Supporting Information

Palladium-catalyzed Cascade Cyclization of Isocyanides with Di-(oiodophenyl)sulfonylguanidines: Access to Heterocyclic Fused Quinazolines

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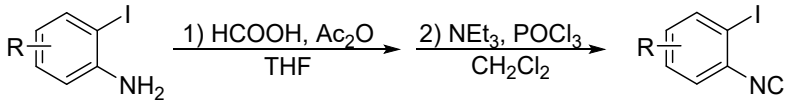
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV-light at 254 nm. Flash column chromatography was performed using Yantai Yinlong flash silica gel (200-300 mesh). Melting points were recorded on an Electrothermal digital melting point apparatus. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400/600 MHz spectrometer in $CDCl_3$ or CD_2Cl_2-d_2 or DMSO-d_6 or DMSO-d_6(0.5 mL)+D_2SO_4(2 drops) with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; h = sextet; m = multiplet; dd = doublet of doublets; br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectroscopy (HRMS) analyses were obtained using a commercial apparatus (ESI Source).

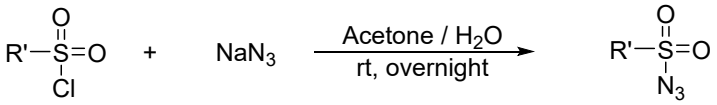
2. Synthesis of the starting materials

2.1. General procedure for the preparation of 1-iodo-2-isocyanobenzene.



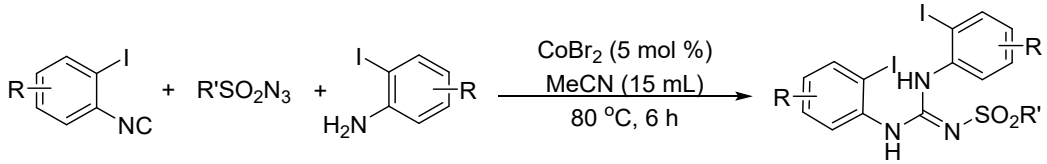
1-Iodo-2-isocyanobenzenes were synthesized according to the literature[1]. A solution of arylamine (1 equiv.) and 98 % formic acid (2 equiv.) in toluene (1.7 M) is refluxed under a condenser attached to a water separator. After the reaction was complete, volatile materials were removed by evaporation. Formanilide was obtained in almost quantitative yield. A solution of formanilide (1 equiv.) and Et_3N (3 equiv.) in dichloromethane (0.5 M) was cooled at 0 °C, then phosphorous oxychloride (1.2 equiv.) was added dropwise. After the reaction was completed, an aqueous saturated solution of sodium carbonate was added to quench the reaction at a sufficiently slow rate in order to maintain 25-30 °C. After stirring for 1h at room temperature, more water and dichloromethane were added and the organic layer was washed with water (3 times), dried with sodium sulfate, and evaporated. The residue was purified by column chromatography.

2.2. General procedure for the preparation of sulfonyl azides.

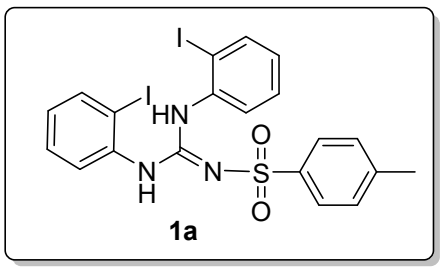


Sulfonyl azides were synthesized according to the literature[2]. To a solution of sodium azide (1.5 equiv.) in water (0.3 M) was added dropwise over 1 h a solution of sulfonyl chloride (1 equiv.) in acetone (1 M) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 11 h. Acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over $MgSO_4$ and solvent was removed under reduced pressure. Crude product was used without further purification.

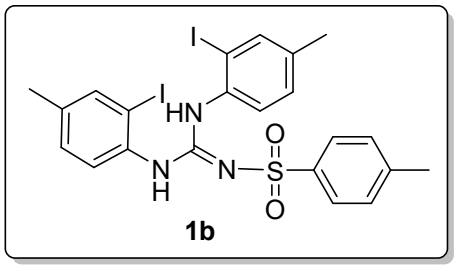
2.3. General procedure for the preparation of di-(*o*-iodophenyl)sulfonylguanidines[1,2].



A mixture of aniline (2 mmol, 1.0 equiv), sulfonyl azides (1.5 equiv), isocyanides (1.2 equiv), $CoBr_2$ (5 mol %) and MeCN (15 mL) were added into a flask and stirred at 80 °C. Then the mixture was vigorously stirred under reflux conditions monitored by TLC analysis (about 6 h). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate (EA) / petroleum ether (PE) / dichloromethane (DCE) (V_{EA}/V_{PE} = 1/10 → DCE) as eluents to afford pure product.

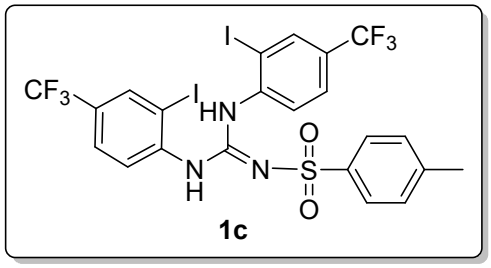


1a was obtained in 99% yield (1221.5 mg). White solid, **mp** = 171.2 – 172.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.94 (s, 2H), 7.92 – 7.87 (m, 2H), 7.74 – 7.69 (m, 2H), 7.44 – 7.32 (m, 6H), 7.08 – 7.02 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.8, 141.7, 140.6, 139.1, 138.5, 129.2, 129.1, 128.8, 128.3, 126.0, 98.8, 21.0. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{17}I_2N_3O_2SNa^+$, m/z: 639.9023, found: 639.9034. **IR (thin film):** ν_{max} 3359, 3266, 1596, 1598, 1571, 1351, 1275, 1140 cm^{-1}.



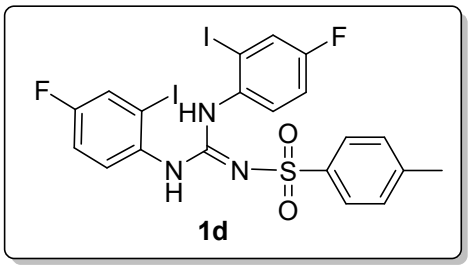
1b was obtained in 88% yield (1135.1 mg). White solid, **mp** = 66.5 – 67.8 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.78 (s,

2H), 7.74 – 7.67 (m, 4H), 7.35 – 7.29 (m, 2H), 7.24 – 7.17 (m, 4H), 2.36 (s, 3H), 2.27 (s, 6H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.2, 141.6, 140.8, 139.2, 138.6, 135.9, 129.8, 129.1, 128.2, 126.0, 99.0, 21.0, 19.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{22}I_2N_3O_2S^+$, m/z: 645.9517, found: 645.9517. **IR (thin film):** ν_{max} 3251, 1582, 1523, 1349, 1267, 1135, 811, 558 cm^{-1}.



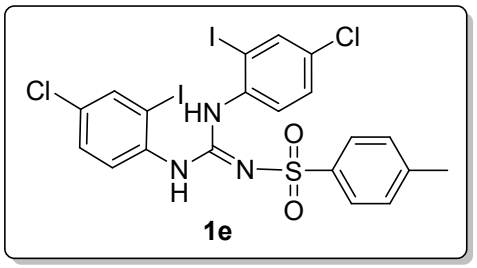
1c

1c was obtained in 50% yield (752.9 mg). Yellow solid, **mp** = 136.5 – 137.5 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.26 (s, 2H), 8.25 – 8.19 (m, 2H), 7.82 – 7.76 (m, 2H), 7.74 – 7.69 (m, 2H), 7.60 – 7.51 (m, 2H), 7.36 – 7.31 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.3, 142.8, 142.1, 140.2, 135.7 (q, $J_{(C-F)}$ = 3.0 Hz), 129.2, 128.5, 128.5 (q, $J_{(C-F)}$ = 32.3 Hz), 126.2, 122.9 (q, $J_{(C-F)}$ = 270.7 Hz), 99.1, 21.0. **^{19}F NMR (376 MHz, DSMO-*d*$_6$)** δ -61.09. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{16}I_2F_6N_3O_2S^+$, m/z: 753.8951, found: 753.8953. **IR (thin film):** ν_{max} 3280, 1591, 1529, 1315, 1122, 1062, 685, 525 cm^{-1}.



1d

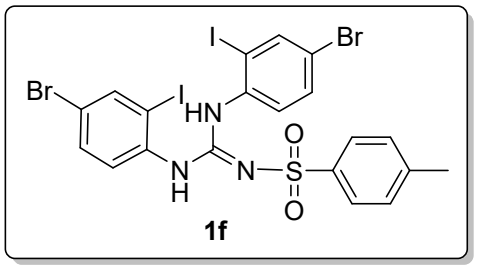
1d was obtained in 80% yield (1046.2 mg). Brown solid, **mp** = 180.1 – 180.4 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.82 (s, 2H), 7.82 – 7.76 (m, 2H), 7.75 – 7.70 (m, 2H), 7.37 – 7.28 (m, 6H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 160.3 (d, $J_{(C-F)}$ = 248 Hz), 153.3, 141.7, 140.7, 135.3 (d, $J_{(C-F)}$ = 3 Hz), 130.1 (d, $J_{(C-F)}$ = 9 Hz), 129.1, 126.0, 125.5 (d, $J_{(C-F)}$ = 24 Hz), 116.0 (d, $J_{(C-F)}$ = 22 Hz), 100.4 (d, $J_{(C-F)}$ = 8 Hz), 21.0. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -113.79. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}I_2F_2N_3O_2S^+$, m/z: 653.9015, found: 653.9029. **IR (thin film):** ν_{max} 3268, 1594, 1575, 1477, 1109, 856, 812, 556 cm^{-1}.



1e

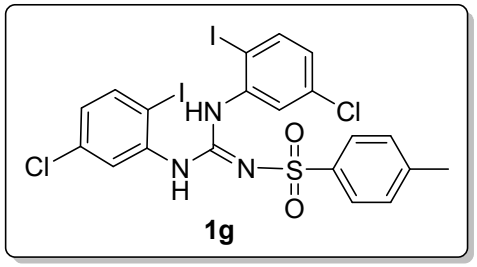
1e was obtained in 92% yield (1261.9 mg). White solid, **mp** = 152.8 – 153.4 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.96 (s, 2H), 7.98 – 7.94 (m, 2H), 7.77 – 7.72 (m,

2H), 7.52 – 7.47 (m, 2H), 7.37 – 7.31 (m, 4H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.8, 141.8, 140.5, 137.9, 137.9, 132.1, 129.8, 129.2, 129.1, 126.1, 100.5, 21.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}Cl_2I_2N_3O_2S^+$, m/z: 685.8424, found: 685.8418. **IR (thin film):** ν_{max} 3259, 1590, 1511, 1108, 1036, 783, 680, 550 cm^{-1}.



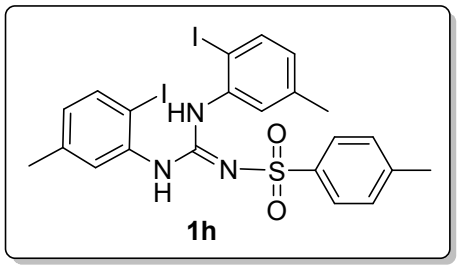
1f

1f was obtained in 75% yield (1160.6 mg). Yellow solid, **mp** = 135.1 – 136.3 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.93 (s, 2H), 8.12 – 8.04 (m, 2H), 7.74 – 7.69 (m, 2H), 7.65 – 7.58 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.7, 141.8, 140.5, 140.5, 138.3, 132.0, 130.2, 129.2, 126.1, 120.5, 101.0, 21.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}Br_2I_2N_3O_2S^+$, m/z: 773.7414, found: 773.7415. **IR (thin film):** ν_{max} 3320, 3257, 1608, 1520, 1376, 1353, 1138, 542 cm^{-1}.



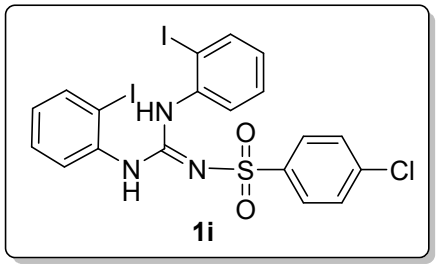
1g

1g was obtained in 87% yield (1193.4 mg). Yellow solid, **mp** = 189.9 – 190.5 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.10 (s, 2H), 7.92 – 7.85 (m, 2H), 7.75 – 7.69 (m, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.17 – 7.11 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.4, 141.9, 140.4, 140.2, 140.0, 133.3, 129.2, 128.7, 128.2, 126.0, 97.2, 21.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{16}Cl_2I_2N_3O_2S^+$, m/z: 685.8424, found: 685.8423. **IR (thin film):** ν_{max} 3328, 3265, 1619, 1571, 1402, 1261, 1091, 713 cm^{-1}.



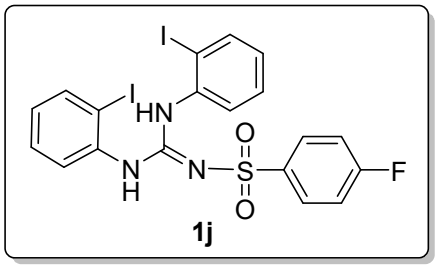
1h

1h was obtained in 94% yield (1214.4 mg). Yellow solid, **mp** = 179.8 – 180.3 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.93 (s, 2H), 7.77 – 7.66 (m, 4H), 7.38 – 7.32 (m, 2H), 7.19 – 7.11 (m, 2H), 6.89 – 6.80 (m, 2H), 2.37 (s, 3H), 2.23 (s, 6H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 152.7, 141.8, 140.7, 138.8, 138.6, 138.1, 129.5, 129.2, 128.7, 126.0, 94.1, 21.0, 20.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{22}I_2N_3O_2S^+$, m/z: 645.9517, found: 645.9523. **IR (thin film):** ν_{max} 3371, 3247, 1603, 1524, 1356, 1106, 806, 684 cm^{-1}.



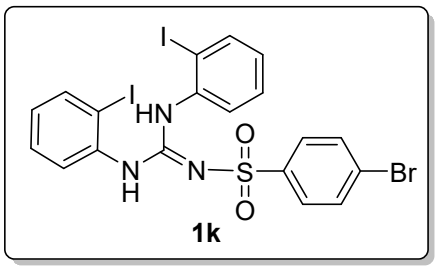
1i

1i was obtained in 91% yield (1159.1 mg). White solid, **mp** = 168.8 – 169.4 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.95 (s, 2H), 7.91 – 7.82 (m, 4H), 7.62 – 7.58 (m, 2H), 7.44 – 7.35 (m, 4H), 7.09 – 7.03 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.0, 142.3, 139.1, 138.5, 136.5, 129.2, 129.0, 128.9, 128.7, 128.1, 99.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{15}ClI_2N_3O_2S^+$, m/z: 637.8658, found: 637.8652. **IR (thin film):** ν_{max} 3364, 3271, 1570, 1526, 1351, 1142, 761, 740 cm^{-1}.



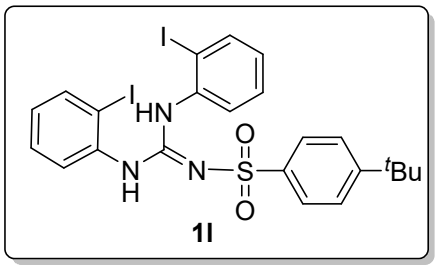
1j

1j was obtained in 85% yield (1055.5 mg). White solid, **mp** = 133.6 – 135.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.98 (s, 2H), 7.99 – 7.85 (m, 4H), 7.48 – 7.34 (m, 6H), 7.11 – 7.02 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.8 (d, $J_{(C\text{-}F)}$ = 248.0 Hz), 153.0, 139.8 (d, $J_{(C\text{-}F)}$ = 3.0 Hz), 139.1, 138.5, 129.2, 129.0 (d, $J_{(C\text{-}F)}$ = 9.0 Hz), 129.0, 128.6, 115.8 (d, $J_{(C\text{-}F)}$ = 22.0 Hz), 99.2. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -107.90. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{15}FI_2N_3O_2S^+$, m/z: 621.8953, found: 621.8964. **IR (thin film):** ν_{max} 3356, 3272, 1573, 1528, 1353, 1222, 1141, 759 cm^{-1}.



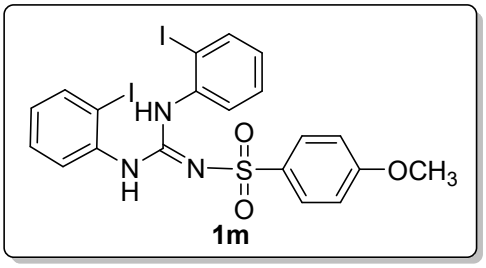
1k

1k was obtained in 85% yield (1157.4 mg). White solid, **mp** = 180.6 – 191.5 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.95 (s, 2H), 7.92 – 7.87 (m, 2H), 7.79 – 7.72 (m, 4H), 7.45 – 7.34 (m, 4H), 7.10 – 7.03 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.0, 142.7, 139.1, 138.4, 131.8, 129.2, 129.0, 128.7, 128.2, 125.4, 99.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{15}BrI_2N_3O_2S^+$, m/z: 681.8152, found: 681.8154. **IR (thin film):** ν_{max} 3364, 3269, 1570, 1377, 1352, 1141, 1062, 746 cm^{-1}.



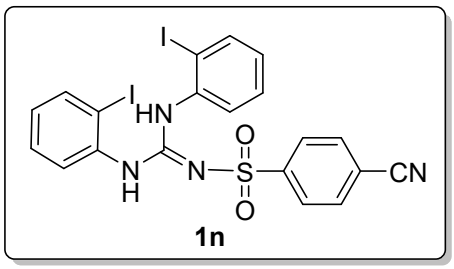
1l

1l was obtained in 88% yield (1159.8 mg). White solid, **mp** = 144.3 – 144.6 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.92 (s, 2H), 7.91 – 7.86 (m, 2H), 7.78 – 7.73 (m, 2H), 7.57 – 7.52 (m, 2H), 7.43 – 7.37 (m, 4H), 7.08 – 7.02 (m, 2H), 1.30 (s, 9H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 154.7, 152.9, 140.6, 139.1, 138.5, 129.2, 128.8, 128.4, 125.9, 125.6, 98.8, 34.7, 30.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{24}I_2N_3O_2S^+$, m/z: 659.9673, found: 659.9675. **IR (thin film):** ν_{max} 3318, 3284, 1603, 1515, 1139, 1125, 789, 646 cm^{-1}.



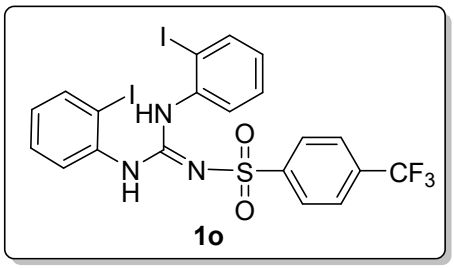
1m

1m was obtained in 75% yield (949.4 mg). Blue solid, **mp** = 149.3 – 150.9 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.92 (s, 2H), 7.93 – 7.86 (m, 2H), 7.78 – 7.72 (m, 2H), 7.43 – 7.34 (m, 4H), 7.08 – 7.01 (m, 4H), 3.81 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 161.7, 152.7, 139.1, 138.6, 135.4, 129.2, 128.8, 128.3, 128.1, 113.9, 98.9, 55.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{18}I_2N_3O_2S^+$, m/z: 633.9153, found: 633.9164. **IR (thin film):** ν_{max} 3356, 3243, 1594, 1522, 1258, 1096, 754, 680 cm^{-1}.



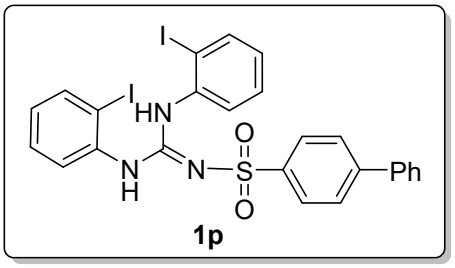
1n

1n was obtained in 92% yield (1155.3 mg). White solid, **mp** = 209.4 – 210.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.98 (s, 2H), 8.05 – 7.96 (m, 4H), 7.93 – 7.87 (m, 2H), 7.46 – 7.33 (m, 4H), 7.11 – 7.04 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.2, 147.3, 139.1, 138.4, 133.1, 129.2, 129.2, 128.9, 127.0, 118.1, 114.2, 99.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{15}I_2N_4O_2S^+$, m/z: 628.9000, found: 628.9003. **IR (thin film):** ν_{max} 3314, 3268, 2217, 1609, 1528, 1255, 1140, 754 cm^{-1}.



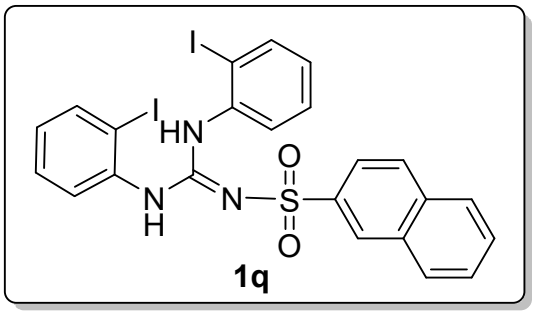
1o

1o was obtained in 91% yield (1221.0 mg). Blue solid, **mp** = 183.3 – 184.5 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.02 (s, 2H), 8.11 – 8.04 (m, 2H), 7.96 – 7.88 (m, 4H), 7.46 – 7.37 (m, 4H), 7.11 – 7.05 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.7, 147.7, 139.6, 138.9, 132.1 (q, $J_{(C-F)}$ = 31.7 Hz), 129.7, 129.6, 129.4, 127.6, 126.5 (q, $J_{(C-F)}$ = 2.8 Hz), 124.2 (q, $J_{(C-F)}$ = 271.0 Hz), 99.9. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -61.36. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{15}F_3I_2N_3O_2S^+$, m/z: 671.8921, found: 671.8926. **IR (thin film):** ν_{max} 3274, 1573, 1530, 1321, 1124, 1061, 759, 728 cm^{-1}.



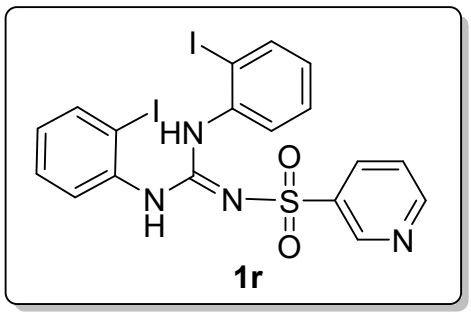
1p

1p was obtained in 87% yield (1181.3 mg). White solid, **mp** = 142.1 – 143.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.99 (d, J = 1.9 Hz, 2H), 7.97 – 7.87 (m, 4H), 7.86 – 7.81 (m, 2H), 7.77 – 7.71 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.38 (m, 5H), 7.10 – 7.02 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.0, 143.2, 142.2, 139.1, 138.8, 138.5, 129.2, 129.1, 128.9, 128.5, 128.3, 127.0, 127.0, 126.8, 99.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{20}I_2N_3O_2S^+$, m/z: 679.9360, found: 679.9366. **IR (thin film):** ν_{max} 3315, 3250, 1573, 1535, 1359, 1138, 740, 684 cm^{-1}.



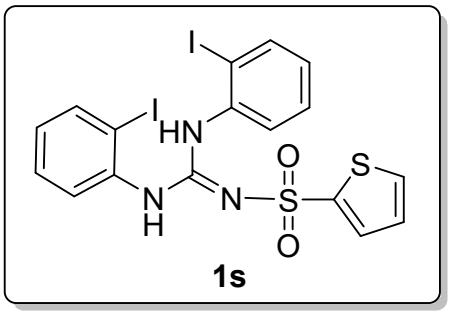
1q

1q was obtained in 85% yield (1110.0 mg). White solid, **mp** = 144.5 – 145.7 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.00 (s, 2H), 8.49 – 8.46 (m, 1H), 8.11 – 8.05 (m, 2H), 8.03 – 7.99 (m, 1H), 7.91 – 7.83 (m, 3H), 7.69 – 7.61 (m, 2H), 7.43 – 7.36 (m, 4H), 7.08 – 7.03 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.0, 140.5, 139.1, 138.5, 133.9, 131.7, 129.2, 129.1, 128.9, 128.8, 128.6, 128.2, 127.8, 127.3, 126.1, 122.6, 99.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{18}I_2N_3O_2S^+$, m/z: 653.9204, found: 653.9208. **IR (thin film):** ν_{max} 3354, 3243, 1599, 1568, 1356, 1116, 1080, 754 cm^{-1}.

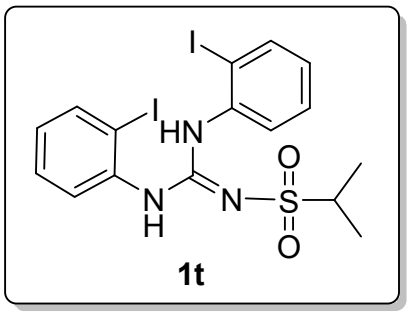


1r

1r was obtained in 83% yield (1002.5 mg). White solid, **mp** = 182.2 – 183.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.00 – 8.95 (m, 3H), 8.77 – 8.72 (m, 1H), 8.22 – 8.18 (m, 1H), 7.92 – 7.87 (m, 2H), 7.60 – 7.55 (m, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.34 (m, 2H), 7.10 – 7.05 (m, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.6, 152.8, 147.2, 140.0, 139.6, 138.9, 134.6, 129.7, 129.6, 129.4, 124.4, 100.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{15}I_2N_4O_2S^+$, m/z: 604.9000, found: 604.9003. **IR (thin film):** ν_{max} 3276, 1543, 1353, 1147, 1111, 1021, 761, 595 cm^{-1}.



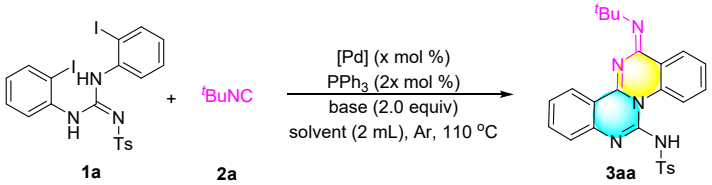
1s was obtained in 95% yield (1147.4 mg). White solid, **mp** = 149.3 – 150.0 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.98 (s, 2H), 7.92 – 7.88 (m, 2H), 7.83 – 7.79 (m, 1H), 7.65 – 7.62 (m, 1H), 7.45 – 7.38 (m, 4H), 7.12 – 7.05 (m, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.1, 144.6, 139.1, 138.4, 131.2, 130.4, 129.2, 129.0, 128.5, 127.0, 99.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{17}H_{14}I_2N_3O_2S_2^+$, m/z: 609.8612, found: 609.8616. **IR (thin film):** ν_{max} 3307, 3274, 1576, 1521, 1346, 1276, 1137, 744 cm^{-1}.



1t was obtained in 45% yield (512.0 mg). Blue solid, **mp** = 132.3 – 133.4 °C. Eluent: PE/EA = 10:1 → DCM. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.91 (s, 2H), 7.95 – 7.89 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.42 (m, 2H), 7.10 – 7.03 (m, 2H), 3.11 (hept, J = 6.7 Hz, 1H), 1.22 (d, J = 6.8 Hz, 6H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 153.0, 139.1, 138.7, 129.2, 128.7, 128.4, 99.0, 53.6, 16.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{18}I_2N_3O_2S^+$, m/z: 569.9204, found: 569.9207. **IR (thin film):** ν_{max} 3295, 3266, 1598, 1516, 1276, 1111, 1053, 750 cm^{-1}.

3. Detailed Optimization of Reaction Conditions

Table S1. Conditions optimization for the synthesis of **3aa** from **1a** and **2a**.

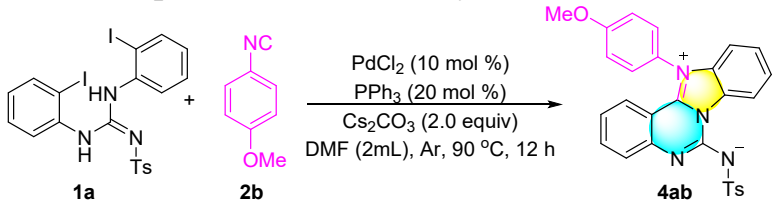


1a **2a** **3aa**

Entry	[Pd] (mol %)	Base	Solvent	Yield (%)
1	$Pd(OAc)_2$ (10)	Cs_2CO_3	Toluene	73
2	$Pd(PPh_3)_4$ (10)	Cs_2CO_3	Toluene	59
3	$Pd(TFA)_2$ (10)	Cs_2CO_3	Toluene	74
4	$PdCl_2$ (10)	Cs_2CO_3	Toluene	76
5	$PdCl_2$ (10)	K_2CO_3	Toluene	trace
6	$PdCl_2$ (10)	Na_2CO_3	Toluene	0
7	$PdCl_2$ (10)	K_3PO_4	Toluene	trace
8	$PdCl_2$ (10)	DBU	Toluene	trace
9	$PdCl_2$ (10)	Cs_2CO_3	1,4-Dioxane	62
10	$PdCl_2$ (10)	Cs_2CO_3	DMF	91
11	$PdCl_2$ (10)	Cs_2CO_3	DMSO	87
12	$PdCl_2$ (5)	Cs_2CO_3	DMF	86
13[b]	$PdCl_2$ (5)	Cs_2CO_3	DMF	67
14[c]	$PdCl_2$ (10)	Cs_2CO_3	DMF	90
15[d]	**$PdCl_2$ (10)**	**Cs_2CO_3**	**DMF**	**92**
16[e]	$PdCl_2$ (10)	Cs_2CO_3	DMF	66
17[f]	$PdCl_2$ (10)	Cs_2CO_3	DMF	45

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (3.0 equiv), [Pd] (x mol %), PPh_3 (2x mol %), base (2.0 equiv), solvent (2.0 mL), Schlenk tube, Ar, 110 °C, 12 h. Isolated yields. [b] Without PPh_3. [c] 100 °C. [d] 90 °C. [e] 80 °C. [f] 70 °C.

Table S2. Conditions optimization for the synthesis of **4ab** from **1a** and **2b**.



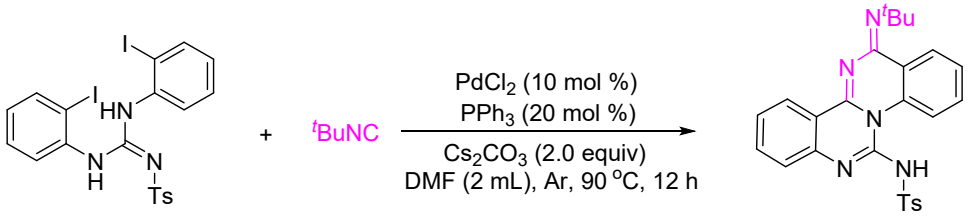
1a **2b** **4ab**

Entry	Base	Solvent	**1a** : **2b** (ratio)	*T* (°C)	Yield (%)[b]
1	Cs_2CO_3	DMF	1 : 3	90	80
2	Cs_2CO_3	DMF	1 : 2.5	90	84
3	**Cs_2CO_3**	**DMF**	**1 : 2**	**90**	**84(80[c])**
4	Cs_2CO_3	DMSO	1 : 2	90	57
5	Cs_2CO_3	1,4-Dioxane	1 : 2	90	trace
6	Cs_2CO_3	Toluene	1 : 2	90	trace
7	K_2CO_3	DMF	1 : 2	90	15
8	Na_2CO_3	DMF	1 : 2	90	5
9	KOH	DMF	1 : 2	90	24
10	DBU	DMF	1 : 2	90	6

11	Cs_2CO_3	DMF	1 : 2	80	78
12	Cs_2CO_3	DMF	1 : 2	70	0

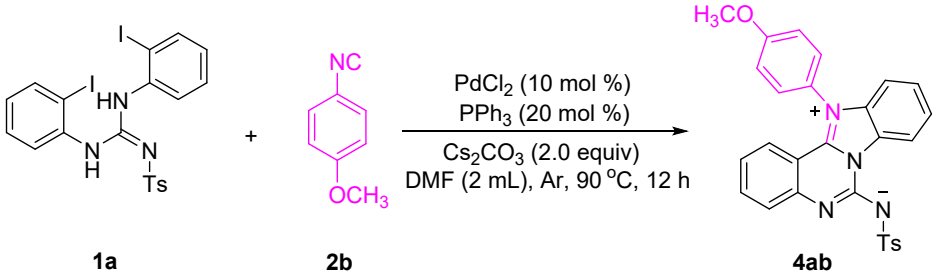
[a] Reaction conditions: **1a** (0.1 mmol), **2b** (X mmol), $PdCl_2$ (10 mol %), PPh_3 (20 mol %), base (2.0 equiv), solvent (2.0 mL), Ar, T °C, 12 h. [b] The yields were determined by LC analysis using diphenyl as an internal standard. [c] Isolated yields.

4. Typical procedure for the synthesis of 3aa and 4ab



1a **2a** **3aa**

In a 25 mL Schlenk tube, to a mixture of $PdCl_2$ (4.4 mg, 0.02 mmol, 10 mol %), PPh_3 (10.4 mg, 0.04 mmol, 20 mol%), Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv), and **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), were added in 2mL DMF. The reaction mixture was stirred at 90 °C (oil bath) under argon atmosphere. After 12 h, the system cooled to room temperature. The mixture was quenched with H_2O, and the crude product was extracted with DCM (3 times). The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by flash column chromatography by using ethyl acetate (EA) / petroleum ether (PE) / dichloromethane (DCE) / methanol (MeOH) (V_{EA} : V_{PE} = 1 : 1 → V_{DCE} : V_{MeOH} = 30 : 1) as eluents to afford pure product **3aa**.

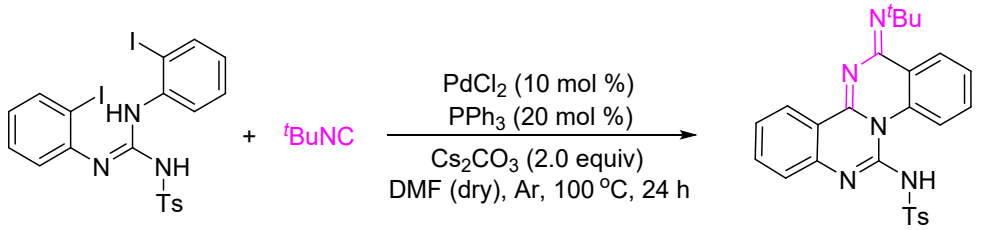


1a **2b** **4ab**

In a 25 mL Schlenk tube, to a mixture of $PdCl_2$ (4.4 mg, 0.02 mmol, 10 mol %), PPh_3 (10.4 mg, 0.04 mmol, 20 mol%), Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv), and **1a** (0.2 mmol, 1.0 equiv), **2b** (0.4 mmol, 2.0 equiv), were added in 2mL DMF. The reaction mixture was stirred at 90 °C (oil bath) under argon atmosphere. After 12 h, the system cooled to room temperature. The mixture was quenched with H_2O, and the crude product was extracted with DCM (3 times). The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by flash

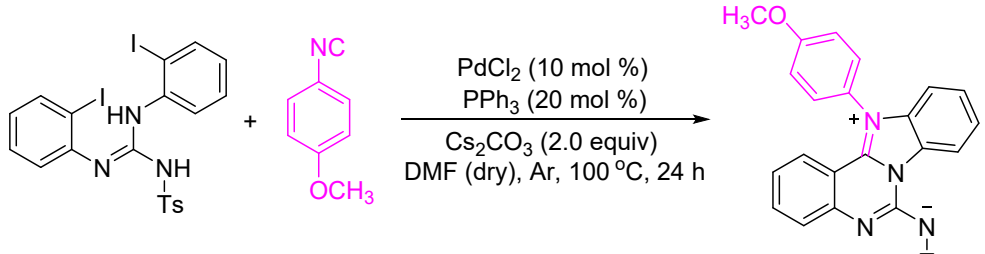
column chromatography by using ethyl acetate (EA) / petroleum ether (PE) / dichloromethane (DCE) / methanol (CH_3OH) (V_{EA} : V_{PE} = 1 : 2 → V_{DCE} : V_{MeOH} = 50 : 1) as eluents to afford pure product **4ab**.

5. Gram-scale synthesis and further transformation



1a 2.5 mmol | **2a** 7.5 mmol | **3aa** 86%, 1.012 g

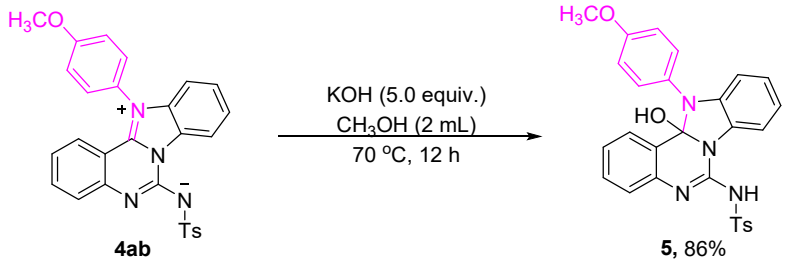
In a 250 mL Schlenk bottle, to a mixture of $PdCl_2$ (0.25 mmol, 10 mol %), PPh_3 (0.50 mmol, 20 mol%), Cs_2CO_3 (5.0 mmol, 2.0 equiv), and **1a** (2.5 mmol, 1.0 equiv), **2a** (7.5 mmol, 3.0 equiv), were added in 25 mL DMF (dry). The reaction mixture was stirred at 100 °C (oil bath) under argon atmosphere. After 24 h, the system cooled to room temperature. The mixture was quenched with H_2O, and the crude product was extracted with DCM (3 times). The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by flash column chromatography by using ethyl acetate (EA) / petroleum ether (PE) / dichloromethane (DCE) / methanol (CH_3OH) (V_{EA} : V_{PE} = 1 : 1 → V_{DCE} : V_{MeOH} = 30 : 1) as eluents to afford pure product **3aa** in 86% yield.



1a 2.5 mmol | **2b** 5.0 mmol | **4ab** 90%, 1.113 g

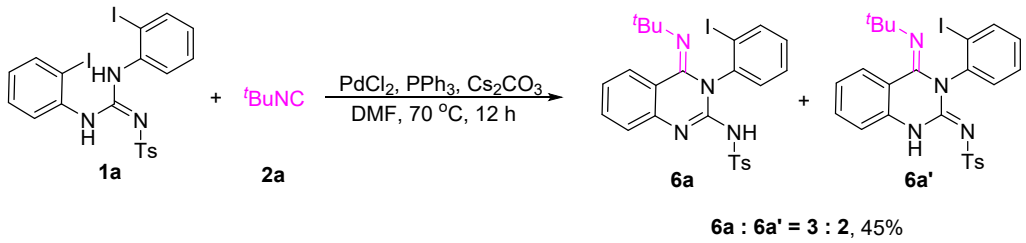
In a 250 mL Schlenk bottle, to a mixture of $PdCl_2$ (0.25 mmol, 10 mol %), PPh_3 (0.50 mmol, 20 mol%), Cs_2CO_3 (5.0 mmol, 2.0 equiv), and **1a** (2.5 mmol, 1.0 equiv), **2b** (5.0 mmol, 2.0 equiv), were added in 25mL DMF (dry). The reaction mixture was stirred at 100 °C (oil bath) under argon atmosphere. After 24 h, the system cooled to room temperature. The mixture was quenched with H_2O, and the crude product was extracted with DCM (3 times). The combined organic layers were dried over Na_2SO_4 and solvent was removed

under reduced pressure. The residue was purified by flash column chromatography by using ethyl acetate (EA) / petroleum ether (PE) / dichloromethane (DCE) / methanol (CH_3OH) (V_{EA} : V_{PE} = 1 : 2 → V_{DCE} : V_{MeOH} = 50 : 1) as eluents to afford pure product **4ab** in 90% yield.



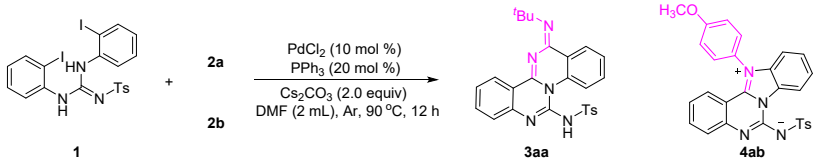
A mixture of **4ab** (0.2 mmol), KOH (1.0 mmol), and CH_3OH (2 mL) was added into a flask and stirred at 70 °C. After 12 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography using DCM/CH_3OH (100:1 V/V) to give the desired product **5** in 86% yield.

6. General procedure for the synthesis of 6



In a 25 mL Schlenk tube, to a mixture of $PdCl_2$ (0.05 mmol, 10 mol %), PPh_3 (0.10 mmol, 20 mol%), Cs_2CO_3 (1.0 mmol, 2.0 equiv), and **1a** (0.50 mmol, 1.0 equiv), **2a** (1.0 mmol, 2.0 equiv), were added in 5mL DMF. The reaction mixture was stirred at 70 °C (oil bath) under argon atmosphere. After 12 h, the system cooled to room temperature. The mixture was quenched with H_2O, and the crude product was extracted with DCM (3 times). The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by flash column chromatography by using ethyl acetate (EA) / petroleum ether (PE) (V_{EA} : V_{PE} = 1 : 2) as eluents to afford pure product **6a** and **6a'** in 45% yield.

7. Control experiments



t-BuNC / 4-OMePhNC (equiv.)	**3aa** Yield (%)	**4ab** Yield (%)
2 / 2	44	trace

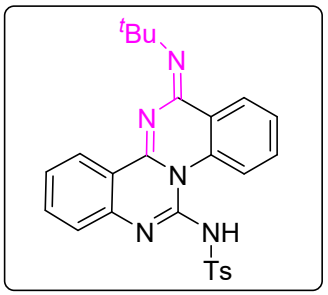
8. References

[1] Jiang, S.; Cao, W.-B.; Xu, X.-P.; Ji, S.-J. Cobalt-catalyzed isocyanide-based three-component cascade for the synthesis of quinazolines. *Org. Lett.* **2021**, *23*, 6740−6744.

[2] Gu, Z.-Y.; Liu, Y.; Wang, F.; Bao, X.; Wang, S.-Y.; Ji, S.-J. Cobalt(II)-catalyzed synthesis of sulfonyl guanidines via nitrene radical coupling with isonitriles: a combined experimental and computational study. *ACS. Catal.* **2017**, *7*, 3893-3899.

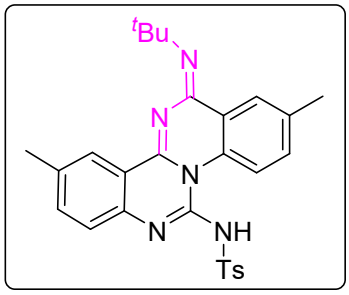
9. Analytic and characterization data for the products

(Z)-N-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3aa)



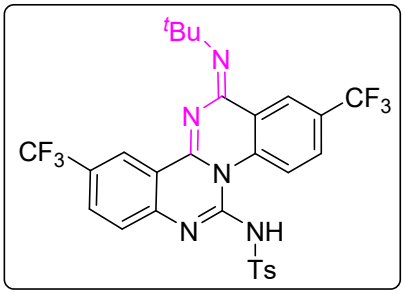
According to the general procedure, **3aa** was obtained in 92% yield (84.8 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.62 – 9.56 (m, 1H), 9.32 (s, 1H), 8.49 – 8.42 (m, 1H), 8.33 – 8.22 (m, 1H), 7.97 – 7.89 (m, 3H), 7.79 – 7.69 (m, 2H), 7.31 – 7.22 (m, 4H), 2.31 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 157.7, 152.4, 148.1, 147.5, 141.4, 140.4, 136.2, 136.0, 132.5, 128.1, 128.0, 127.9, 126.1, 124.6, 124.3, 122.8, 122.7, 115.7, 115.2, 55.1, 28.5, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{26}N_5O_2S^+$, m/z: 472.1802, found: 472.1816. **IR (thin film):** ν_{max} 2964, 2918, 1584, 1426, 1272, 1134, 1078, 751 cm^{-1}.

(Z)-N-(13-(*tert*-butylimino)-2,10-dimethyl-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ba)



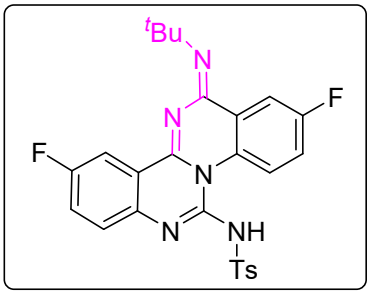
According to the general procedure, **3ba** was obtained in 95% yield (94.8 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.58 – 9.47 (m, 1H), 9.16 (s, 1H), 8.31 – 8.22 (m, 1H), 8.06 – 8.00 (m, 1H), 7.94 C 7.85 (m, 2H), 7.79 – 7.72 (m, 1H), 7.59 – 7.51 (m, 1H), 7.28 – 7.17 (m, 3H), 2.51 (s, 3H), 2.37 (s, 3H), 2.30 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 157.4, 151.7, 147.2, 146.3, 141.5, 140.2, 137.9, 137.6, 134.1, 133.6, 131.9, 128.0, 128.0, 124.8, 124.3, 123.7, 122.6, 115.4, 114.9, 55.0, 28.5, 21.0, 20.9, 20.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{30}N_5O_2S^+$, m/z: 500.2115, found: 500.2133. **IR (thin film):** ν_{max} 3275, 2919, 1583, 1425, 1229, 1134, 815, 665 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-2,10-bis(trifluoromethyl)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ca)



According to the general procedure, **3ca** was obtained in 88% yield (106.9 mg). Yellow solid, **mp** = 209.3 – 210.1 °C. Eluent: PE/EA = 1:1. **^{1}H NMR (600 MHz, CD_2Cl_2-d_2)** δ 9.51 (d, J = 9.2 Hz, 1H), 8.55 (s, 1H), 8.49 (s, 1H), 8.40 (s, 1H), 8.04 (d, J = 7.9 Hz, 2H), 7.91 (d, J = 9.2 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H), 1.76 (s, 9H). **^{13}C NMR (150 MHz, CD_2Cl_2-d_2)** δ 158.1, 153.9, 151.7, 149.3, 142.6, 140.7, 139.1, 132.8 (q, $J_{(C-F)}$ = 2.3 Hz), 130.1 (q, $J_{(C-F)}$ = 33.6 Hz), 129.5 (q, $J_{(C-F)}$ = 2.9 Hz), 129.1, 128.8, 126.4, 125.0 (q, $J_{(C-F)}$ = 4.2 Hz), 124.9 (q, $J_{(C-F)}$ = 32.5 Hz), 124.5 (q, $J_{(C-F)}$ = 269.5 Hz), 124.2, 123.7 (q, $J_{(C-F)}$ = 275.5 Hz), 122.8 (q, $J_{(C-F)}$ = 3.0 Hz), 116.2, 115.0, 57.4, 29.0, 21.8. **^{19}F NMR (564 MHz, CD_2Cl_2-d_2)** δ -62.85, -62.88. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{28}H_{23}N_5F_6O_2SNa^+$, m/z: 630.1369, found: 630.1357. **IR (thin film):** ν_{max} 3229, 2921, 1588, 1567, 1312, 1138, 1081, 842 cm^{-1}.

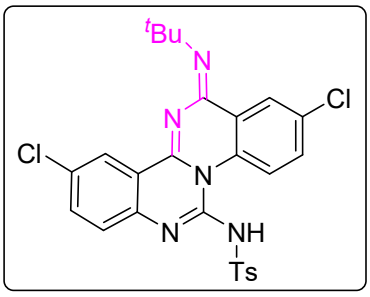
(Z)-*N*-(13-(*tert*-butylimino)-2,10-difluoro-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3da)



According to the general procedure, **3da** was obtained in 50% yield (50.7 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.80 – 9.76 (m, 1H), 9.29 (s, 1H), 8.44 – 8.41 (m, 1H), 7.94 – 7.84 (m, 4H), 7.67 – 7.64 (m, 1H), 7.37 – 7.34 (m, 1H), 7.26 – 7.23 (m, 2H), 2.31 (s, 3H), 1.65 (s, 9H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 160.1 (d, $J_{(C-F)}$ = 246.0 Hz), 157.3 (d, $J_{(C-F)}$ = 238.5 Hz), 157.2, 151.9 (d, $J_{(C-F)}$ = 4.5 Hz), 147.2, 145.1, 141.2, 140.4, 133.1, 128.1, 128.0, 126.9 (d, $J_{(C-F)}$ = 9.0 Hz), 126.0 (d, $J_{(C-F)}$ = 7.5 Hz), 125.1 (d, $J_{(C-F)}$ = 22.5 Hz), 120.6 (d, $J_{(C-F)}$ = 22.5 Hz), 117.7 (d, $J_{(C-F)}$ = 9.0 Hz), 115.5 (d, $J_{(C-F)}$ = 9.0 Hz), 110.0 (d, $J_{(C-F)}$ = 25.5 Hz), 109.8 (d, $J_{(C-F)}$ = 24.0 Hz), 55.4, 28.4, 20.9. **^{19}F NMR (564 MHz, DMSO-d_6)** δ -111.31, -111.33, -111.34, -111.35, -118.32, -118.32, -118.33, -118.34. **HRMS (ESI)** calcd for

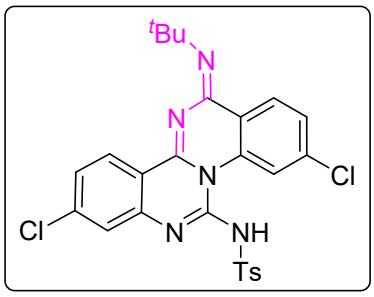
[M+H]$^+$ $C_{26}H_{24}N_5F_2O_2S^+$, m/z: 508.1614, found: 508.1631. **IR (thin film):** ν_{max} 3273, 1572, 1432, 1272, 1197, 1077, 825, 664 cm^{-1}.

(Z)-N-(13-(*tert*-butylimino)-2,10-dichloro-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ea)



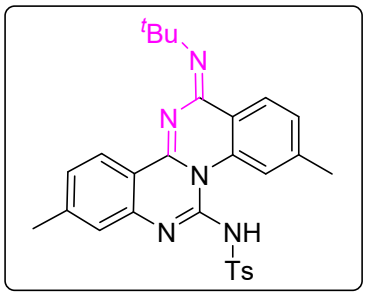
According to the general procedure, **3ea** was obtained in 65% yield (70.1 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.64 (d, *J* = 9.5 Hz, 1H), 9.43 (s, 1H), 8.65 (d, *J* = 2.4 Hz, 1H), 8.14 (d, *J* = 2.5 Hz, 1H), 8.04 (dd, *J* = 9.5, 2.3 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.73 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 1.65 (s, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 156.9, 151.7, 147.6, 146.9, 141.1, 140.5, 136.0, 135.1, 132.5, 132.4, 128.1, 128.0, 126.5, 126.3, 124.8, 124.6, 123.8, 117.3, 116.1, 55.5, 28.4, 20.9. **HRMS (ESI)** calcd for [M+H]$^+$ $C_{26}H_{24}Cl_2N_5O_2S^+$, m/z: 540.1023, found: 540.1024. **IR (thin film):** ν_{max} 3295, 2917, 2847, 1582, 1502, 1424, 1274, 1132, 1076 cm^{-1}.

(Z)-N-(13-(*tert*-butylimino)-3,9-dichloro-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ga)



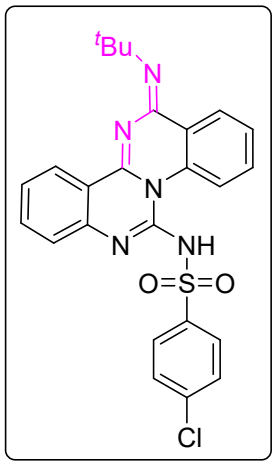
According to the general procedure, **3ga** was obtained in 65% yield (70.1 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.70 (s, 1H), 9.45 (s, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 3H), 7.30 (dd, *J* = 22.3, 9.6 Hz, 4H), 2.32 (s, 3H), 1.64 (s, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 157.4, 152.5, 149.0, 147.8, 141.0, 140.9, 140.7, 137.4, 137.1, 128.3, 128.2, 128.1, 127.8, 126.8, 123.2, 123.1, 122.5, 114.6, 114.1, 55.4, 28.5, 20.9. **HRMS (ESI)** calcd for [M+H]$^+$ $C_{26}H_{24}Cl_2N_5O_2S^+$, m/z: 540.1023, found: 540.1031. **IR (thin film):** ν_{max} 3302, 1563, 1455, 1272, 1133, 1079, 770, 661 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-3,9-dimethyl-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ha)



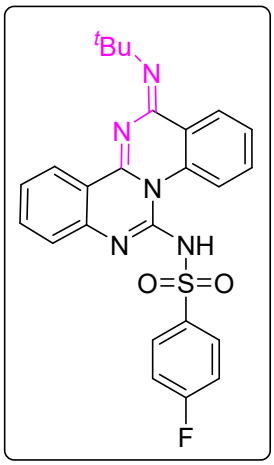
According to the general procedure, **3ha** was obtained in 67% yield (66.9 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.36 (s, 1H), 9.15 (s, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.3 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.14 – 7.09 (m, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 1.65 (s, 9H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 157.5, 152.3, 148.3, 147.5, 146.9, 143.0, 141.7, 140.4, 136.3, 128.9, 128.2, 127.6, 125.9, 124.7, 124.5, 123.8, 122.7, 113.4, 113.0, 54.9, 28.6, 22.1, 21.7, 20.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{28}H_{29}N_5O_2SNa^+$, m/z: 522.1934, found: 522.1953. **IR (thin film):** ν_{max} 3299, 1568, 1451, 1243, 1131, 1078, 875, 824 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-chlorobenzenesulfonamide (3ia)



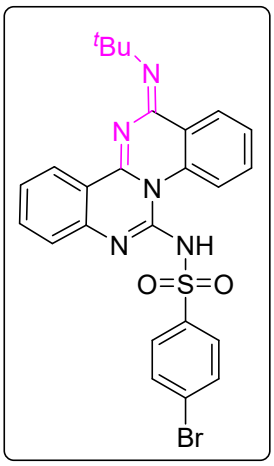
According to the general procedure, **3ia** was obtained in 86% yield (84.5 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.47 – 9.38 (m, 1H), 8.71 (s, 1H), 8.37 – 8.27 (m, 2H), 8.23 – 8.15 (m, 2H), 7.70 – 7.63 (m, 1H), 7.46 – 7.34 (m, 4H), 7.25 – 7.14 (m, 2H), 1.82 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.0, 152.9, 148.6, 147.6, 142.4, 137.2, 136.2, 136.1, 132.1, 130.0, 128.1, 127.6, 126.5, 125.4, 125.3, 123.6, 122.5, 115.9, 115.2, 56.2, 29.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{23}ClN_5O_2S^+$, m/z: 492.1256, found: 492.1245. **IR (thin film):** ν_{max} 3423, 1559, 1443, 1373, 1290, 1198, 1140, 1076 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-fluorobenzenesulfonamide (3ja)



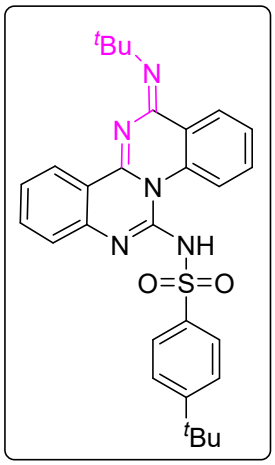
According to the general procedure, **3ja** was obtained in 78% yield (74.1 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.48 (d, J = 8.8 Hz, 1H), 8.56 (s, 1H), 8.36 – 8.33 (m, 1H), 8.28 – 8.23 (m, 3H), 7.68 – 7.65 (m, 1H), 7.45 – 7.42 (m, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.16 – 7.11 (m, 2H), 1.82 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.3 (d, $J_{(C-F)}$ = 250.5 Hz), 158.0, 153.0, 148.8, 147.6, 139.8 (d, $J_{(C-F)}$ = 3.0 Hz), 136.2, 136.2, 132.2, 131.0 (d, $J_{(C-F)}$ = 9.0 Hz), 127.6, 126.5, 125.3, 125.1, 123.5, 122.6, 115.9, 115.2, 114.9 (d, $J_{(C-F)}$ = 22.5 Hz), 56.2, 29.2. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -109.10. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{23}FN_5O_2S^+$, m/z: 476.1551, found: 476.1557. **IR (thin film):** ν_{max} 2915, 1561, 1509, 1431, 1228, 1135, 1079, 898, 855 cm^{-1}.

(Z)-4-bromo-N-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)benzenesulfonamide (3ka)



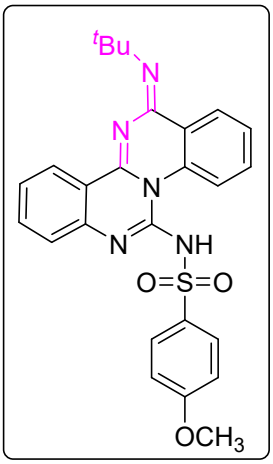
According to the general procedure, **3ka** was obtained in 35% yield (37.5 mg). Yellow solid, **mp** = 219.2 – 220.0 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.59 – 9.57 (m, 1H), 9.35 (s, 1H), 8.48 – 8.46 (m, 1H), 8.32 – 8.29 (m, 1H), 7.99 – 7.94 (m, 3H), 7.81 – 7.78 (m, 1H), 7.76 – 7.72 (m, 1H), 7.69 – 7.61 (m, 2H), 7.33 – 7.28 (m, 2H), 1.67 (s, 9H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 157.8, 152.5, 147.9, 147.4, 143.6, 136.2, 136.1, 132.6, 130.6, 130.2, 127.9, 126.1, 124.7, 124.3, 124.1, 123.1, 122.8, 115.7, 115.4, 55.2, 28.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{23}N_5O_2SBr^+$, m/z: 536.0751, found: 536.0754. **IR (thin film):** ν_{max} 3266, 1587, 1565, 1430, 1234, 1132, 1079, 900, 738 cm^{-1}.

(Z)-4-(*tert*-butyl)-N-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)benzenesulfonamide (3la)



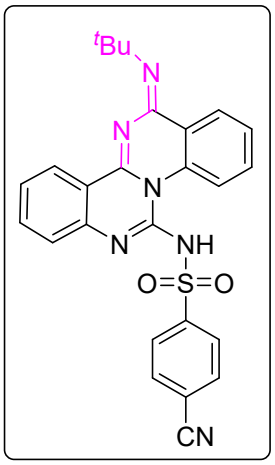
According to the general procedure, **3la** was obtained in 89% yield (91.4 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.46 (d, J = 8.8 Hz, 1H), 8.76 (s, 1H), 8.34 – 8.31 (m, 2H), 8.20 – 8.15 (m, 2H), 7.66 – 7.62 (m, 1H), 7.51 – 7.47 (m, 2H), 7.40 – 7.36 (m, 2H), 7.22 – 7.15 (m, 2H), 1.81 (s, 9H), 1.33 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.0, 154.4, 152.9, 149.0, 147.7, 140.9, 136.1, 136.0, 131.9, 128.2, 127.5, 126.4, 125.6, 125.5, 124.9, 123.2, 122.4, 115.8, 115.2, 56.1, 35.1, 31.4, 29.2. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{29}H_{31}N_5O_2SNa^+$, m/z: 536.2090, found: 536.2076. **IR (thin film):** ν_{max} 3289, 2919, 1561, 1426, 1236, 1078, 1014, 817, 754 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methoxybenzenesulfonamide (3ma)



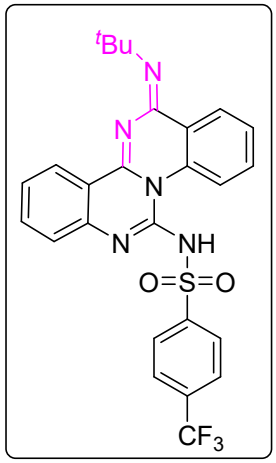
According to the general procedure, **3ma** was obtained in 70% yield (68.2 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, CD_2Cl_2-d_2)** δ 9.51 – 9.46 (m, 1H), 8.38 (dd, J = 8.2, 1.5 Hz, 1H), 8.30 (s, 1H), 8.22 (dd, J = 8.2, 1.5 Hz, 1H), 8.16 – 8.11 (m, 2H), 7.71 – 7.66 (m, 1H), 7.54 – 7.49 (m, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.30 – 7.20 (m, 2H), 6.99 – 6.94 (m, 2H), 3.83 (s, 3H), 1.80 (s, 9H). **^{13}C NMR (100 MHz, CD_2Cl_2-d_2)** δ 162.2, 158.4, 153.5, 149.4, 148.3, 136.7, 136.7, 136.4, 132.5, 130.8, 128.1, 127.1, 125.2, 125.0, 123.5, 123.0, 116.2, 115.7, 113.3, 56.5, 56.0, 29.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{26}N_5O_3S^+$, m/z: 488.1751, found: 488.1732. **IR (thin film):** ν_{max} 3247, 2969, 1577, 1431, 1251, 1231, 1129, 895, 823 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-cyanobenzenesulfonamide (3na)



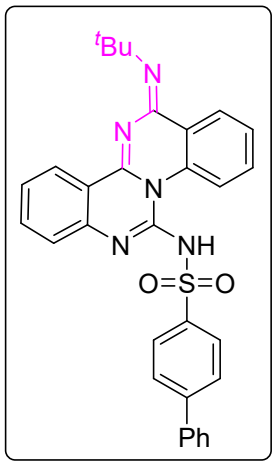
According to the general procedure, **3na** was obtained in 81% yield (78.1 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, DMSO-d_6+D_2SO_4)** δ 8.48 – 8.41 (m, 2H), 8.28 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.80 – 7.73 (m, 1H), 7.72 – 7.66 (m, 1H), 7.56 – 7.49 (m, 1H), 1.62 (s, 9H). **^{13}C NMR (100 MHz, DMSO-d_6+D_2SO_4)** δ 157.7, 152.4, 148.8, 147.6, 147.4, 136.0, 136.0, 132.6, 131.9, 128.8, 127.9, 126.0, 124.7, 124.2, 123.3, 122.9, 118.3, 115.7, 115.5, 112.9, 55.2, 28.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{23}N_6O_2S^+$, m/z: 483.1598, found: 483.1578. **IR (thin film):** ν_{max} 3319, 2918, 2232, 1564, 1432, 1234, 1128, 1076, 755 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-(trifluoromethyl)benzenesulfonamide (3oa)



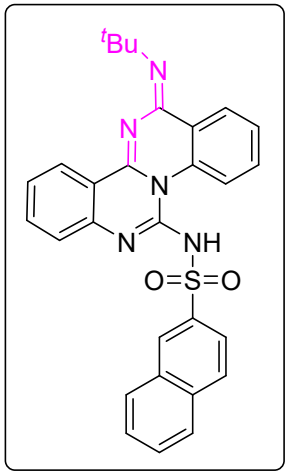
According to the general procedure, **3oa** was obtained in 88% yield (92.4 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.54 (d, J = 8.9 Hz, 1H), 8.41 – 8.32 (m, 4H), 8.19 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.69 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 1.82 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 157.9, 153.1, 148.6, 147.6, 147.5, 136.4, 136.3, 132.7 (q, $J_{(C-F)}$ = 30.0 Hz), 132.5, 129.0, 127.9, 126.5, 125.4, 125.0 (q, $J_{(C-F)}$ = 4.5 Hz), 124.7, 123.9 (q, $J_{(C-F)}$ = 271.0 Hz), 123.8, 122.9, 115.9, 115.2, 56.2, 29.2. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -62.76. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{26}H_{22}F_3N_5O_2SNa^+$, m/z: 548.1338, found: 548.1345. **IR (thin film):** ν_{max} 3282, 1562, 1517, 1449, 1319, 1277, 1167, 1129, 750 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-[1,1'-biphenyl]-4-sulfonamide (3pa)



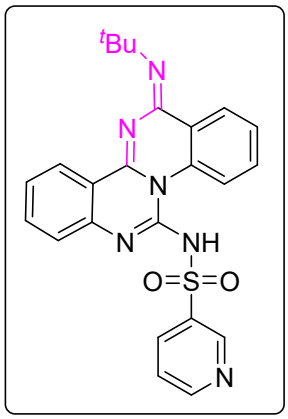
According to the general procedure, **3pa** was obtained in 91% yield (97.0 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.53 (d, J = 8.8 Hz, 1H), 8.61 (s, 1H), 8.37 – 8.27 (m, 4H), 7.71 – 7.60 (m, 5H), 7.48 – 7.40 (m, 4H), 7.39 – 7.34 (m, 1H), 7.25 – 7.18 (m, 2H), 1.83 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.0, 153.0, 149.0, 147.8, 143.8, 142.6, 140.4, 136.2, 136.1, 132.2, 129.0, 129.0, 128.0, 127.6, 127.5, 126.6, 126.4, 125.5, 125.1, 123.3, 122.6, 115.8, 115.2, 56.1, 29.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{31}H_{28}N_5O_2S^+$, m/z: 534.1958, found: 534.1942. **IR (thin film):** ν_{max} 3275, 2919, 1560, 1507, 1428, 1358, 1235, 1135, 1080, 854 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)naphthalene-2-sulfonamide (3qa)



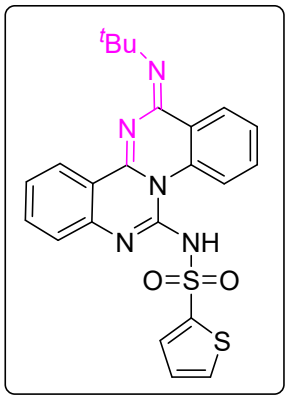
According to the general procedure, **3qa** was obtained in 91% yield (92.3 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.66 (d, J = 8.9 Hz, 1H), 9.33 (s, 1H), 8.68 (s, 1H), 8.48 – 8.45 (m, 1H), 8.27 – 8.24 (m, 1H), 8.17 – 8.14 (m, 1H), 8.09 – 8.05 (m, 1H), 8.00 – 7.92 (m, 3H), 7.81 – 7.77 (m, 1H), 7.71 – 7.67 (m, 1H), 7.60 – 7.56 (m, 2H), 7.33 – 7.29 (m, 1H), 7.26 – 7.22 (m, 1H), 1.65 (s, 9H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 157.7, 152.4, 148.0, 147.5, 141.2, 136.2, 136.0, 133.6, 132.6, 131.7, 128.9, 128.4, 127.9, 127.6, 127.5, 127.1, 126.7, 126.1, 124.7, 124.7, 124.3, 122.9, 122.8, 115.7, 115.3, 55.2, 28.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{29}H_{26}N_5O_2S^+$, m/z: 508.1802, found: 508.1807. **IR (thin film):** ν_{max} 3077, 1570, 1427, 1274, 1116, 1070, 899, 752 cm^{-1}.

(Z)-N-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)pyridine-3-sulfonamide (3ra)



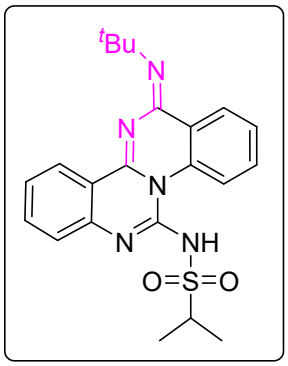
According to the general procedure, **3ra** was obtained in 95% yield (87.0 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.58 (d, J = 8.9 Hz, 1H), 9.36 (s, 1H), 9.21 – 9.03 (m, 1H), 8.64 – 8.26 (m, 4H), 8.02 – 7.90 (m, 1H), 7.83 – 7.67 (m, 2H), 7.56 – 7.45 (m, 1H), 7.35 – 7.21 (m, 2H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 158.0, 152.4, 147.5, 146.9, 145.9, 145.1, 141.5, 140.6, 136.3, 135.8, 132.8, 128.2, 126.2, 125.2, 125.0, 124.1, 123.5, 123.0, 115.9, 115.8, 55.6, 28.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{23}N_6O_2S^+$, m/z: 459.1598, found: 459.1581. **IR (thin film):** ν_{max} 3266, 1589, 1564, 1434, 1280, 1143, 1097, 900, 753 cm^{-1}.

(Z)-N-(13-(tert-butylimino)-13H-quinazolino[3,4-a]quinazolin-6-yl)thiophene-2-sulfonamide (3sa)



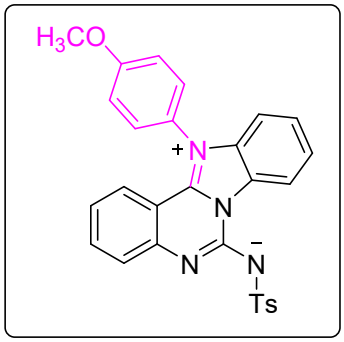
According to the general procedure, **3sa** was obtained in 96% yield (88.9 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.54 (d, J = 8.9 Hz, 1H), 9.36 (s, 1H), 8.47 (d, J = 8.2 Hz, 1H), 8.37 – 8.33 (m, 1H), 7.98 – 7.94 (m, 1H), 7.82 – 7.76 (m, 2H), 7.74 – 7.63 (m, 2H), 7.48 (d, J = 8.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.04 – 7.00 (m, 1H), 1.68 (s, 9H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 157.8, 152.5, 147.8, 147.5, 145.7, 145.6, 136.1, 136.1, 132.5, 130.7, 130.1, 127.9, 126.2, 125.9, 124.7, 124.4, 123.2, 122.8, 115.5, 55.2, 28.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{22}N_5O_2S^+$, m/z: 464.1210, found: 464.1226. **IR (thin film):** ν_{max} 3292, 1586, 1566, 1430, 1273, 1236, 1123, 902, 762 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)propane-2-sulfonamide (3ta)



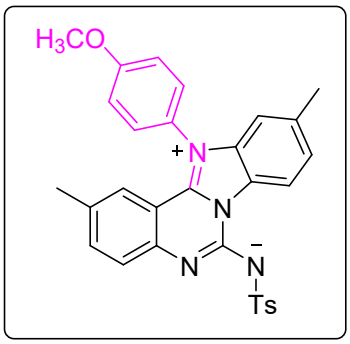
According to the general procedure, **3ta** was obtained in 70% yield (59.2 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (400 MHz, DMSO-d_6+D_2SO_4)** δ 8.68 (d, J = 8.8 Hz, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.96 – 7.83 (m, 3H), 7.77 – 7.70 (m, 1H), 7.53 – 7.46 (m, 1H), 3.36 (hept, J = 6.7 Hz, 1H), 1.63 (s, 9H), 1.23 (d, J = 6.8 Hz, 6H). **^{13}C NMR (100 MHz, DMSO-d_6+D_2SO_4)** δ 159.4, 152.8, 145.3, 137.9, 137.6, 135.7, 134.2, 129.6, 127.4, 126.6, 126.6, 123.5, 118.3, 116.6, 116.0, 57.6, 54.9, 29.4, 16.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{26}N_5O_2S^+$, m/z: 424.1802, found: 424.1806. **IR (thin film):** ν_{max} 3331, 1598, 1580, 1564, 1449, 1276, 1108, 893, 755 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4ab)



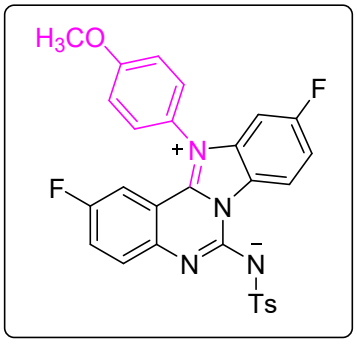
According to the general procedure, **4ab** was obtained in 80% yield (79.0 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.28 – 9.24 (m, 1H), 8.05 – 8.01 (m, 2H), 7.78 – 7.68 (m, 5H), 7.56 (d, J = 8.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 7.09 – 7.04 (m, 1H), 6.99 – 6.95 (m, 1H), 3.94 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 161.2, 149.0, 145.9, 145.0, 141.1, 140.6, 134.8, 134.6, 129.4, 128.1, 128.1, 127.9, 126.4, 126.1, 126.0, 125.4, 123.5, 122.6, 119.1, 116.3, 111.3, 107.5, 55.8, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{23}N_4O_3S^+$, m/z: 495.1486, found: 495.1474. **IR (thin film):** ν_{max} 1664, 1590, 1506, 1473, 1251, 1145, 1082, 754, 554 cm^{-1}.

(12-(4-methoxyphenyl)-2,10-dimethylbenzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4bb)



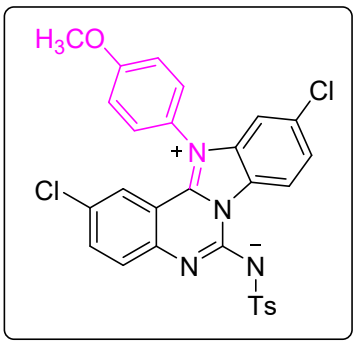
According to the general procedure, **4bb** was obtained in 85% yield (88.7 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.09 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.06 (s, 1H), 6.65 (s, 1H), 3.94 (s, 3H), 2.48 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.3, 147.2, 145.6, 144.5, 141.2, 140.5, 138.2, 136.3, 134.8, 131.5, 129.5, 128.1, 128.1, 126.6, 126.1, 126.0, 124.5, 122.5, 118.7, 116.1, 110.8, 107.3, 55.9, 21.2, 21.1, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{30}H_{27}N_4O_3S^+$, m/z: 523.1799, found: 523.1819. **IR (thin film):** ν_{max} 1583, 1512, 1488, 1253, 1140, 1085, 811, 661, 552 cm^{-1}.

(2,10-difluoro-12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4db)



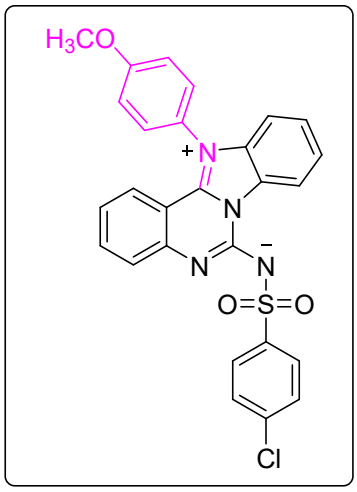
According to the general procedure, **4db** was obtained in 51% yield (54.1 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.30 – 9.25 (m, 1H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.75 – 7.63 (m, 5H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.21 (m, 3H), 6.47 – 6.43 (m, 1H), 3.94 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.5, 161.3 (d, $J_{(C-F)}$ = 244.5 Hz), 156.4 (d, $J_{(C-F)}$ = 239.7 Hz), 146.1, 145.5, 140.8 (d, $J_{(C-F)}$ = 20.9 Hz), 135.5 (d, $J_{(C-F)}$ = 13.2 Hz), 129.4, 128.8, 128.7, 128.1 (d, $J_{(C-F)}$ = 11.0 Hz), 125.1, 124.2 (d, $J_{(C-F)}$ = 24.7 Hz), 123.1, 120.9 (d, $J_{(C-F)}$ = 9.8 Hz), 116.4, 113.8 (d, $J_{(C-F)}$ = 24.8 Hz), 107.5 (d, $J_{(C-F)}$ = 26.5 Hz), 107.2 (d, $J_{(C-F)}$ = 10.4 Hz), 98.7, 98.5, 55.9, 20.9. **^{19}F NMR (564 MHz, DMSO-*d*$_6$)** δ -110.89, -110.90, -110.91, -110.93, -116.91, -116.93, -116.94, -116.96. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{28}H_{20}F_2N_4O_3SNa^+$, m/z: 553.1116, found: 553.1127. **IR (thin film):** ν_{max} 1593, 1509, 1482, 1253, 1135, 1084, 836, 550 cm^{-1}.

(Z)-*N*-(13-(*tert*-butylimino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)propane-2-sulfonamide (4eb)



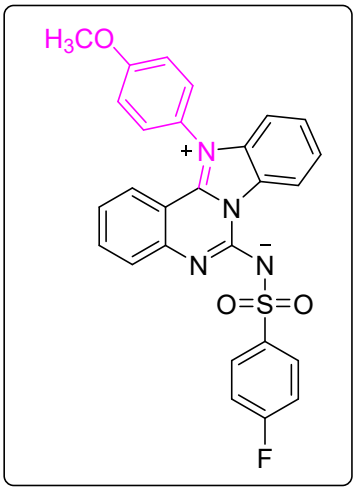
According to the general procedure, **4eb** was obtained in 39% yield (43.8 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.22 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.90 – 7.87 (m, 1H), 7.77 – 7.71 (m, 3H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 3H), 2.32 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.6, 147.8, 145.9, 145.0, 140.9, 140.7, 135.4, 135.1, 132.7, 129.3, 128.2, 128.1, 126.2, 126.1, 125.3, 125.0, 122.3, 120.5, 116.5, 111.2, 108.3, 55.9, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{21}F_2N_4O_3S^+$, m/z: 563.0706, found: 563.0710. **IR (thin film):** ν_{max} 1590, 1470, 1434, 1259, 1090, 939, 813, 552 cm^{-1}.

((4-chlorophenyl)sulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4ib)



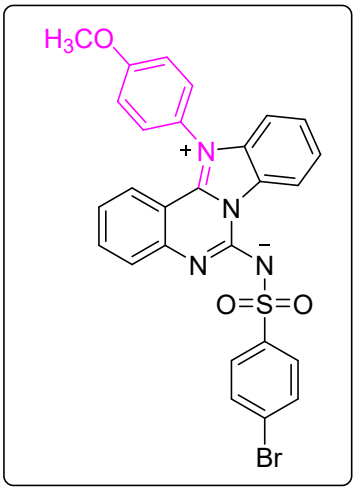
According to the general procedure, **4ib** was obtained in 86% yield (88.4 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.25 (d, *J* = 8.4 Hz, 1H), 8.17 – 8.12 (m, 2H), 7.80 – 7.70 (m, 5H), 7.60 – 7.53 (m, 3H), 7.38 – 7.35 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.99 – 6.97 (m, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.7, 145.9, 145.0, 142.8, 135.4, 134.8, 134.6, 130.1, 129.4, 128.0, 127.8, 126.4, 126.1, 125.9, 125.5, 123.5, 122.9, 119.1, 116.3, 111.4, 107.8, 55.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{27}H_{19}ClN_4O_3SNa^+$, m/z: 537.0758, found: 537.0745. **IR (thin film):** ν_{max} 1585, 1514, 1474, 1254, 1140, 1087, 892, 757, 550 cm^{-1}.

((4-fluorophenyl)sulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4jb)



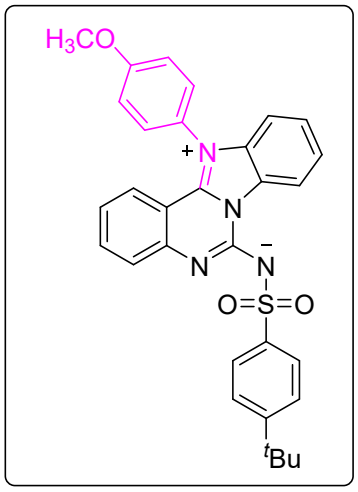
According to the general procedure, **4jb** was obtained in 77% yield (76.7 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 (d, *J* = 8.3 Hz, 1H), 8.23 – 8.16 (m, 2H), 7.79 – 7.70 (m, 5H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.32 – 7.25 (m, 3H), 7.10 – 7.07 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 163.3 (d, $J_{(C-F)}$ = 247.5 Hz), 161.2, 148.8, 145.9, 145.0, 140.3, 134.8, 134.6, 130.9 (d, $J_{(C-F)}$ = 9.0 Hz), 129.4, 127.9, 126.4, 126.0, 125.9, 125.5, 123.5, 122.8, 119.1, 116.3, 114.6 (d, $J_{(C-F)}$ = 21.0 Hz), 111.3, 107.7, 55.8. **^{19}F NMR (564 MHz, DMSO-*d*$_6$)** δ -109.84, -109.86, -109.87, -109.88, -109.89. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{27}H_{20}FN_4O_3S^+$, m/z: 499.1235, found: 499.1218. **IR (thin film):** ν_{max} 1586, 1514, 1475, 1254, 1140, 1084, 754, 550 cm^{-1}.

((4-bromophenyl)sulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4kb)



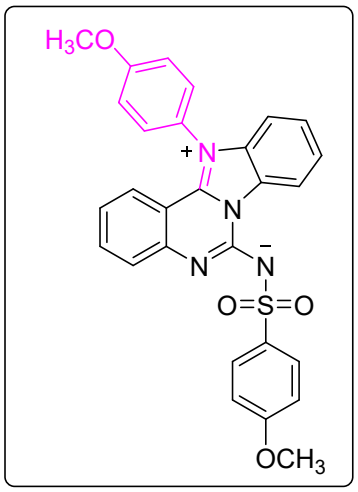
According to the general procedure, **4kb** was obtained in 30% yield (33.5 mg). Brown solid, **mp** = 246.1 – 247.3 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.25 (d, *J* = 8.4 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.79 – 7.67 (m, 7H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.7, 145.9, 145.0, 143.2, 134.9, 134.6, 130.7, 130.3, 129.4, 128.0, 126.4, 126.1, 125.9, 125.5, 124.3, 123.5, 122.9, 119.1, 116.3, 111.4, 107.8, 55.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{27}H_{20}BrN_4O_3S^+$, m/z: 559.0434, found: 559.0443. **IR (thin film):** ν_{max} 1584, 1514, 1475, 1253, 1139, 1084, 753, 603, 549 cm^{-1}.

((4-(*tert*-butyl)phenyl)sulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4lb)



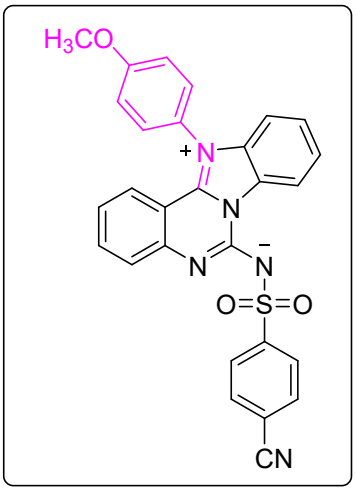
According to the general procedure, **4lb** was obtained in 78% yield (83.6 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 (d, *J* = 8.4 Hz, 1H), 8.10 – 8.06 (m, 2H), 7.78 – 7.69 (m, 5H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.38 – 7.35 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 1.26 (s, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 153.5, 149.0, 146.0, 145.0, 141.1, 134.8, 134.6, 129.4, 127.9, 126.5, 126.1, 126.0, 125.4, 124.5, 123.5, 122.6, 119.2, 116.3, 111.3, 107.6, 55.8, 34.61, 30.98. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{31}H_{29}N_4O_3S^+$, m/z: 537.1955, found: 537.1947. **IR (thin film):** ν_{max} 2963, 1585, 1513, 1475, 1394, 1253, 1144, 1083, 758, 568 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)((4-methoxyphenyl)sulfonyl)amide (4mb)



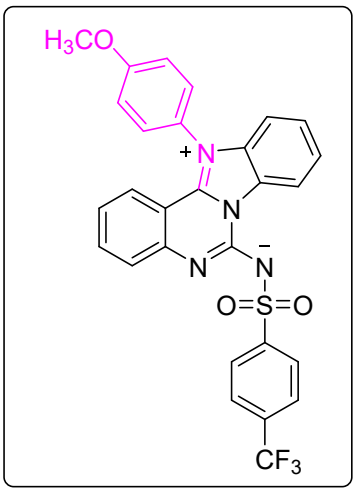
According to the general procedure, **4mb** was obtained in 72% yield (73.7 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 (d, *J* = 8.3 Hz, 1H), 8.10 – 8.06 (m, 2H), 7.78 – 7.69 (m, 5H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.01 – 6.95 (m, 3H), 3.94 (s, 3H), 3.77 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.6, 161.4, 149.4, 146.4, 145.4, 136.3, 135.2, 135.1, 130.5, 129.8, 128.3, 126.9, 126.5, 126.4, 125.8, 123.9, 123.0, 119.6, 116.7, 113.2, 111.7, 107.9, 56.2, 55.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{28}H_{22}N_4O_4SNa^+$, m/z: 533.1254, found: 533.1244. **IR (thin film):** ν_{max} 1586, 1513, 1254, 1138, 1086, 889, 751, 563, 551 cm^{-1}.

((4-cyanophenyl)sulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4nb)



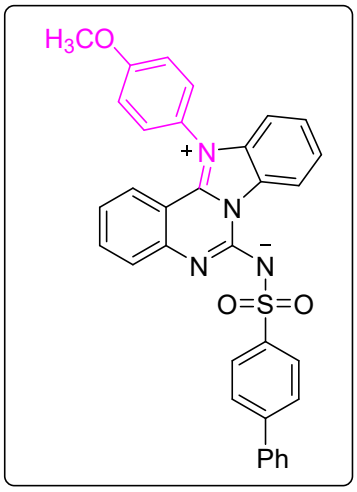
According to the general procedure, **4nb** was obtained in 20% yield (20.2 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 – 9.23 (m, 1H), 8.31 – 8.26 (m, 2H), 7.99 – 7.94 (m, 2H), 7.80 – 7.77 (m, 1H), 7.76 – 7.71 (m, 4H), 7.58 – 7.55 (m, 1H), 7.39 – 7.36 (m, 2H), 7.29 – 7.26 (m, 1H), 7.13 – 7.10 (m, 1H), 7.00 – 6.98 (m, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.5, 148.3, 145.8, 145.0, 134.9, 134.6, 132.0, 129.3, 128.9, 128.0, 126.4, 126.0, 125.9, 125.6, 123.5, 123.2, 119.0, 118.3, 116.3, 113.1, 111.4, 107.9, 55.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{20}N_5O_3S^+$, m/z: 506.1282, found: 506.1264. **IR (thin film):** ν_{max} 2228, 1586, 1513, 1475, 1393, 1252, 1139, 1084, 753, 562 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)((4-(trifluoromethyl)phenyl)sulfonyl)amide (4ob)



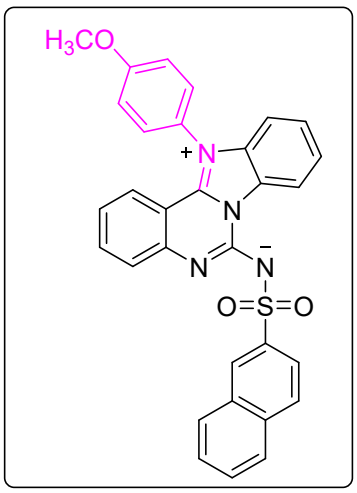
According to the general procedure, **4ob** was obtained in 82% yield (89.9 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.80 – 7.77 (m, 1H), 7.76 – 7.70 (m, 4H), 7.59 (d, J = 8.3 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.27 (d, J = 8.2 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.00 – 6.97 (m, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.6, 147.9, 145.9, 145.0, 134.9, 134.6, 130.7 (q, $J_{(C-F)}$ = 32.0 Hz), 129.3, 129.0, 128.0, 126.4, 126.0, 125.9, 125.6, 124.9 (q, $J_{(C-F)}$ = 3.0 Hz), 123.9 (q, $J_{(C-F)}$ = 270.5 Hz), 123.5, 123.1, 119.0, 116.3, 111.4, 107.9, 55.8. **^{19}F NMR (564 MHz, DMSO-*d*$_6$)** δ -61.26. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{28}H_{19}F_3N_4O_3SNa^+$, m/z: 571.1022, found: 571.1016. **IR (thin film):** ν_{max} 1584, 1514, 1324, 1153, 1087, 892, 752, 545 cm^{-1}.

([1,1'-biphenyl]-4-ylsulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4pb)



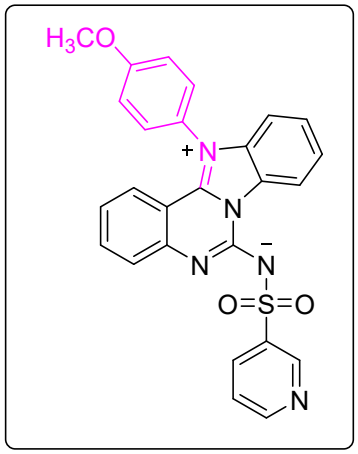
According to the general procedure, **4pb** was obtained in 78% yield (86.7 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.29 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.67 (m, 9H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.9, 146.0, 145.1, 142.8, 142.3, 139.2, 134.8, 134.6, 129.4, 129.0, 128.7, 128.0, 127.9, 126.9, 126.5, 126.1, 126.0, 125.5, 123.5, 122.7, 119.1, 116.3, 111.3, 107.7, 55.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{33}H_{25}N_4O_3S^+$, m/z: 557.1642, found: 557.1634. **IR (thin film):** ν_{max} 1586, 1513, 1476, 1213, 1141, 1087, 753, 593 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(naphthalen-2-ylsulfonyl)amide (4qb)



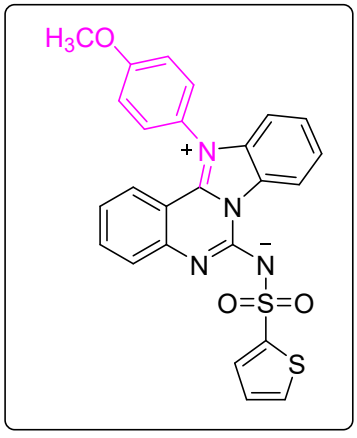
According to the general procedure, **4qb** was obtained in 90% yield (95.4 mg). Brown solid, **mp** = 220.1 – 221.1 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.30 (d, *J* = 8.3 Hz, 1H), 8.81 (d, *J* = 1.9 Hz, 1H), 8.21 – 8.15 (m, 2H), 7.99 – 7.93 (m, 2H), 7.80 – 7.77 (m, 1H), 7.74 – 7.67 (m, 4H), 7.61 – 7.56 (m, 3H), 7.37 – 7.33 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.95 – 6.92 (m, 1H), 3.92 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 148.8, 145.9, 145.0, 140.9, 134.8, 134.6, 133.7, 131.7, 129.3, 128.9, 128.6, 127.9, 127.7, 127.5, 127.2, 126.7, 126.4, 126.0, 125.9, 125.5, 124.8, 123.5, 122.7, 119.1, 116.3, 111.3, 107.6, 55.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{31}H_{23}N_4O_3S^+$, m/z: 531.1486, found: 531.1473. **IR (thin film):** ν_{max} 1584, 1512, 1474, 1252, 1123, 890, 743, 548 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(pyridin-3-ylsulfonyl)amide (4rb)



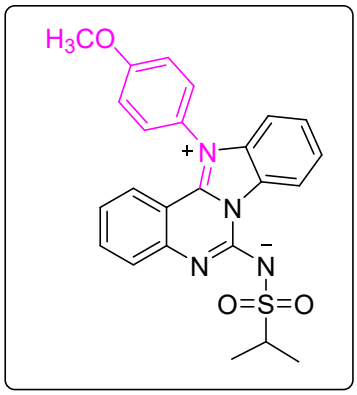
According to the general procedure, **4rb** was obtained in 79% yield (76.0 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.30 – 9.22 (m, 2H), 8.66 – 8.62 (m, 1H), 8.52 – 8.48 (m, 1H), 7.81 – 7.77 (m, 1H), 7.76 – 7.70 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.39 – 7.36 (m, 2H), 7.27 (d, J = 8.2 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.00 – 6.97 (m, 1H), 3.94 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 151.3, 148.8, 148.5, 145.9, 145.0, 139.7, 136.1, 134.9, 134.6, 129.3, 128.0, 126.4, 126.1, 125.9, 125.6, 123.6, 123.1, 123.0, 119.0, 116.3, 111.4, 107.9, 55.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{20}N_5O_3S^+$, m/z: 482.1282, found: 482.1285. **IR (thin film):** ν_{max} 1586, 1512, 1395, 1297, 1250, 1151, 1100, 759, 554 cm^{-1}.

(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(thiophen-2-ylsulfonyl)amide (4sb)



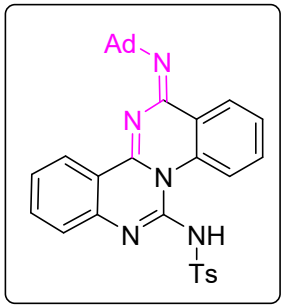
According to the general procedure, **4sb** was obtained in 80% yield (77.8 mg). Brown solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.22 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.79 – 7.70 (m, 7H), 7.39 – 7.37 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.07 – 7.04 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 161.2, 148.7, 146.0, 145.3, 145.1, 134.9, 134.6, 130.9, 130.3, 129.4, 128.0, 126.4, 126.2, 126.1, 125.9, 125.5, 123.6, 123.0, 119.0, 116.3, 111.4, 107.8, 55.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{25}H_{18}N_4O_3S_2Na^+$, m/z: 509.0712, found: 509.0725. **IR (thin film):** ν_{max} 1590, 1514, 1475, 1250, 1213, 1134, 753, 587, 545 cm^{-1}.

(isopropylsulfonyl)(12-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)amide (4tb)



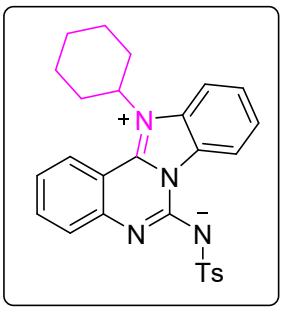
According to the general procedure, **4tb** was obtained in 69% yield (61.5 mg). Grey solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.23 (d, *J* = 8.3 Hz, 1H), 7.83 – 7.69 (m, 5H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.08 (hept, *J* = 6.9 Hz, 1H), 3.95 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.2, 149.4, 146.5, 145.1, 134.8, 134.7, 129.4, 127.9, 126.6, 126.0, 125.4, 123.6, 122.4, 119.1, 116.3, 111.3, 107.3, 55.8, 50.3, 16.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{23}N_4O_3S^+$, m/z: 469.1305, found: 469.1305. **IR (thin film):** ν_{max} 2918, 1586, 1505, 1471, 1395, 1242, 1105, 888, 750, 549 cm^{-1}.

N-((*Z*)-13-(((3*s*,5*s*,7*s*)-adamantan-1-yl)imino)-13*H*-quinazolino[3,4-*a*]quinazolin-6-yl)-4-methylbenzenesulfonamide (3ac)



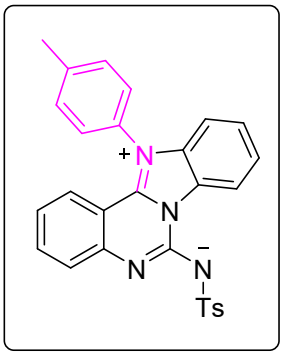
According to the general procedure, **3ac** was obtained in 83% yield (91.1 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 2:1 → DCM/CH_3OH = 30:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.56 (d, *J* = 8.9 Hz, 1H), 9.21 (s, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.97 – 7.89 (m, 3H), 7.79 – 7.71 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.38 (d, *J* = 2.9 Hz, 6H), 2.31 (s, 3H), 2.19 – 2.16 (m, 3H), 1.79 – 1.73 (m, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 157.7, 152.2, 147.4, 141.3, 140.4, 136.3, 136.0, 132.6, 128.1, 128.0, 127.9, 125.9, 124.7, 124.2, 123.0, 122.7, 115.6, 115.3, 56.1, 40.3, 35.9, 29.0, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{32}H_{32}N_5O_2S^+$, m/z: 550.2271, found: 550.2275. **IR (thin film):** ν_{max} 3297, 2905, 1585, 1564, 1450, 1229, 1132, 1080, 750, 550 cm^{-1}.

(12-cyclohexylbenzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4ad)



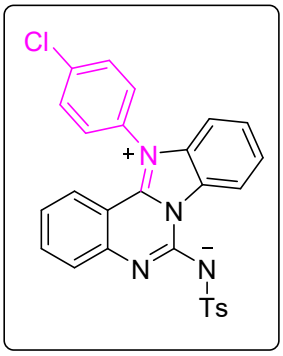
According to the general procedure, **4ad** was obtained in 51% yield (47.9 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.34 – 9.31 (m, 1H), 8.36 – 8.33 (m, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.82 – 7.79 (m, 1H), 7.74 – 7.69 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 5.21 (t, *J* = 12.3 Hz, 1H), 2.53 (s, 1H), 2.47 (s, 1H), 2.30 (s, 3H), 2.17 (d, *J* = 12.3 Hz, 2H), 1.94 (d, *J* = 13.1 Hz, 2H), 1.74 (d, *J* = 12.4 Hz, 1H), 1.64 – 1.53 (m, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 149.1, 145.8, 145.1, 141.2, 140.5, 134.5, 130.9, 128.1, 128.0, 127.4, 126.9, 126.3, 125.0, 124.6, 123.1, 119.5, 114.8, 107.6, 60.3, 29.6, 25.4, 24.2, 20.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{27}H_{26}N_4O_2SNa^+$, m/z: 493.1668, found: 493.1653. **IR (thin film):** ν_{max} 2941, 1587, 1502, 1483, 1261, 1136, 1086, 897, 741, 543 cm^{-1}.

(12-(*p*-tolyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4ag)



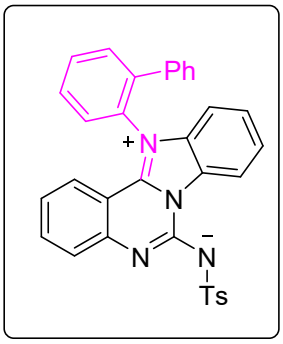
According to the general procedure, **4ag** was obtained in 85% yield (81.3 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.26 (d, J = 8.3 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.78 – 7.75 (m, 1H), 7.73 – 7.68 (m, 4H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 149.0, 145.9, 144.8, 141.7, 141.1, 140.6, 134.8, 134.4, 131.6, 131.2, 128.1, 128.1, 127.9, 127.8, 126.5, 126.1, 125.5, 123.5, 122.6, 119.1, 111.2, 107.5, 21.1, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{23}N_4O_2S^+$, m/z: 479.1536, found: 479.1515. **IR (thin film):** ν_{max} 1588, 1504, 1473, 1143, 1086, 890, 725, 549 cm^{-1}.

(12-(4-chlorophenyl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide(4ah)



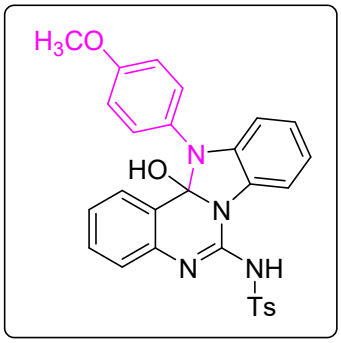
According to the general procedure, **4ah** was obtained in 70% yield (69.7 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.27 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.91 – 7.88 (m, 2H), 7.79 – 7.76 (m, 1H), 7.74 – 7.69 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.11 – 7.08 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 149.0, 145.9, 144.9, 141.0, 140.6, 136.5, 134.9, 134.3, 132.7, 131.4, 130.2, 128.1, 128.1, 128.0, 126.5, 126.1, 125.6, 123.4, 122.8, 119.2, 111.3, 107.3, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{27}H_{20}ClN_4O_2S^+$, m/z: 499.0990, found: 499.1007. **IR (thin film):** ν_{max} 1586, 1505, 1473, 1146, 1083, 887, 749, 548 cm^{-1}.

(12-([1,1'-biphenyl]-2-yl)benzo[4,5]imidazo[1,2-*c*]quinazolin-12-ium-6-yl)(tosyl)amide (4ai)



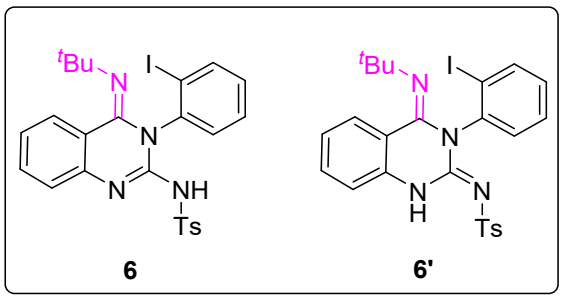
According to the general procedure, **4ai** was obtained in 82% yield (88.6 mg). Yellow solid, **mp**>250 °C. Eluent: EA/PE = 1:2 → DCM/CH_3OH = 50:1. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.17 – 9.12 (m, 1H), 8.03 – 7.96 (m, 3H), 7.90 – 7.82 (m, 3H), 7.77 – 7.74 (m, 1H), 7.72 – 7.69 (m, 1H), 7.66 – 7.63 (m, 1H), 7.58 – 7.55 (m, 1H), 7.30 – 7.26 (m, 3H), 7.16 – 7.13 (m, 1H), 7.10 – 7.06 (m, 4H), 7.04 – 7.01 (m, 2H), 2.32 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 149.2, 145.8, 144.7, 141.0, 140.7, 139.9, 136.2, 135.3, 133.4, 132.5, 132.3, 131.0, 130.6, 129.0, 128.6, 128.3, 128.2, 128.1, 127.7, 126.3, 126.1, 125.8, 123.2, 123.1, 119.1, 111.5, 106.9, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{33}H_{25}N_4O_2S^+$, m/z: 541.1693, found: 541.1690. **IR (thin film):** ν_{max} 1589, 1503, 1473, 1138, 1080, 742, 688, 550 cm^{-1}.

12-(4-methoxyphenyl)-6-((4-methylphenyl)sulfonamido)-12,12a-dihydrobenzo[4,5]imidazo[1,2-*c*]quinazoline 12-oxide (5)



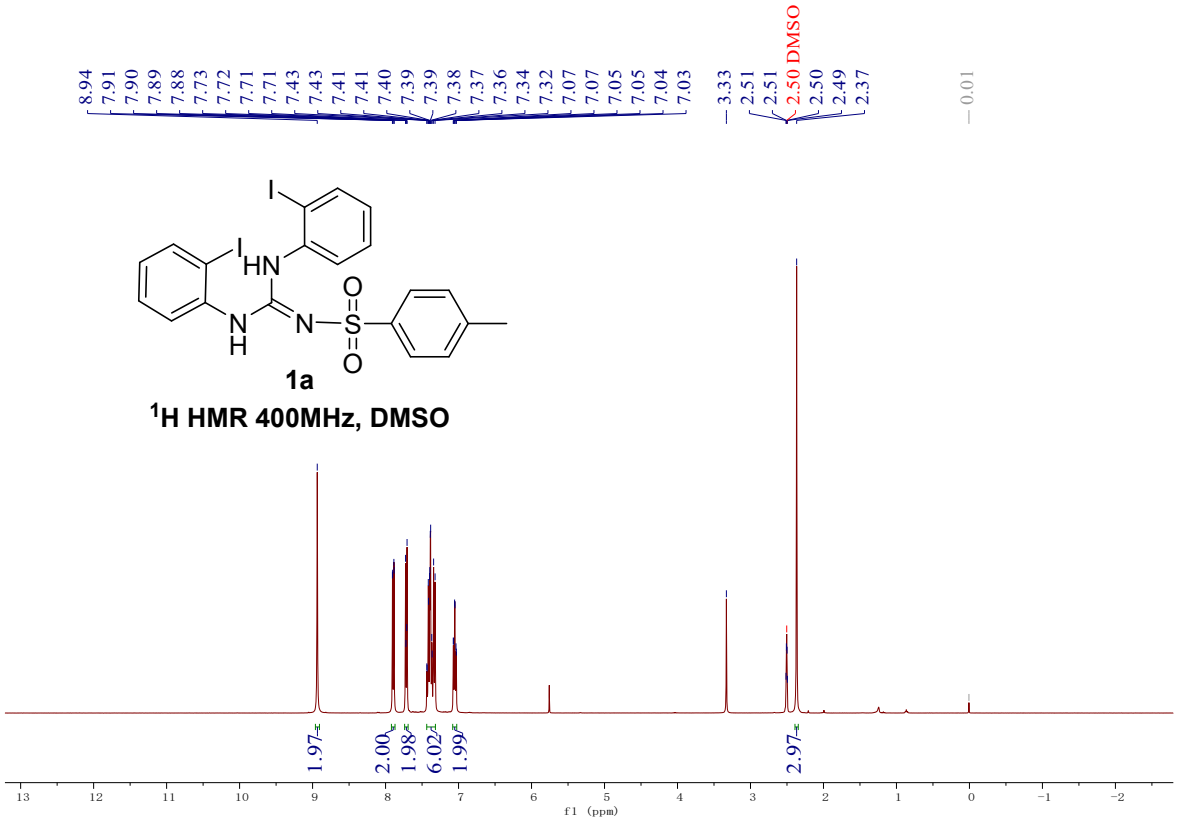
According to the general procedure, **5** was obtained in 86% yield (88.1 mg). Grey solid, **mp** = 230.0 – 230.5 °C. Eluent: DCM/CH_3OH = 100:1. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.19 (s, 1H), 8.02 – 7.98 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.62 – 7.58 (m, 2H), 7.50 (s, 1H), 7.41 – 7.36 (m, 1H), 7.18 – 7.09 (m, 4H), 6.98 – 6.94 (m, 1H), 6.85 – 6.79 (m, 4H), 6.75 – 6.70 (m, 1H), 3.71 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 160.6, 154.8, 149.2, 142.6, 142.0, 140.2, 138.1, 135.1, 134.9, 129.8, 129.2, 129.0, 127.1, 125.6, 124.4, 123.3, 122.5, 117.6, 117.3, 116.6, 114.2, 113.6, 55.2, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{25}N_4O_4S^+$, m/z: 513.1591, found: 513.1595. **IR (thin film):** ν_{max} 3383, 1620, 1579, 1509, 1437, 1243, 1076, 759, 573 cm^{-1}.

(*E*)-*N*-(4-(*tert*-butylimino)-3-(2-iodophenyl)-3,4-dihydroquinazolin-2-yl)-4-methylbenzenesulfonamide 6a and N-((2*E*,4*E*)-4-(*tert*-butylimino)-3-(2-iodophenyl)-3,4-dihydroquinazolin-2(1*H*)-ylidene)-4-methylbenzenesulfonamide 6a' (6a / 6a' = 3 : 2)

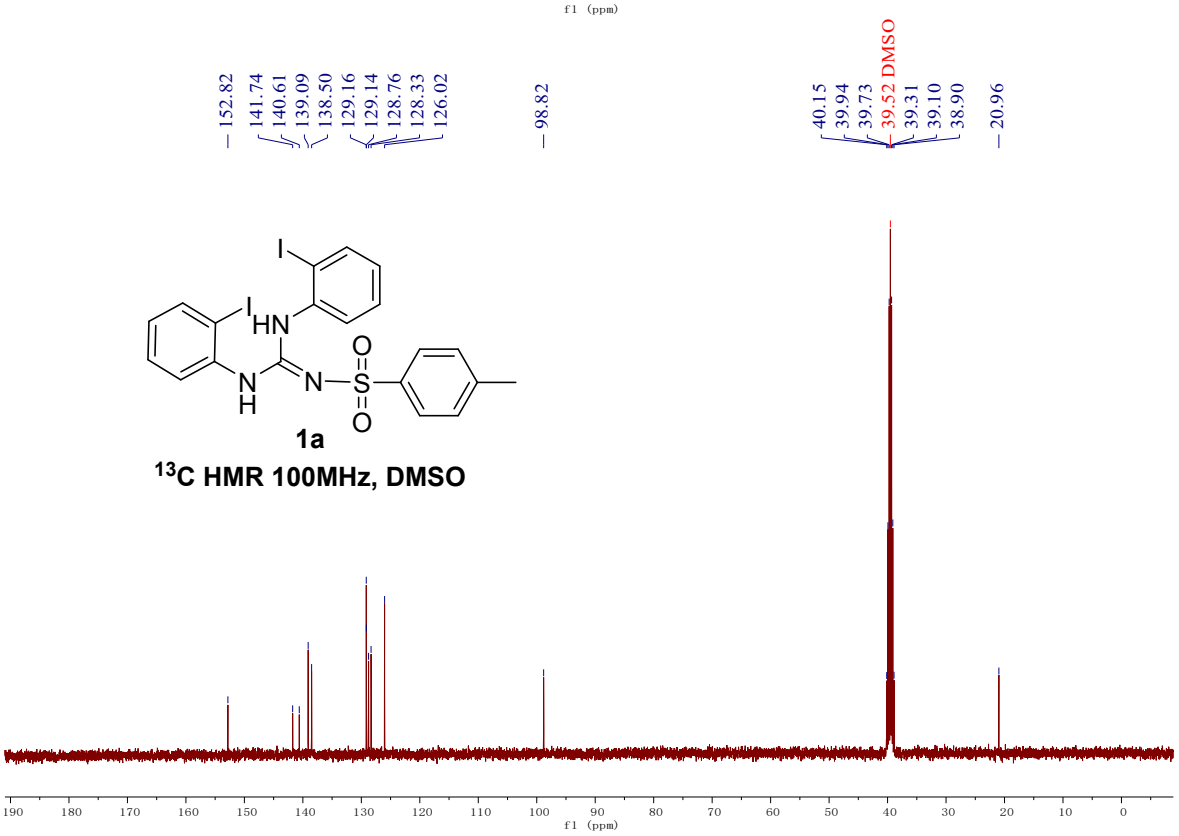


According to the general procedure, **6a** and **6a'** were obtained in 45% yield (128.7 mg). White solid, **mp** = 179.6 – 180.9 °C. Eluent: EA/PE = 1:2. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.58 (s, 1H), 7.91 – 7.82 (m, 2H), 7.78 – 7.54 (m, 4H), 7.44 – 7.31 (m, 2H), 7.28 – 7.16 (m, 3H), 7.10 – 7.05 (m, 1H), 2.31 (d, *J* = 11.5 Hz, 3H), 1.31 (s, 3H), 1.18 (s, 6H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 158.2, 153.0, 149.8, 148.9, 141.9, 141.8, 141.6, 140.5, 140.3, 139.9, 138.8, 138.4, 138.0, 137.1, 136.4, 132.6, 131.4, 131.0, 130.5, 129.8, 129.5, 129.1, 128.9, 128.5, 127.9, 127.7, 125.6, 125.4, 123.5, 121.2, 117.7, 115.2, 109.6, 100.7, 99.6, 59.5, 53.5, 30.6, 30.0, 20.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{26}IN_4O_2S^+$, m/z: 595.0635, found: 595.0651. **IR (thin film):** ν_{max} 3244, 2961, 1606, 1575, 1074, 811, 691, 566 cm^{-1}.

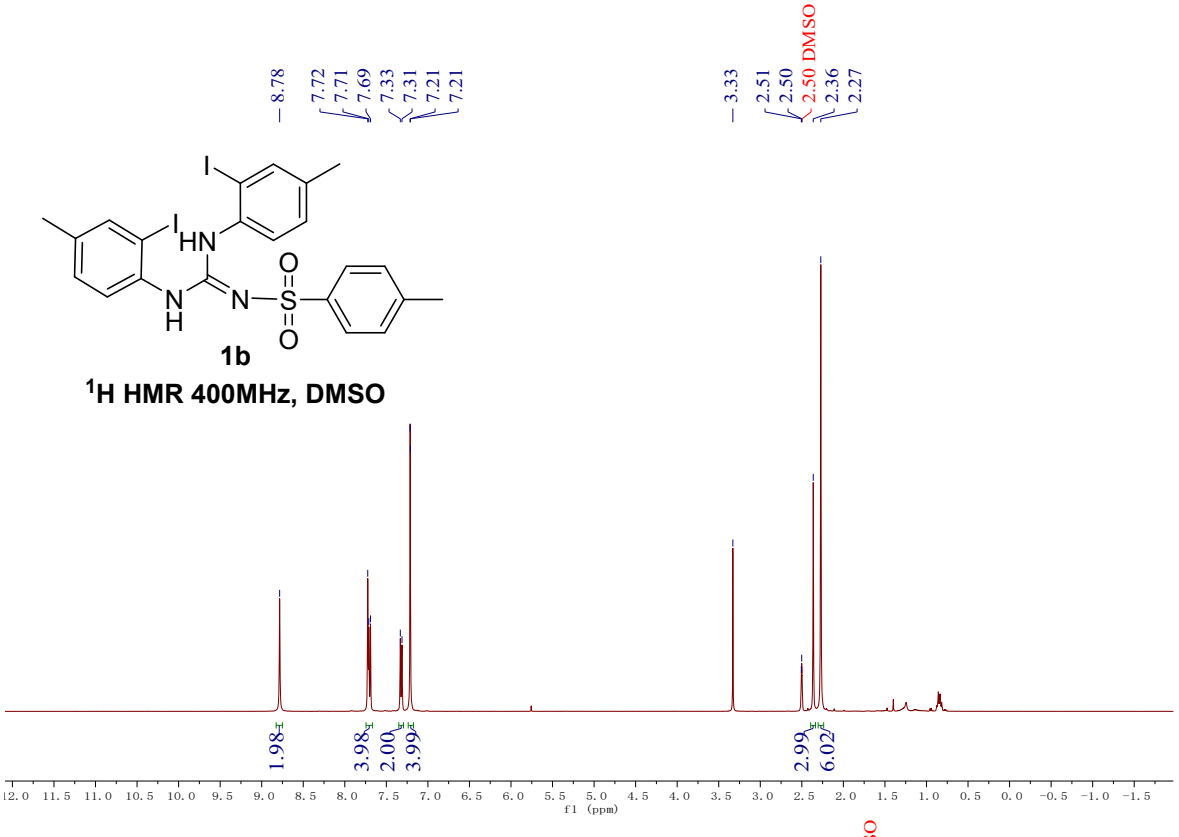
10. ^{1}H, ^{13}C and ^{19}F NMR spectra of new substrates and all products



^{1}H HMR 400MHz, DMSO

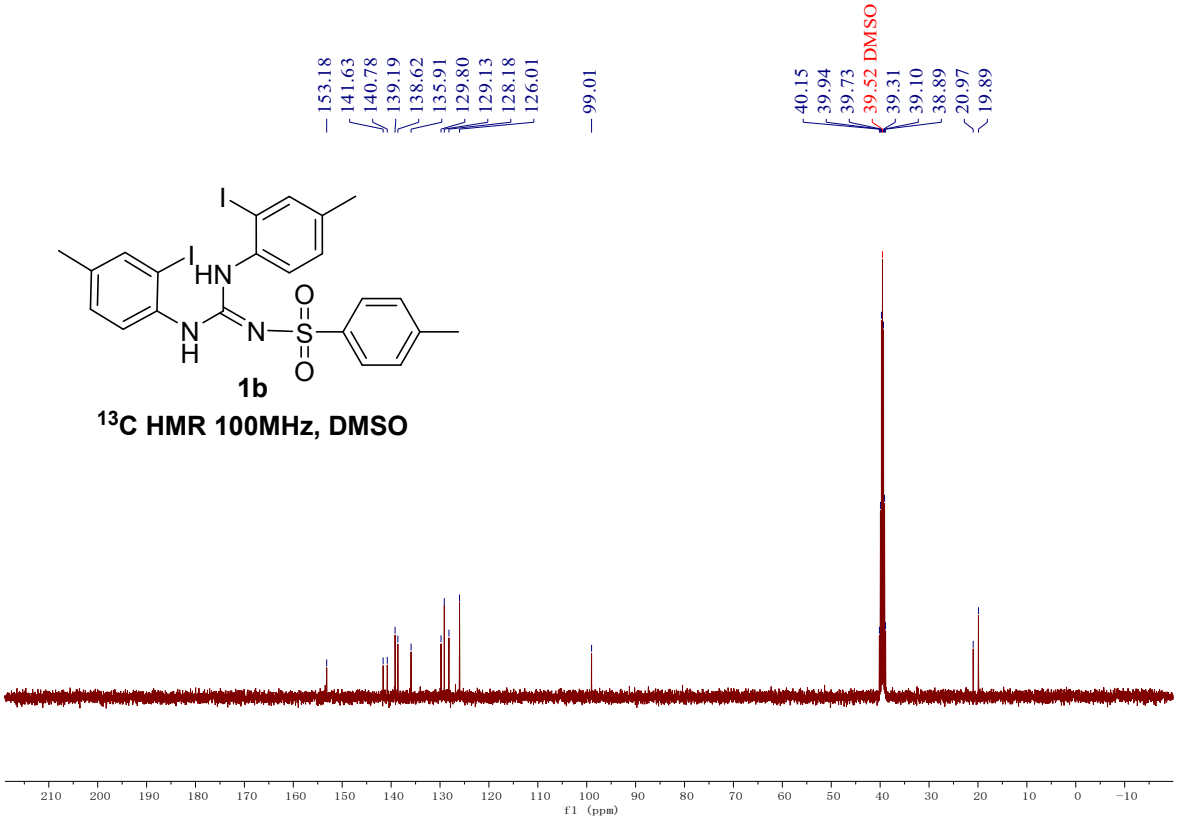


^{13}C HMR 100MHz, DMSO



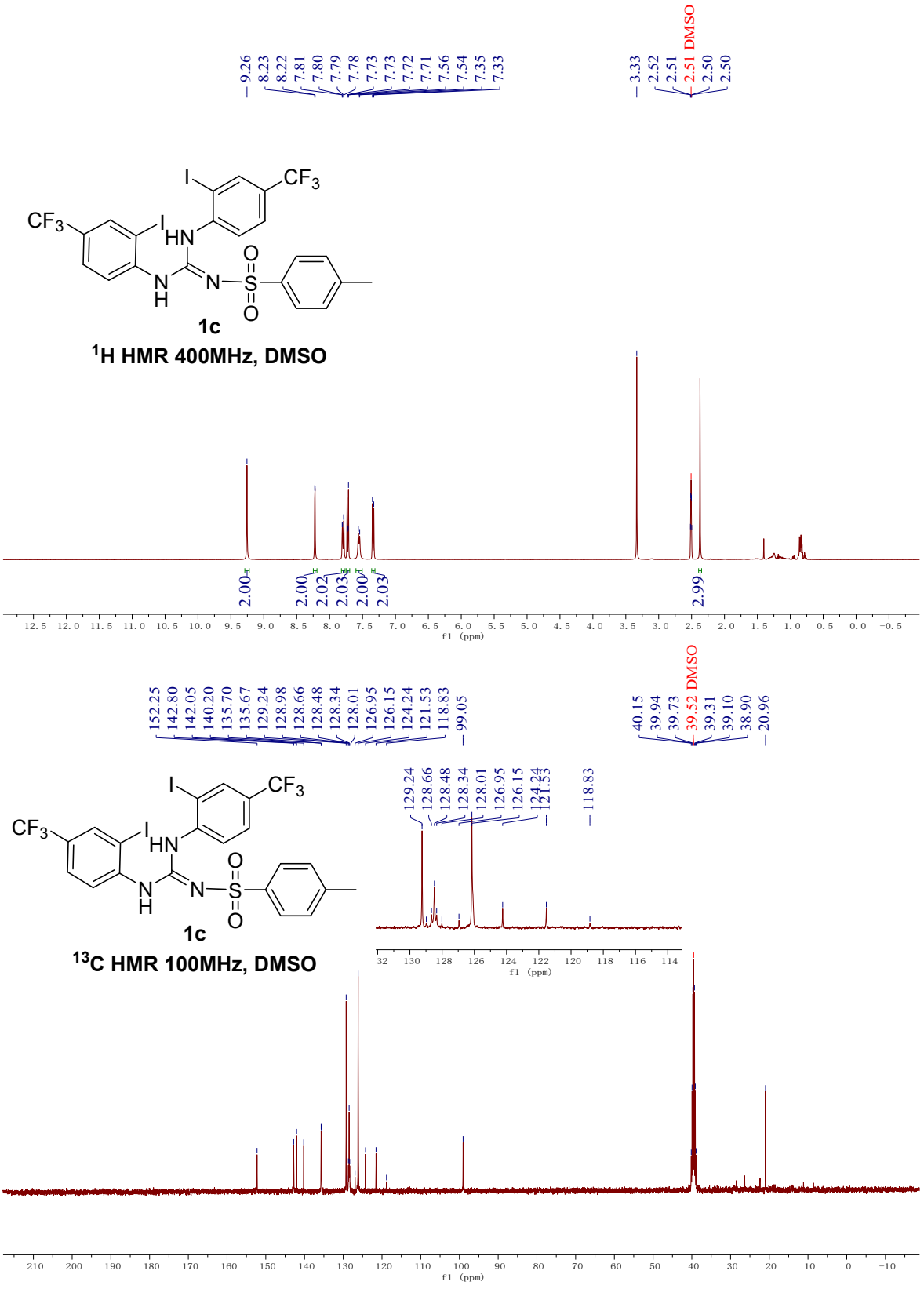
1b

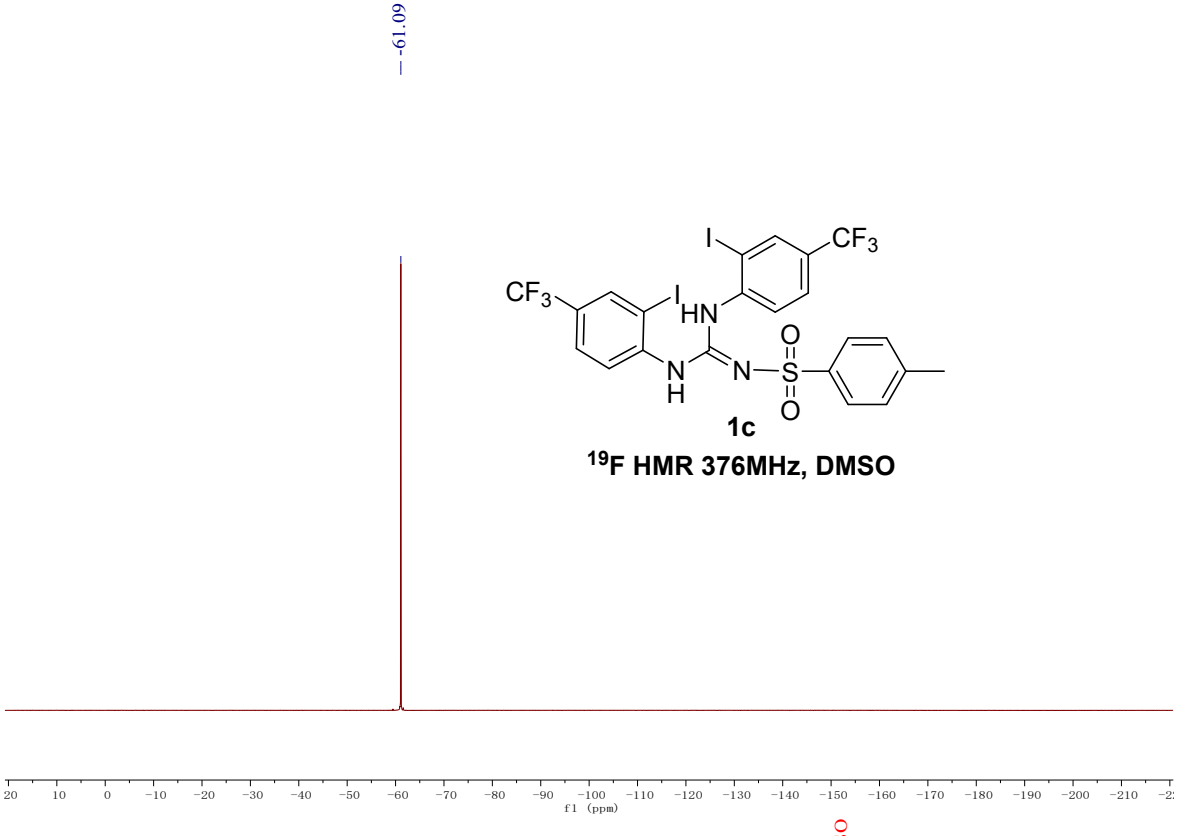
^{1}H HMR 400MHz, DMSO



1b

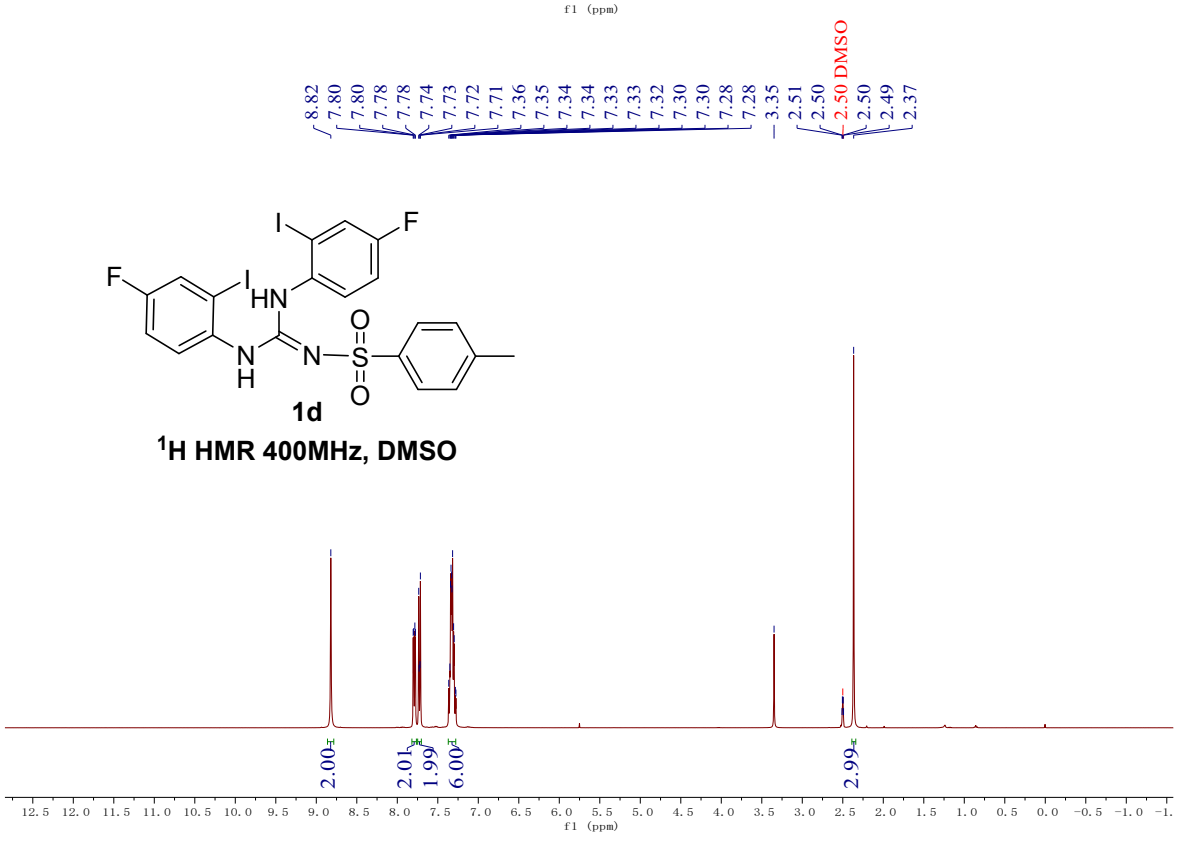
^{13}C HMR 100MHz, DMSO


9.26
8.23
8.22
7.81
7.80
7.79
7.78
7.73
7.73
7.72
7.71
7.56
7.54
7.35
7.33
3.33
2.52
2.51
2.51 DMSO
2.50
2.50
I
CF3
CF3
I
HN
O
N
N
S
O
H
O
1c
1H HMR 400MHz, DMSO
2.00
2.00
2.02
2.03
2.00
2.03
2.99
f1 (ppm)
152.25
142.80
142.05
140.20
135.70
135.67
129.24
128.98
128.66
128.48
128.34
128.01
126.95
126.15
124.24
121.53
118.83
99.05
40.15
39.94
39.73
39.52 DMSO
39.31
39.10
38.90
20.96
1c
13C HMR 100MHz, DMSO
f1 (ppm)
f1 (ppm)



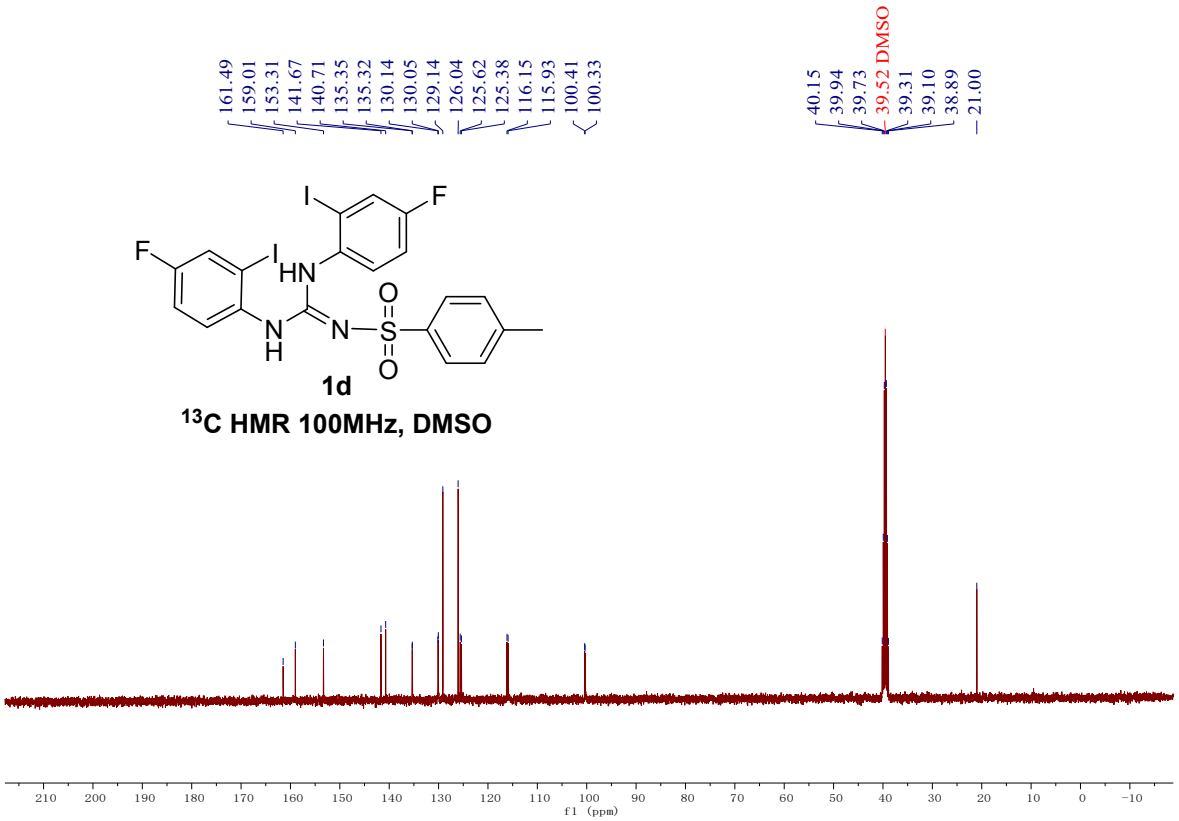
1c

^{19}F HMR 376MHz, DMSO



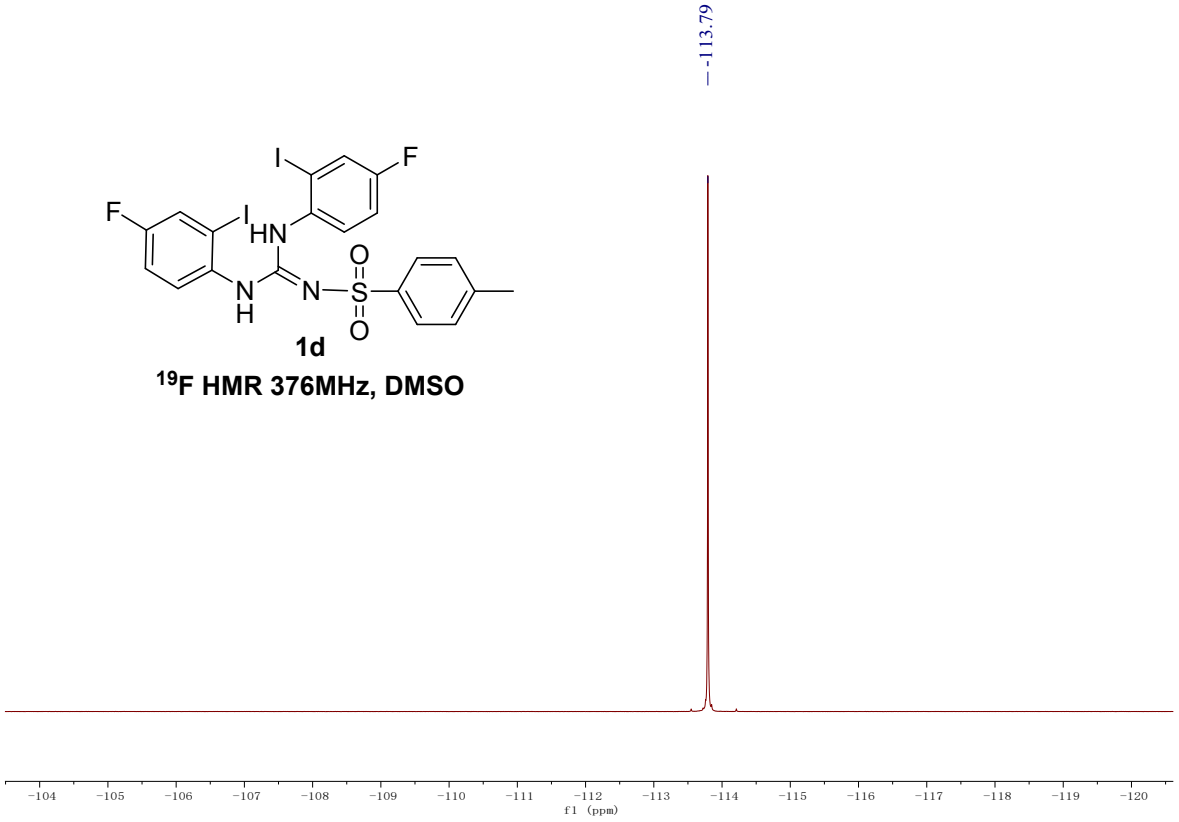
1d

^{1}H HMR 400MHz, DMSO



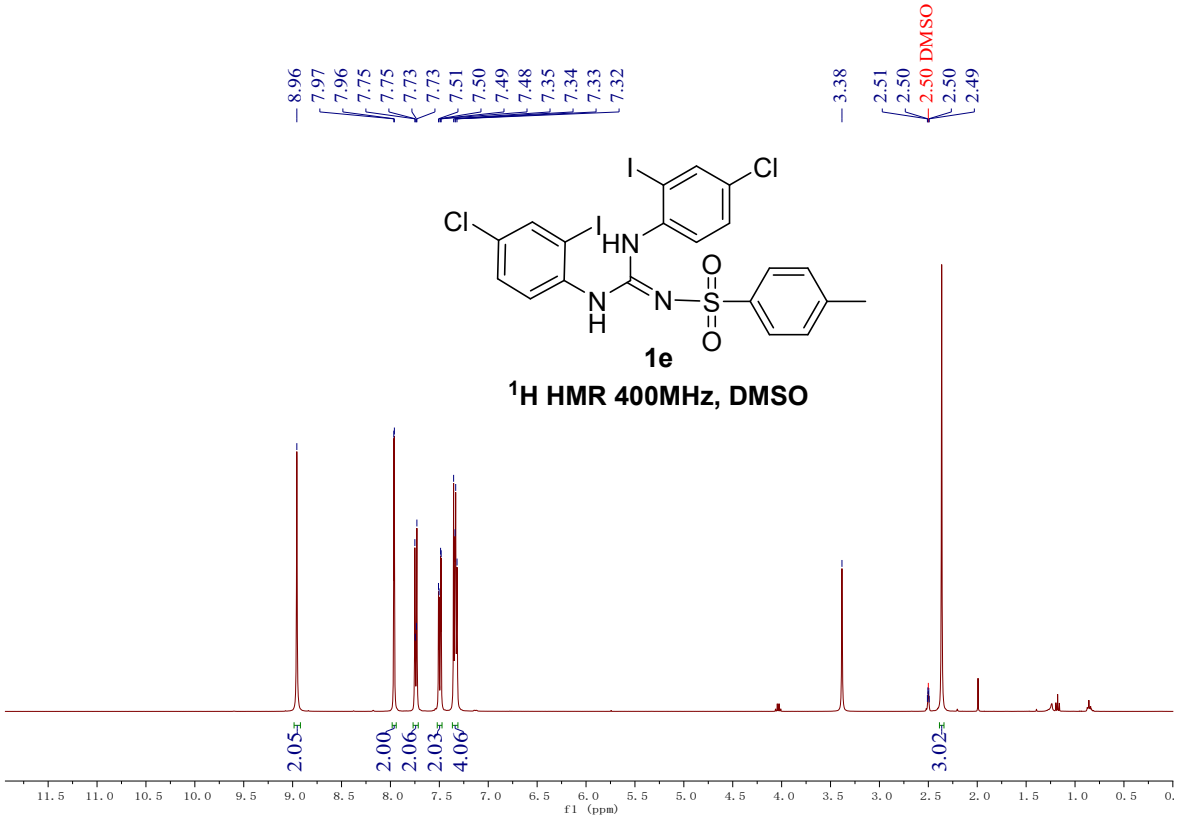
1d

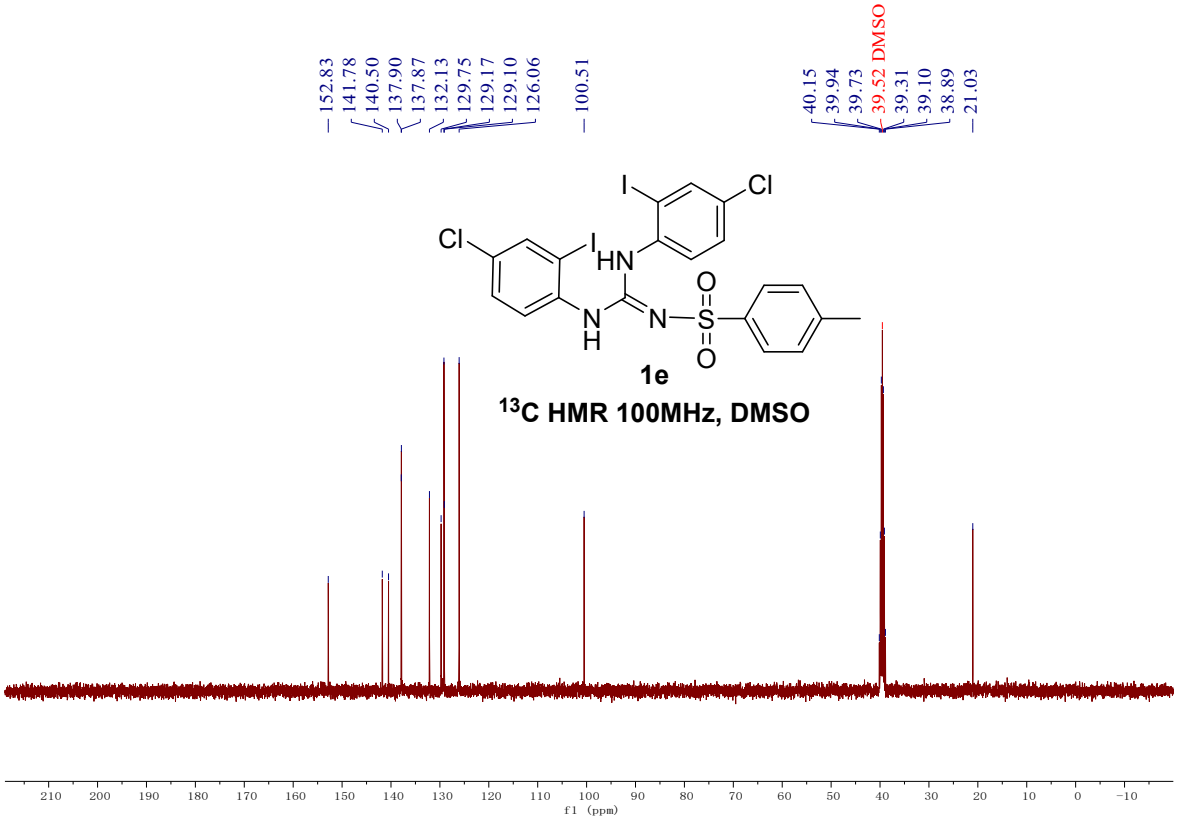
^{13}C HMR 100MHz, DMSO

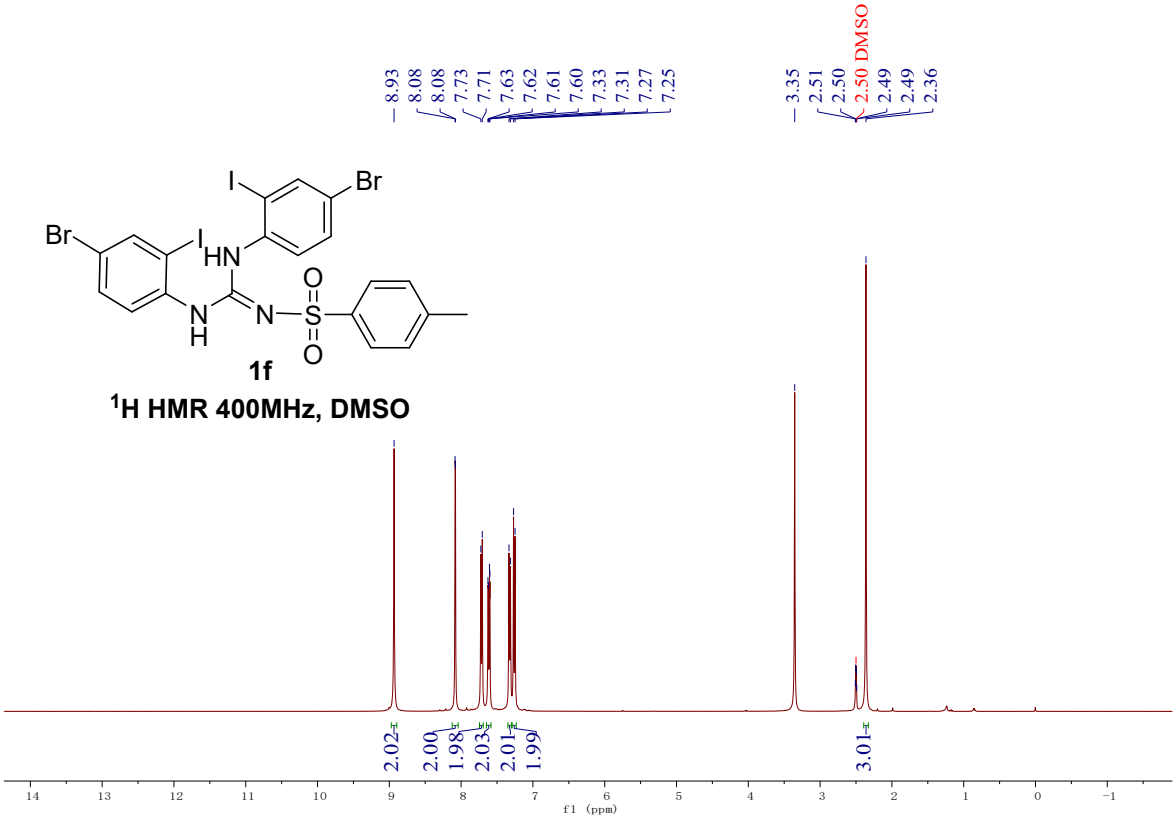


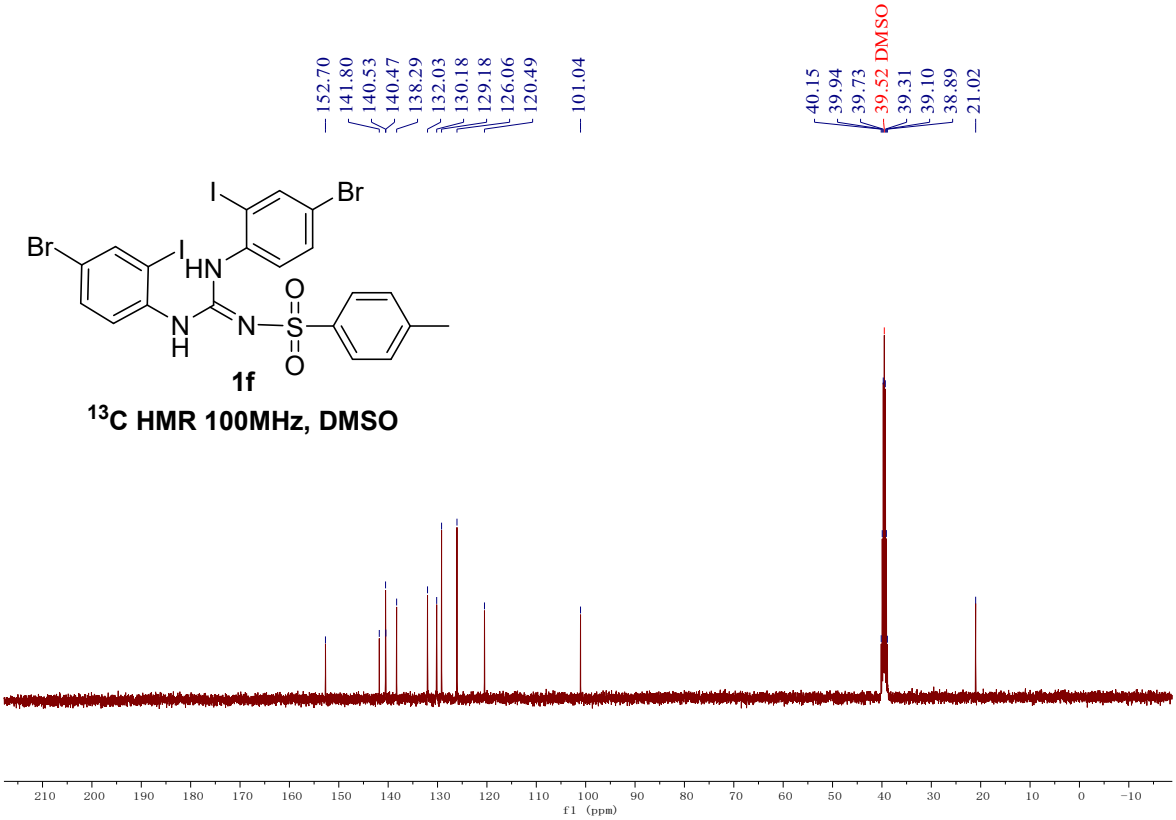
1d

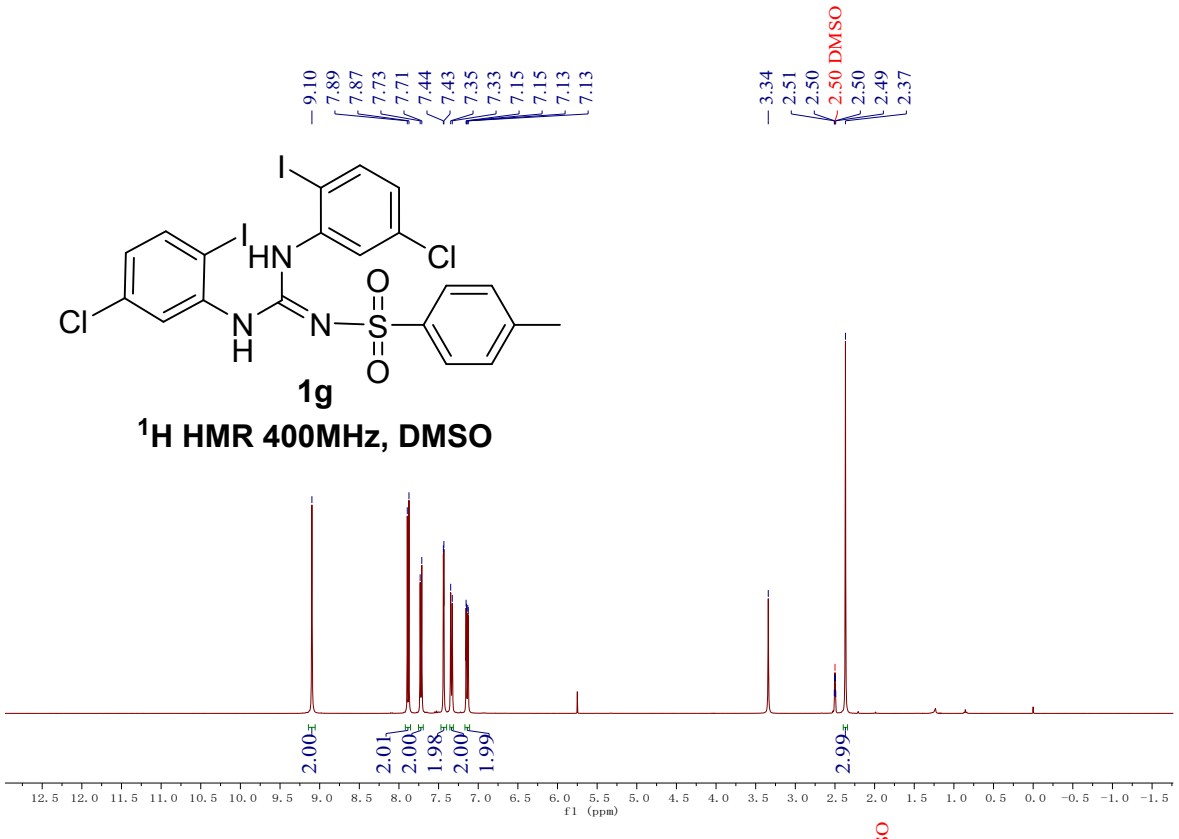
^{19}F HMR 376MHz, DMSO


8.96
7.97
7.96
7.75
7.75
7.73
7.73
7.51
7.50
7.49
7.48
7.35
7.34
7.33
7.32
3.38
2.51
2.50
2.50 DMSO
2.50
2.49
I
Cl
Cl
I
HN
N
H
N
S
O
O
O
1e
1H HMR 400MHz, DMSO
2.05
2.00
2.06
2.03
4.06
3.02
f1 (ppm)

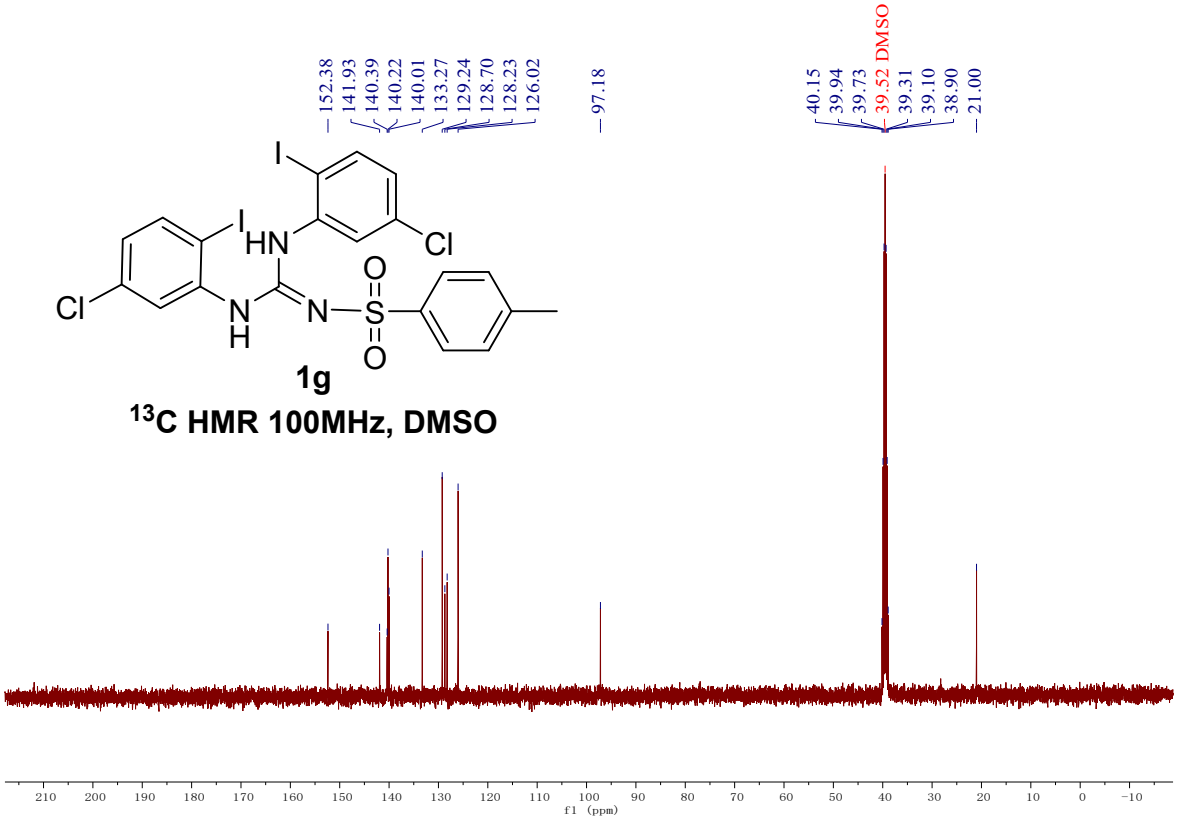

152.83
141.78
140.50
137.90
137.87
132.13
129.75
129.17
129.10
126.06
100.51
40.15
39.94
39.73
39.52 DMSO
39.31
39.10
38.89
21.03
I
Cl
Cl
I
HN
N
H
N
S
O
O
O
1e
13C HMR 100MHz, DMSO
f1 (ppm)


8.93
8.08
8.08
7.73
7.71
7.63
7.62
7.61
7.60
7.33
7.31
7.27
7.25
3.35
2.51
2.50
2.50 DMSO
2.49
2.49
2.36
Br
I
HN
N
H
N
S
O
O
Br
I
1f
1H HMR 400MHz, DMSO
2.02
2.00
1.98
2.03
2.01
1.99
3.01
f1 (ppm)

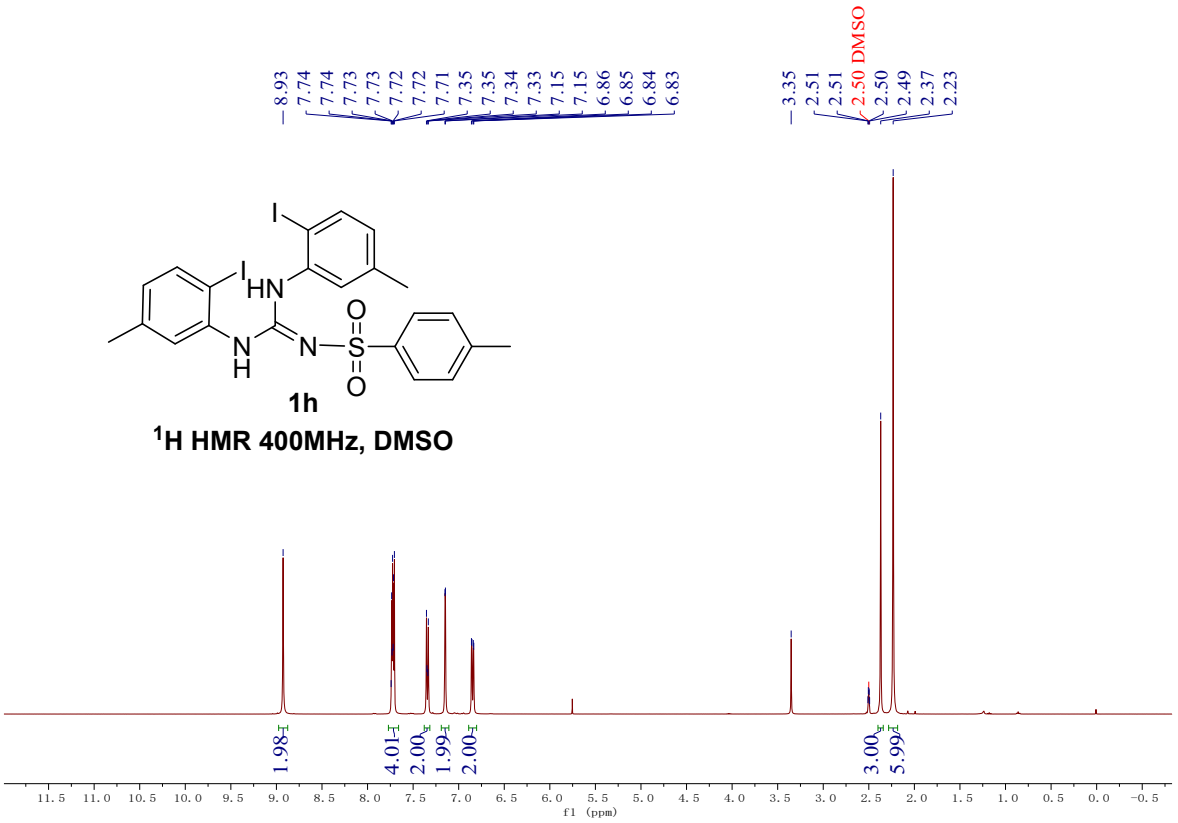

152.70
141.80
140.53
140.47
138.29
132.03
130.18
129.18
126.06
120.49
101.04
40.15
39.94
39.73
39.52 DMSO
39.31
39.10
38.89
21.02
Br
I
HN
N
H
N
S
O
O
Br
I
1f
13C HMR 100MHz, DMSO
f1 (ppm)



^{1}H HMR 400MHz, DMSO

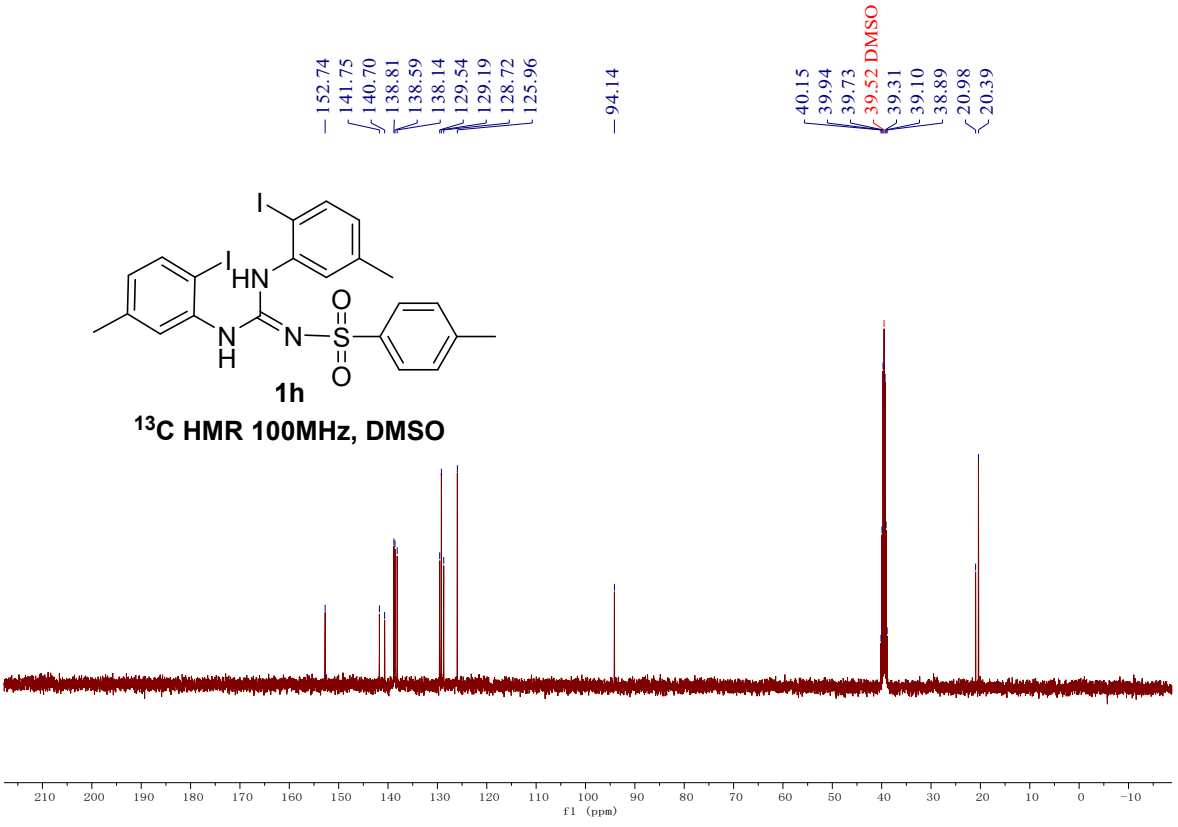


^{13}C HMR 100MHz, DMSO



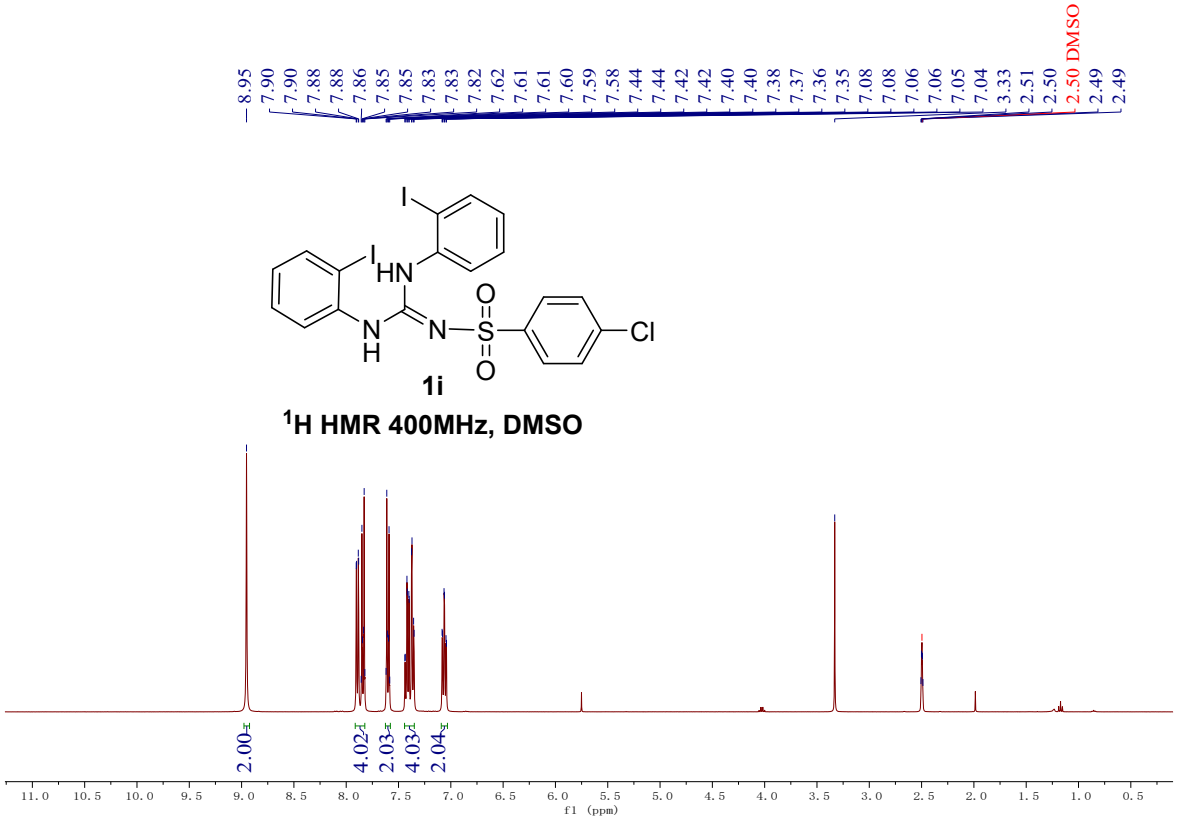
1h

^{1}H HMR 400MHz, DMSO

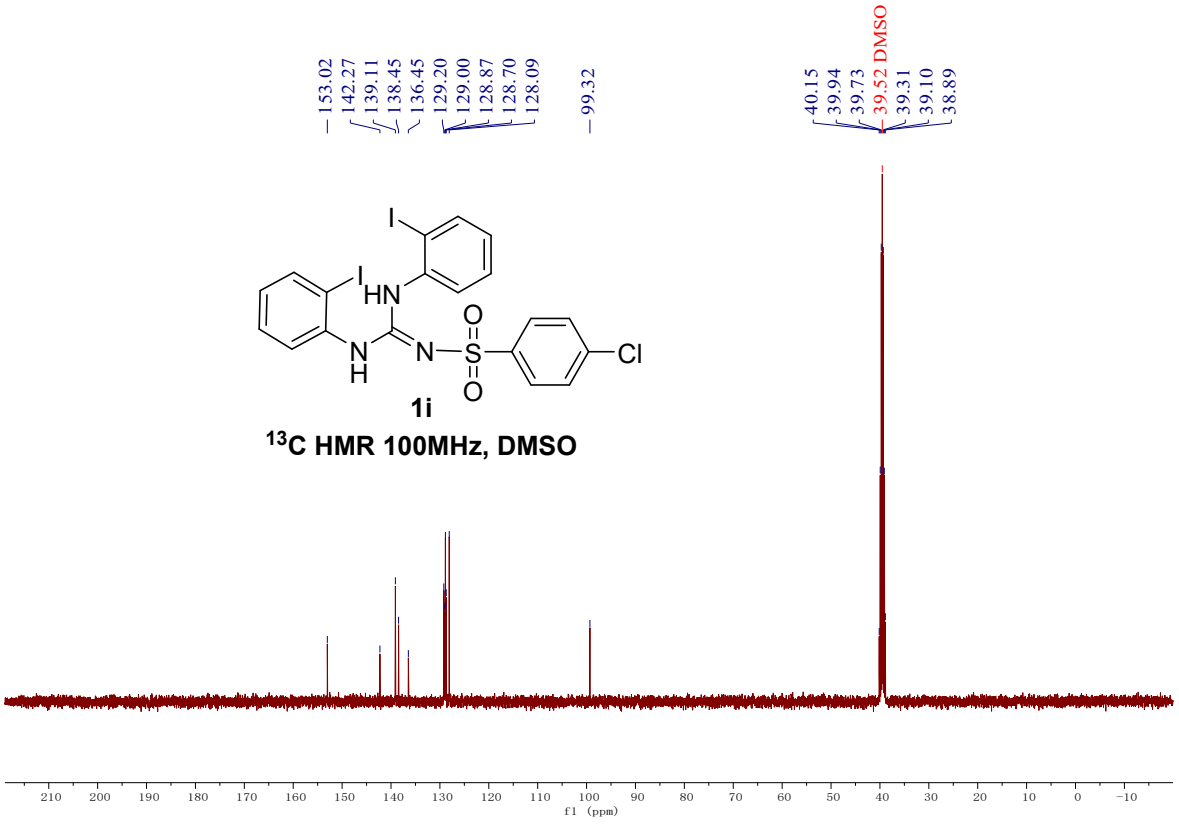


1h

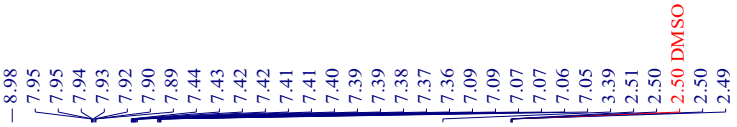
^{13}C HMR 100MHz, DMSO

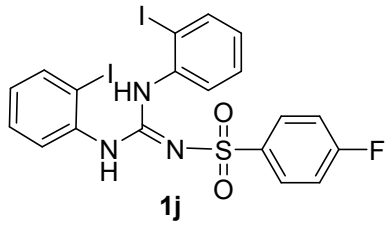


^{1}H HMR 400MHz, DMSO



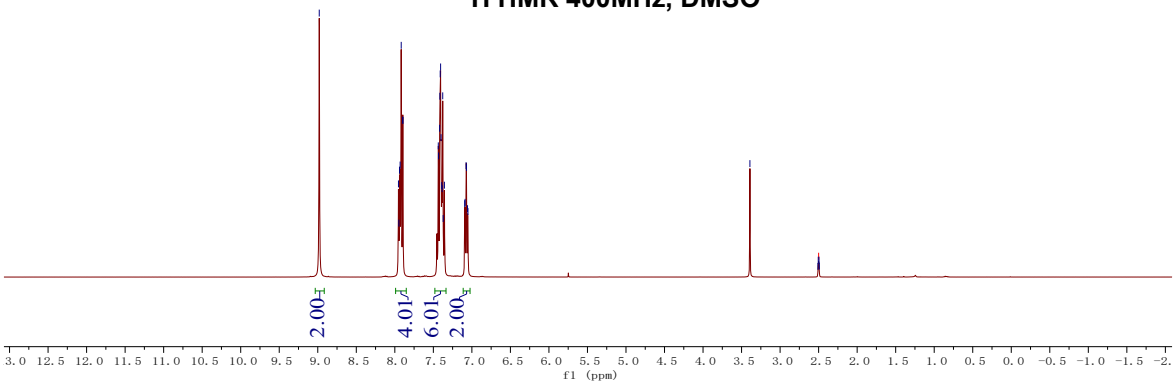
^{13}C HMR 100MHz, DMSO

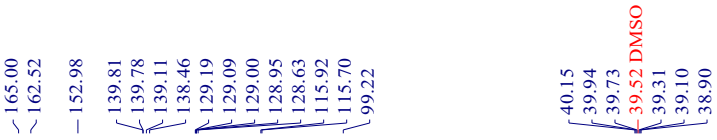


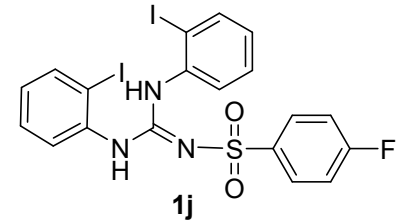


1j

^{1}H HMR 400MHz, DMSO

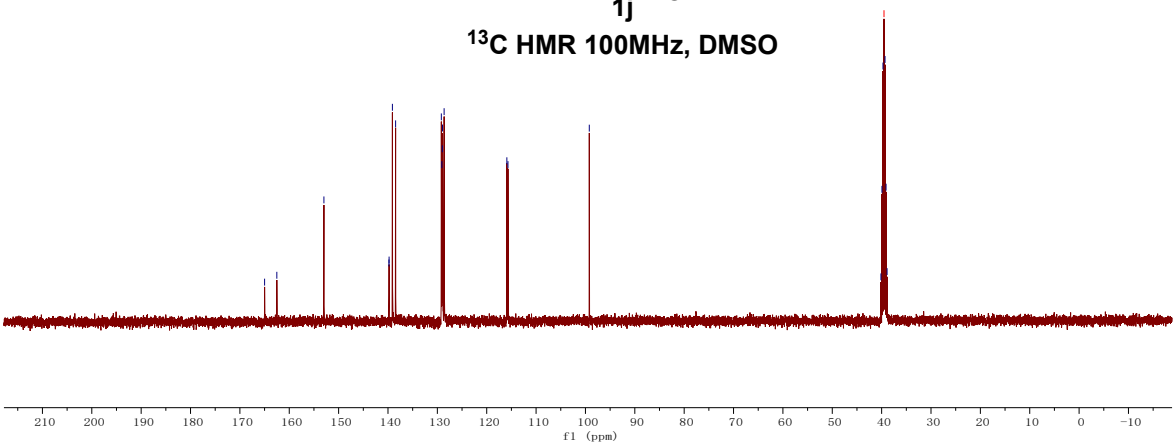


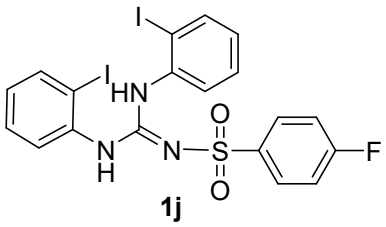




1j

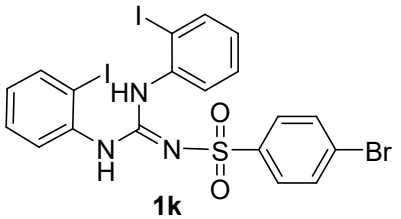
^{13}C HMR 100MHz, DMSO





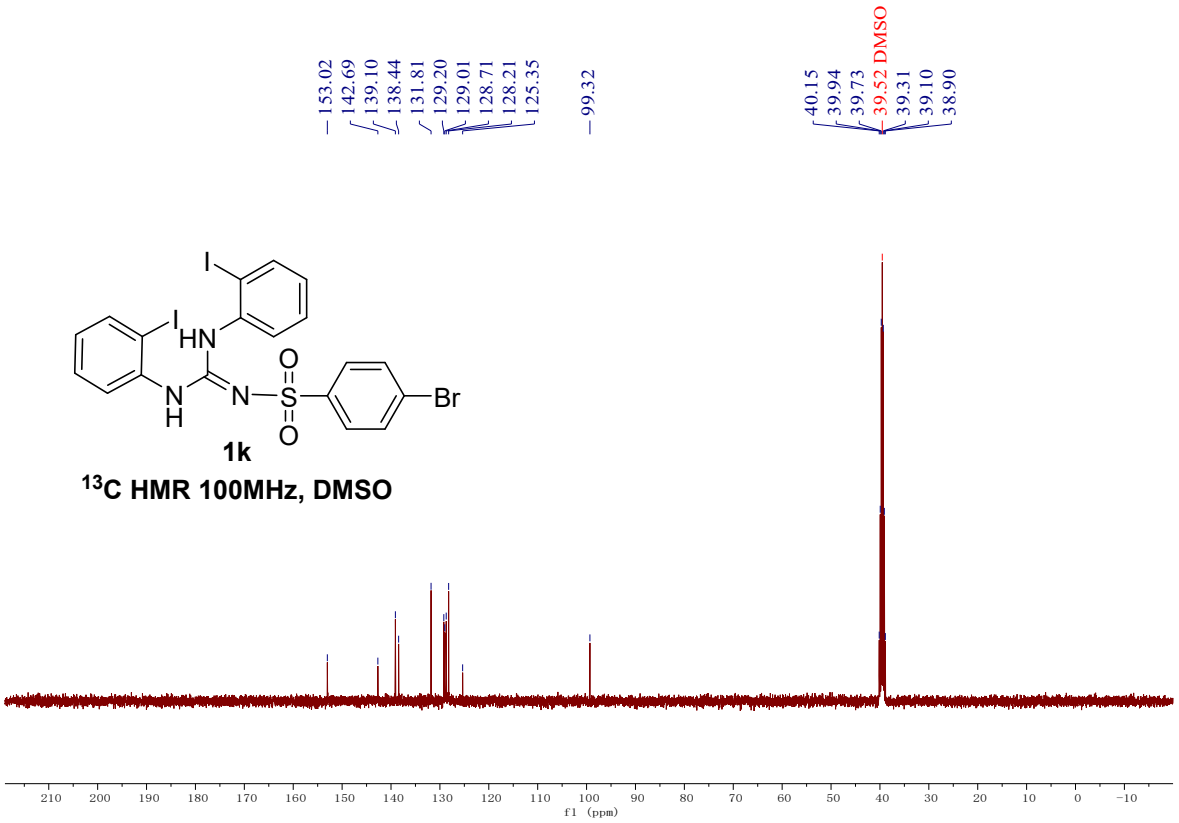
1j

^{19}F HMR 376MHz, DMSO



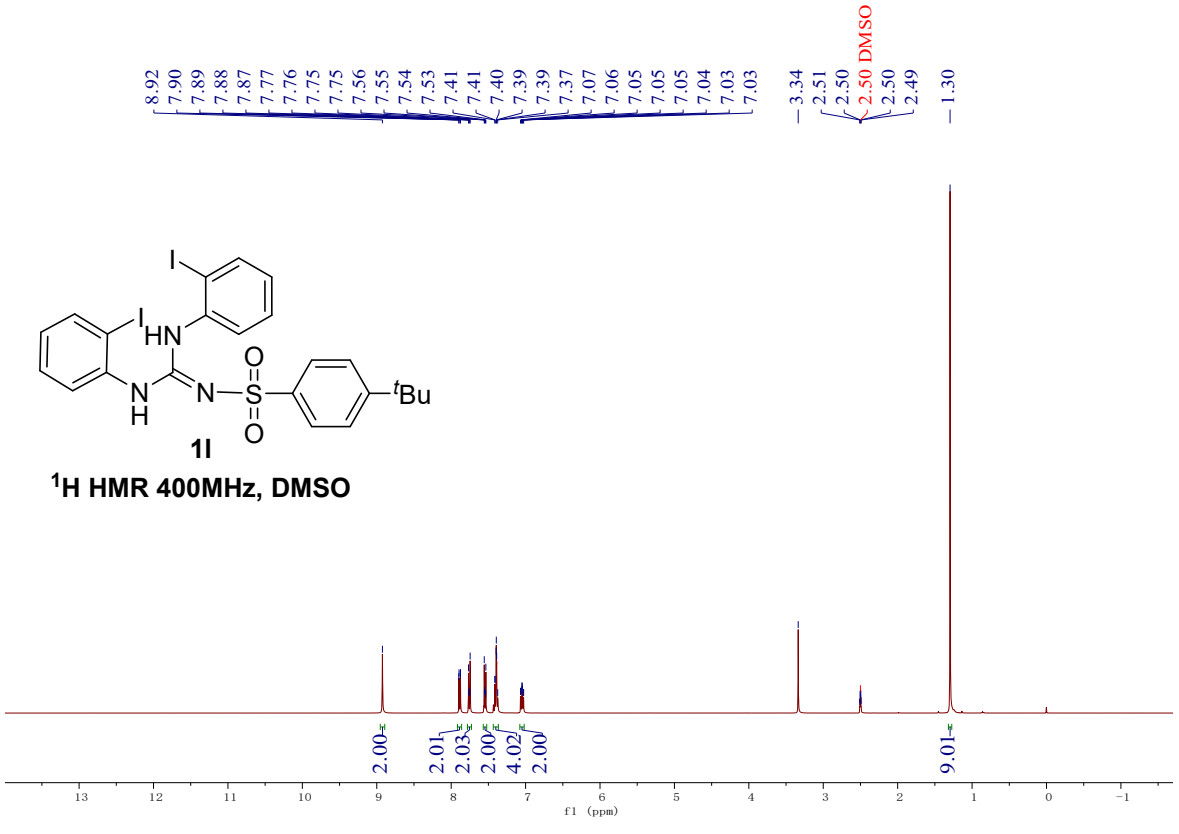
1k

^{1}H HMR 400MHz, DMSO



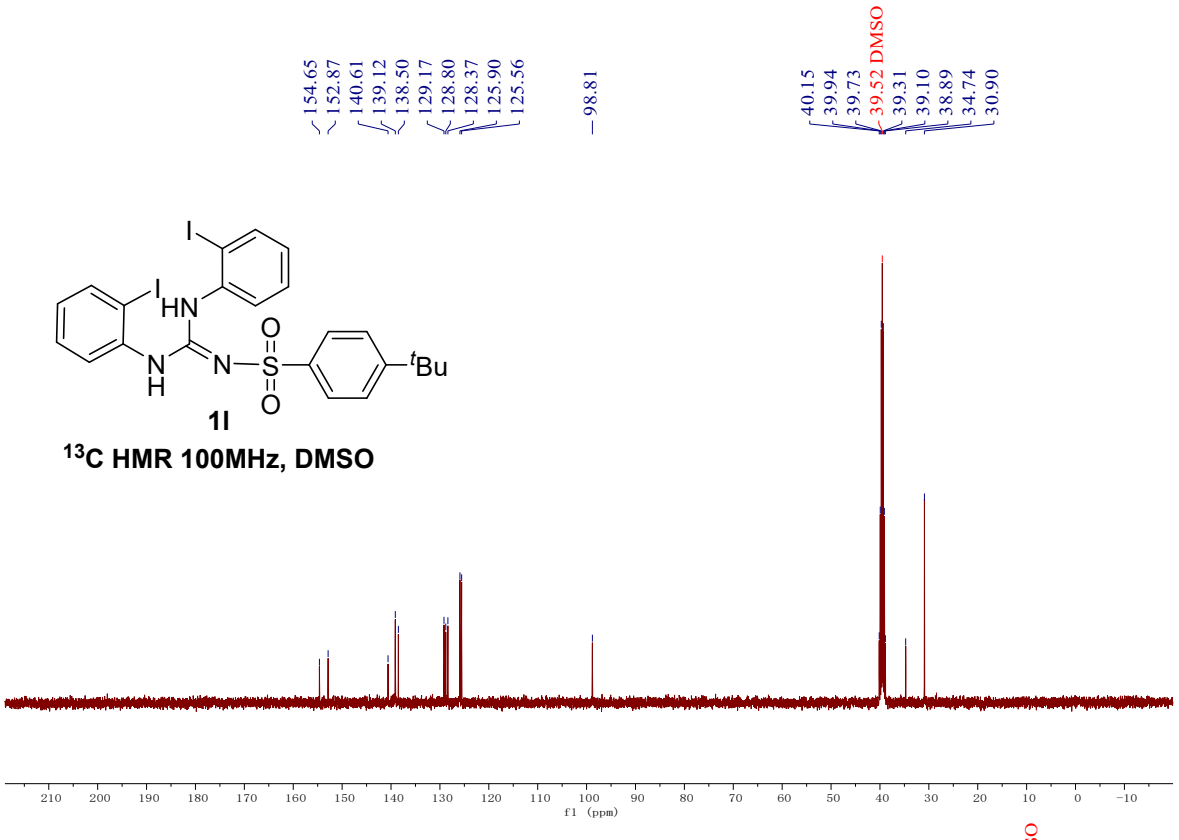
1k

^{13}C HMR 100MHz, DMSO



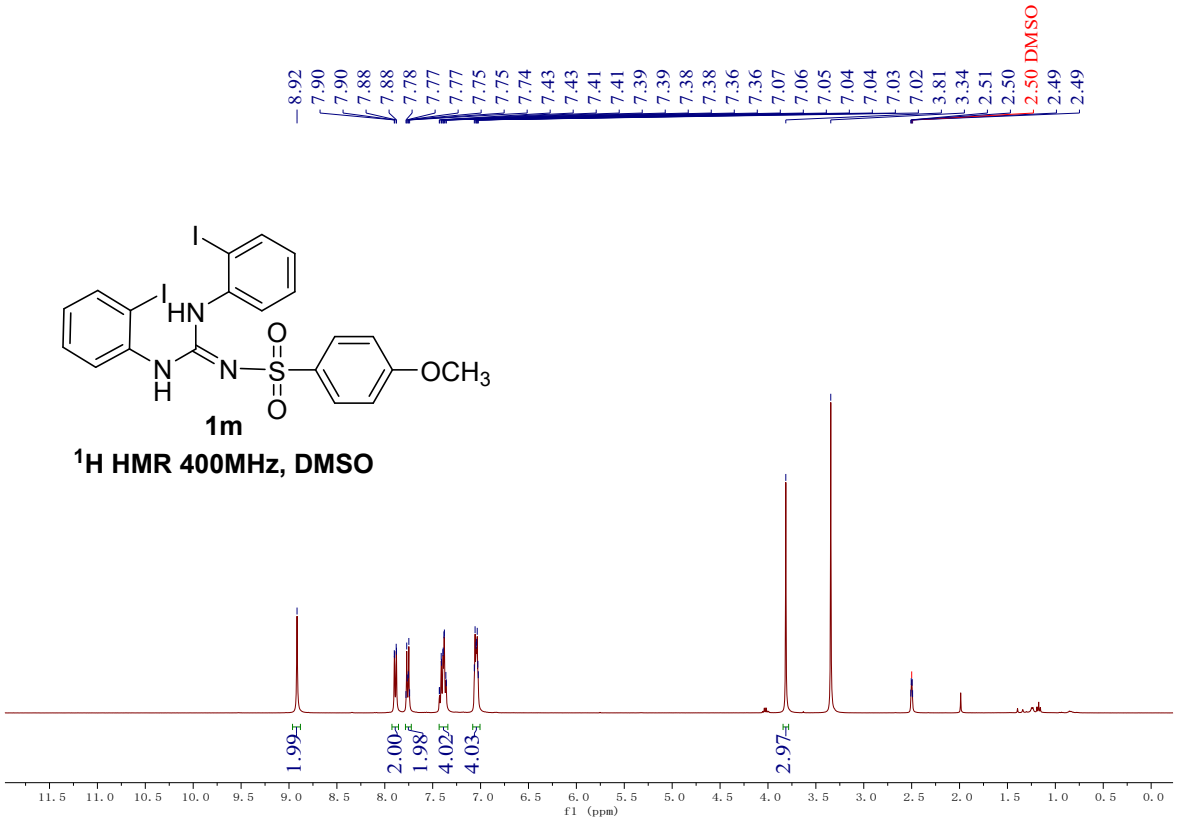
1l

^{1}H HMR 400MHz, DMSO



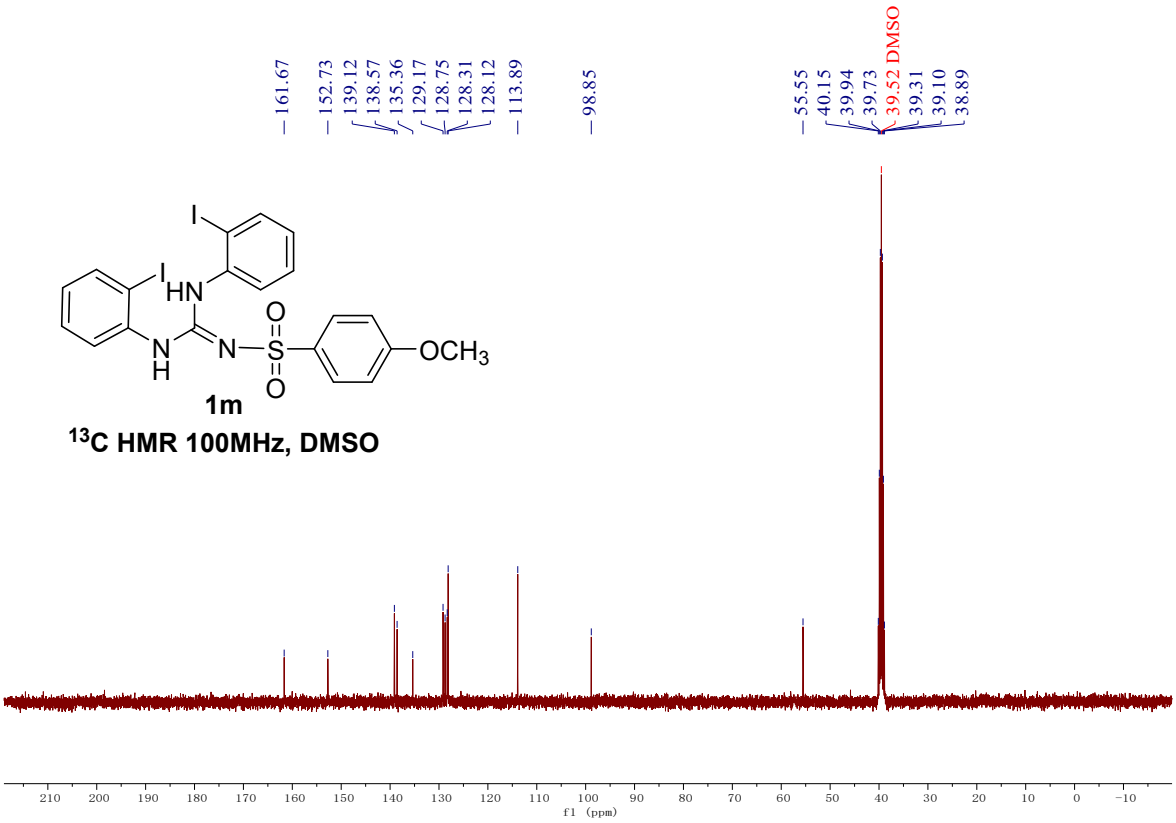
1l

^{13}C HMR 100MHz, DMSO



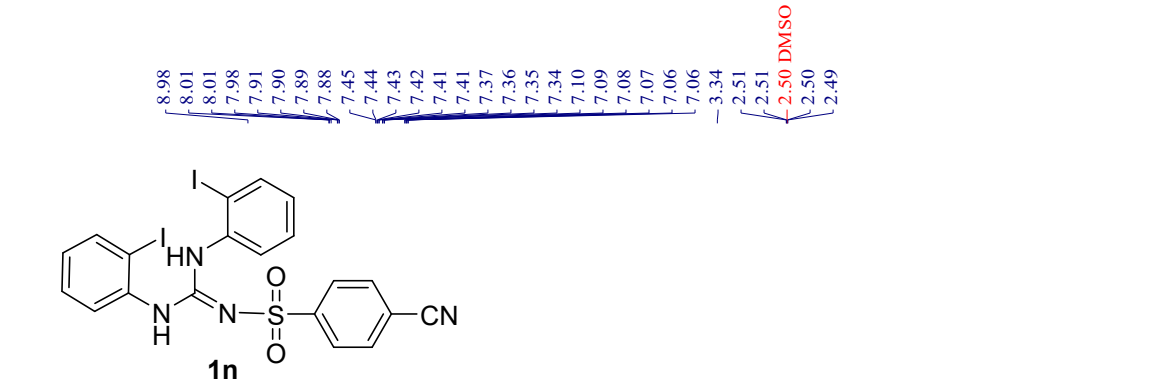
1m

^{1}H HMR 400MHz, DMSO



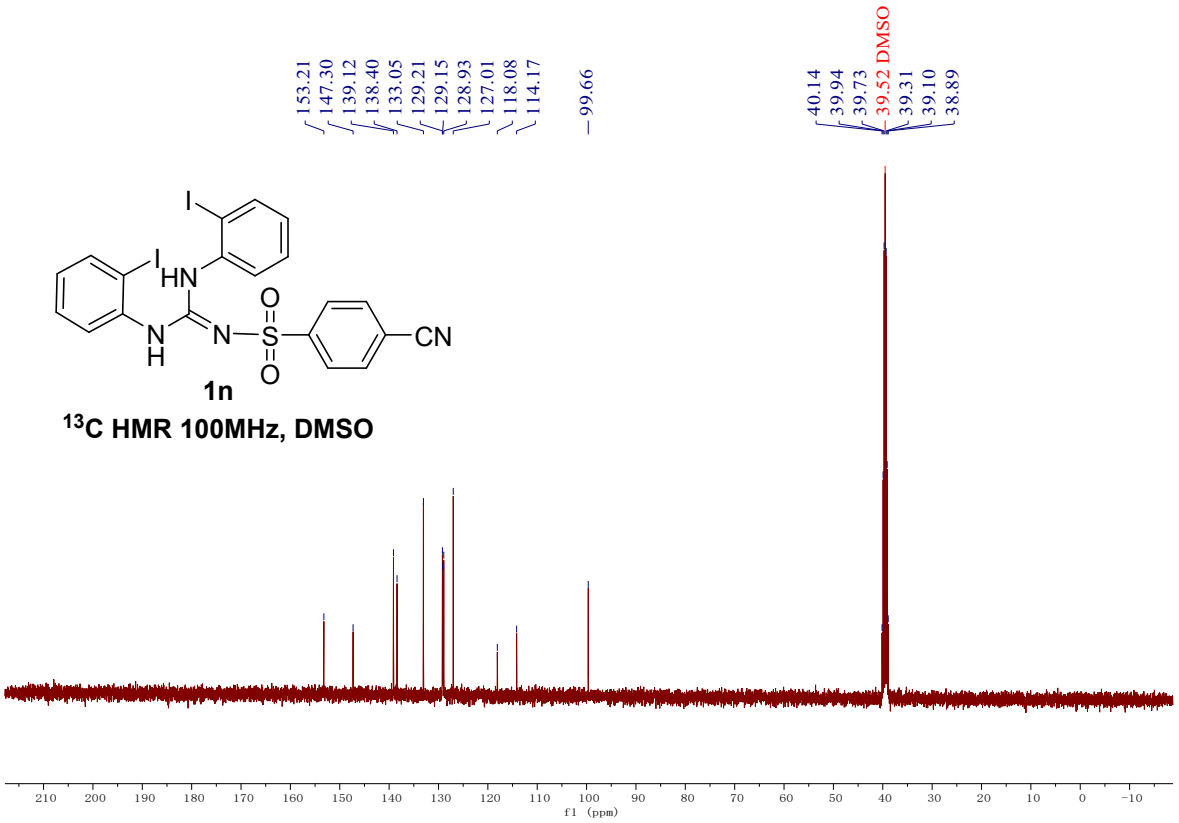
1m

^{13}C HMR 100MHz, DMSO



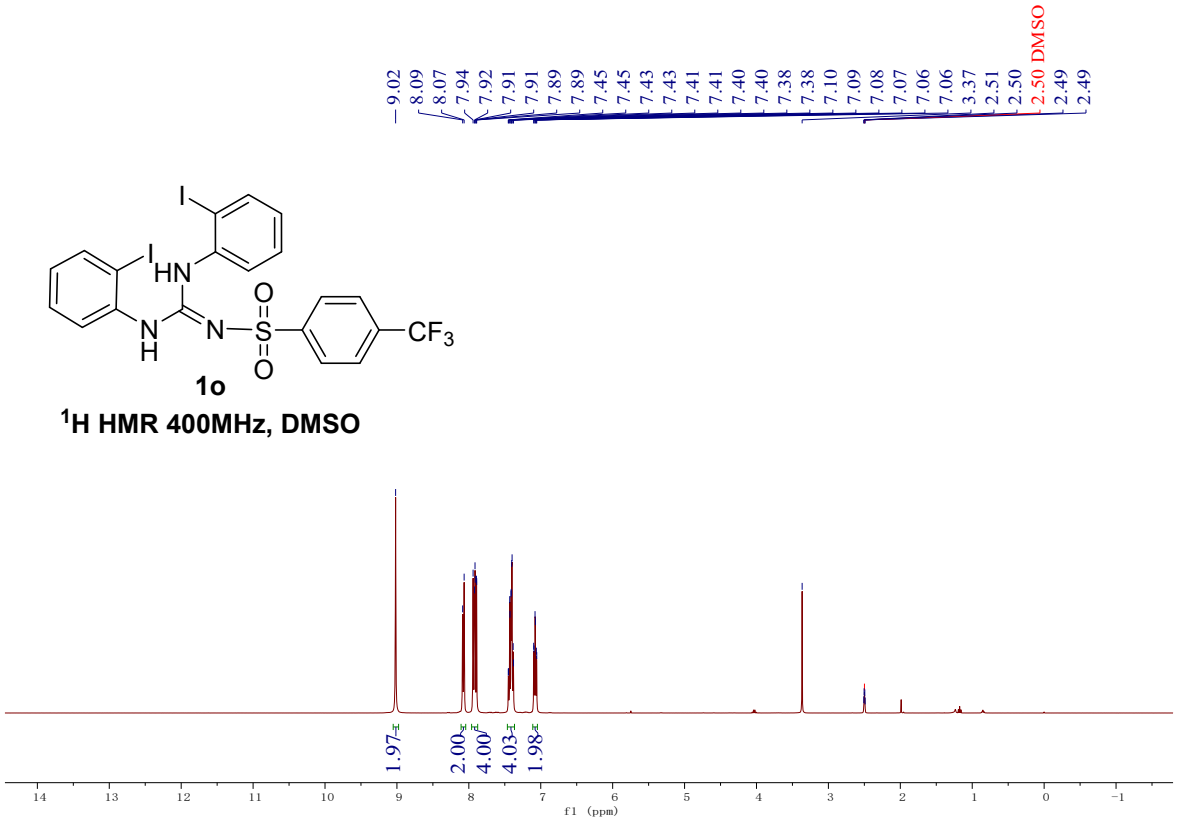
1n

^{1}H HMR 400MHz, DMSO



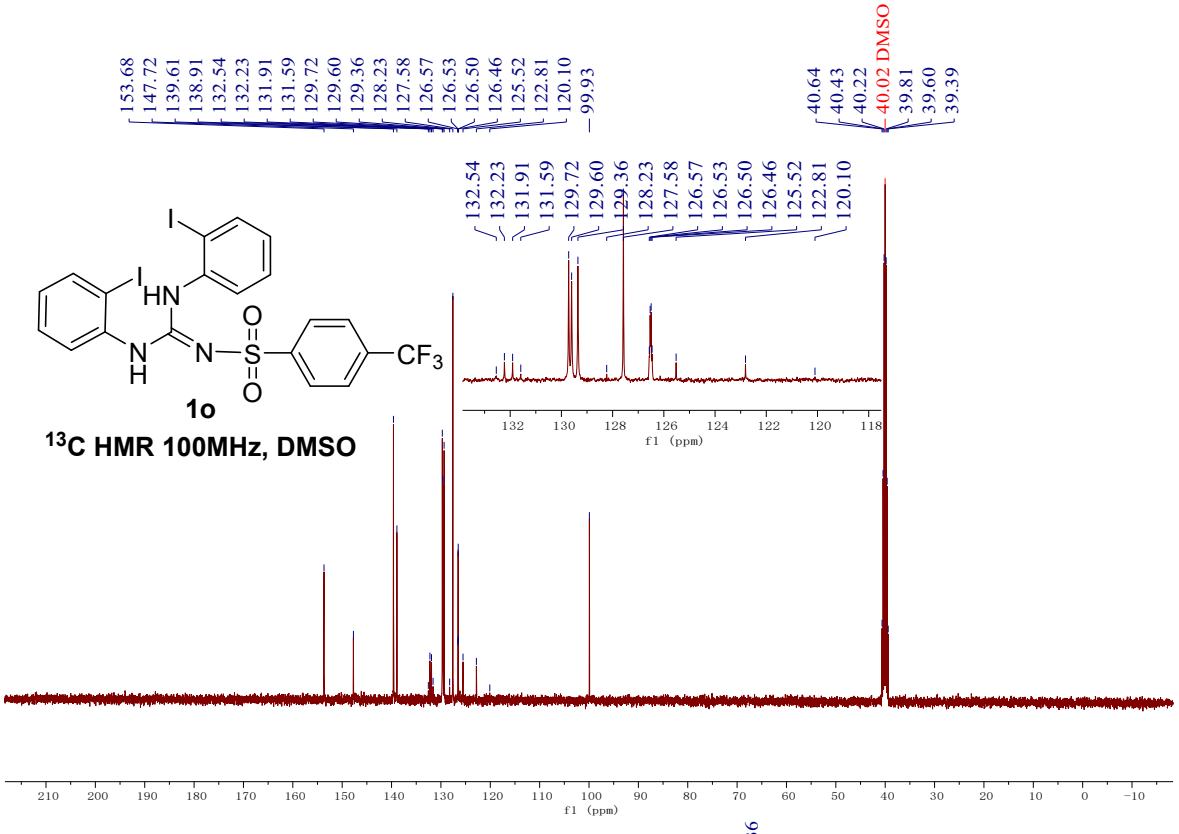
1n

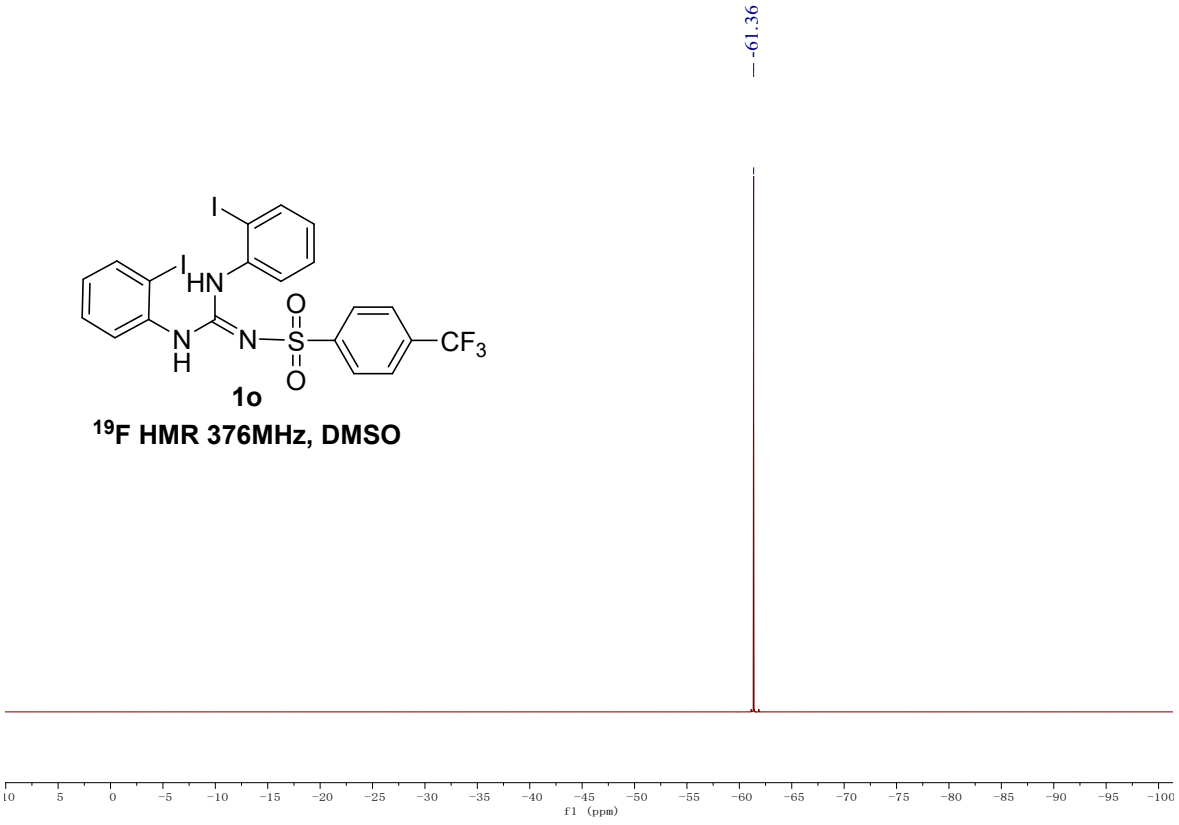
^{13}C HMR 100MHz, DMSO

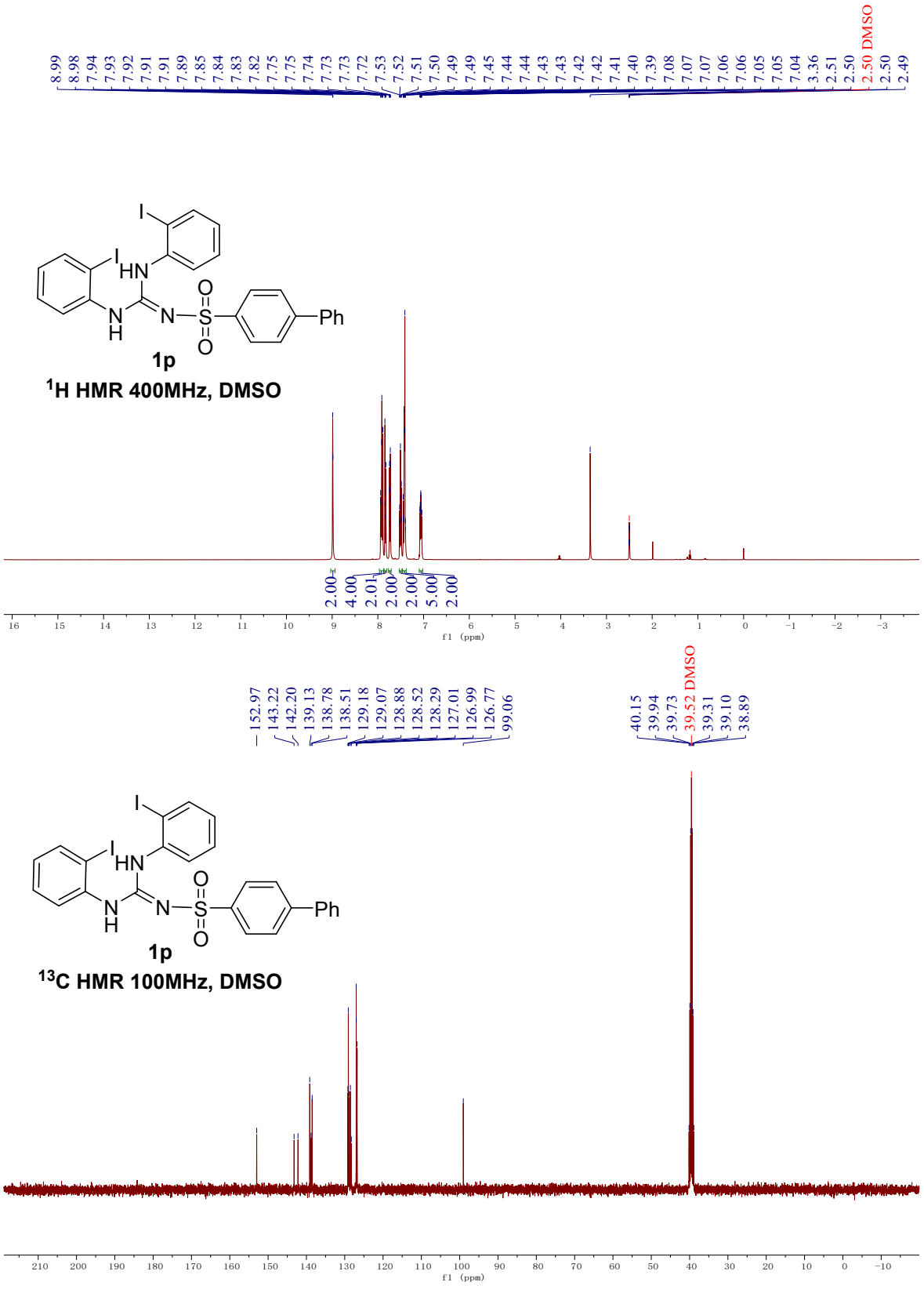


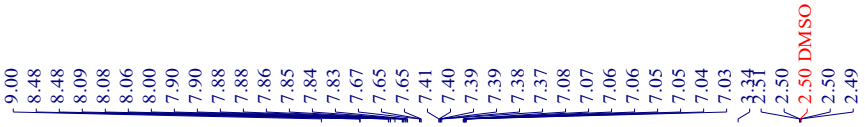
1o

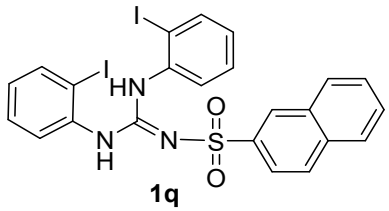
^{1}H HMR 400MHz, DMSO


153.68
147.72
139.61
138.91
132.54
132.23
131.91
131.59
129.72
129.60
129.36
128.23
127.58
126.57
126.53
126.50
126.46
125.52
122.81
120.10
99.93
40.64
40.43
40.22
40.02 DMSO
39.81
39.60
39.39
I
HN
N
H
N
S
O
O
CF3
1o
13C HMR 100MHz, DMSO
f1 (ppm)


-61.36
I
HN
N
H
N
S
O
O
CF3
1o
19F HMR 376MHz, DMSO
f1 (ppm)

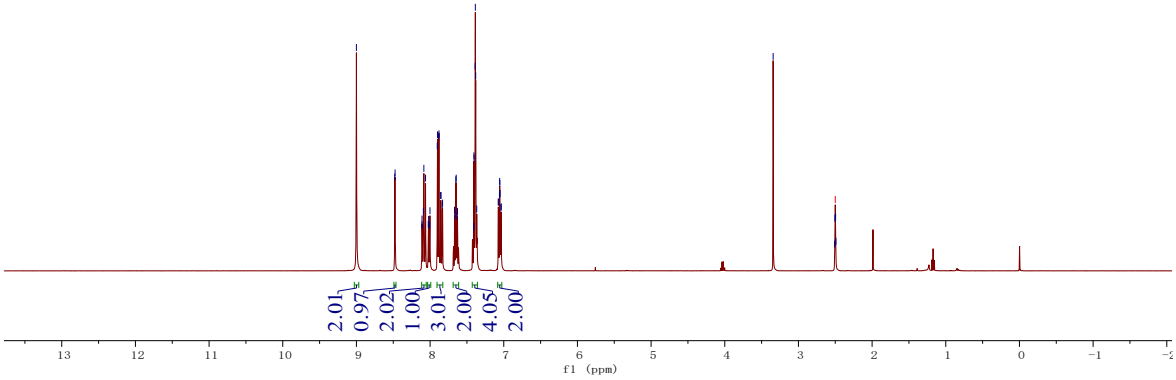

8.99
8.98
7.94
7.93
7.92
7.91
7.91
7.89
7.85
7.84
7.83
7.82
7.75
7.75
7.74
7.73
7.73
7.72
7.53
7.52
7.51
7.50
7.49
7.49
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.08
7.07
7.07
7.06
7.06
7.05
7.05
7.04
3.36
2.51
2.50
2.50 DMSO
2.50
2.49
I
I
HN
N
H
N
S
O
O
Ph
1p
1H HMR 400MHz, DMSO
2.00
4.00
2.01
2.00
2.00
5.00
2.00
f1 (ppm)
152.97
143.22
142.20
139.13
138.78
138.51
129.18
129.07
128.88
128.52
128.29
127.01
126.99
126.77
99.06
40.15
39.94
39.73
39.52 DMSO
39.31
39.10
38.89
I
I
HN
N
H
N
S
O
O
Ph
1p
13C HMR 100MHz, DMSO
f1 (ppm)

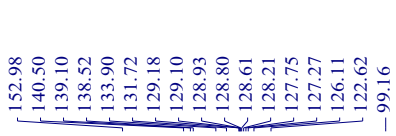


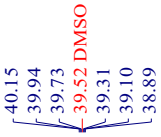


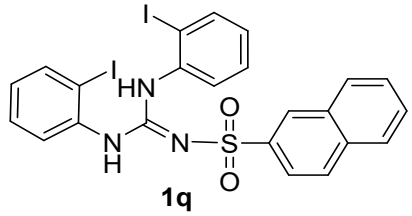
1q

^{1}H HMR 400MHz, DMSO



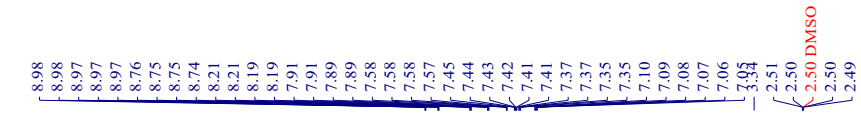


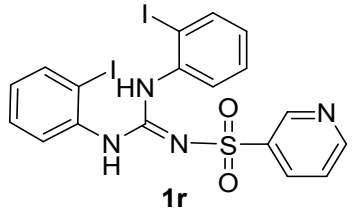




1q

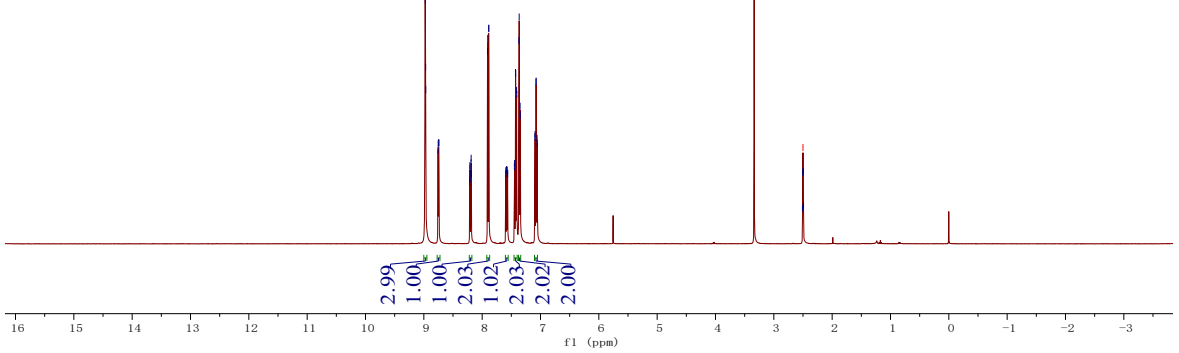
^{13}C HMR 100MHz, DMSO

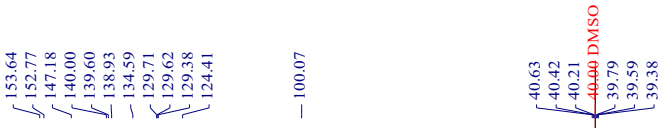


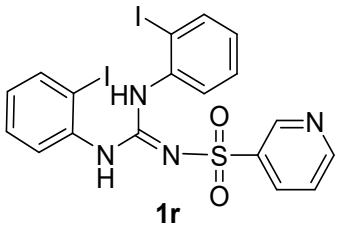


1r

^{1}H HMR 400MHz, DMSO

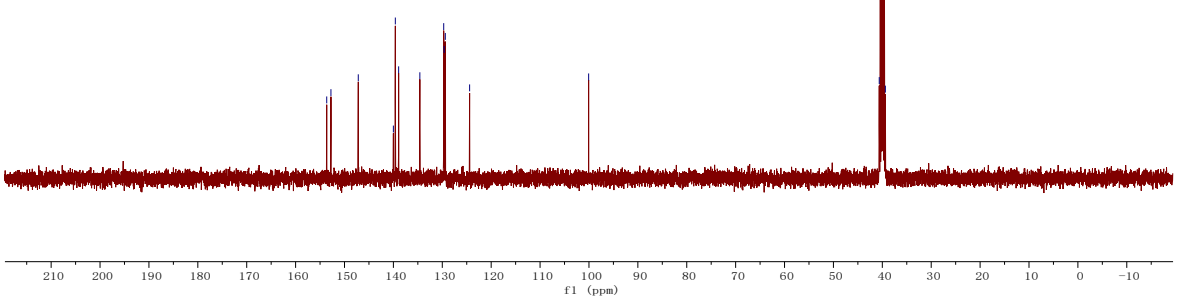


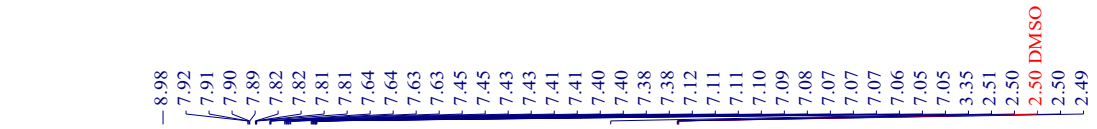


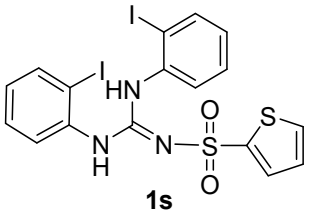


1r

^{13}C HMR 100MHz, DMSO

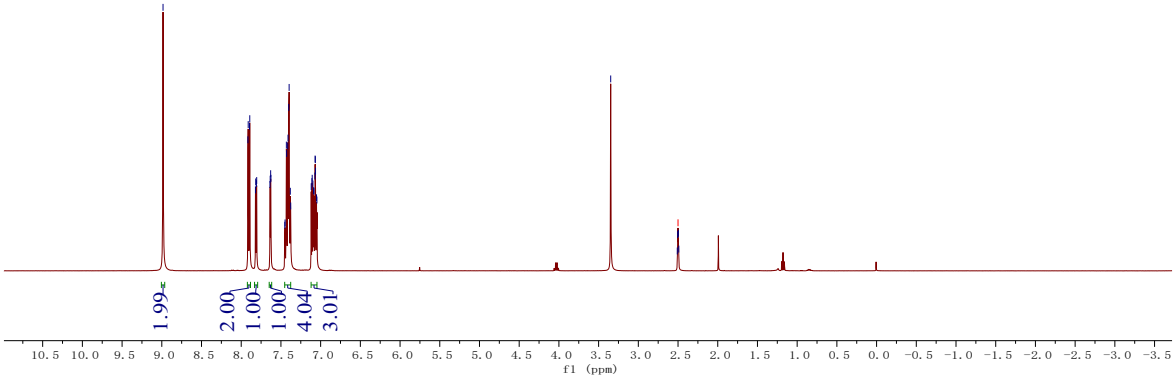


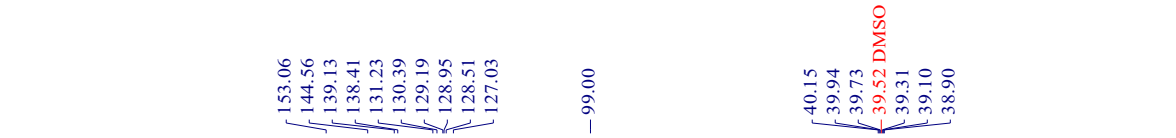


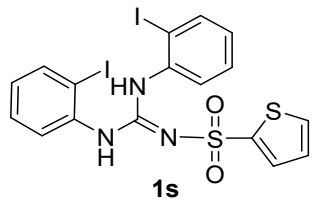


1s

^{1}H HMR 400MHz, DMSO

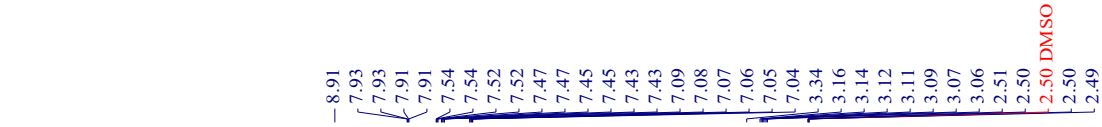


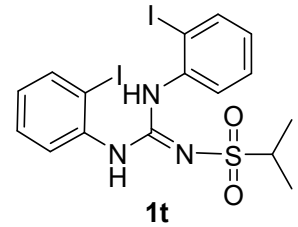




1s

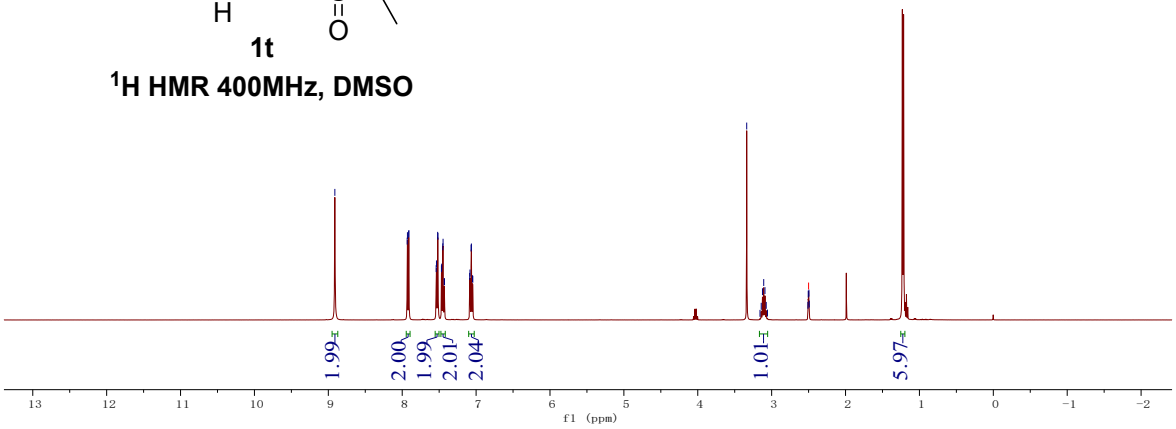
^{13}C HMR 100MHz, DMSO

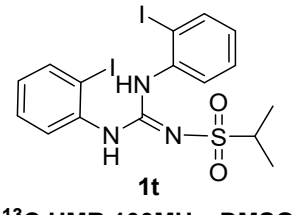




1t

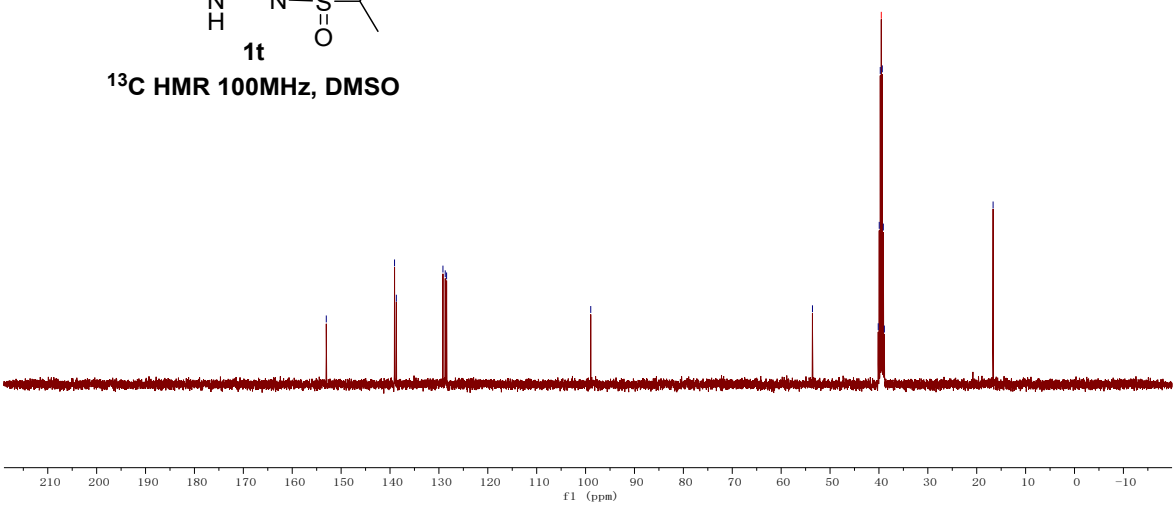
^{1}H HMR 400MHz, DMSO

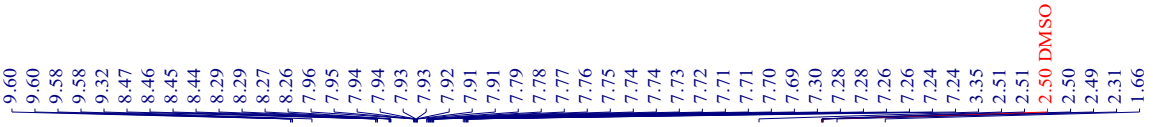


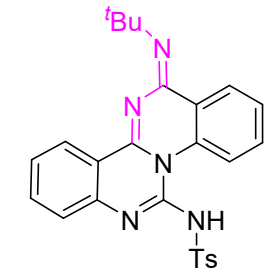


1t

^{13}C HMR 100MHz, DMSO

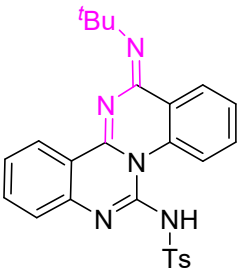






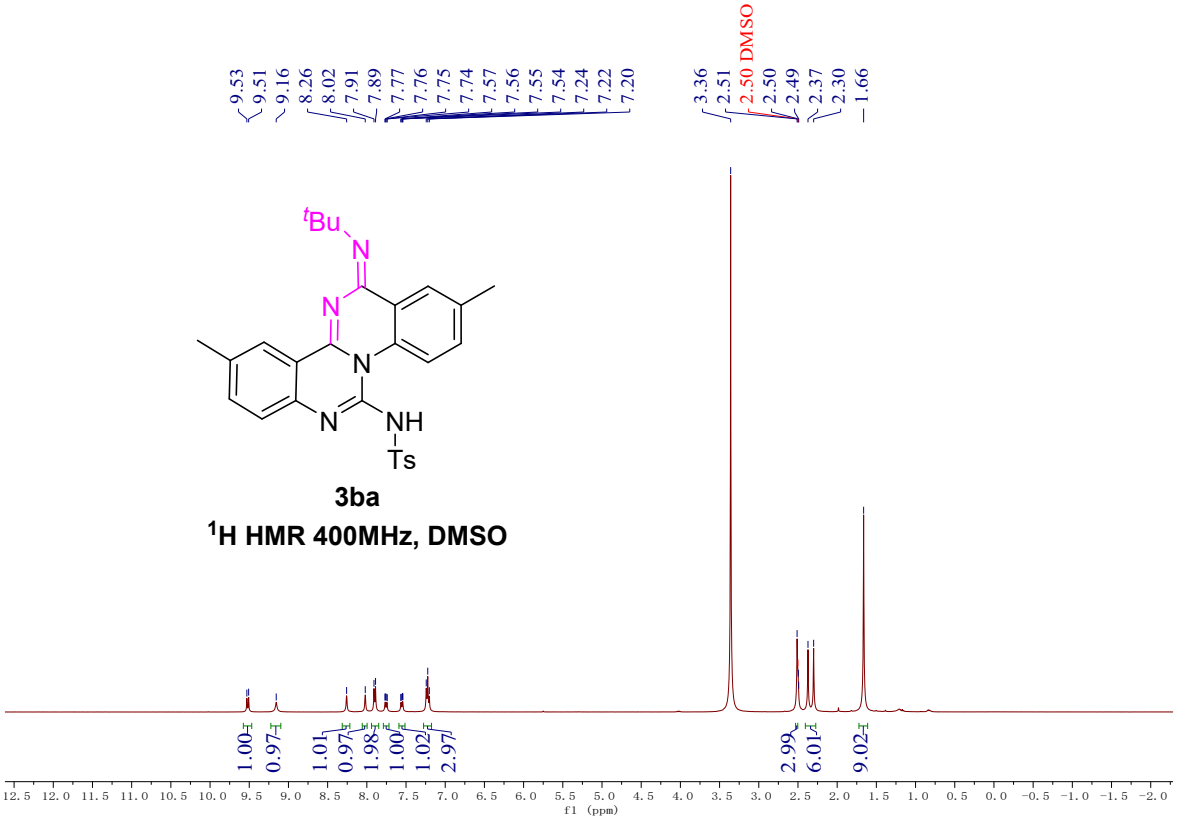
3aa

^{1}H HMR 400MHz, DMSO



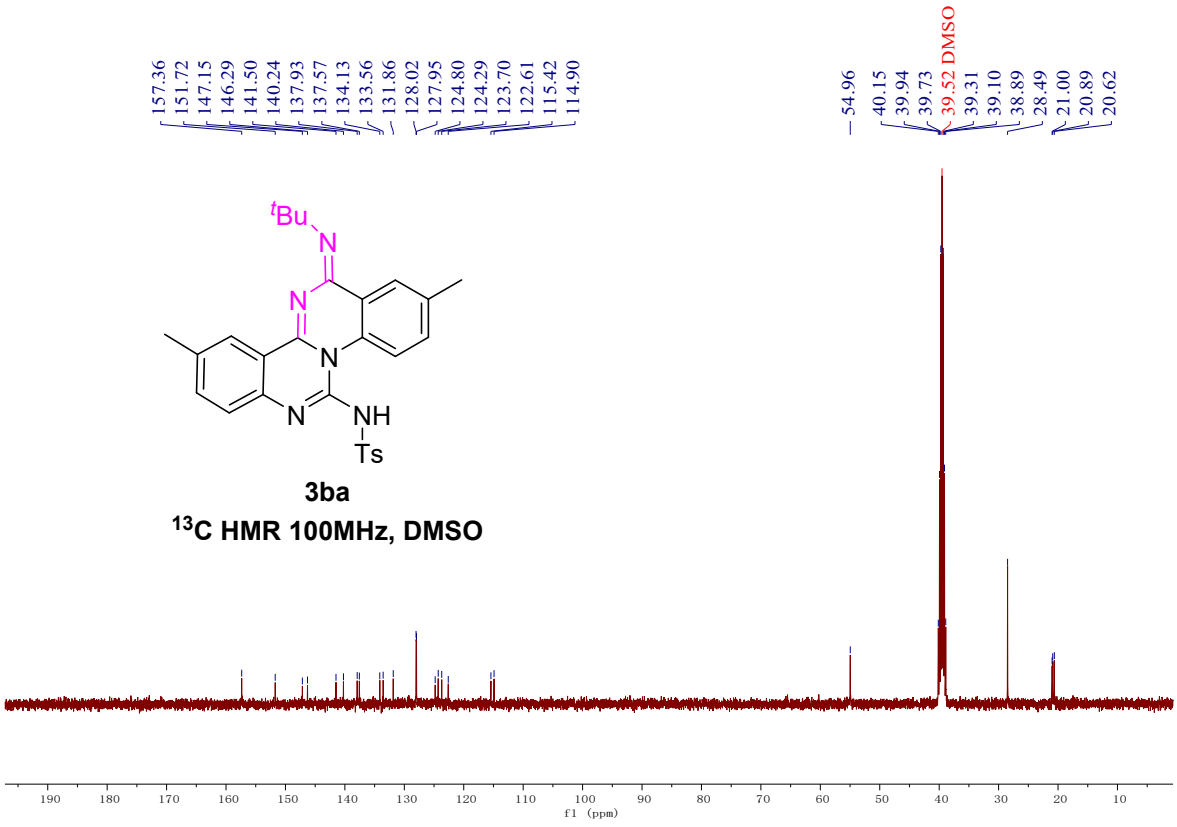
3aa

^{13}C HMR 100MHz, DMSO



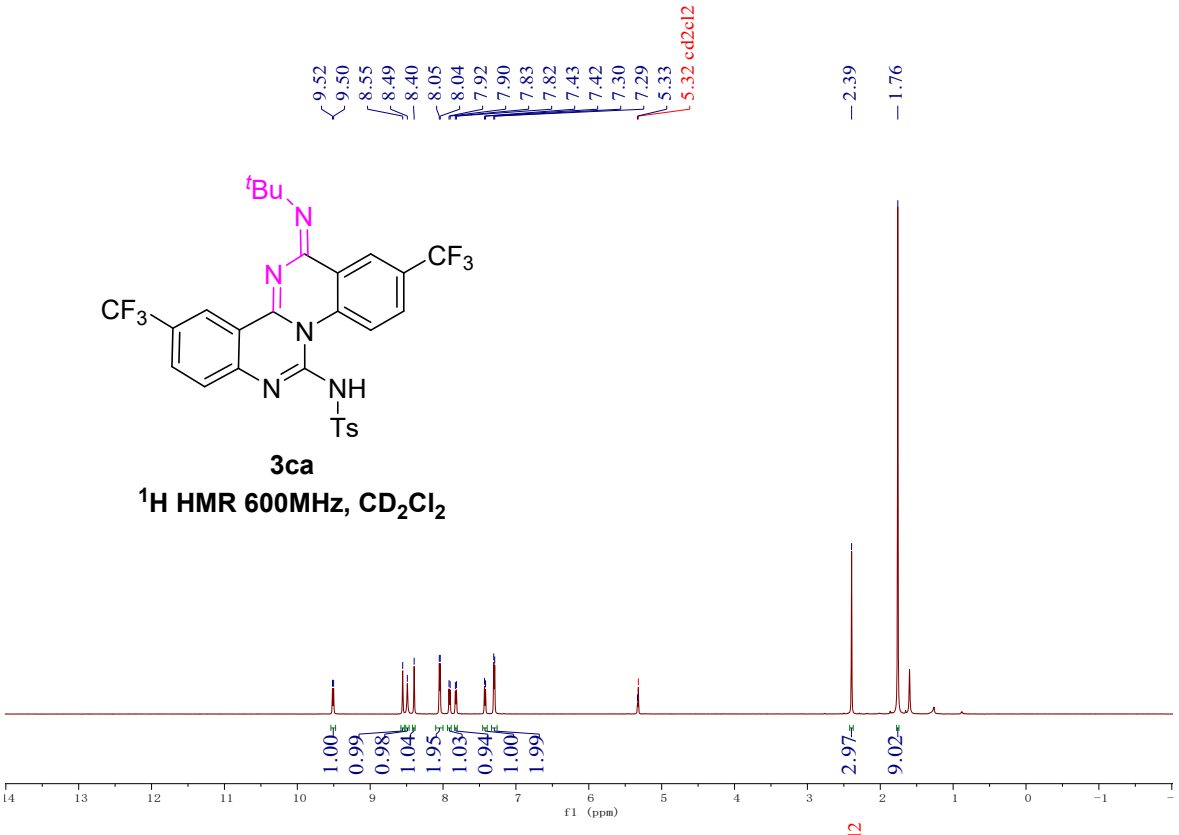
3ba

^{1}H HMR 400MHz, DMSO



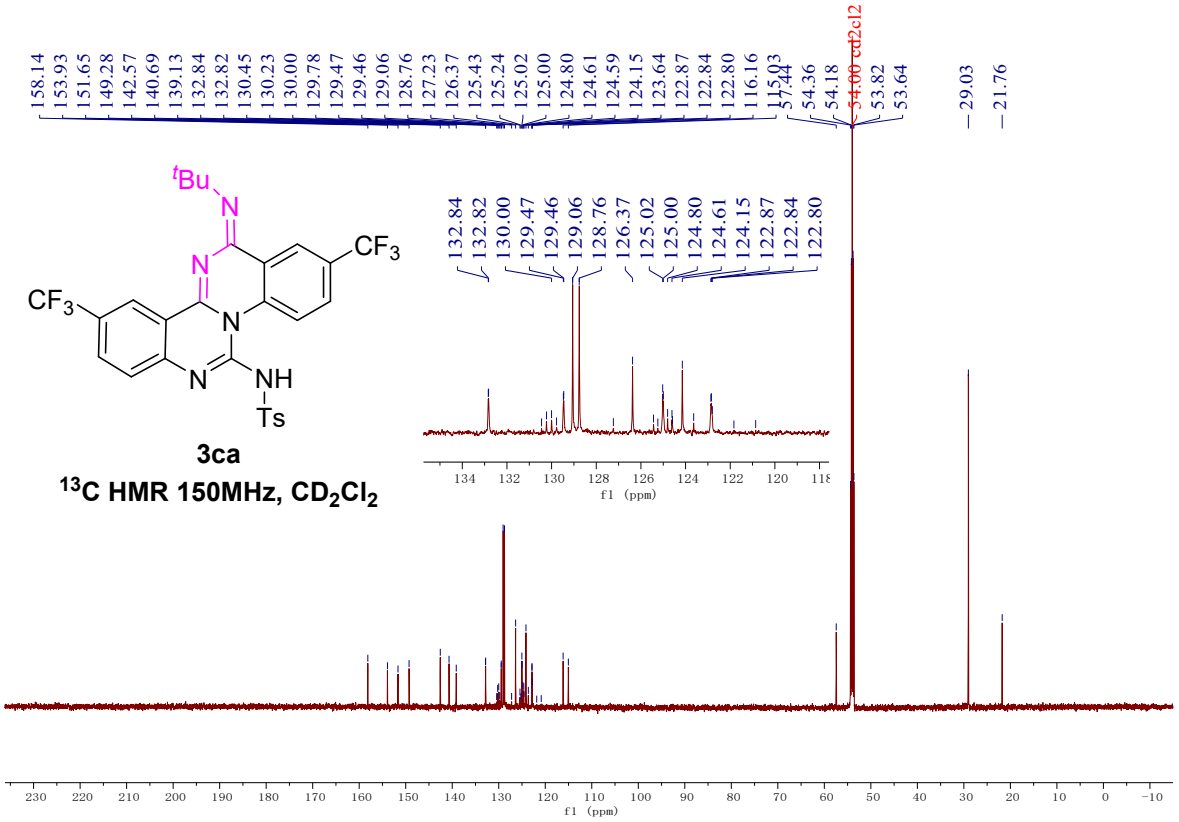
3ba

^{13}C HMR 100MHz, DMSO



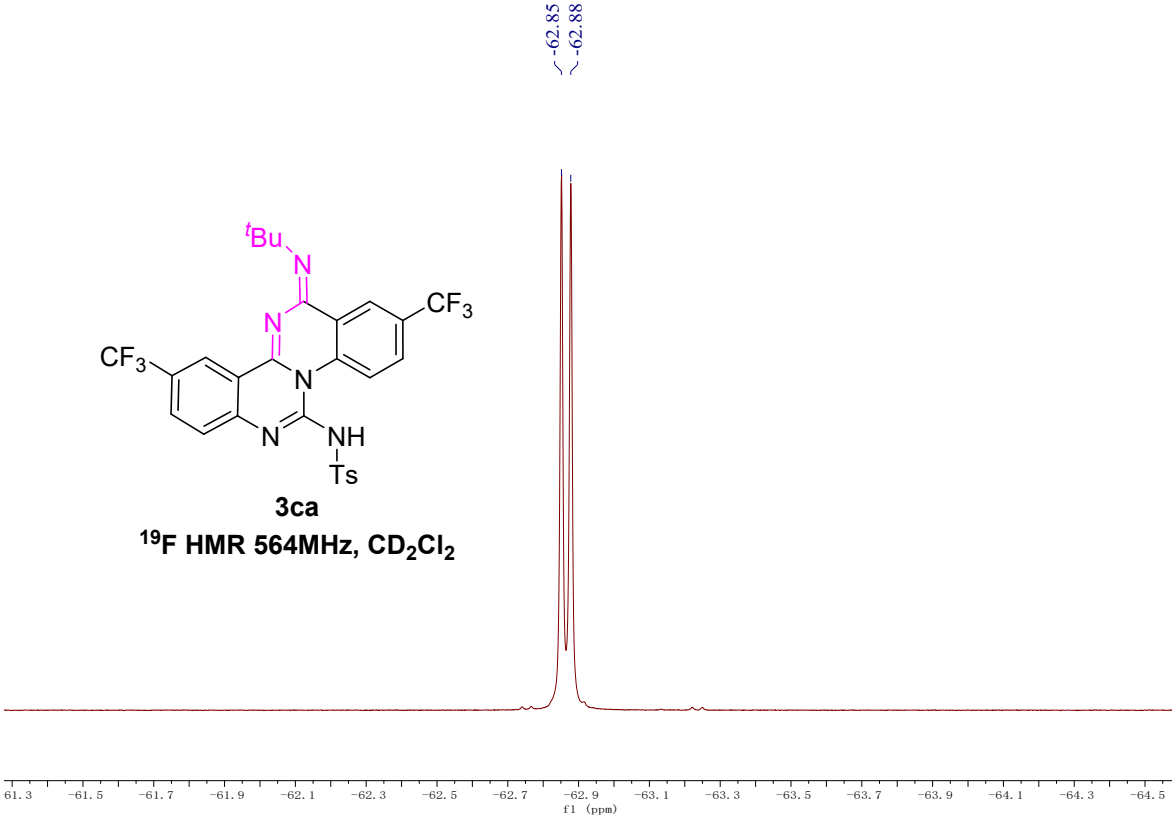
3ca

^{1}H HMR 600MHz, CD_2Cl_2



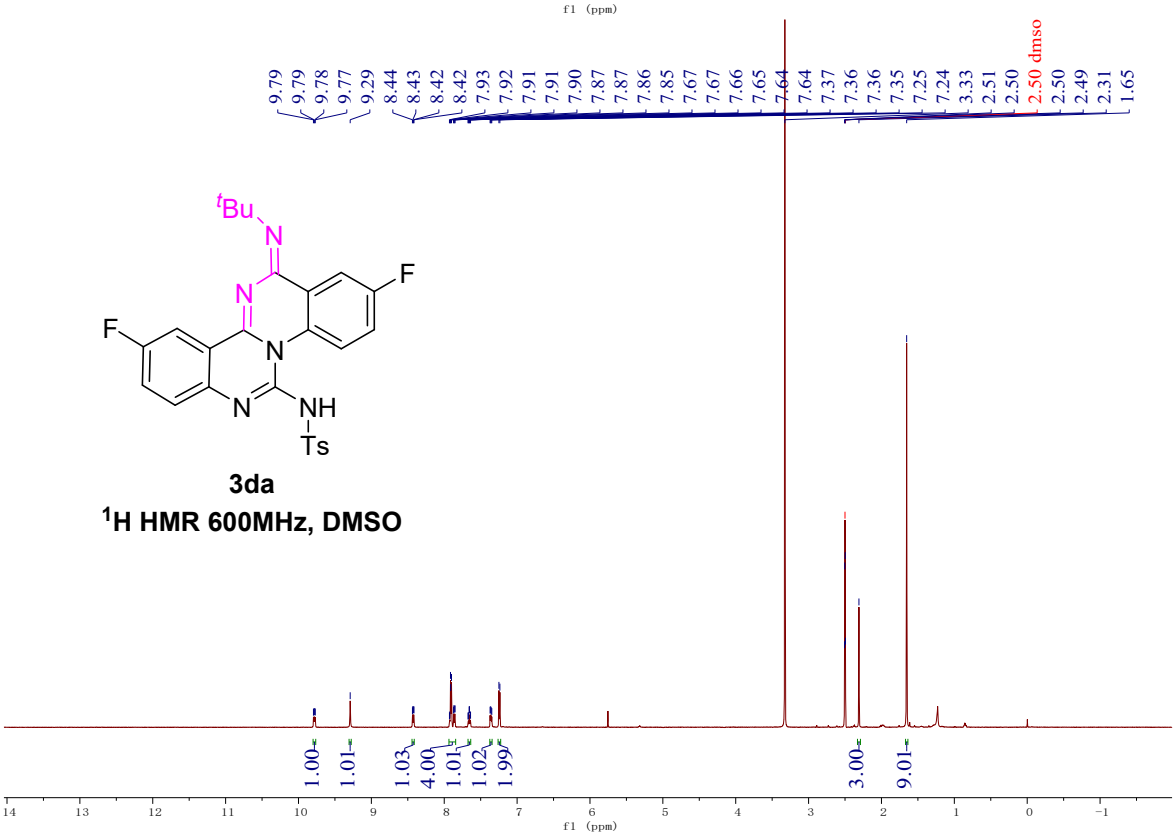
3ca

^{13}C HMR 150MHz, CD_2Cl_2



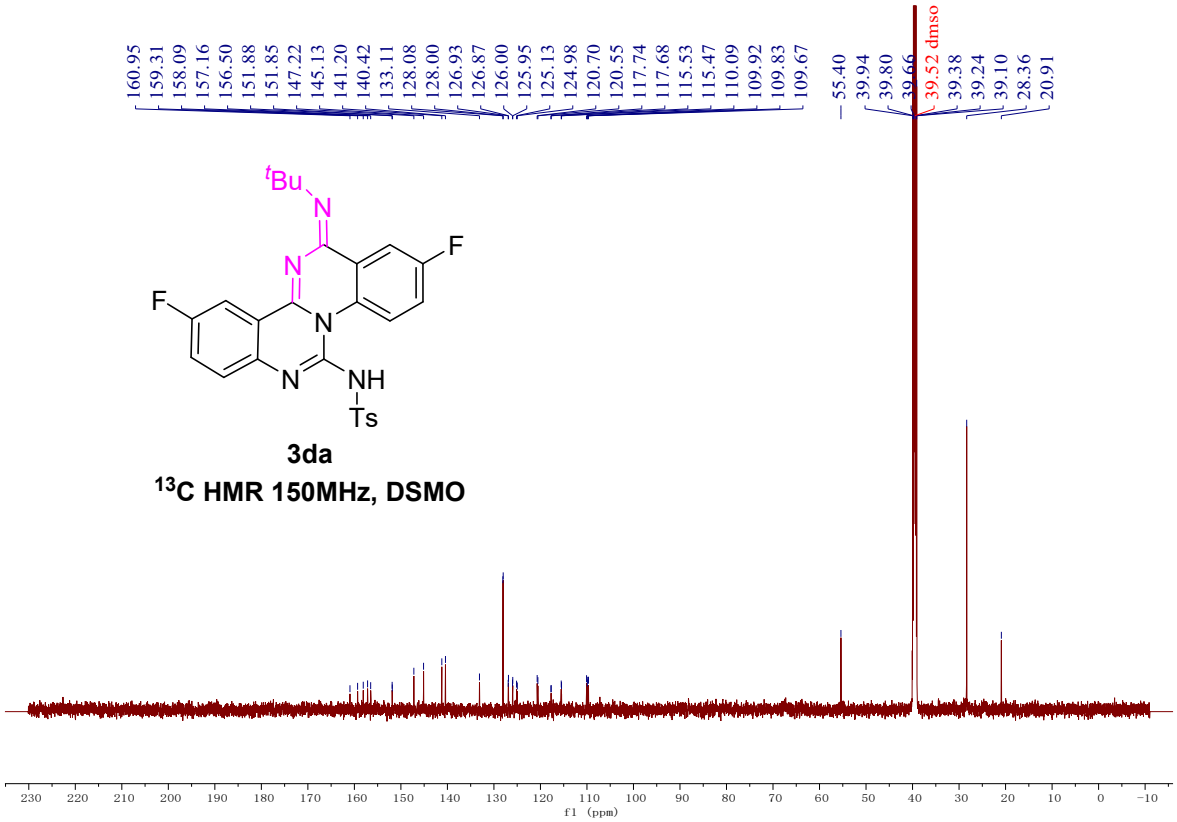
3ca

^{19}F HMR 564MHz, CD_2Cl_2



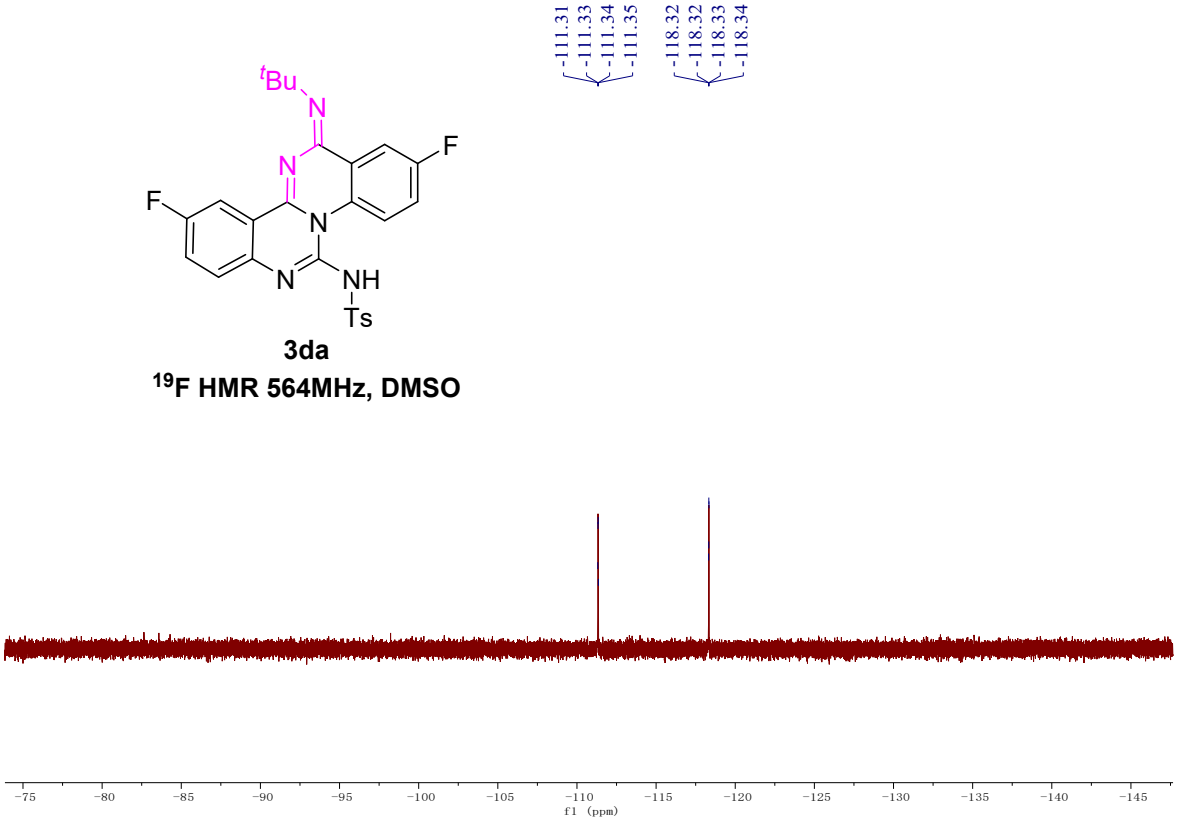
3da

^{1}H HMR 600MHz, DMSO



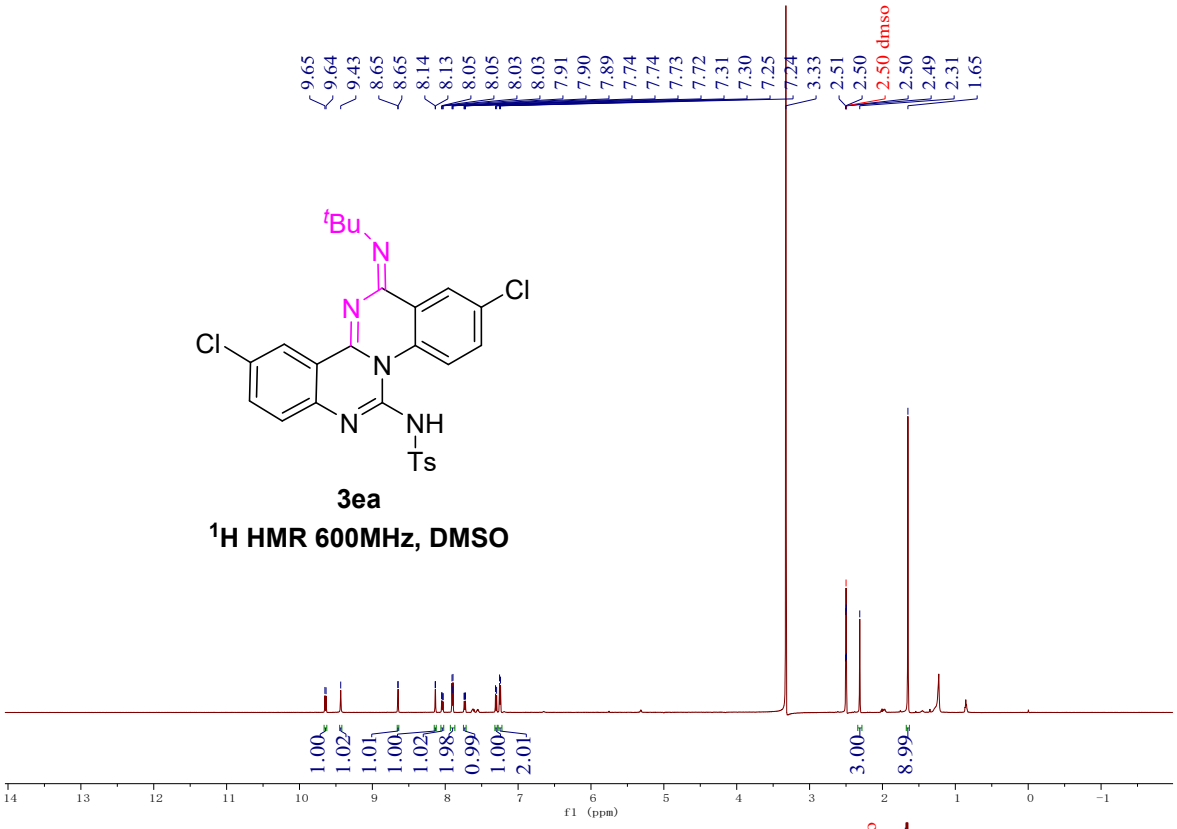
3da

^{13}C HMR 150MHz, DSMO



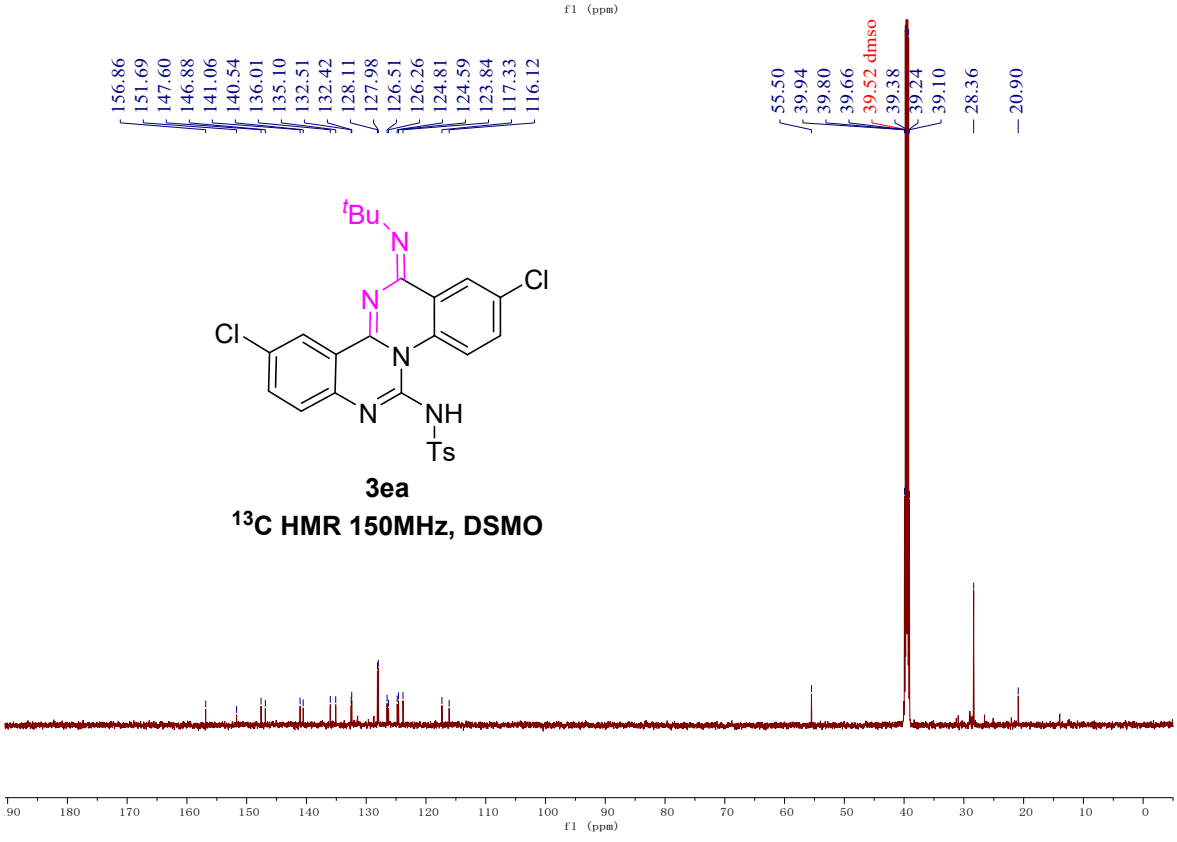
3da

^{19}F HMR 564MHz, DMSO



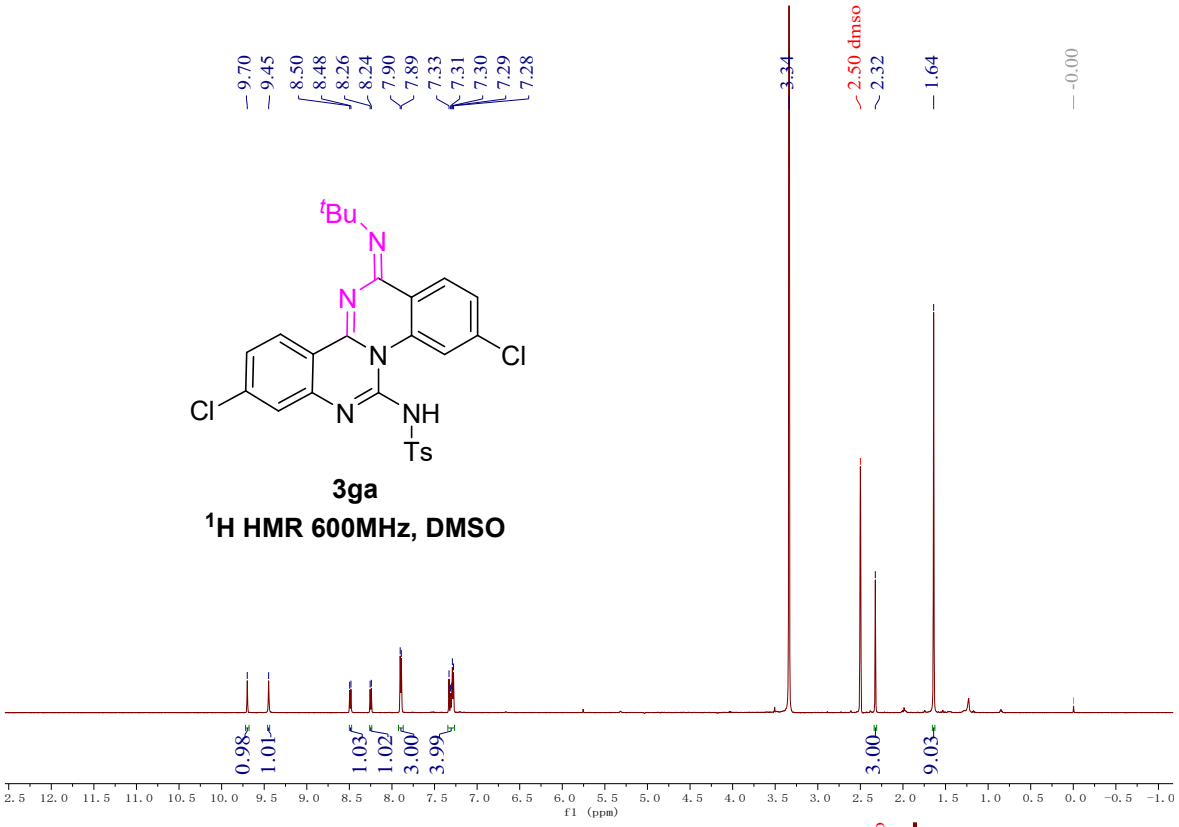
3ea

^{1}H HMR 600MHz, DMSO



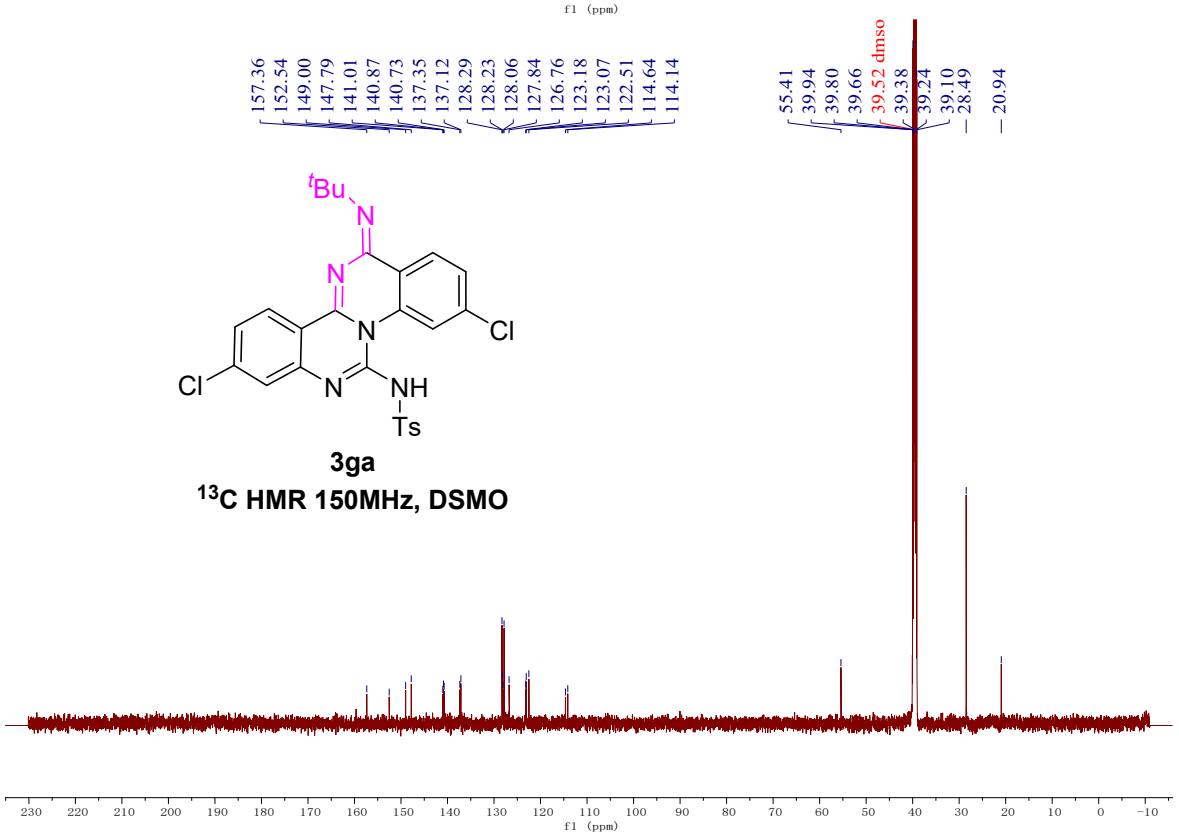
3ea

^{13}C HMR 150MHz, DSMO



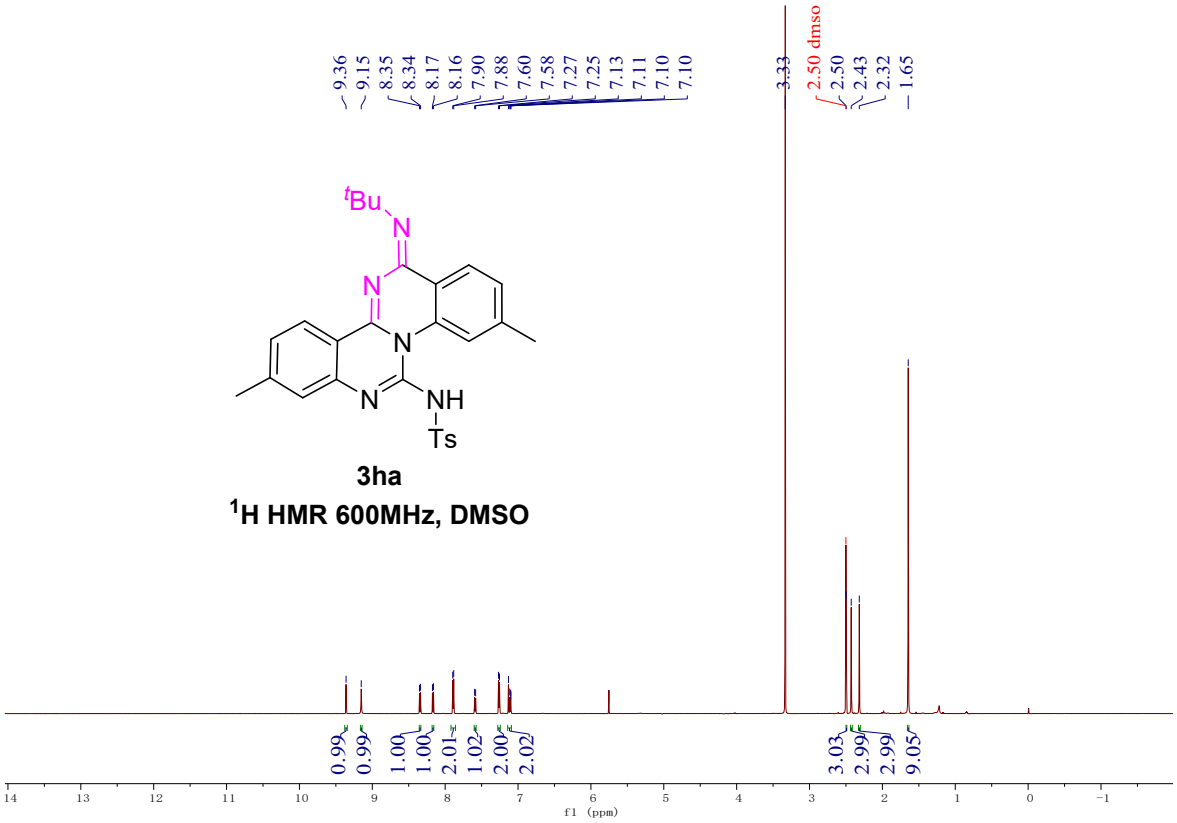
3ga

^{1}H HMR 600MHz, DMSO



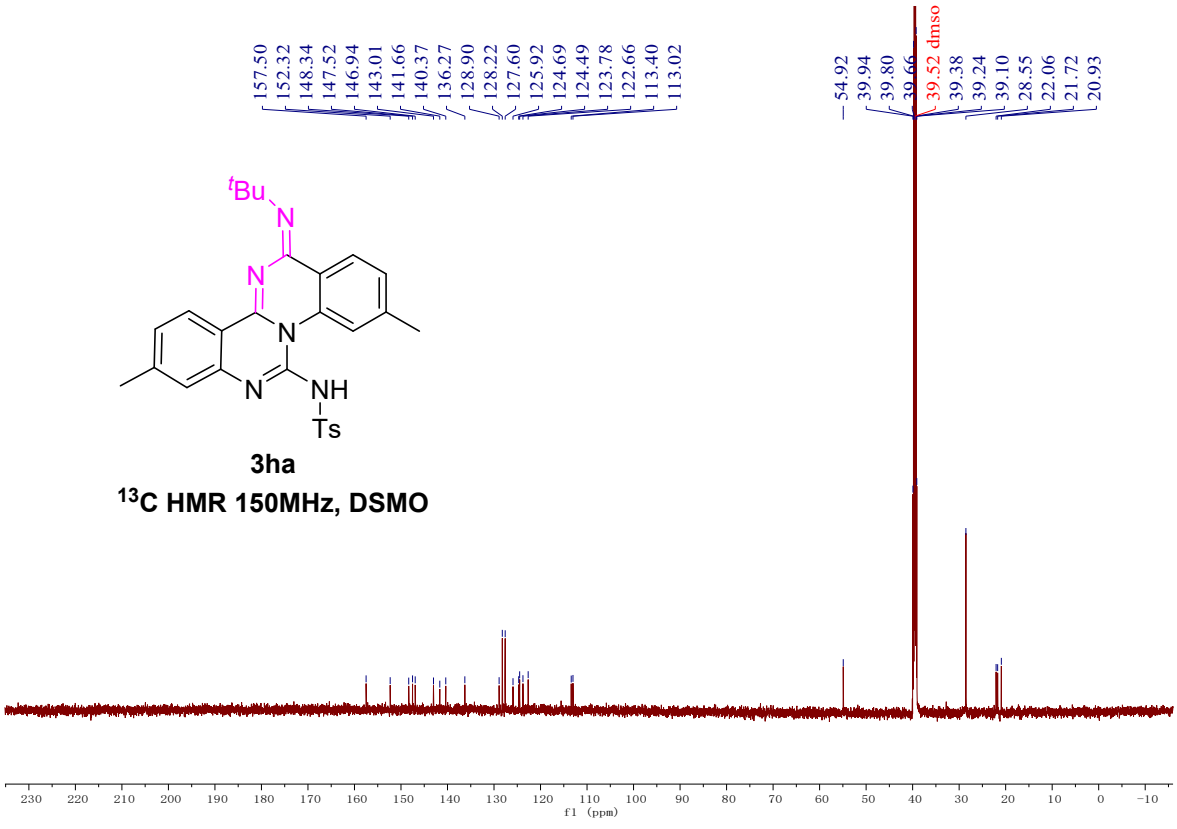
3ga

^{13}C HMR 150MHz, DSMO



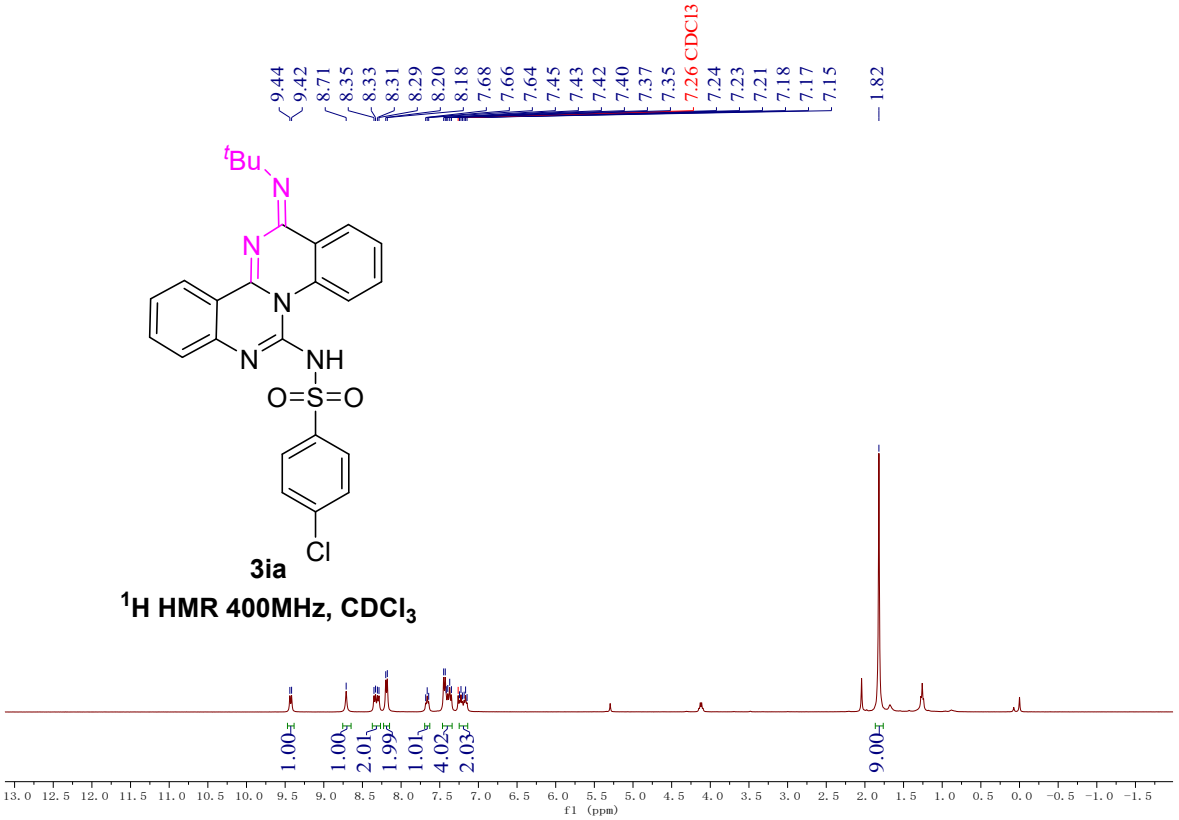
3ha

^{1}H HMR 600MHz, DMSO



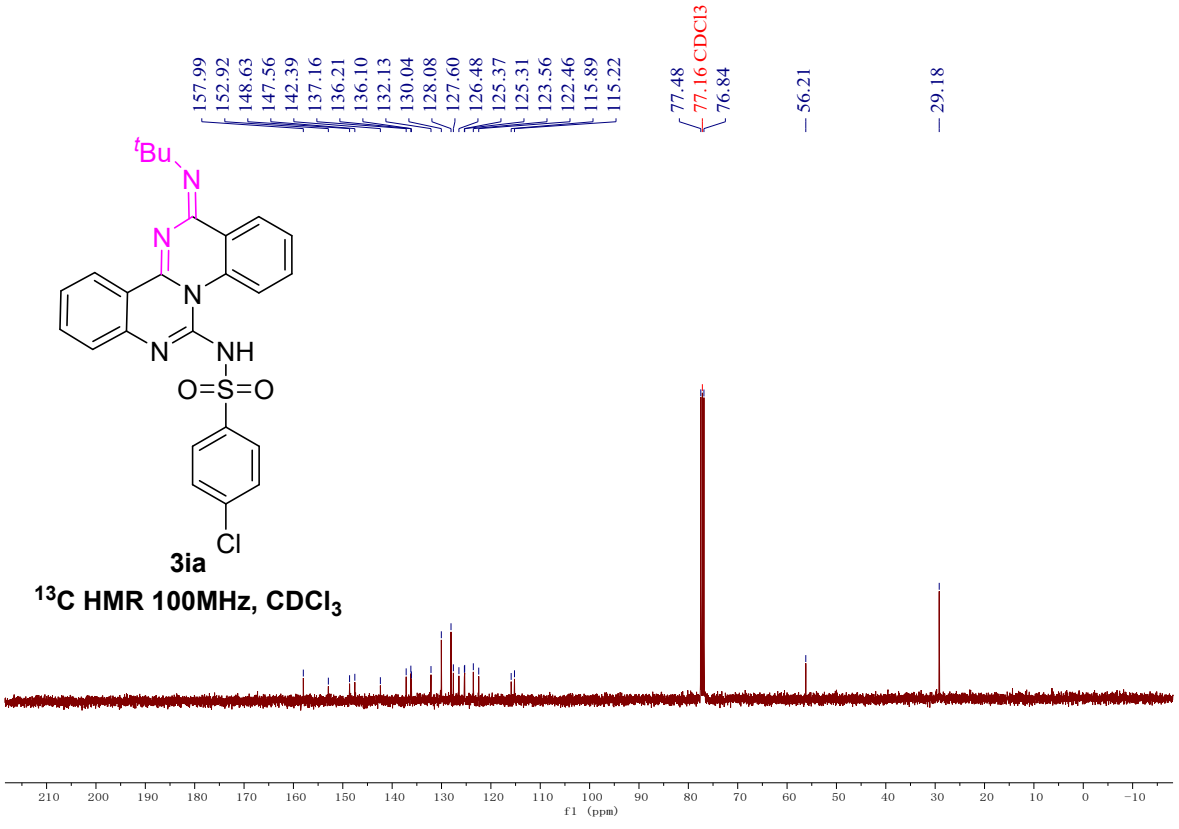
3ha

^{13}C HMR 150MHz, DSMO



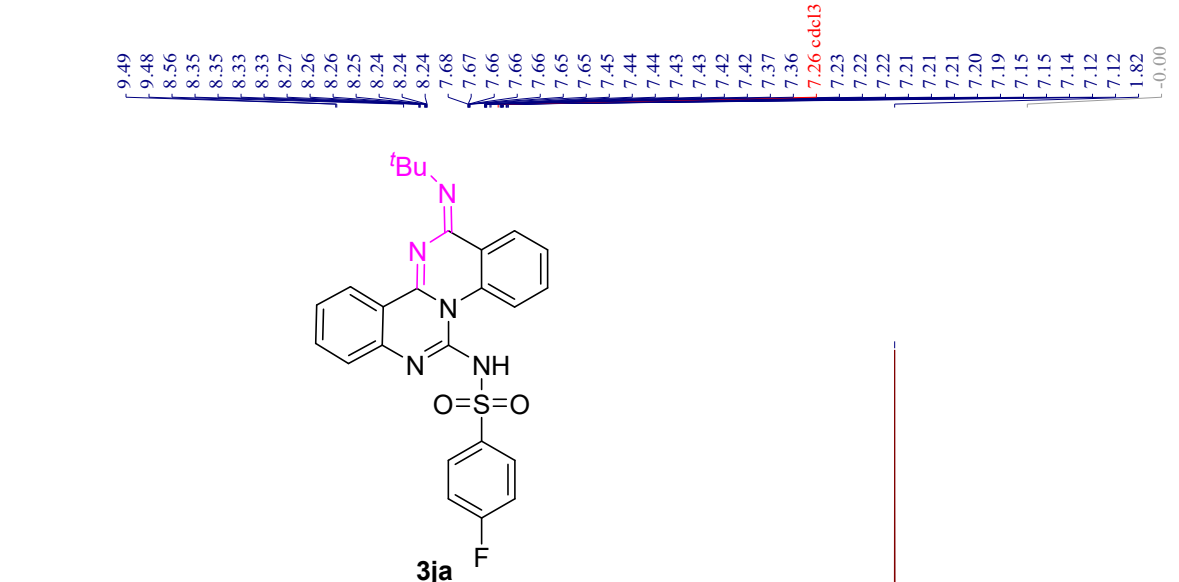
3ia

^{1}H HMR 400MHz, $CDCl_3$



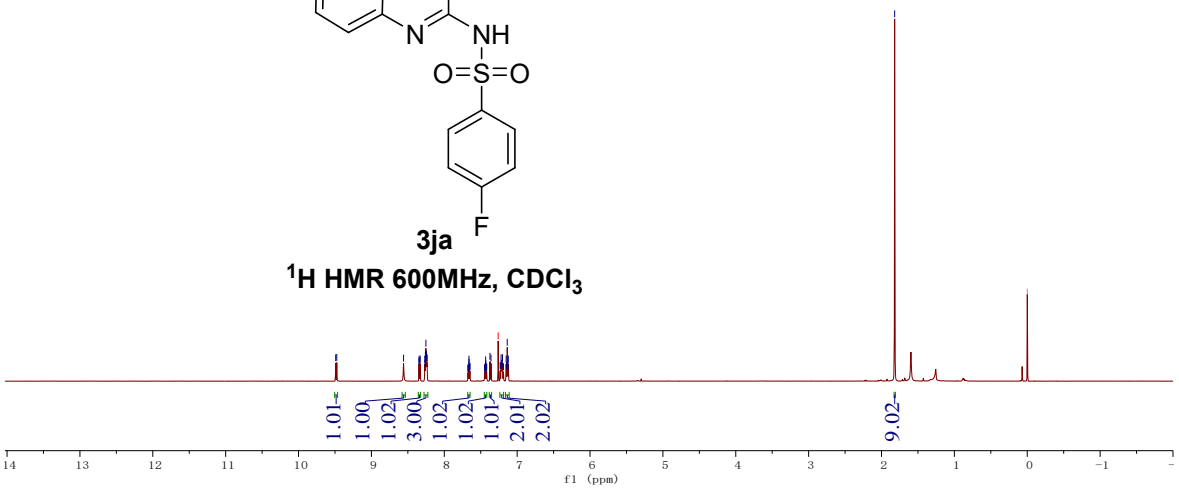
3ia

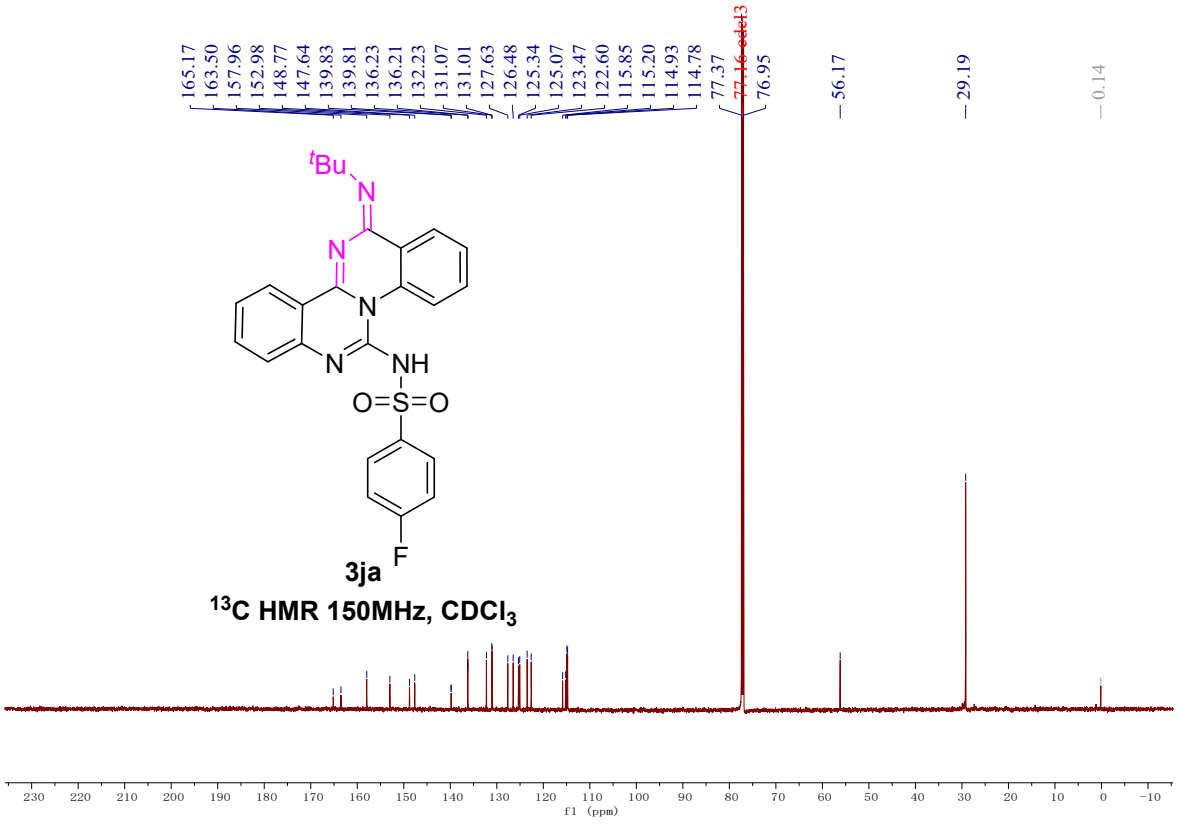
^{13}C HMR 100MHz, $CDCl_3$



3ja

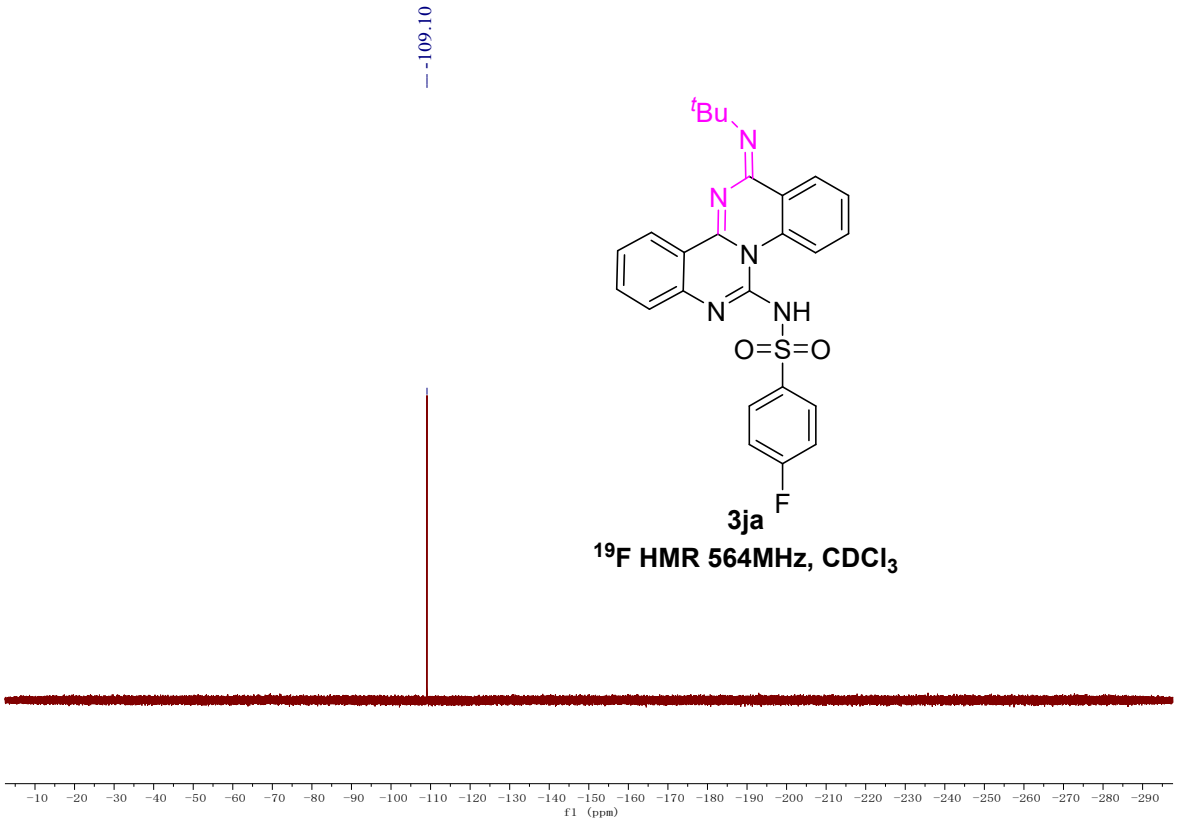
^{1}H HMR 600MHz, $CDCl_3$





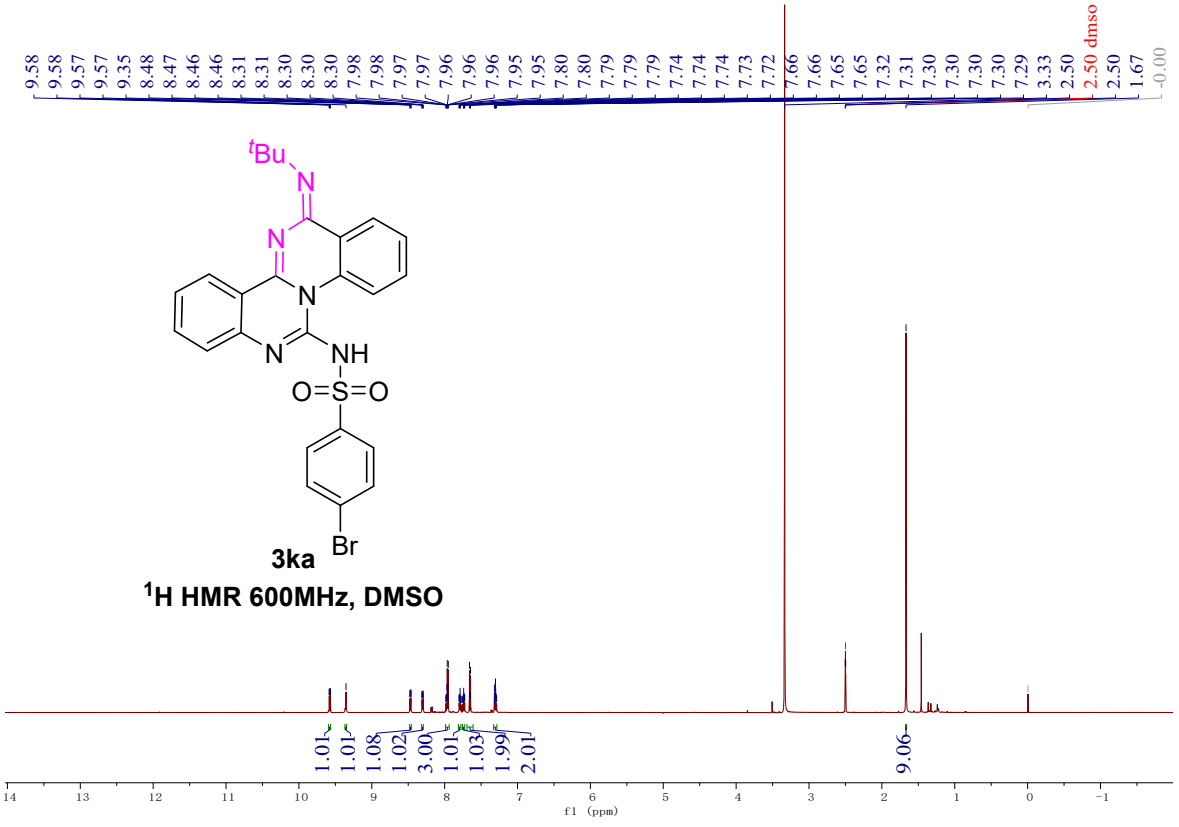
3ja

^{13}C HMR 150MHz, $CDCl_3$



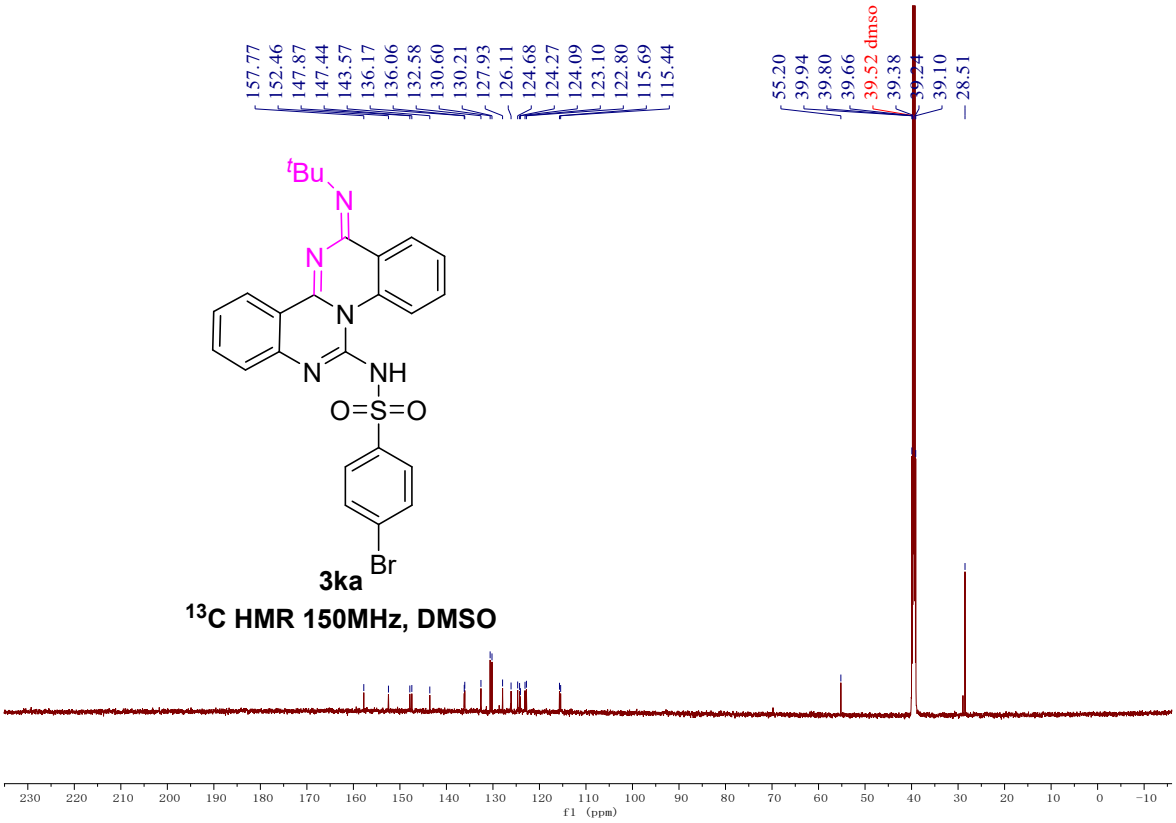
3ja

^{19}F HMR 564MHz, $CDCl_3$



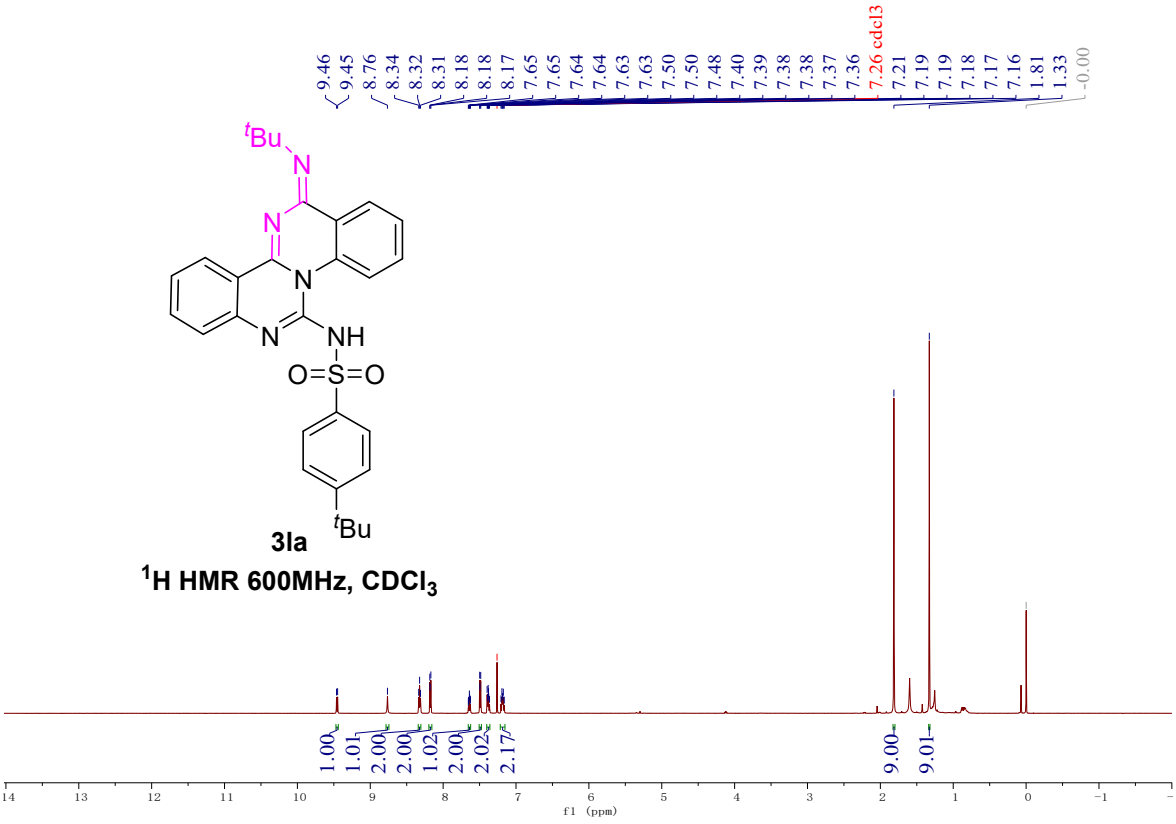
3ka

^{1}H HMR 600MHz, DMSO



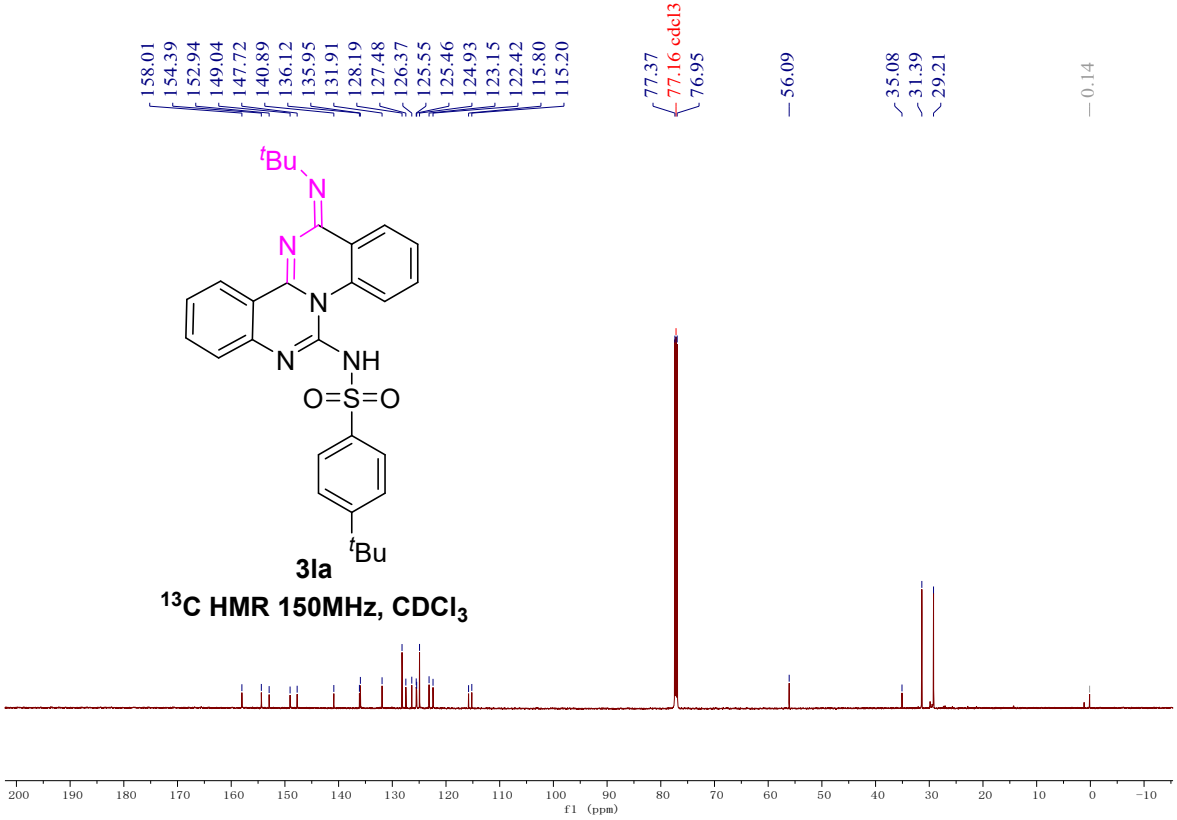
3ka

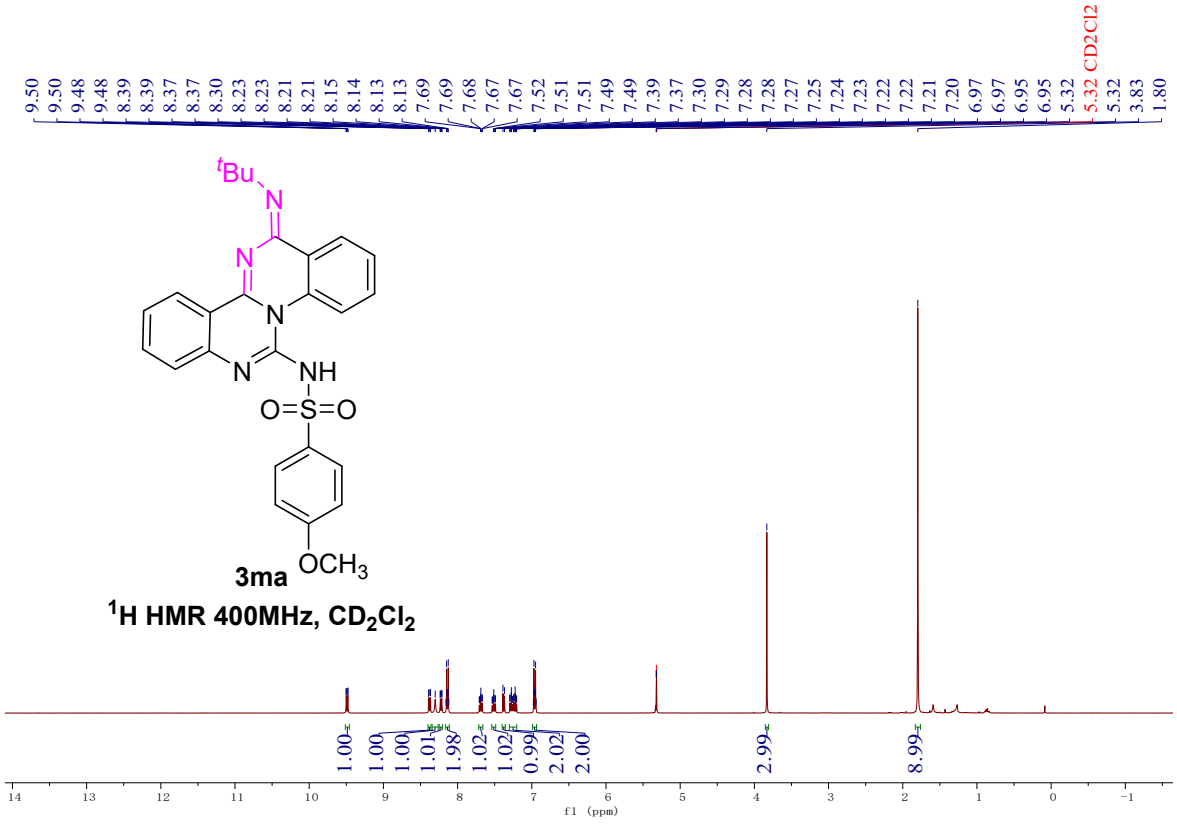
^{13}C HMR 150MHz, DMSO

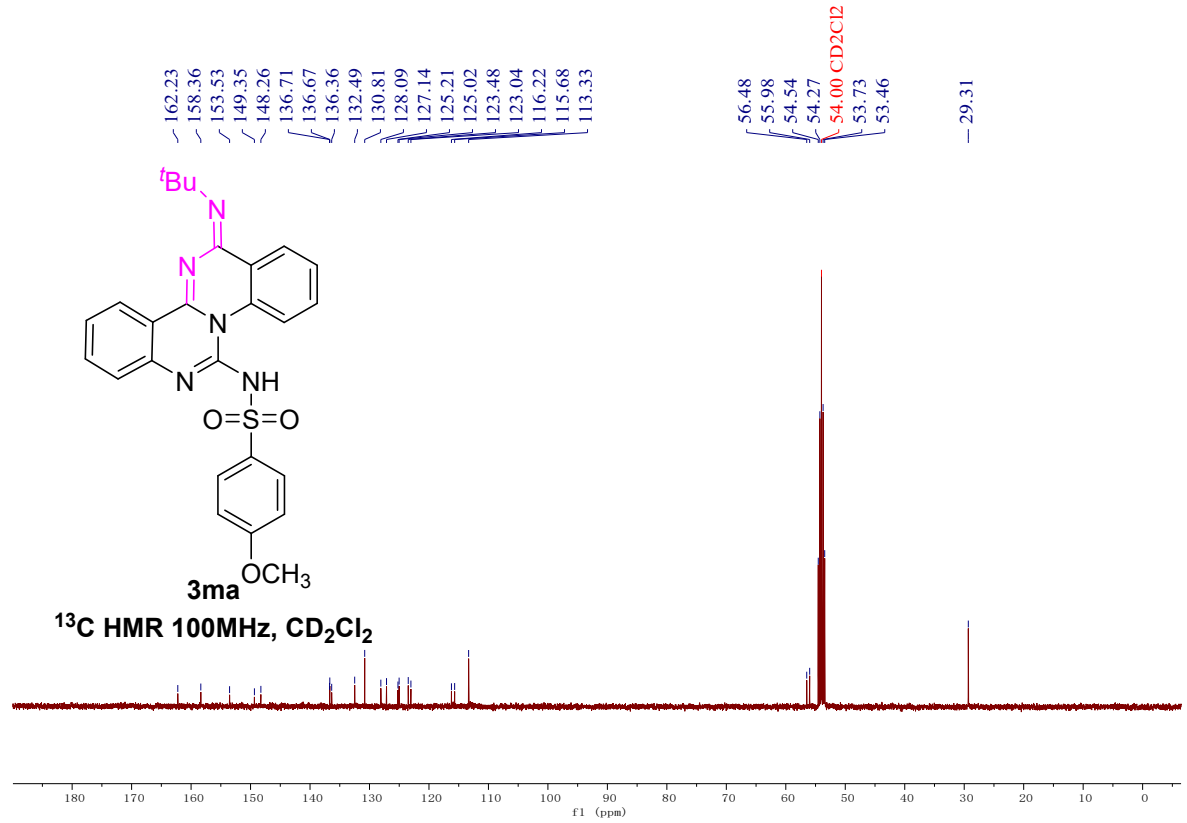


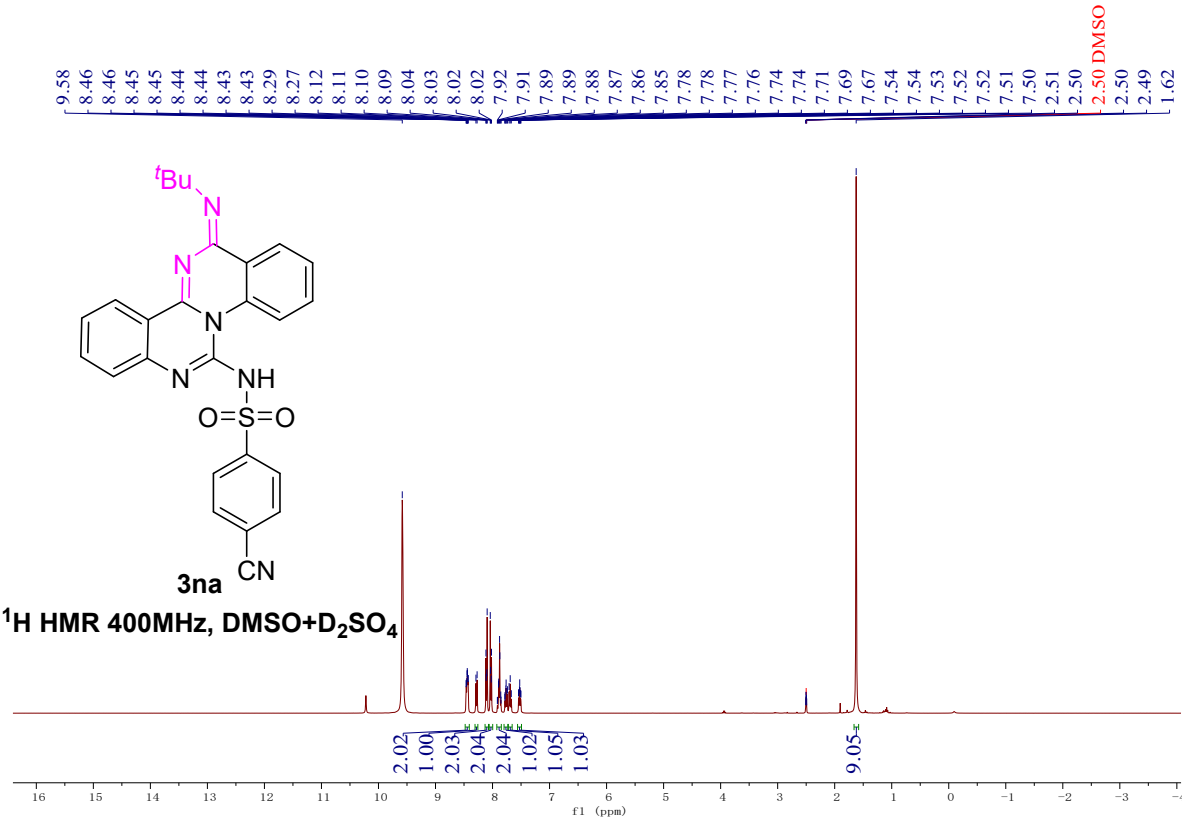
3la

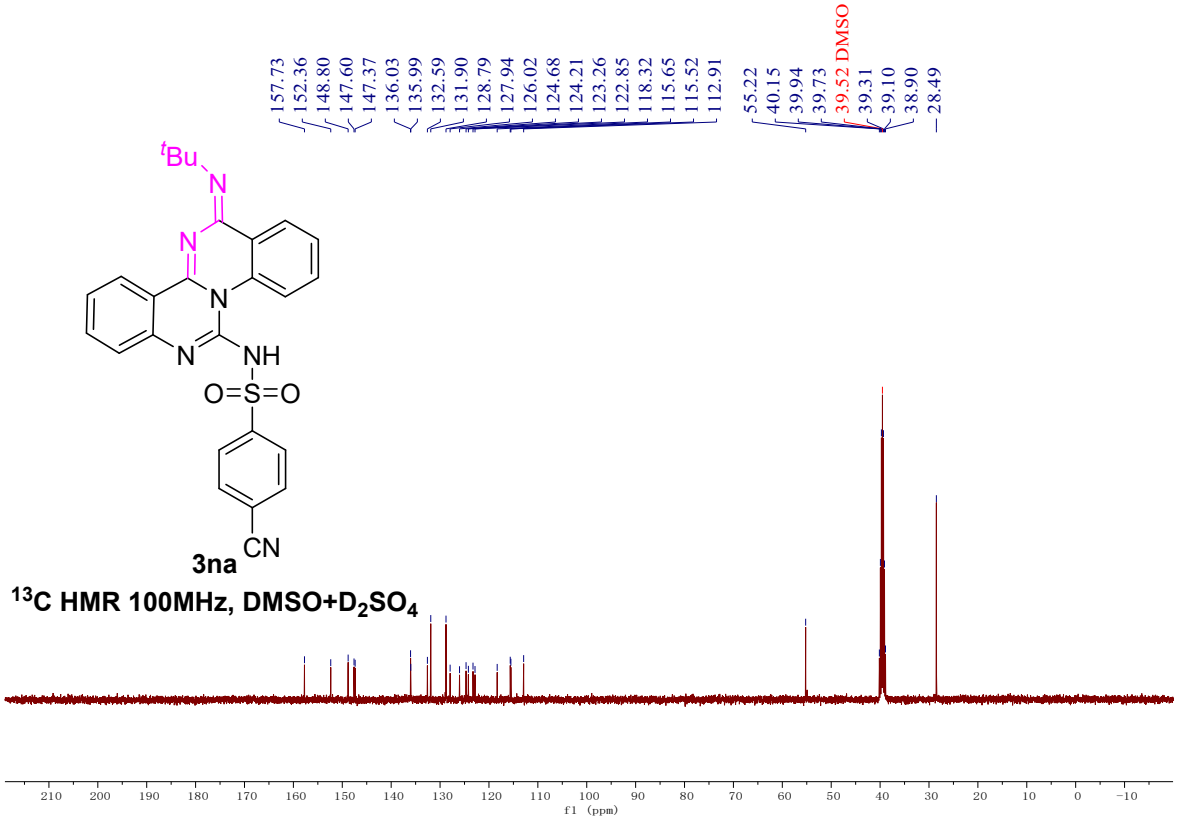
^{1}H HMR 600MHz, $CDCl_3$


158.01
154.39
152.94
149.04
147.72
140.89
136.12
135.95
131.91
128.19
127.48
126.37
125.55
125.46
124.93
123.15
122.42
115.80
115.20
77.37
77.16 cdcl3
76.95
56.09
35.08
31.39
29.21
0.14
tBu
N
N
N
N
NH
O=S=O
tBu
3la
13C HMR 150MHz, CDCl3
f1 (ppm)


9.50
9.50
9.48
9.48
8.39
8.39
8.37
8.37
8.30
8.23
8.23
8.21
8.21
8.15
8.14
8.13
8.13
7.69
7.69
7.68
7.67
7.67
7.52
7.51
7.51
7.49
7.49
7.39
7.37
7.30
7.29
7.28
7.28
7.27
7.25
7.24
7.23
7.22
7.22
7.21
7.20
6.97
6.97
6.95
6.95
5.32
5.32 CD2Cl2
3.83
1.80
tBu
N
N
N
N
NH
O=S=O
OCH3
3ma
1H HMR 400MHz, CD2Cl2
1.00
1.00
1.00
1.01
1.98
1.02
1.02
0.99
2.02
2.00
2.99
8.99
f1 (ppm)

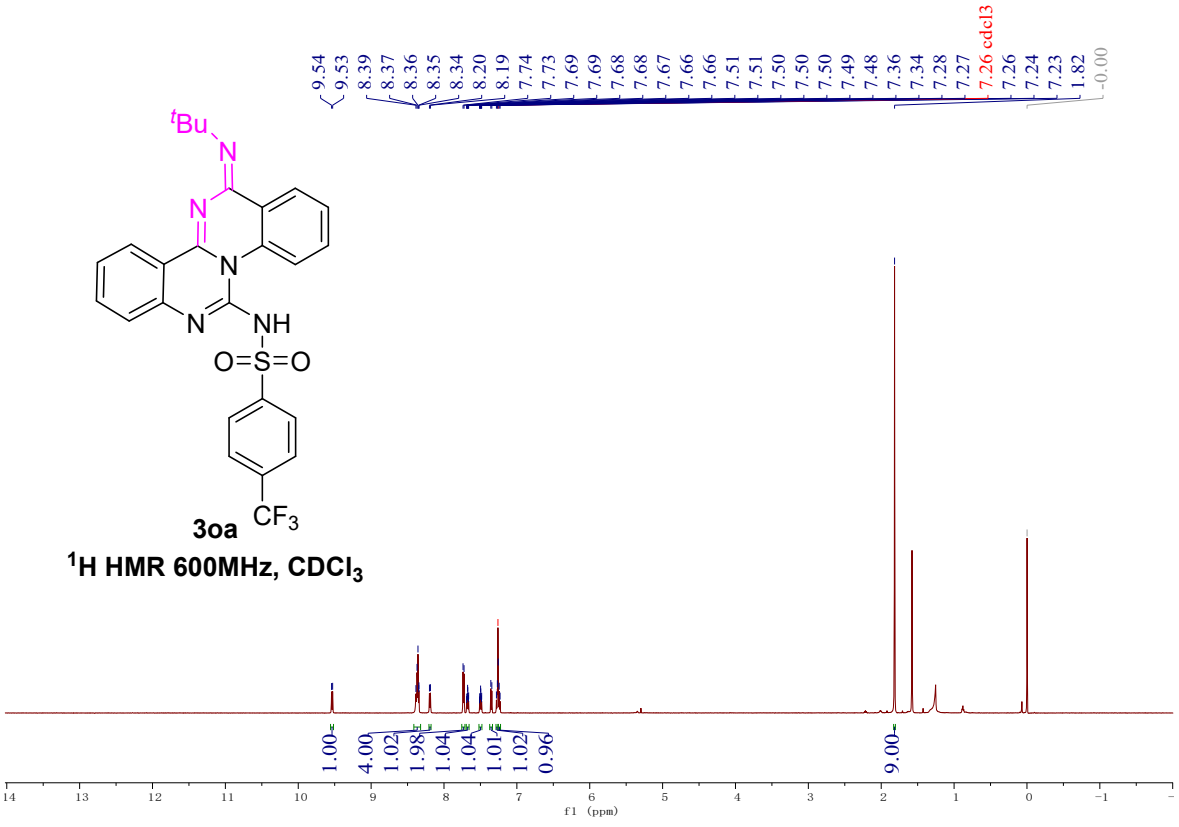

162.23
158.36
153.53
149.35
148.26
136.71
136.67
136.36
132.49
130.81
128.09
127.14
125.21
125.02
123.48
123.04
116.22
115.68
113.33
56.48
55.98
54.54
54.27
54.00 CD2Cl2
53.73
53.46
29.31
tBu
N
N
N
N
NH
O=S=O
OCH3
3ma
13C HMR 100MHz, CD2Cl2
f1 (ppm)


9.58
8.46
8.46
8.45
8.45
8.44
8.44
8.43
8.43
8.29
8.27
8.12
8.11
8.10
8.09
8.04
8.03
8.02
8.02
7.92
7.91
7.89
7.89
7.88
7.87
7.86
7.85
7.78
7.78
7.77
7.76
7.74
7.74
7.71
7.69
7.67
7.54
7.54
7.53
7.52
7.52
7.51
7.50
2.51
2.50
2.50 DMSO
2.50
2.49
1.62
tBu
N
N
N
N
NH
O=S=O
CN
3na
1H HMR 400MHz, DMSO+D2SO4
2.02
1.00
2.03
2.04
2.04
1.02
1.05
1.03
9.05
f1 (ppm)



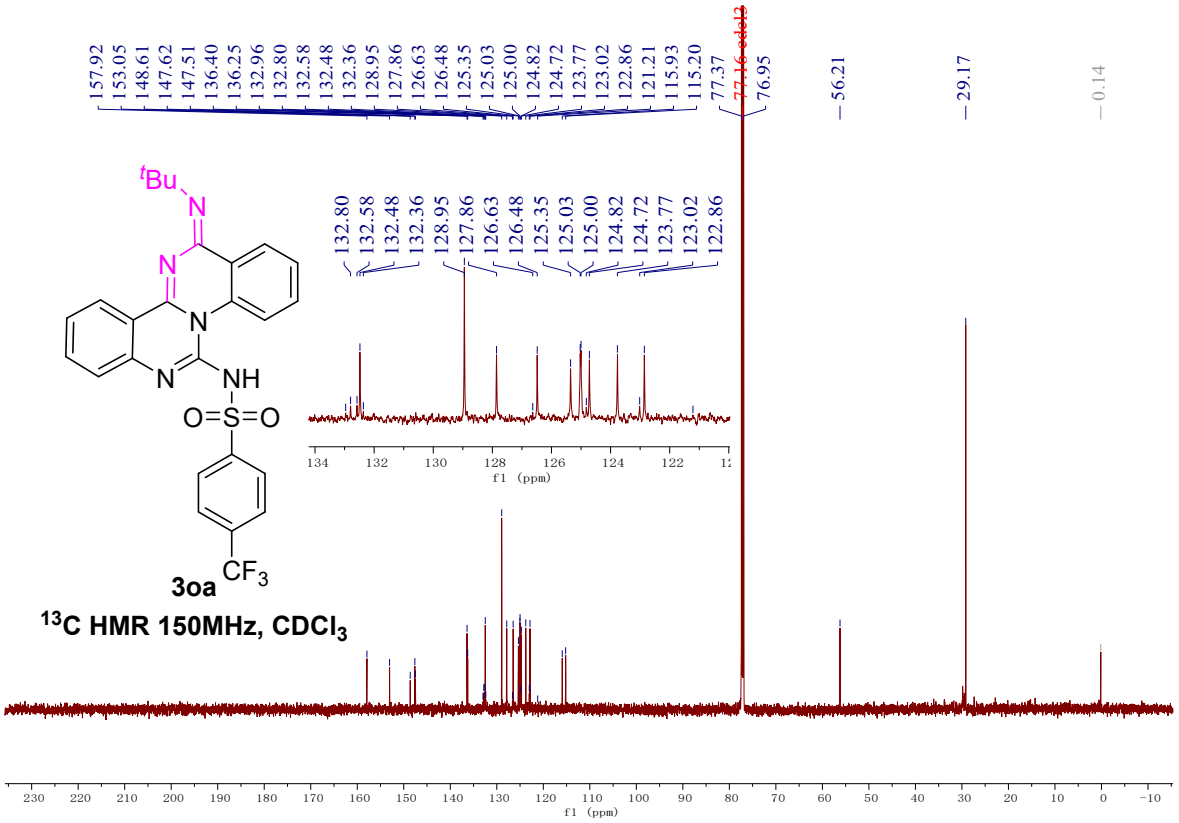
3na

^{13}C HMR 100MHz, DMSO+D_2SO_4



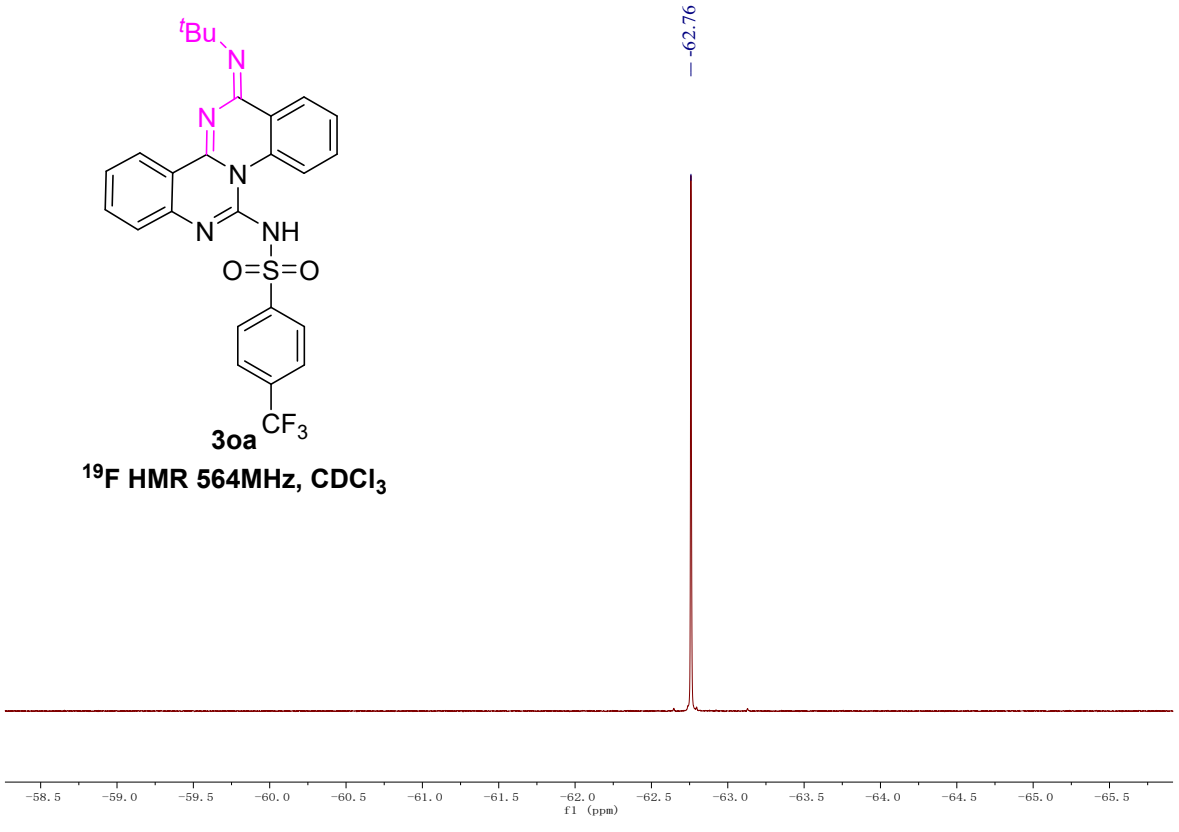
3oa

^{1}H HMR 600MHz, $CDCl_3$



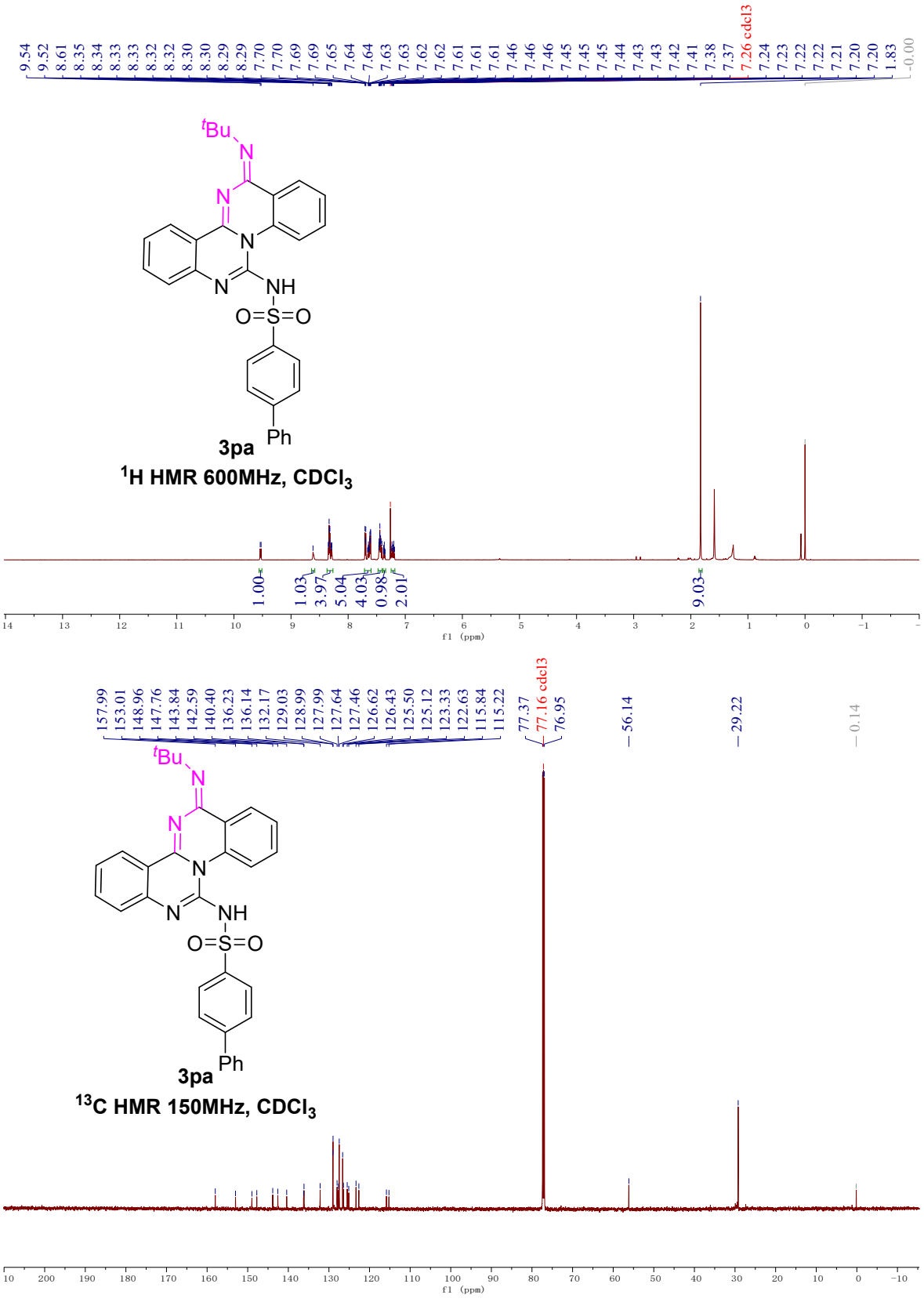
3oa

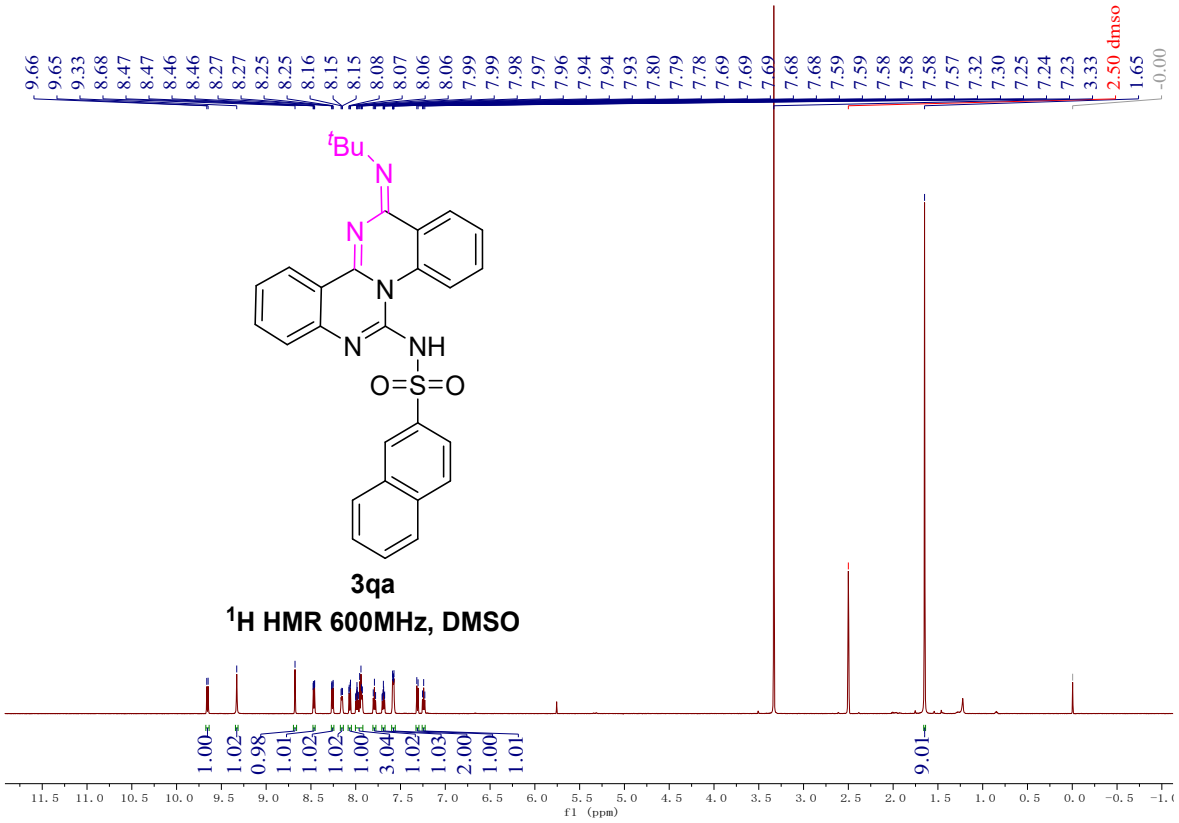
^{13}C HMR 150MHz, $CDCl_3$



3oa

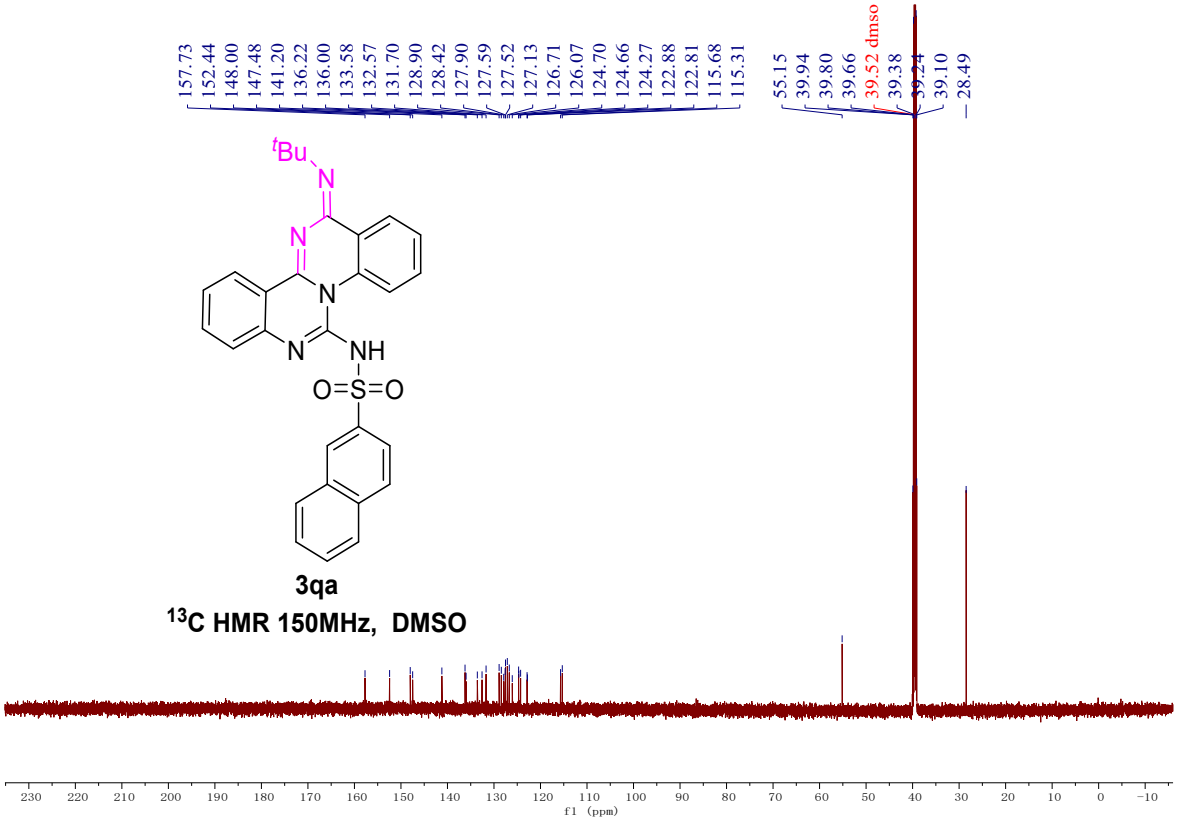
^{19}F HMR 564MHz, $CDCl_3$


9.54
9.52
8.61
8.35
8.34
8.33
8.33
8.32
8.32
8.30
8.30
8.29
8.29
7.70
7.70
7.69
7.69
7.65
7.64
7.64
7.63
7.63
7.62
7.62
7.61
7.61
7.61
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.38
7.37
7.26 cdcl3
7.24
7.23
7.22
7.22
7.21
7.20
7.20
1.83
0.00
tBu
N
N
N
N
NH
O=S=O
Ph
3pa
1H HMR 600MHz, CDCl3
1.00
1.03
3.97
5.04
4.03
0.98
2.01
9.03
f1 (ppm)
157.99
153.01
148.96
147.76
143.84
142.59
140.40
136.23
136.14
132.17
129.03
128.99
127.99
127.64
127.46
126.62
126.43
125.50
125.12
123.33
122.63
115.84
115.22
77.37
77.16 cdcl3
76.95
56.14
29.22
0.14
tBu
N
N
N
N
NH
O=S=O
Ph
3pa
13C HMR 150MHz, CDCl3
f1 (ppm)



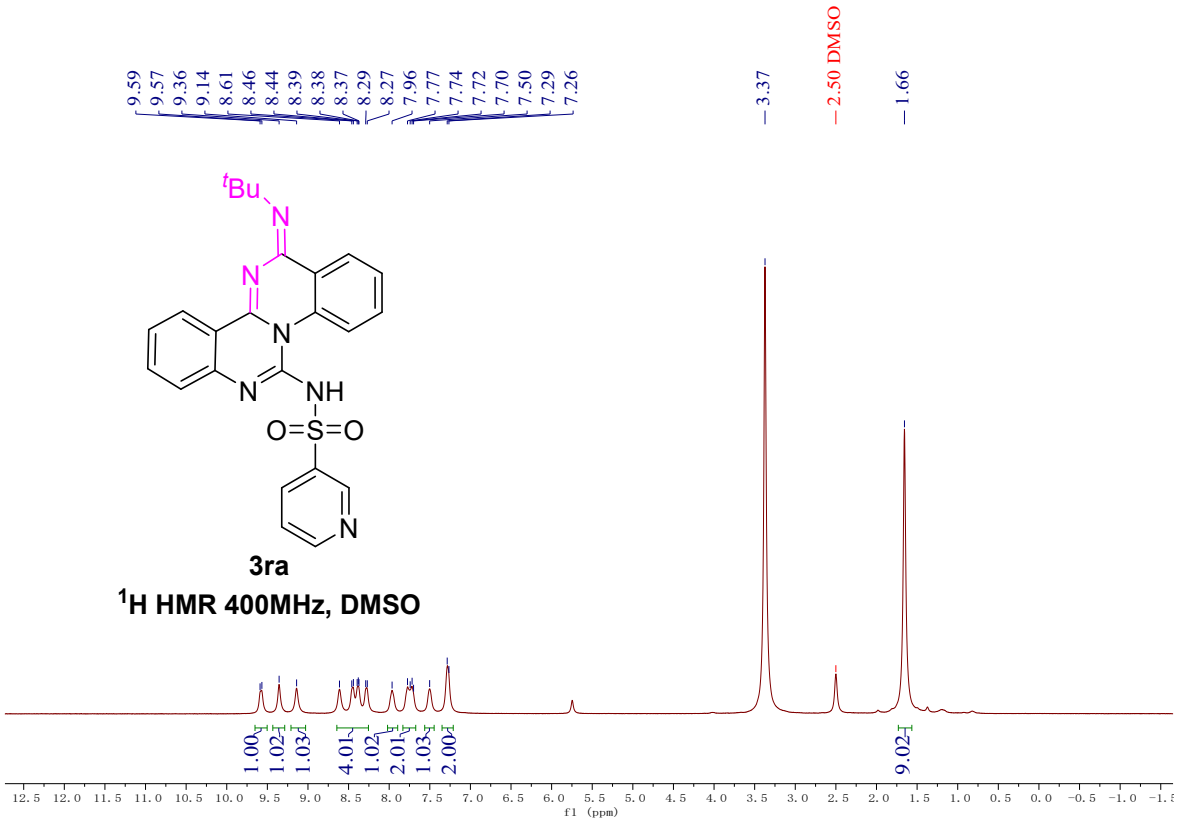
3qa

^{1}H HMR 600MHz, DMSO



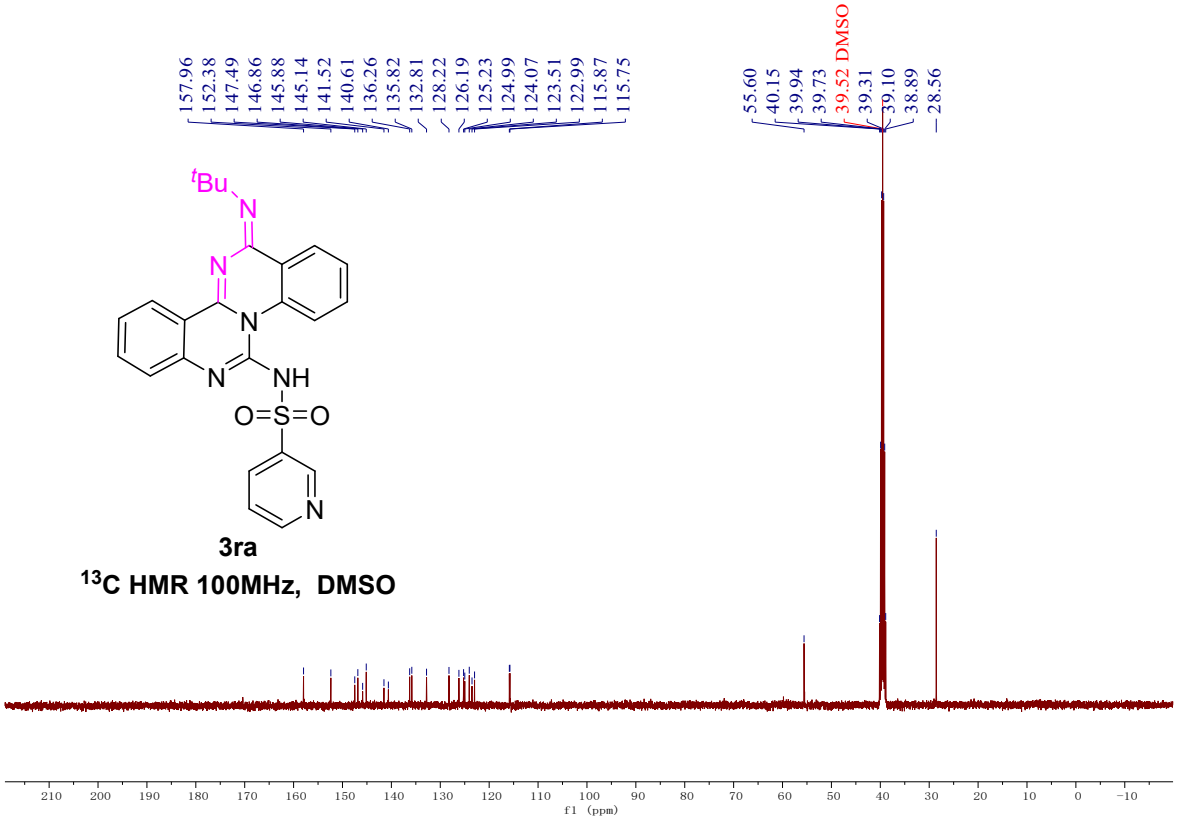
3qa

^{13}C HMR 150MHz, DMSO



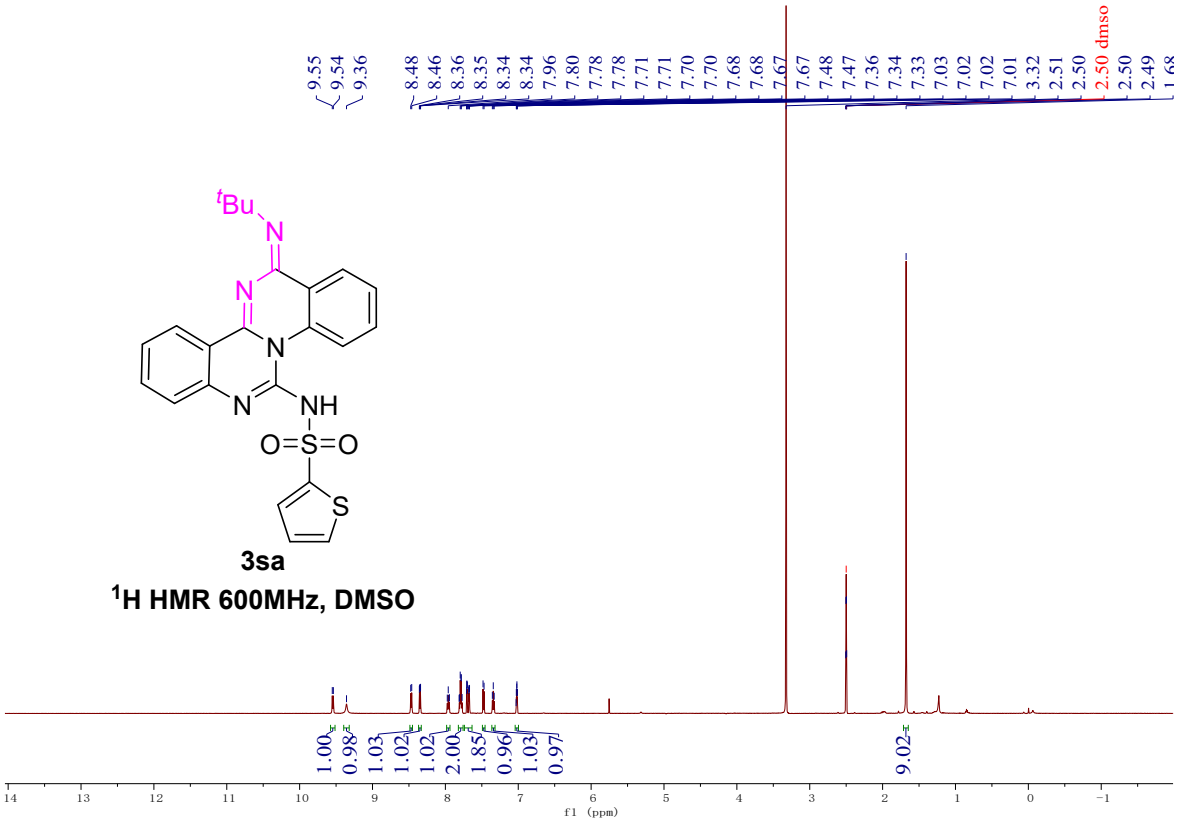
3ra

^{1}H HMR 400MHz, DMSO



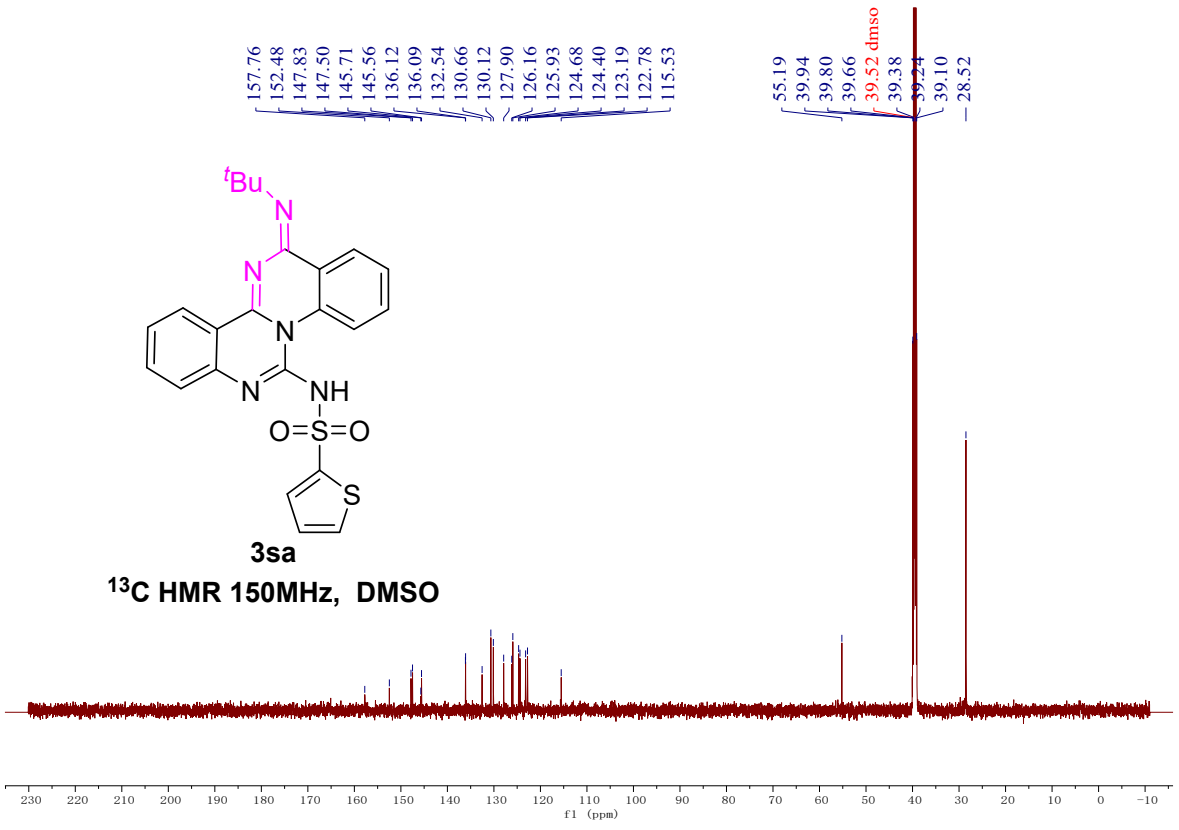
3ra

^{13}C HMR 100MHz, DMSO



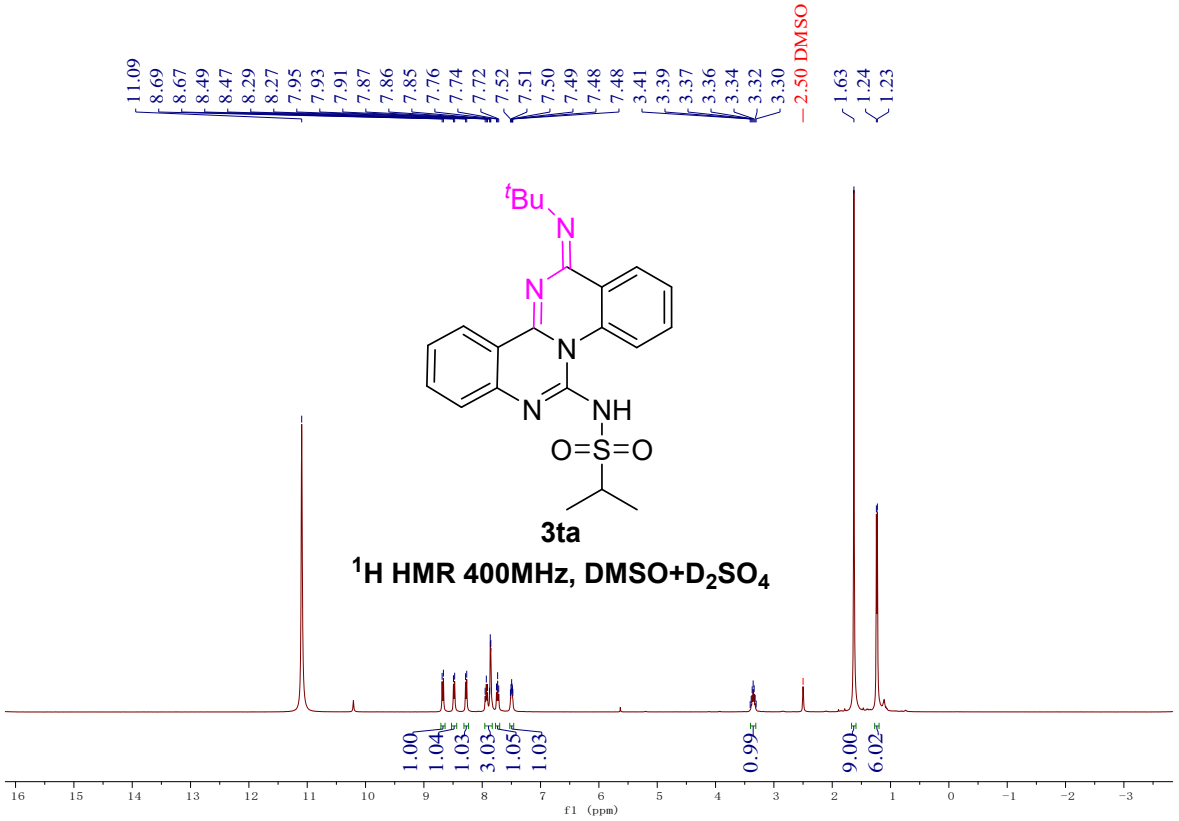
3sa

^{1}H HMR 600MHz, DMSO



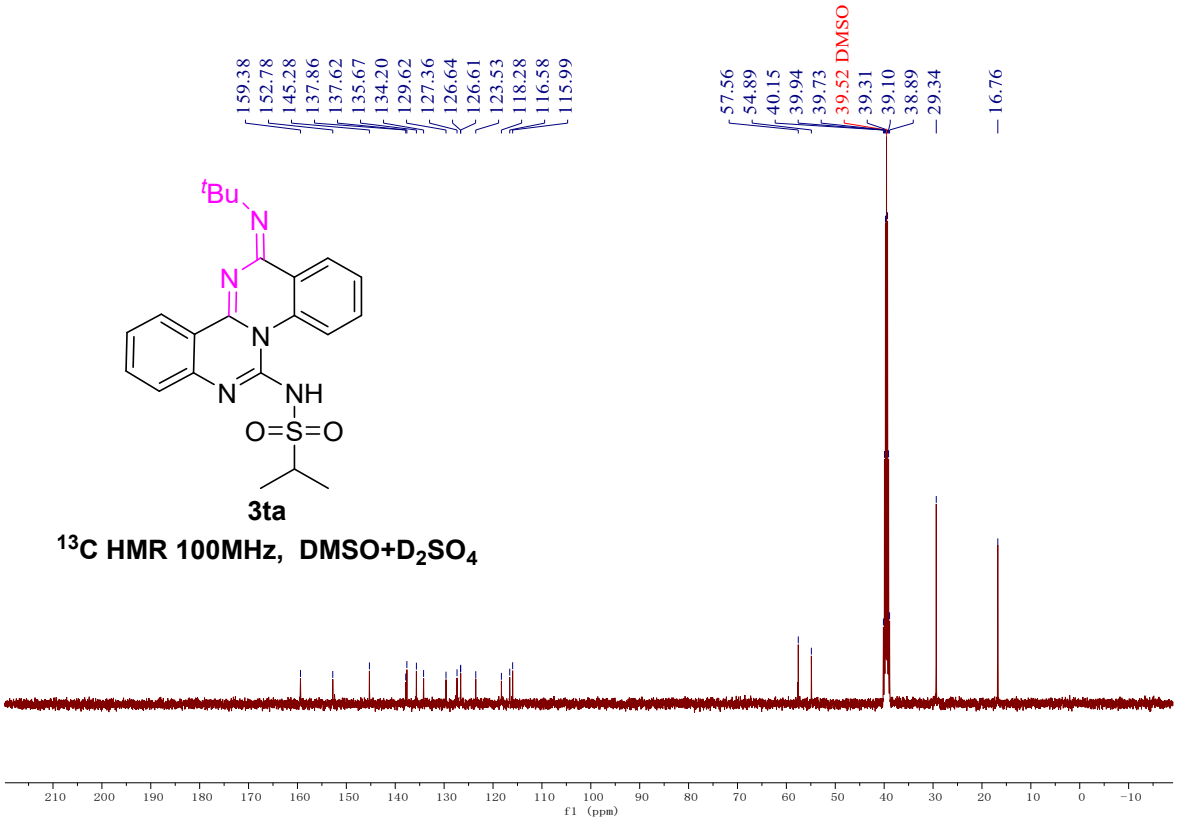
3sa

^{13}C HMR 150MHz, DMSO



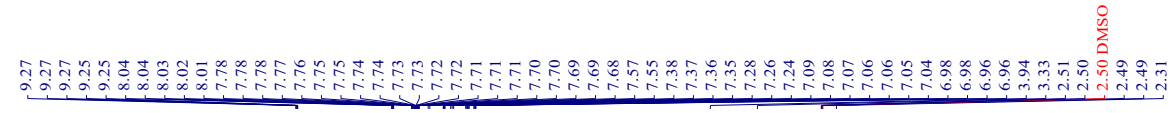
3ta

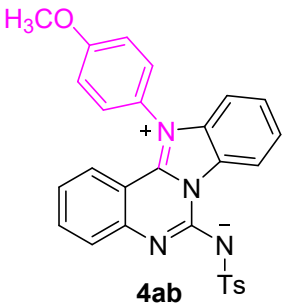
^{1}H HMR 400MHz, DMSO+D_2SO_4



3ta

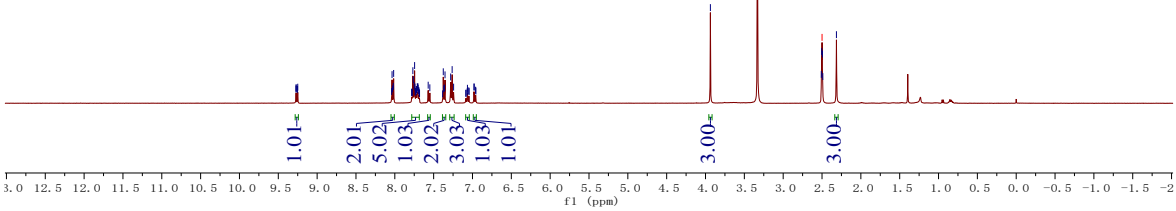
^{13}C HMR 100MHz, DMSO+D_2SO_4

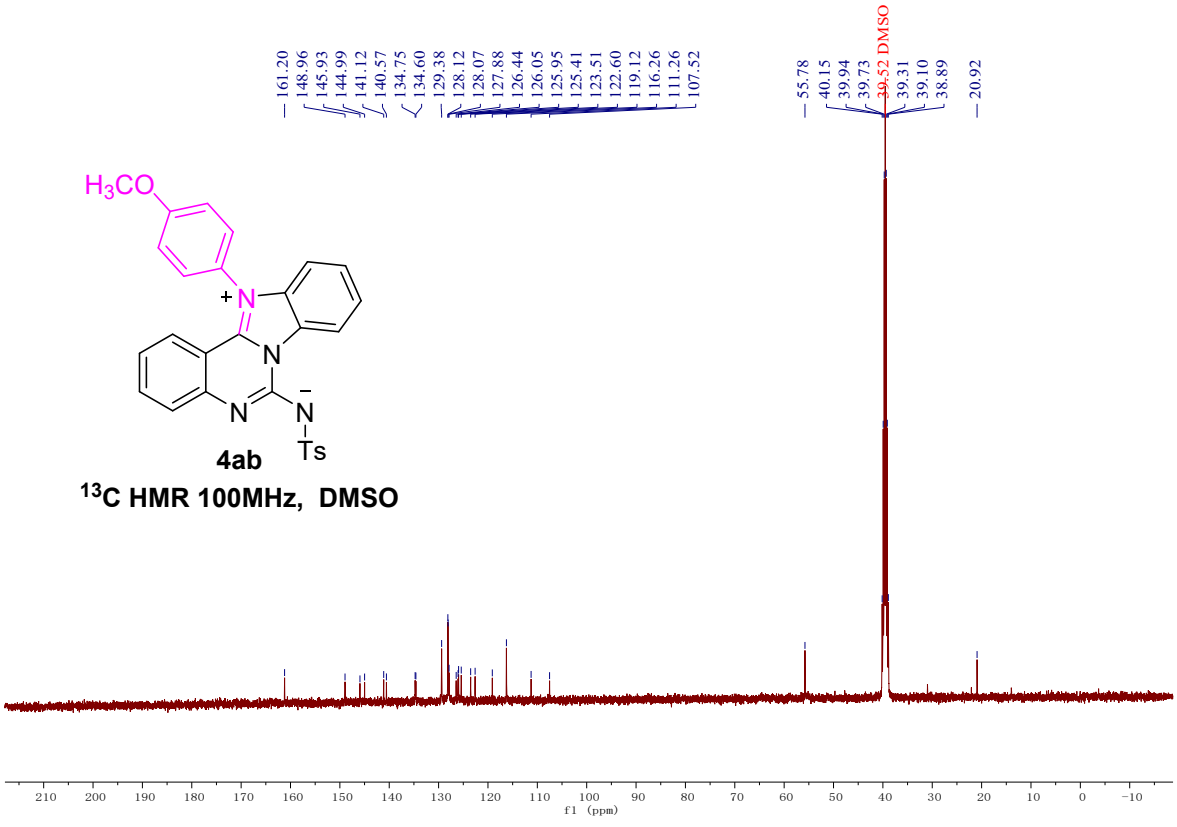




4ab

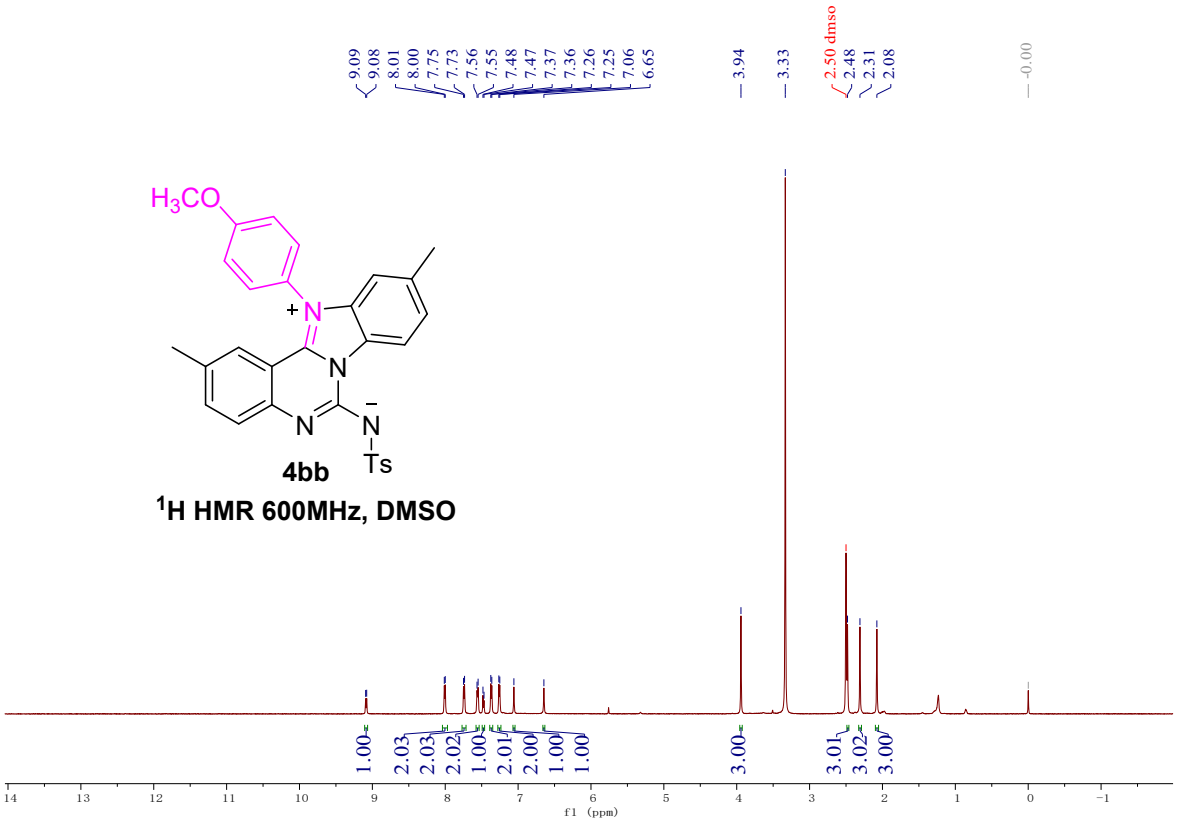
^{1}H HMR 400MHz, DMSO





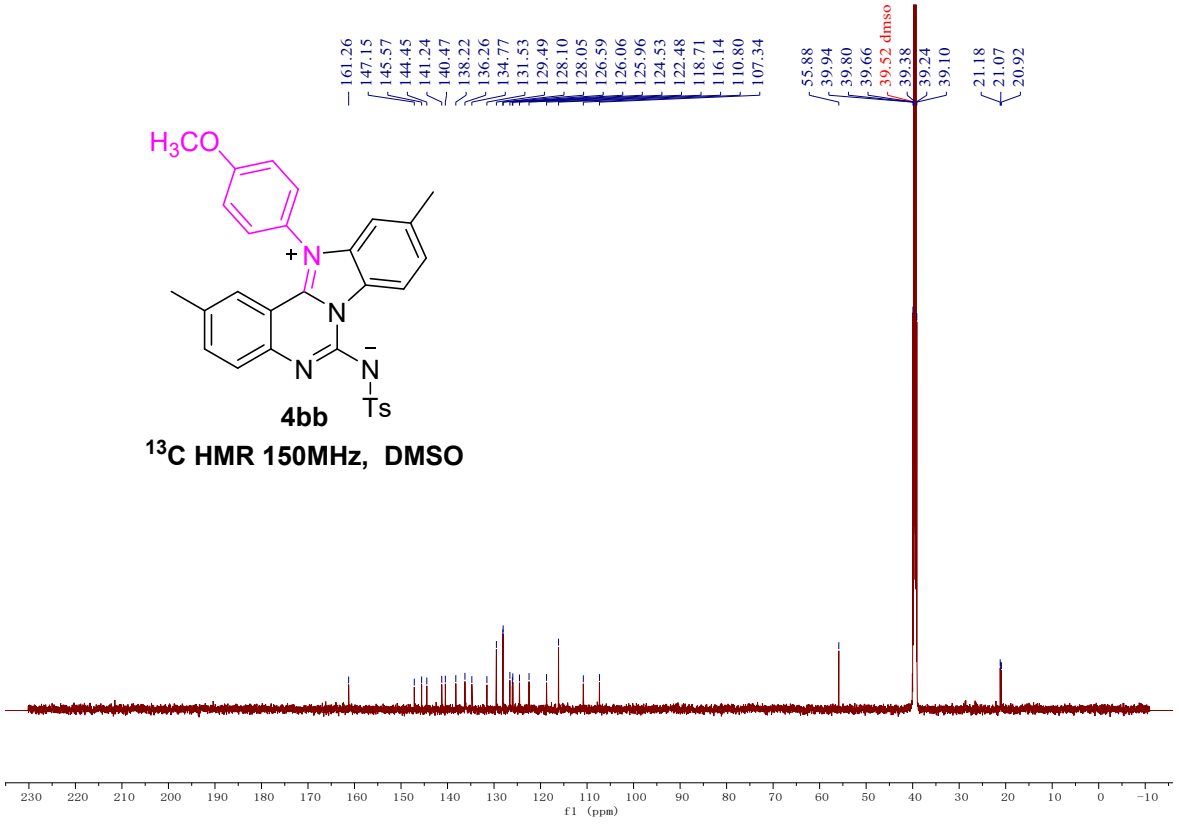
4ab

^{13}C HMR 100MHz, DMSO



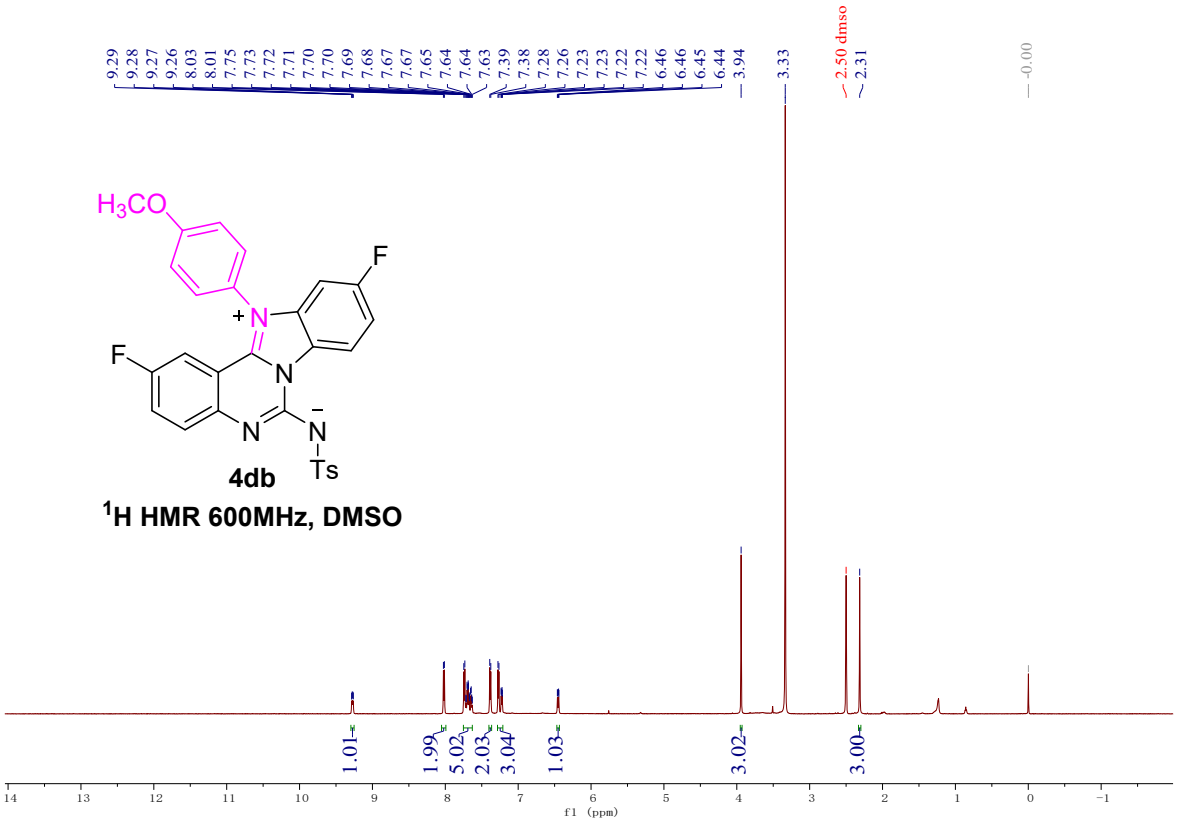
4bb

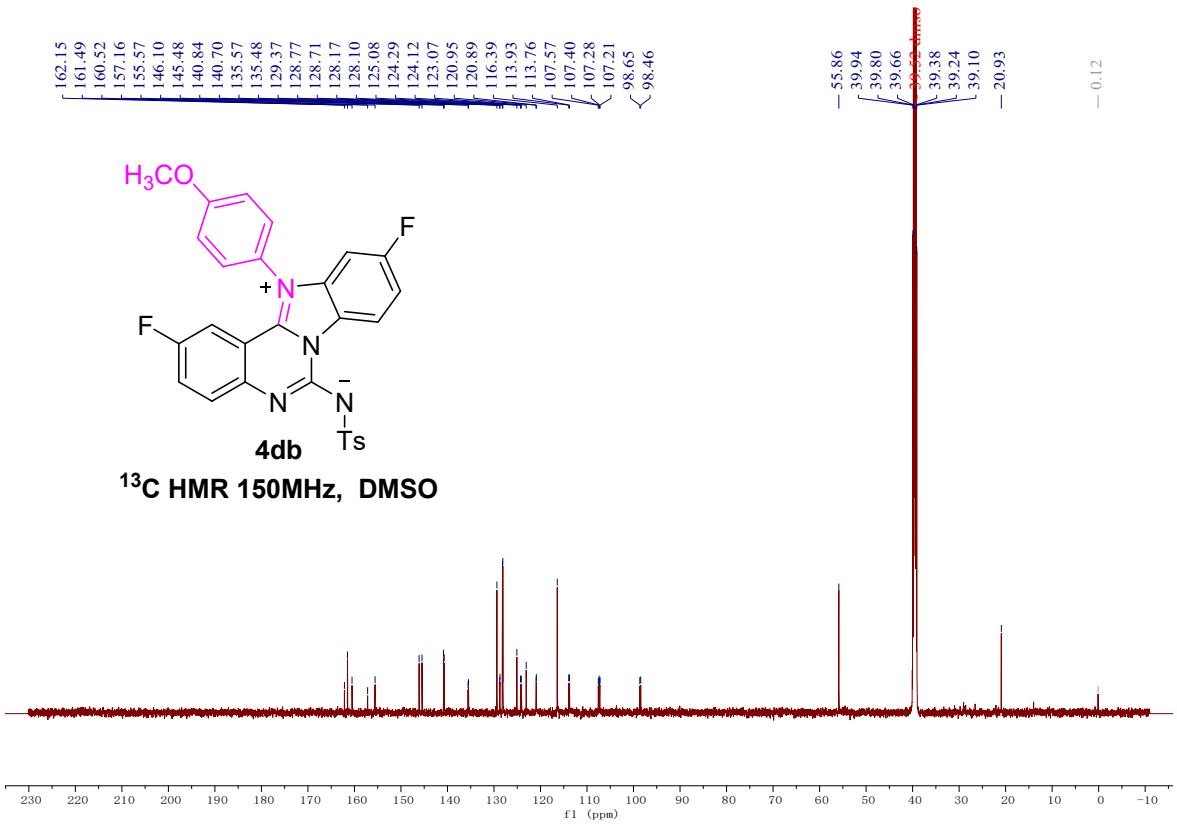
^{1}H HMR 600MHz, DMSO

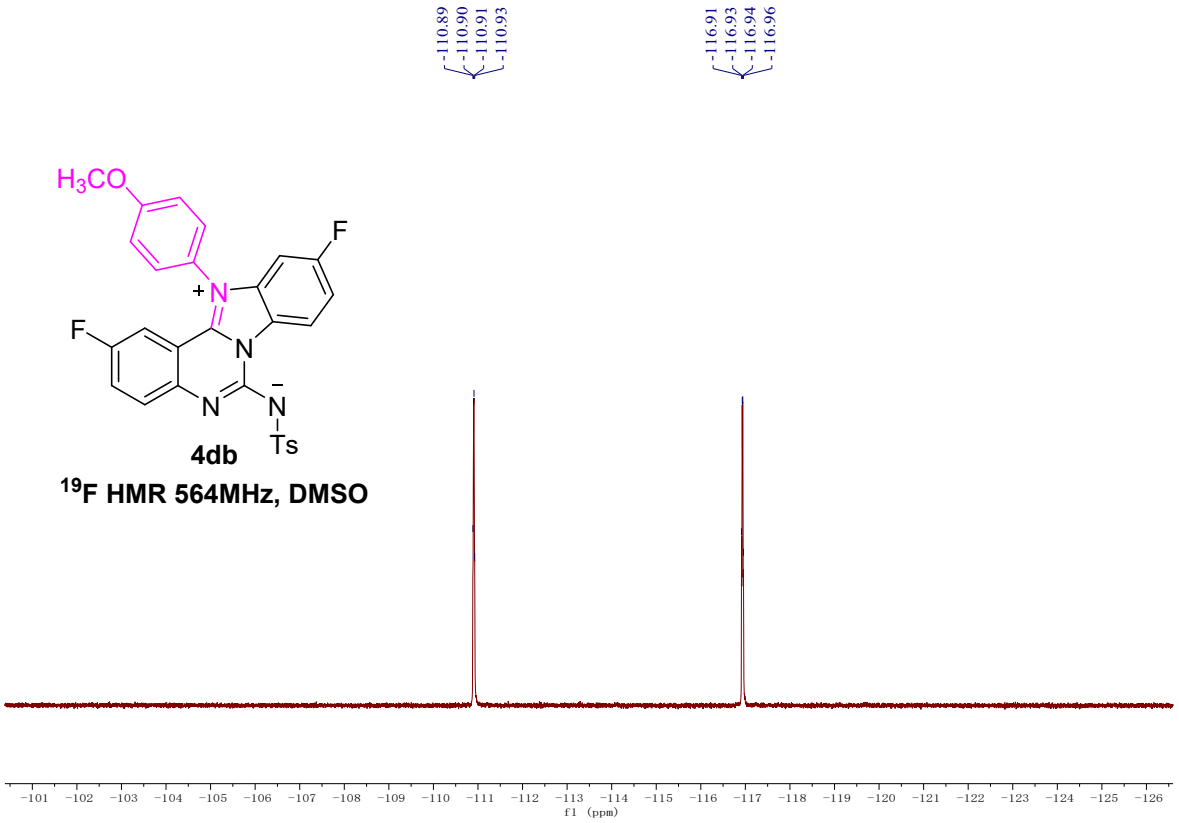


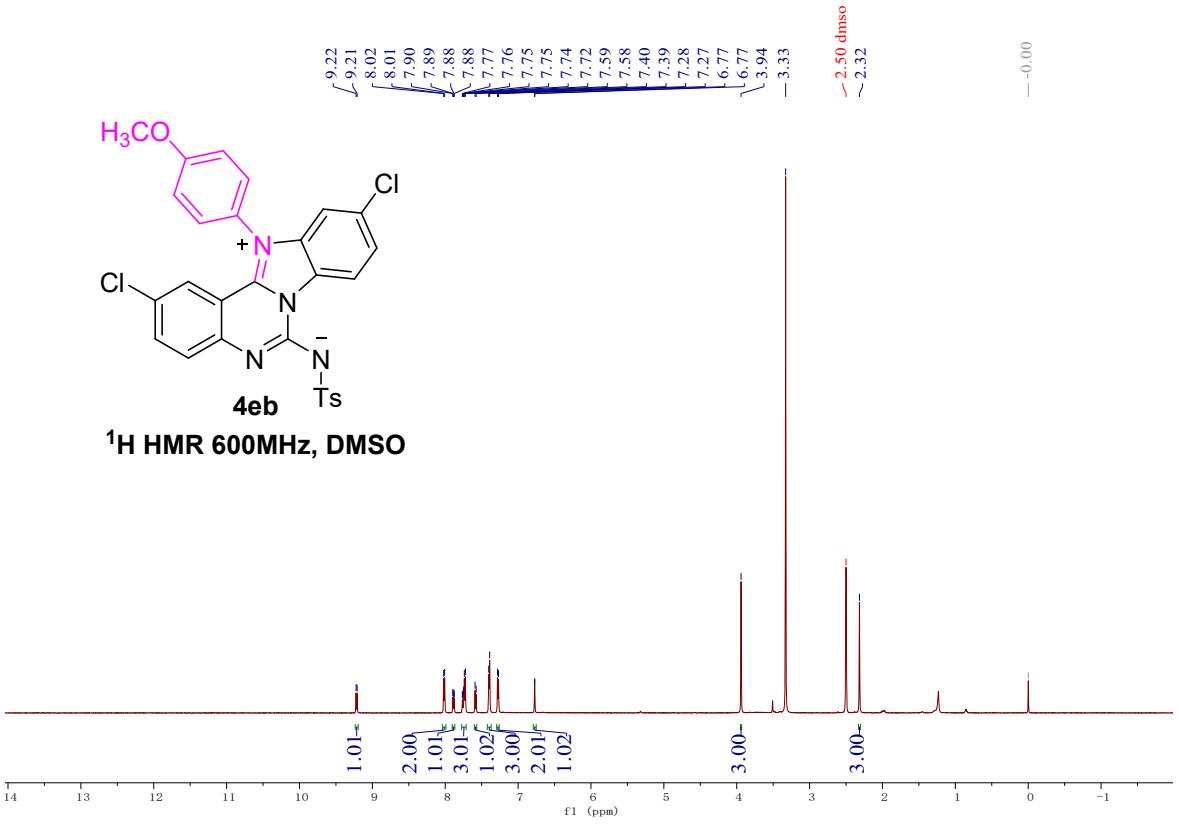
4bb

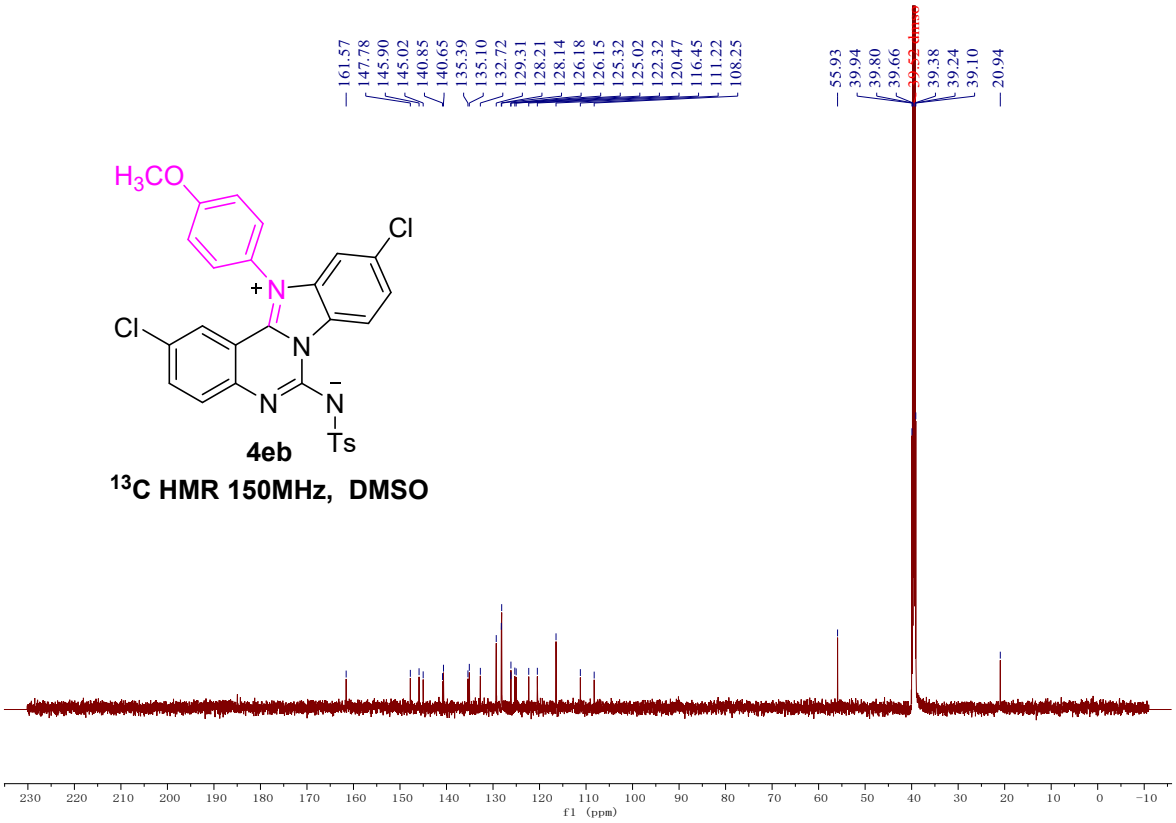
^{13}C HMR 150MHz, DMSO

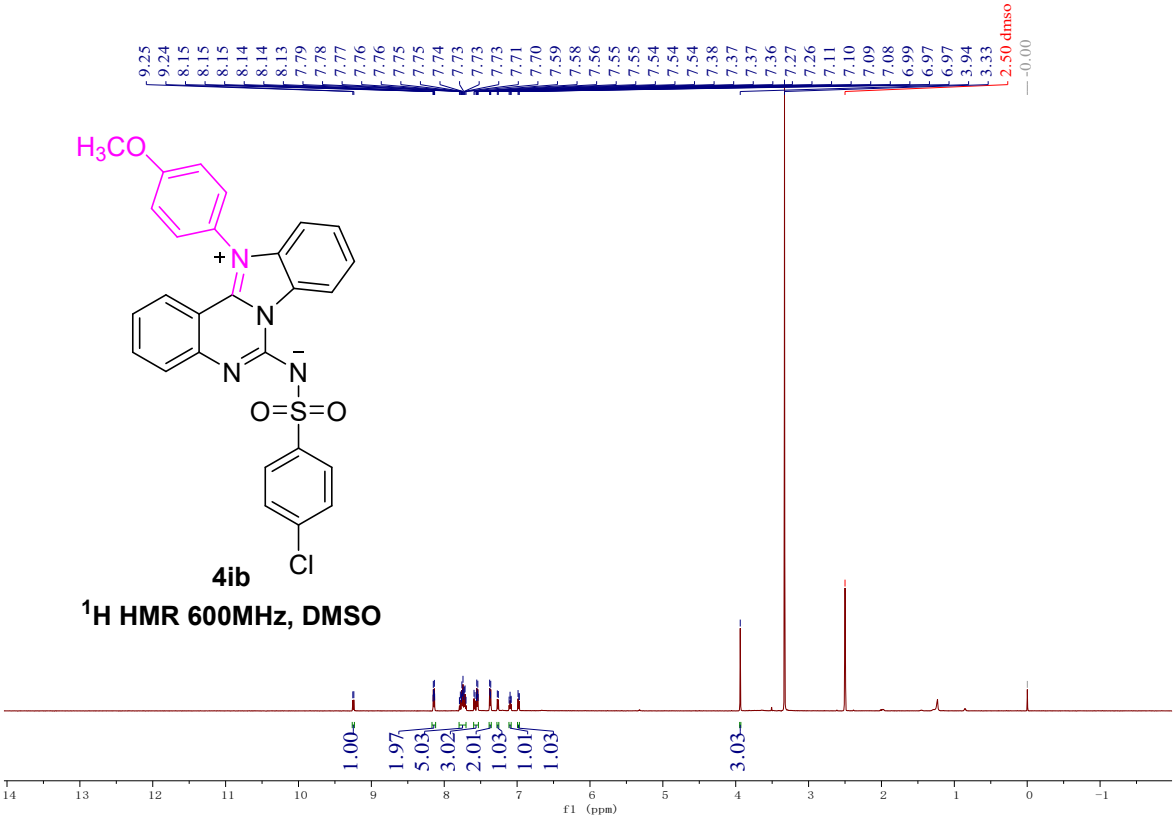

9.29
9.28
9.27
9.26
8.03
8.01
7.75
7.73
7.72
7.71
7.70
7.70
7.69
7.68
7.67
7.67
7.65
7.64
7.64
7.63
7.39
7.38
7.28
7.26
7.23
7.23
7.22
7.22
6.46
6.46
6.45
6.44
3.94
3.33
2.50 dmso
2.31
-0.00
H3CO
F
N
F
N
N
N
Ts
4db
1H HMR 600MHz, DMSO
1.01
1.99
5.02
2.03
3.04
1.03
3.02
3.00
f1 (ppm)

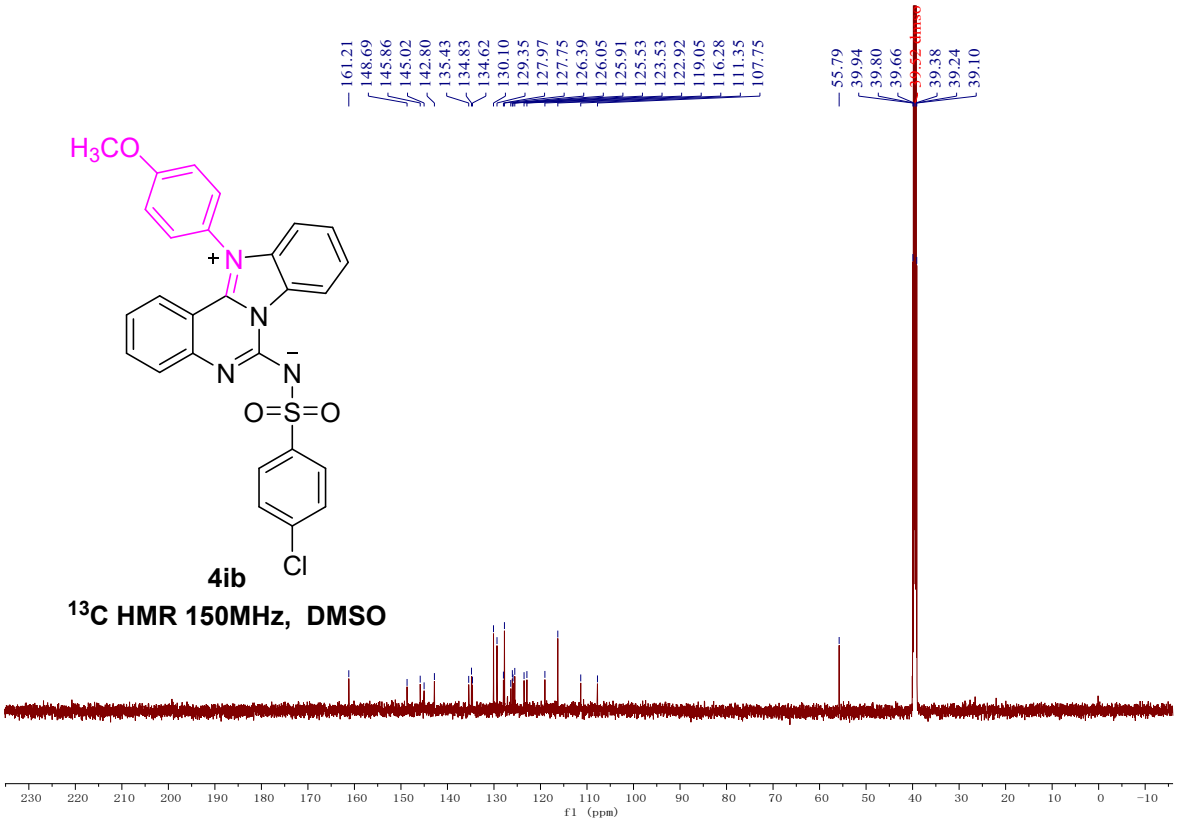

162.15
161.49
160.52
157.16
155.57
146.10
145.48
140.84
140.70
135.57
135.48
129.37
128.77
128.71
128.17
128.10
125.08
124.29
124.12
123.07
120.95
120.89
116.39
113.93
113.76
107.57
107.40
107.28
107.21
98.65
98.46
55.86
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
20.93
0.12
H3CO
F
N
F
N
N
N
Ts
4db
13C HMR 150MHz, DMSO
f1 (ppm)

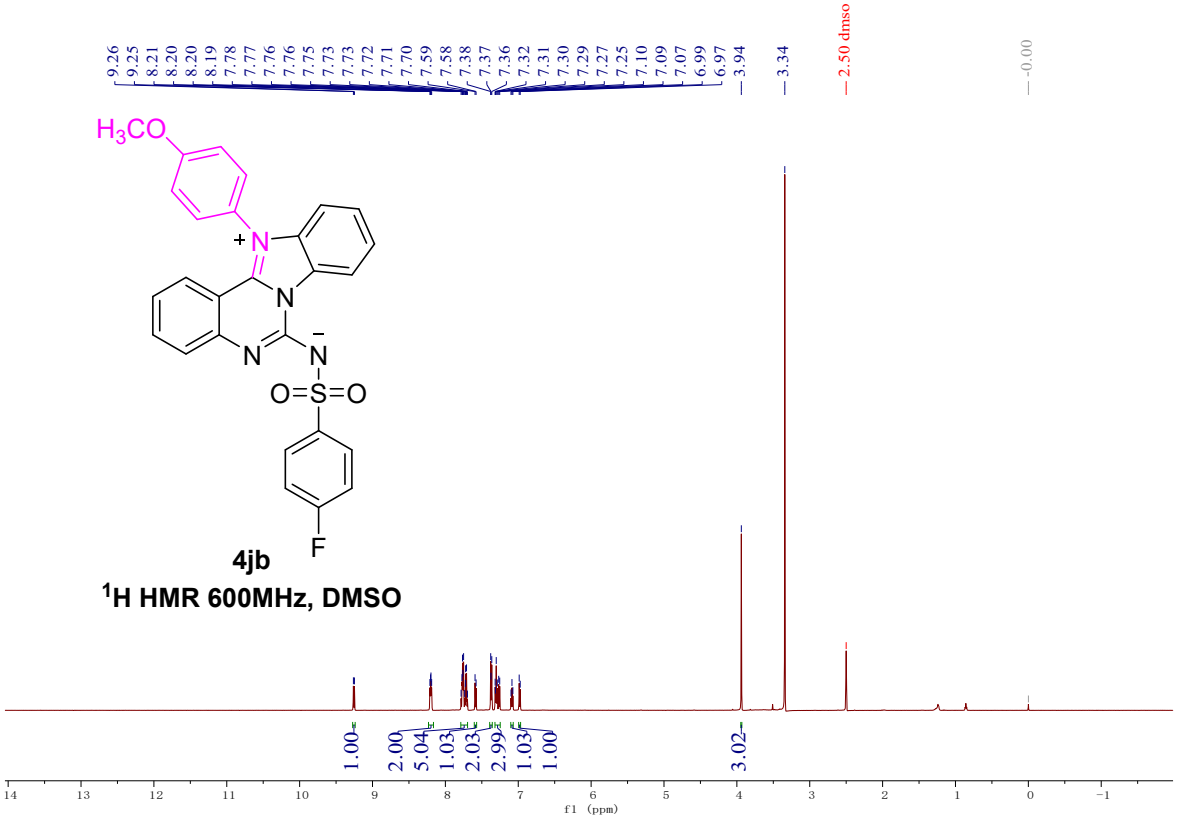

-110.89
-110.90
-110.91
-110.93
-116.91
-116.93
-116.94
-116.96
H3CO
F
F
N
N
N
N
Ts
4db
19F HMR 564MHz, DMSO
f1 (ppm)

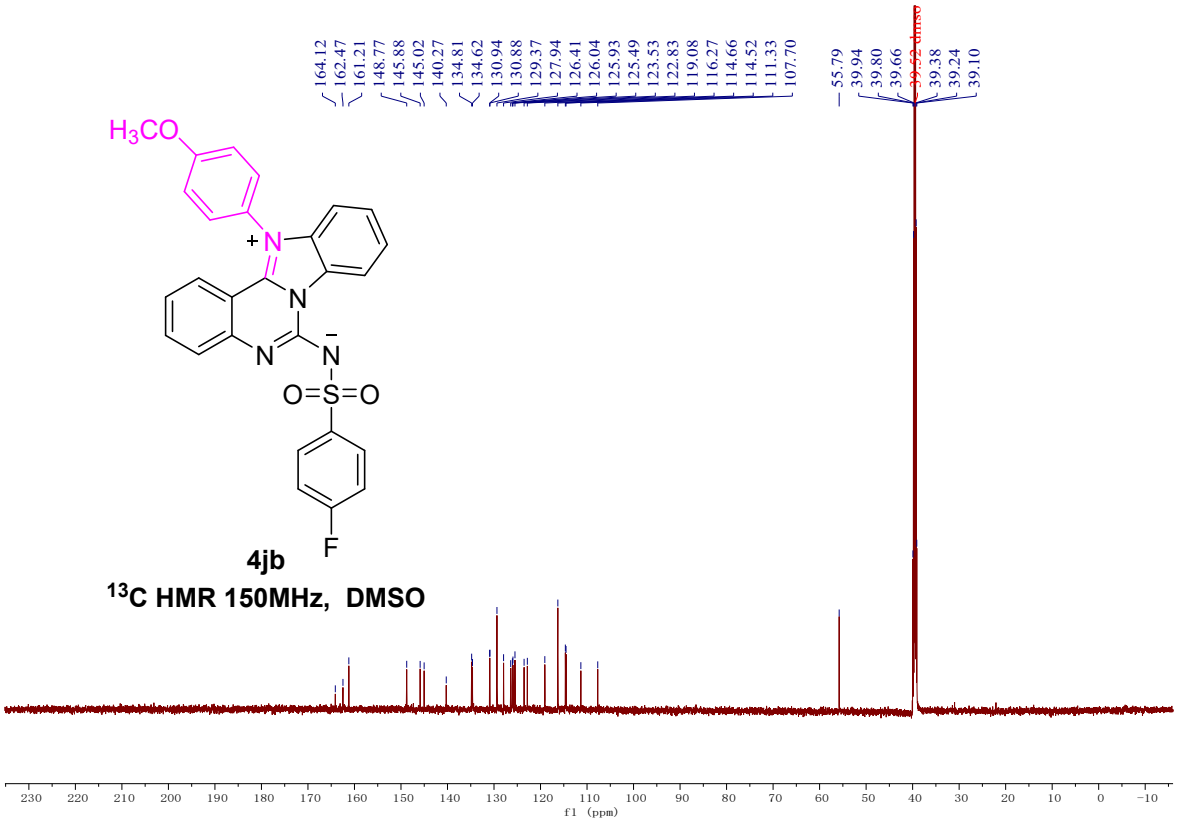

9.22
9.21
8.02
8.01
7.90
7.89
7.88
7.88
7.77
7.76
7.75
7.75
7.74
7.72
7.59
7.58
7.40
7.39
7.28
7.27
6.77
6.77
3.94
3.33
2.50 dmso
2.32
0.00
H3CO
Cl
Cl
N
N
N
N
Ts
4eb
1H HMR 600MHz, DMSO
1.01
2.00
1.01
3.01
1.02
3.00
2.01
1.02
3.00
3.00
f1 (ppm)

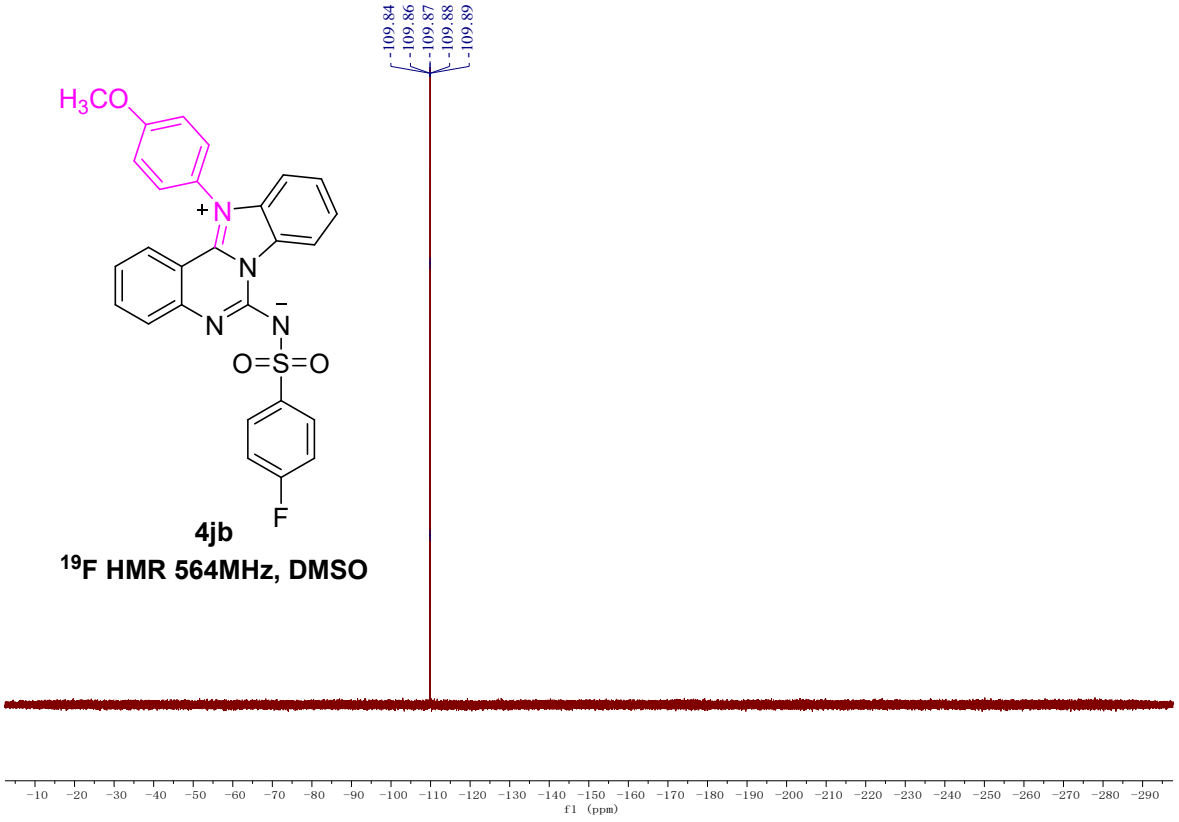

161.57
147.78
145.90
145.02
140.85
140.65
135.39
135.10
132.72
129.31
128.21
128.14
126.18
126.15
125.32
125.02
122.32
120.47
116.45
111.22
108.25
55.93
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
20.94
H3CO
Cl
Cl
N
N
N
N
Ts
4eb
13C HMR 150MHz, DMSO
f1 (ppm)

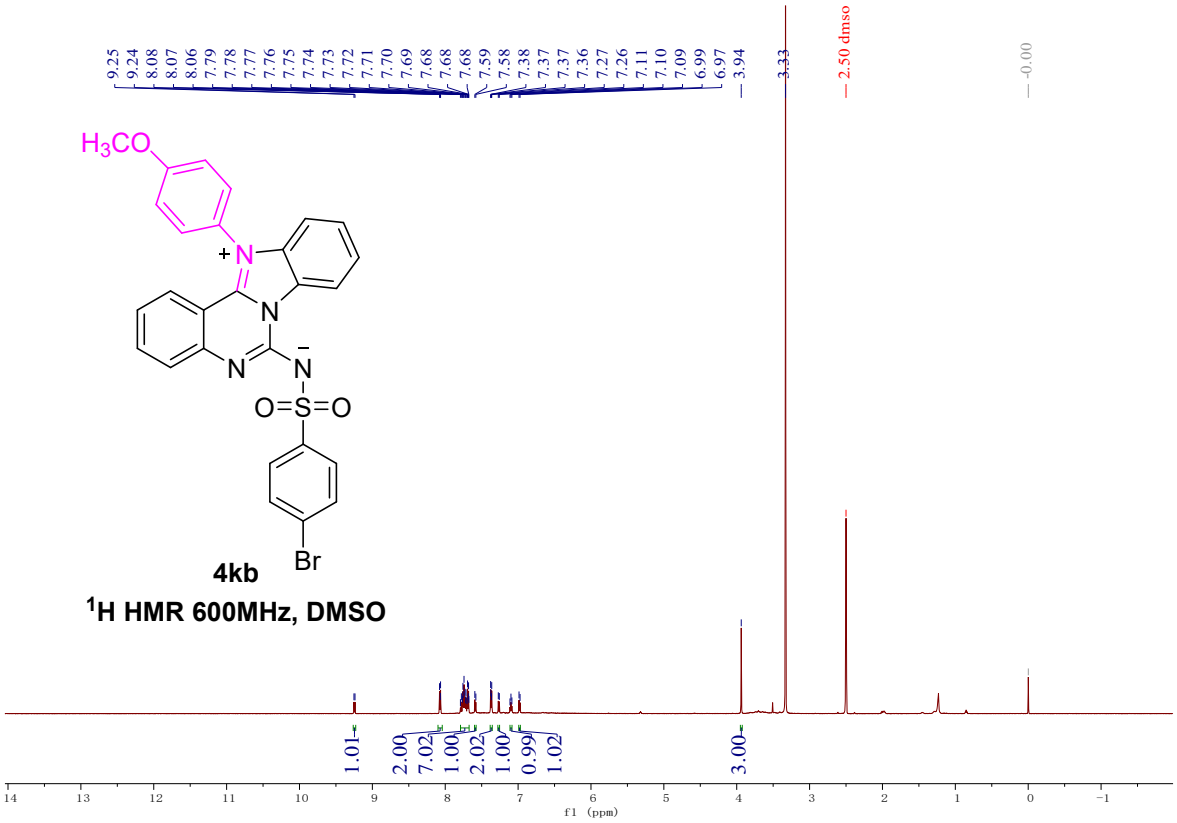

9.25
9.24
8.15
8.15
8.14
8.14
8.13
7.79
7.78
7.77
7.76
7.76
7.75
7.75
7.74
7.73
7.73
7.73
7.71
7.70
7.59
7.58
7.56
7.55
7.55
7.54
7.54
7.54
7.38
7.37
7.37
7.36
7.27
7.26
7.11
7.10
7.09
7.08
6.99
6.97
6.97
3.94
3.33
2.50 dmso
0.00
H3CO
N
N
N
O=S=O
Cl
4ib
1H HMR 600MHz, DMSO
1.00
1.97
5.03
3.02
2.01
1.03
1.01
1.03
3.03
f1 (ppm)

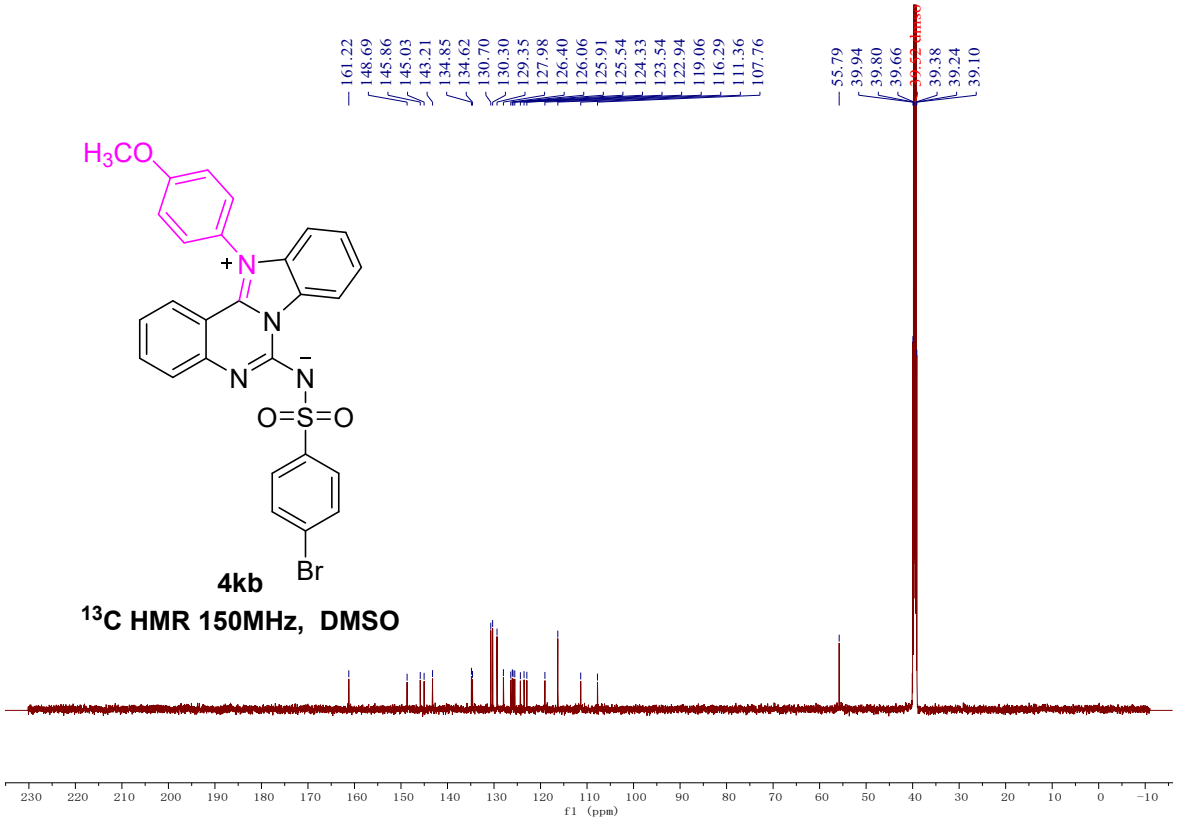

161.21
148.69
145.86
145.02
142.80
135.43
134.83
134.62
130.10
129.35
127.97
127.75
126.39
126.05
125.91
125.53
123.53
122.92
119.05
116.28
111.35
107.75
55.79
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
Cl
4ib
13C HMR 150MHz, DMSO
f1 (ppm)


9.26
9.25
8.21
8.20
8.20
8.19
7.78
7.77
7.76
7.76
7.75
7.73
7.73
7.72
7.71
7.70
7.59
7.58
7.38
7.37
7.36
7.32
7.31
7.30
7.29
7.27
7.25
7.10
7.09
7.07
6.99
6.97
3.94
3.34
2.50 dmso
0.00
H3CO
N
N
N
N
O=S=O
F
4jb
1H HMR 600MHz, DMSO
1.00
2.00
5.04
1.03
2.03
2.99
1.03
1.00
3.02
f1 (ppm)


164.12
162.47
161.21
148.77
145.88
145.02
140.27
134.81
134.62
130.94
130.88
129.37
127.94
126.41
126.04
125.93
125.49
123.53
122.83
119.08
116.27
114.66
114.52
111.33
107.70
55.79
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
F
4jb
13C HMR 150MHz, DMSO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-109.84
-109.86
-109.87
-109.88
-109.89
H3CO
N
N
N
N
O=S=O
F
4jb
19F HMR 564MHz, DMSO
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)


9.25
9.24
8.08
8.07
8.06
7.79
7.78
7.77
7.76
7.75
7.74
7.73
7.72
7.71
7.70
7.69
7.68
7.68
7.68
7.59
7.58
7.38
7.37
7.37
7.36
7.27
7.26
7.11
7.10
7.09
6.99
6.97
3.94
3.33
2.50 dmso
-0.00
H3CO
N
N
N
N
O=S=O
Br
4kb
1H HMR 600MHz, DMSO
1.01
2.00
7.02
1.00
2.02
1.00
0.99
1.02
3.00
f1 (ppm)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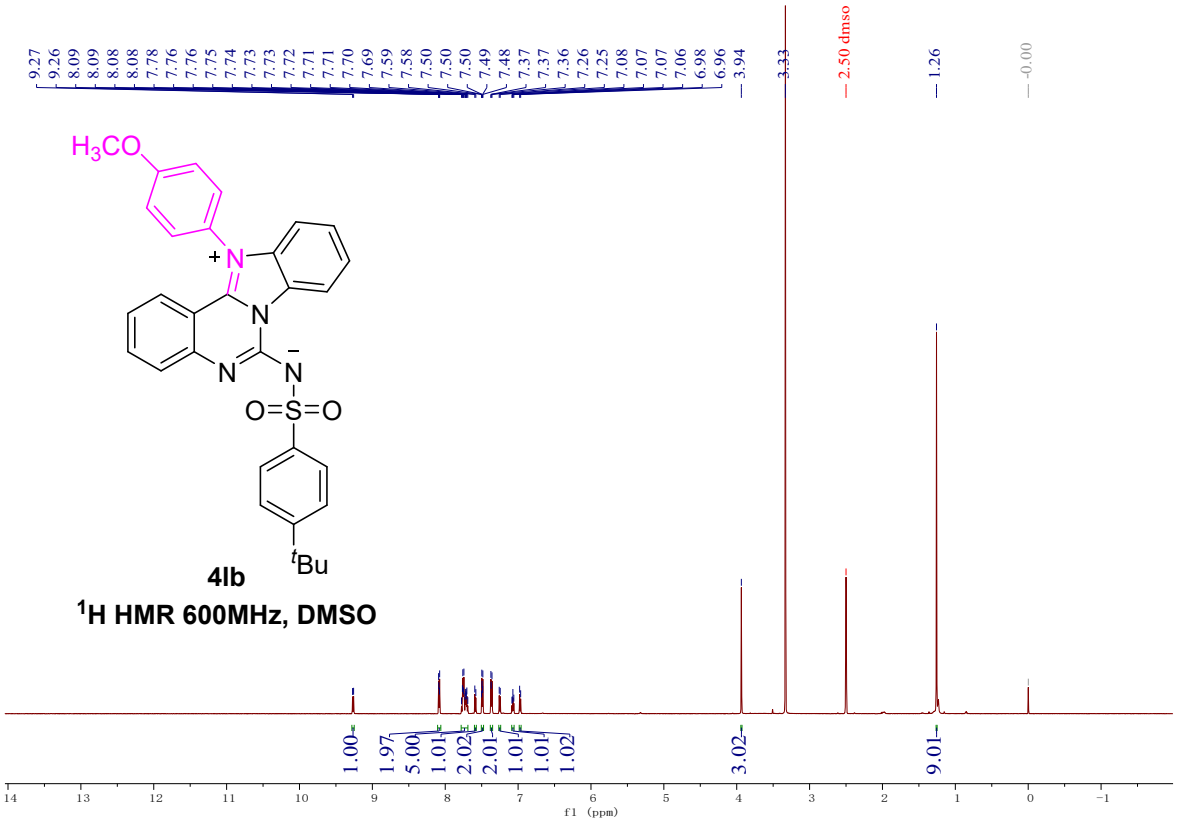
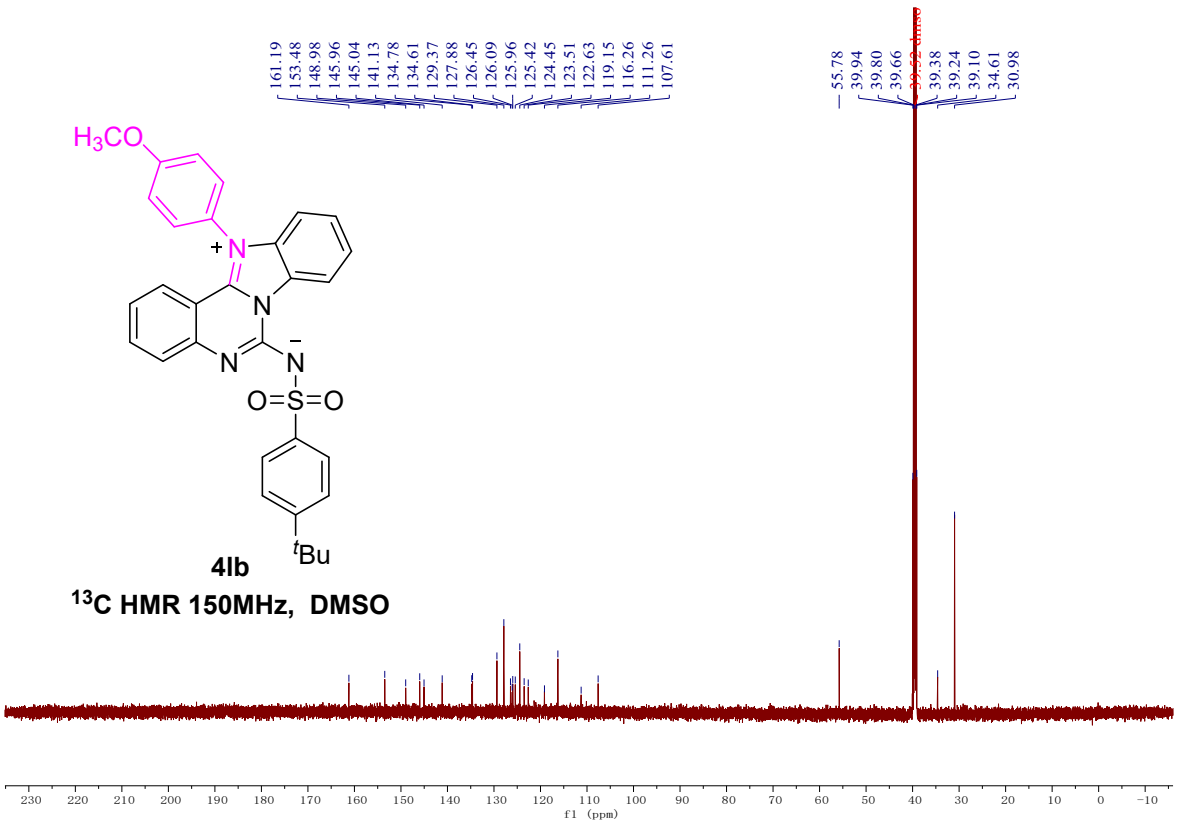
145.86
145.03
143.21
134.85
134.62
130.70
130.30
129.35
127.98
126.40
126.06
125.91
125.54
124.33
123.54
122.94
119.06
116.29
111.36
107.76
55.79
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
Br
4kb
13C HMR 150MHz, DMSO
f1 (ppm)


9.27
9.26
8.09
8.09
8.08
8.08
7.78
7.76
7.76
7.75
7.74
7.73
7.73
7.72
7.71
7.71
7.70
7.69
7.59
7.58
7.50
7.50
7.50
7.49
7.48
7.37
7.37
7.36
7.26
7.25
7.08
7.07
7.07
7.06
6.98
6.96
3.94
3.33
2.50 dmso
1.26
-0.00
H3CO
N
N
N
N
O=S=O
tBu
4lb
1H HMR 600MHz, DMSO
1.00
1.97
5.00
1.01
2.02
2.01
1.01
1.01
1.02
3.02
9.01
f1 (ppm)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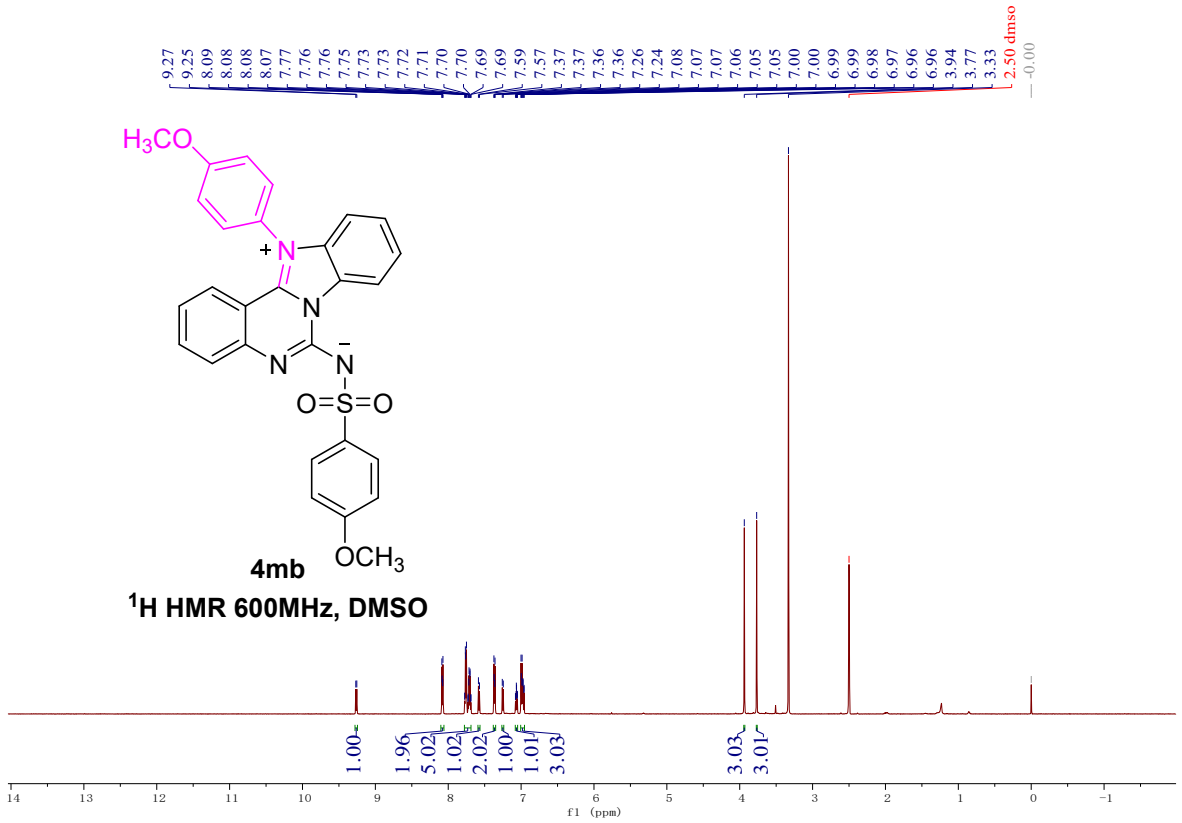
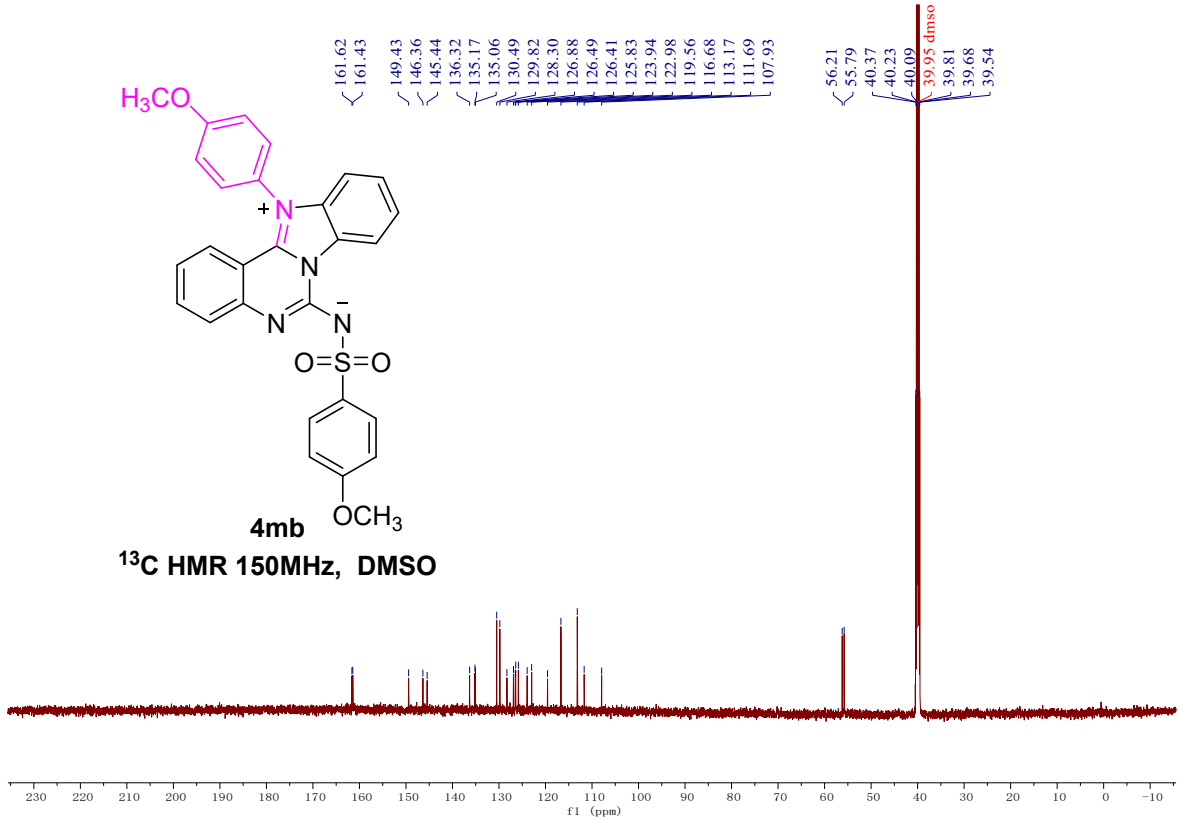
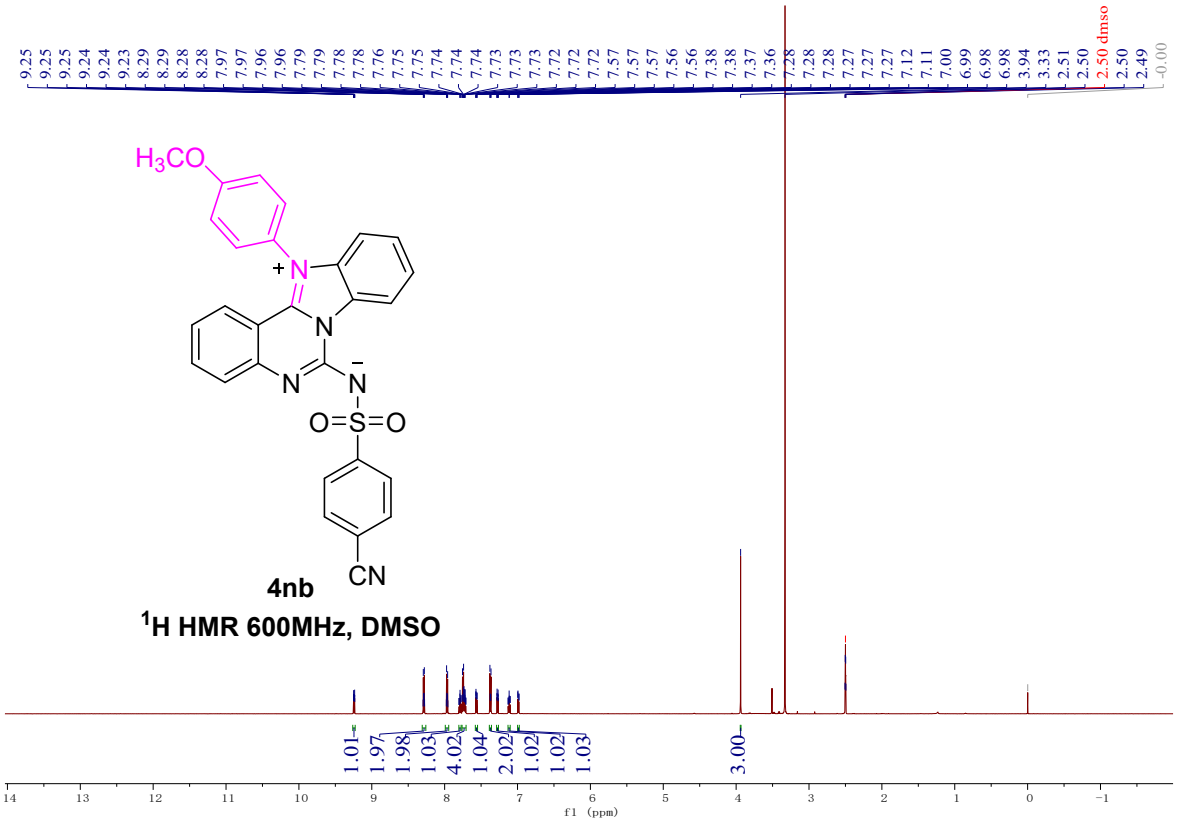
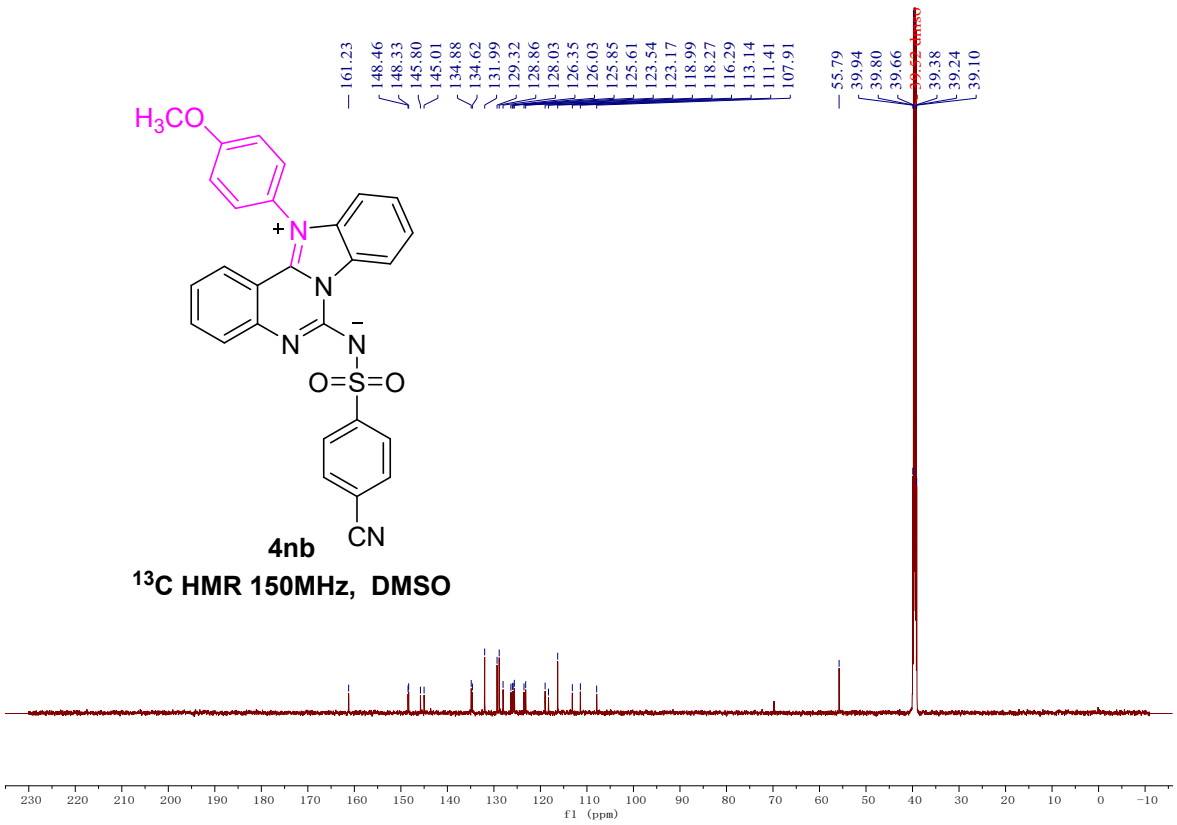
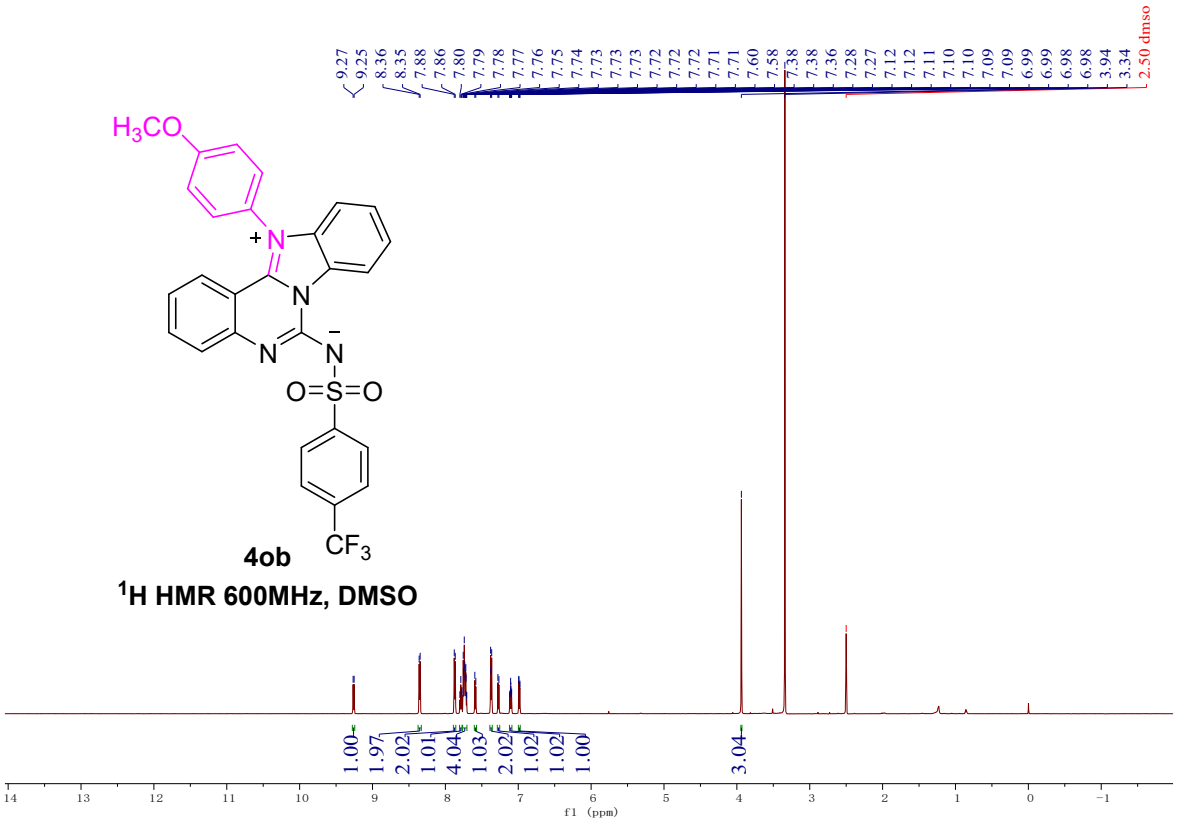
153.48
148.98
145.96
145.04
141.13
134.78
134.61
129.37
127.88
126.45
126.09
125.96
125.42
124.45
123.51
122.63
119.15
116.26
111.26
107.61
55.78
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
34.61
30.98
H3CO
N
N
N
N
O=S=O
tBu
4lb
13C HMR 150MHz, DMSO
f1 (ppm)

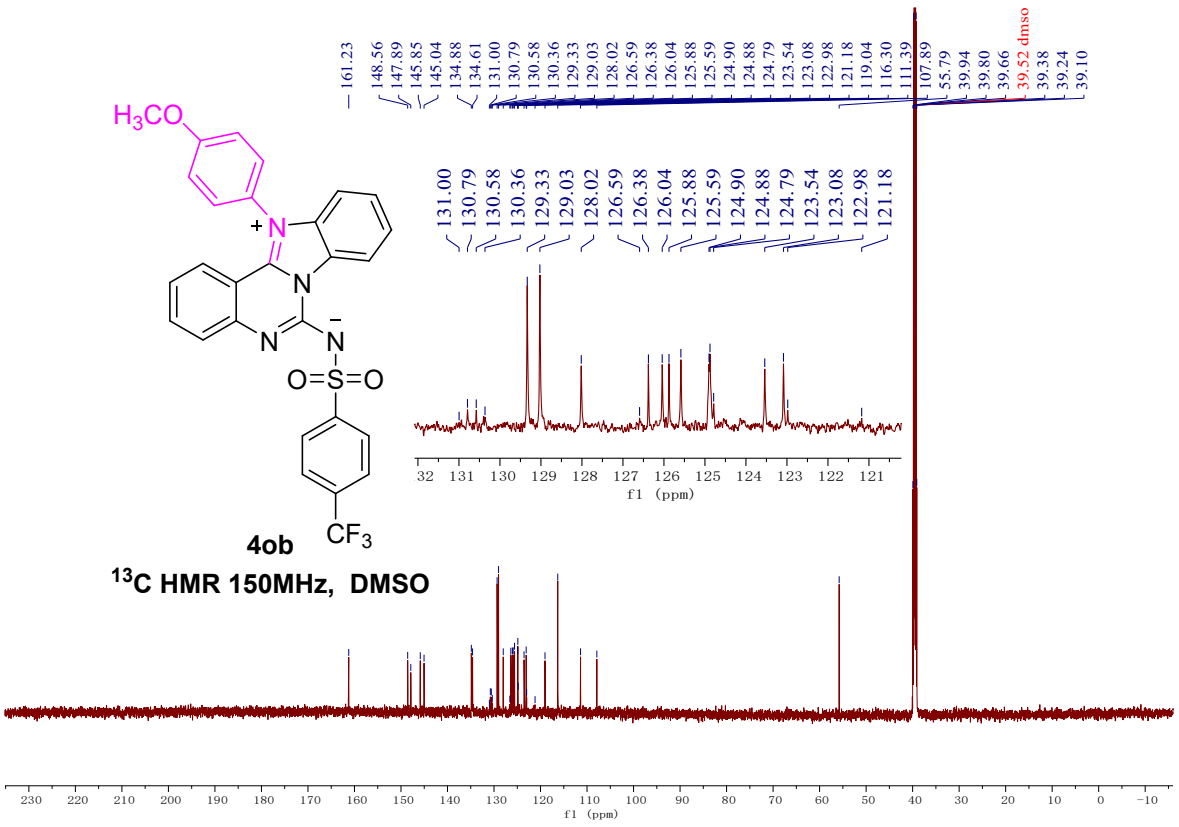

9.27
9.25
8.09
8.08
8.08
8.07
7.77
7.76
7.76
7.75
7.73
7.73
7.72
7.71
7.70
7.70
7.69
7.69
7.59
7.57
7.37
7.37
7.36
7.36
7.26
7.24
7.08
7.07
7.07
7.06
7.05
7.05
7.00
7.00
6.99
6.99
6.98
6.97
6.96
6.96
3.94
3.77
3.33
2.50 dmso
-0.00
H3CO
N
N
N
N
O=S=O
OCH3
4mb
1H HMR 600MHz, DMSO
1.00
1.96
5.02
1.02
2.02
1.00
1.01
3.03
3.03
3.01
f1 (ppm)

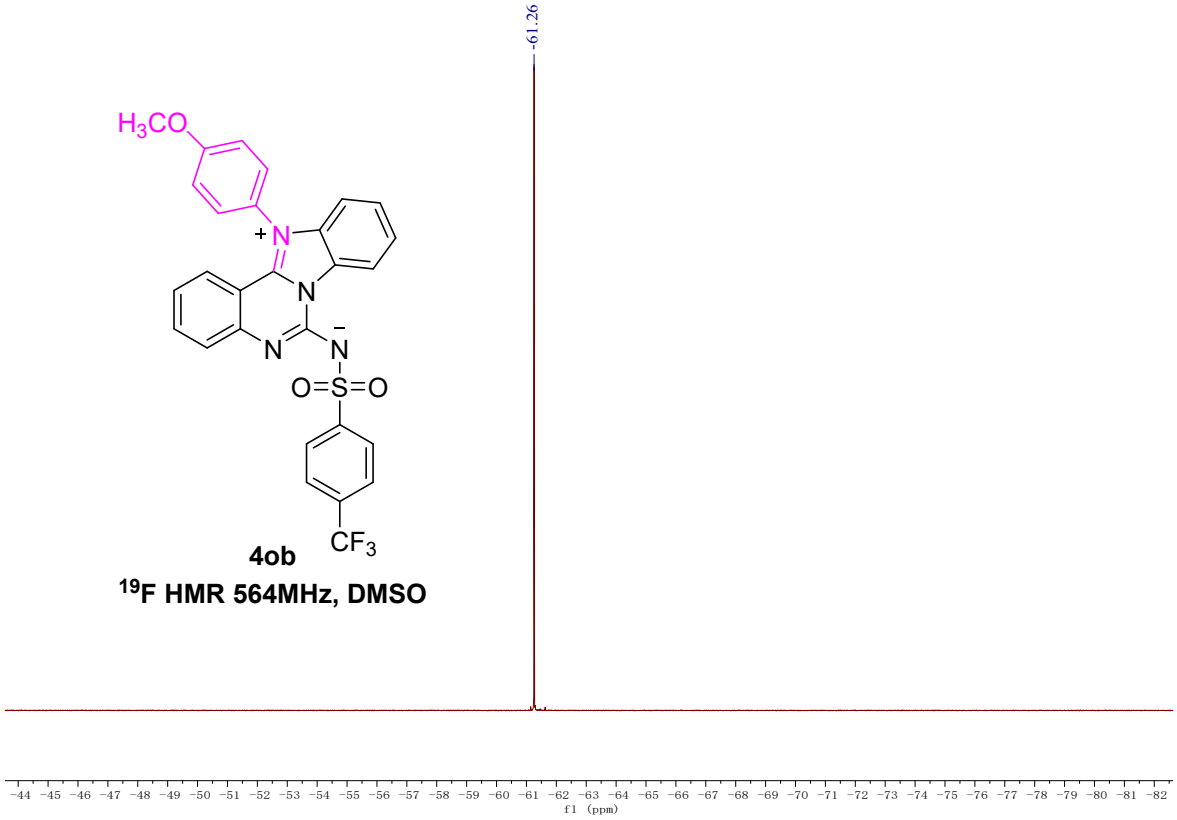

161.62
161.43
149.43
146.36
145.44
136.32
135.17
135.06
130.49
129.82
128.30
126.88
126.49
126.41
125.83
123.94
122.98
119.56
116.68
113.17
111.69
107.93
56.21
55.79
40.37
40.23
40.09
39.95 dmso
39.81
39.68
39.54
H3CO
N
N
N
N
O=S=O
OCH3
4mb
13C HMR 150MHz, DMSO
f1 (ppm)


H3CO
N
N
N
N
O=S=O
CN
4nb
1H HMR 600MHz, DMSO
1.01
1.97
1.98
1.03
4.02
1.04
2.02
1.02
1.02
1.03
3.00
f1 (ppm)


H3CO
N
N
N
N
O=S=O
CN
4nb
13C HMR 150MHz, DMSO
f1 (ppm)

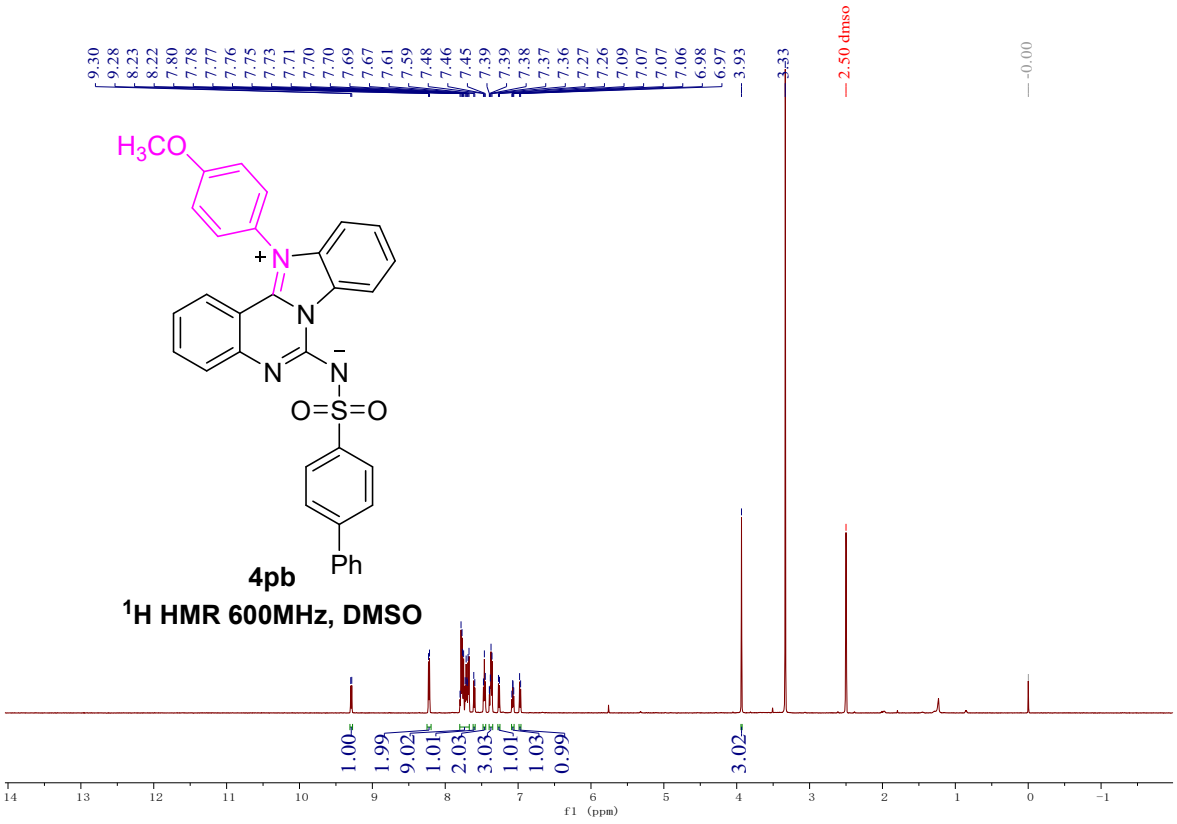

9.27
9.25
8.36
8.35
7.88
7.86
7.80
7.79
7.78
7.77
7.76
7.75
7.74
7.73
7.73
7.73
7.72
7.72
7.72
7.71
7.71
7.60
7.58
7.38
7.38
7.36
7.28
7.27
7.12
7.12
7.11
7.10
7.10
7.09
7.09
6.99
6.99
6.98
6.98
3.94
3.34
2.50 dmso
H3CO
N
N
N
N
O=S=O
CF3
4ob
1H HMR 600MHz, DMSO
1.00
1.97
2.02
1.01
4.04
1.03
2.02
1.02
1.02
1.00
3.04
f1 (ppm)


161.23
148.56
147.89
145.85
145.04
134.88
134.61
131.00
130.79
130.58
130.36
129.33
129.03
128.02
126.59
126.38
126.04
125.88
125.59
124.90
124.88
124.79
123.54
123.08
122.98
121.18
119.04
116.30
111.39
107.89
55.79
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
CF3
4ob
13C HMR 150MHz, DMSO
f1 (ppm)



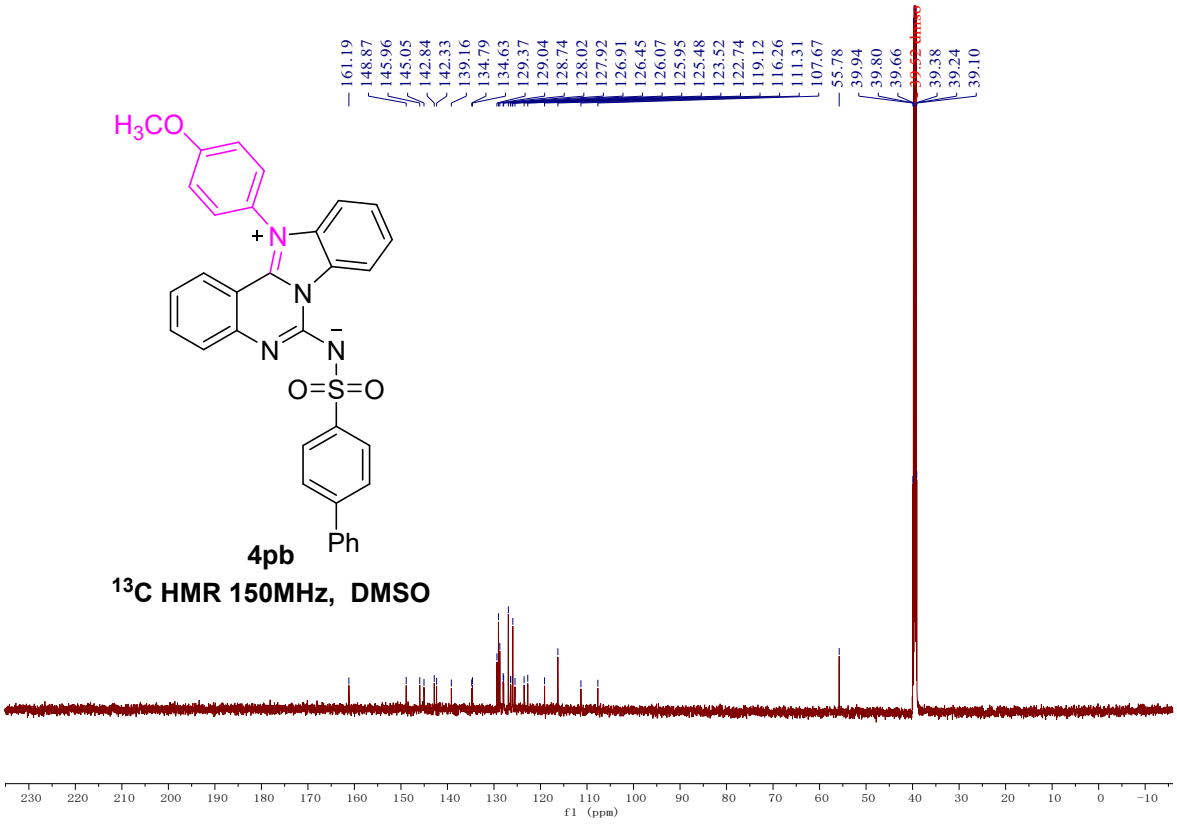
4ob

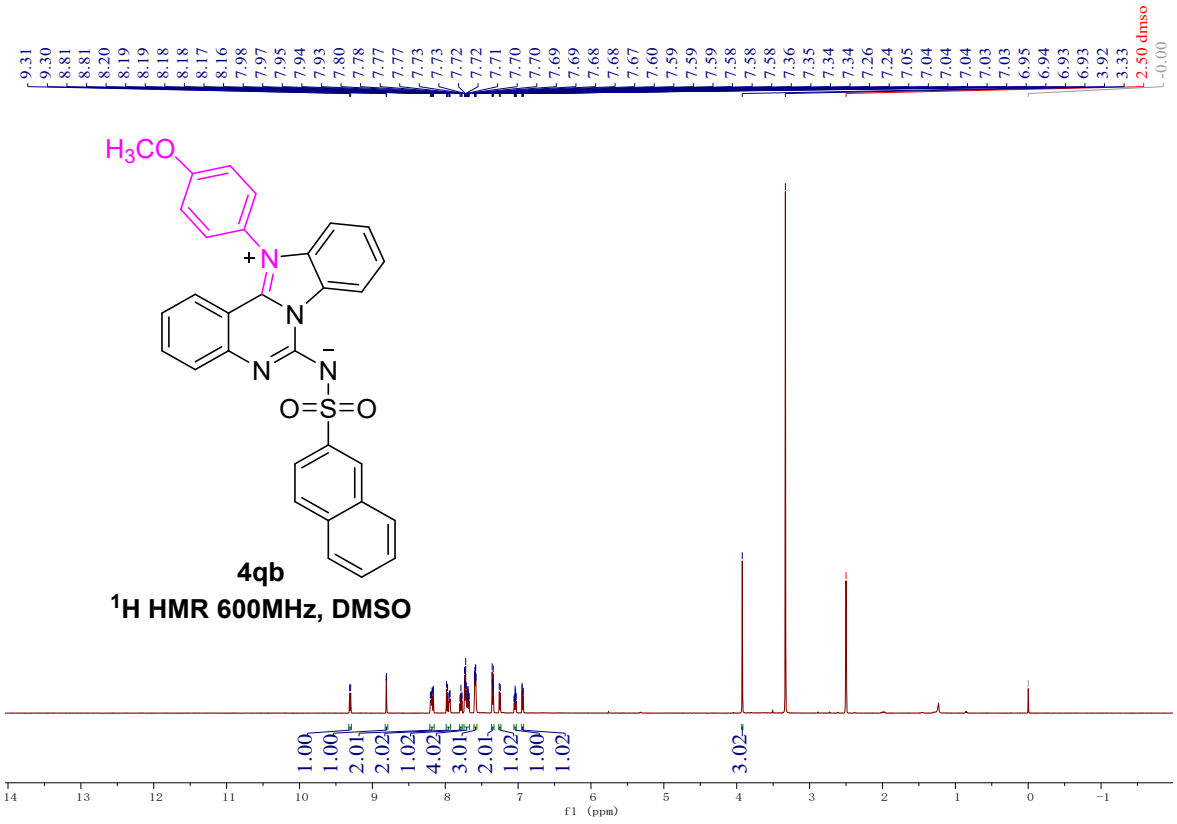
^{19}F HMR 564MHz, DMSO

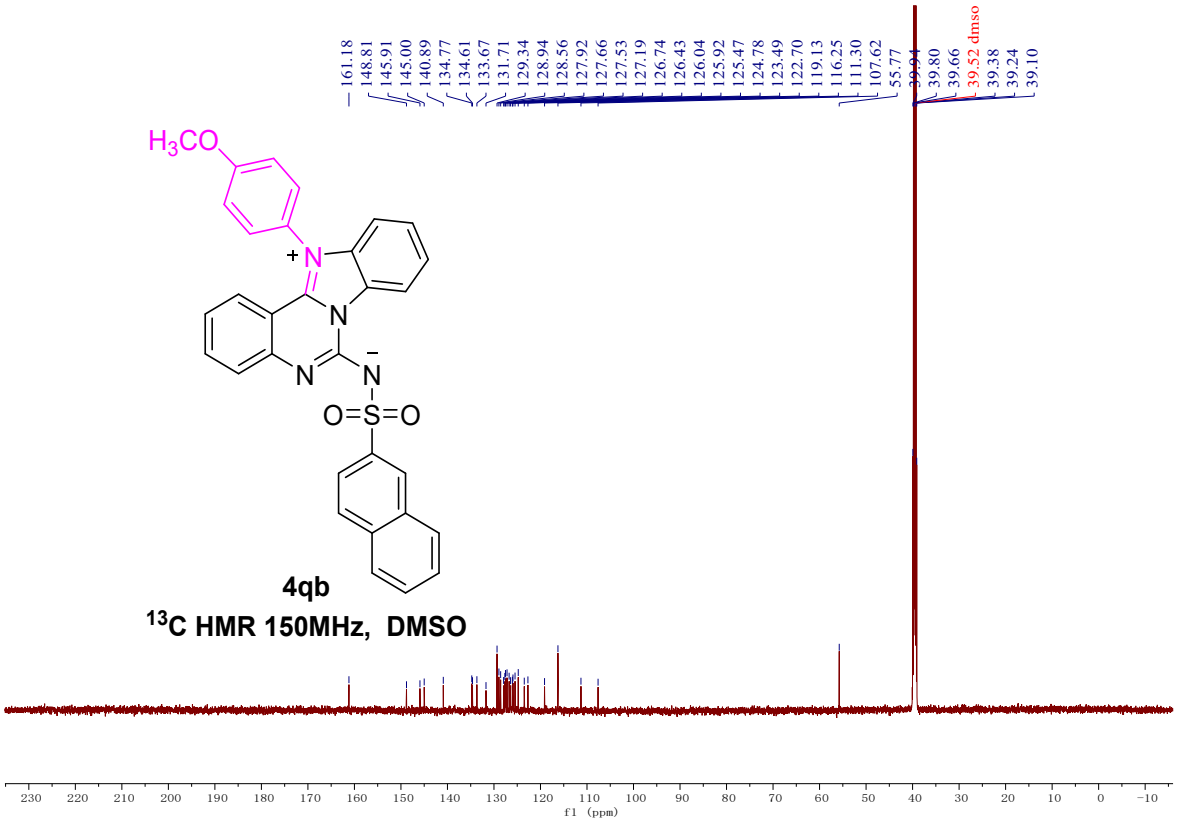


4pb

^{1}H HMR 600MHz, DMSO

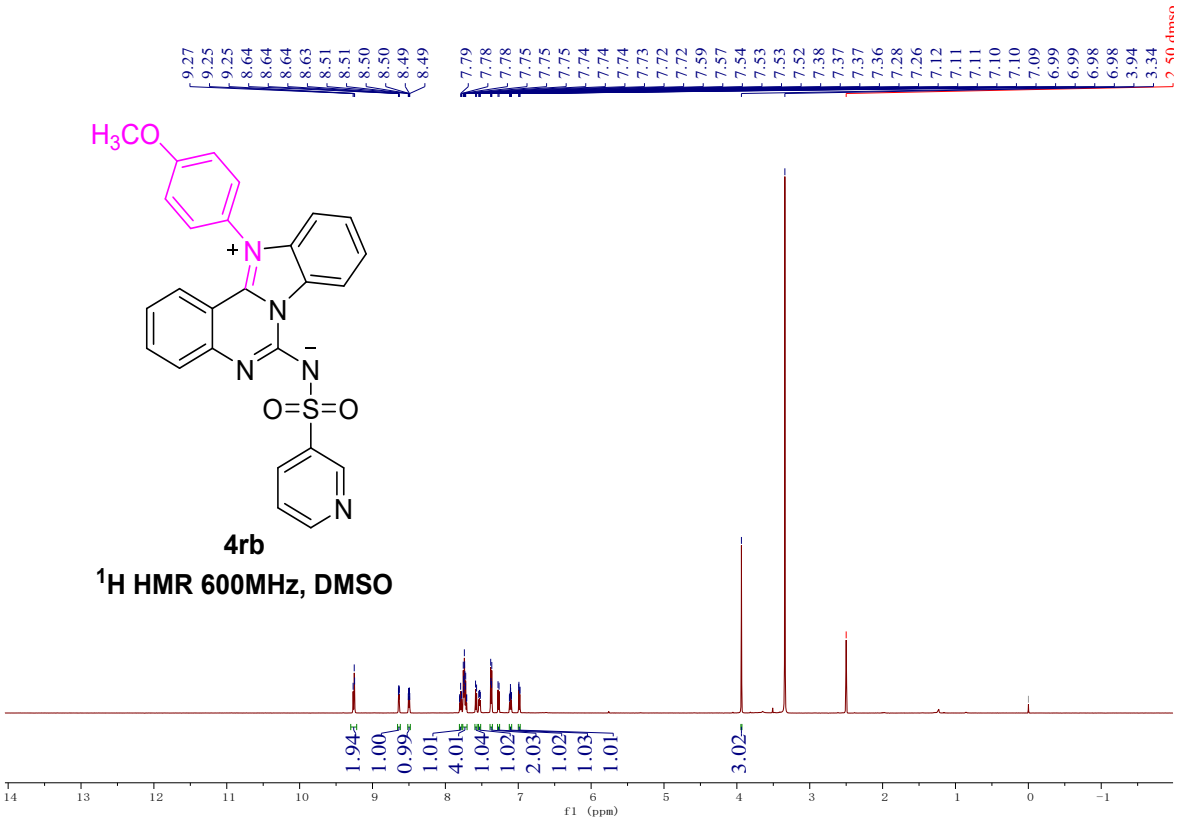

H3CO
N
N
N
N
O=S=O
Ph
4pb
13C HMR 150MHz, DMSO
f1 (ppm)


H3CO
N
N
N
N
O=S=O
4qb
1H HMR 600MHz, DMSO
f1 (ppm)



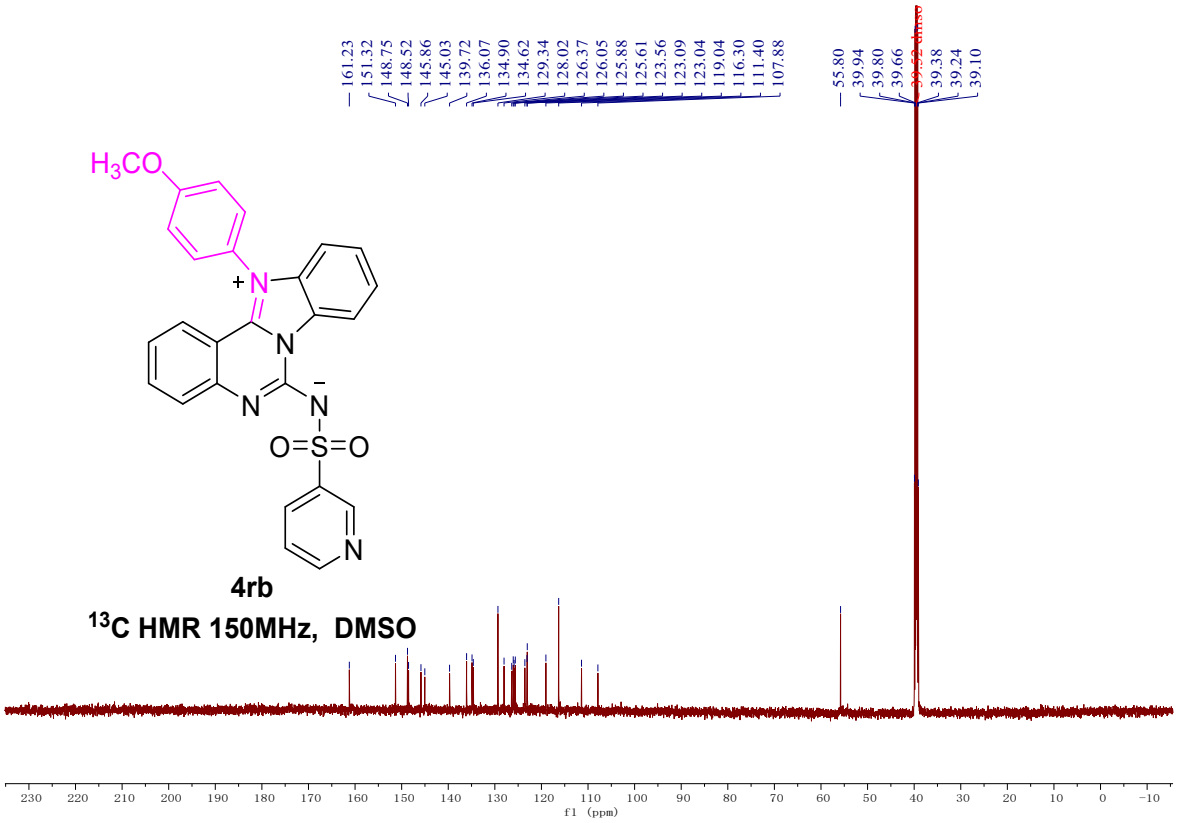
4qb

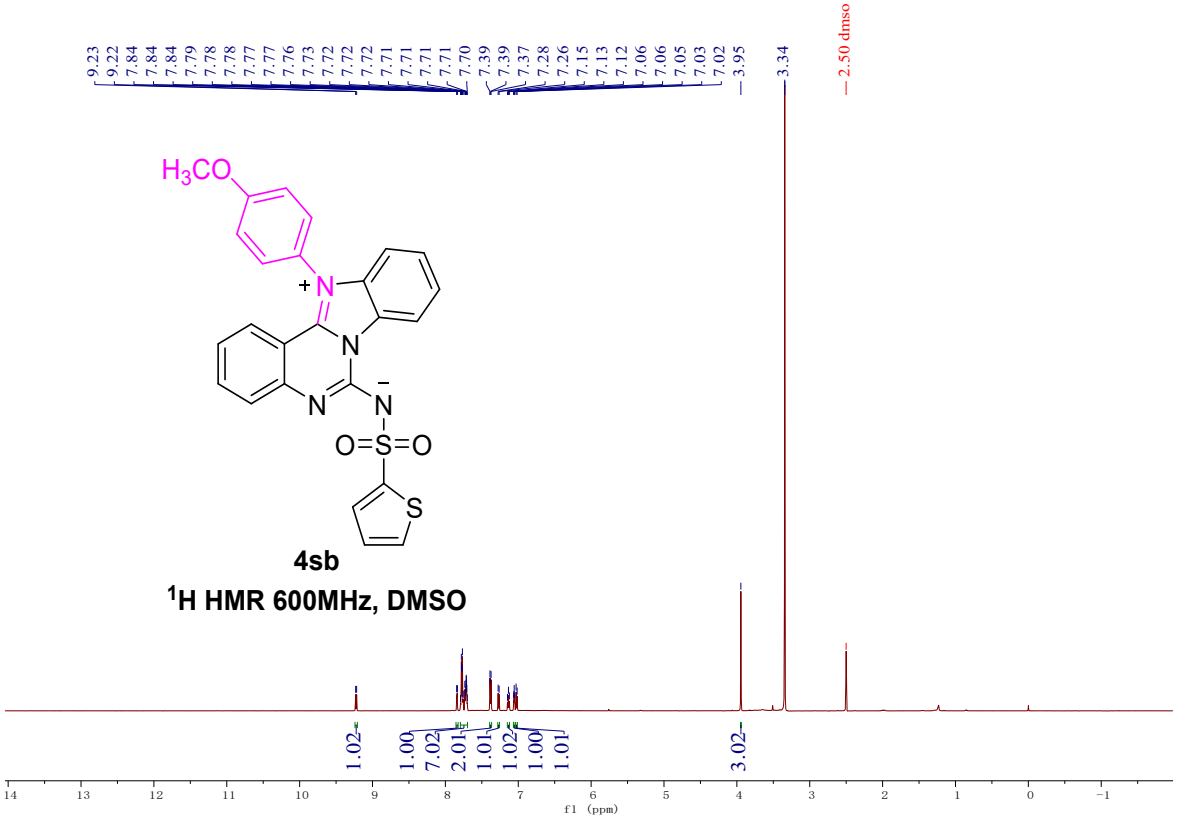
^{13}C HMR 150MHz, DMSO

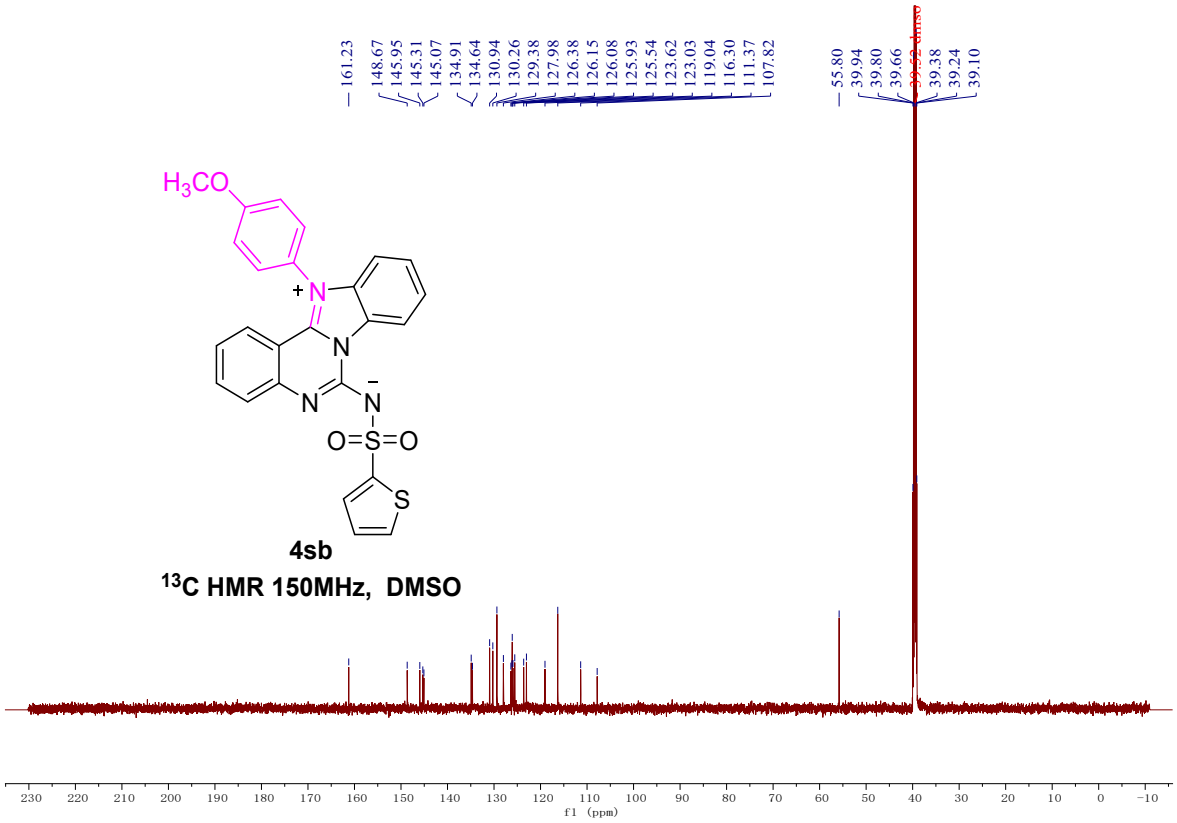


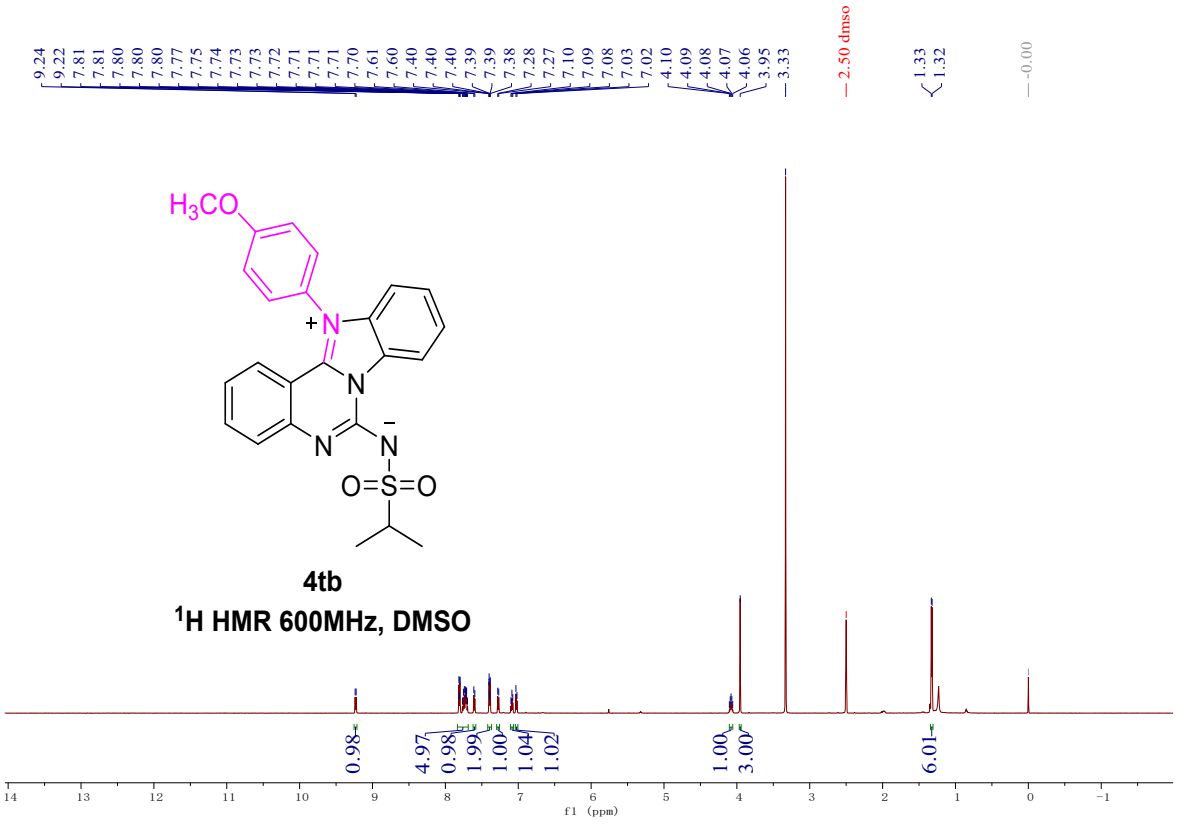
4rb

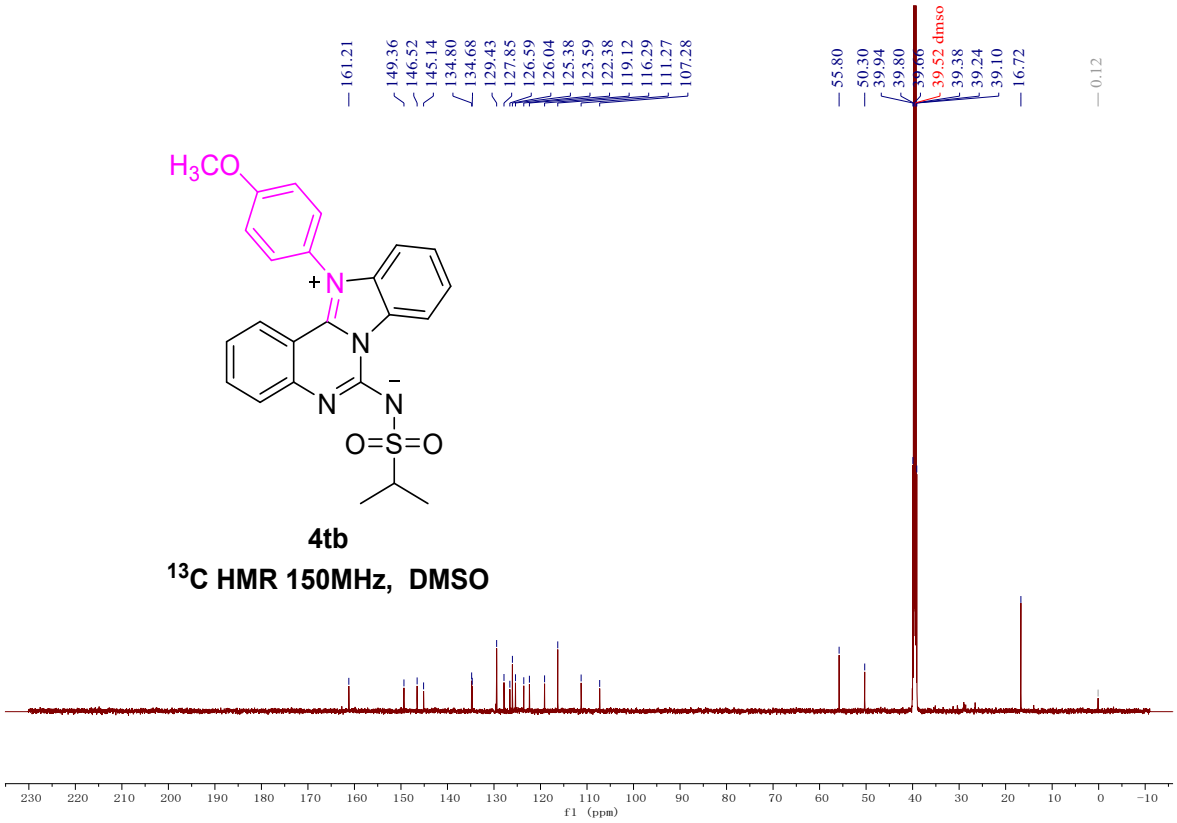
^{1}H HMR 600MHz, DMSO


161.23
151.32
148.75
148.52
145.86
145.03
139.72
136.07
134.90
134.62
129.34
128.02
126.37
126.05
125.88
125.61
123.56
123.09
123.04
119.04
116.30
111.40
107.88
55.80
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
N
4rb
13C HMR 150MHz, DMSO
f1 (ppm)


9.23
9.22
7.84
7.84
7.84
7.79
7.78
7.78
7.77
7.77
7.76
7.73
7.72
7.72
7.72
7.71
7.71
7.71
7.71
7.70
7.39
7.39
7.37
7.28
7.26
7.15
7.13
7.12
7.06
7.06
7.05
7.03
7.02
3.95
3.34
2.50 dmso
H3CO
N
N
N
N
O=S=O
S
4sb
1H HMR 600MHz, DMSO
1.02
1.00
7.02
2.01
1.01
1.02
1.00
1.01
3.02
f1 (ppm)

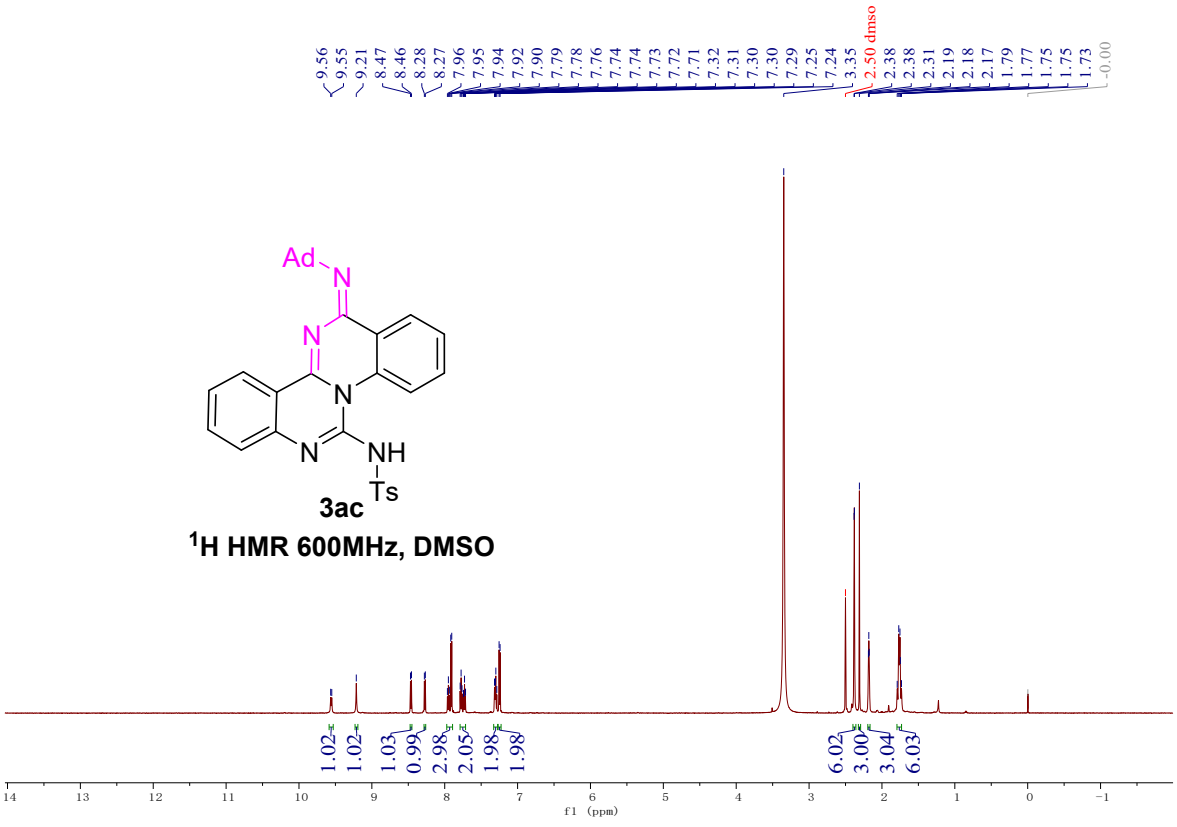

161.23
148.67
145.95
145.31
145.07
134.91
134.64
130.94
130.26
129.38
127.98
126.38
126.15
126.08
125.93
125.54
123.62
123.03
119.04
116.30
111.37
107.82
55.80
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
H3CO
N
N
N
N
O=S=O
S
4sb
13C HMR 150MHz, DMSO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.24
9.22
7.81
7.81
7.80
7.80
7.80
7.77
7.75
7.74
7.73
7.73
7.72
7.71
7.71
7.71
7.70
7.61
7.60
7.40
7.40
7.40
7.39
7.39
7.38
7.28
7.27
7.10
7.09
7.08
7.03
7.02
4.10
4.09
4.08
4.07
4.06
3.95
3.33
2.50 dmso
1.33
1.32
0.00
H3CO
N
N
N
N
O=S=O
4tb
1H HMR 600MHz, DMSO
0.98
4.97
0.98
1.99
1.00
1.04
1.02
1.00
3.00
6.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



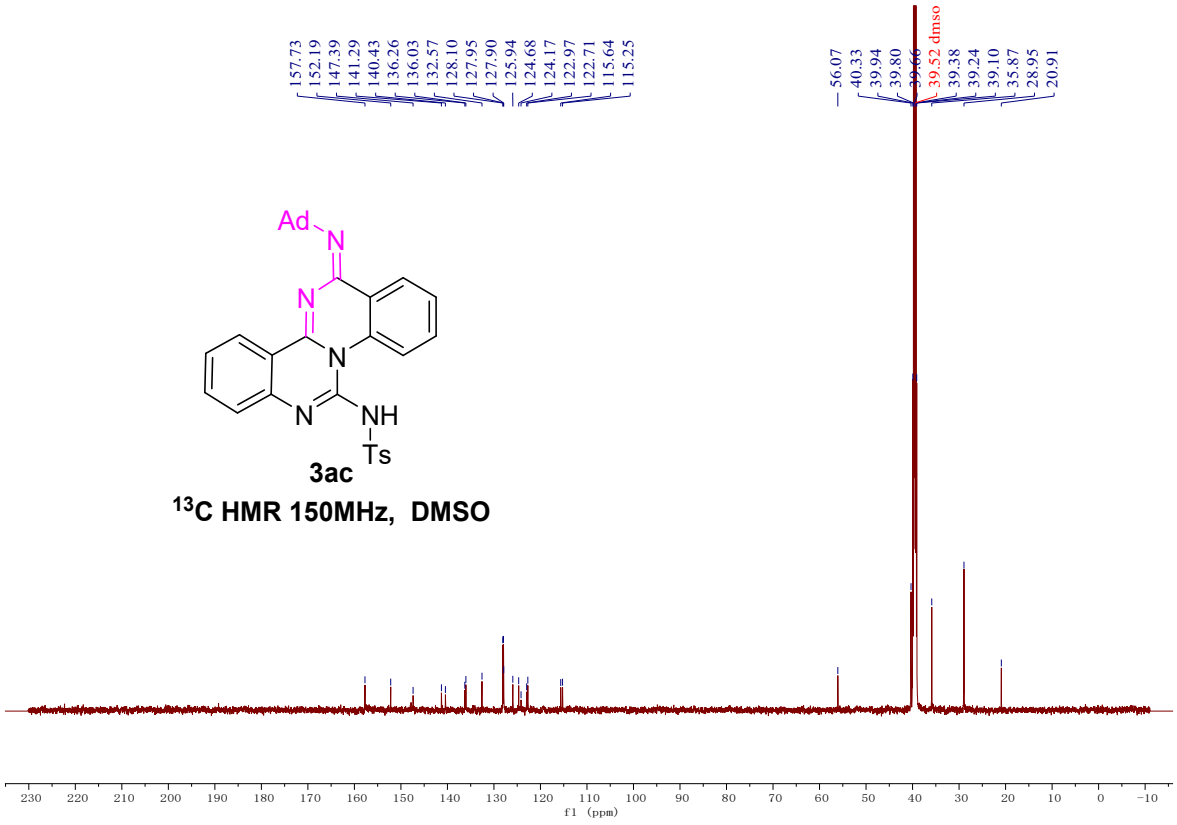
4tb

^{13}C HMR 150MHz, DMSO



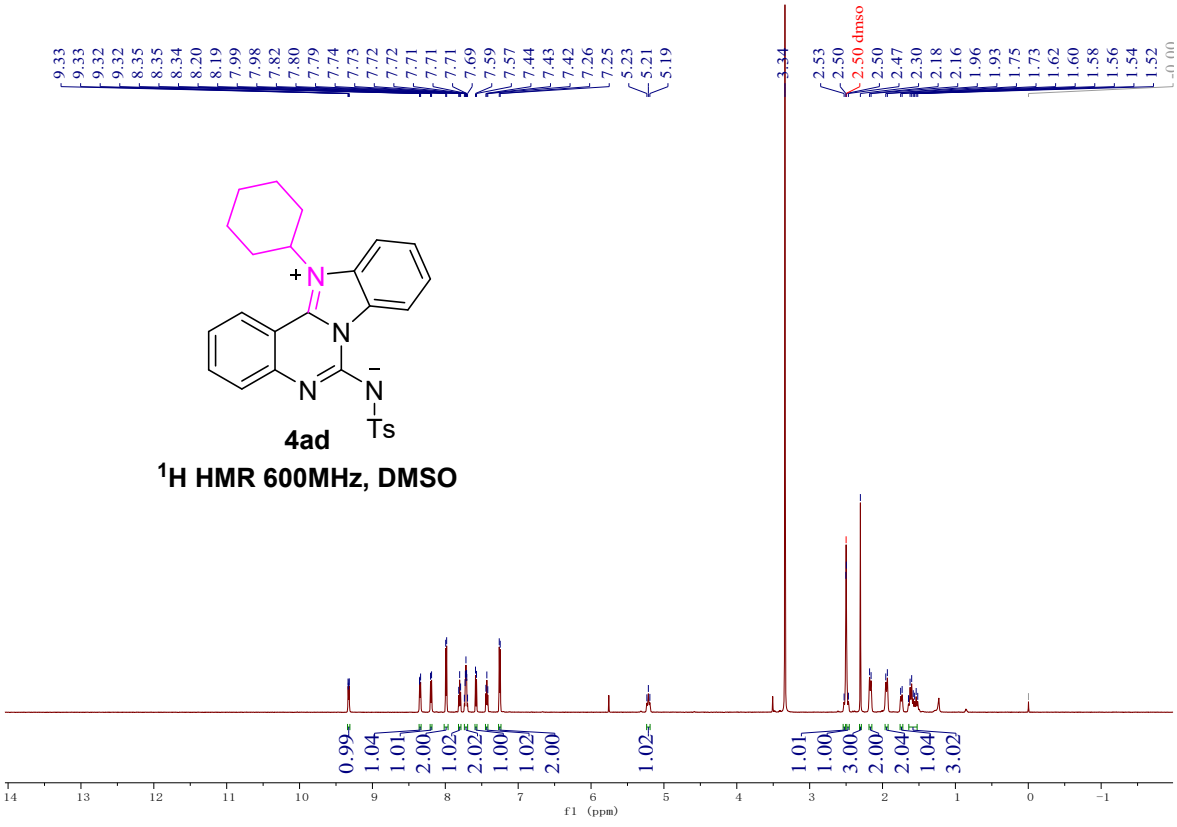
3ac

^{1}H HMR 600MHz, DMSO



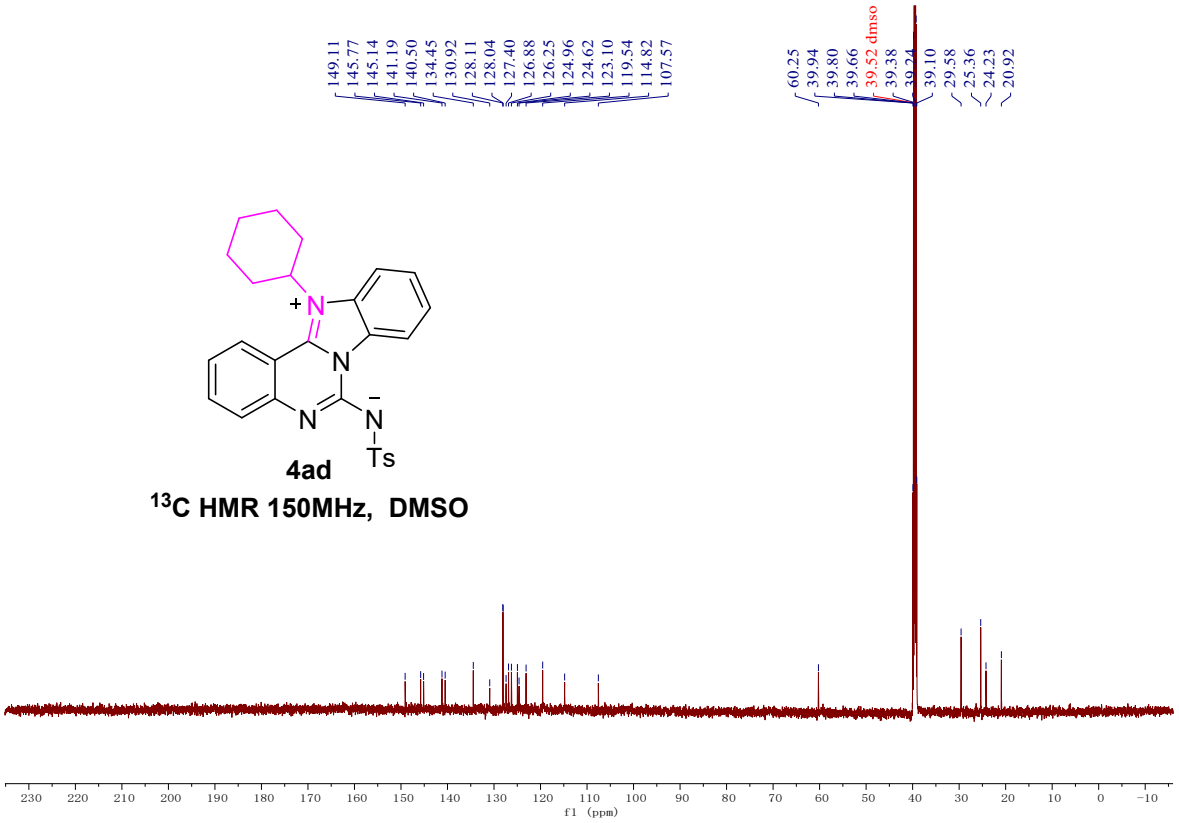
3ac

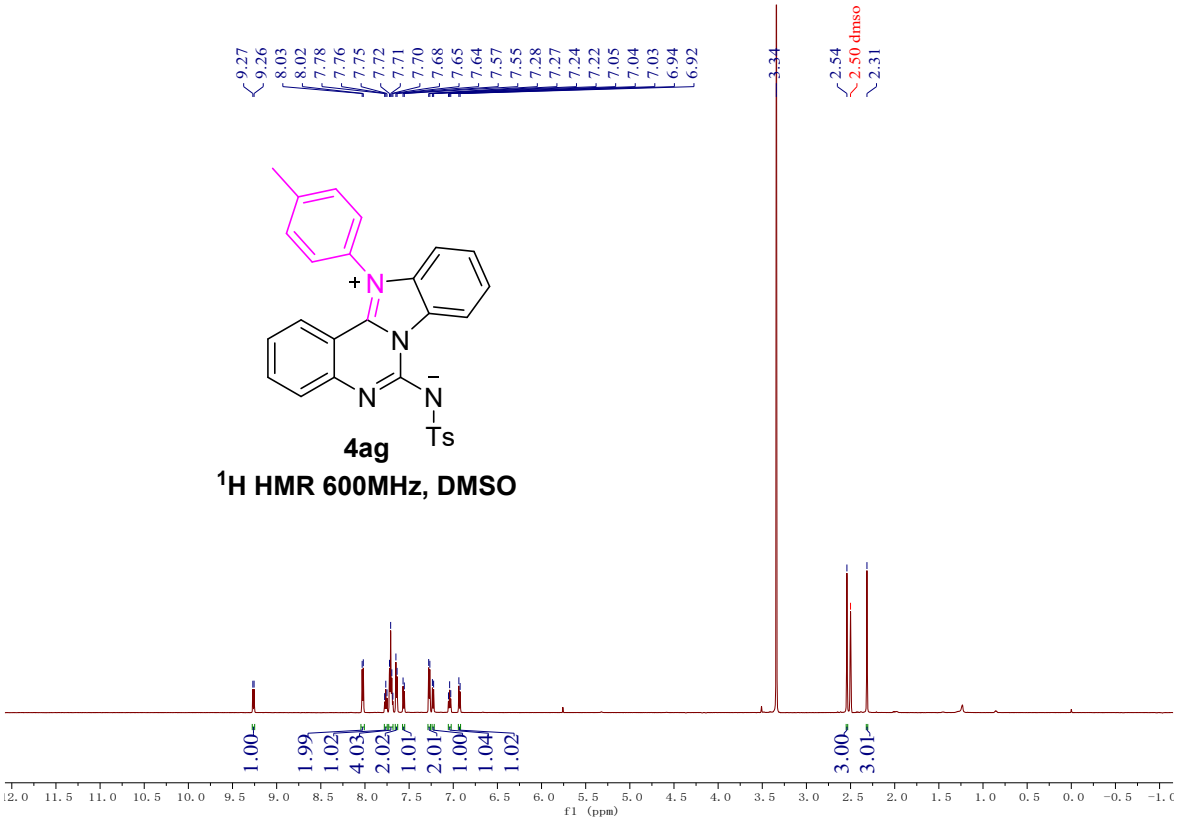
^{13}C HMR 150MHz, DMSO

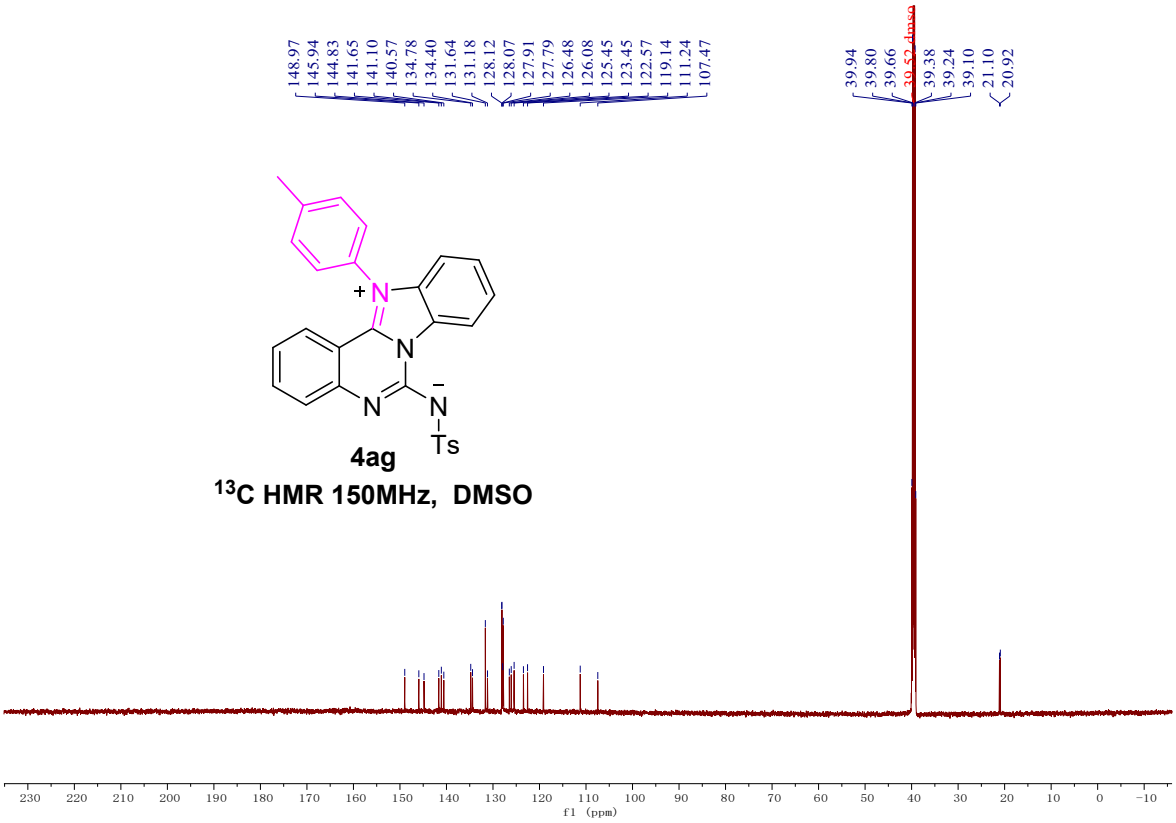


4ad

^{1}H HMR 600MHz, DMSO

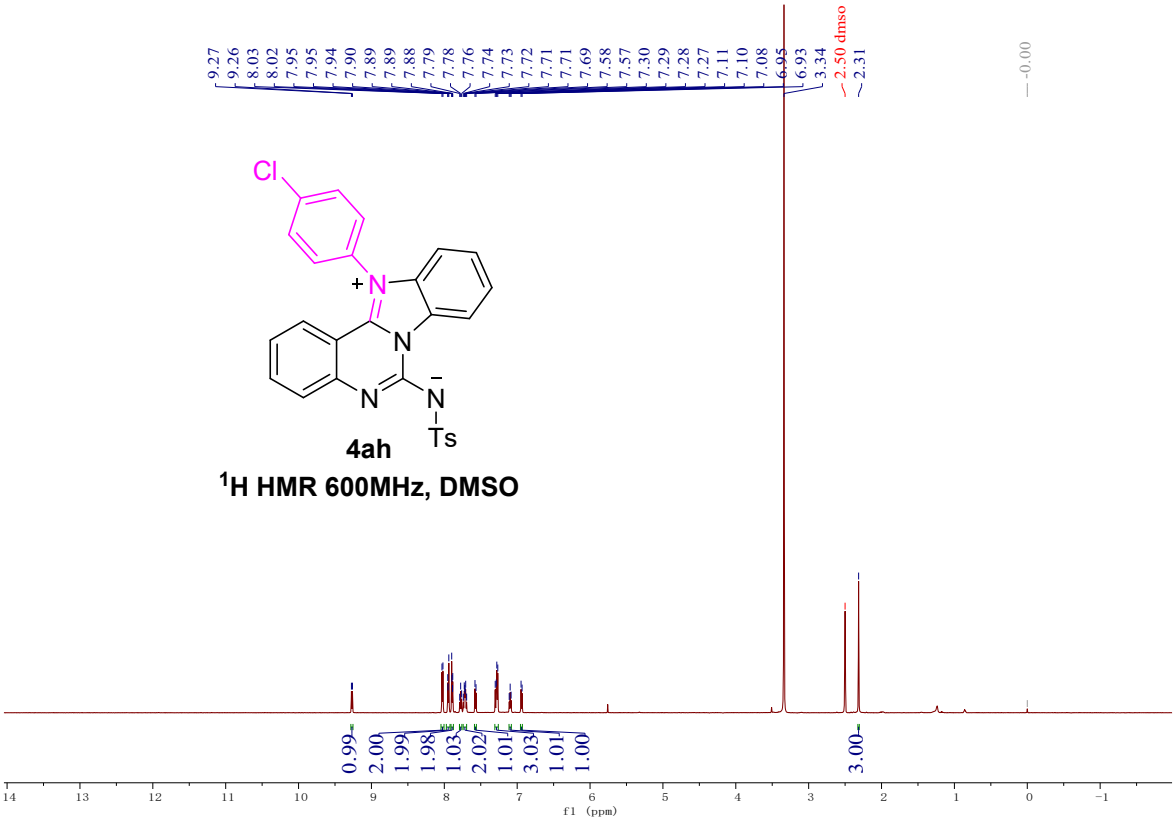

149.11
145.77
145.14
141.19
140.50
134.45
130.92
128.11
128.04
127.40
126.88
126.25
124.96
124.62
123.10
119.54
114.82
107.57
60.25
39.94
39.80
39.66
39.52 dmso
39.38
39.24
39.10
29.58
25.36
24.23
20.92
N
N
N
N
Ts
4ad
13C HMR 150MHz, DMSO
f1 (ppm)


9.27
9.26
8.03
8.02
7.78
7.76
7.75
7.72
7.71
7.70
7.68
7.65
7.64
7.57
7.55
7.28
7.27
7.24
7.22
7.05
7.04
7.03
6.94
6.92
3.34
2.54
2.50 dmso
2.31
N
N
N
N
Ts
4ag
1H HMR 600MHz, DMSO
1.00
1.99
1.02
4.03
2.02
1.01
2.01
1.00
1.04
1.02
3.00
3.01
f1 (ppm)



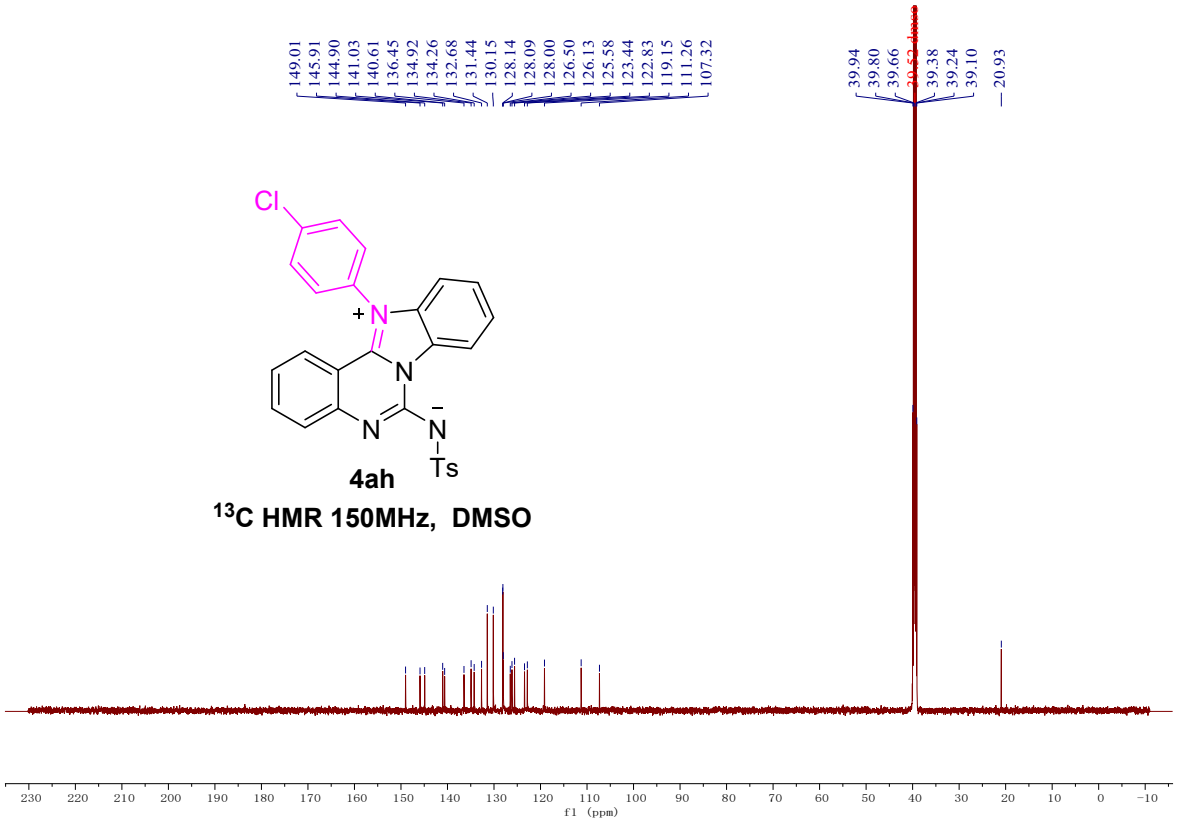
4ag

^{13}C HMR 150MHz, DMSO



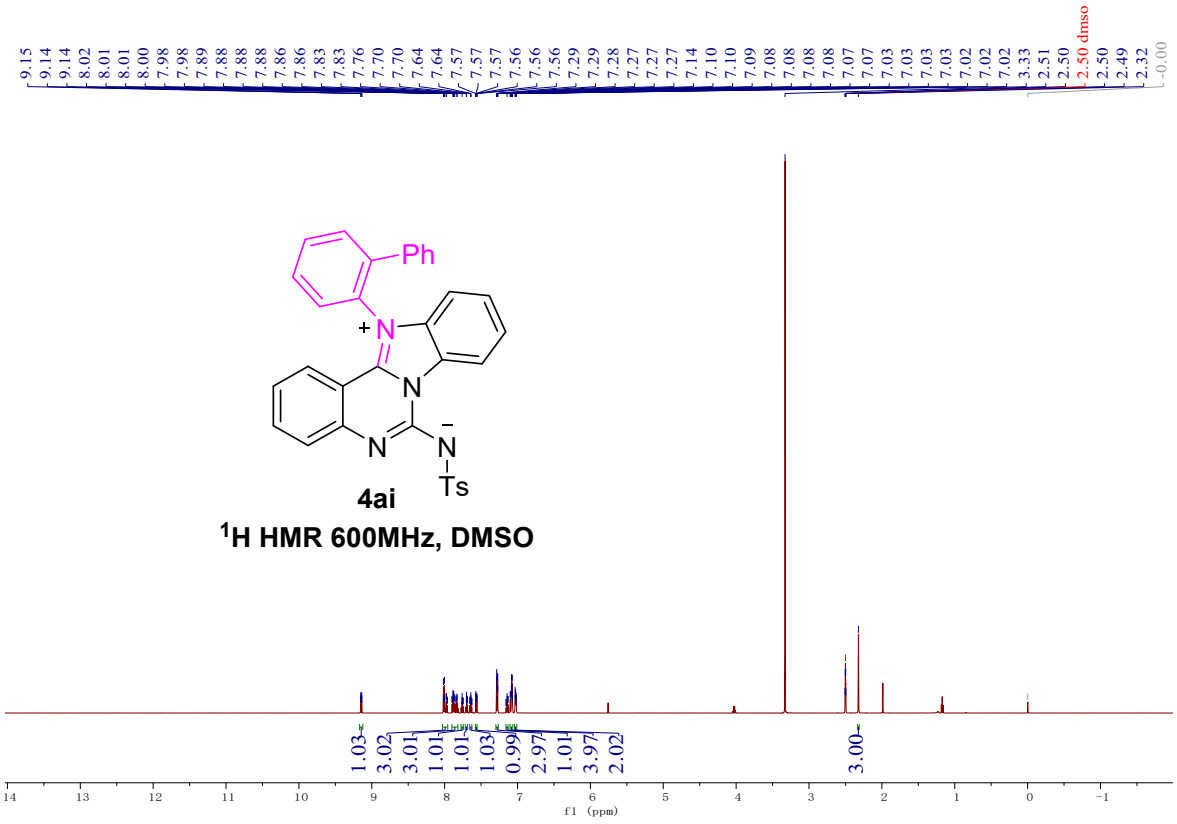
4ah

^{1}H HMR 600MHz, DMSO



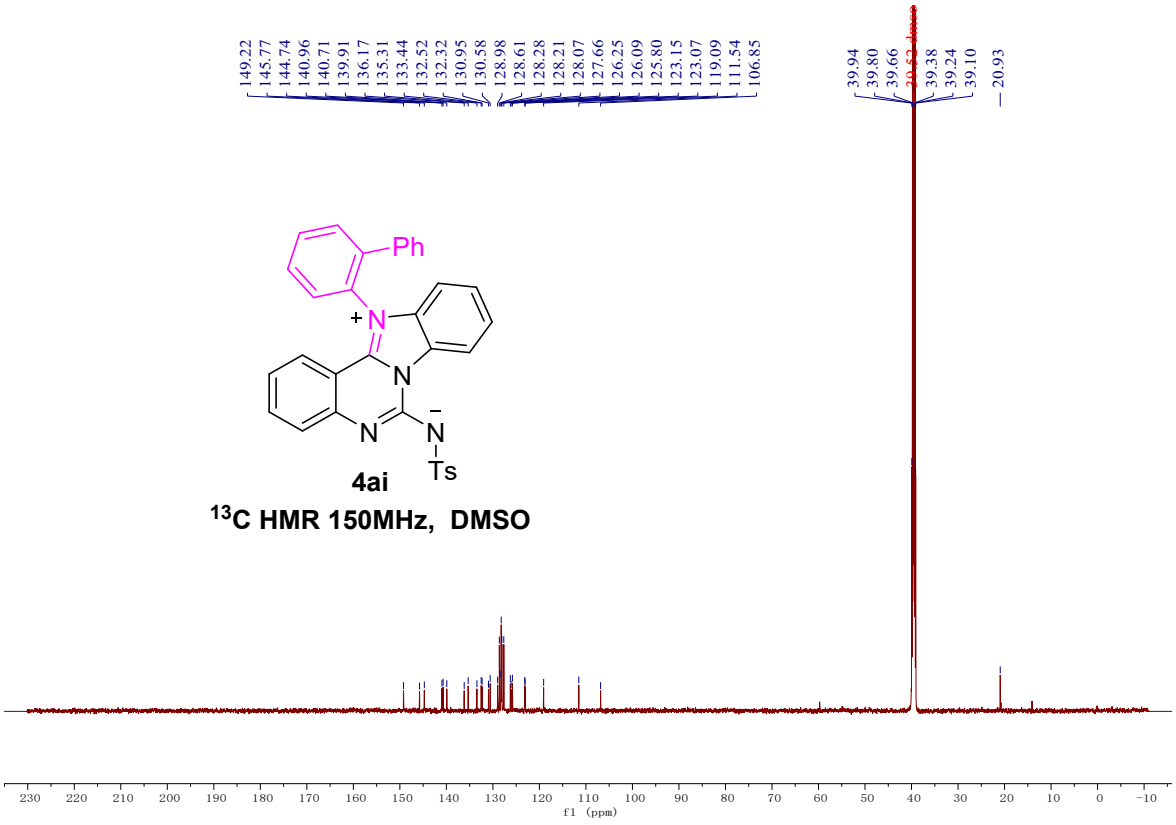
4ah

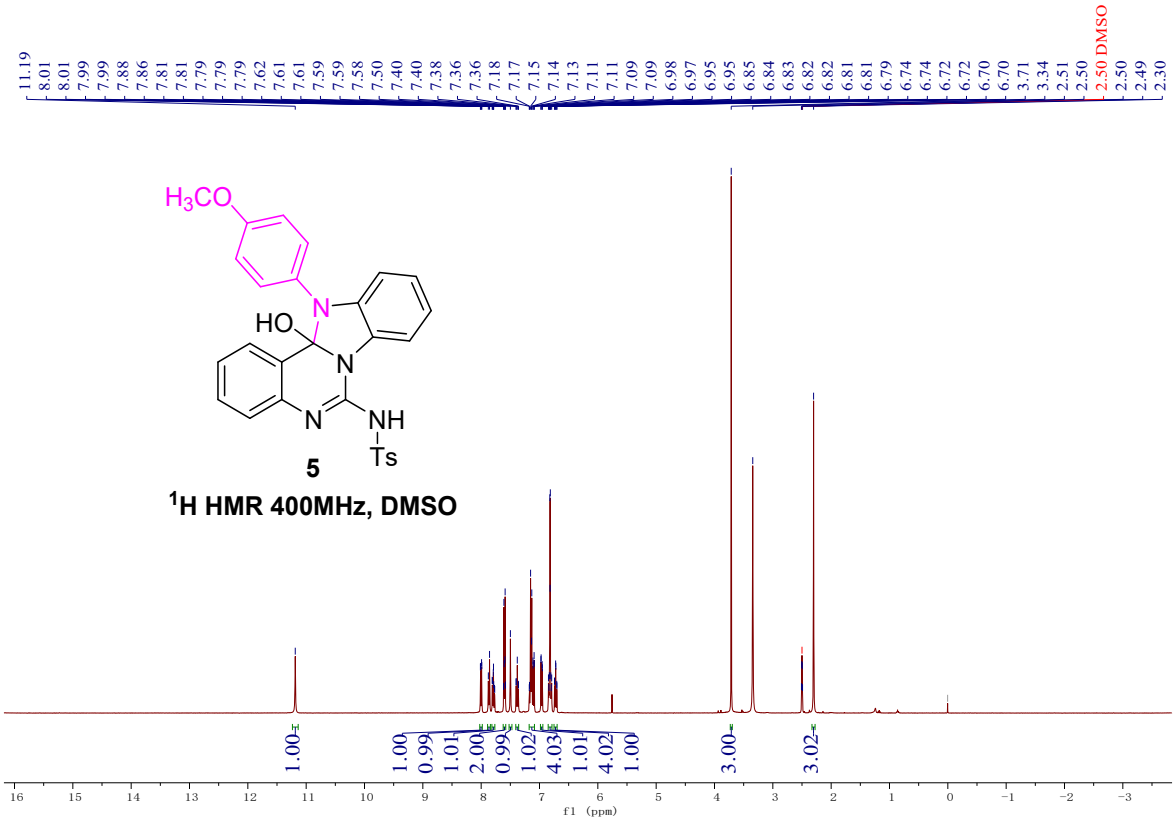
^{13}C HMR 150MHz, DMSO

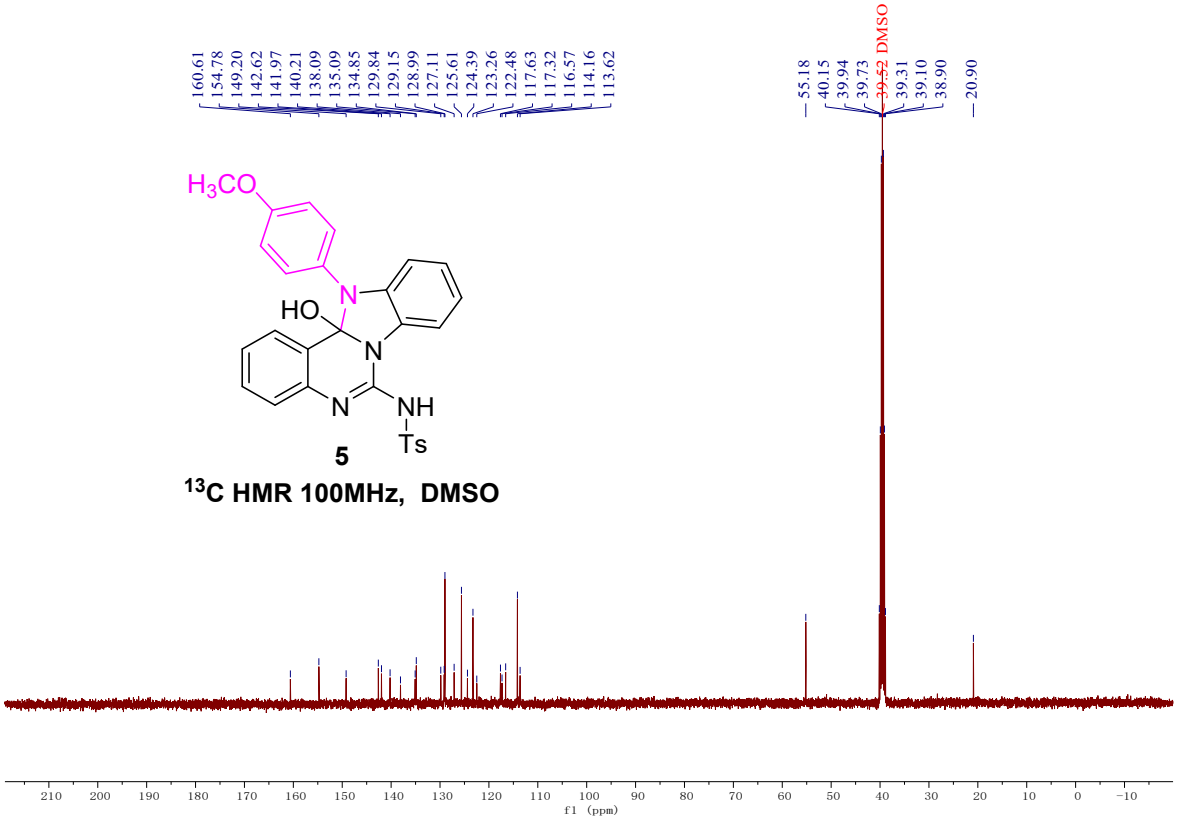


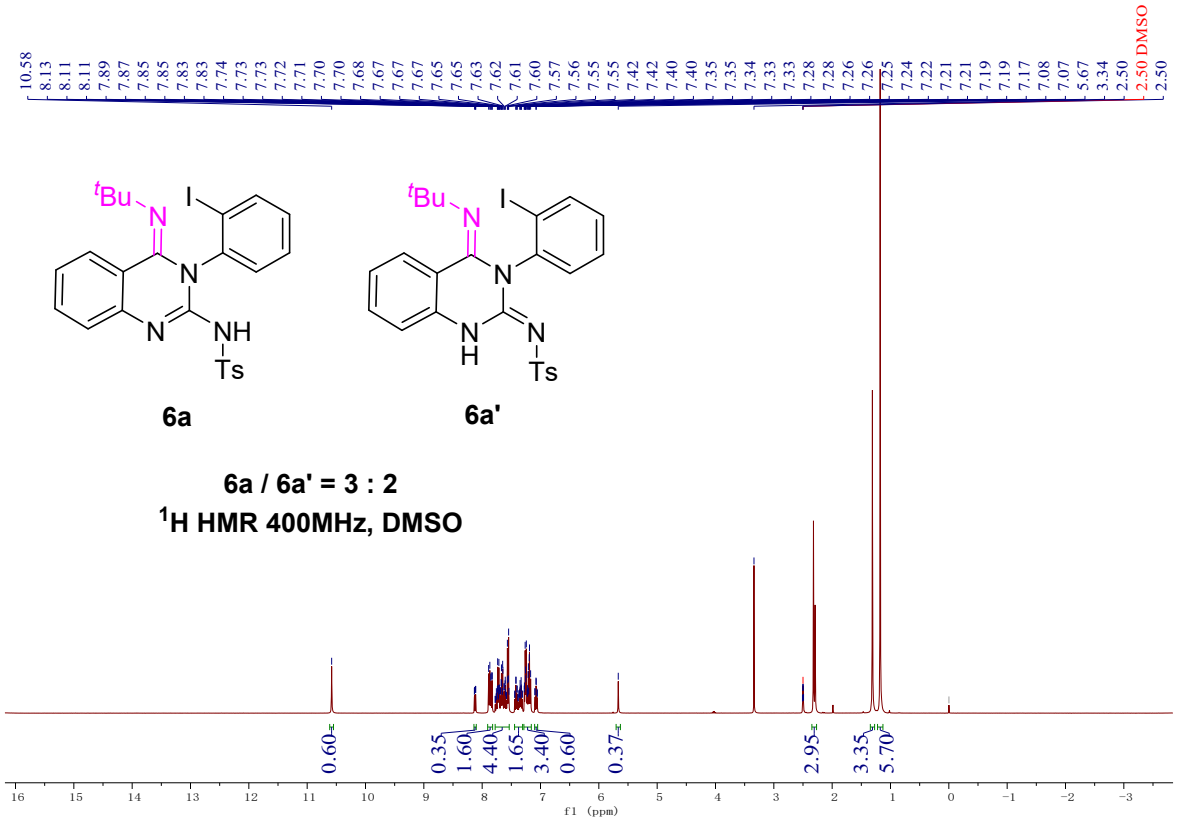
4ai

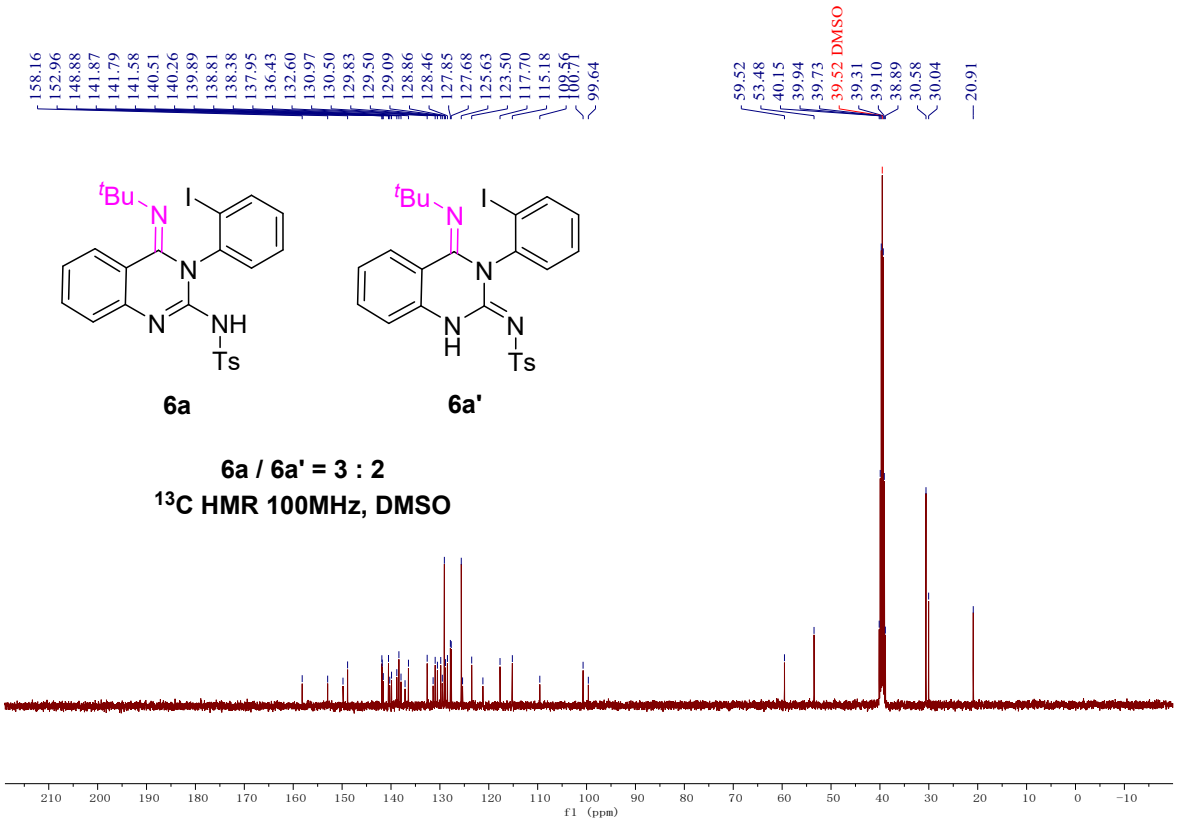
^{1}H HMR 600MHz, DMSO


149.22
145.77
144.74
140.96
140.71
139.91
136.17
135.31
133.44
132.52
132.32
130.95
130.58
128.98
128.61
128.28
128.21
128.07
127.66
126.25
126.09
125.80
123.15
123.07
119.09
111.54
106.85
39.94
39.80
39.66
39.52
39.38
39.24
39.10
20.93
Ph
N
N
N
N
Ts
4ai
13C HMR 150MHz, DMSO
f1 (ppm)

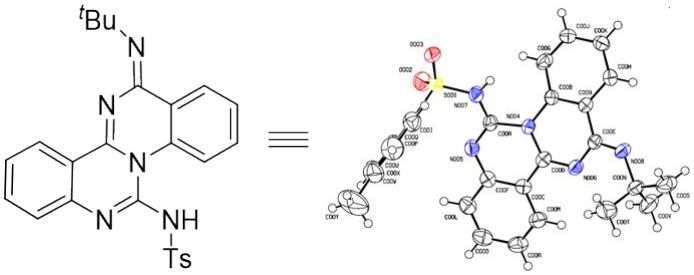

11.19
8.01
8.01
7.99
7.99
7.88
7.86
7.81
7.81
7.79
7.79
7.79
7.79
7.62
7.61
7.61
7.59
7.59
7.58
7.50
7.40
7.40
7.38
7.36
7.36
7.18
7.17
7.15
7.14
7.13
7.11
7.11
7.09
7.09
6.98
6.97
6.95
6.95
6.85
6.84
6.83
6.82
6.82
6.81
6.81
6.79
6.74
6.74
6.72
6.72
6.70
6.70
3.71
3.34
2.51
2.50
2.50 DMSO
2.50
2.49
2.30
H3CO
N
HO
N
N
NH
Ts
5
1H HMR 400MHz, DMSO
1.00
1.00
0.99
1.01
2.00
0.99
1.02
4.03
1.01
4.02
1.00
3.00
3.02
f1 (ppm)


160.61
154.78
149.20
142.62
141.97
140.21
138.09
135.09
134.85
129.84
129.15
128.99
127.11
125.61
124.39
123.26
122.48
117.63
117.32
116.57
114.16
113.62
55.18
40.15
39.94
39.73
39.52 DMSO
39.31
39.10
38.90
20.90
H3CO
HO
N
N
N
NH
Ts
5
13C HMR 100MHz, DMSO
f1 (ppm)


10.58
8.13
8.11
8.11
7.89
7.87
7.85
7.85
7.83
7.83
7.74
7.73
7.73
7.72
7.71
7.70
7.70
7.68
7.67
7.67
7.67
7.65
7.65
7.63
7.62
7.61
7.60
7.57
7.56
7.55
7.55
7.42
7.42
7.40
7.40
7.35
7.35
7.34
7.33
7.33
7.28
7.28
7.26
7.26
7.25
7.24
7.22
7.21
7.21
7.19
7.19
7.17
7.08
7.07
5.67
3.34
2.50
2.50 DMSO
tBu
N
I
N
N
NH
Ts
6a
tBu
N
I
N
N
H
N
Ts
6a'
6a / 6a' = 3 : 2
1H HMR 400MHz, DMSO
0.60
0.35
1.60
4.40
1.65
3.40
0.60
0.37
2.95
3.35
5.70
f1 (ppm)



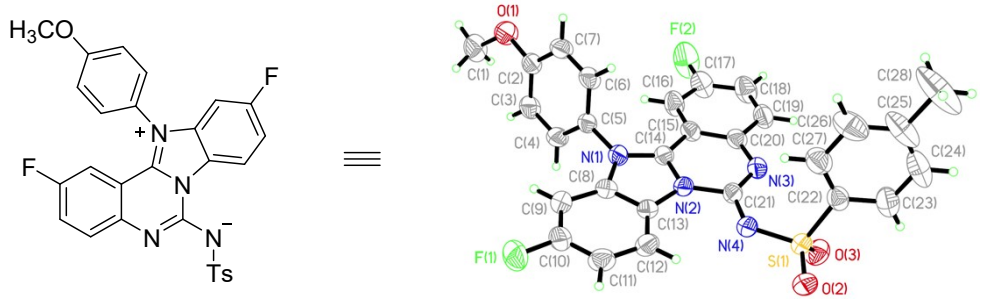
11. Crystal data and structure refinement for 3aa and 4db



Crystal data and structure refinement for **3aa**.

Crystal number	CCDC 2224853
Empirical formula	$C_{26}H_{25}O_2N_5S$
Formula weight:	471.57
Unit cell parameters:	*a* = 13.132 (3) Å *a*= 90
	b = 13.230 (4) Å *b*= 112
	c = 14.822 (4) Å = 82
Temperature	296 K
Wavelength	0.71073 Å
Crystal system	monoclinic

Volume	2379.6 (11) Å^3
Calculated density	1.316 Mg/m^3
Absorption coefficient	0.170 mm^{-1}
F (000)	992
Crystal size	0.40× 0.20 × 0.10 mm^3
Correction-type	multi-scan
h, k, l max	17,17,19
Tmin, Tmax	0.960/0.983
Data completeness	0.998



Crystal data and structure refinement for **4db**.

Crystal number	CCDC 2224861
Empirical formula	$C_{28}H_{20}F_2N_4O_3S$
Formula weight:	530.54
Unit cell parameters:	a = 10.8435 (7) Å a = 74
	b = 12.5404 (8) Å b = 68
	c = 18.9000 (13) Å = 82
Temperature	296 K
Wavelength	0.71013 Å
Crystal system	triclinic
Volume	2483.4 (3) Å^3
Calculated density	1.419 Mg/m^3
Absorption coefficient	0.184 mm^{-1}
F (000)	1096
Crystal size	0.50× 0.40 × 0.20 mm^3

Correction-type	multi-scan
h, k, l max	10,10,13
Tmin, Tmax	0.915/0.964
Data completeness	0.996