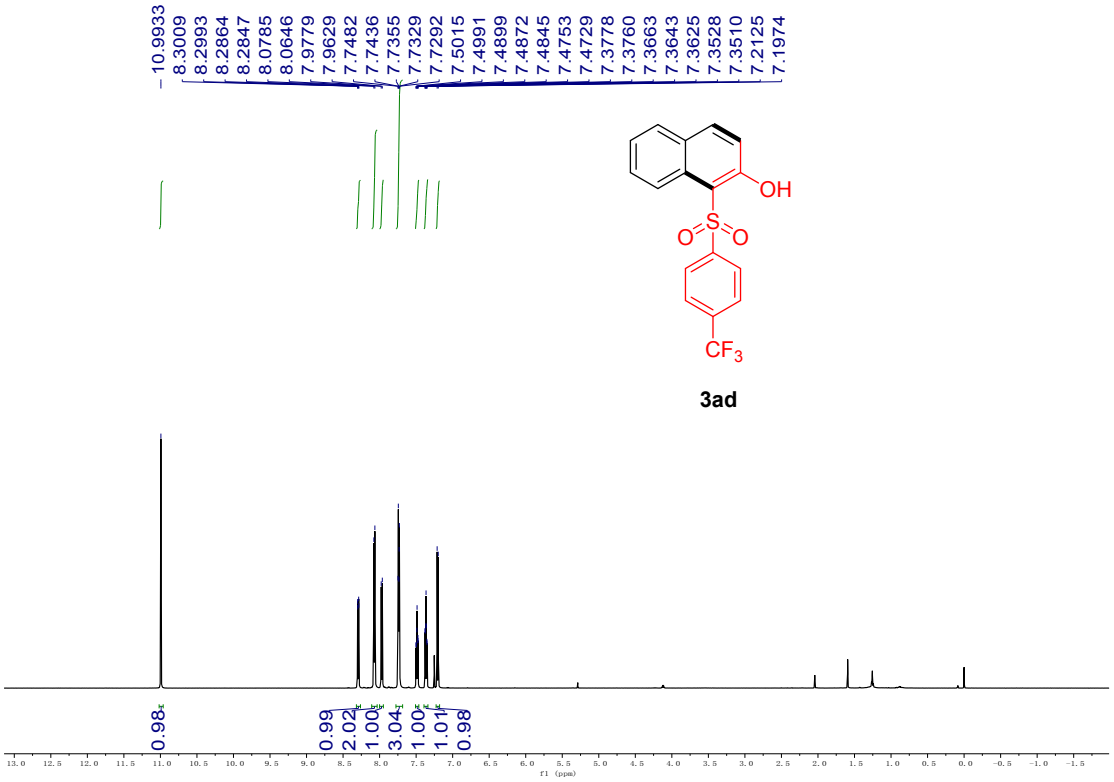
3ab

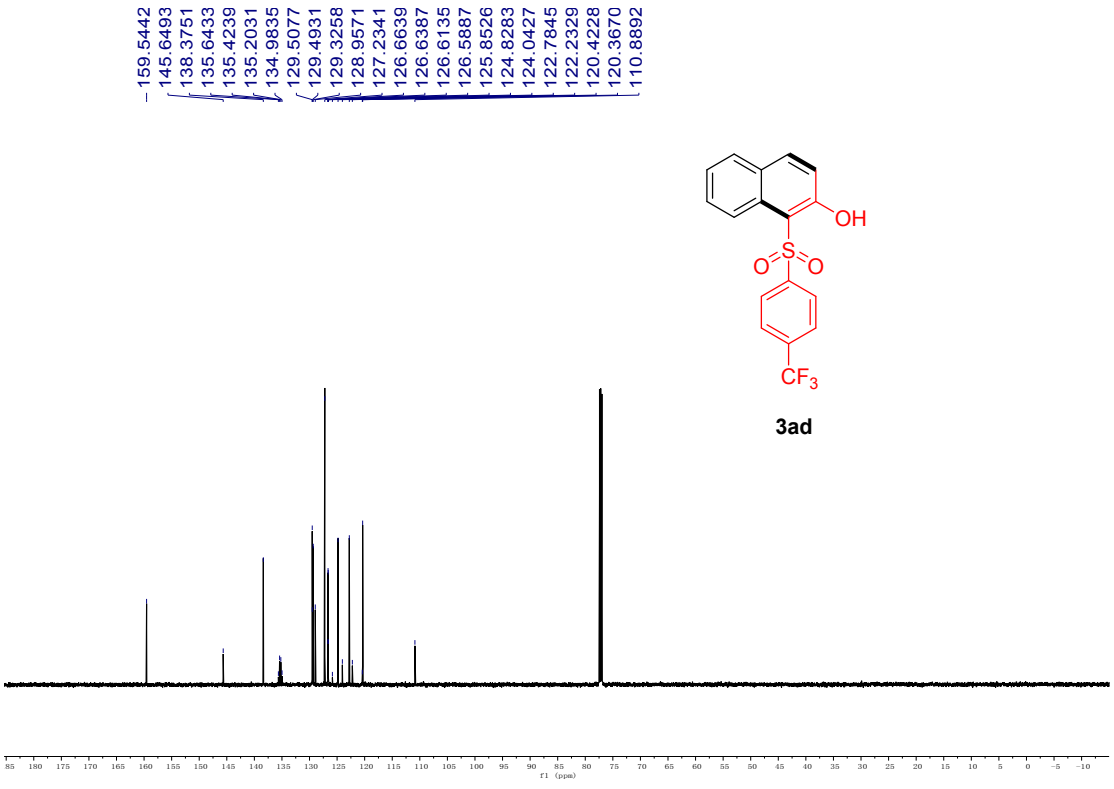
^{1}H and ^{13}C NMR spectra for compound **3ac**

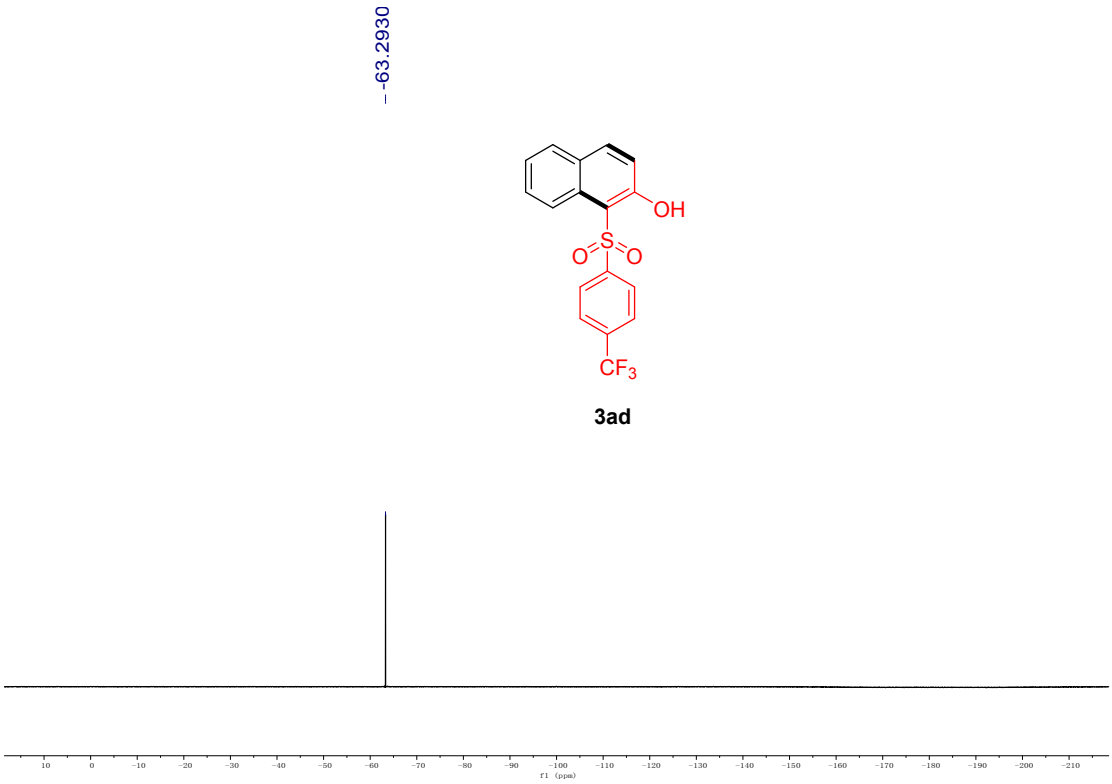




^{1}H, ^{13}C and ^{19}F NMR spectra for compound **3ad**

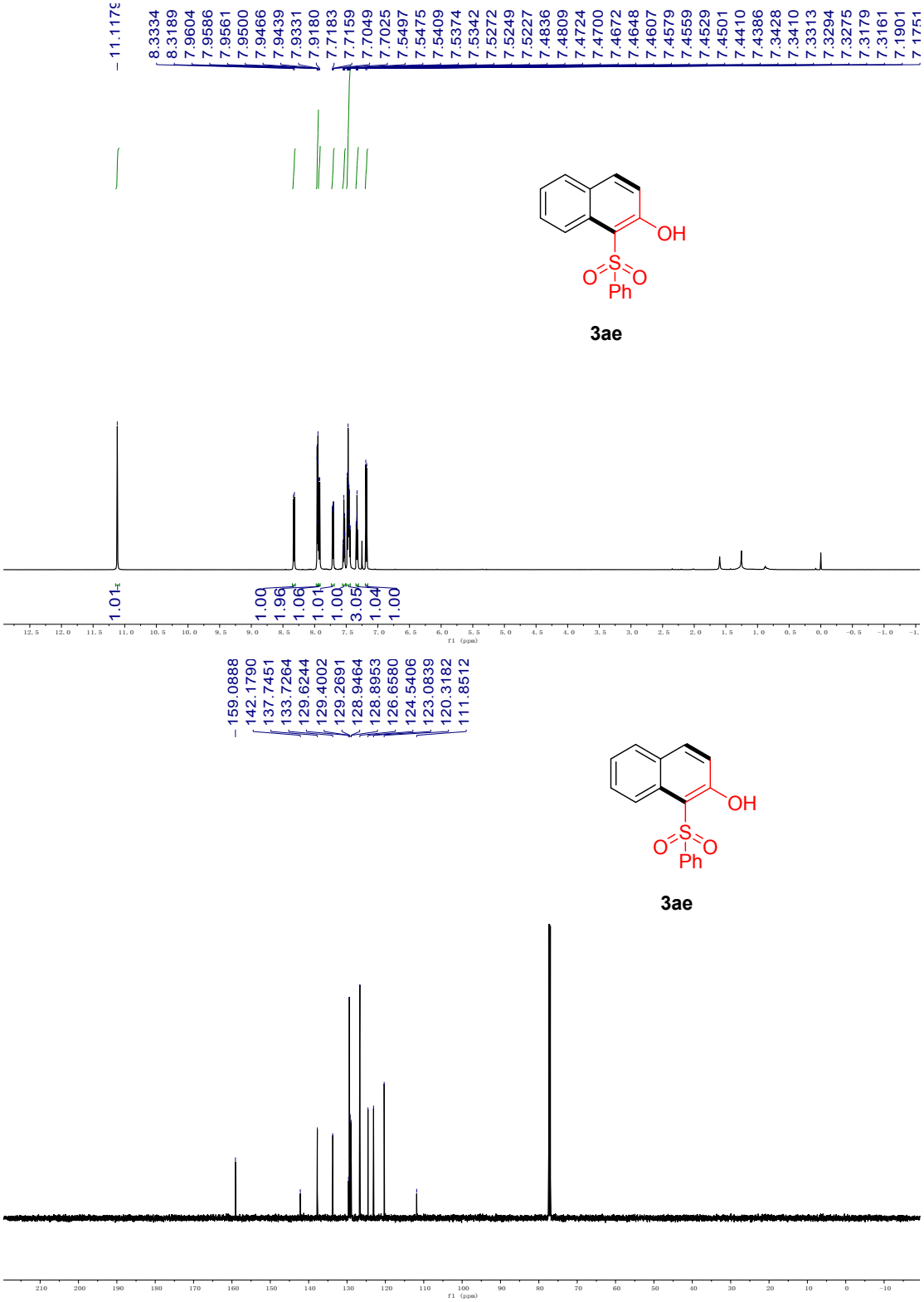




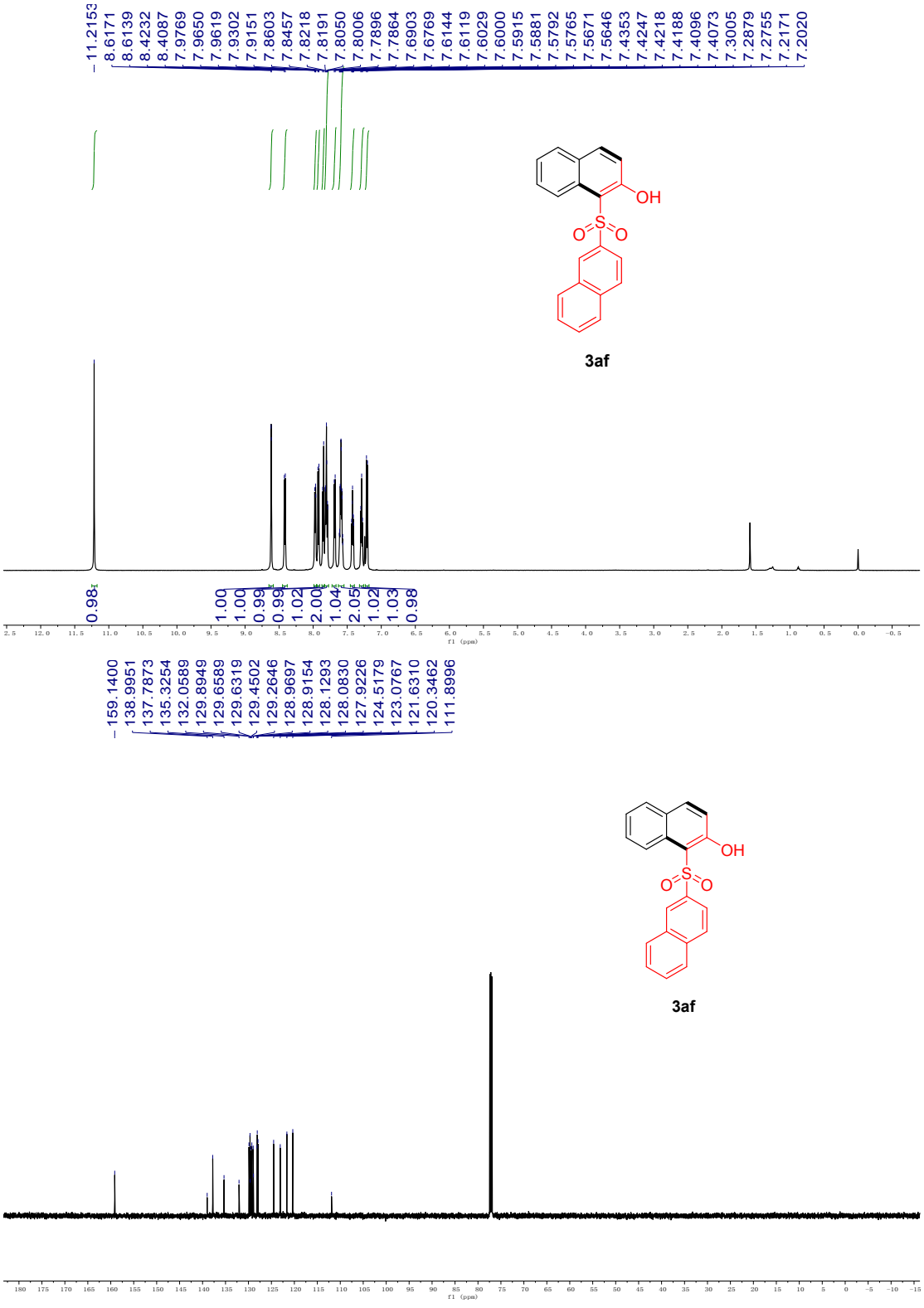

-63.2930
OH
O
S
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3ad

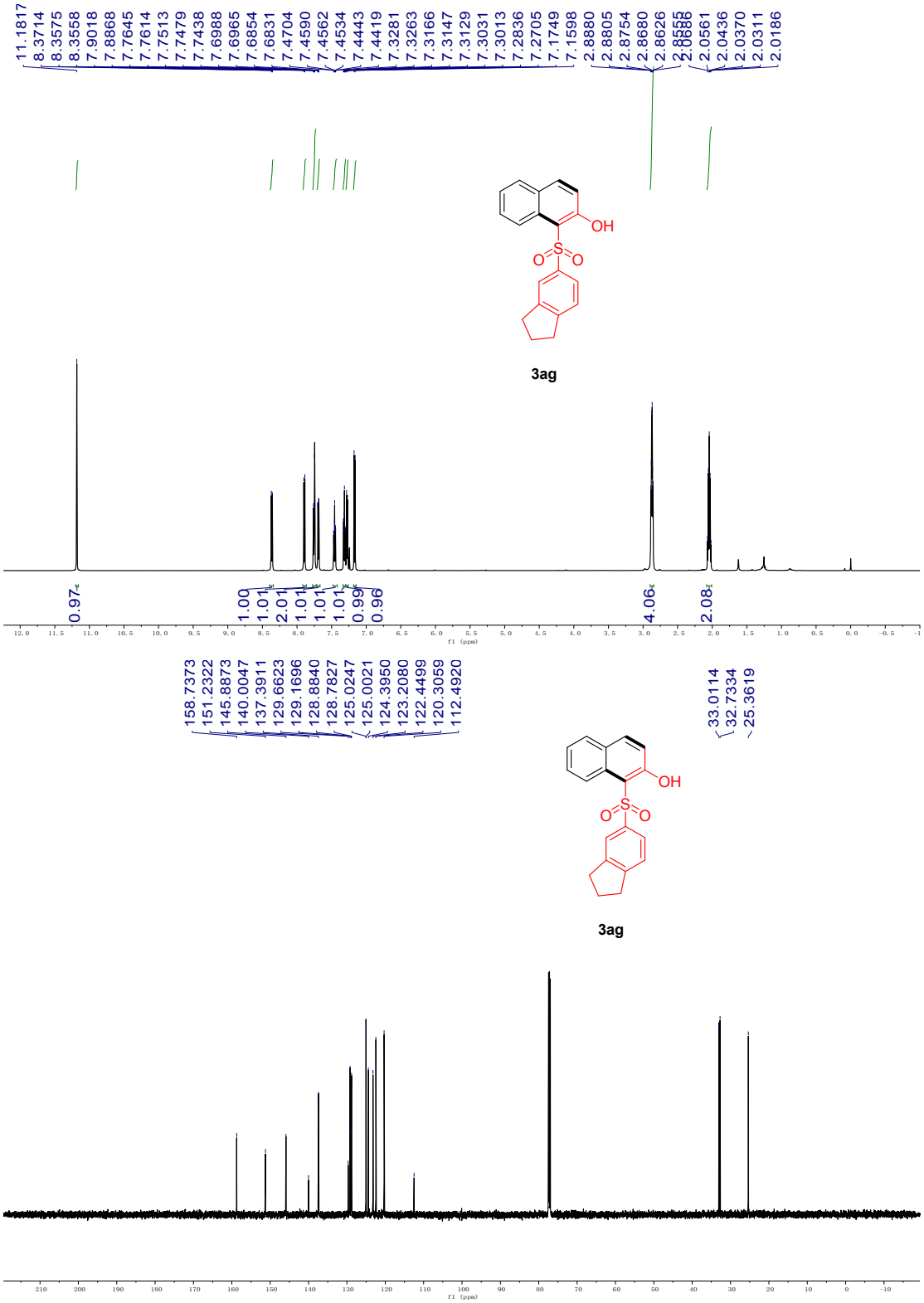
^{1}H and ^{13}C NMR spectra for compound **3ae**



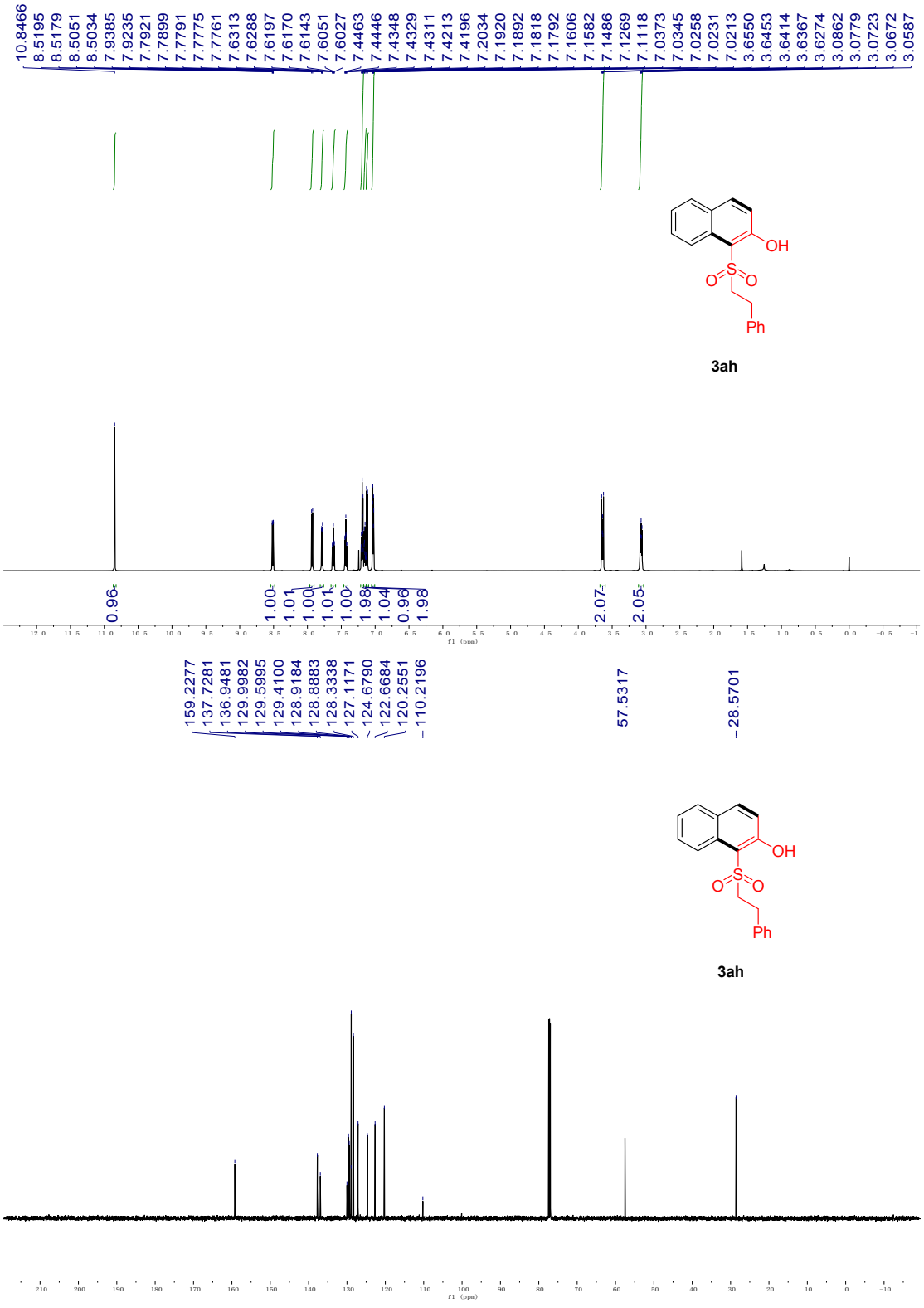
^{1}H and ^{13}C NMR spectra for compound **3af**



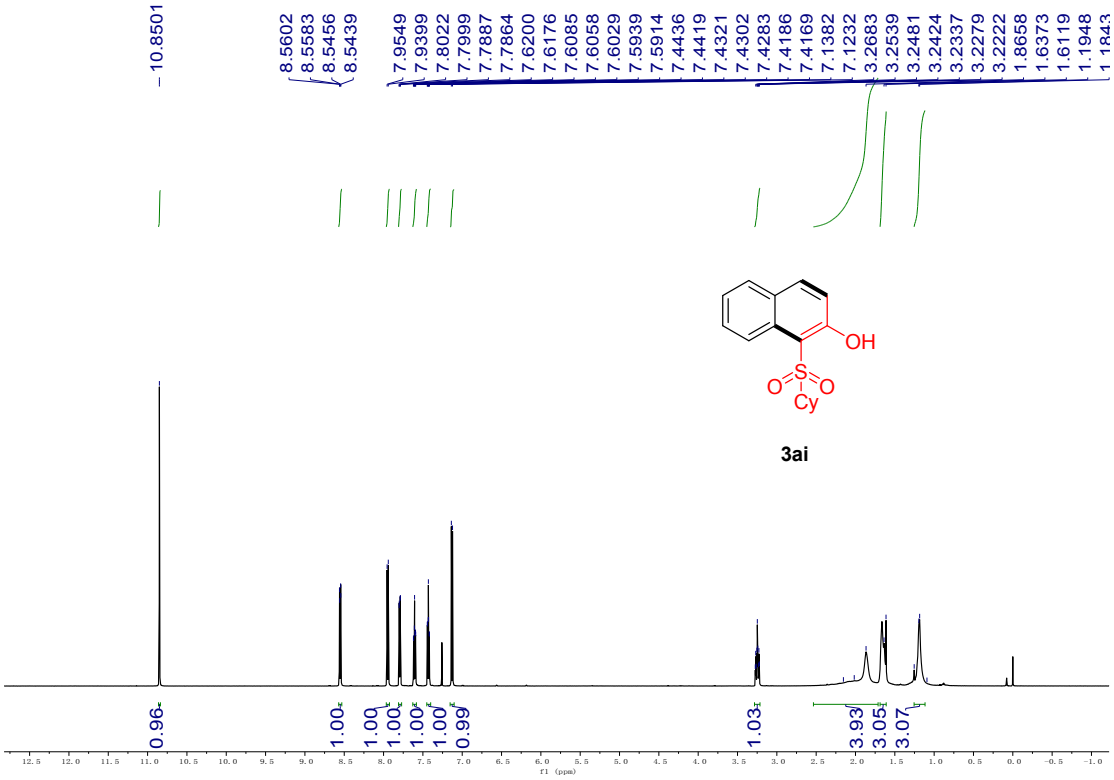
^{1}H and ^{13}C NMR spectra for compound **3ag**



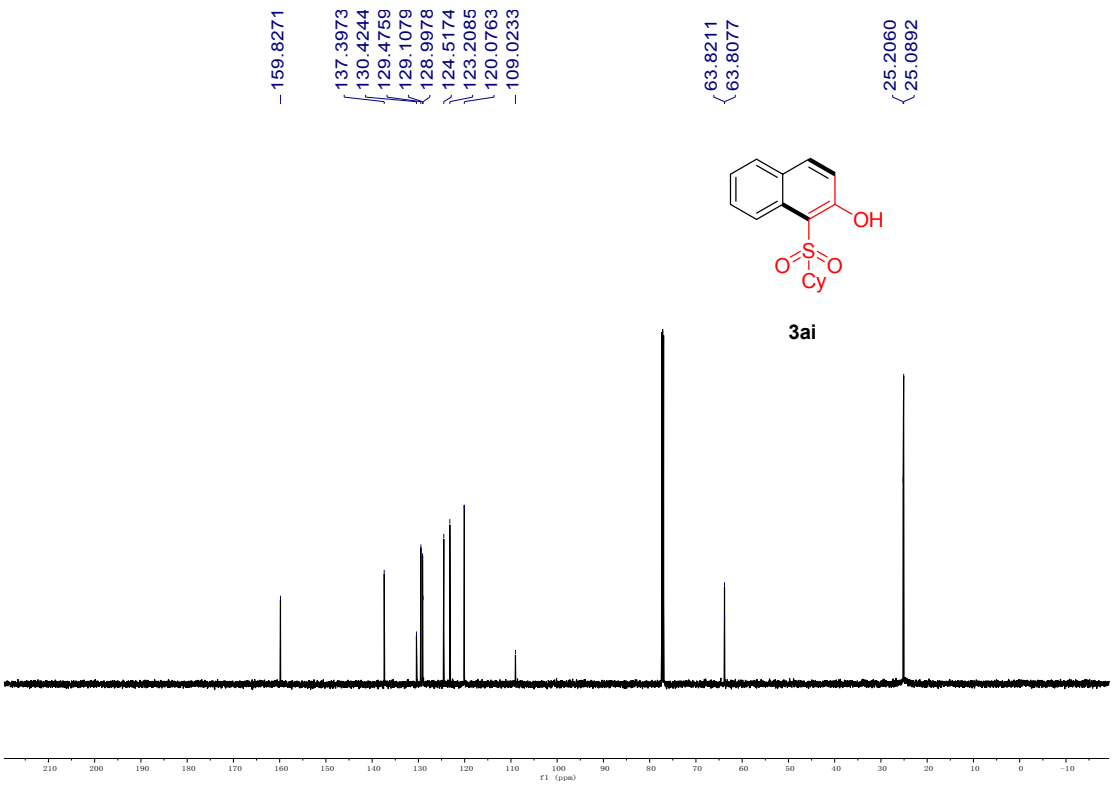
^{1}H and ^{13}C NMR spectra for compound **3ah**



^{1}H and ^{13}C NMR spectra for compound **3ai**

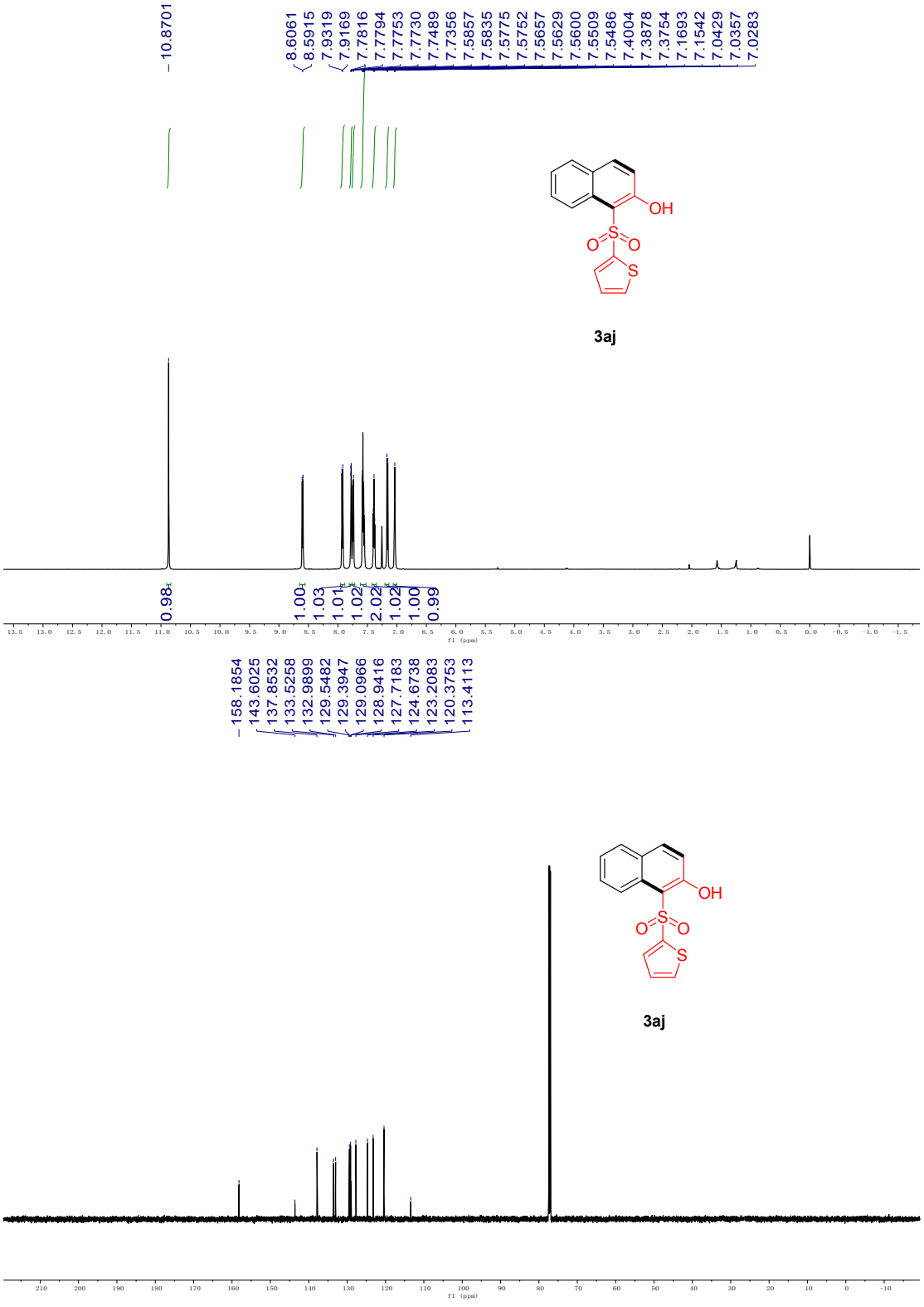


3ai

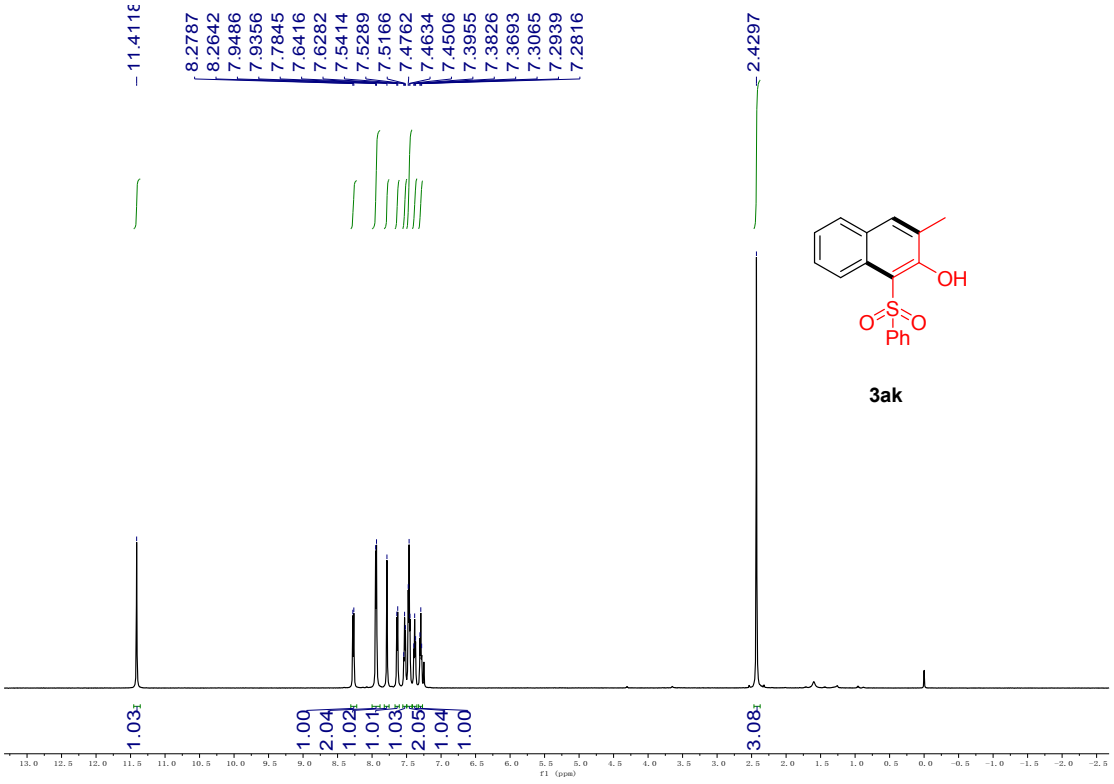


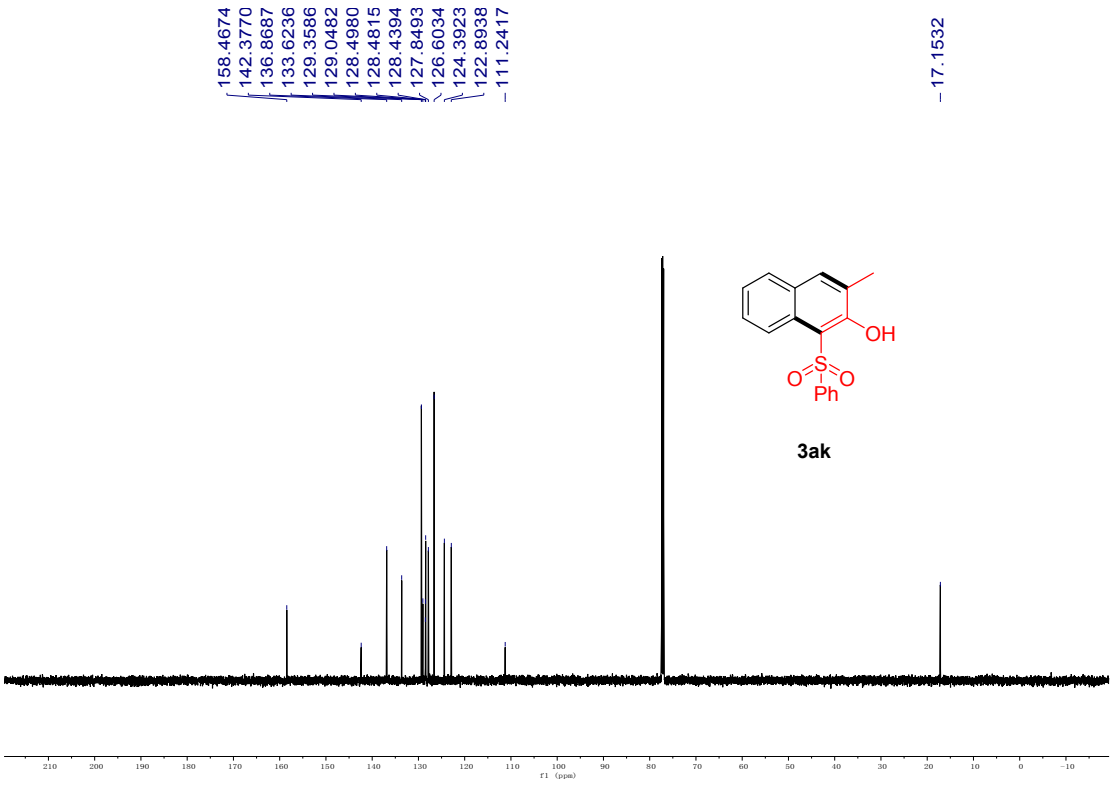
3ai

^{1}H and ^{13}C NMR spectra for compound **3aj**

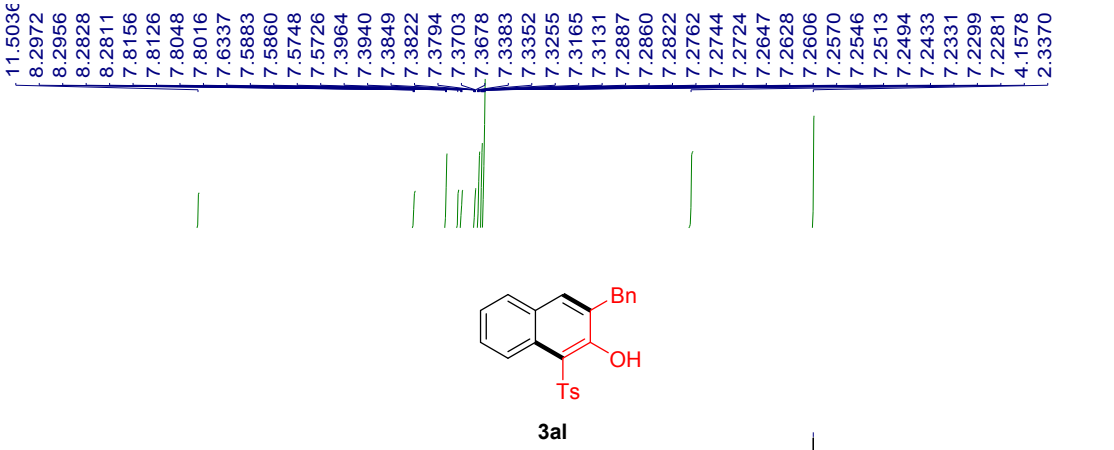


^{1}H and ^{13}C NMR spectra for compound **3ak**

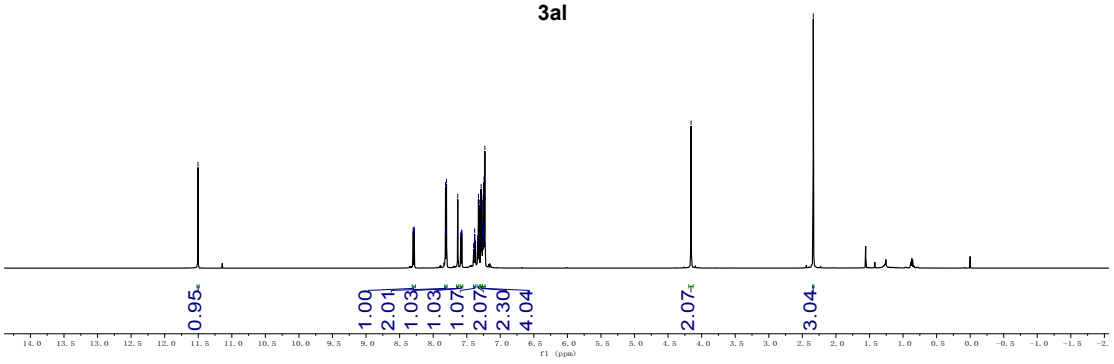


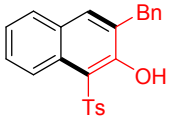


^{1}H and ^{13}C NMR spectra for compound **3al**

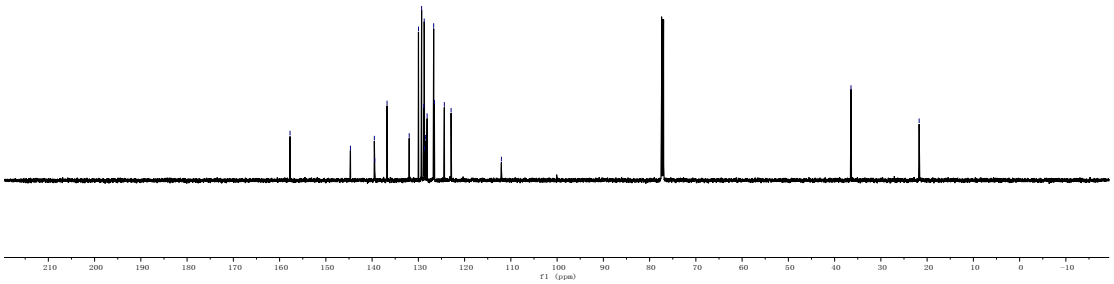


3al

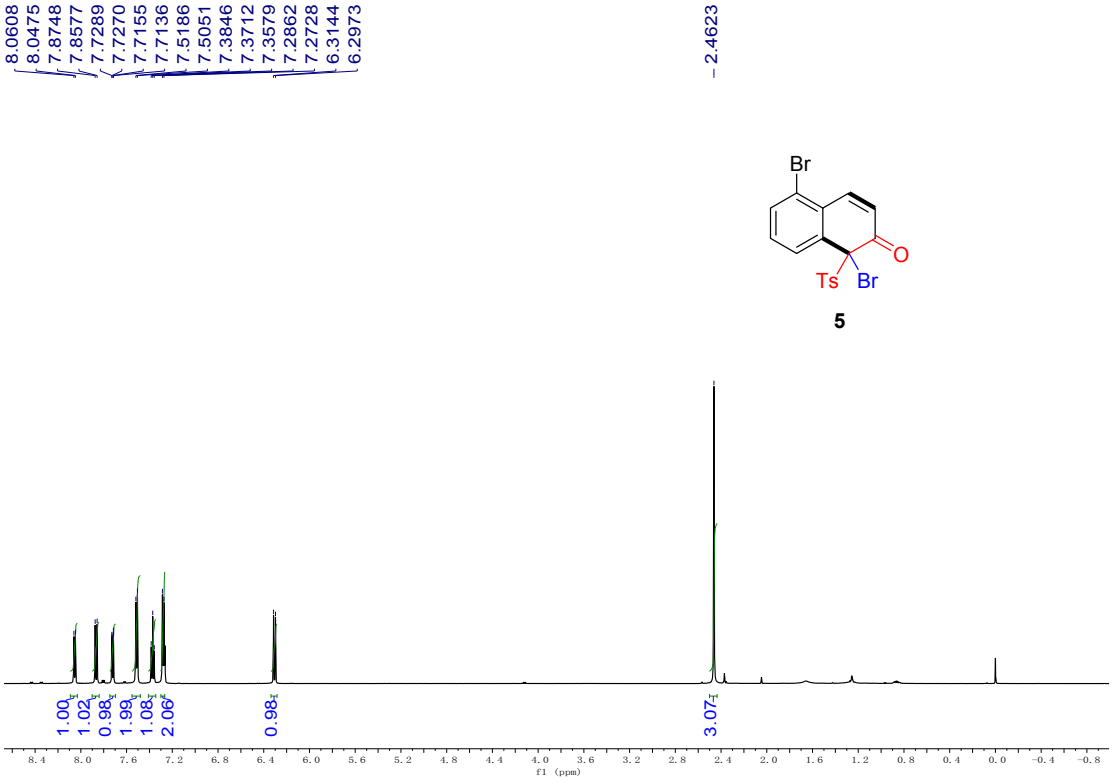


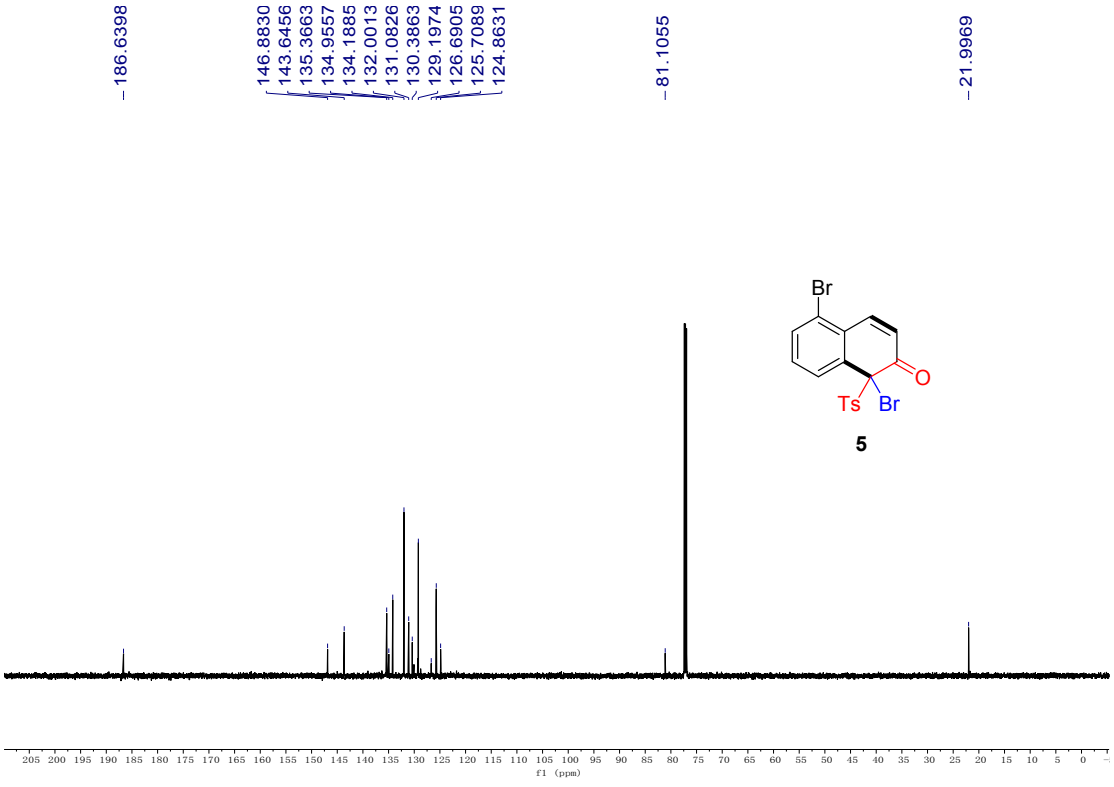


3al



^{1}H and ^{13}C NMR spectra for compound **5**





^{1}H and ^{13}C NMR spectra for compound **6**