

Supporting Information for

Cobalt-Catalyzed Condensation of Sulfonyl Azides with *o*- Diisocyanoarenes and Anilines: A New Approach to *N*-Sulfonyl Guanidines

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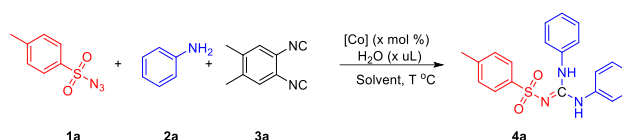
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I. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Anhydrous MeCN, was purchased from Sam Chemical Technology (Shanghai) Co., Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 200-300 mesh silica gel was used. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on a BRUKER 400 MHz spectrometer in CDCl_3 or $\text{DMSO-}d_6$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI source.

II. Optimization of reaction condition: Effects of water.



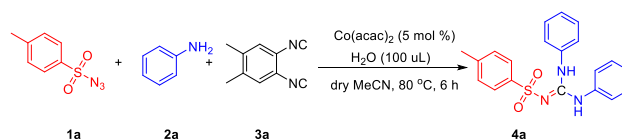
Entry	[Co]. (mol %)	H_2O (x μL)	Solvent	T ($^\circ\text{C}$)	Time (h)	Yield (%) ^b
1	$\text{CoC}_2\text{O}_4(5)$	----	MeCN	80	6	60 ^a
2	$\text{CoC}_2\text{O}_4(5)$	----	MeCN	80	6	63 ^c
3	$\text{CoC}_2\text{O}_4(5)$	----	MeCN	80	6	54 ^d
4	$\text{CoC}_2\text{O}_4(5)$	10	MeCN	80	6	40
5	$\text{CoC}_2\text{O}_4(5)$	50	MeCN	80	6	50
6	$\text{CoC}_2\text{O}_4(5)$	100	MeCN	80	6	63

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.44 mmol), **3a** (0.4 mmol), catalyst (5 mol %), dry solvent (2 mL), 6 h.

^bIsolated yield. ^cMeCN without molecular sieve (commercial available MeCN). ^dDry MeCN (2 mL), under Ar atmosphere.

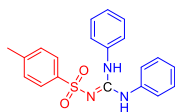
III. General procedure and product characterization

1. General procedure for the formation of **4aaa**



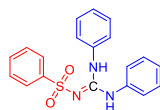
In a 25 mL oven-dried reaction tube, a mixture of TsN_3 **1a** (0.2 mmol, 1 equiv), aniline **2a** (0.44 mmol, 2.2 equiv), 1,2-dicyano-4,5-dimethylbenzene **3a** (0.4 mmol, 2 equiv), $\text{Co}(\text{acac})_2$ (5 mol %), were added in 2 mL dry MeCN with 100 μL H_2O . The tube was sealed with a rubber cap and the resulting mixture was stirred at 80 $^\circ\text{C}$ for 6 h (checked by TLC). After 6 h, cooled to rt. The system was evaporated under the reduced pressure directly. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether (EA : PE = 1 : 50~1 : 4) as eluents to afford pure product **4aaa** in 77% yield.

2. Product characterization



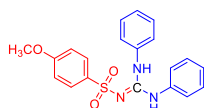
N-(bis(phenylamino)methylene)-4-methylbenzenesulfonamide (4a)

Yield: 77% (56.2 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, J = 8.3 Hz, 2H), 7.26 (t, J = 7.8 Hz, 4H), 7.16 (h, J = 7.9, 7.4 Hz, 8H), 2.33 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 151.9, 142.5, 140.5, 135.8, 129.7, 129.4, 126.7, 126.2, 124.3, 21.6. **IR (ATR):** ν = 3262, 3195, 3154, 3057, 3041, 2962, 1668, 1598, 1542, 1491, 1441, 1372, 865, 749, 670 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₉N₃O₂S [M+Na]⁺: 388.1096, found: 388.1100.



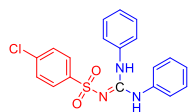
N-(bis(phenylamino)methylene)benzenesulfonamide (4b)

Yield: 80% (56.5 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.10 (s, 2H), 7.78 (dd, J = 8.1, 1.6 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.24 – 7.19 (m, 4H), 7.11 – 7.03 (m, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.3, 143.4, 137.5, 131.8, 129.0, 128.9, 125.7, 125.0, 123.3. **IR (ATR):** ν = 3284, 3063, 2960, 1671, 1574, 1537, 1492, 1451, 1362, 895, 744, 687 cm⁻¹; **HRMS (ESI):** calcd. for C₁₉H₁₇N₃O₂S [M+Na]⁺: 374.0939, found: 374.0936.



N-(bis(phenylamino)methylene)-4-methoxybenzenesulfonamide (4c)

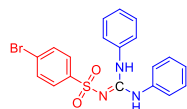
Yield: 74% (56.6 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.06 (s, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.11 (d, J = 8.2 Hz, 4H), 7.06 (t, J = 7.8 Hz, 2H), 7.03 – 7.00 (m, 2H), 3.75 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 161.7, 152.1, 137.6, 135.4, 128.9, 127.8, 124.9, 123.2, 114.1, 55.6. **IR (ATR):** ν = 3278, 1594, 1574, 1538, 1492, 1451, 1397, 1360, 1300, 1057, 893, 745, 671 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₉N₃O₃S [M+H]⁺: 382.1225, found: 382.1221.



N-(bis(phenylamino)methylene)-4-chlorobenzenesulfonamide (4d)

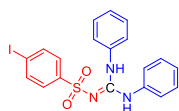
Yield: 64% (49.3 mg isolated). Yellowish brown solid. m.p.: 122.2–122.7 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.17 (s, 2H), 7.90 – 7.77 (m, 2H), 7.70 – 7.54 (m, 2H), 7.30

(td, $J = 7.3, 1.9$ Hz, 4H), 7.19 – 7.10 (m, 6H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.3, 142.3, 137.4, 136.5, 129.1, 128.9, 127.7, 125.1, 123.4. IR (ATR): $\nu = 3398, 3294, 2924, 1674, 1605, 1580, 1527, 1452, 1393, 1250, 1065, 897, 740, 680$ cm^{-1} ; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{16}\text{ClN}_3\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 408.0549, found: 408.0540.



***N*-(bis(phenylamino)methylene)-4-bromobenzenesulfonamide (4e)**

Yield: 63% (54.3 mg isolated). Yellowish brown solid. m.p.: 138.2-139.1 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 9.17 (s, 2H), 7.78 (d, $J = 8.5$ Hz, 4H), 7.30 (t, $J = 7.6$ Hz, 4H), 7.15 (dd, $J = 14.0, 7.3$ Hz, 6H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.3, 142.7, 137.4, 128.9, 127.8, 125.1, 123.5. IR (ATR): $\nu = 3396, 3293, 2954, 1605, 1579, 1525, 1390, 1064, 846, 766, 673$ cm^{-1} ; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{16}\text{BrN}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 430.0225, found: 430.0225.



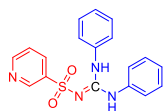
***N*-(bis(phenylamino)methylene)-4-iodobenzenesulfonamide (4f)**

Yield: 67% (63.7 mg isolated). Yellowish brown solid. m.p.: 128.2-128.9 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 9.16 (s, 2H), 7.96 – 7.93 (m, 2H), 7.61 – 7.57 (m, 2H), 7.32 – 7.27 (m, 4H), 7.17 – 7.11 (m, 6H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.3, 143.1, 137.8, 137.4, 128.9, 127.6, 125.1, 123.4, 99.4. IR (ATR): $\nu = 3397, 3390, 3291, 3243, 1673, 1603, 1577, 1391, 1066, 897, 766, 698, 507, 436$ cm^{-1} ; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{16}\text{IN}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 478.0086, found: 478.0070.



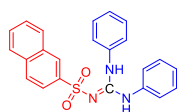
***N*-(bis(phenylamino)methylene)-4-(trifluoromethyl)benzenesulfonamide (4g)**

Yield: 65% (54.2 mg isolated). Yellowish brown solid. m.p.: 129.4-130.8 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 9.19 (s, 2H), 7.94 (dd, $J = 41.0, 8.1$ Hz, 4H), 7.31 – 7.03 (m, 10H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 152.4, 147.3, 137.3, 131.5 (d, $J = 32.0$ Hz), 132.8, 126.7 (d, $J = 7.0$ Hz), 126.2 (d, $J = 3.0$ Hz), 125.2, 123.5, 123.6 (d, $J = 271.0$ Hz). IR (ATR): $\nu = 3393, 3293, 2964, 1674, 1576, 1531, 1394, 1321, 1125, 1061, 859, 764, 698$ cm^{-1} ; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 420.0994, found: 420.0974.



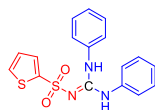
***N*-(bis(phenylamino)methylene)pyridine-3-sulfonamide (4h)**

Yield: 66% (46.4 mg isolated). Yellowish brown solid. m.p.: 163.4–164.2 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.17 (s, 2H), 8.98 – 8.90 (m, 1H), 8.73 (d, *J* = 4.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.11 (dd, *J* = 12.3, 7.5 Hz, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.4, 152.3(5), 146.4, 139.6, 137.3, 133.7, 128.9, 125.2, 124.1, 123.6. **IR (ATR):** ν = 3333, 1730, 1595, 1575, 1496, 1454, 1371, 1277, 1107, 1026, 896, 769, 674 cm⁻¹; **HRMS (ESI):** calcd. for C₁₈H₁₆N₄O₂S [M+Na]⁺: 375.0892, found: 375.0889.



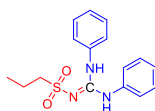
***N*-(bis(phenylamino)methylene)naphthalene-2-sulfonamide (4i)**

Yield: 62% (49.4 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.99 – 7.93 (m, 3H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.60 (qd, *J* = 6.9, 1.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 4H), 7.28 – 7.22 (m, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 152.0, 140.3, 135.7, 134.6, 132.3, 129.7, 129.3, 129.1, 128.3, 127.9, 127.3, 126.8, 126.6, 124.4, 122.4. **IR (ATR):** ν = 3396, 3289, 2958, 2924, 2853, 1740, 1677, 1595, 1580, 1494, 1450, 1375, 1260, 1140, 1074, 895, 746, 690 cm⁻¹; **HRMS (ESI):** calcd. for C₂₃H₁₉N₃O₂S [M+H]⁺: 402.1276, found: 402.1264.



***N*-(bis(phenylamino)methylene)thiophene-2-sulfonamide (4j)**

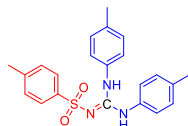
Yield: 79% (56.6 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.16 (s, 2H), 7.83 (d, *J* = 4.6 Hz, 1H), 7.62 – 7.52 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.13 (dd, *J* = 17.3, 7.9 Hz, 7H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.5, 144.6, 137.3, 131.4, 130.0, 128.9, 127.2, 125.2, 123.4. **IR (ATR):** ν = 3330, 3284, 1673, 1612, 1575, 1543, 1494, 1452, 1368, 1275, 1131, 1068, 894, 740, 681 cm⁻¹; **HRMS (ESI):** calcd. for C₁₇H₁₅N₃O₂S₂ [M+H]⁺: 358.0684, found: 358.0686.



***N*-(bis(phenylamino)methylene)propane-1-sulfonamide (4k)**

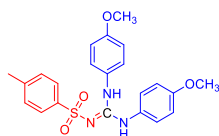
Yield: 48% (30.3 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.00 (s, 2H), 7.33 – 7.27 (m, 8H), 7.15 – 7.09 (m, 2H), 3.05 – 2.97 (m, 2H), 2.26 (d, *J* = 11.0 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 152.1, 135.9,

129.7, 126.6, 124.2, 56.8, 17.5, 13.2. **IR (ATR):** $\nu = 3330, 3285, 2952, 2926, 2854, 1672, 1615, 1542, 1493, 1451, 1380, 1293, 1119, 1082, 895, 804, 747, 694 \text{ cm}^{-1}$; **HRMS (ESI):** calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 340.1096, found: 340.1095.



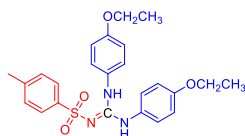
***N*-(bis(*p*-tolylamino)methylene)-4-methylbenzenesulfonamide (4l)**

Yield: 60% (47.2 mg isolated). Yellowish brown solid. m.p.: 113.1-113.9 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 8.89 (s, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 4H), 6.99 (d, $J = 8.4$ Hz, 4H), 2.32 (s, 3H), 2.20 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.5, 141.8, 140.8, 134.7, 134.4, 129.4, 129.3, 125.7, 123.7, 21.0, 20.5. **IR (ATR):** $\nu = 3320, 3284, 2917, 2858, 1674, 1572, 1539, 1399, 1360, 1286, 1140, 1101, 876, 767, 690 \text{ cm}^{-1}$; **HRMS (ESI):** calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 394.1589, found: 394.1590.



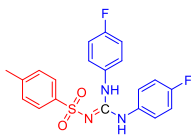
***N*-(bis((4-methoxyphenyl)amino)methylene)-4-methylbenzenesulfonamide (4m)**

Yield: 59% (50.2 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 4H), 6.85 (d, $J = 8.6$ Hz, 4H), 3.78 (s, 6H), 2.41 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.0, 142.2, 140.8, 129.3, 126.1, 114.8, 114.1, 55.6, 21.6. **IR (ATR):** $\nu = 3284, 2956, 2927, 2836, 1678, 1594, 1579, 1506, 1440, 1391, 1360, 1242, 1234, 1098, 878, 802, 745, 669 \text{ cm}^{-1}$; **HRMS (ESI):** calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$: 448.1307, found: 448.1306.



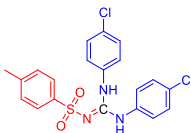
***N*-(bis((4-ethoxyphenyl)amino)methylene)-4-methylbenzenesulfonamide (4n)**

Yield: 46% (41.7 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 8.71 (s, 2H), 7.67 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 4H), 6.82 (d, $J = 8.8$ Hz, 4H), 3.95 (q, $J = 6.9$ Hz, 4H), 2.35 (s, 3H), 1.27 (t, $J = 6.9$ Hz, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 156.3, 153.2, 141.6, 141.0, 129.6, 129.3, 126.0, 125.6, 114.6, 63.2, 20.9, 14.6. **IR (ATR):** $\nu = 3323, 3279, 3049, 2975, 2922, 1683, 1587, 1531, 1506, 1394, 1363, 1290, 1235, 1139, 1101, 825, 804, 775, 671 \text{ cm}^{-1}$; **HRMS (ESI):** calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 454.1801, found: 454.1799.



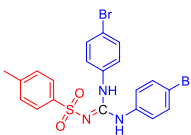
***N*-bis((4-fluorophenyl)amino)methylene)-4-methylbenzenesulfonamide (4o)**

Yield: 54% (43.7 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.02 (s, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.11 (m, 8H), 2.37 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 159.6 (d, *J* = 240.0 Hz), 152.7, 141.8, 140.7, 133.5 (d, *J* = 3.0 Hz), 129.3, 126.2 (d, *J* = 8.0 Hz), 125.7, 115.5 (d, *J* = 23 Hz), 20.9. **IR (ATR):** ν = 3322, 3249, 3078, 2930, 1674, 1582, 1541, 1505, 1366, 1213, 1140, 1090, 1067, 829, 812, 777, 690 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₇F₂N₃O₂S [M+Na]⁺: 424.0907, found: 424.0908.



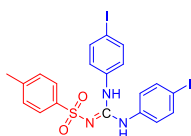
***N*-bis((4-chlorophenyl)amino)methylene)-4-methylbenzenesulfonamide (4p)**

Yield: 49% (43.7 mg isolated). Yellowish brown solid. m.p.: 116.7-117.3 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 3H), 7.29 (d, *J* = 8.6 Hz, 5H), 7.16 (d, *J* = 8.7 Hz, 4H), 2.41 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 151.6, 142.8, 140.2, 134.2, 132.4, 129.8, 129.5, 126.1, 125.8, 21.6. **IR (ATR):** ν = 3342, 3273, 1671, 1616, 1573, 1530, 1488, 1384, 1261, 1137, 1100, 1013, 867, 824, 771, 682 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₇Cl₂N₃O₂S [M+Na]⁺: 456.0316, found: 456.0314.



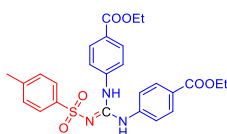
***N*-bis((4-bromophenyl)amino)methylene)-4-methylbenzenesulfonamide (4q)**

Yield: 33% (34.7 mg isolated). Yellowish brown solid. m.p.: 186.4-187.3 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (s, 4H), 2.42 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 151.4, 142.8, 140.2, 134.8, 132.8, 129.5, 126.2, 126.0, 120.2, 21.6. **IR (ATR):** ν = 3406, 3248, 1734, 1675, 1615, 1528, 1483, 1380, 1248, 1135, 1061, 1010, 873, 813, 763, 656 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₇Br₂N₃O₂S [M+Na]⁺: 543.9306, found: 543.9302.



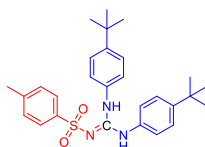
***N*-(bis((4-iodophenyl)amino)methylene)-4-methylbenzenesulfonamide (4r)**

Yield: 37% (45.1 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.17 (s, 2H), 7.72 – 7.68 (m, 2H), 7.65 – 7.59 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.95 (m, 4H), 2.37 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 151.6, 142.0, 140.4, 137.5, 137.4, 129.4, 125.8, 125.4, 89.5, 21.0. **IR (ATR):** ν = 3401, 3255, 2961, 2922, 2853, 1723, 1674, 1583, 1525, 1484, 1378, 1259, 1133, 1017, 871, 797, 663 cm⁻¹; **HRMS (ESI):** calcd. for C₂₀H₁₇I₂N₃O₂S [M+Na]⁺: 639.9029, found: 639.9028.



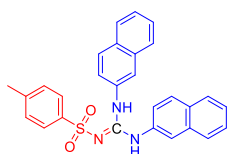
diethyl 4,4'-(((tosylimino)methylene)bis(azanediyl))dibenzoate (4s)

Yield: 46% (46.5 mg isolated). Yellowish brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 4H), 7.86 – 7.81 (m, 2H), 7.34 – 7.27 (m, 6H), 4.34 (q, *J* = 7.1 Hz, 4H), 2.42 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 165.8, 150.7, 143.0, 140.1, 139.9, 131.2, 129.6, 128.0, 126.2, 122.8, 61.3, 21.6, 14.4. **IR (ATR):** ν = 3273, 2961, 2920, 2854, 1709, 1596, 1533, 1364, 1270, 1092, 852, 759, 679 cm⁻¹; **HRMS (ESI):** calcd. for C₂₆H₂₇N₃O₆S [M+H]⁺: 510.1699, found: 510.1693.



***N*-(bis((4-(tert-butyl)phenyl)amino)methylene)-4-methylbenzenesulfonamide (4t)**

Yield: 50% (47.4 mg isolated). Yellowish brown solid. m.p.: 125.9-126.7 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.00 (s, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 4H), 7.06 (d, *J* = 8.6 Hz, 4H), 2.35 (s, 3H), 1.23 (s, 18H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.4, 147.3, 141.8, 140.7, 134.8, 129.4, 125.7, 125.6, 122.9, 34.1, 31.1, 20.9. **IR (ATR):** ν = 3306, 2958, 2907, 2866, 1615, 1574, 1515, 1355, 1264, 1088, 905, 805, 686 cm⁻¹; **HRMS (ESI):** calcd. for C₂₈H₃₅N₃O₂S [M+H]⁺: 478.2528, found: 478.2531.

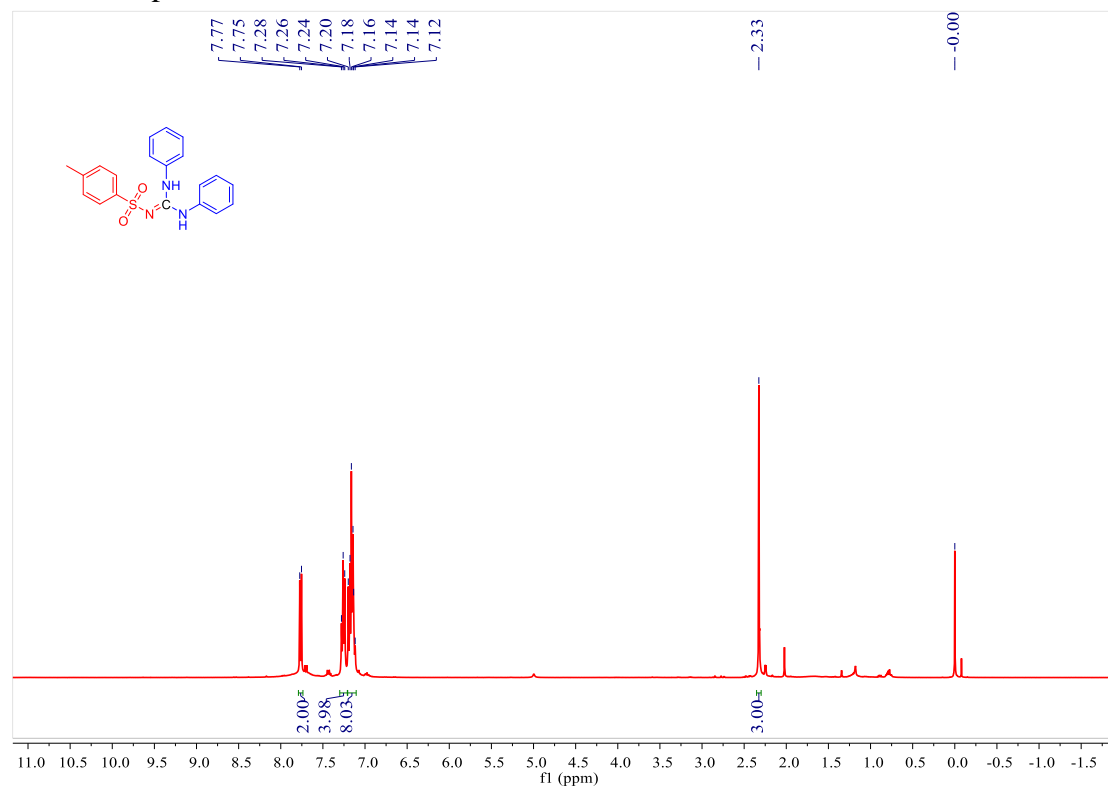


***N*-(bis(naphthalen-2-ylamino)methylene)-4-methylbenzenesulfonamide (4v)**

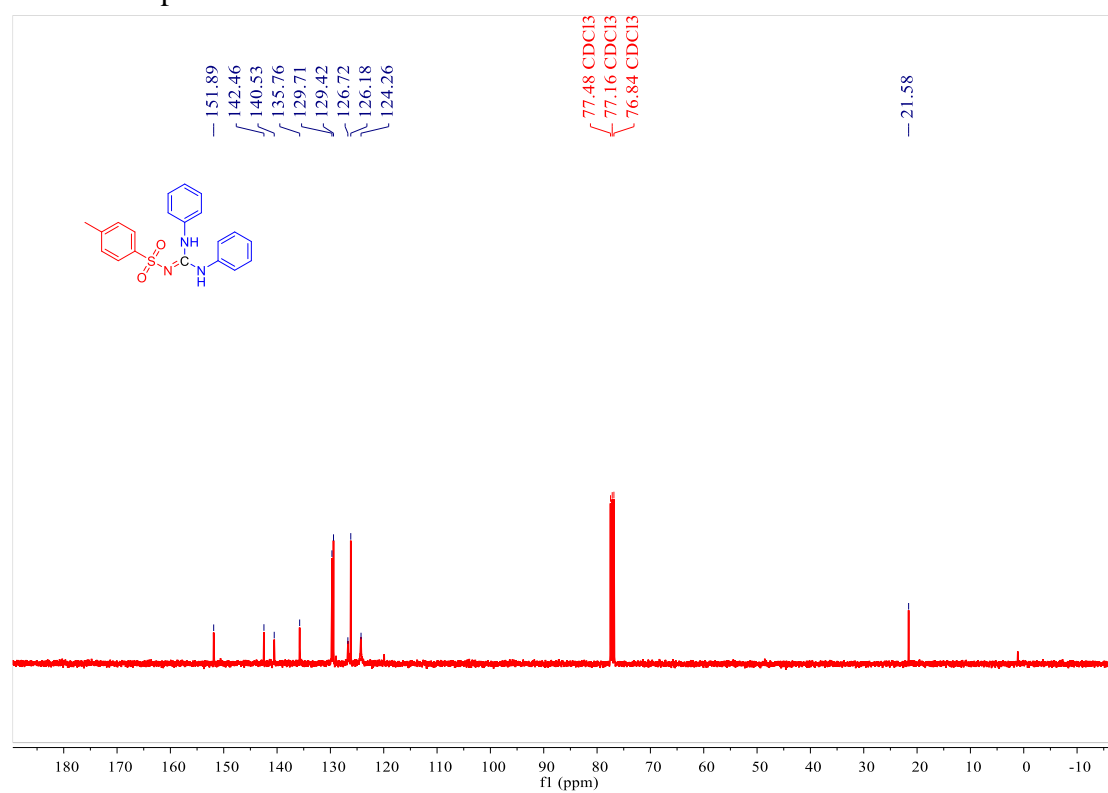
Yield: 31% (28.7 mg isolated). Yellowish brown solid. m.p.: 204.9-205.8 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.41 (s, 2H), 7.88 – 7.75 (m, 8H), 7.70 (d, *J* = 2.2 Hz, 2H), 7.51 – 7.39 (m, 6H), 7.34 (dd, *J* = 8.8, 2.2 Hz, 2H), 2.40 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.2, 141.9, 140.8, 135.1, 133.1, 130.7, 129.5, 128.5, 127.5, 127.3, 126.5, 125.8, 125.5, 123.2, 120.5, 21.0. **IR (ATR):** ν = 3252, 3241, 2236, 2167, 1739, 1612, 1578, 1555, 1327, 1239, 1001, 858, 817, 711, 669 cm⁻¹; **HRMS (ESI):** calcd. for C₂₈H₂₃N₃O₂S [M+H]⁺: 466.1589, found: 466.1573.

IV. Copies of ^1H NMR and ^{13}C NMR Spectra

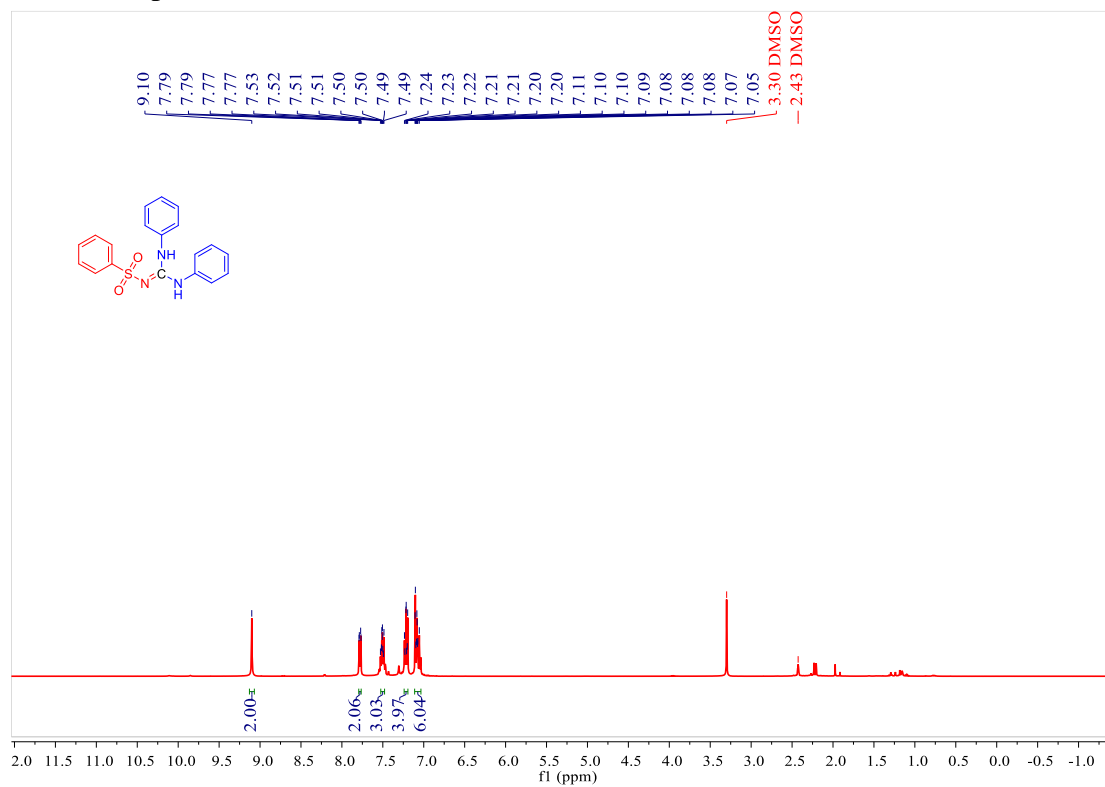
^1H NMR Spectra of **4a**



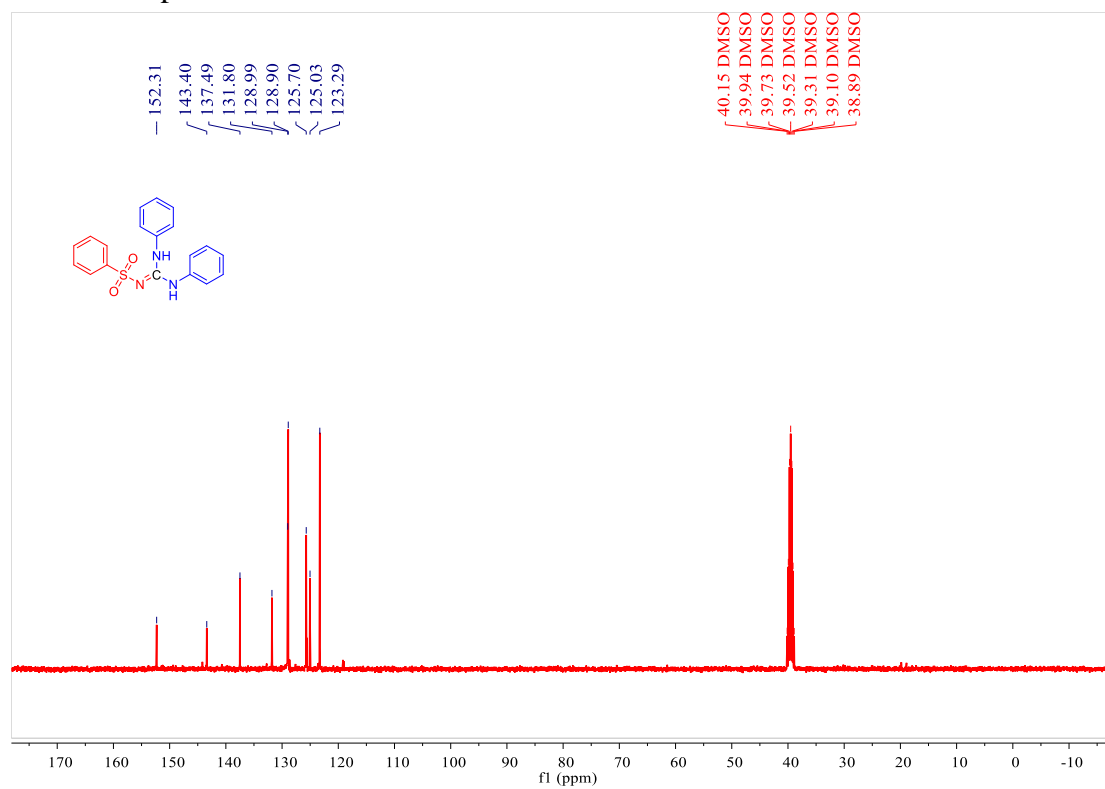
^{13}C NMR Spectra of **4a**



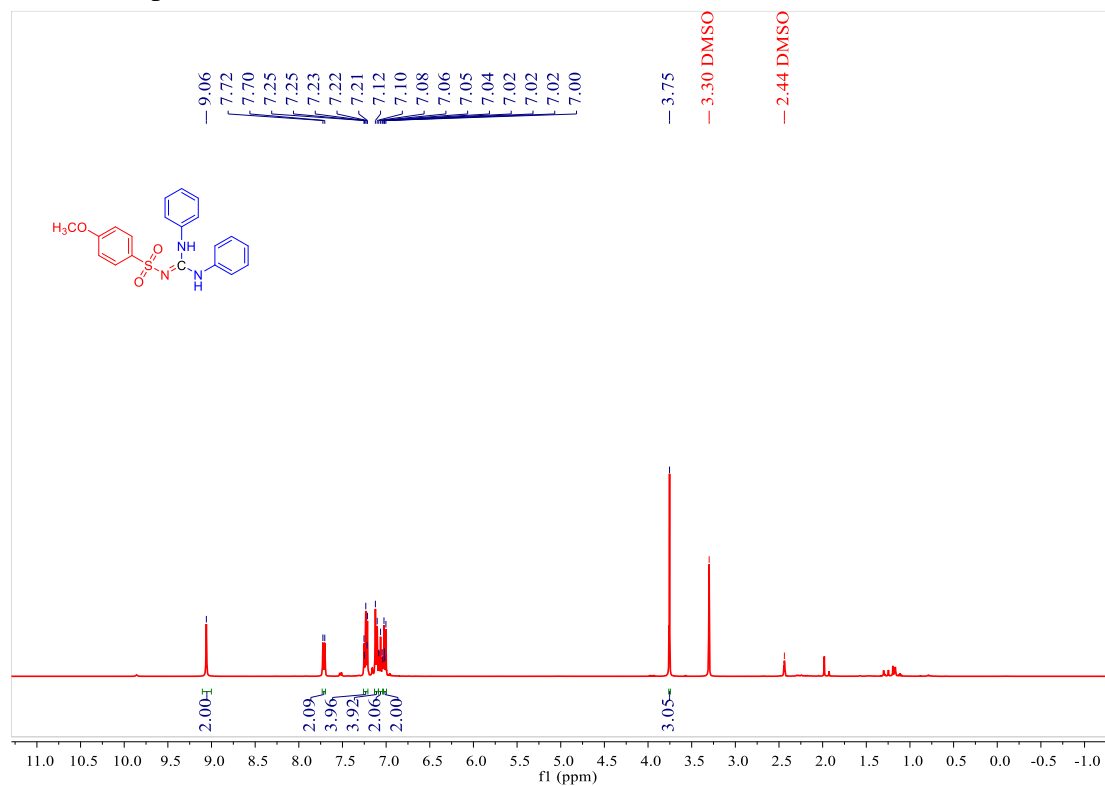
¹H NMR Spectra of **4b**



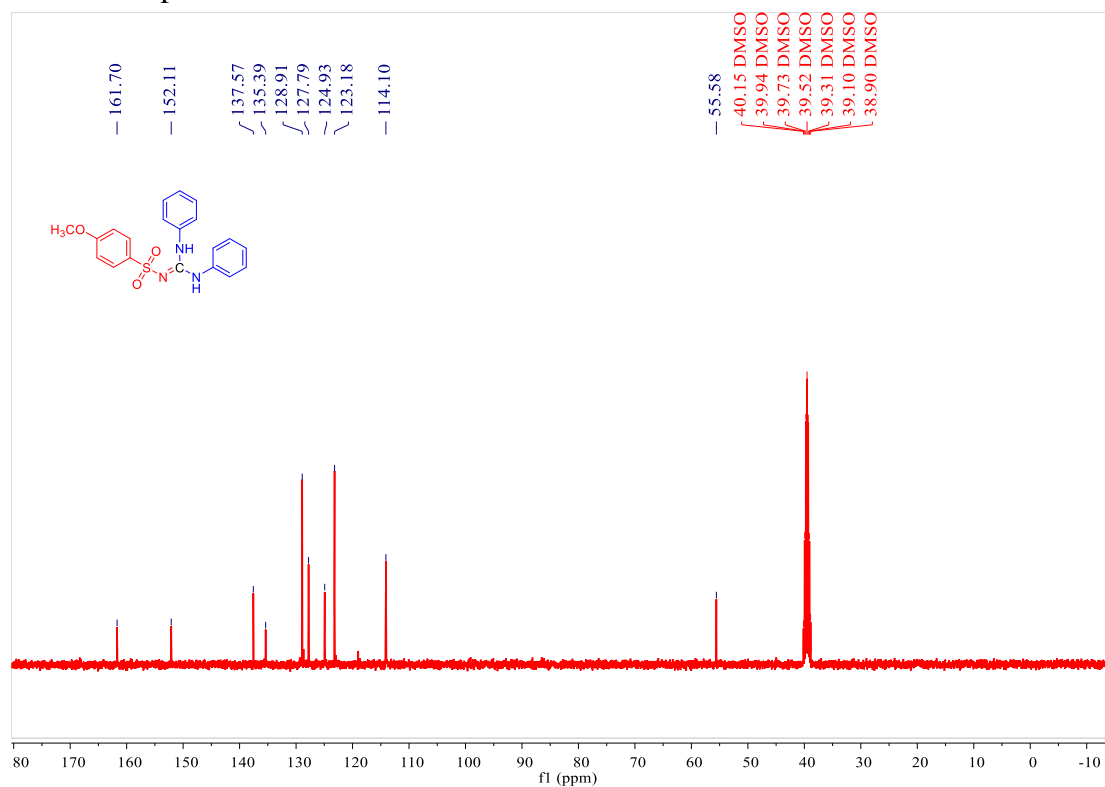
¹³C NMR Spectra of **4b**



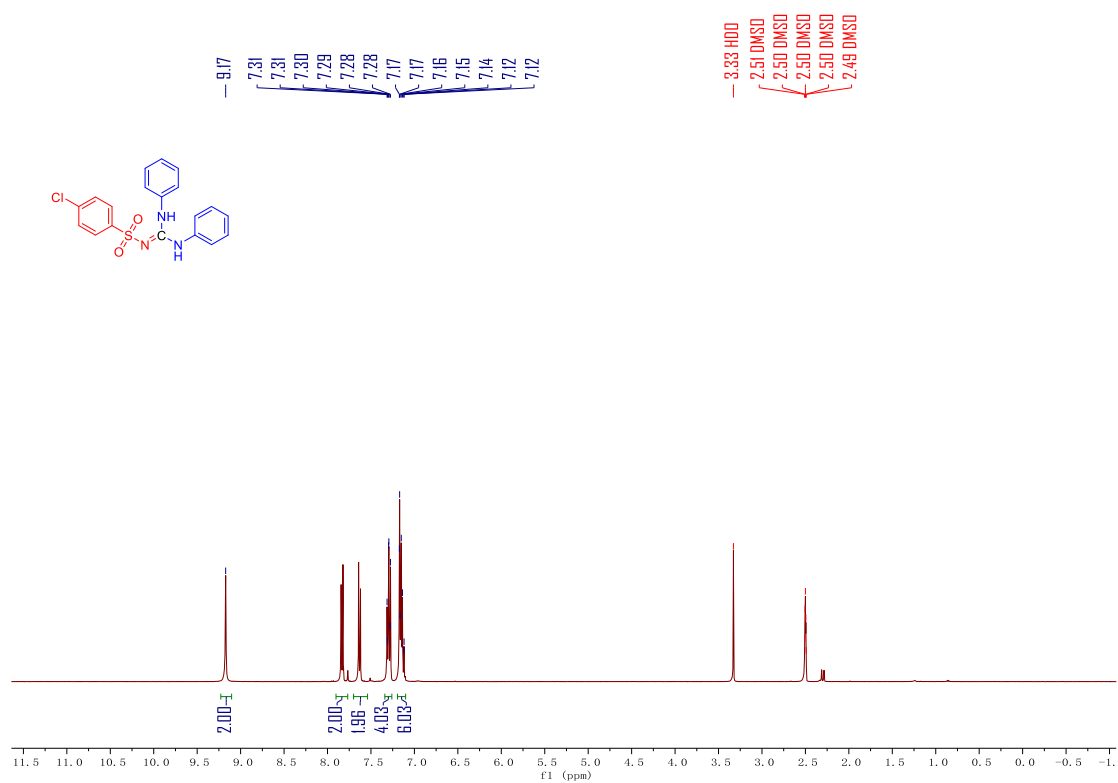
¹H NMR Spectra of **4c**



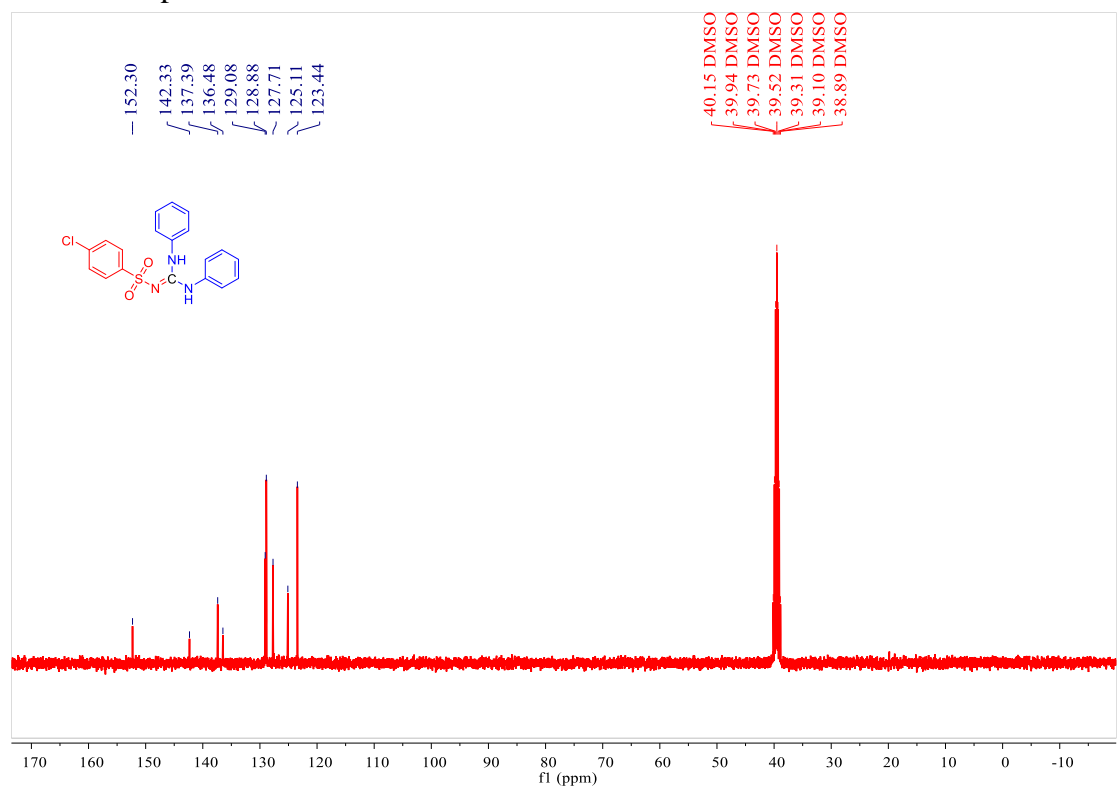
¹³C NMR Spectra of **4c**



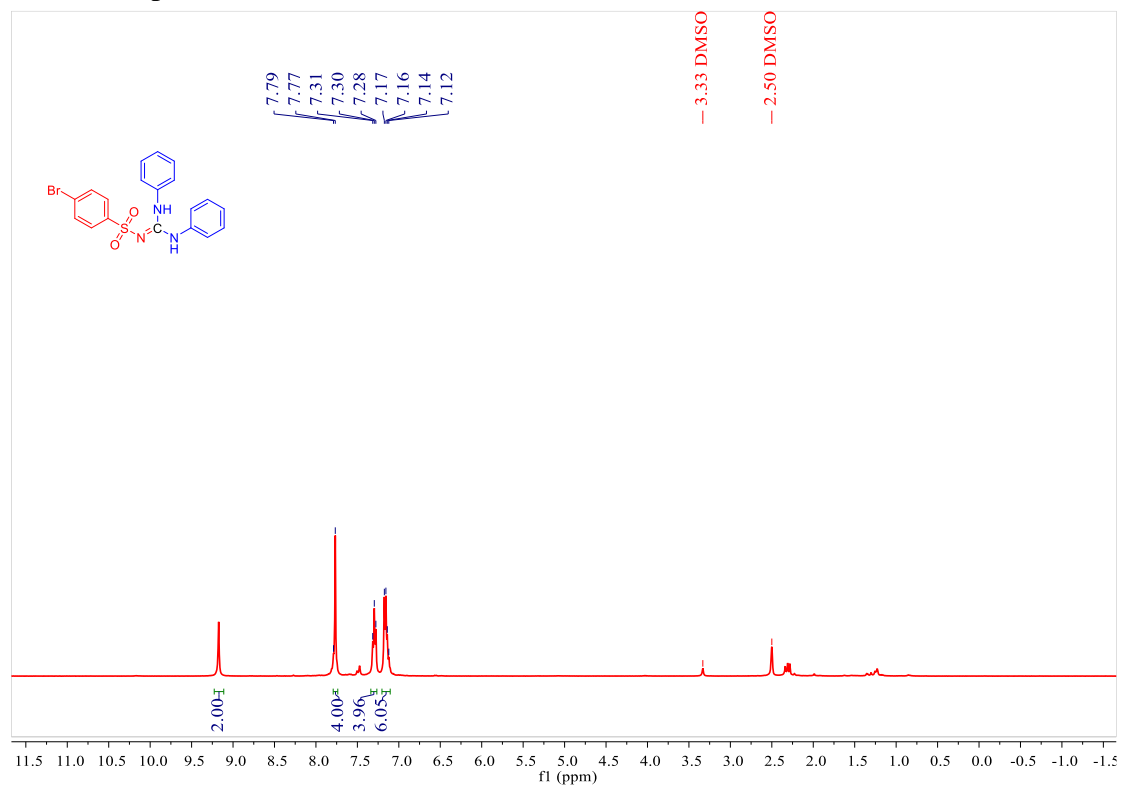
¹H NMR Spectra of **4d**



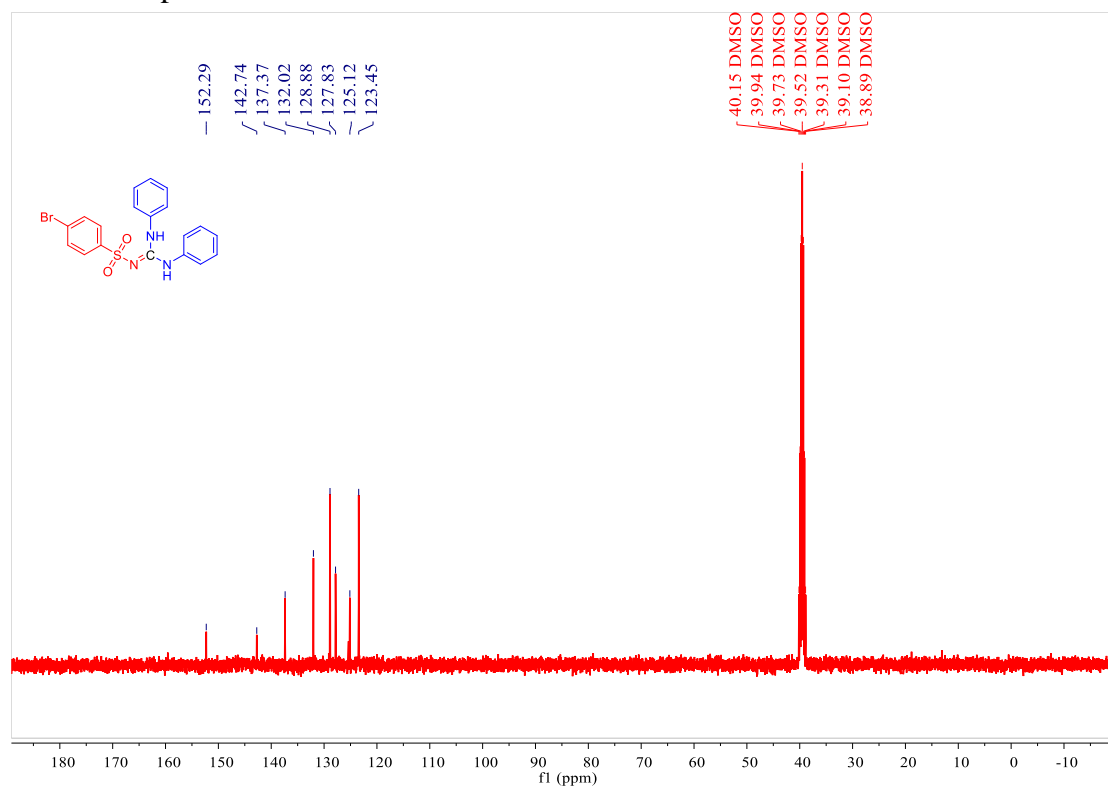
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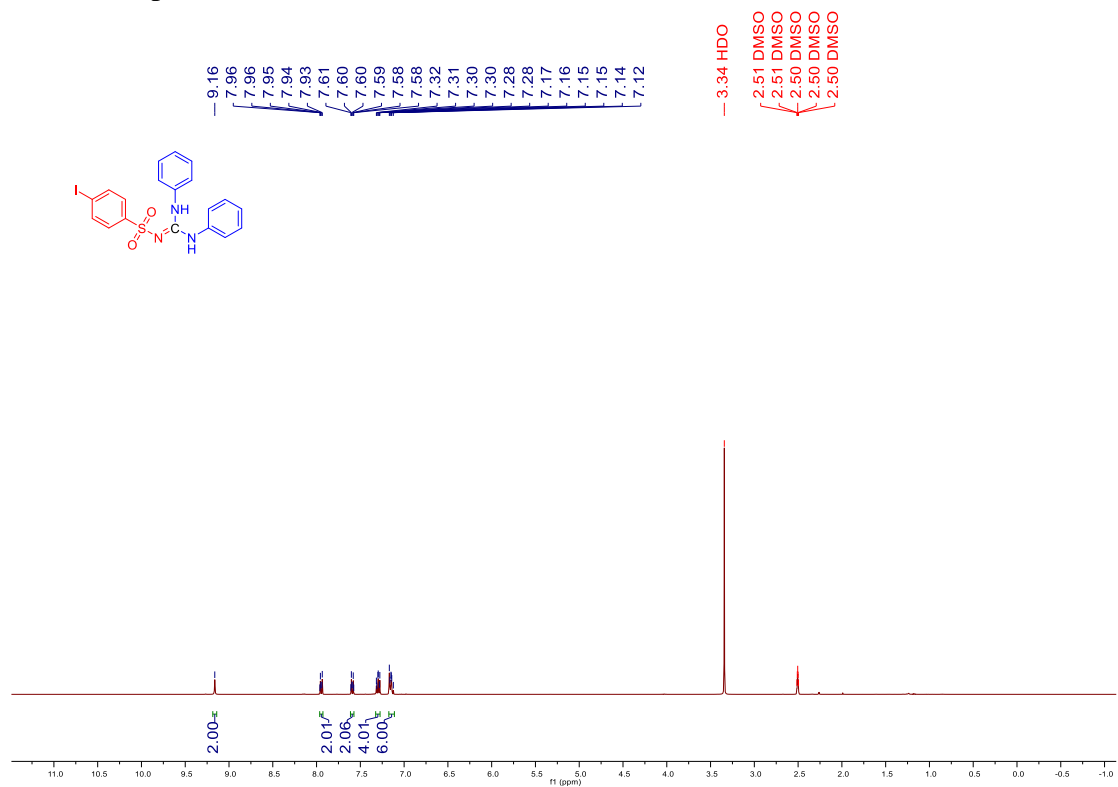
¹H NMR Spectra of 4e



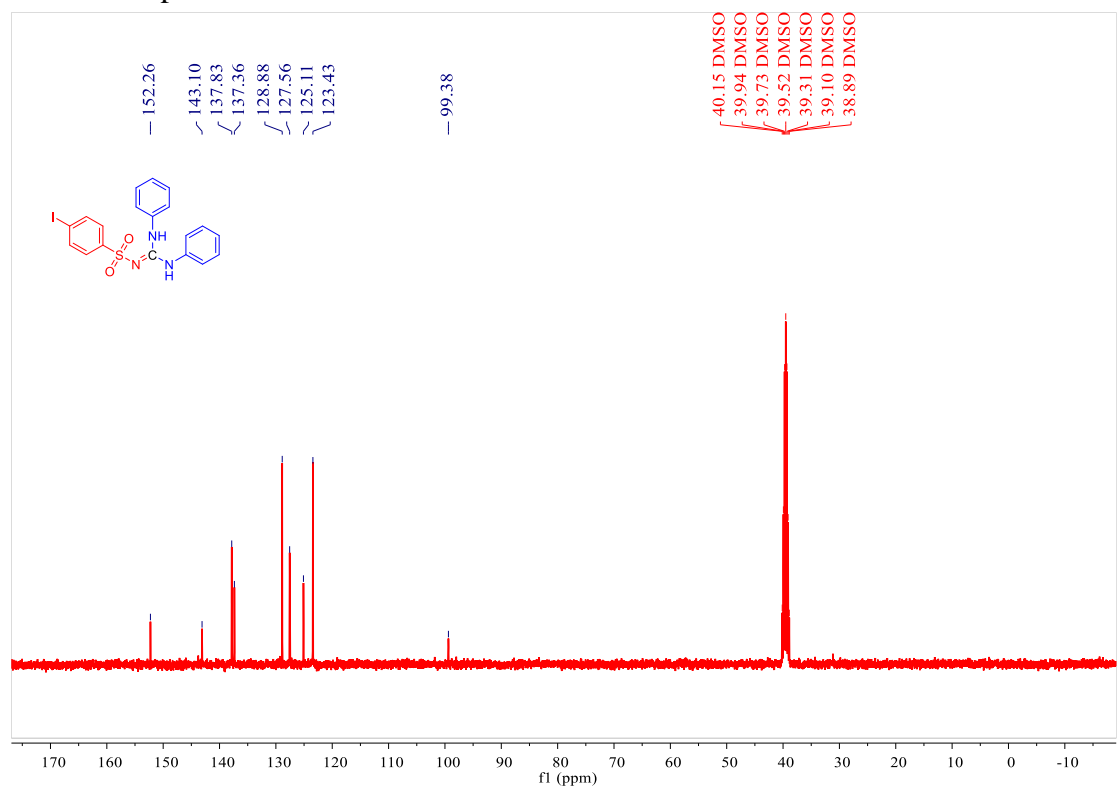
¹³C NMR Spectra of 4e



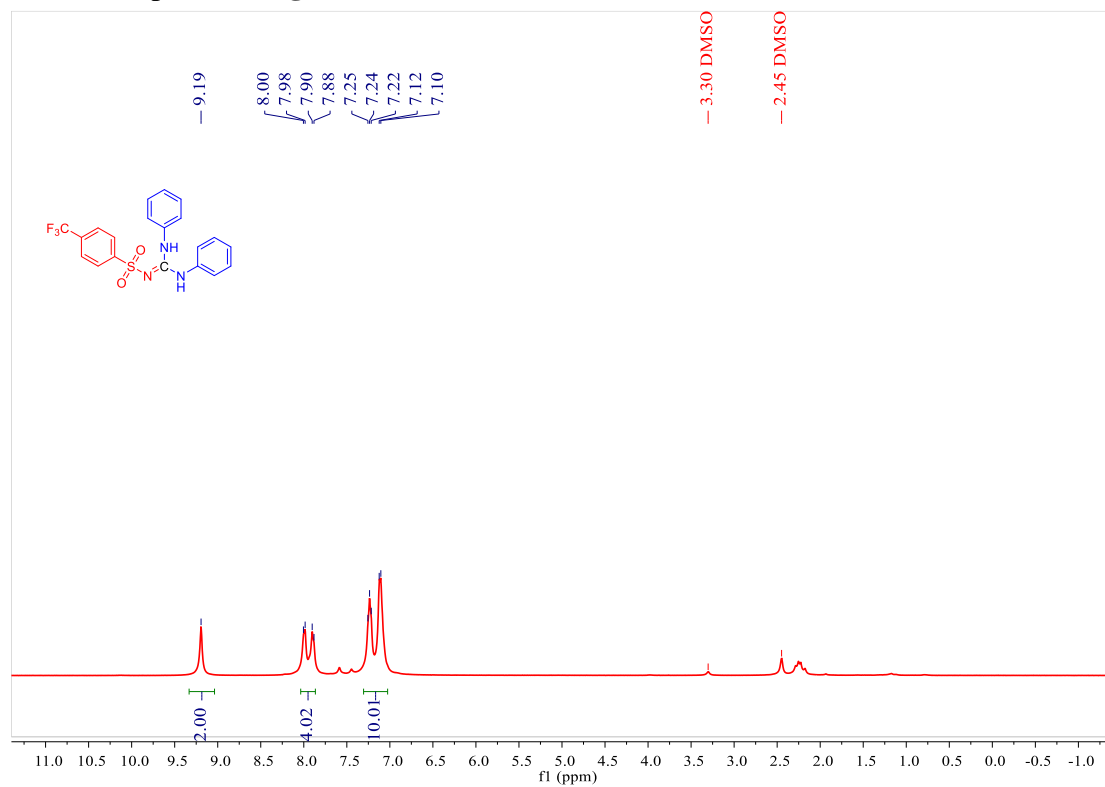
¹H NMR Spectra of 4f



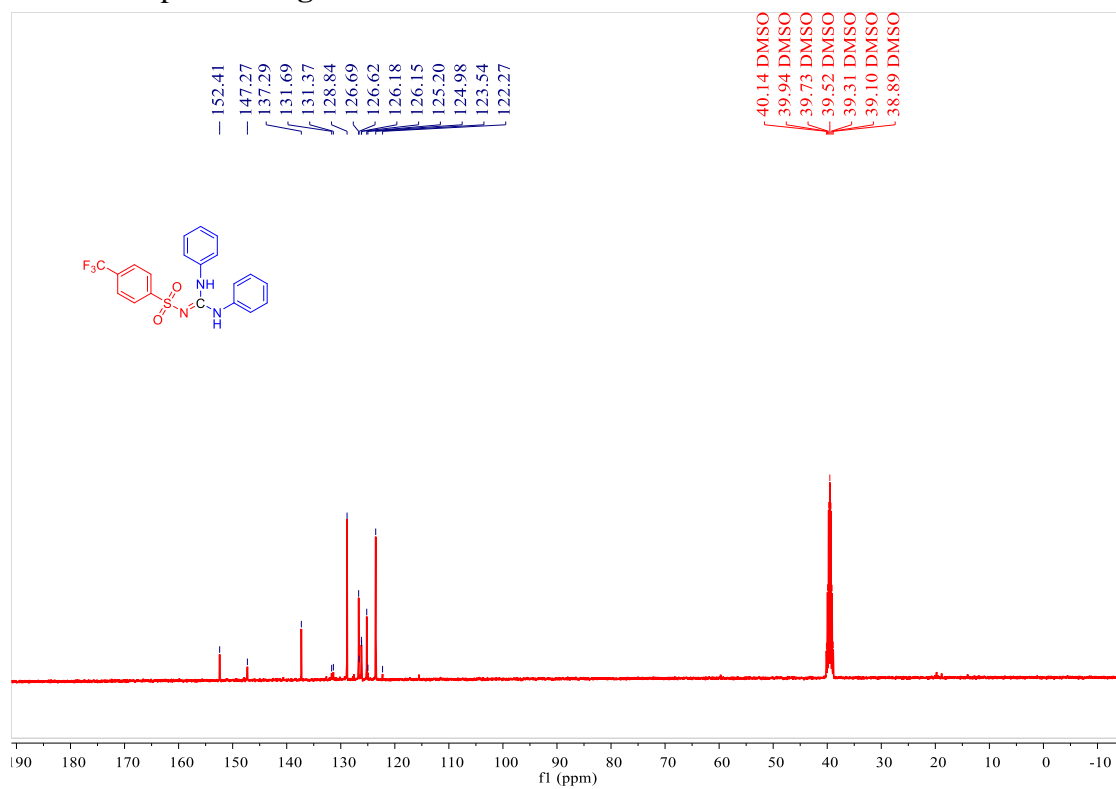
¹³C NMR Spectra of 4f



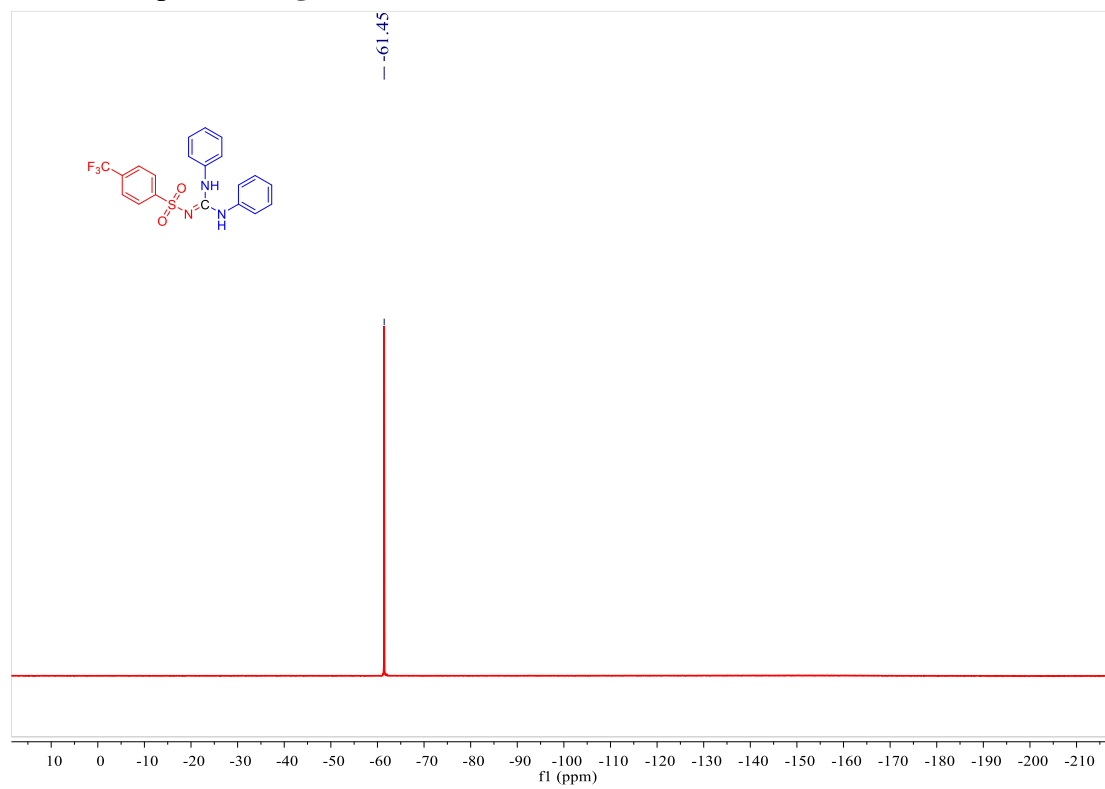
¹H NMR Spectra of **4g**



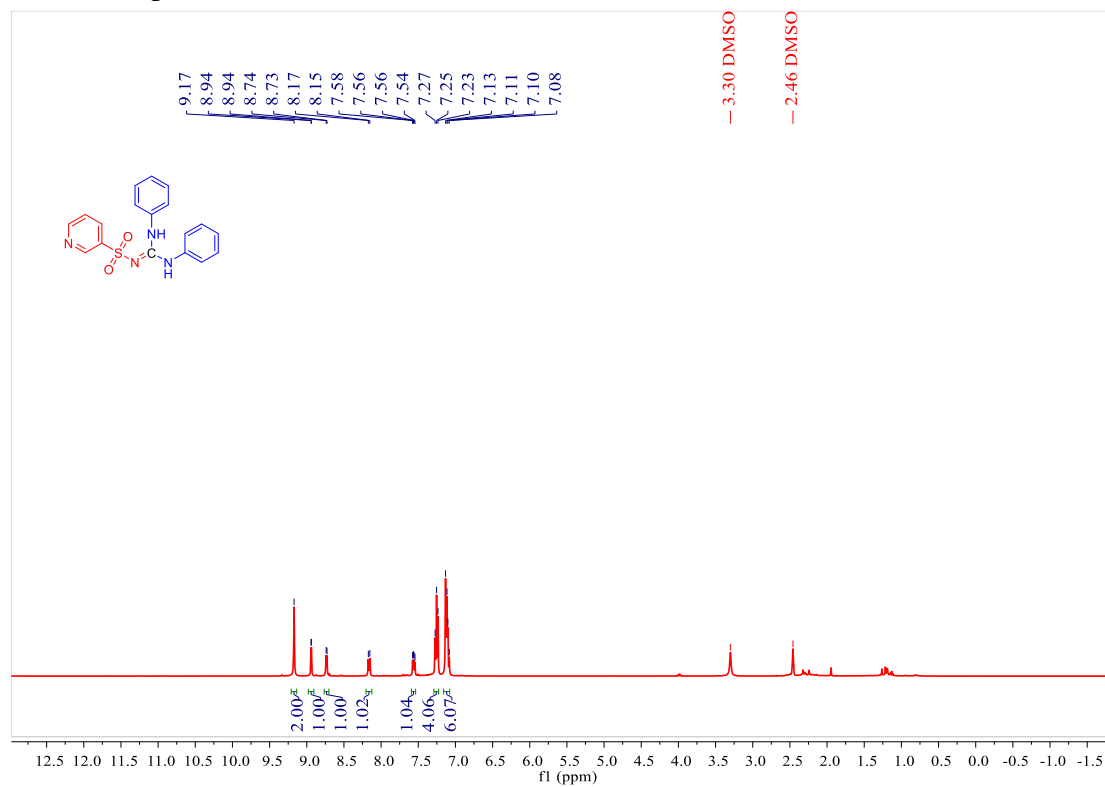
¹³C NMR Spectra of **4g**



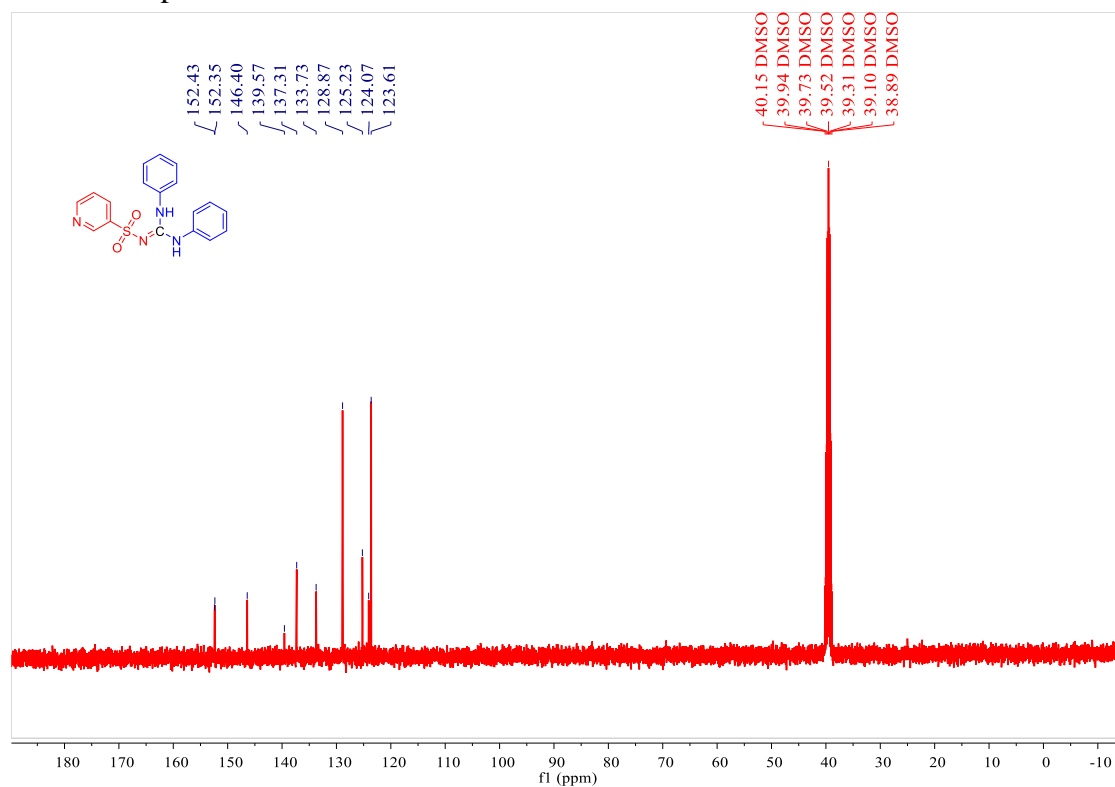
¹⁹F NMR Spectra of **4g**



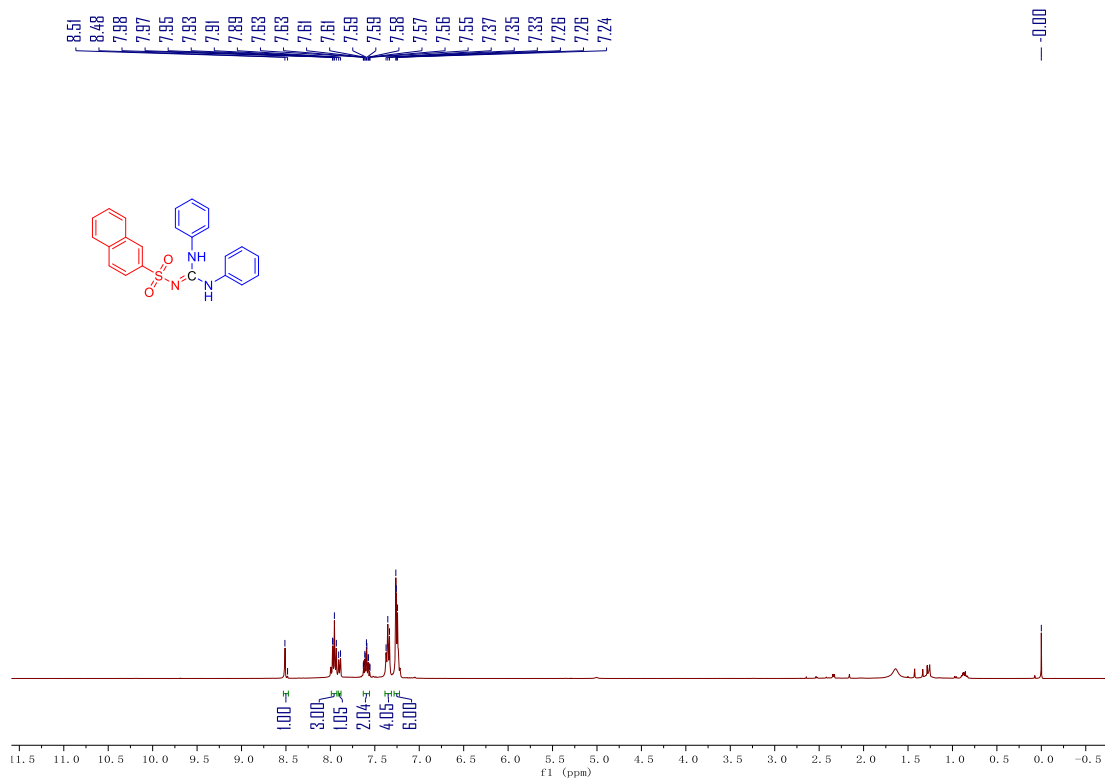
¹H NMR Spectra of **4h**



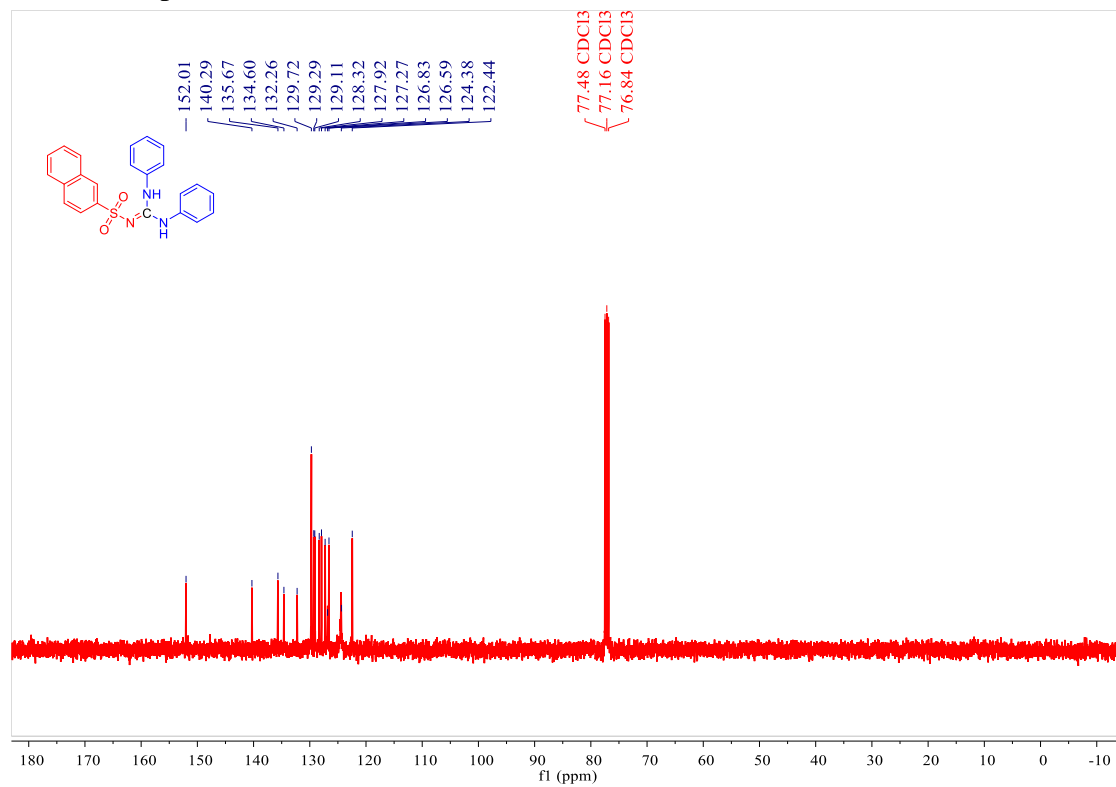
¹³C NMR Spectra of **4h**



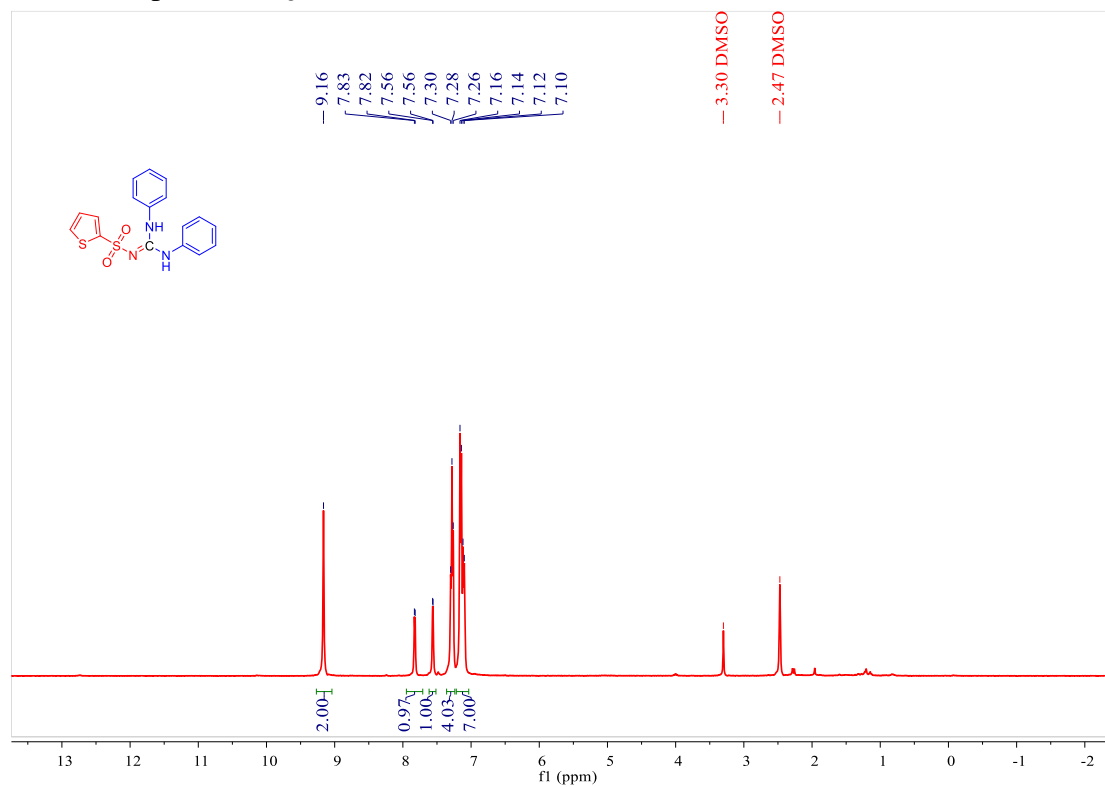
¹H NMR Spectra of **4i**



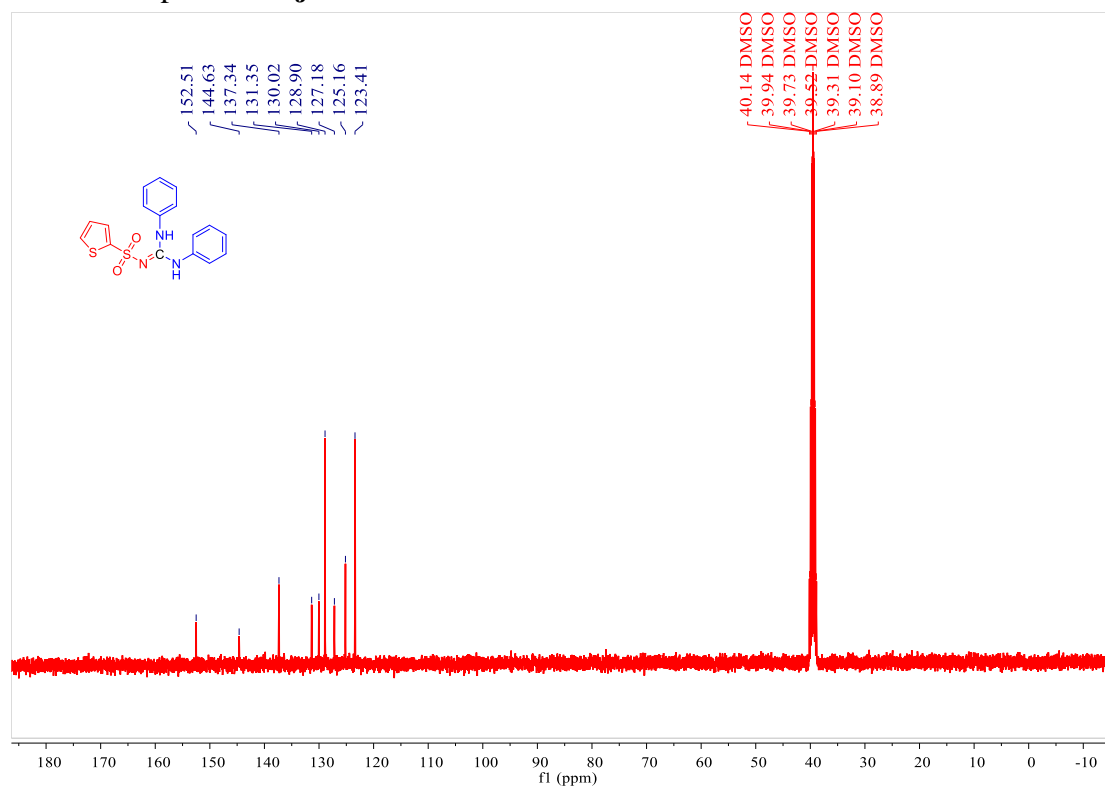
¹³C NMR Spectra of **4i**



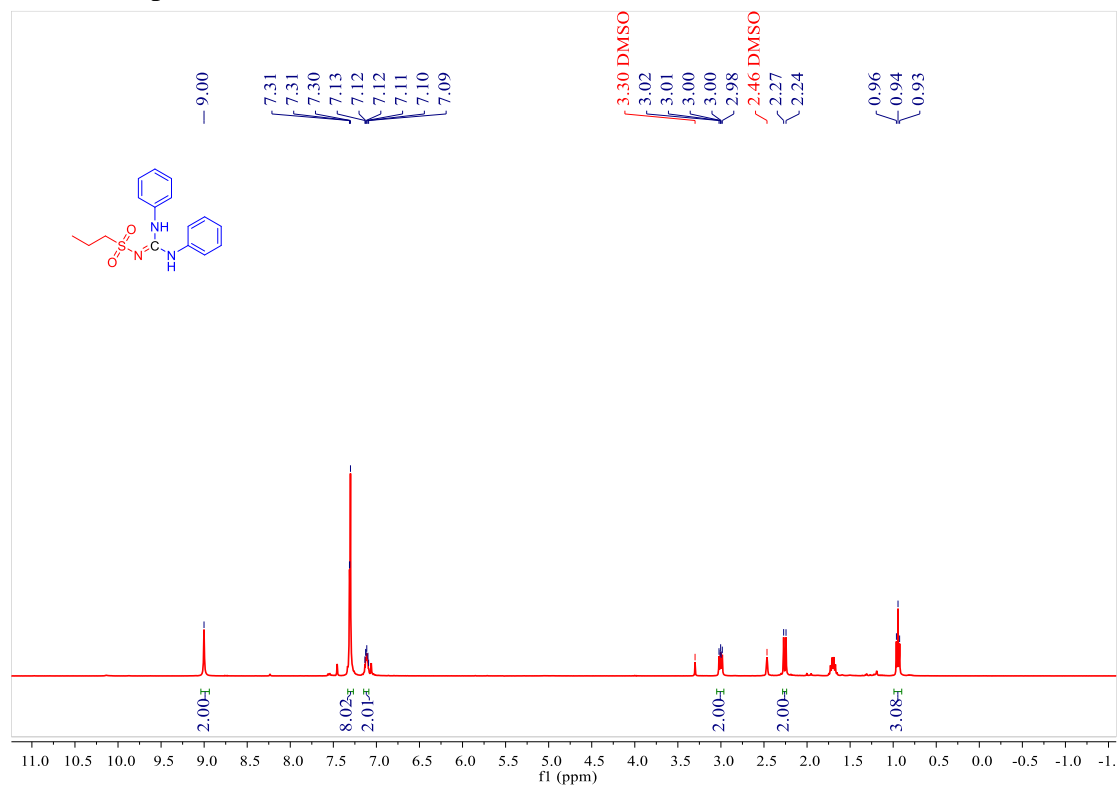
¹H NMR Spectra of **4j**



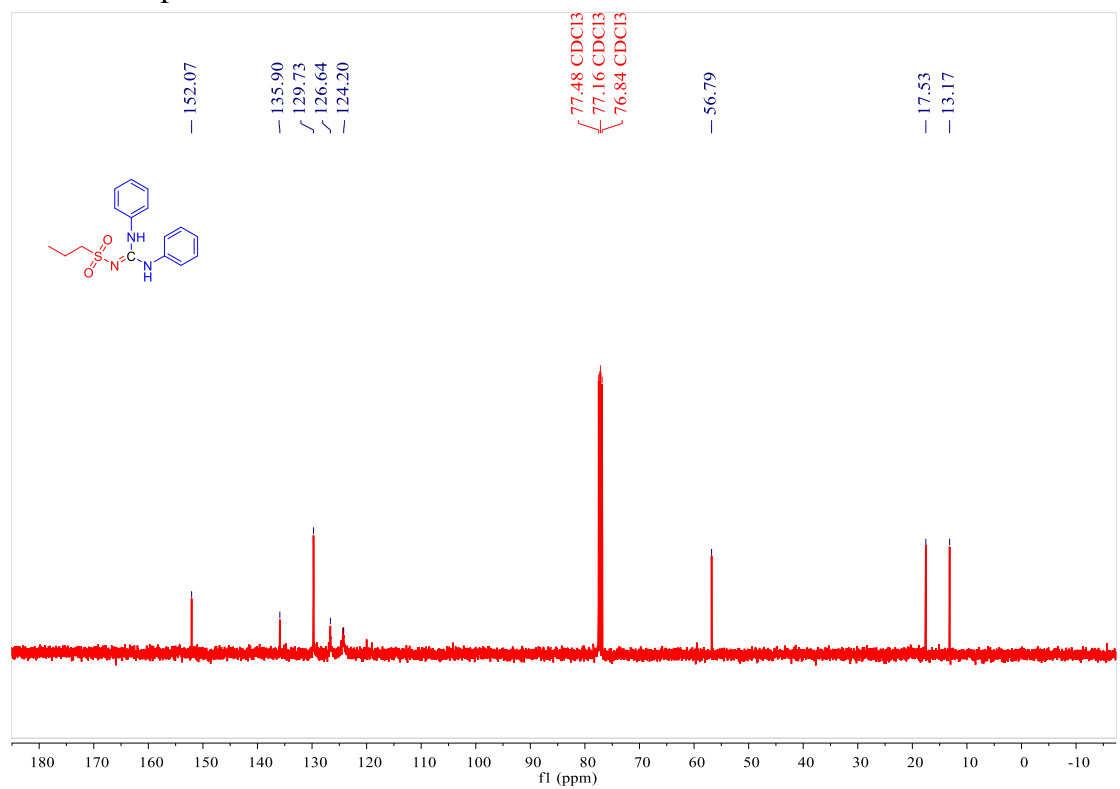
¹³C NMR Spectra of **4j**



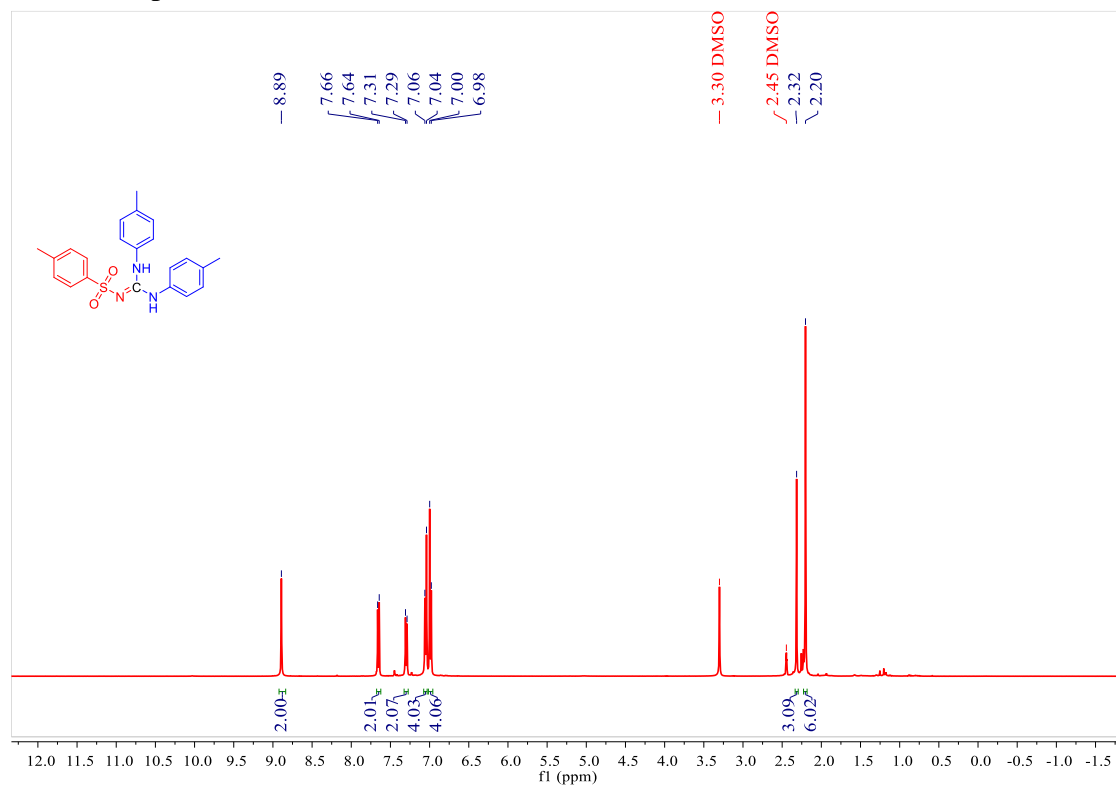
¹H NMR Spectra of **4k**



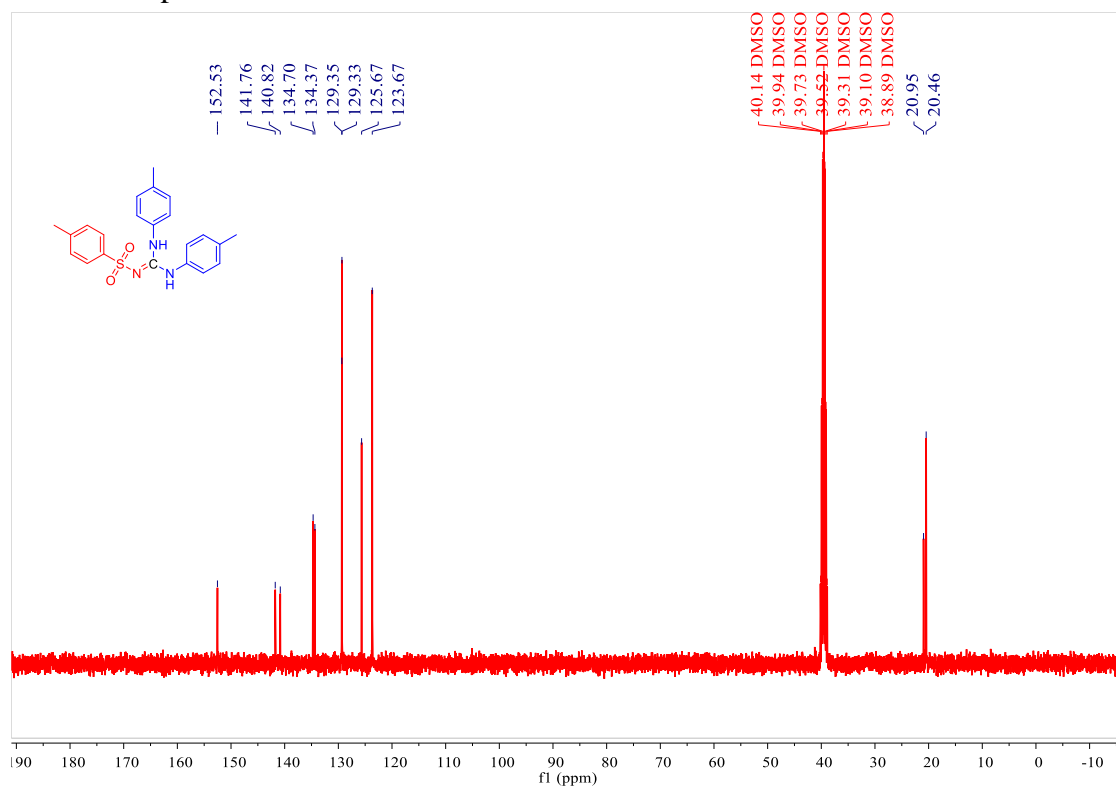
¹³C NMR Spectra of **4k**



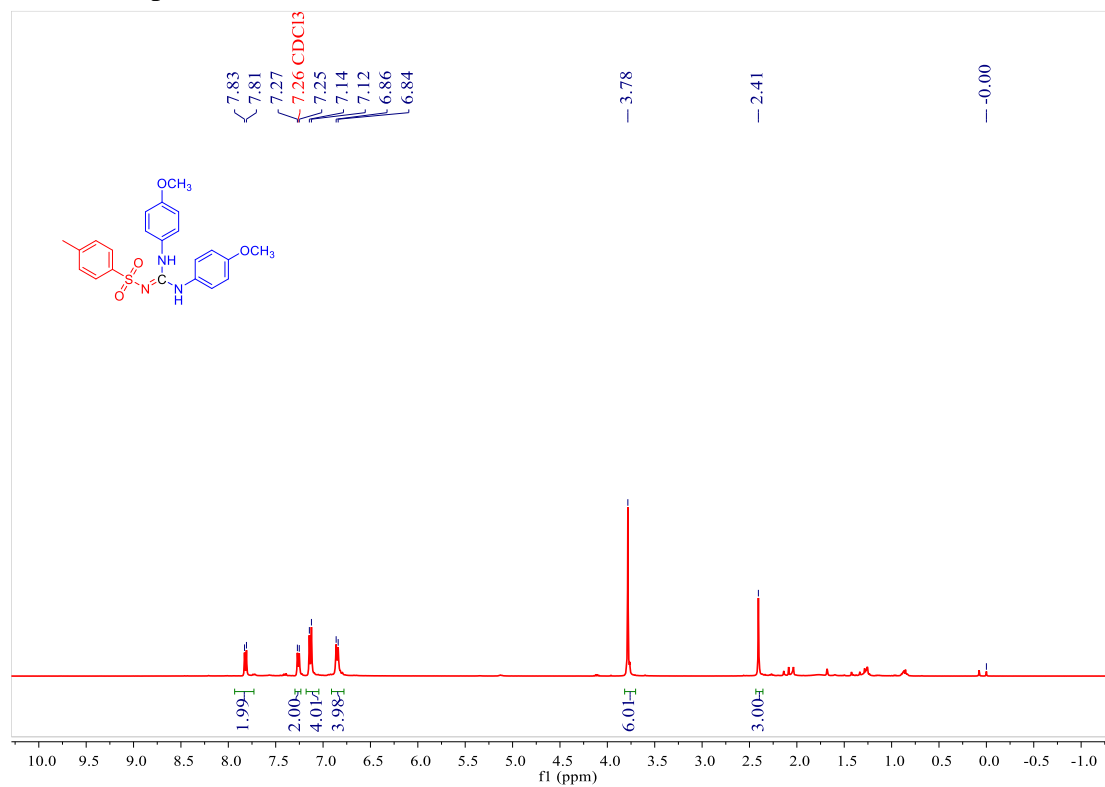
¹H NMR Spectra of **41**



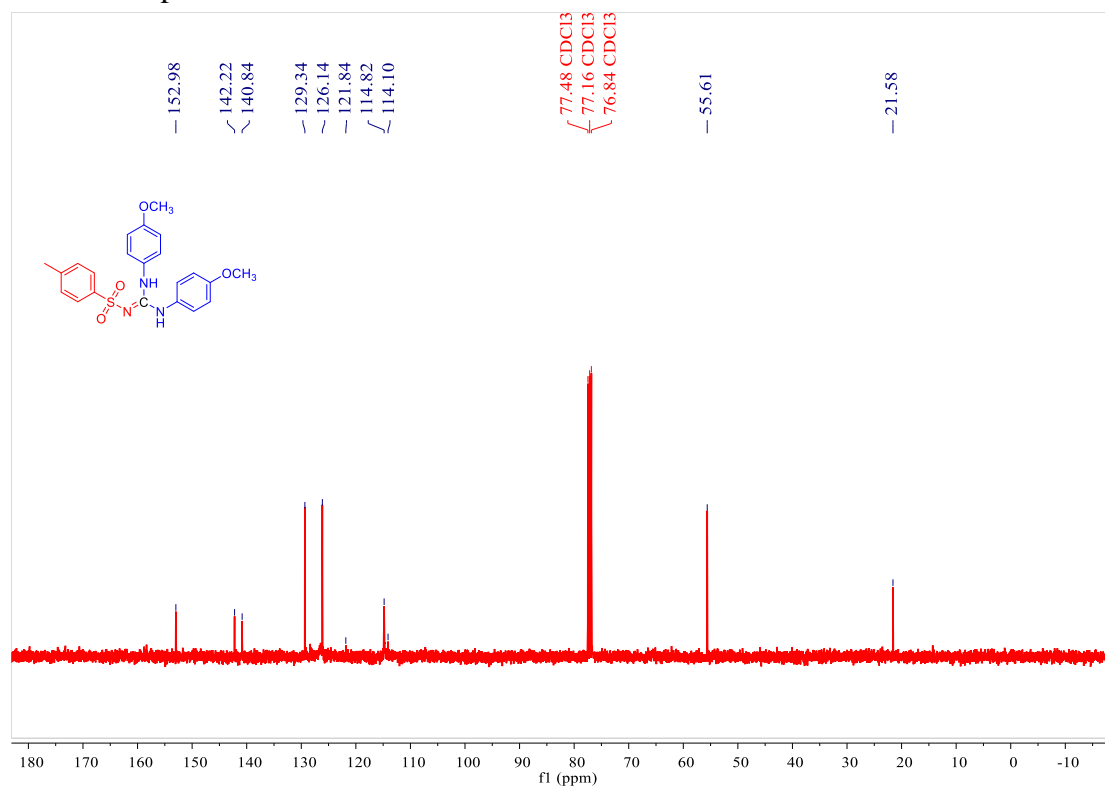
¹³C NMR Spectra of **41**



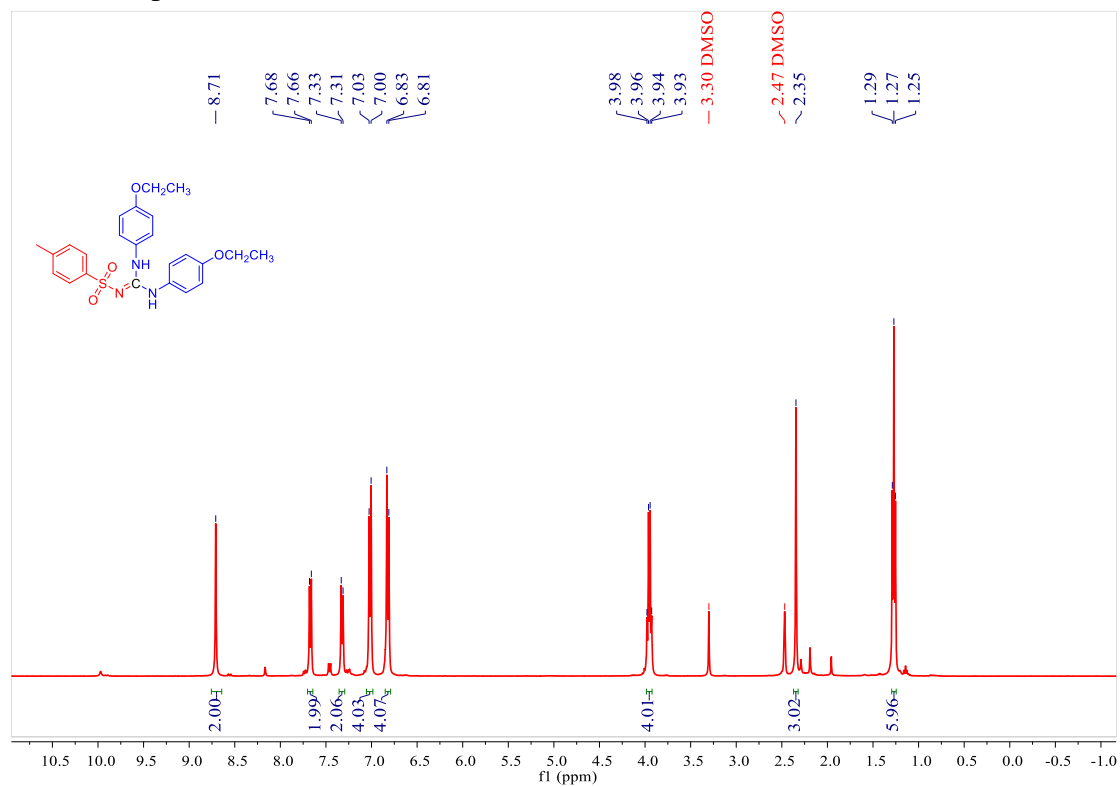
¹H NMR Spectra of **4m**



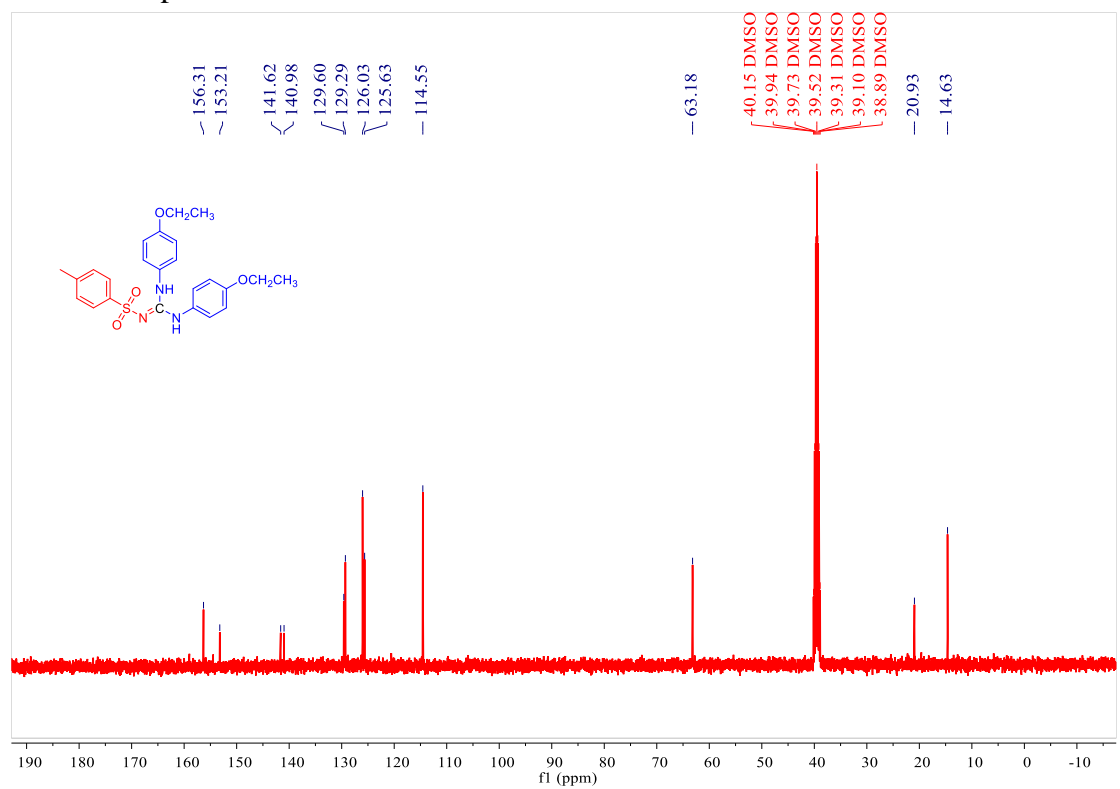
¹³C NMR Spectra of **4m**



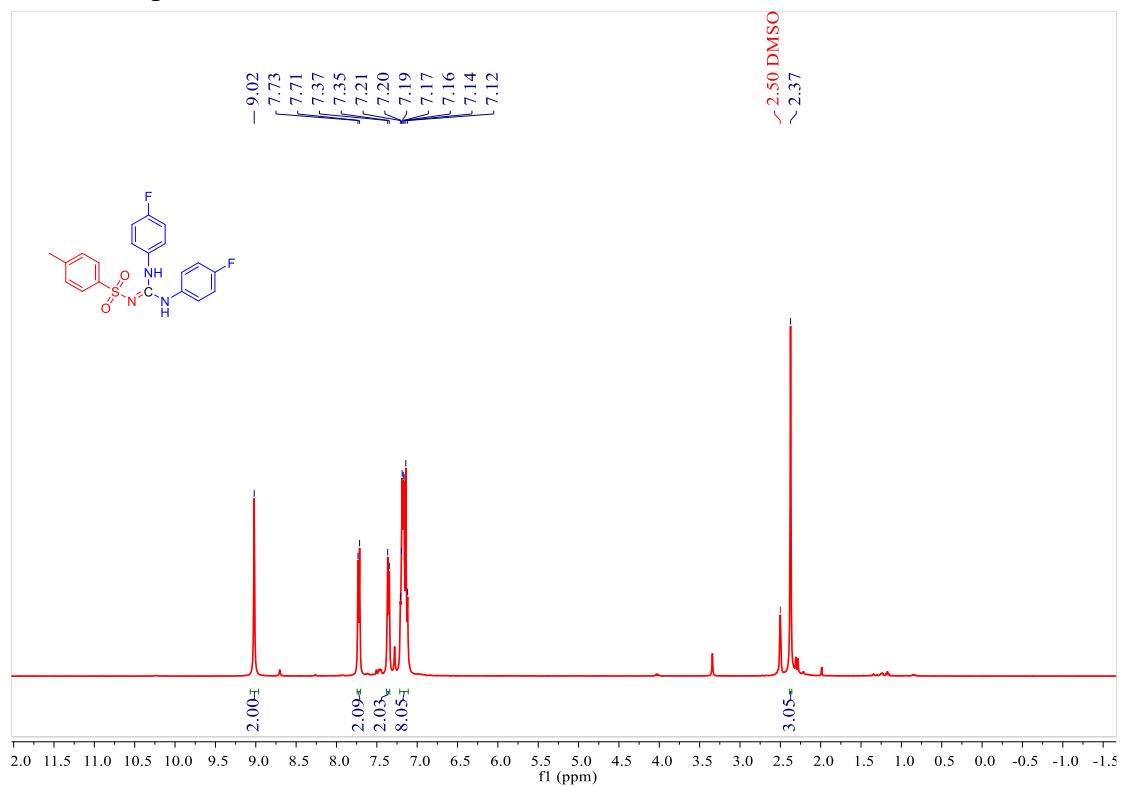
¹H NMR Spectra of **4n**



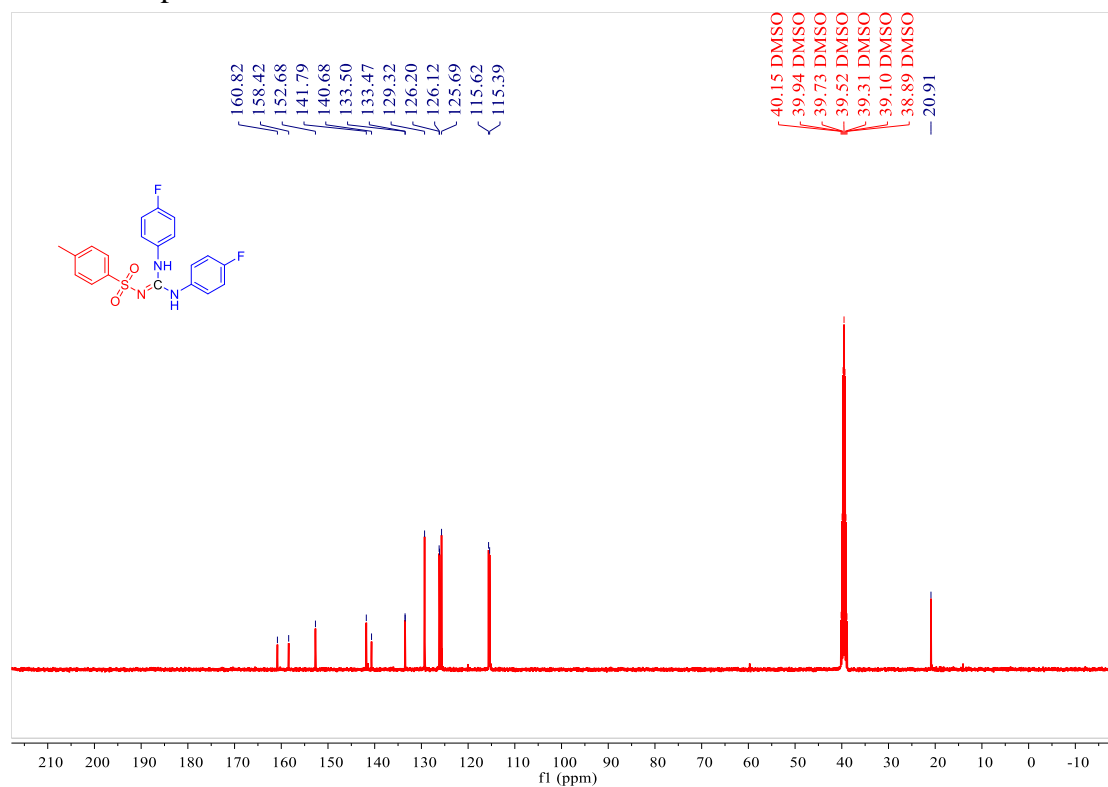
¹³C NMR Spectra of **4n**



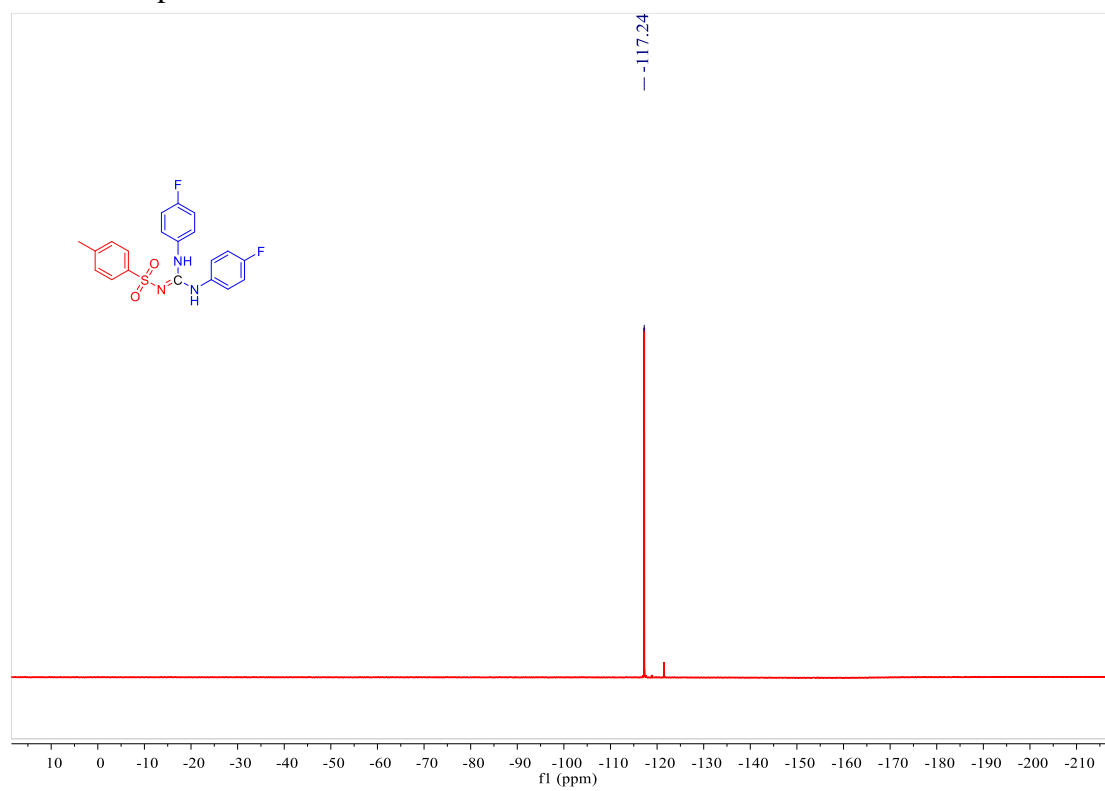
¹H NMR Spectra of **4o**



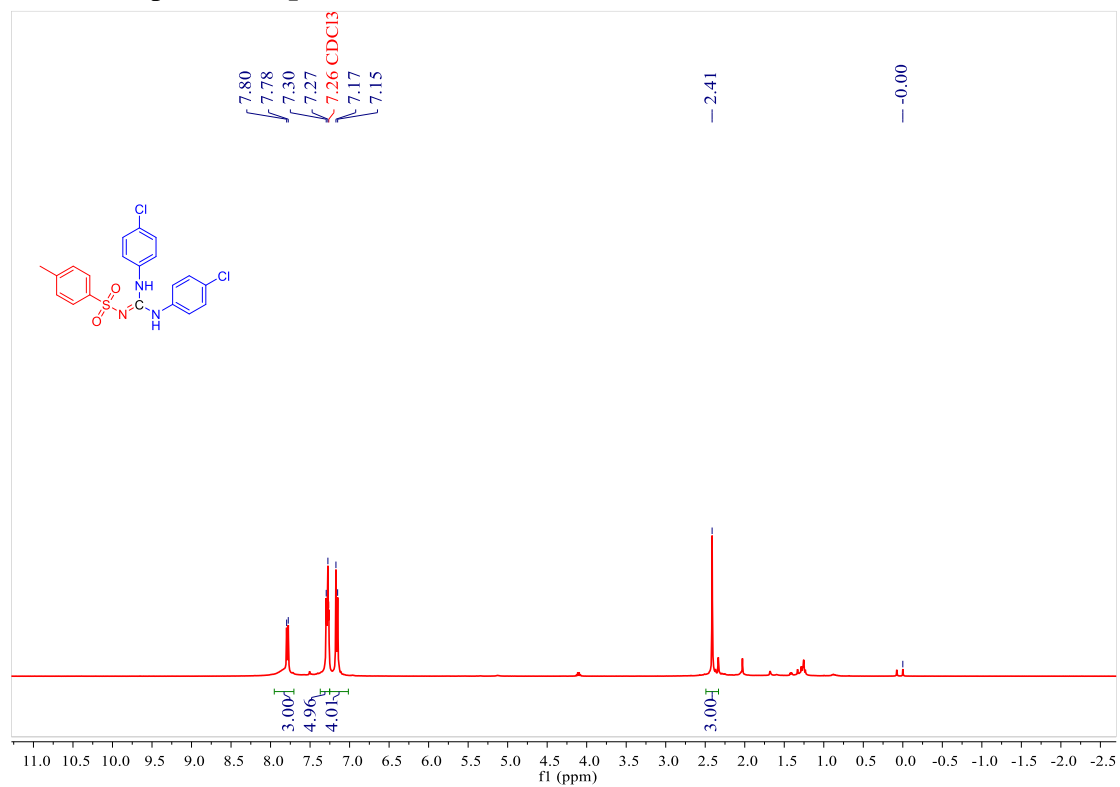
¹³C NMR Spectra of **4o**



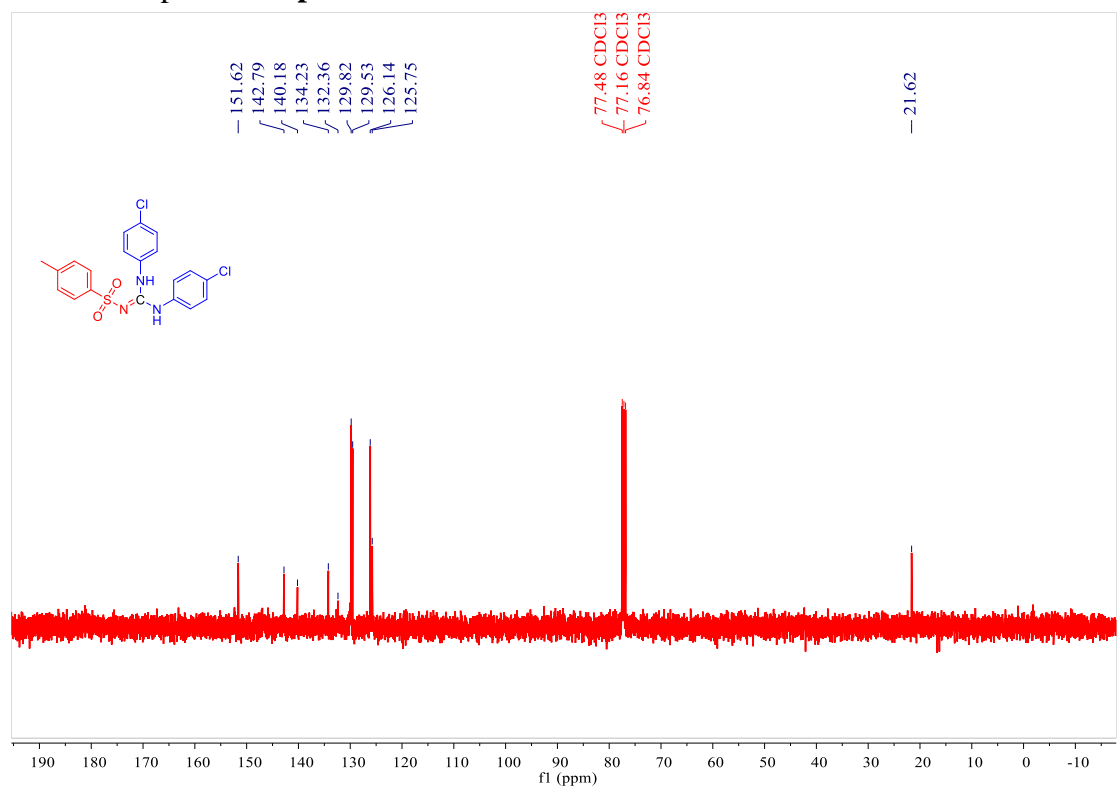
¹⁹F NMR Spectra of **4o**



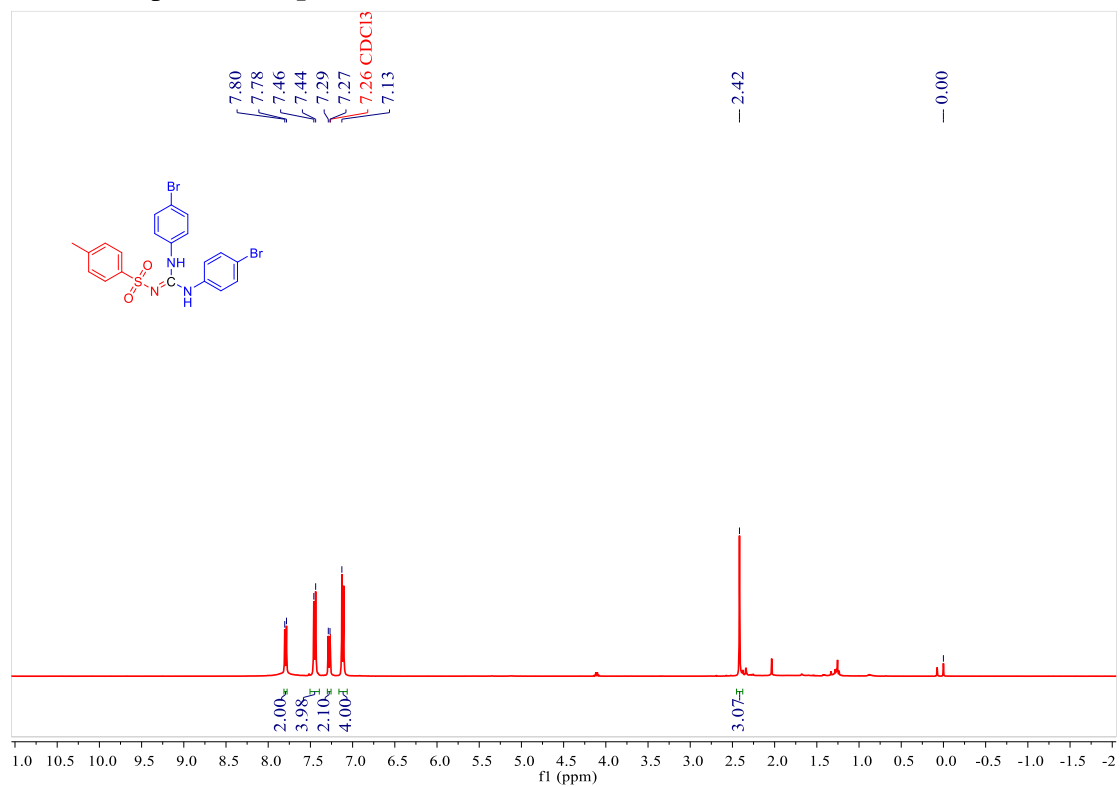
¹H NMR Spectra of **4p**



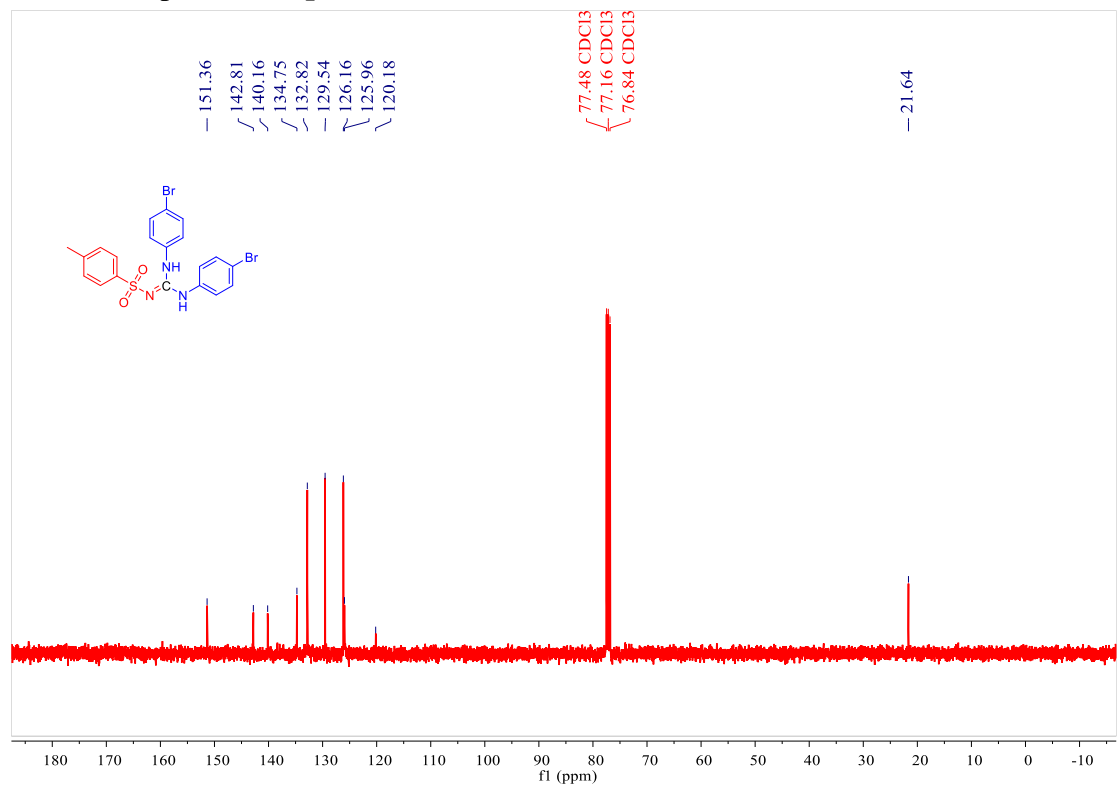
¹³C NMR Spectra of **4p**



¹H NMR Spectra of **4q**

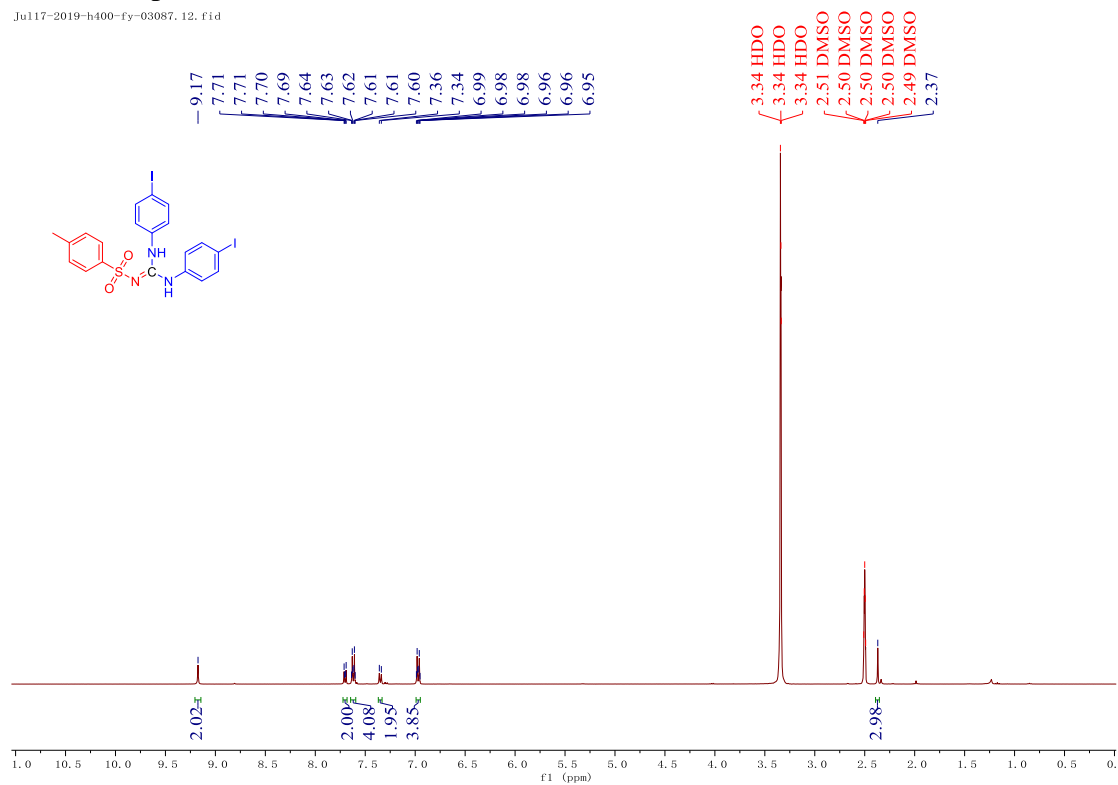


¹³C NMR Spectra of **4q**

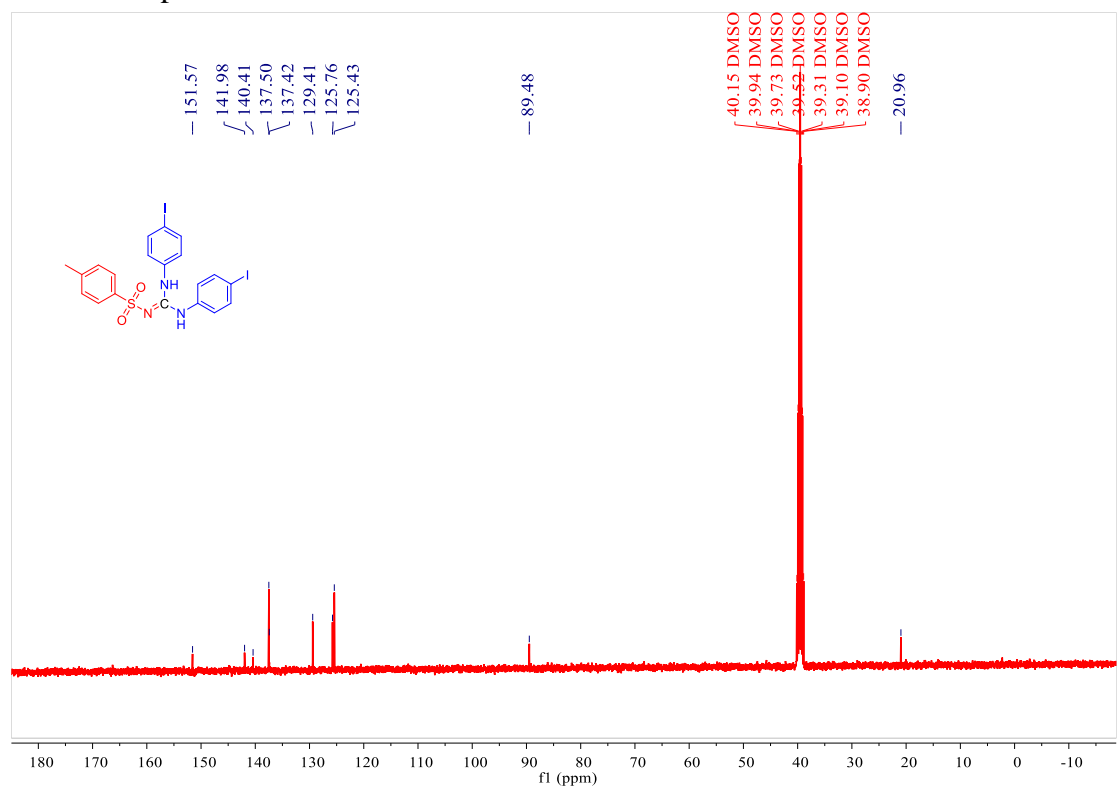


¹H NMR Spectra of 4r

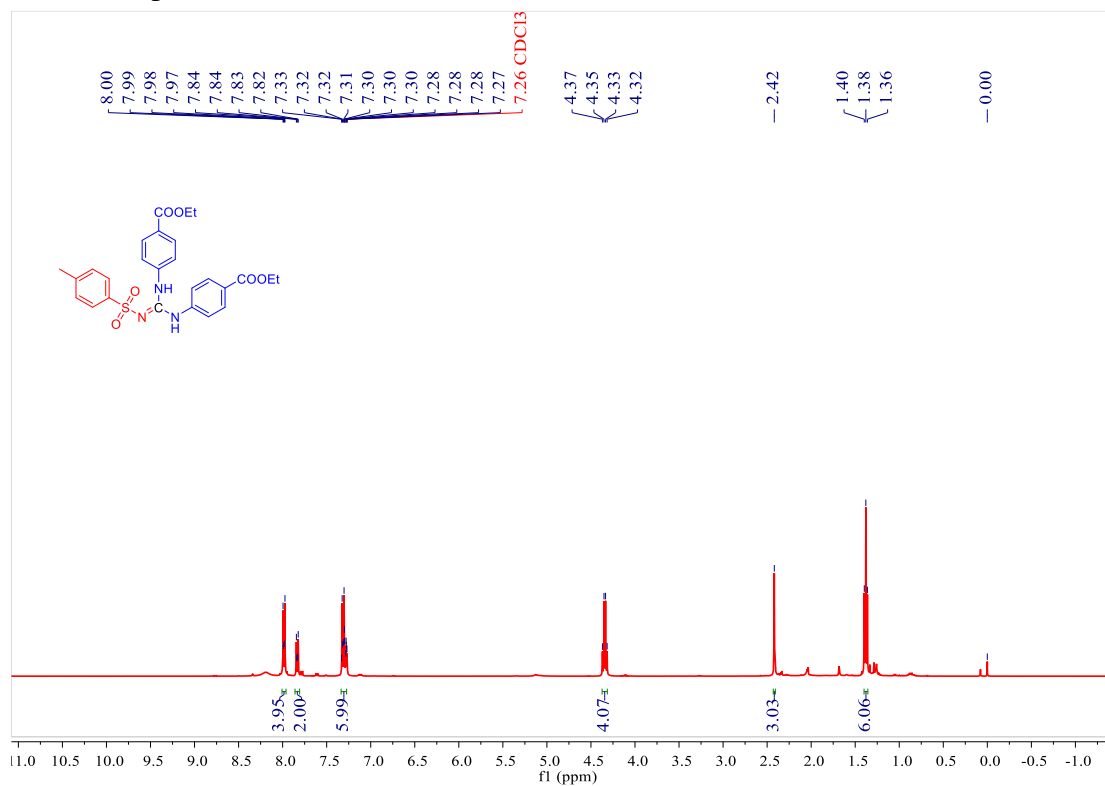
Ju117-2019-h400-fy-03087. 12. fid



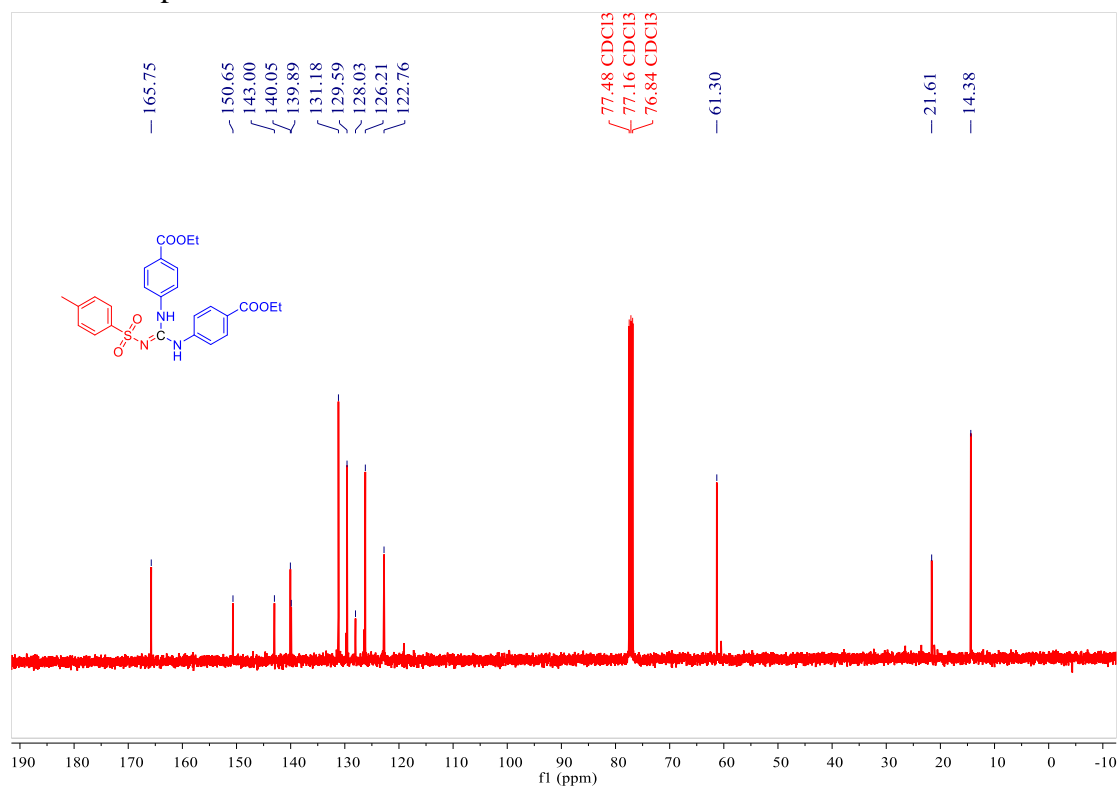
¹³C NMR Spectra of 4r



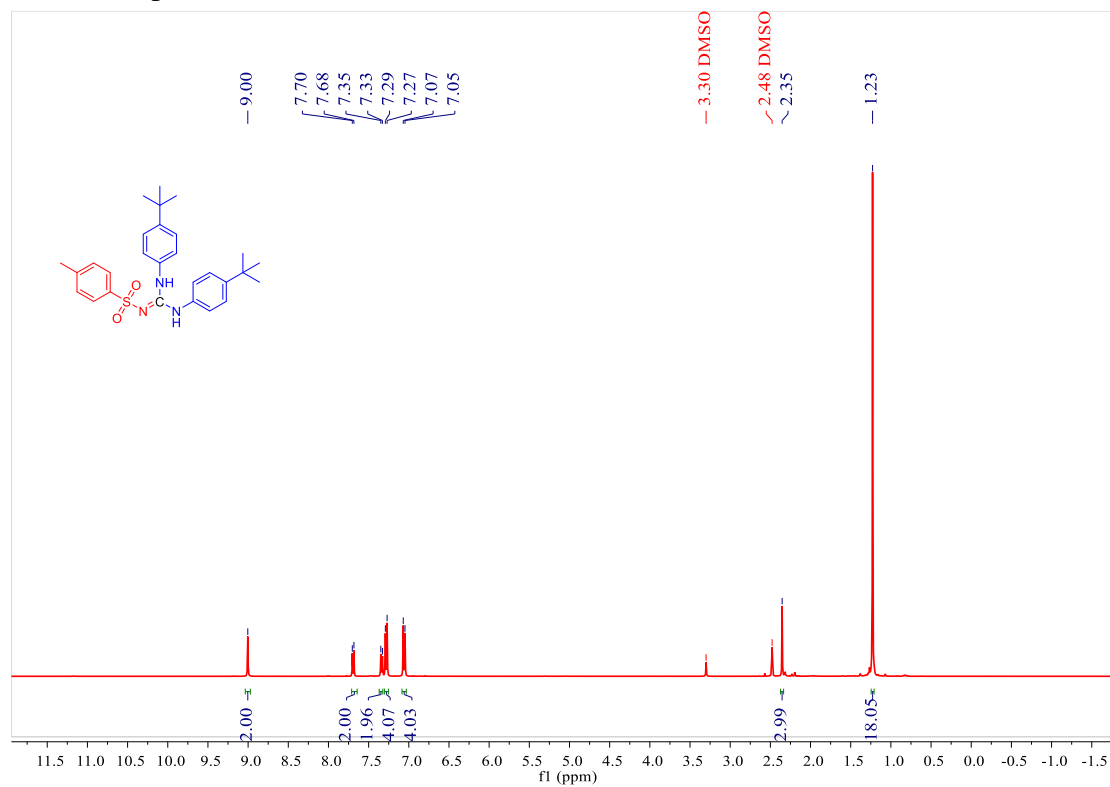
¹H NMR Spectra of 4s



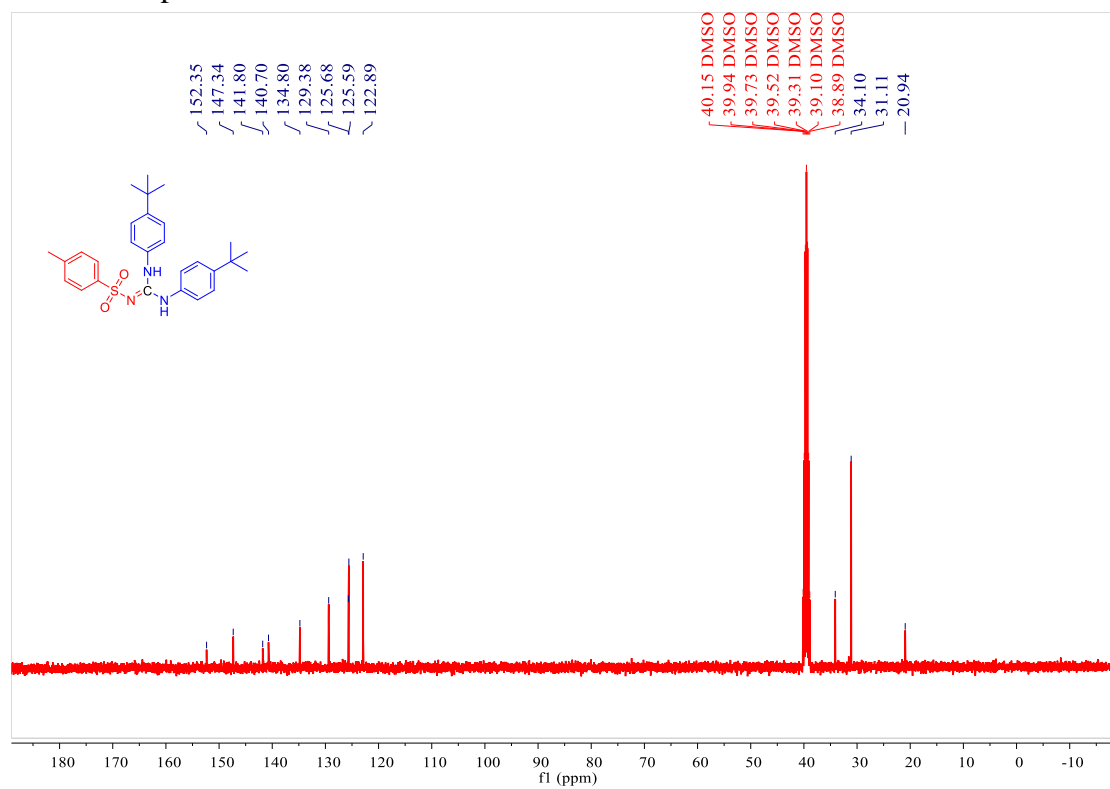
¹³C NMR Spectra of 4s



¹H NMR Spectra of **4t**

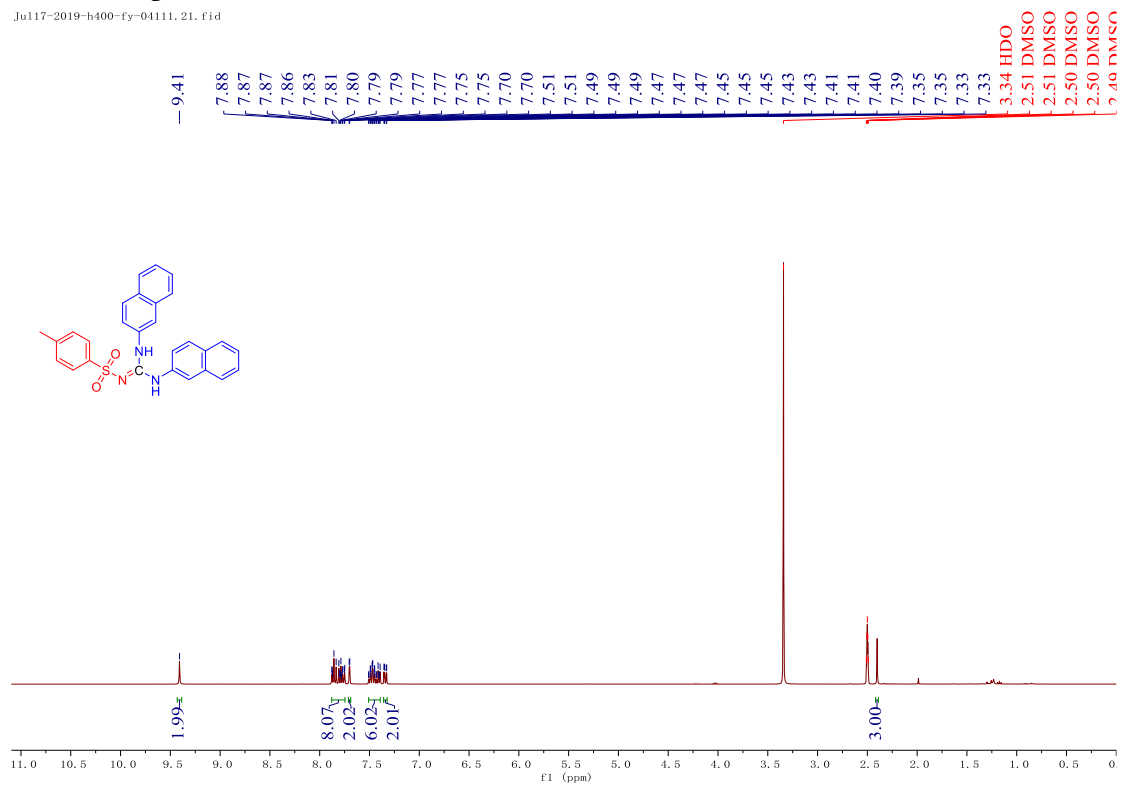


¹³C NMR Spectra of **4t**

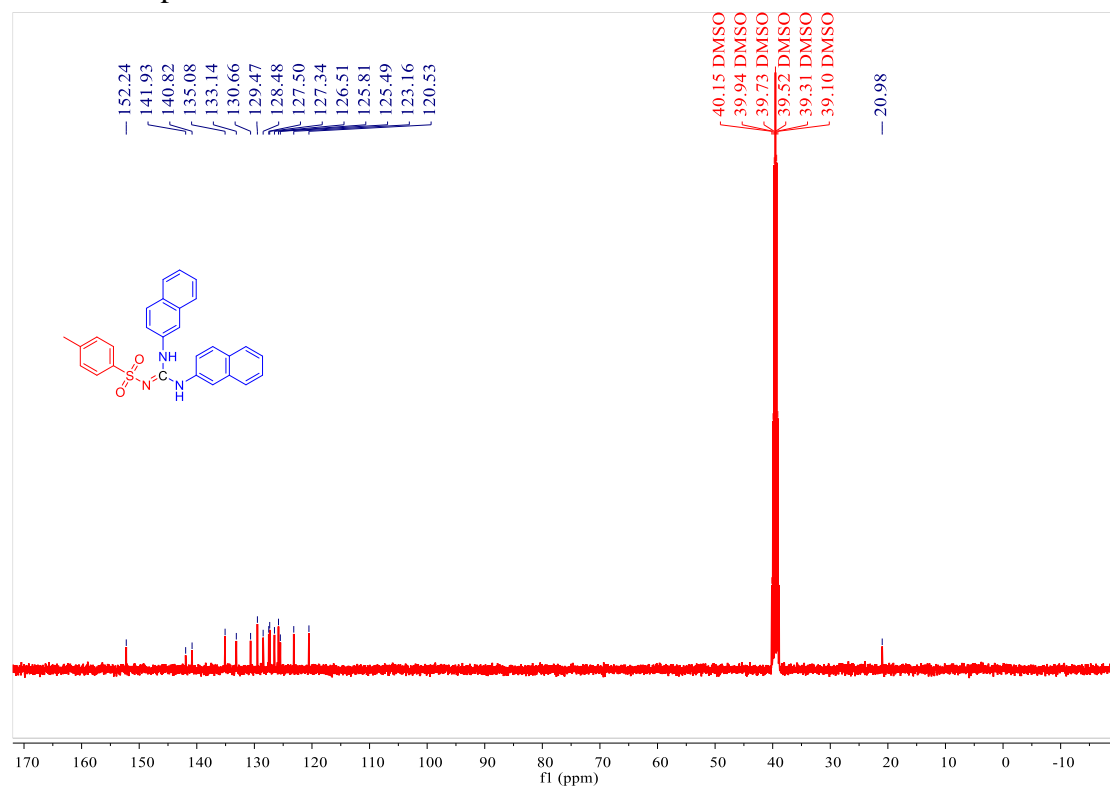


¹H NMR Spectra of 4v

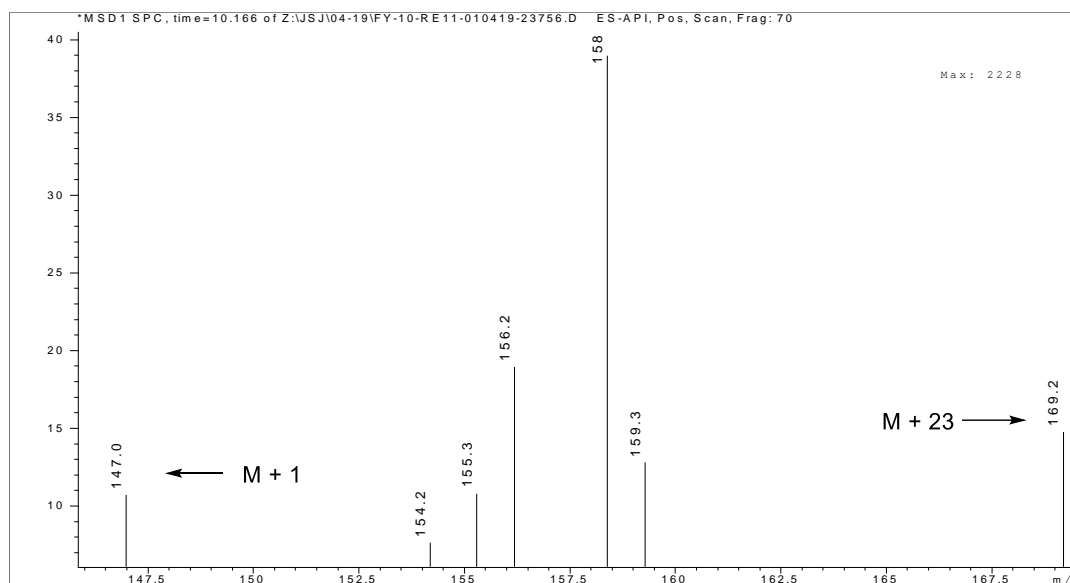
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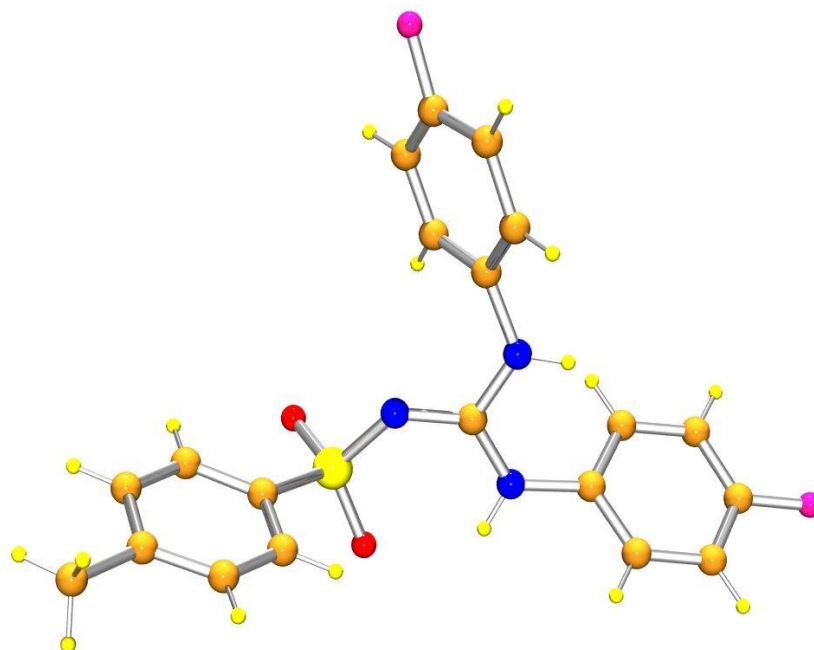
¹³C NMR Spectra of 4v



V. The MS Spectra of 4'



VI. X-Ray Structure of 4o



CCDC 1913025 (**4aea**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.