Electronic Supplementary Information

Electrochemically generated N-iodoaminium species as the key intermediates for selective methyl sulphonylimination of tertiary amines

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1. General and Experimental Details

1.1 General information

All commercially available reagents (AR grade) were directly used as received without further purification, including organic solvents. Electrochemical reactions were performed on a DJS-292B potentiostat (made in China) in the constant current mode. All yields of products refer to the isolated yields after chromatography.

^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded on a Bruker AV-400 spectrometer in $CDCl_3$. For ^{1}H NMR, $CDCl_3$ (δ = 7.26 ppm) or tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; for ^{13}C NMR, $CDCl_3$ (δ = 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration.

GC analysis was performed on 7890B/Agilent, while GC-MS analysis was performed on 7890A-5975C/Agilent. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

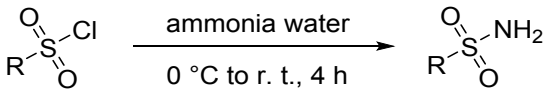
1.2 Substrates preparation

Substrates (CAS No.) purchased from commercial sources:

1	70-55-3	**2**	88-19-7
4	6292-59-7	**5**	98-10-2
7	30058-40-3	**8**	402-46-0
9	17260-71-8	**10**	701-34-8
11	830-43-3	**12**	3119-02-6
13	1513-45-7	**15**	1129-26-6
17	121-61-9	**18**	6339-87-3
20	4563-33-1	**21**	3144-09-0
22	421-85-2	**24**	68291-97-4
25	169590-42-5		
a	626-67-5	**b**	7378-99-6
c	103-83-3	**d**	75-50-3 (4.2 mol/L in ethanol)
e	598-56-1	**f**	996-35-0
g	98-94-2	**h**	120-29-6

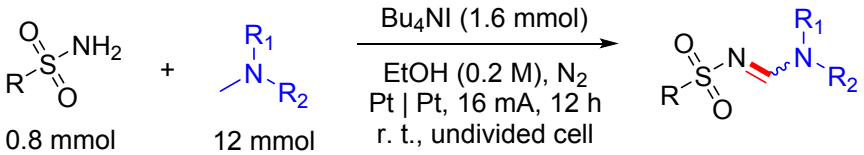
i	2155-94-4	**j**	109-02-4
k	120-94-5	**l**	121-69-7
m	68-12-2		

Sulfonamides **3**, **6**, **14**, **16**, **19**, **23** were obtained from their corresponding sulfonyl chlorides:



Sulfonyl chloride (5 mmol) was dropwise added to excess amount of ammonia water (3.0 mL, 25% - 28% ammonia content) at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 4 hours. The mixture was extracted with dichloromethane (DCM) and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the obtained solid was further purified by recrystallization using petroleum ether (PE) from ethyl acetate (EA).

1.3 General Procedure for the condensation between sulfonamides and tertiary amines (GP1)



To a 25 mL three-necked flask was added sulfonamide (1.0 equiv, 0.8 mmol) and Bu_4NI (2.0 equiv, 1.6 mmol, 591.0 mg), followed by N-methyl-N,N-dialkylamine (15 equiv, 12 mmol) and solvent ethanol (4.0 mL). The flask was then equipped with two platinum plate electrodes (10×10×0.2 mm, the distance between them was approximately 2 cm) and a N_2 balloon with a three-way valve. The atmosphere was replaced to N_2 by pump under low temperature for several times. The constant current (16 mA) electrolysis was performed at room temperature for the indicated time. After the electrolysis, the solvent was removed under reduced pressure, and the resulting mixture was purified by column chromatography on silica gel (eluted with PE/EA) to afford the desired condensation product.

Observations during every electrolysis: When the constant current is on, the reaction mixture around the anode starts to get colored immediately, which gradually changes the color of the whole system from clearly colorless to dark brown. Meanwhile, small bubbles of gas evolution are observed on the surface of the cathode (**Fig. S1**, **S2**).

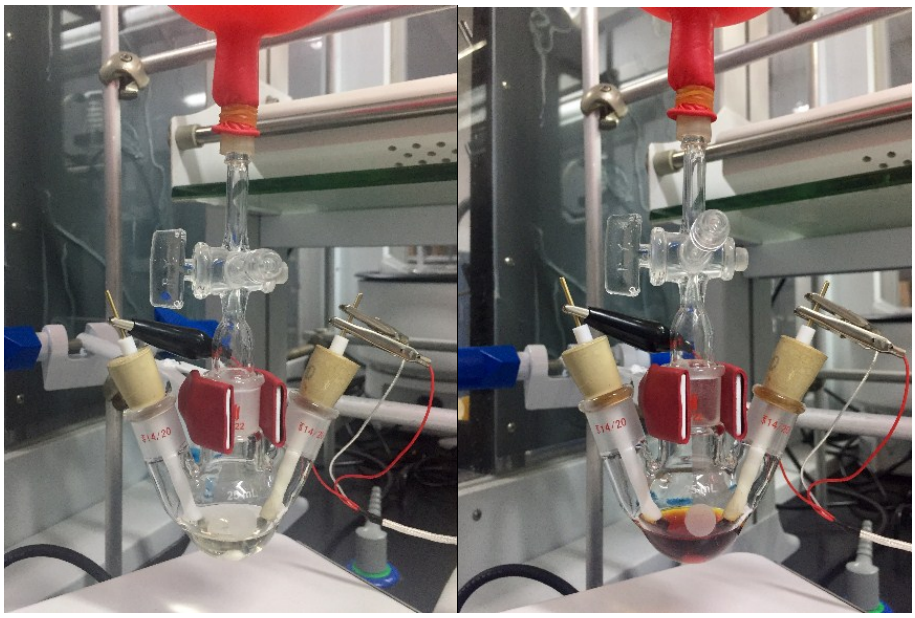


Fig. S1. Reaction setup and the color change after electrolysis
(Left: before electrolysis; Right: after electrolysis for 12 h)

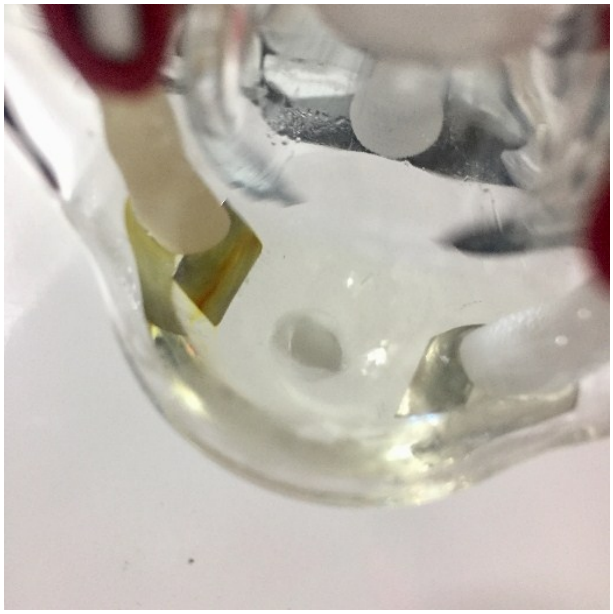
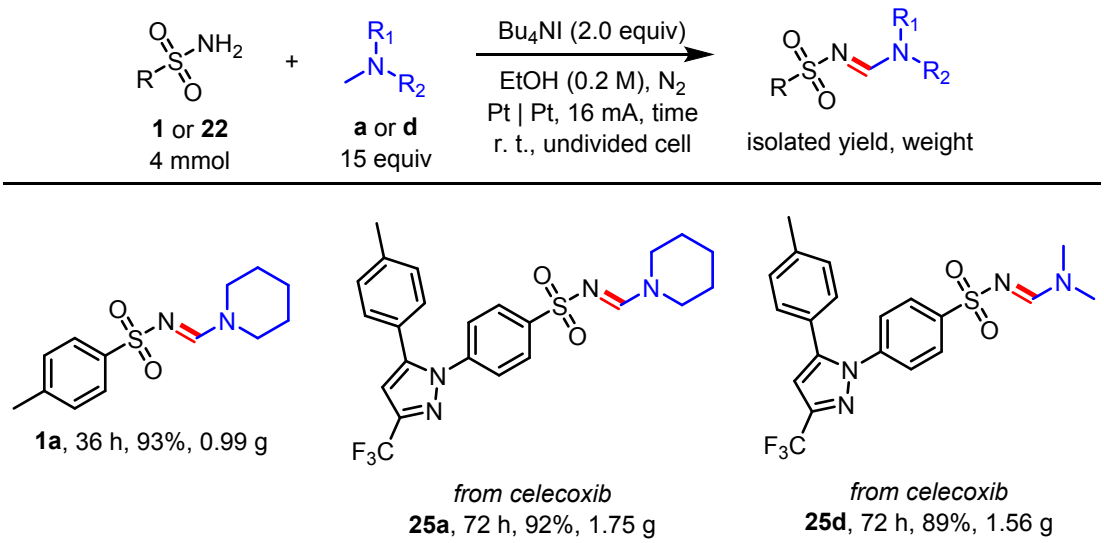


Fig. S2. During the electrolysis
(Left: anode, right: cathode; picture was taken shortly after the constant current was on)

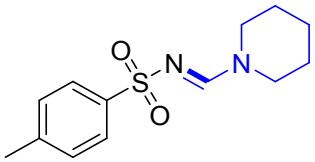
1.4 General Procedure for the gram scale syntheses (GP2)



Each gram scale reaction was carried out using electrodes of same size and identical current with small scale ones, but for a prolonged reaction time:

To a 50 mL three-necked flask was added sulfonamide (1 equiv, 4 mmol) and Bu_4NI (2 equiv, 8 mmol, 2.955 g), followed by N-methyl containing tertiary amine (15 equiv, 60 mmol) and solvent ethanol (20 mL). The flask was then equipped with two platinum plate electrodes (10×10×0.2 mm, the distance between them was approximately 3 cm) and a N_2 balloon through a three-way valve. The atmosphere was then replaced to N_2 by pump under low temperature for several times. The constant current (16 mA) electrolysis was performed at room temperature for indicated time. The resulting mixture was purified by column chromatography on silica gel (eluted with PE/EA) to afford the desired condensation product.

2. Characterization Data for the products



4-methyl-N-(piperidin-1-ylmethylene)benzenesulfonamide[1] (**1a**, E/Z > 20:1)

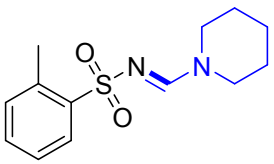
White solid, 204.5 mg, 96% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

Beige solid, 0.99 g, 93% isolated yield from the reaction between **1** (685.0 mg, 4.0 mmol) and **a** (7.3 mL, 60 mmol) following **GP2**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.77 – 7.71 (m, 2H), 7.23 (d, J = 7.9 Hz, 2H), 3.57 (t, J = 5.7 Hz, 2H), 3.39 (t, J = 5.3 Hz, 2H), 2.38 (s, 3H), 1.69 – 1.61 (m, 4H), 1.58 – 1.53 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.32, 142.40, 139.75, 129.36, 126.50, 51.95, 44.69, 26.47, 24.90, 24.00, 21.54.

GC-MS (EI): 266.1, 201.2, 111.1, 91.1, 84.2, 65.1.



2-methyl-N-(piperidin-1-ylmethylene)benzenesulfonamide (**2a**, E/Z > 20:1)

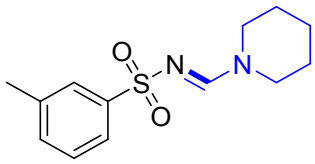
Colorless oil, 196.0 mg, 92% isolated yield from the reaction between **2** (137.0 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.04 – 7.94 (m, 1H), 7.43 – 7.34 (m, 1H), 7.31 – 7.23 (m, 2H), 3.66 – 3.57 (m, 2H), 3.40 (t, J = 5.3 Hz, 2H), 2.69 (s, 3H), 1.75 – 1.65 (m, 4H), 1.63 – 1.56 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.58, 140.78, 137.43, 132.16, 132.02, 127.63, 125.88, 51.99, 44.79, 26.54, 24.97, 24.09, 20.68.

GC-MS (EI): 266.1, 182.0, 159.1, 111.1, 91.1, 84.1, 65.1.

HRMS (ESI) calcd for $C_{13}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 267.1162; found: 267.1163.



3-methyl-N-(piperidin-1-ylmethylene)benzenesulfonamide (**3a**, E/Z > 20:1)

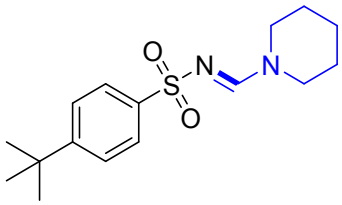
Colorless oil, 179.0 mg, 84% isolated yield from the reaction between **3** (137.0 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.74 – 7.61 (m, 2H), 7.38 – 7.27 (m, 2H), 3.63 – 3.56 (m, 2H), 3.41 (t, J = 5.2 Hz, 2H), 2.40 (s, 3H), 1.72 – 1.65 (m, 4H), 1.63 – 1.54 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.42, 142.41, 138.89, 132.66, 128.68, 126.98, 126.96, 123.64, 52.03, 44.78, 26.51, 24.94, 24.05, 21.46.

GC-MS (EI): 266.1, 155.0, 111.1, 91.1, 84.1, 65.1, 56.1.

HRMS (ESI) calcd for $C_{13}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 267.1162; found: 267.1167.



4-(tert-butyl)-N-(piperidin-1-ylmethylene)benzenesulfonamide (**4a**, E/Z > 20:1)

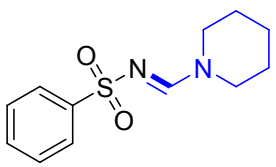
Colorless crystal, 231.9 mg, 94% isolated yield from the reaction between **4** (170.6 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.83 – 7.76 (m, 2H), 7.49 – 7.43 (m, 2H), 3.62 – 3.57 (m, 2H), 3.42 – 3.37 (m, 2H), 1.72 – 1.63 (m, 4H), 1.62 – 1.54 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.43, 155.44, 139.68, 126.36, 125.79, 52.00, 44.76, 35.12, 31.24, 26.51, 24.95, 24.07.

GC-MS (EI): 308.2, 229.2, 207.1, 159.1, 111.1, 84.1.

HRMS (ESI) calcd for $C_{16}H_{25}N_2O_2S^+$ m/z $[M+H]^+$: 309.1631; found: 309.1638.



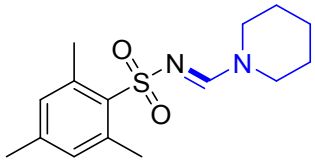
N-(piperidin-1-ylmethylene)benzenesulfonamide[2] (**5a**, E/Z > 20:1)

White solid, 183.7 mg, 91% isolated yield from the reaction between **5** (125.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.93 – 7.84 (m, 2H), 7.53 – 7.41 (m, 3H), 3.62 – 3.56 (m, 2H), 3.41 (t, J = 5.2 Hz, 2H), 1.71 – 1.62 (m, 4H), 1.61 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 142.65, 131.87, 128.80, 126.53, 52.05, 44.80, 26.52, 24.95, 24.04.

GC-MS (EI): 252.1, 207.1, 141.0, 111.1, 84.1, 77.1, 51.1.



2,4,6-trimethyl-N-(piperidin-1-ylmethylene)benzenesulfonamide (**6a**, E/Z > 20:1)

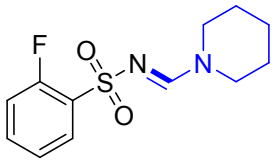
Light yellow oil, 209.6 mg, 89% isolated yield from the reaction between **6** (159.4 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 6.89 (s, 2H), 3.59 – 3.53 (m, 2H), 3.40 – 3.34 (m, 2H), 2.65 (s, 6H), 2.26 (s, 3H), 1.69 – 1.60 (m, 4H), 1.60 – 1.53 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.79, 141.14, 138.37, 136.68, 131.48, 51.75, 44.57, 26.44, 24.87, 24.02, 23.07, 20.92.

GC-MS (EI): 294.1, 229.1, 146.1, 119.1, 103.1, 91.1, 84.1.

HRMS (ESI) calcd for $C_{15}H_{23}N_2O_2S^+$ m/z $[M+H]^+$: 295.1475; found: 295.1473.



2-fluoro-N-(piperidin-1-ylmethylene)benzenesulfonamide (**7a**, E/Z > 20:1)

Colorless crystal, 168.7 mg, 78% isolated yield from the reaction between **7** (140.1 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

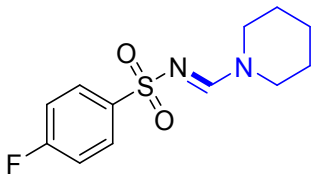
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 2.8 Hz, 1H), 7.98 (td, J = 7.6, 1.8 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.23 (td, J = 7.7, 1.1 Hz, 1H), 7.16 – 7.06 (m, 1H), 3.64 – 3.58 (m, 2H), 3.50 – 3.43 (m, 2H), 1.73 – 1.66 (m, 4H), 1.63 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.29, 158.86, 157.77, 134.29, 134.20, 130.20, 130.06, 129.62, 124.28, 124.25, 116.87, 116.66, 52.28, 45.02, 26.67, 25.05, 24.05.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.30.

GC-MS (EI): 270.1, 159.0, 111.1, 95.1, 84.1, 75.1, 56.1.

HRMS (ESI) calcd for $C_{12}H_{16}FN_2O_2S^+$ m/z $[M+H]^+$: 271.0911; found: 271.0916.



4-fluoro-N-(piperidin-1-ylmethylene)benzenesulfonamide (**8a**, E/Z > 20:1)

Light yellow oil, 194.6 mg, 90% isolated yield from the reaction between **8** (140.1 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

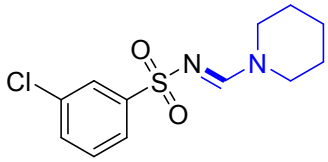
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.91 – 7.84 (m, 2H), 7.15 – 7.07 (m, 2H), 3.61 – 3.55 (m, 2H), 3.41 (t, J = 5.2 Hz, 2H), 1.70 – 1.62 (m, 4H), 1.61 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89, 163.38, 157.34, 138.82, 138.79, 129.20, 129.11, 115.99, 115.77, 52.08, 44.81, 26.49, 24.93, 23.98.

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.26.

GC-MS (EI): 270.1, 185.1, 159.0, 111.2, 95.1, 84.2.

HRMS (ESI) calcd for $C_{12}H_{16}FN_2O_2S^+$ m/z $[M+H]^+$: 271.0911; found: 271.0918.



3-chloro-N-(piperidin-1-ylmethylene)benzenesulfonamide (**9a**, E/Z > 20:1)

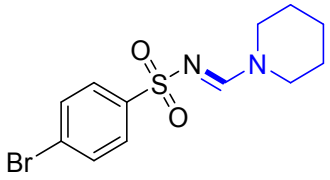
Beige crystal, 188.1 mg, 82% isolated yield from the reaction between **9** (153.3 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 (t, J = 1.9 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.49 – 7.43 (m, 1H), 7.39 (t, J = 7.9 Hz, 1H), 3.63 – 3.57 (m, 2H), 3.43 (t, J = 5.0 Hz, 2H), 1.71 – 1.65 (m, 4H), 1.63 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.53, 144.36, 134.80, 131.96, 130.16, 126.75, 124.73, 52.18, 44.93, 26.50, 24.95, 23.99.

GC-MS (EI): 288.0, 286.1, 175.0, 111.1, 84.1, 75.1.

HRMS (ESI) calcd for $C_{12}H_{16}ClN_2O_2S^+$ m/z $[M+H]^+$: 287.0616; found: 287.0620.



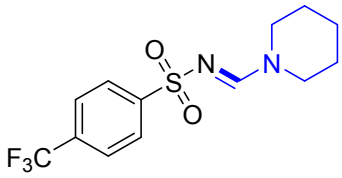
4-bromo-N-(piperidin-1-ylmethylene)benzenesulfonamide[2] (**10a**, E/Z > 20:1)

Light yellow solid, 148.4 mg, 56% isolated yield from the reaction between **10** (188.9 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol), along with 78.7 mg debrominated product **5a** (39% isolated yield) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.78 – 7.66 (m, 2H), 7.61 – 7.51 (m, 2H), 3.62 – 3.52 (m, 2H), 3.45 – 3.35 (m, 2H), 1.72 – 1.61 (m, 4H), 1.61 – 1.51 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 141.87, 132.04, 128.25, 126.61, 52.15, 44.89, 26.55, 24.98, 24.02.

GC-MS (EI): 332.0, 330.0, 220.9, 218.9, 156.9, 155.0, 111.1, 84.1.



N-(piperidin-1-ylmethylene)-4-(trifluoromethyl)benzenesulfonamide (**11a**, E/Z > 20:1)

Light yellow solid, 138.4 mg, 54% isolated yield from the reaction between **11** (180.2 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol), along with 78.8 mg defluorinated product **1a** (37% isolated yield) following **GP1**.

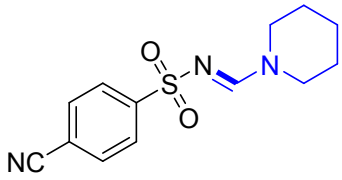
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.75 – 7.68 (m, 2H), 3.61 (t, J = 5.7 Hz, 2H), 3.44 (t, J = 5.2 Hz, 2H), 1.73 – 1.65 (m, 4H), 1.63 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58, 146.24, 133.78, 133.46, 127.14, 125.99, 125.96, 125.92, 124.93, 122.22, 52.25, 44.99, 26.55, 24.99, 24.01.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.00.

GC-MS (EI): 320.1, 237.1, 209.0, 145.0, 111.1, 125.0, 95.0.

HRMS (ESI) calcd for $C_{13}H_{16}F_3N_2O_2S^+$ m/z $[M+H]^+$: 321.0879; found: 321.0874.



4-cyano-N-(piperidin-1-ylmethylene)benzenesulfonamide (**12a**, E/Z > 20:1)

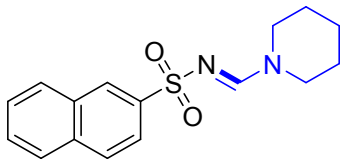
White solid, 110.9 mg, 50% isolated yield from the reaction between **12** (145.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 – 7.94 (m, 2H), 7.77 – 7.70 (m, 2H), 3.59 (t, J = 5.6 Hz, 2H), 3.44 (t, J = 5.1 Hz, 2H), 1.73 – 1.64 (m, 4H), 1.63 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 146.90, 132.67, 127.24, 117.77, 115.42, 52.26, 45.00, 26.47, 24.93, 23.89.

GC-MS (EI): 277.1, 166.0, 111.1, 102.0, 84.1, 56.1, 42.1.

HRMS (ESI) calcd for $C_{13}H_{16}N_3O_2S^+$ m/z $[M+H]^+$: 278.0958; found: 278.0951.



N-(piperidin-1-ylmethylene)naphthalene-2-sulfonamide (**13a**, E/Z > 20:1)

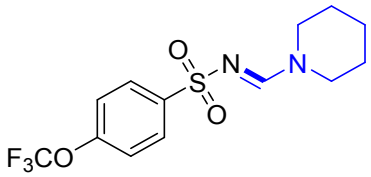
Light yellow solid, 186.3 mg, 77% isolated yield from the reaction between **14** (165.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.18 (s, 1H), 7.95 – 7.89 (m, 2H), 7.88 – 7.84 (m, 2H), 7.61 – 7.53 (m, 2H), 3.62 – 3.56 (m, 2H), 3.41 (t, J = 5.2 Hz, 2H), 1.70 – 1.62 (m, 4H), 1.60 – 1.53 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.47, 139.54, 134.58, 132.30, 129.27, 129.05, 128.34, 127.91, 127.27, 127.10, 122.69, 52.06, 44.81, 26.51, 24.94, 24.03.

GC-MS (EI): 302.1, 237.2, 210.2, 127.1, 111.1, 84.1, 56.1.

HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 303.1162; found: 303.1168.



N-(piperidin-1-ylmethylene)-4-(trifluoromethoxy)benzenesulfonamide (**14a**, E/Z > 20:1)

Light yellow oil, 139.9 mg, 52% isolated yield from the reaction between **13** (192.9 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

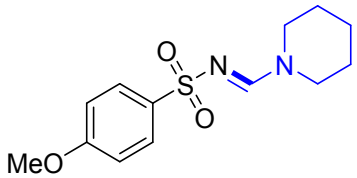
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.98 – 7.88 (m, 2H), 7.33 – 7.24 (m, 2H), 3.65 – 3.58 (m, 2H), 3.44 (t, J = 5.1 Hz, 2H), 1.74 – 1.66 (m, 4H), 1.64 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 151.56, 141.27, 128.67, 121.68, 120.85, 119.11, 52.16, 44.91, 26.52, 24.97, 24.01.

^{19}F NMR (376 MHz, $CDCl_3$) δ 57.72.

GC-MS (EI): 336.1, 251.1, 225.0, 203.1, 161.1, 111.1, 84.1.

HRMS (ESI) calcd for $C_{13}H_{16}F_3N_2O_3S^+$ m/z $[M+H]^+$: 337.0828; found: 337.0805.



4-methoxy-N-(piperidin-1-ylmethylene)benzenesulfonamide (**15a**, E/Z > 20:1)

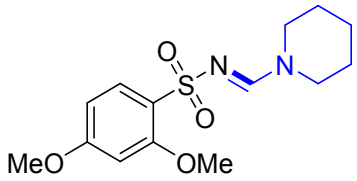
Light yellow solid, 178.5 mg, 79% isolated yield from the reaction between **15** (149.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 – 7.75 (m, 2H), 6.96 – 6.89 (m, 2H), 3.83 (s, 3H), 3.60 – 3.54 (m, 2H), 3.39 (t, J = 5.2 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.61 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.31, 157.20, 134.61, 128.58, 113.95, 55.64, 51.97, 44.71, 26.52, 24.94, 24.07.

GC-MS (EI): 282.1, 171.0, 155.0, 111.1, 92.1, 84.1.

HRMS (ESI) calcd for $C_{13}H_{19}N_2O_3S^+$ m/z $[M+H]^+$: 283.1111; found: 283.1116.



2,4-dimethoxy-N-(piperidin-1-ylmethylene)benzenesulfonamide (**16a**, E/Z > 20:1)

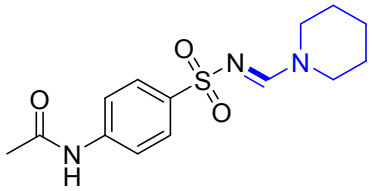
Light yellow oil, 147.5 mg, 59% isolated yield from the reaction between **16** (173.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.92 (d, J = 8.7 Hz, 1H), 6.49 (dd, J = 8.7, 2.3 Hz, 1H), 6.42 (d, J = 2.3 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.58 – 3.53 (m, 2H), 3.43 (t, J = 5.2 Hz, 2H), 1.72 – 1.60 (m, 4H), 1.58 – 1.49 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.32, 159.53, 157.74, 131.34, 122.45, 104.06, 99.49, 56.02, 55.71, 51.92, 44.67, 26.76, 25.07, 24.11.

GC-MS (EI): 312.1, 217.2, 153.0, 113.1, 111.1, 84.1, 55.1.

HRMS (ESI) calcd for $C_{14}H_{21}N_2O_4S^+$ m/z $[M+H]^+$: 313.1217; found: 313.1215.



N-(4-(N-(piperidin-1-ylmethylene)sulfamoyl)phenyl)acetamide (**17a**, E/Z > 20:1)

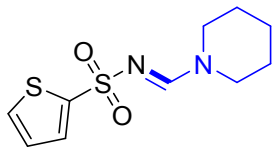
Light yellow solid, 207.9 mg, 84% isolated yield from the reaction between **17** (171.4 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.03 (s, 1H), 7.73 – 7.68 (m, 2H), 7.62 (d, J = 8.9 Hz, 2H), 3.55 – 3.49 (m, 2H), 3.37 (t, J = 5.2 Hz, 2H), 2.13 (s, 3H), 1.57 – 1.68 (m, 4H), 1.56 – 1.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.64, 157.25, 141.87, 136.87, 127.31, 119.53, 52.03, 44.74, 26.40, 24.84, 24.54, 23.87.

GC-MS (EI): 309.1, 281.0, 207.0, 134.0, 111.1, 84.1, 65.0, 56.1.

HRMS (ESI) calcd for $C_{14}H_{20}N_3O_3S^+$ m/z $[M+H]^+$: 310.1220; found: 310.1220.



N-(piperidin-1-ylmethylene)thiophene-2-sulfonamide (**18a**, E/Z > 20:1)

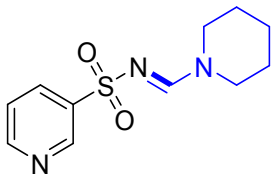
Light yellow crystal, 179.8 mg, 87% isolated yield from the reaction between **18** (130.6 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.57 (dd, J = 3.7, 1.4 Hz, 1H), 7.48 (dd, J = 5.0, 1.3 Hz, 1H), 7.01 (dd, J = 5.0, 3.7 Hz, 1H), 3.65 – 3.59 (m, 2H), 3.42 (t, J = 5.3 Hz, 2H), 1.73 – 1.64 (m, 4H), 1.64 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.54, 144.34, 130.65, 130.58, 127.05, 52.18, 44.96, 26.59, 25.01, 24.04.

GC-MS (EI): 258.1, 194.1, 161.1, 147.0, 111.2, 84.2.

HRMS (ESI) calcd for $C_{10}H_{15}N_2O_2S_2^+$ m/z $[M+H]^+$: 259.0569; found: 259.0561.



N-(piperidin-1-ylmethylene)pyridine-3-sulfonamide (**19a**, E/Z > 20:1)

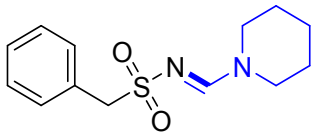
White solid, 158.1 mg, 78% isolated yield from the reaction between **19** (126.6 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 2.3 Hz, 1H), 8.72 (dd, J = 4.9, 1.6 Hz, 1H), 8.18 (dt, J = 8.0, 2.0 Hz, 1H), 8.14 (s, 1H), 7.40 (dd, J = 8.0, 4.8 Hz, 1H), 3.67 – 3.58 (m, 2H), 3.45 (t, J = 5.1 Hz, 2H), 1.75 – 1.67 (m, 4H), 1.63 – 1.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.51, 152.43, 147.71, 139.22, 134.31, 123.53, 52.29, 45.03, 26.55, 24.98, 24.01.

GC-MS (EI): 253.1, 191.0, 133.0, 111.1, 84.1, 78.1, 51.0.

HRMS (ESI) calcd for $C_{11}H_{16}N_3O_2S^+$ m/z $[M+H]^+$: 254.0958; found: 254.0953.



1-phenyl-N-(piperidin-1-ylmethylene)methanesulfonamide (**20a**, E/Z > 20:1)

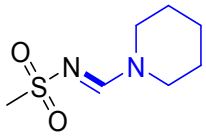
White solid, 151.3 mg, 71% isolated yield from the reaction between **20** (137.0 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.37 – 7.28 (m, 5H), 4.25 (s, 2H), 3.56 (t, J = 5.7 Hz, 2H), 3.20 – 3.12 (m, 2H), 1.70 – 1.61 (m, 2H), 1.61 – 1.53 (m, 2H), 1.52 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.61, 131.14, 130.68, 128.49, 128.33, 59.83, 51.75, 44.62, 26.60, 25.04, 24.06.

GC-MS (EI): 266.1, 202.1, 175.0, 159.0, 111.1, 91.1, 84.1.

HRMS (ESI) calcd for $C_{13}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 267.1162; found: 267.1156.



N-(piperidin-1-ylmethylene)methanesulfonamide (**21a**, E/Z = 1:0.09)

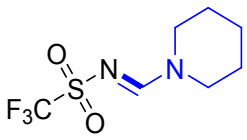
White solid, 94.4 mg, 62% isolated yield from the reaction between **21** (76.1 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), δ 7.97 (s, 0.09H), 3.61 – 3.55 (m, 2H), 3.47 – 3.42 (m, 0.18H), 3.42 – 3.36 (m, 2H), 3.30 – 3.25 (m, 0.18H), 3.07 (s, 0.27H), 2.92 (s, 3H), 1.71 – 1.54 (m, 6.54H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.95, 157.42, 51.92, 51.88, 46.92, 44.62, 44.59, 44.55, 43.39, 42.08, 40.68, 26.61, 26.43, 25.12, 24.87, 24.74, 24.00.

GC-MS (EI): 190.0, 175.0, 159.0, 111.1, 84.1, 56.1, 42.1.

HRMS (ESI) calcd for $C_7H_{15}N_2O_2S^+$ m/z $[M+H]^+$: 191.0849; found: 191.0845.



1,1,1-trifluoro-N-(piperidin-1-ylmethylene)methanesulfonamide[3] (**22a**, E/Z > 20:1)

Beige solid, 70.3 mg, 36% isolated yield from the reaction between **22** (119.1 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 3.76 – 3.69 (m, 2H), 3.57 – 3.49 (m, 2H), 1.78 – 1.71 (m, 4H), 1.71 – 1.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.09, 119.77 (q, J = 321.3 Hz), 52.95, 45.83, 26.57, 25.07, 23.72.

^{19}F NMR (376 MHz, $CDCl_3$) δ 78.52.

GC-MS (EI): 244.1, 175.1, 161.1, 111.1, 84.1, 69.1, 56.1.

N-(piperidin-1-ylmethylene)cyclopropanesulfonamide (**23a**, E/Z = 1:0.15)

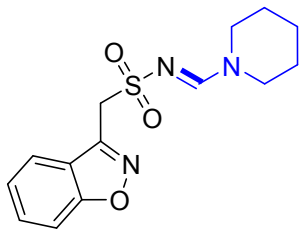
Light yellow oil, 119.4 mg, 69% isolated yield from the reaction between **23** (96.9 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.97 (s, 0.15H), 3.64 – 3.57 (m, 2H), 3.48 – 3.43 (m, 0.3H), 3.42 – 3.35 (m, 2H), 3.31 – 3.25 (m, 0.3H), 2.61 – 2.51 (m, 0.15H), 2.45 – 2.36 (m, 1H), 1.73 – 1.47 (m, 6.9H), 1.20 – 1.05 (m, 2.3H), 1.02 – 0.83 (m, 2.3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.90, 157.51, 51.84, 46.90, 44.59, 40.69, 32.42, 31.39, 26.65, 26.48, 25.15, 24.91, 24.78, 24.06, 6.00, 5.52.

GC-MS (EI): 216.1, 175.1, 159.1, 111.1, 84.1, 56.1, 41.1.

HRMS (ESI) calcd for $C_9H_{17}N_2O_2S^+$ m/z $[M+H]^+$: 217.1005; found: 217.1002.



1-(benzo[d]isoxazol-3-yl)-N-(piperidin-1-ylmethylene)methanesulfonamide (**24a**, E/Z > 20:1)

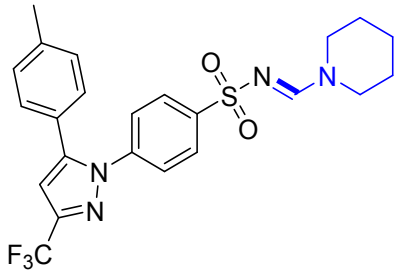
Light yellow solid, 113.1 mg, 46% isolated yield from the reaction between **24** (169.8 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 1H), 7.66 (s, 1H), 7.60 – 7.53 (m, 2H), 7.41 – 7.32 (m, 1H), 4.71 (s, 2H), 3.58 – 3.52 (m, 2H), 3.25 – 3.19 (m, 2H), 1.69 – 1.61 (m, 3H), 1.59 – 1.48 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.67, 158.34, 150.51, 130.31, 124.13, 122.87, 121.22, 109.93, 52.05, 50.67, 44.99, 26.50, 24.90, 23.97.

GC-MS (EI): 307.2, 207.1, 175.0, 132.2, 111.1, 84.1, 77.1.

HRMS (ESI) calcd for $C_{14}H_{18}N_3O_3S^+$ m/z $[M+H]^+$: 308.1063; found: 308.1060.



N-(piperidin-1-ylmethylene)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (**25a**, E/Z > 20:1)

Light yellow crystal, 346.9 mg, 91% isolated yield from the reaction between **25** (305.1 mg, 0.8 mmol) and **a** (1.46 mL, 12 mmol) following **GP1**.

Light yellow solid, 1.75 g, 92% isolated yield from the reaction between **25** (1.53 g, 4.0 mmol) and **a** (7.3 mL, 60 mmol) following **GP2**.

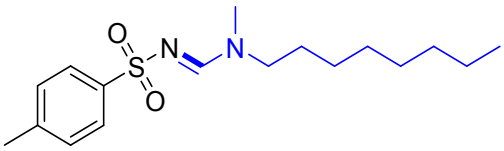
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.89 – 7.83 (m, 2H), 7.43 – 7.37 (m, 2H), 7.19 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 6.72 (s, 1H), 3.63 – 3.55 (m, 2H), 3.42 (t, J = 5.2 Hz, 2H), 2.37 (s, 3H), 1.73 – 1.64 (m, 4H), 1.63 – 1.55 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.43, 145.23, 143.90 (q, J = 38.5 Hz), 142.31, 141.87, 139.73, 129.79, 128.79, 127.63, 125.80, 125.39, 121.21 (q, J = 269.0 Hz), 106.08, 106.07, 52.17, 44.89, 26.53, 24.95, 23.98, 21.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ 62.41.

GC-MS (EI): 476.2, 457.2, 300.1, 255.1, 111.1, 84.1, 56.1.

HRMS (ESI) calcd for $C_{23}H_{24}F_3N_4O_2S^+$ m/z $[M+H]^+$: 477.1567; found: 477.1560.



N-methyl-N-octyl-N'-tosylformimidamide (**1b**, E/Z = 1:0.45)

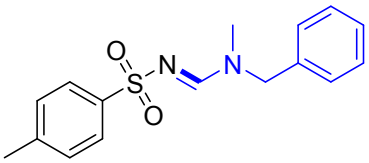
Light yellow oil, 236.2 mg, 91% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **b** (2.47 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.11 (s, 0.45H), 7.78 – 7.71 (m, 2.9H), 7.26 – 7.20 (m, 2.9H), 3.41 (t, J = 7.2 Hz, 0.9H), 3.30 (t, J = 7.2 Hz, 2H), 3.07 (s, 1.35H), 2.96 (s, 3H), 2.38 (s, 1.35H), 2.38 (s, 3H), 1.63 – 1.47 (m, 2.9H), 1.32 – 1.15 (m, 14.5H), 0.91 – 0.82 (m, 4.35H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.16, 158.93, 142.46, 142.32, 139.94, 139.82, 129.40, 129.34, 126.57, 126.47, 54.89, 48.23, 39.51, 33.62, 31.80, 31.76, 29.24, 29.17, 29.14, 28.09, 26.64, 26.33, 26.12, 22.68, 21.54, 14.13.

GC-MS (EI): 324.2, 309.2, 295.1, 267.1, 253.1, 169.2, 147.1, 91.1.

HRMS (ESI) calcd for $C_{17}H_{29}N_2O_2S^+$ m/z $[M+H]^+$: 325.1944; found: 325.1948.



N-benzyl-N-methyl-N'-tosylformimidamide (**1c**, E/Z = 1:0.64)

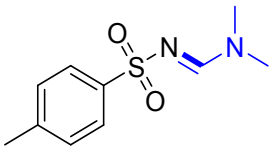
White solid, 164.5 mg, 68% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **c** (1.80 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.25 (s, 1H), 7.83 – 7.75 (m, 3.28H), 7.41 – 7.32 (m, 3.28H), 7.31 – 7.24 (m, 4.92H), 7.22 – 7.14 (m, 3.28H), 4.63 (s, 1.28H), 4.47 (s, 2H), 3.00 (s, 1.92H), 2.90 (s, 3H), 2.41 (s, 1.92H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 157.84, 142.47, 139.86, 129.41, 126.62, 126.54, 55.47, 47.08, 33.62, 29.32, 21.58, 20.89, 18.85.

GC-MS (EI): 302.1, 237.2, 147.1, 120.1, 106.1, 91.1, 65.1.

HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 303.1162; found: 303.1157.



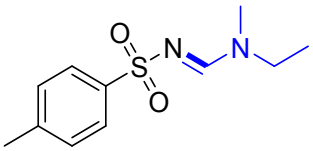
N,N-dimethyl-N'-tosylformimidamide[1] (**1d**, E/Z > 20:1)

White solid, 173.8 mg, 96% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **d** (4.2 M solution in ethanol, 2.86 mL, 12 mmol) following **GP1** (solvent ethanol applied was 2 mL).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.80 – 7.73 (m, 2H), 7.25 (d, J = 8.1 Hz, 2H), 3.11 (s, 3H), 3.00 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.18, 142.55, 139.63, 129.41, 126.59, 41.57, 35.59, 21.58.

GC-MS (EI): 226.1, 161.1, 147.1, 91.1, 71.1, 44.1.



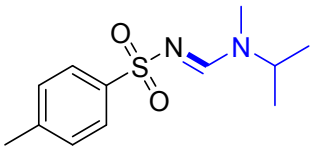
N-ethyl-N-methyl-N'-tosylformimidamide[4] (**1e**, E/Z = 1:0.52)

Light yellow oil, 134.6 mg, 70% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **e** (1.30 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.09 (s, 0.52H), 7.79 – 7.74 (m, 3.04H), 7.29 – 7.22 (m, 3.04H), 3.48 (q, J = 7.2 Hz, 1.04H), 3.39 (q, J = 7.2 Hz, 2H), 3.08 (s, 1.56H), 2.98 (s, 3H), 2.40 (s, 1.56H), 2.40 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 1.56H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.76, 158.53, 142.45, 142.36, 139.85, 139.74, 129.36, 129.34, 126.53, 126.44, 49.52, 43.05, 38.91, 33.11, 21.50, 13.88, 11.29.

GC-MS (EI): 240.1, 155.0, 147.1, 91.0, 85.1, 65.1, 58.1, 42.1



N-isopropyl-N-methyl-N'-tosylformimidamide (**1f**, E/Z = 1:0.26)

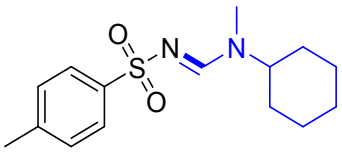
Light yellow oil, 162.8 mg, 80% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **f** (1.46 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.09 (s, 0.26H), 7.83 – 7.71 (m, 2.52H), 7.30 – 7.21 (m, 2.52H), 4.67 (hept, J = 6.7 Hz, 0.26H) 3.75 (hept, J = 6.7 Hz, 1H), 2.97 (s, 0.78H), 2.91 (s, 3H), 2.40 (s, 0.78H), 2.40 (s, 3H), 1.27 (d, J = 6.7 Hz, 6H), 1.14 (d, J = 6.8 Hz, 1.56H).

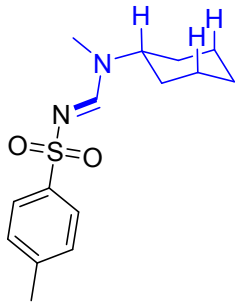
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 157.84, 142.47, 139.86, 129.41, 126.62, 126.54, 55.47, 47.08, 33.62, 29.32, 21.58, 20.89, 18.85.

GC-MS (EI): 254.1, 239.1, 157.0, 147.1, 120.1, 99.1, 91.1.

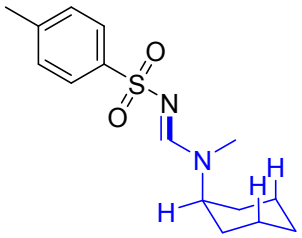
HRMS (ESI) calcd for $C_{12}H_{19}N_2O_2S^+$ m/z $[M+H]^+$: 255.1162; found: 255.1166.



N-cyclohexyl-N-methyl-N'-tosylformimidamide[5] (**1g**, E/Z > 20:1, eq./ax. = 1:0.23)



E-1g$_{eq.}$
(equatorial isomer)



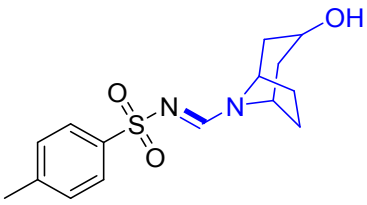
E-1g$_{ax.}$
(axial isomer)

Beige solid, 183.7 mg, 78% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **g** (1.80 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.10 (s, 0.23H), 7.82 – 7.72 (m, 2.46H), 7.30 – 7.20 (m, 2.46H), 4.33 – 4.18 (m, 0.23H), 3.32 – 3.20 (m, 1H), 2.99 (s, 0.69H), 2.94 (d, J = 0.7 Hz, 3H), 2.40 (s, 3.69H), 1.93 – 1.03 (m, 12.3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15, 158.06, 142.44, 139.93, 129.42, 126.62, 126.56, 63.73, 55.09, 31.48, 30.84, 29.11, 25.49, 25.25, 25.13, 21.59.

GC-MS (EI): 294.1, 213.1, 155.0, 147.1, 139.2, 91.1.



N-((3-hydroxy-8-azabicyclo[3.2.1]octan-8-yl)methylene)-4-methylbenzenesulfonamide (**1h**, E/Z > 20:1)

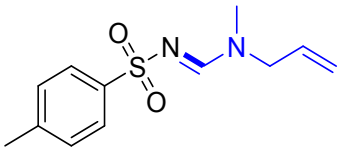
White solid, 69.1 mg, 28% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **h** (1.69 g, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 1H), 7.79 – 7.71 (m, 2H), 7.29 – 7.21 (m, 2H), 4.61 – 4.52 (m, 1H), 4.14 (s, 1H), 4.04 – 3.96 (m, 1H), 2.39 (d, J = 2.4 Hz, 3H), 2.36 – 2.27 (m, 2H), 2.18 – 2.08 (m, 1H), 2.03 – 1.87 (m, 4H), 1.85 – 1.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.37, 142.46, 139.89, 129.44, 126.51, 64.43, 58.58, 52.70, 41.75, 38.57, 27.80, 27.19, 21.57.

GC-MS (EI): 308.1, 281.1, 243.2, 207.0, 153.1, 109.0, 91.1, 68.1.

HRMS (ESI) calcd for $C_{15}H_{21}N_2O_3S^+$ m/z $[M+H]^+$: 309.1267; found: 309.1263.



N-allyl-N-methyl-N'-tosylformimidamide (**1i**, E/Z = 1:0.55)

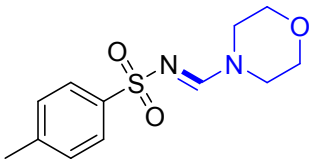
Light yellow solid, 62.6 mg, 31% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **i** (1.42 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.18 (s, 0.55H), 7.79 – 7.73 (m, 3.1H), 7.29 – 7.22 (m, 3.1H), 5.82 – 5.63 (m, 1.55H), 5.35 – 5.15 (m, 3.1H), 4.04 (dt, J = 6.3, 1.4 Hz, 1.1H), 3.92 (dt, J = 6.0, 1.4 Hz, 2H), 3.06 (s, 1.65H), 2.96 (s, 3H), 2.40 (s, 4.65H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15, 159.09, 142.57, 142.49, 139.67, 139.58, 131.40, 130.26, 129.69, 129.41, 129.37, 126.60, 126.51, 120.18, 119.62, 56.99, 50.63, 38.87, 33.60, 21.53.

GC-MS (EI): 252.1, 155.0, 97.1, 91.1, 83.1, 70.1, 44.1.

HRMS (ESI) calcd for $C_{12}H_{17}N_2O_2S^+$ m/z $[M+H]^+$: 253.1005; found: 253.1008.



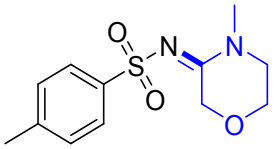
4-methyl-N-(morpholinomethylene)benzenesulfonamide[1] (**1j**, E/Z > 20:1)

White solid, 34.3 mg, 16% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **j** (1.31 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.79 – 7.73 (m, 2H), 7.31 – 7.22 (m, 2H), 3.77 – 3.72 (m, 2H), 3.67 (s, 4H), 3.51 – 3.45 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 142.84, 139.32, 129.52, 126.74, 66.95, 66.07, 50.44, 44.35, 21.62.

GC-MS (EI): 268.0, 254.9, 225.0, 154.9, 113.0, 91.1, 65.0.



4-methyl-N-(4-methylmorpholin-3-ylidene)benzenesulfonamide (**1j'**, E/Z > 20:1)

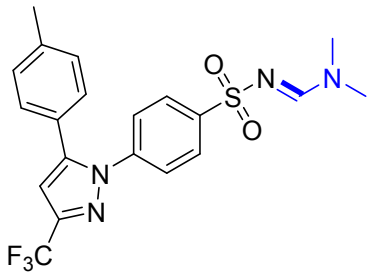
Light yellow solid, 19.3 mg, 9% isolated yield from the reaction between **1** (137.0 mg, 0.8 mmol) and **j** (1.31 mL, 12 mmol) following **GP1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.29 – 7.24 (m, 2H), 4.91 (s, 2H), 3.92 – 3.82 (m, 2H), 3.43 (t, J = 5.3 Hz, 2H), 3.08 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 142.35, 140.73, 129.34, 126.47, 66.35, 63.10, 48.96, 37.88, 21.60.

GC-MS (EI): 268.0, 203.1, 155.0, 113.1, 91.1, 65.1, 42.1.

HRMS (ESI) calcd for $C_{12}H_{17}N_2O_3S^+$ m/z $[M+H]^+$: 269.0954; found: 269.0959.



N,N-dimethyl-N'-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonyl)formimidamide (**25d**, E/Z > 20:1)

Colorless crystal, 1.56 g, 89% isolated yield from the reaction between **25** (1.53 g, 0.8 mmol) and **d** (4.2 M solution in ethanol, 14.3 mL, 60 mmol) following **GP2** (additional solvent ethanol applied was 10 mL).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.91 – 7.83 (m, 2H), 7.44 – 7.36 (m, 2H), 7.19 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 6.72 (s, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.35, 145.23, 143.92 (q, J = 38.3 Hz), 142.14, 141.95, 139.74, 129.80, 128.79, 127.67, 125.81, 125.37, 121.21 (q, J = 269.1 Hz), 106.13, 106.12, 41.71, 35.71, 21.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ 62.41.

GC-MS (EI): 436.1, 417.1, 357.1, 330.2, 300.1, 255.1, 119.0, 71.1.

HRMS (ESI) calcd for $C_{20}H_{20}F_3N_4O_2S^+$ m/z $[M+H]^+$: 437.1254; found: 437.1259.

3. Mechanistic Studies

3.1 Attempts using Raman spectroscopy to detect the active species

The measurement was conducted using the same method as reported in literature[6]. Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with thermoelectrically cooled CCD camera and fiber-optic cable for excitation and collection of Raman spectra. The 532-nm beam of the diode YAG laser was used as the excitation source. The laser power at the sample was about 150 mW. The laser beam was focused on a point in the reaction mixture in the glass capillary. But unfortunately, no discernible Raman peak characteristic to any active species was observed.

(1) **Standard 1**: NaI (45 mg, 0.3 mmol) was added to a solution of I_2 (25.4 mg, 0.1 mmol) in EtOH (0.2 mL, in 5 mL test vial) at room temperature. The resulting mixture was stirred for 1 h and was then drawn into the glass capillary, after which an equal volume of 10 M NaOH aq. was charged in it. The Raman spectrum was measured after 10 s.

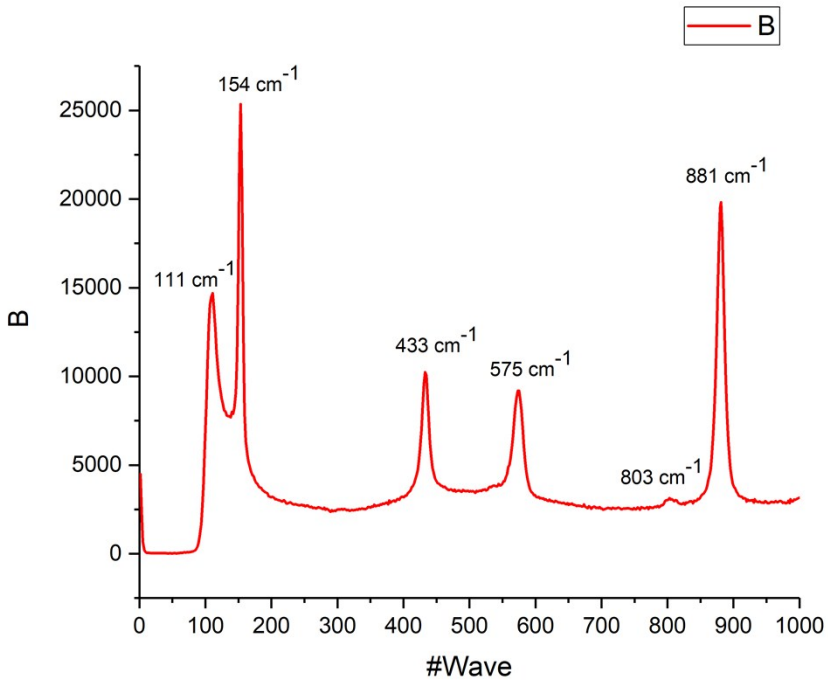


Fig. S3. Raman spectrum of a solution of I_2 (0.5 M) and NaI (1.5 M) in EtOH in the presence of an equal volume of 10 M NaOH aq.

(2) **Control 1**: EtOH was drawn into the glass capillary and the Raman spectrum was collected at room temperature.

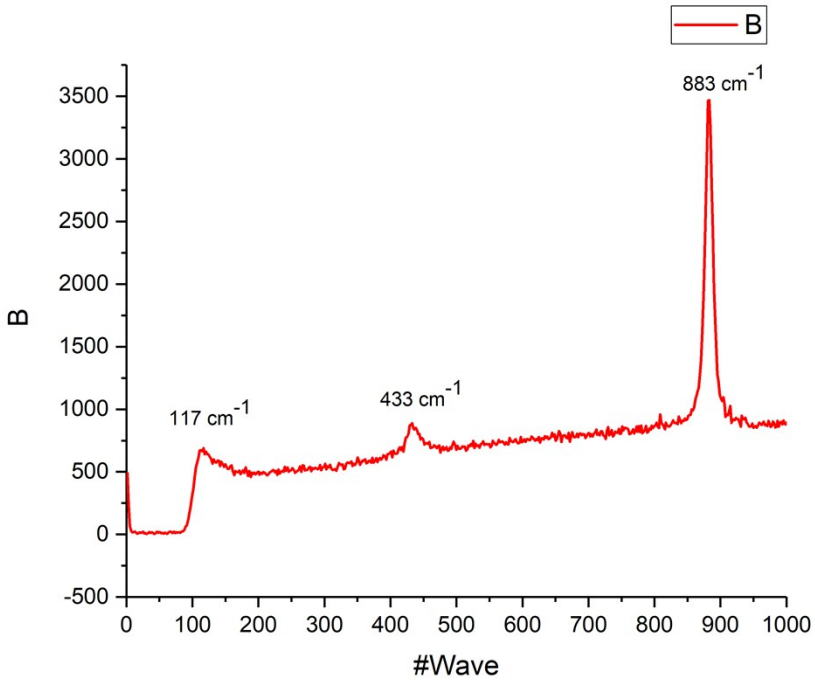


Fig. S4. Raman spectrum of EtOH

(3) **Control 2**: I_2 (126.9 mg, 0.5 mmol) was dissolved in EtOH (1 mL, in 5 mL volume of test vial) at room temperature. The mixture was drawn into the glass capillary and the Raman spectrum was collected.

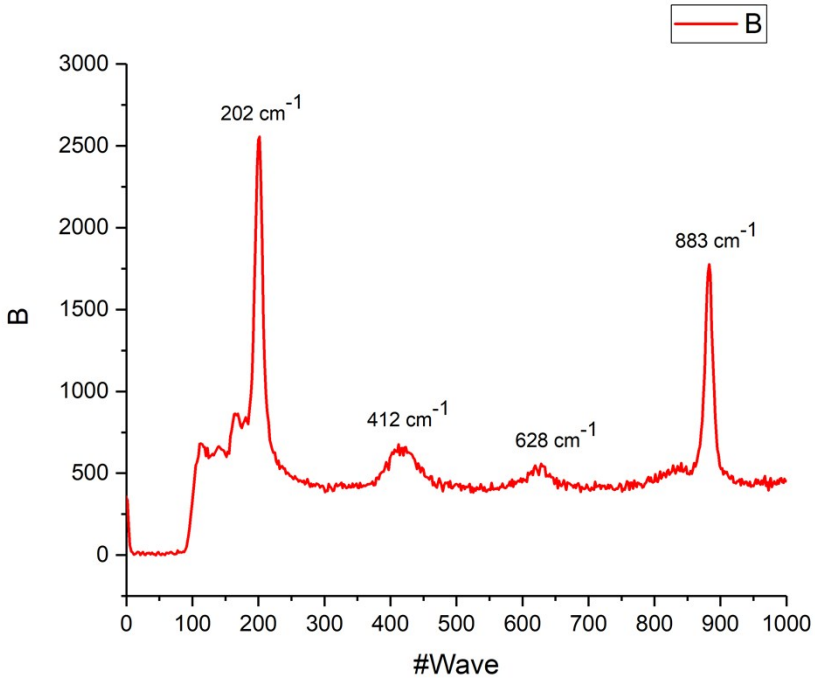


Fig. S5. Raman spectrum of a solution of I_2 (0.5 M) in EtOH

(4) **Control 3**: Bu_4NI (369.4 mg, 1 mmol) was dissolved in EtOH (1 mL, in 5 mL volume of test vial) at room temperature. The mixture was drawn into the glass capillary and the Raman spectrum was collected.

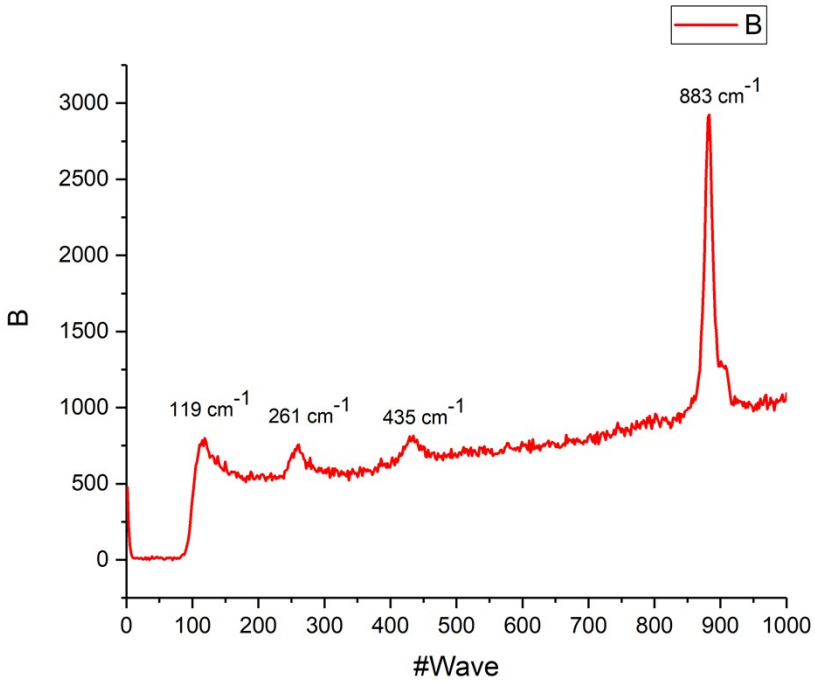


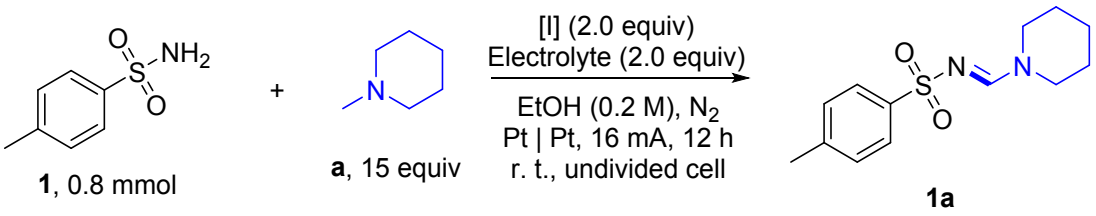
Fig. S6. Raman spectrum of a solution of Bu_4NI (1.0 M) in EtOH

(5) **Reaction**: In a 10 mL three-necked flask, Bu_4NI (369.4 mg, 1 mmol) was dissolved in EtOH (1 mL) at room temperature. The flask was then equipped with two platinum electrodes and the atmosphere was exchanged to N_2. Electrolysis was carried out with a 16 mA constant current for 30 s, 3 min and 10 min, at each time point a portion of mixture was drawn into the glass capillary and the Raman spectrum was measured immediately.

However, the Raman spectra collected were exactly the same with **Control 3** (without electrolysis), which might probably be attributed to the short life of the *in situ* formed active species. Thus, the attempts using Raman spectroscopy to detect active species failed.

3.2 Control experiments for the investigation of active iodine-containing species

Table S1. Examination of iodine species under neutral conditions



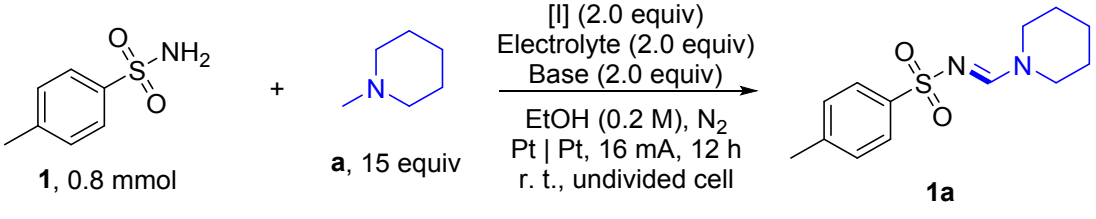
1, 0.8 mmol + **a**, 15 equiv → **1a**

Entry	[I]	Electrolyte	Current	Isolated yield of **1a**
1		Bu_4NI (2)	On	96%
2		Bu_4NI (2)	Off	N.D.
3		Bu_4NI_3 (0.67)	On or Off	< 1% or N.D.
4	I_2 (1)	Bu_4NBF_4	On or Off	< 1% or N.D.
5		NaI (2)	On	81%
6		NaI (2)	Off	N.D.
7	NaI (2)	Bu_4NBF_4	On	80%
8	$NaIO_3$ (2)	Bu_4NBF_4	On or Off	< 1% or N.D.
9	$NaIO_4$ (2)	Bu_4NBF_4	On or Off	< 1% or N.D.
10	$PhI(OAc)_2$ (2)	Bu_4NBF_4	On or Off	< 1% or N.D.
11	NIS (2)	Bu_4NBF_4	On or Off	< 1% or N.D.

* The total iodine element in each reaction was 2.0 equiv to $TsNH_2$ (**1**); numbers given in the parentheses are the equivalents of the reagents, the same in Table S2. N.D.: not detected.

Under otherwise additive-free conditions, all control experiments carried without constant current electrolysis provided no detectable signal of **1a** upon GC-MS analysis. Only trace amount of **1a** could be detected or isolated from the electrolytic reactions using iodine species other than I^-. Among the tested reagents, only NaI worked and showed a lower efficiency than Bu_4NI (Table S1, entry 5). The reaction using a combination of NaI and Bu_4NBF_4 could not gave a comparable performance with Bu_4NI (Table S1, entry 7), which also indicated the inertness of Bu_4NBF_4 as a supporting electrolyte. Additionally, the colored species I_2 and I_3^-, which were both proven inert for this transformation (Table S1, entry 3, 4), could be side products based on the color change observed during every typical electrolysis.

Table S2. Examination of iodine species under basic conditions



1, 0.8 mmol + **a**, 15 equiv → **1a**

Entry	[I]	Electrolyte	Base	Current	Isolated yield of **1a**
1	I_2 (1)	Bu_4NBF_4	NaOH	On	76%

2	I_2 (1)	-	NaOH	Off	30%
3	NaI (2)	-	NaOH	Off	N. D.
4	$NaIO_3$ (2)	-	NaOH	Off	N. D.
5	-	-	NaOH	Off	N. D.
6	I_2 (1)	-	EtONa	Off	36%

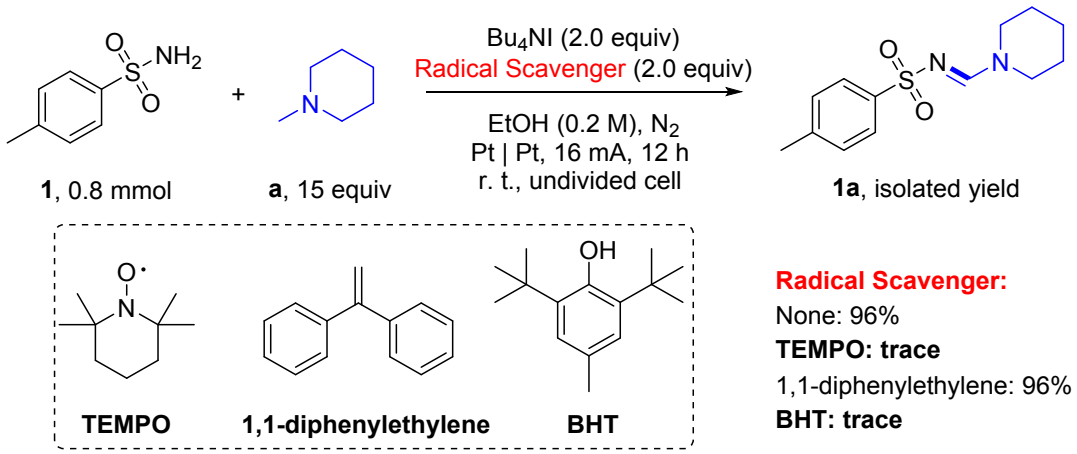
In the subsequent attempt with I_2, additional NaOH (2 equiv) was added to the reaction system, and the corresponding product **1a** was acquired in 76% yield after 12 h electrolysis (Table S2, entry 1). At this stage, we still believed the occurrence of the condensation was due to the generation of NaI from the reaction of I_2 and NaOH as well as the subsequent disproportionation of the *in situ* formed unstable NaIO (Eq. S1). To verify this speculation, one more control experiment was conducted by switching off the electricity under otherwise identical conditions with entry 1 (Table S2, entry 2). Surprisingly, the condensation still proceeded to deliver **1a** in 30% yield, which was obviously beyond the above I^-/electricity theory. Under such circumstances, further control experiments were conducted to rule out certain scenarios (Table S2, entry 3-5). The results demonstrated that neither NaI/NaOH, $NaIO_3$/NaOH combinations nor NaOH alone is capable of promoting this CDC without electricity, from which the active species could be limited to the short lived IO^- (containing positively charged iodine).

Transformation of 1 equiv I_2 in the presence of 2 equiv NaOH:

$$3\,I_2 + 6\,NaOH \longrightarrow \underset{\text{(unstable under ambient conditions)}}{3\,NaI + 3\,NaIO + 3\,H_2O} \longrightarrow 5\,NaI + NaIO_3 + 3\,H_2O \quad \textbf{Eq. S1}$$

Further attempt using EtONa instead of NaOH as the base also worked, providing a slightly better performance than NaOH (Table S2, entry 6). Based on these studies, an *in situ* generated iodonium (I^+) mediated pathway is plausible.

3.3 Radical scavenger addition experiments



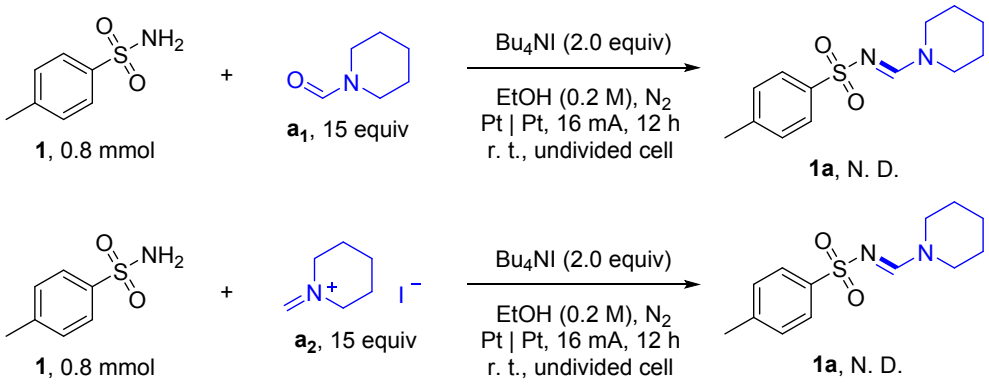
Scheme S1. Radical scavenger addition experiments

Three parallel radical scavenger addition experiments were conducted using **1** and **a** as substrates with 2 equiv TEMPO, 1,1-diphenylethylene and BHT respectively. The results showed that TEMPO and BHT could effectively inhibit the reaction, although no radical adduct formation was detected in both reactions, while addition of 1,1-diphenylethylene made no difference to the reaction efficiency.

After the redox potentials of all components collected via cyclic voltammetry (see section **3.5**), a conclusion was drawn that both TEMPO and BHT would not be preferentially oxidized. However, we believe that the inhibition of the reaction is more likely due to the quenching of the *in situ* formed hypervalent iodine species, rather than the suppression of a radical process by the two reagents.

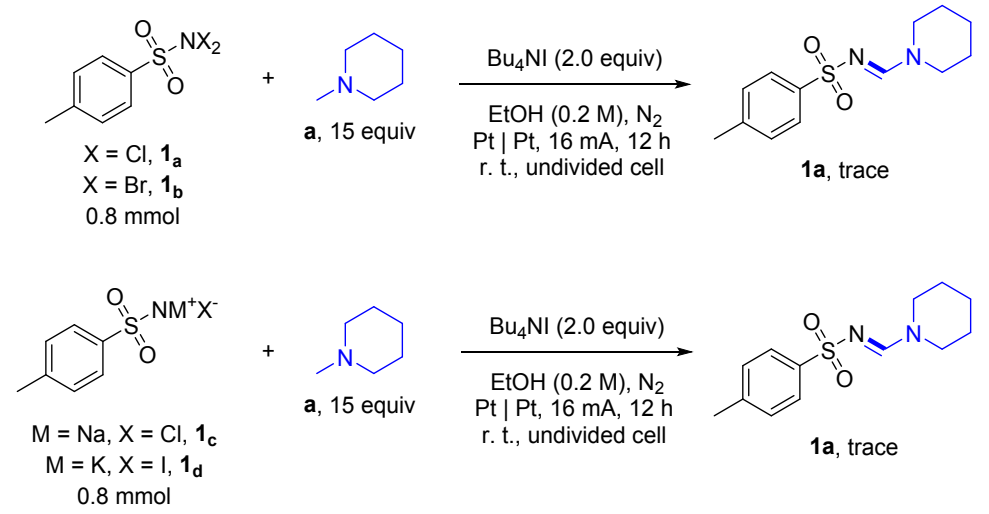
3.4 Examination of possible intermediates

First, hypothetical intermediates $\mathbf{a_1}$ and $\mathbf{a_2}$[7] were respectively applied as condensation partners in place of tertiary amine **a** to run reactions with sulfonamide **1** (Scheme S2). The results suggested that this condensation is not likely via either a formamide or a piperidinium intermediate (The iminium salt $\mathbf{a_2}$ is found almost insoluble in the reaction solvent ethanol, which could also be the reason for its inertness as a condensation partner, thus we still conducted computational studies on this scenario, for details please see Scheme S7 and Fig. S13).



Scheme S2. Examination of possible intermediates of **a**

Subsequently, $\mathbf{1_a}$ (CAS: 473-34-7), $\mathbf{1_b}$[8], $\mathbf{1_c}$ (CAS: 127-65-1) **and** $\mathbf{1_d}$[9] were successively subjected to the standard conditions with condensation partner **a** (Scheme S3). All of the reactions yielded only negligible amount of product **1a**, thus the possibility of related intermediates could also be eliminated.



Scheme S3. Examination of possible intermediates of **1**

3.5 Electrochemical potential measurements via cyclic voltammetry (CV)

Cyclic voltammograms were collected with a CHI 760E Potentiostat. Samples were prepared with 0.1 mmol of substrate, dissolved in 10 mL of 0.1 M Bu_4NBF_4 in ethanol. Measurements employed a glassy carbon working electrode, platinum plate counter electrode and a 3 M KCl silver-silver chloride reference electrode. The scan rate applied was 0.1 V/s. Maximum current (C_p) of each substrate was obtained using Origin and the potential ($E_{p/2}$) was determined at half of this value ($C_{p/2}$).

(1) Bu_4NI

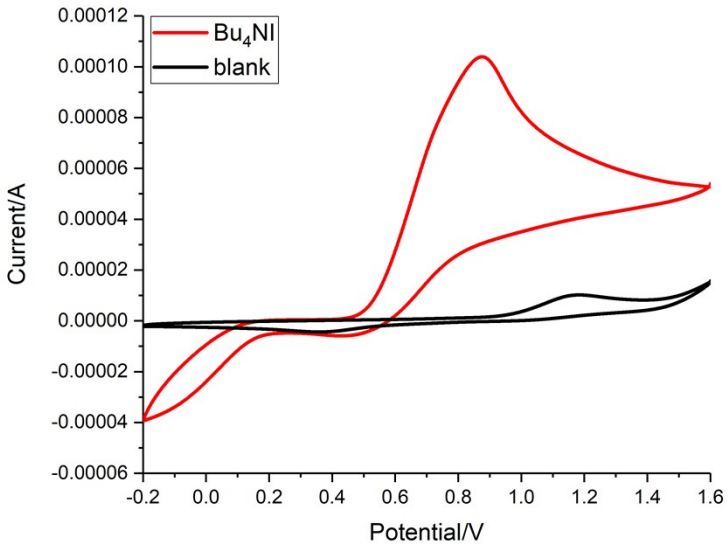


Fig. S7. CV plot of 10 mM Bu_4NI in 0.1 M Bu_4NBF_4 EtOH solution

$E_{p/2}$ (Bu_4NI) = 0.66 V (vs. Ag | AgCl)

(2) $TsNH_2$ (**1**)

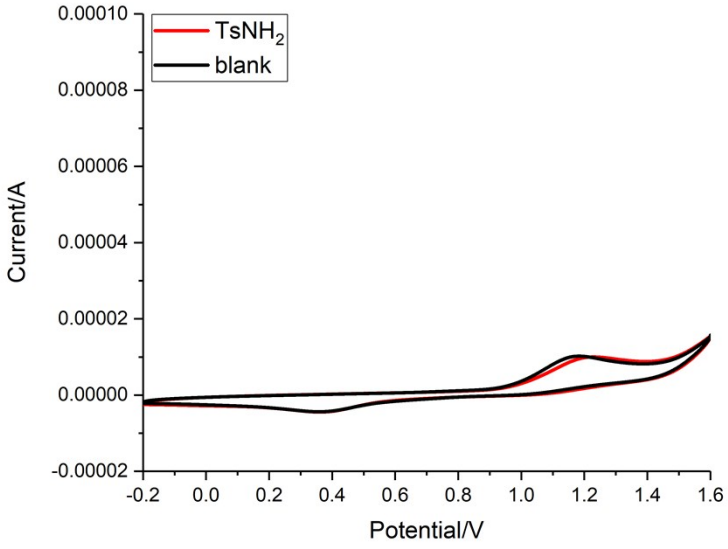


Fig. S8. CV plot of 10 mM $TsNH_2$ (**1**) in 0.1 M Bu_4NBF_4 EtOH solution

No obvious redox peak was found in the CV plot of $TsNH_2$ (even when the scan region was extended to 3.0 V).

(3) N-methylpiperidine (**a**)

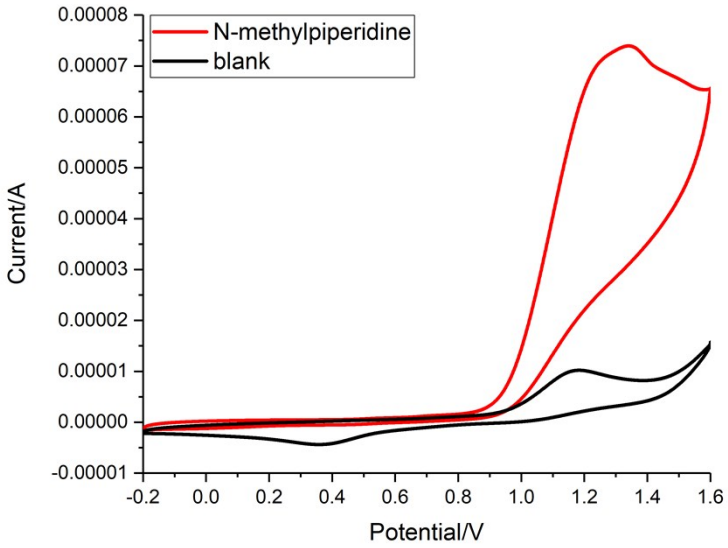


Fig. S9. CV plot of 10 mM N-methylpiperidine (**a**) in 0.1 M Bu_4NBF_4 EtOH solution

$E_{p/2}$ (N-methylpiperidine) = 1.09 V (vs. Ag | AgCl)

(4) TEMPO and BHT

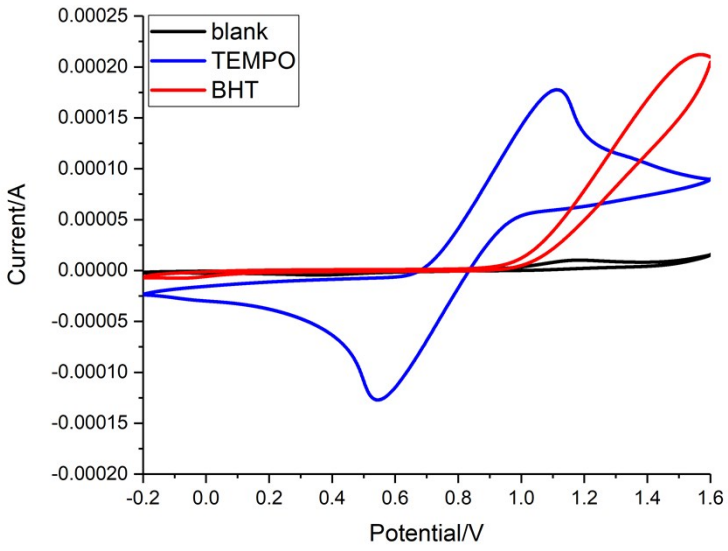


Fig. S10. CV plots of 10 mM radical scavengers in 0.1 M Bu_4NBF_4 EtOH solution

$E_{p/2}$ (TEMPO) = 0.90 V (vs. Ag | AgCl)

$E_{p/2}$ (BHT) = 1.26 V (vs. Ag | AgCl)

By comparing the oxidation potentials of the two radical scavengers with Bu_4NI, a conclusion can be reached that neither of the two radical scavengers would be preferentially oxidized than I^-.

(5) Some other N-methyl tertiary amines

CV data of several N-methyl tertiary amines were collected (both reactive and inert examples).

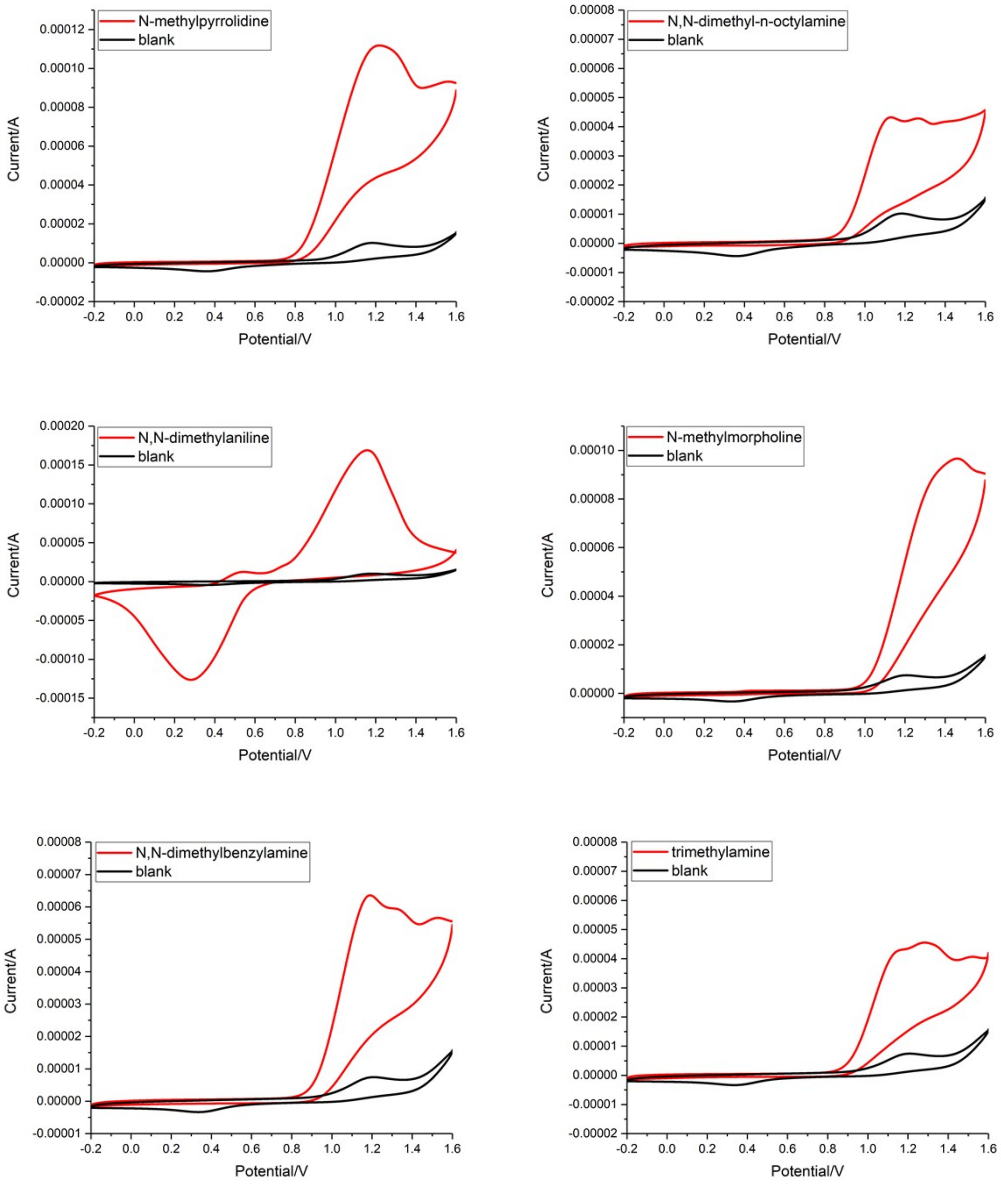


Fig. S11. CV plots of 10 mM other N-methyl tertiary amines in 0.1 M Bu_4NBF_4 EtOH solution

The oxidation potentials of these tertiary amines as well as compounds tested above are summarized in **Table S3** (no oxidation peak of N,N-dimethylformamide (**m**) was detected in -0.2 V ~ 3.0V region).

Table S3. Oxidation potentials ($E_{p/2}$s, in EtOH) of compounds investigated in this work

Entry	Compound	$E_{p/2}$	Reaction with **1**
1	Bu_4NI	0.66 V	-
2	$TsNH_2$ (**1**)	>1.6 V	-
3	N-methylpiperidine (**a**)	1.09 V	R

4	N,N-dimethyl-n-octylamine (**b**)	0.99 V	R
5	N,N-dimethylbenzylamine (**c**)	1.03 V	R
6	trimethylamine (**d**)	1.02 V	R
7	N-methylmorpholine (**j**)	1.18 V	R[a]
8	N-methylpyrrolidine (**k**)	0.99 V	NR
9	N,N-dimethylaniline (**l**)	0.93 V	NR
10	N,N-dimethylformamide (**m**)	>1.6 V	NR
11	TEMPO	0.90 V	-
12	BHT	1.26 V	-

a 24 mA constant current was applied.

The inertness of N,N-dimethylformamide (**m**) might be attributed to its high oxidation potential, but for **k** and **l** with low oxidation potentials, it could not be explained from this point. Thus, we believe that this transformation is not via a simple redox pathway which could also be realized by anodic oxidation without the iodine species, theoretically.

(6) $TsNH_2$ (**1**) and/or EtONa

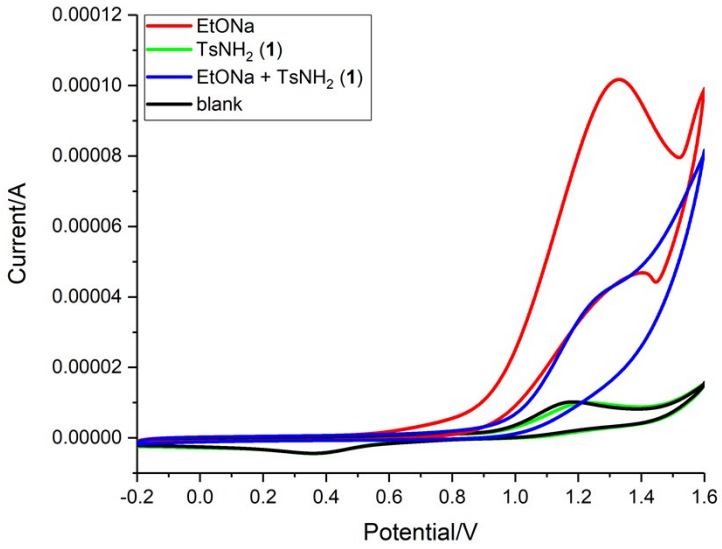


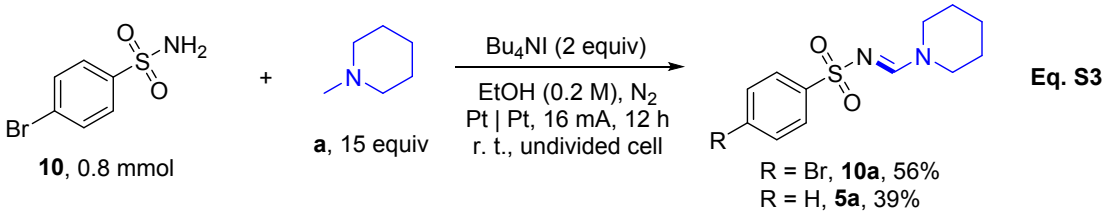
Fig. S12. CV plots of 10 mM $TsNH_2$ (**1**) and/or 10 mM EtONa in 0.1 M Bu_4NBF_4 EtOH solution

The CV plot of EtONa showed an obvious oxidation peak at 1.33 V ($E_{p/2}$ is 1.10 V), while the peak was reduced dramatically after addition of 1 equiv $TsNH_2$ (**1**), which indicated an interaction between **1** and EtO^- (Eq. S2).

$$TsNH_2 + EtO^- \longrightarrow TsNH^- + EtOH \qquad \textbf{Eq. S2}$$

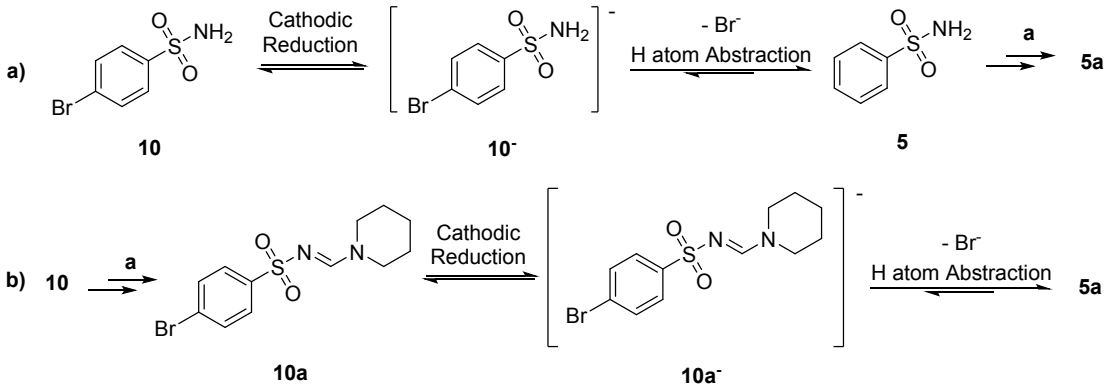
3.6 Investigation and possible mechanism for the dehalogenative condensations

In the reactions between **10** and **a**, **11** and **a** under standard conditions, desired CDC product **10a** and **11a** were isolated in 56% and 54% yield respectively, along with 39% and 37% yield of debrominated product **5a** and defluorinated (×3 times) product **1a**. The possible mechanism for the dehalogenation was investigated with the former reaction (Eq. S3).



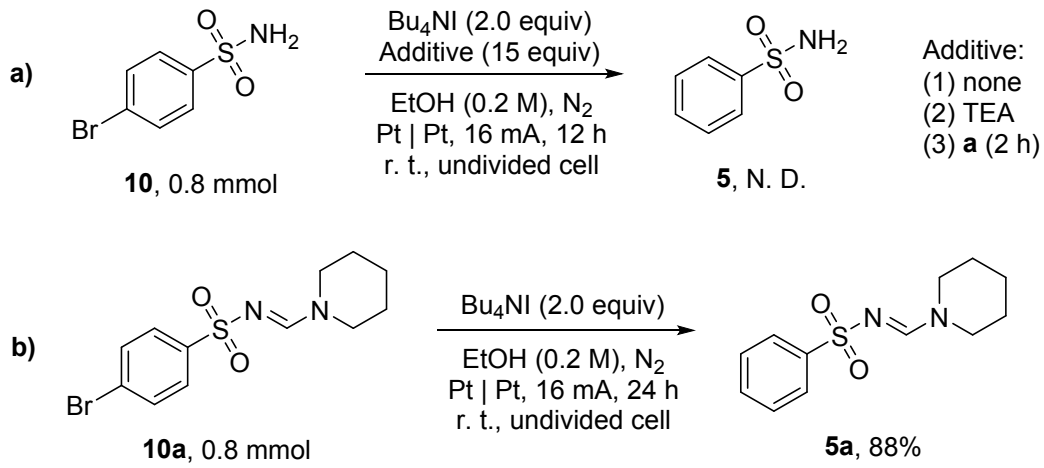
Eq. S3

Two possible mechanism scenarios were conceived in Scheme S4, the difference lies in the sequential order of debromination and the CDC process.



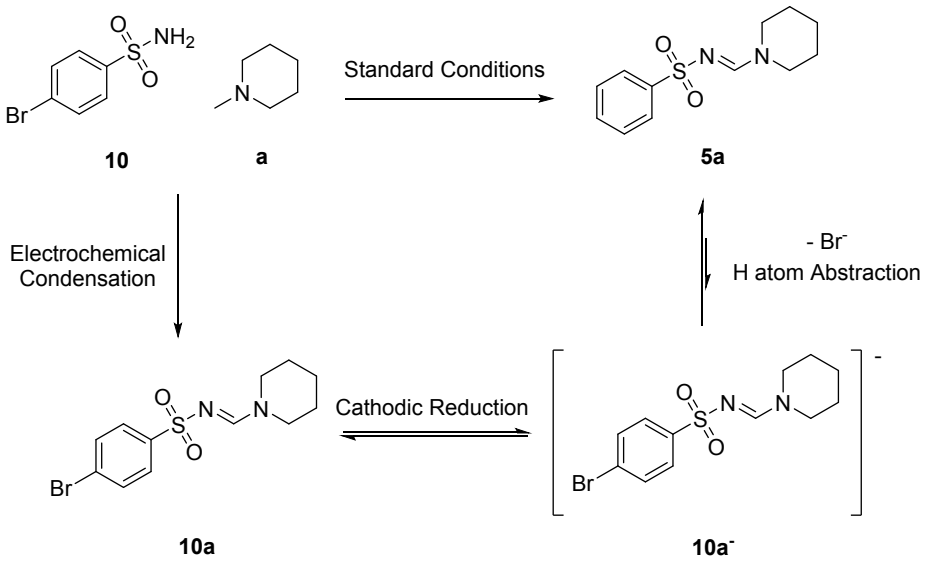
Scheme S4. Two possible mechanism scenarios for deBr CDC between **10** and **a**

A series of control experiments were conducted (Scheme S5). No formation of **5** could be detected in the reactions of **10** under standard conditions with (1) no additive; (2) triethylamine in place of **a**; (3) **a**, but in a shortened time (Scheme S5-a). While in another experiment, **10a** was successfully converted into **5a** in 88% isolated yield after electrolysis for 24 h (Scheme S5-b).



Scheme S5. Control experiments for the deBr CDC

The above results demonstrated that the debromination occurs after the condensation process, thus a mechanism was proposed in Scheme S6.



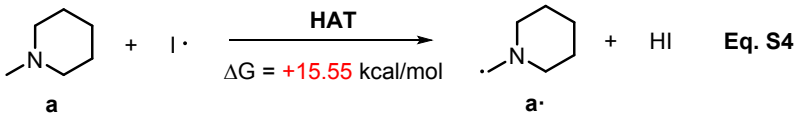
Scheme S6. Plausible mechanism for the deBr CDC between **10** and **a**

3.7 Computational studies

All computations were carried out with the Gaussian09 program.[10] All structures were fully optimized in ethanol solvent via the SMD model[11] using the B3LYP functional[12,13]. The B3LYP functional has been successfully used for a similar system.[10] An all-electron 6-31+G(d,p) basis set was used for all atoms. The harmonic vibrational frequency calculations were performed to ensure that either a minimum or first-order saddle point was obtained. Unless otherwise stated, the

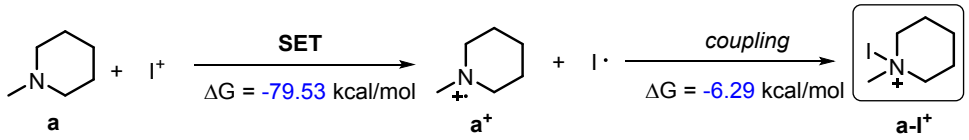
energies reported in this paper are Gibbs free energies under 298.15 K and 1 atm with solvent effect corrections.

The first examined was the iodine radical promoted HAT hypothesis. The Gibbs free energies of all participants were calculated in solvent ethanol under the standard state, and a positive ΔG value was acquired for this step, which indicated that it is an endothermic and non-spontaneous process thermodynamically (Eq. S4).



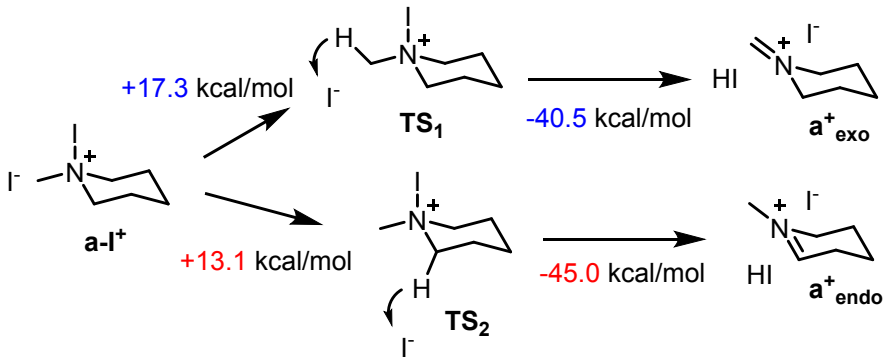
Eq. S4

Next, an SET process between tertiary amine **a** and the postulated active species I^+ was evaluated, in which a ΔG value of -79.53 kcal/mol was obtained (Eq. S5), suggesting that the positively charged iodine species is sufficiently oxidizing to acquire an electron from **a**. Moreover, a stable adduct (**a-I**$^+$) was discovered as a crucial intermediate of this CDC process, which could be formed either by further coupling of radical cation **a**$^+$ with the accompanied iodine radical, or directly from the addition of I^+ to the nitrogen atom of tertiary amine **a**. **a-I**$^+$ was regarded as a key intermediate for this transformation, because under otherwise identical conditions using Bu_4NBF_4 or Bu_4NPF_6 as the supporting electrolyte, a could still be oxidized by anode to afford **a**$^+$, but only trace amounts of **1a** was furnished in these reactions without the involvement of iodine species.



Eq. S5

Therefore, the following chemistry of this cationic intermediate **a-I**$^+$ was subsequently investigated. To reach the putative imine cation species **IV** (Scheme S7 and Fig. S13), an anion-assisted deprotonation of **a-I**$^+$ was conceived, taking the most abundantly existed I^- as a proton abstractor (Scheme S7). However, the free energy profile revealed that the formation of an endocyclic C=N bond (**a**$^+_{endo}$) is far more favorable than an exocyclic one (**a**$^+_{exo}$), with both a lower barrier and a more stable product (Fig. S13). Such a result would lead to an opposite regioselectivity to our experimental results. In combination with one control experiment above (the second reaction in Scheme S2), **we deem that the reaction pathway is unlikely via such an imine cation intermediate.**



Scheme S7. Hypothesis and free energy calculation of the formation of two imine cation intermediates

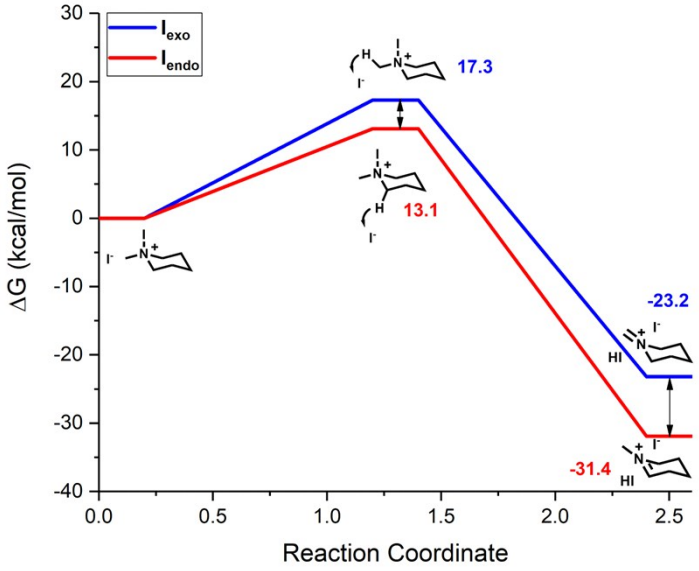
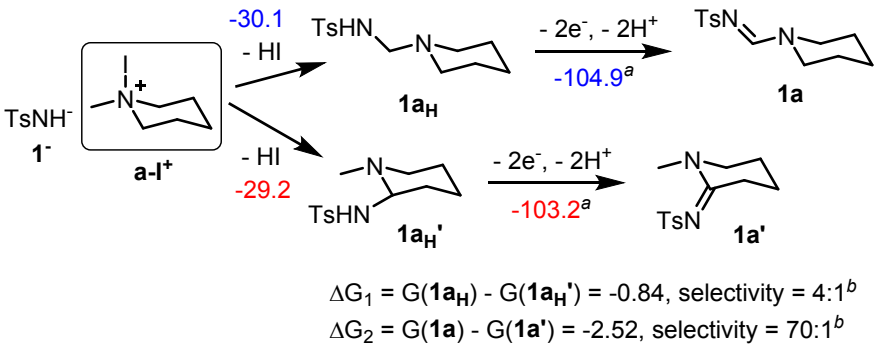


Fig. S13. Free energy profile of the formation of two imine cation intermediates

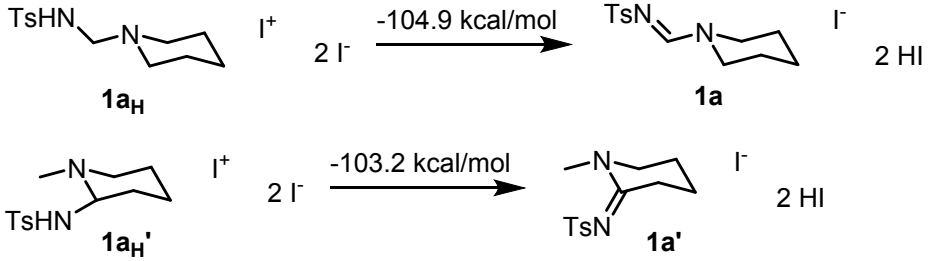
Under such circumstances, we then examined the coupling between $TsNH^-$ (**1**$^-$) and **a-I**$^+$ with the loss of one molecule HI in one step (Scheme S8). Indeed, it was found that both of the processes producing exo- and endo- coupling intermediates (**1a$_H$** and **1a$_H$'**) are exothermic, with the isomer **1a$_H$** more stable than **1a$_H$'** by 0.84 kcal/mol (ΔG_1) as the products. Notably, the final product **1a** upon further oxidation is 2.52 kcal/mol (ΔG_2) more stable than the product **1a'**, leading to a theoretical selectivity up to 70:1,[14] which is in good agreement with our experimental outcomes.



Scheme S8. Free energy evaluation and the calculated selectivity of the regioisomers

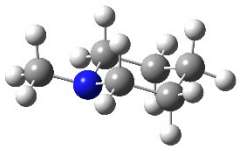
a ΔG was calculated using an I^+ as the oxidant, see the contents below; *b* the selectivity was calculated by Boltzmann distribution under standard state. All energies are in kcal/mol.

The transformation of putative intermediates **1a$_H$** and **1a$_H$'** to their corresponding final condensation products **1a** and **1a'** were calculated as two-electron oxidation processes with I^+ as the oxidant (Scheme S9).



Scheme S9. The oxidation of **1a$_H$** to **1a** and **1a$_H$'** to **1a'**

Calculated data for the related species:

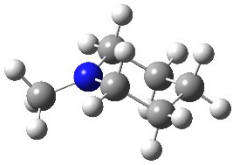


N-methylpiperidine (**a**), Charge = 0, Multiplicity = 1

20 atoms, 56 electrons, neutral, singlet, -291.090235 Hartree

H	-0.264188009	-0.1031351614	2.1690611685
C	-0.9732624145	0.0853122813	1.3546202558
C	-1.6539139506	-1.2190784341	0.9304671953

C	-1.8266449993	-0.2770826525	-1.4003135025
C	-1.1393349159	0.9909491457	-0.8861580912
H	-0.8833593477	-1.9572168723	0.6685533788
H	-2.2137278119	-1.6254573475	1.7821140316
H	-1.7382927625	0.7871826689	1.7471634613
H	-1.0679368616	-0.9505385222	-1.8222419164
H	-2.5100231254	-0.0096008266	-2.2159610232
H	-0.5498999006	1.4547647549	-1.6855684625
H	-1.9110205589	1.7288871983	-0.5829216492
N	-0.2386243627	0.7007527346	0.2393412876
C	0.4528609218	1.910467809	0.6770262028
H	1.1491806094	1.6705100958	1.4878899237
H	-0.2427530119	2.690345172	1.0438193558
H	1.0275541433	2.334043754	-0.1537912708
C	-2.5817698811	-0.9915711984	-0.270967479
H	-2.9945637123	-1.9442736301	-0.6254169936
H	-3.4347140487	-0.3720819694	0.0426161273

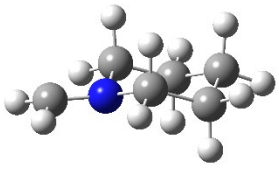


N-methylpiperidine cation (**a**$^{+}$), Charge = 1, Multiplicity = 1

20 atoms, 55 electrons, +1 charged, singlet, -290.905695 Hartree

H	-0.6156419536	0.2857687308	2.3493427412
C	-1.2842531918	0.2944857254	1.4885420958
C	-1.5791166981	-1.1356739241	0.9631280961
C	-1.7524218562	-0.1905551635	-1.3753328043

C	-1.4536588419	1.2183384956	-0.7973013084
H	-0.6259990678	-1.6472338933	0.7851314102
H	-2.1014067564	-1.6707711193	1.7626563568
H	-2.2305858864	0.7813103577	1.7588399773
H	-0.8119083367	-0.6333786165	-1.7234008229
H	-2.39861716	-0.0499357087	-2.2476969173
H	-0.9009369142	1.8416229536	-1.5002306682
H	-2.4004237585	1.7075199343	-0.5328349377
N	-0.6810482613	1.0763611212	0.4239504562
C	0.6551686645	1.6101691012	0.5406676977
H	1.2445375113	0.9966279378	1.2254183687
H	0.585034399	2.6285201486	0.9574451846
H	1.120719346	1.671869407	-0.445297568
C	-2.4130544094	-1.0829165336	-0.3203888105
H	-2.5335577351	-2.0963367516	-0.7210448784
H	-3.4172630943	-0.7026131978	-0.0922616805

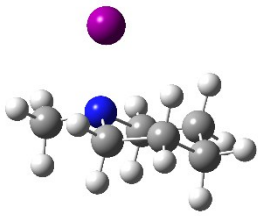


N-methylpiperidine radical (**a**·), Charge = 0, Multiplicity = 2

19 atoms, 55 electrons, neutral, doublet, -290.448591 Hartree

H	-0.3305762473	0.0029297546	2.2024953827
C	-1.0924399188	0.1245317325	1.426244303
C	-1.5534481258	-1.2372290909	0.9004415022
C	-1.8789291457	-0.197869294	-1.3736391776
C	-1.410842876	1.1411220219	-0.7980268414

H	-0.6753703307	-1.8199680333	0.5903076695
H	-2.0350914892	-1.7871727915	1.7181303979
H	-1.9469864785	0.6573488786	1.8818218533
H	-1.0198814836	-0.7197064406	-1.8169378511
H	-2.593414656	-0.0042462109	-2.18299561
H	-0.8680866455	1.7191508201	-1.5523966584
H	-2.2863061769	1.7406103466	-0.4884091846
N	-0.5198838522	0.946574178	0.3527924724
C	0.277840248	2.0128625825	0.7259540657
H	0.8870831095	1.8811675116	1.6156483782
H	0.645450506	2.6523198288	-0.0715510362
C	-2.5131446829	-1.076384586	-0.2865386289
H	-2.7826309481	-2.0573376485	-0.6963094284
H	-3.4457068064	-0.6082775596	0.0608773917

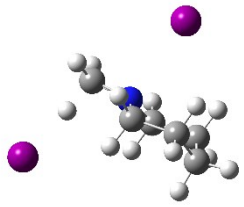


Cation intermediate (**a-I**$^{+}$), Charge = 1, Multiplicity = 1

21 atoms, 108 electrons, +1 charged, singlet, -302.331358 Hartree

H	-0.820313783	2.1047334622	-0.3241017034
C	-0.2940761134	1.2491752881	0.1020008465
C	1.196473722	1.2614297093	-0.2100048997
C	1.1964857095	-1.2614247546	-0.2099872194
C	-0.2940643106	-1.2491800421	0.1020183329
H	1.3485995965	1.3667059048	-1.2907782117
H	1.6107345413	2.1615393828	0.2578802645

H	-0.4622666441	1.2353056553	1.1856226496
H	1.3486125651	-1.3667145108	-1.2907590951
H	1.6107551663	-2.1615239959	0.2579103088
H	-0.8202936492	-2.10474951	-0.3240718986
H	-0.4622548772	-1.2352968297	1.1856399757
C	-2.4262209631	-0.0000127707	0.0698127279
H	-2.9226164528	0.8959413607	-0.302079037
H	-2.4142531044	-0.0000055146	1.1627458347
H	-2.9226083453	-0.8959764871	-0.3020668626
C	1.898432505	0.0000094651	0.3091847777
H	2.9480793758	0.0000123497	-0.0032108228
H	1.8877037425	0.0000170853	1.4072808475
I	-1.0779880671	-0.0000250197	-2.6044869025
N	-0.9990185138	-0.0000094581	-0.3976014629

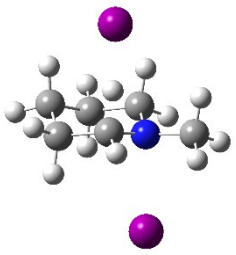


Transition state 1 (**TS1**), Charge = 0, Multiplicity = 1

22 atoms, 162 electrons, neutral, singlet, -313.927144 Hartree

H	-0.0813841094	0.3967468944	2.1442569351
C	0.0364523585	1.0941851936	1.3136688883
C	-1.104987529	2.1024481308	1.2269442936
C	-0.9408501766	2.0596411319	-1.283476322
C	0.1998989181	1.0515421877	-1.1865413984
H	-2.0574769778	1.5613336032	1.2555703526
H	-1.0535753532	2.7271874537	2.1252013625

H	0.9963117867	1.6254050069	1.4507131023
H	-1.8827165003	1.5157772863	-1.4174901823
H	-0.771525644	2.6536372426	-2.1880792662
H	0.1896529593	0.3259935112	-2.0011926733
H	1.1706054521	1.5799294432	-1.2154464088
C	1.1268041002	-0.732278234	0.1601530501
H	1.2124116796	-1.3277589654	-0.7479235936
H	1.0923149167	-1.2965954863	1.0912125308
H	2.2377245927	-0.1839714881	0.2233852959
C	-1.0174197651	2.9560337285	-0.0428244039
H	-1.8899873999	3.6148584976	-0.1111080313
H	-0.1295920335	3.6009424165	0.0042264935
I	4.1126960344	0.5887065281	0.3329287785
N	0.2347936837	0.3021536959	0.0843368057
I	-2.3924219932	-1.2593127783	-0.0610206091

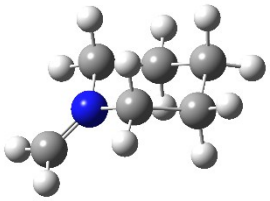


Transition state 2 (**TS2**), Charge = 0, Multiplicity = 1

22 atoms, 162 electrons, neutral, singlet, -313.933844 Hartree

H	-0.8786724359	-0.6333147551	-1.284825715
C	-0.769036045	0.221191375	-0.614427078
C	-0.4210713881	1.5348414064	-1.2840100871
C	0.5603641658	2.3003002556	0.9051074199
H	0.5488534947	1.368684876	-1.780438846
H	-1.1604912081	1.7340269588	-2.06486758

H	1.606142672	2.2122974999	0.5888926724
H	0.5187406217	3.06356043	1.6896131582
H	-1.9276647655	0.3474168713	-0.1922694852
C	-0.3230448759	2.6904894882	-0.2847386404
H	0.0816981844	3.5790332639	-0.7808011865
H	-1.3300435194	2.9488978341	0.0670107715
I	-3.9246231028	0.528497739	0.3088032557
N	-0.064350091	-0.1041105365	0.5297625154
I	2.675372751	-0.6084219704	-0.2861421946
C	-0.3467587515	-1.4219950627	1.1108745397
H	-0.3078261958	-2.1845024332	0.333792164
H	0.3722434255	-1.6387219963	1.8990341981
H	-1.3607706695	-1.3822858538	1.5371075185
C	0.1262751995	0.9764473525	1.5252996892
H	0.8335533227	0.6156550376	2.2725513843
H	-0.8596197888	1.0815122199	2.0103795258

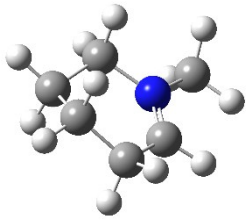


Imine cation ($\mathbf{a}^{+}_{\mathbf{exo}}$), Charge = 1, Multiplicity = 1

19 atoms, 54 electrons, +1 charged, singlet, -290.335854 Hartree

H	-0.5150324065	0.1883004123	2.3264971557
C	-1.2359523348	0.215030284	1.5086388093
C	-1.5152762408	-1.1745980576	0.9259382185
C	-1.8413184748	-0.1334998711	-1.3519182829
C	-1.559095314	1.2468711162	-0.748963239

H	-0.5613750847	-1.6493313037	0.6638486488
H	-1.9749476654	-1.7777563363	1.716105122
H	-2.1620469145	0.6834185407	1.8584025191
H	-0.9087063607	-0.540254274	-1.7627412408
H	-2.5338579705	0.0069219859	-2.1886573255
H	-1.0554928695	1.914066166	-1.4493685811
H	-2.4859185297	1.7175859765	-0.4042900215
N	-0.6948510255	1.1051725839	0.4502991347
C	0.4470333327	1.6720297022	0.5459380347
H	1.0485310484	1.5218654083	1.4379097222
H	0.8047992904	2.3001352319	-0.2648944137
C	-2.4252686401	-1.0929166235	-0.3066571057
H	-2.5519976713	-2.0892133995	-0.743876823
H	-3.4215921688	-0.7434015422	-0.0043013317

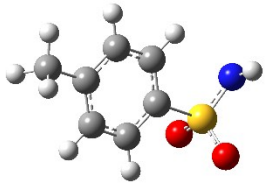


Imine cation ($\mathbf{a}^{+}_{\mathbf{endo}}$), Charge = 1, Multiplicity = 1

19 atoms, 54 electrons, +1 charged, singlet, -290.349668 Hartree

C	-0.5526312256	-0.4531736505	-0.5168403944
C	-1.3789354289	-1.6691217196	-0.31175138
C	-3.2872778691	-0.0802526412	0.009015524
C	-2.3066493541	1.0600483335	0.253169558
H	-1.567302556	-2.0749791264	-1.3184572358
H	-0.7400540368	-2.4135460192	0.180157867
H	0.4551493312	-0.5651481379	-0.9115661414

H	-3.5438752713	-0.1193529451	-1.0570460075
H	-4.2071341444	0.1403733439	0.5592959505
H	-2.6216071346	1.9802343039	-0.2445295711
H	-2.1877383224	1.2766346254	1.3205575209
N	-0.9459156553	0.7487534238	-0.2666135748
C	-0.0685384958	1.9132842557	-0.4655756291
H	-0.0244709945	2.476803177	0.4700215251
H	-0.4961910385	2.545978302	-1.2474825094
H	0.9296285799	1.5808897446	-0.7497095411
C	-2.6820932111	-1.4148380079	0.4518567255
H	-3.3794200701	-2.2382642301	0.2735115331
H	-2.4771361026	-1.3872790318	1.5288297804

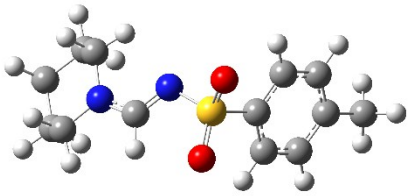


TsNH$^-$ (**1**$^-$), Charge = -1, Multiplicity = 1

19 atoms, 90 electrons, -1 charged, singlet, -874.955688 Hartree

C	2.6736381379	-0.0002095289	0.0098105165
C	1.9365609894	-1.1902910259	-0.1402516501
C	0.5427897905	-1.1837180876	-0.1272957394
C	-0.1450748813	0.026529051	0.0392514085
C	0.5651229843	1.2163785328	0.1910828843
C	1.965713291	1.1977649571	0.1732256372
H	2.4633658395	-2.1333179822	-0.2694472204
H	-0.0033136537	-2.114857114	-0.2478370025
H	0.0304893748	2.1516673598	0.326273431

H	2.5109745015	2.1313307501	0.2904560641
C	4.1829334537	-0.0262318669	-0.0007817018
H	4.5729356594	-0.6083119392	0.843563624
H	4.5646916488	-0.4941599053	-0.9161601174
H	4.5994269264	0.9833429193	0.0645565815
S	-1.9651783869	0.0278577787	0.0740672709
O	-2.3443142797	-0.6583576125	-1.2182402833
O	-2.3175853931	-0.7738578144	1.2963000889
N	-2.5165916043	1.4919696479	0.2411367944
H	-2.4464718482	1.9653890201	-0.6629457666

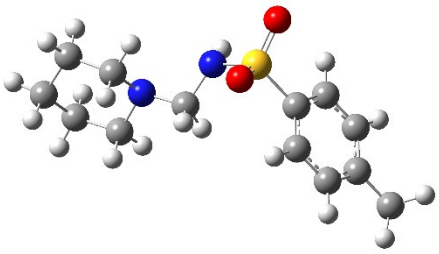


Final product (**1a**), Charge = 0, Multiplicity = 1

36 atoms, 142 electrons, neutral, singlet, -1164.132383 Hartree

H	-2.2806501424	0.9468385996	-1.1525345224
C	-3.1109801716	0.4668407529	-0.6353635725
C	-3.5785293731	-0.7966766368	-1.3678684472
C	-4.1448767323	-1.8497240084	0.8588238431
C	-3.6752462078	-0.5702050371	1.5581876724
H	-2.7124121944	-1.4485584907	-1.5428472999
H	-3.9675860598	-0.5021360469	-2.3494880246
H	-3.9347823692	1.1893869838	-0.5601464386
H	-3.3114555018	-2.5637344117	0.8201355364
H	-4.937347596	-2.3049251488	1.4643210711
H	-4.5257014571	0.1069411042	1.7145502588

H	-3.2301506054	-0.7863177967	2.5319831937
N	-2.6798242785	0.1385963411	0.734344507
C	-4.645547366	-1.5515967445	-0.5619546368
H	-5.5584184221	-0.9417408692	-0.5050054663
H	-4.9153892302	-2.4838042337	-1.0717006139
S	0.8434562495	1.4668122303	1.2790338219
C	2.0219315574	0.3876521907	0.4646699686
O	1.2033928513	2.863222992	0.9352557304
O	0.8284946091	1.1156093693	2.7250971296
C	2.3231188415	-0.8536336446	1.0296449016
C	2.6016336422	0.7895164241	-0.7438810786
C	3.2191666944	-1.699182249	0.3712292989
H	1.87330507	-1.1580618281	1.9691496194
C	3.4919343377	-0.0693287088	-1.3868086916
H	2.3664799031	1.7574100548	-1.174663119
C	3.8167880911	-1.3245615358	-0.8422506245
H	3.4582832674	-2.663518585	0.812042273
H	3.9449846339	0.2422312882	-2.3247982648
C	4.7969497691	-2.232161801	-1.5422493755
H	5.8122098955	-1.8182968788	-1.4948655232
H	4.8175954573	-3.2259548281	-1.0859854026
H	4.5446066806	-2.3437451884	-2.6028326314
C	-1.4958145981	0.4781531967	1.2253299871
H	-1.3133912251	0.1720897179	2.2566409096
N	-0.5946580203	1.1504064268	0.5304280107

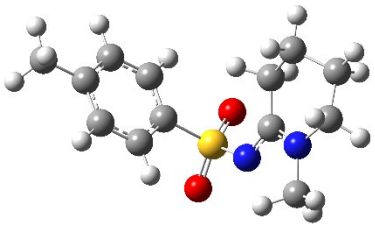


Intermediate (**1a$_H$**), Charge = 0, Multiplicity = 1

38 atoms, 144 electrons, neutral, singlet, -1165.302492 Hartree

H	2.0999832447	12.1959873288	5.5679104215
C	2.1951851785	12.8089234079	4.6671781212
C	1.7752612817	14.2519276107	4.9562351707
C	3.4233732349	15.0010307154	3.2031810242
C	3.7873417424	13.5313149878	2.9760922115
H	2.3645315516	14.6355358048	5.8003377791
H	0.7230959358	14.2612651615	5.2663964517
H	1.5239579589	12.3747411756	3.9002379465
H	4.1265336091	15.4347348608	3.9273198831
H	3.5503068574	15.5481642663	2.2609090091
H	3.1707138932	13.1248305617	2.1505945197
H	4.8362159592	13.443907775	2.6721515411
N	3.5944839389	12.7431376862	4.2067542657
C	1.9874049857	15.1447766422	3.726096484
H	1.282688073	14.8461768734	2.9364329966
H	1.769528603	16.1925266154	3.9670760984
S	4.3167730877	9.1134462194	5.5261971955
C	5.6133186255	8.4360388613	4.490082519
O	4.6876267653	8.8821520569	6.9375824913
O	3.0252049047	8.6058647363	5.0255177851
C	5.2946144938	7.9080256697	3.2370321198
C	6.9385192973	8.4790076982	4.9424433385

C	6.3226202575	7.4124456684	2.430561353
H	4.2651365878	7.8733959739	2.8967368688
C	7.9479461905	7.9806921977	4.1222591199
H	7.1794617243	8.885853632	5.9196316925
C	7.6592185362	7.4393653313	2.8557535365
H	6.0768947869	6.9961539692	1.4572526285
H	8.9768762882	8.0081669286	4.4722040385
C	8.7651457432	6.8912270042	1.9900679315
H	9.2092957903	5.9979741339	2.4468869755
H	8.3967433909	6.6162556977	0.9978006182
H	9.5709136818	7.6243714202	1.869066645
C	4.0461355452	11.3735758733	4.0278931216
H	4.9665418732	11.3856602339	3.4343954511
H	3.3041172859	10.744985148	3.5120527188
N	4.2885708848	10.7733619908	5.3573594083
H	5.0897182108	11.1859980817	5.8373185192



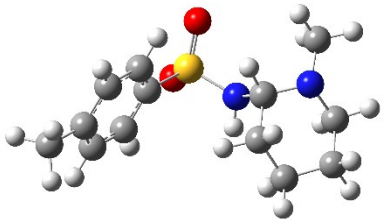
Competitive product (**1a'**), Charge = 0, Multiplicity = 1

36 atoms, 142 electrons, neutral, singlet, -1164.128367 Hartree

H	4.7882537777	0.737635508	0.5252723234
C	3.7780781834	1.1573795972	0.4957234129
C	3.6356761698	2.1367551915	-0.6597545116
C	1.4412236645	1.1347377844	-1.2789896013
H	4.0816886161	1.7124906695	-1.5686364169

H	4.1957693005	3.0446511508	-0.4121784988
H	3.6029322032	1.662595332	1.4545446513
H	0.3575985444	1.2779272398	-1.2600415082
H	1.6942530797	0.8500351773	-2.3071933586
N	2.8403178853	0.0137089147	0.41569841
C	3.1428543956	-1.1070423179	1.3139054914
H	3.5126642536	-1.9691108815	0.7485180154
H	2.2495790805	-1.4093528355	1.8644971701
H	3.9101400402	-0.7851360144	2.0188437459
C	2.1585561422	2.4317438569	-0.8995780154
H	2.0232888213	3.1630142853	-1.7030416634
H	1.7117377355	2.8585542727	0.0077275361
S	-0.2221296419	-1.5102091235	-1.2797085857
C	-1.6003268839	-0.5637416736	-0.6111516392
O	-0.524965218	-2.9427644282	-1.0254676248
O	-0.0652456362	-1.1319225074	-2.7106311393
C	-1.9436427019	-0.7245870941	0.7379224491
C	-2.3352542036	0.284027108	-1.4404579216
C	-3.0289622082	-0.018768116	1.2511803697
H	-1.3745864292	-1.3902403481	1.3797951639
C	-3.4251480326	0.9810578741	-0.9081883187
H	-2.0664260503	0.4001217141	-2.4850114791
C	-3.7887980281	0.8442385182	0.4388348752
H	-3.2949543805	-0.1422034625	2.2982192455
H	-3.9984351835	1.6399755289	-1.5551237074
C	-4.9636095873	1.5953039401	1.0136171764
H	-5.7167465147	0.9022163587	1.4077169556
H	-4.6503940986	2.2361664351	1.8466622839
H	-5.4426289447	2.2258862208	0.2592432062
C	1.7806685242	-0.0508946802	-0.3973959113

N	1.0968713256	-1.1994061953	-0.3666205809

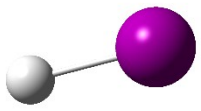


Competitive intermediate (**1a$_H$'**), Charge = 0, Multiplicity = 1

38 atoms, 144 electrons, neutral, singlet, -1165.301150 Hartree

H	19.6202977128	-7.9743157131	24.4189107191
C	19.5487225967	-8.0419559625	23.3281462554
C	20.1446819048	-6.7887226216	22.6824826459
C	20.8959196679	-8.235531588	20.7601535625
H	21.1606654271	-6.6356416965	23.0707760228
H	19.5497009311	-5.9146177634	22.9734561812
H	18.472148408	-8.1182989369	23.0852540801
H	20.8535867522	-8.3954064342	19.6774723875
H	21.9548032747	-8.181109502	21.0402551827
N	20.2750640023	-9.2538365526	22.9121570388
C	19.8567906177	-10.434450945	23.665511215
H	20.4537948601	-11.2998881279	23.3608472581
H	18.7917562718	-10.6840638523	23.526528212
H	20.0285688751	-10.2584724108	24.732451225
C	20.1947259365	-6.9275463533	21.1555341285
H	20.7210212336	-6.0775610633	20.705729084
H	19.1723350199	-6.9043512719	20.7511479891
S	18.6542118362	-11.0841905742	19.9435264971
C	19.5485419596	-10.8811948437	18.4013030112
O	17.2082022971	-11.0492736142	19.6327482102

O	19.2160006784	-12.2659865126	20.6270570055
C	19.0029944143	-10.0714576396	17.3975630324
C	20.7872438663	-11.5041558662	18.2308739734
C	19.7139745513	-9.8912730036	16.2127685944
H	18.037718618	-9.5937650352	17.5330745347
C	21.483835893	-11.3106941512	17.035342894
H	21.2003333251	-12.1361679208	19.0096374372
C	20.9628049651	-10.5066282466	16.010178254
H	19.290705722	-9.2659221201	15.430742469
H	22.446234614	-11.7971446169	16.8996654634
C	21.705872489	-10.3237500637	14.7110339498
H	21.2570475635	-10.9382053526	13.9197582413
H	21.6649695116	-9.282580115	14.3733505801
H	22.7551211278	-10.6178987836	14.8062519501
C	20.2957503324	-9.4579700849	21.4732297439
H	20.9084911693	-10.3415754822	21.2786515288
N	18.9245771639	-9.7759977073	20.9269910702
H	18.3907844099	-8.9743974708	20.5944383719



Hydrogen iodide (HI), Charge = 0, Multiplicity = 1

2 atoms, 54 electrons, neutral, singlet, -12.032500 Hartree

H	-1.1315395425	-0.9992835108	-0.324078518
I	-2.5622414575	-0.3282474892	0.024152518

Iodine radical ($I^{\cdot}$), Charge = 0, Multiplicity = 2

1 atom, 53 electrons, neutral, doublet, -11.415635 Hartree

Iodide anion (I^{-}), Charge = -1, Multiplicity = 1

1 atom, 54 electrons, -1 charged, singlet, -11.623371 Hartree

Iodide cation (I^{+}), Charge = 1, Multiplicity = 1

1 atom, 52 electrons, +1 charged, singlet, -11.104363 Hartree

4. Reference

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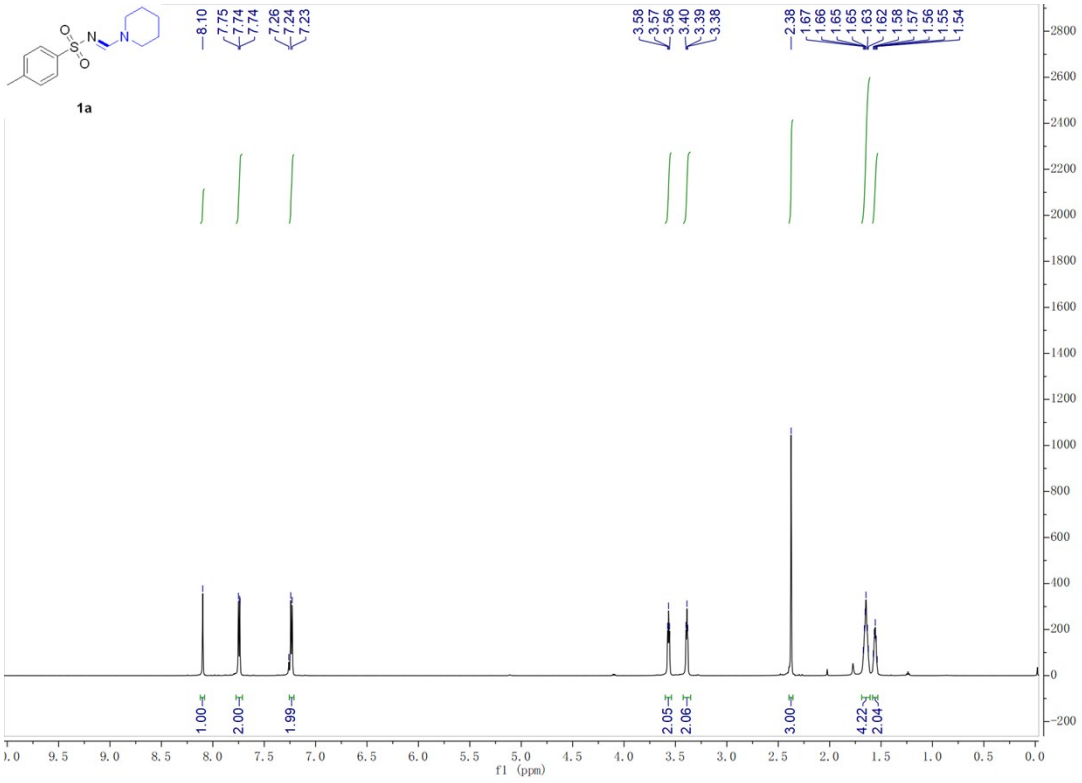
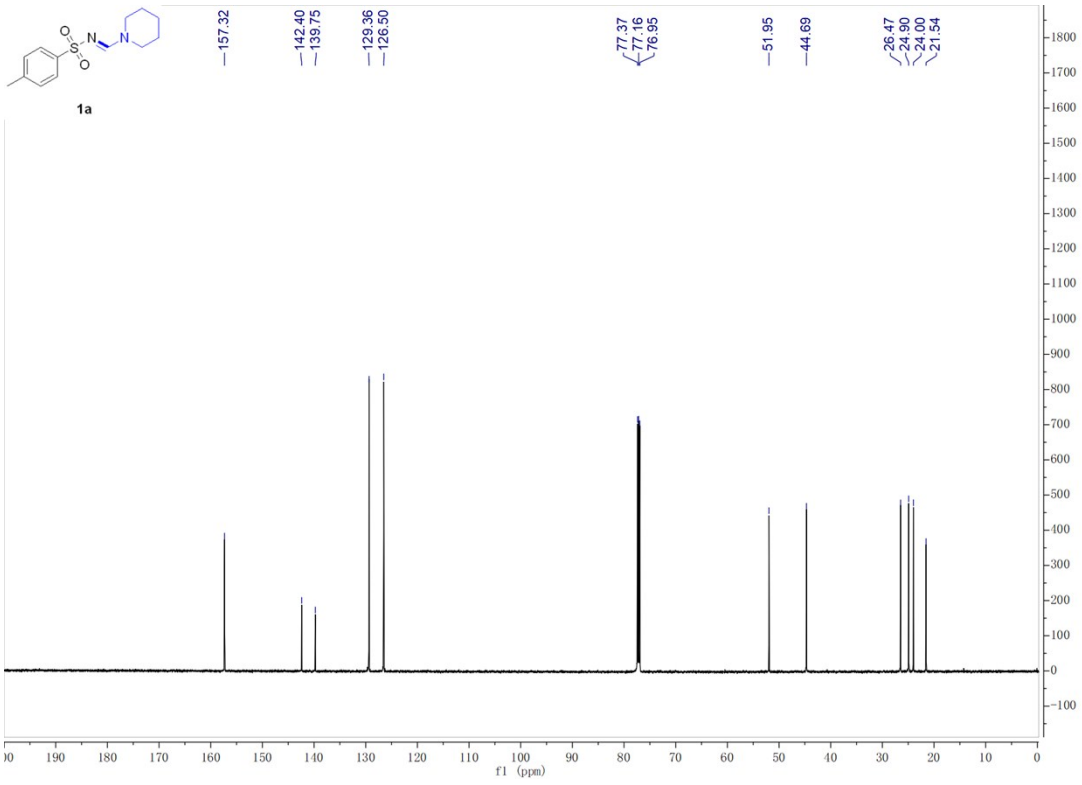
[14] D. P. Curran, C.-H. Lin, N. DeMello, J. Junggebauer, *J. Am. Chem. Soc.* 1998, 120, 342−351.

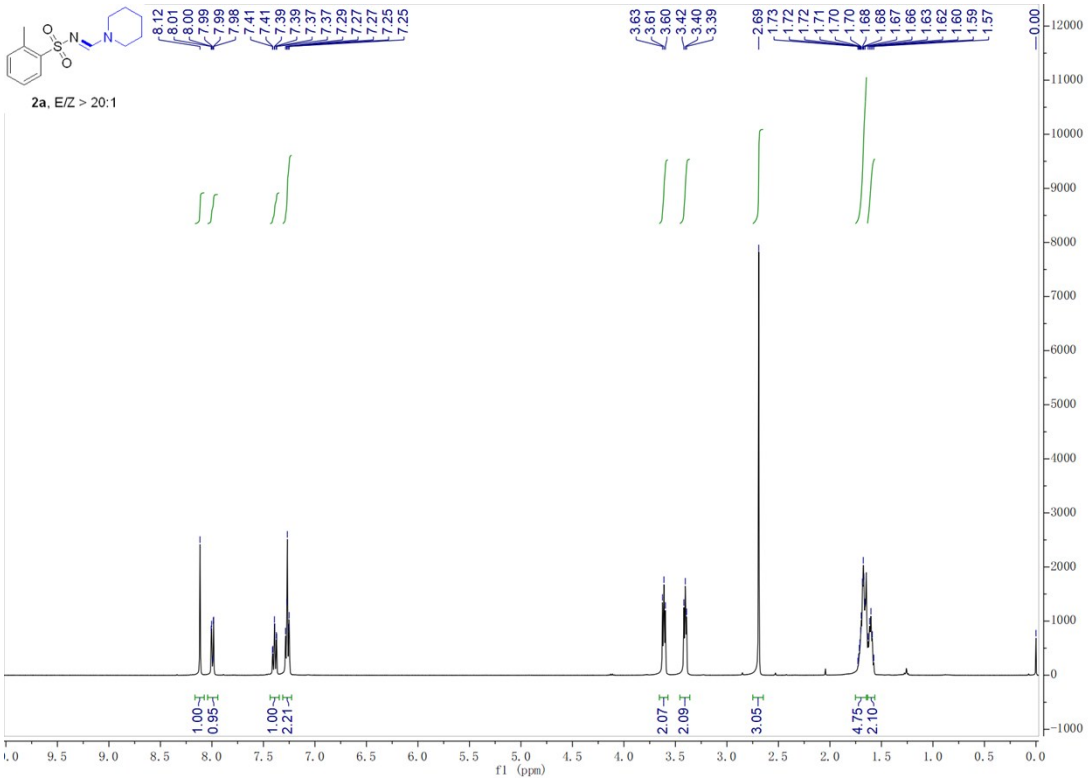
5. NMR spectra of the products

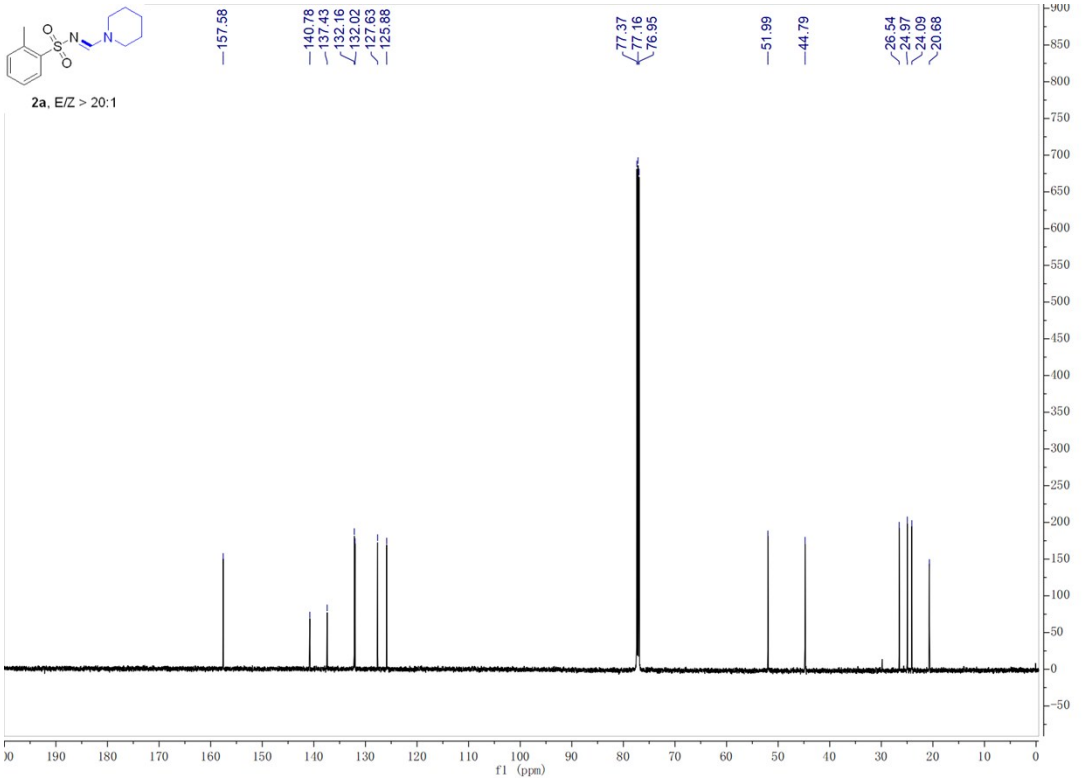
1a ^{1}H, ^{13}C, $CDCl_3$



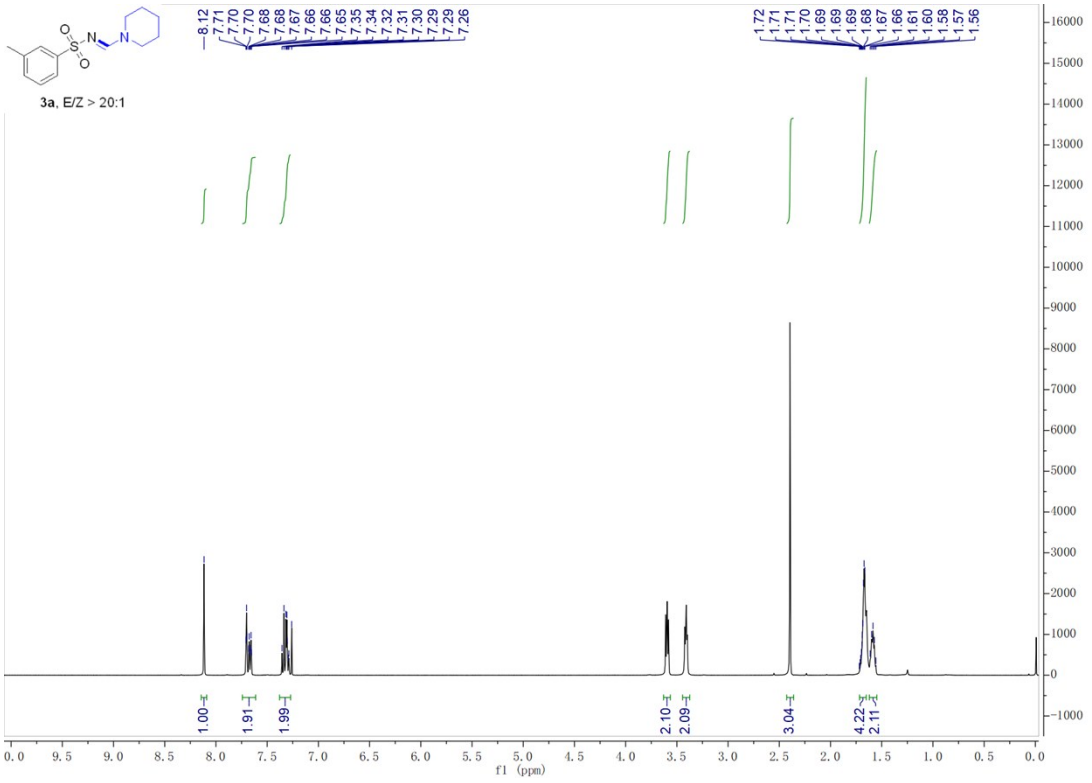


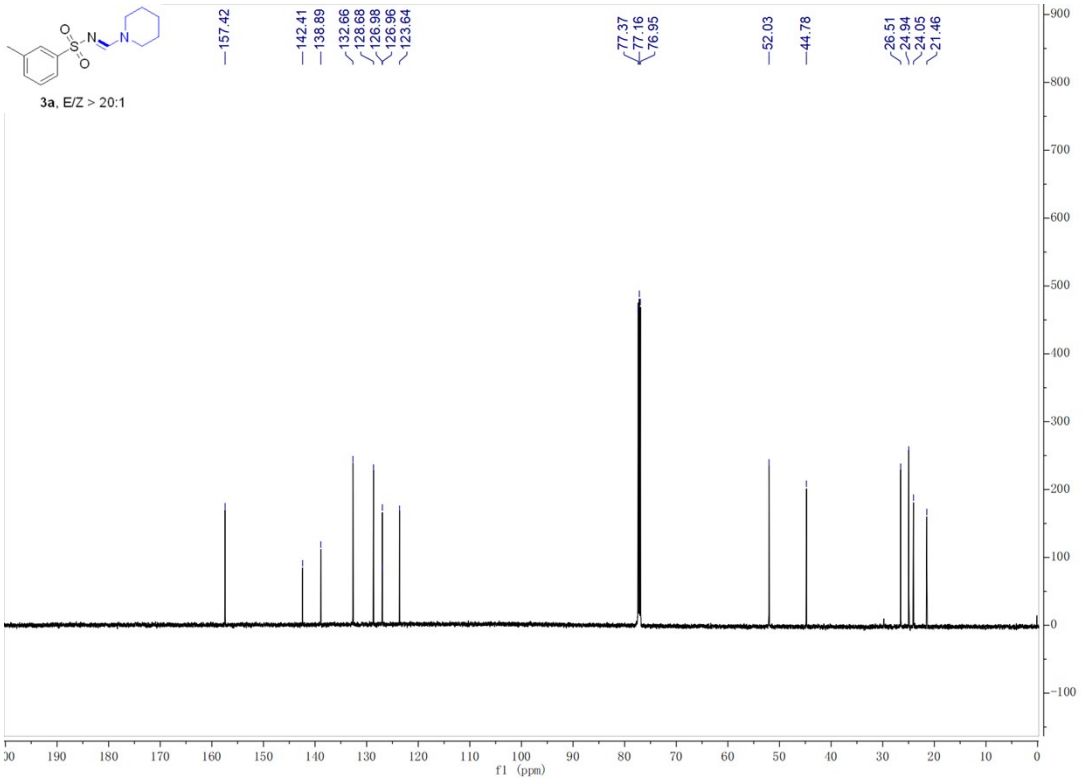
2a ^{1}H, ^{13}C, $CDCl_3$



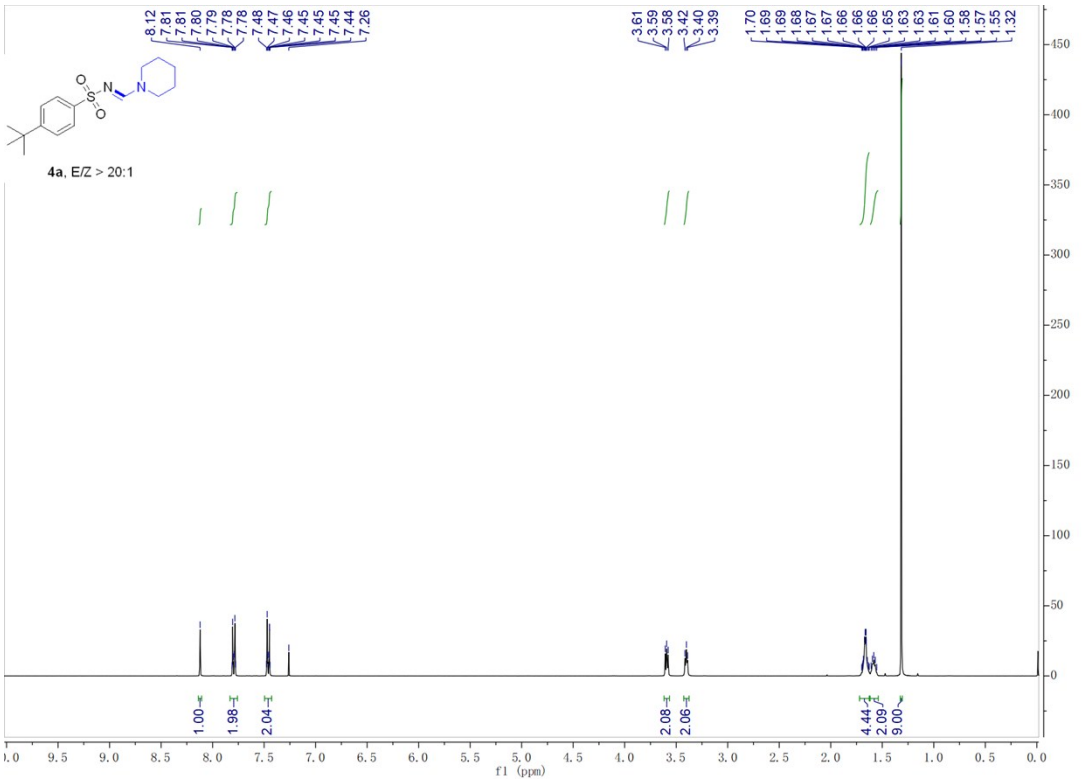


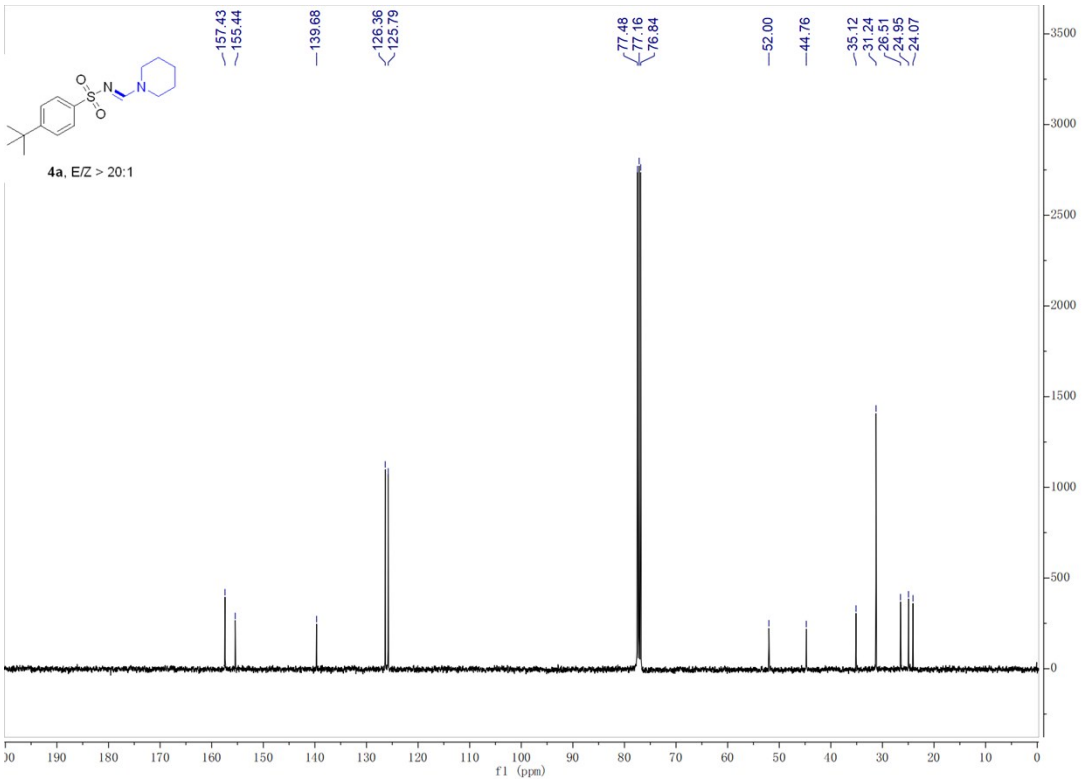
3a ^{1}H, ^{13}C, $CDCl_3$



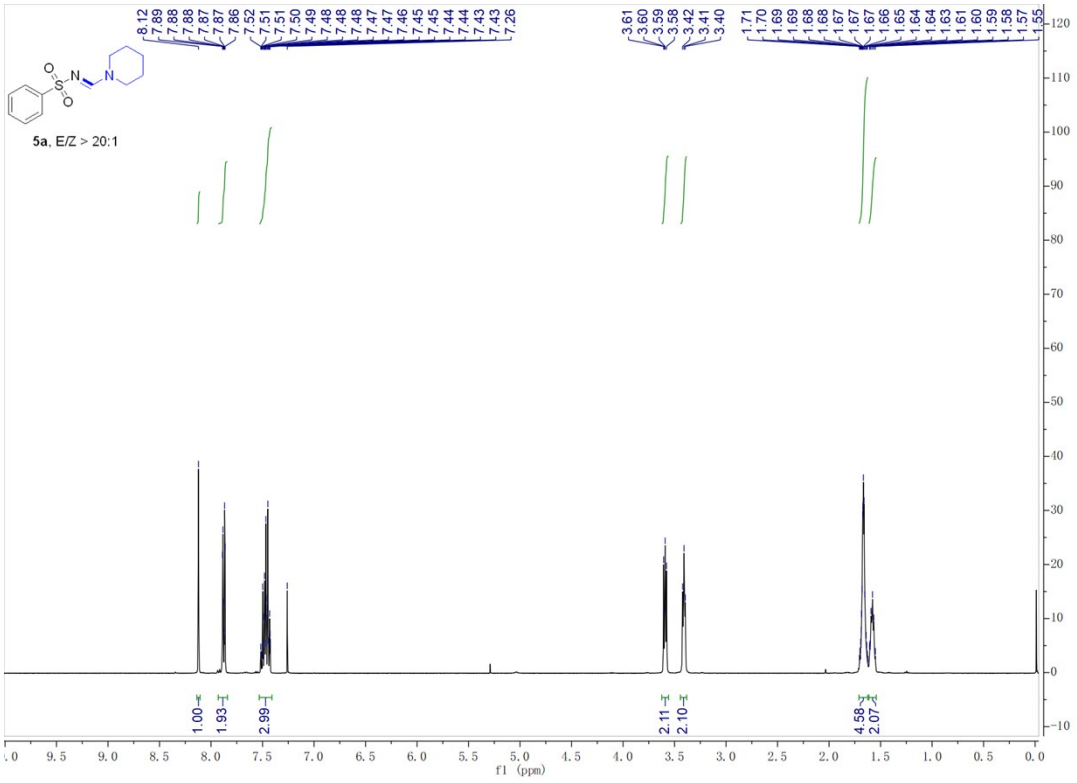


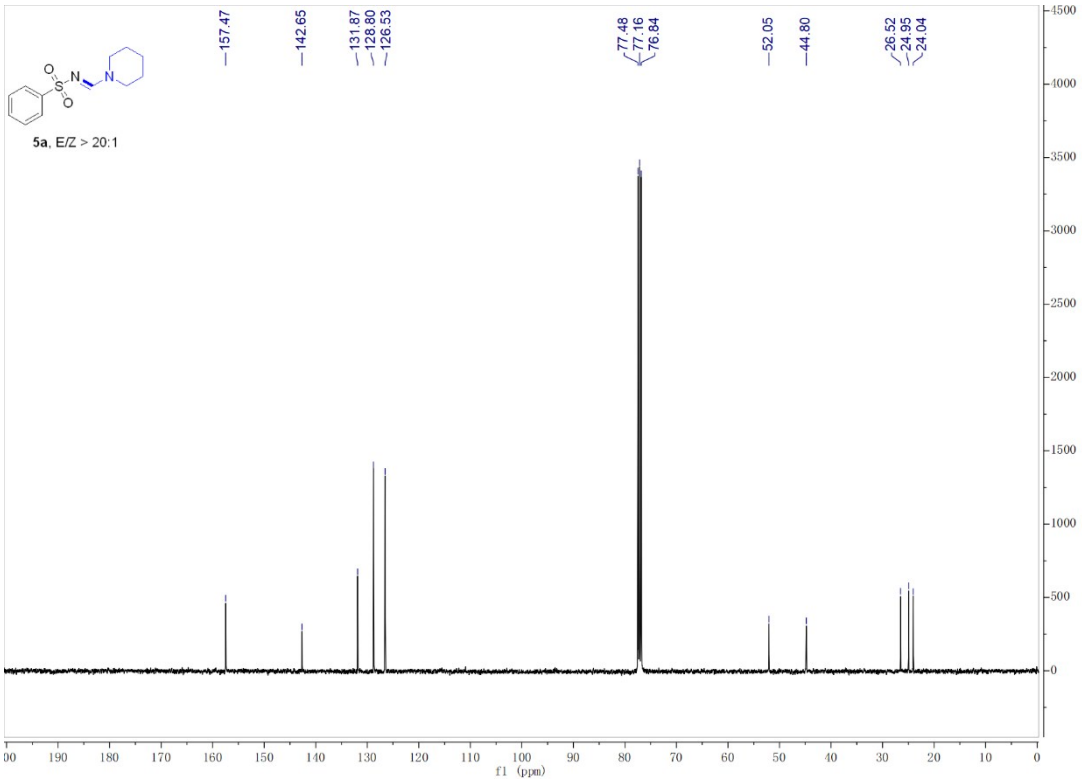
4a ^{1}H, ^{13}C, $CDCl_3$



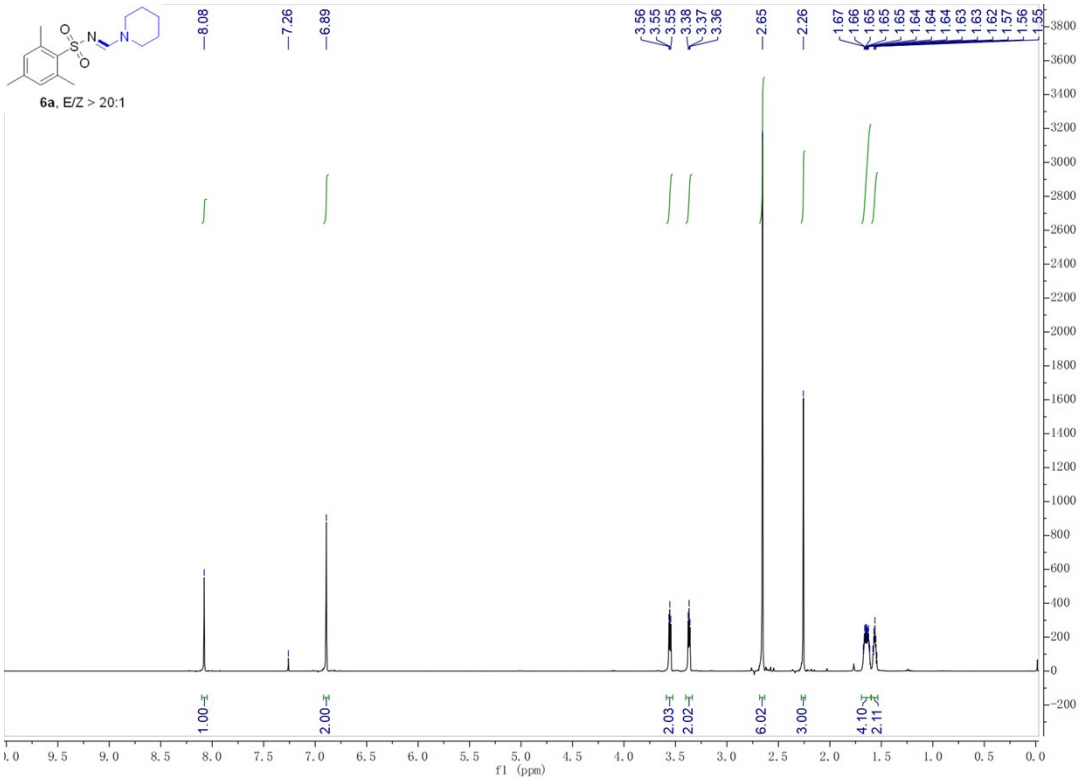


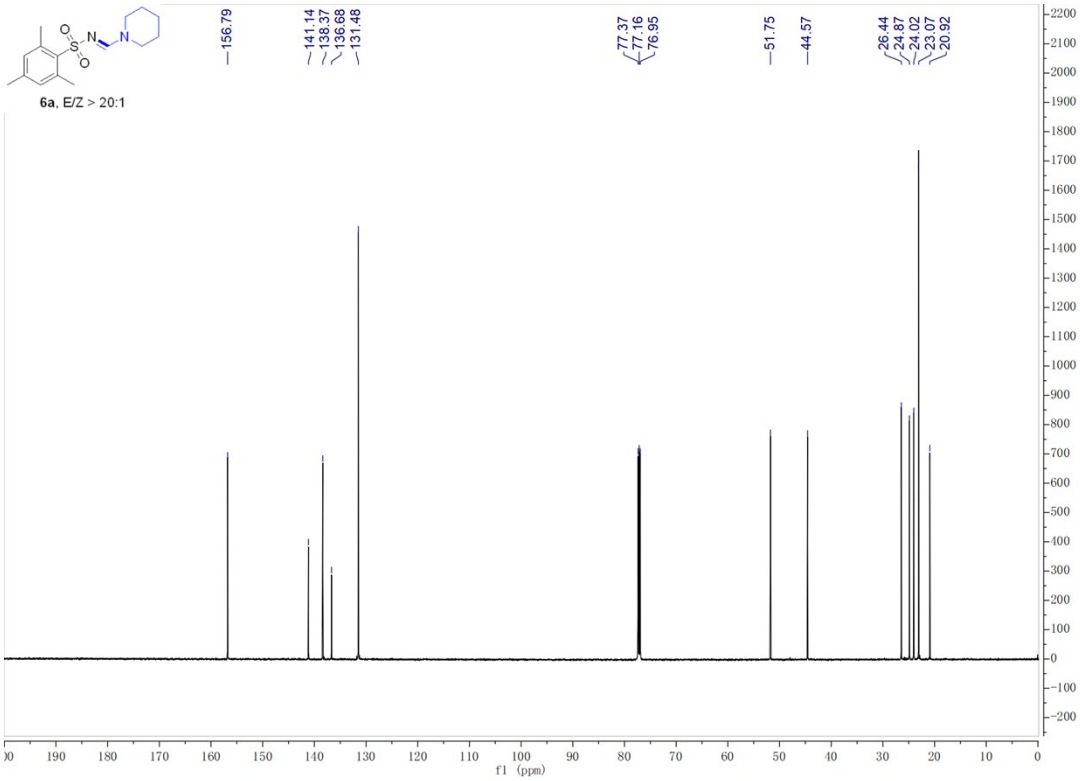
5a ^{1}H, ^{13}C, $CDCl_3$



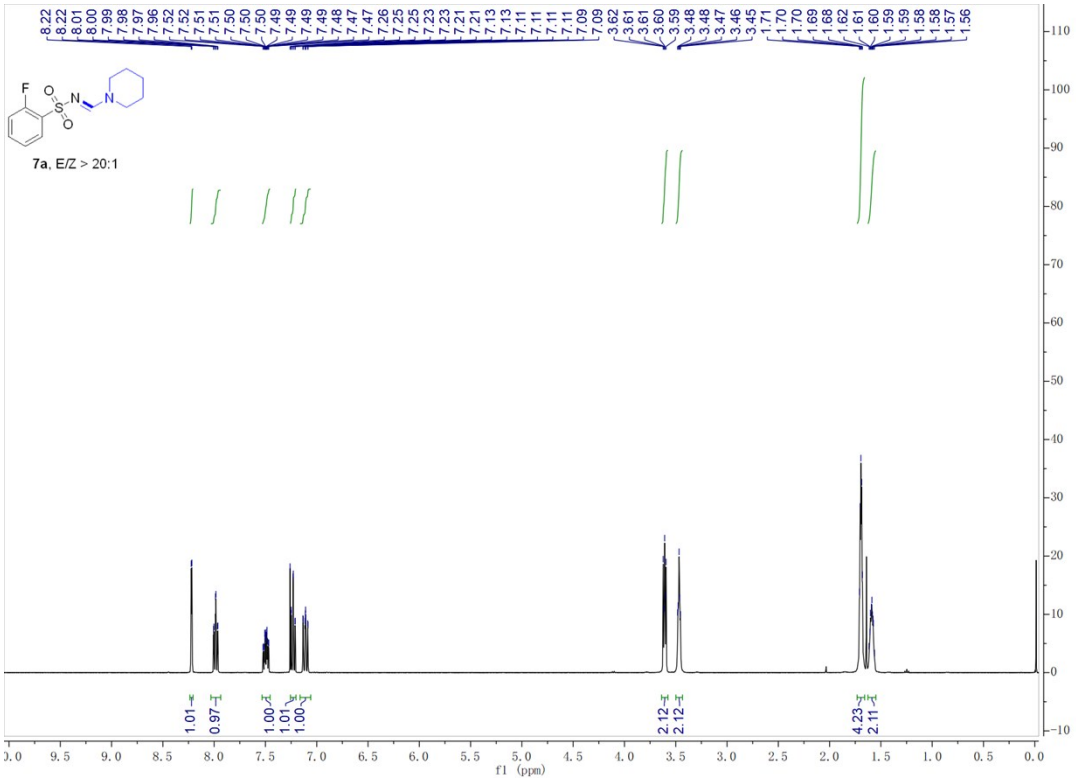


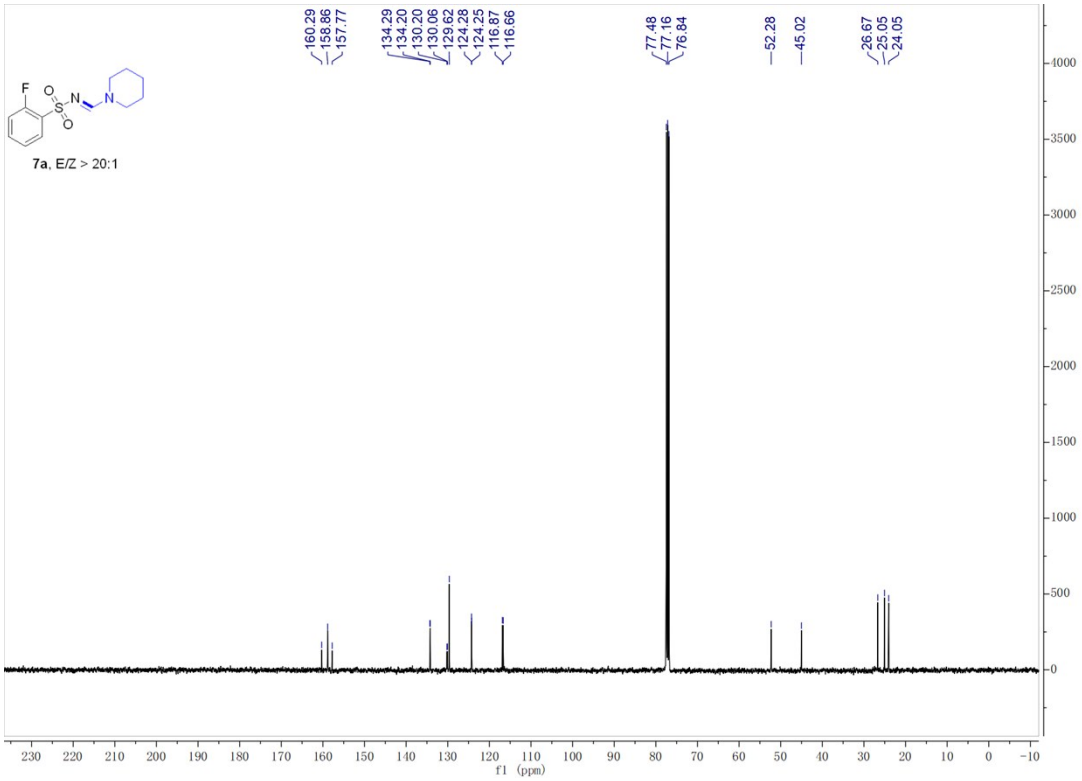
6a ^{1}H, ^{13}C, $CDCl_3$

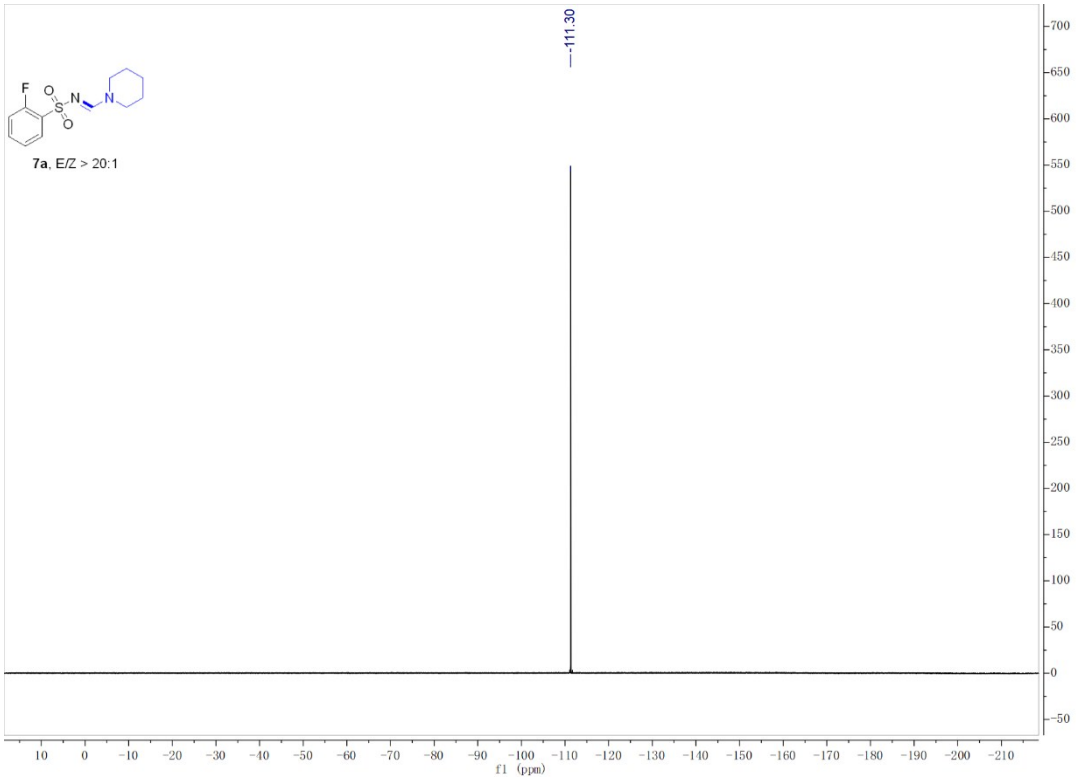




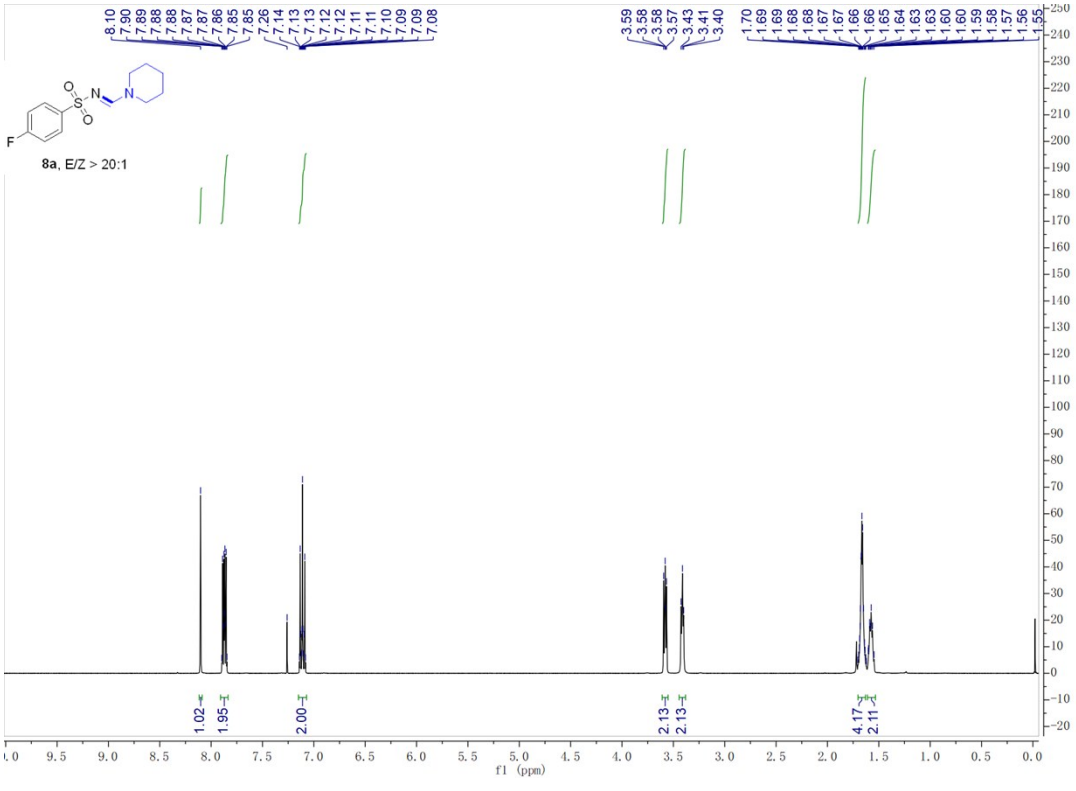
7a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

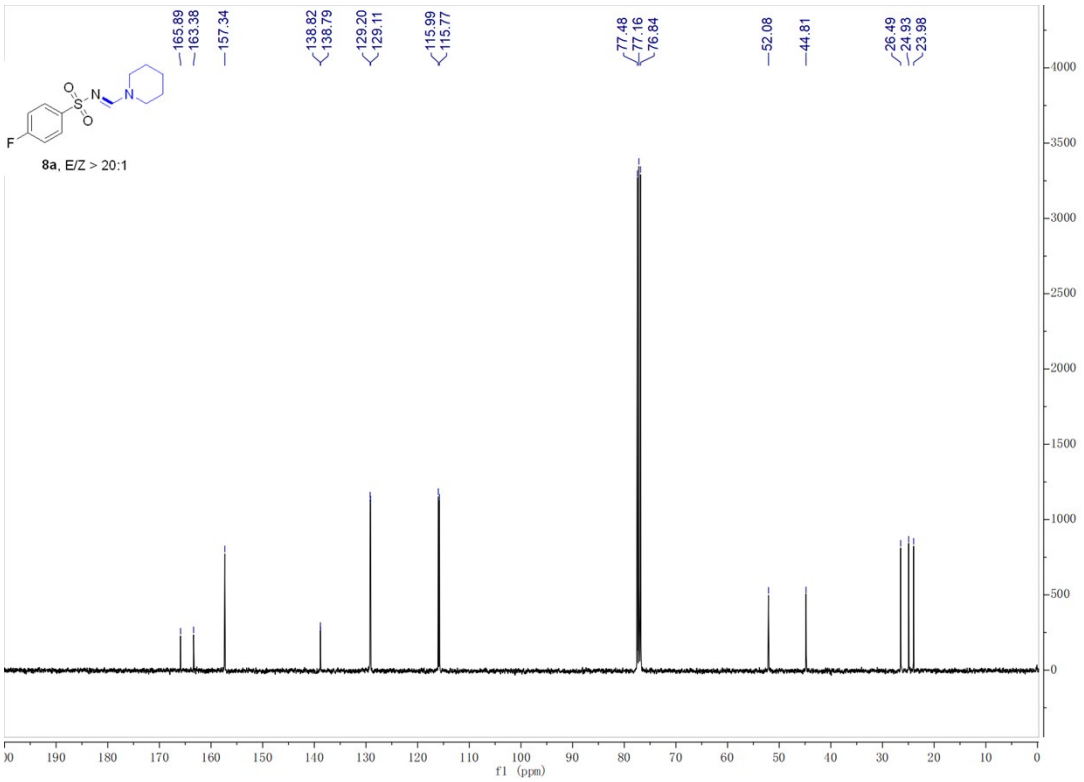


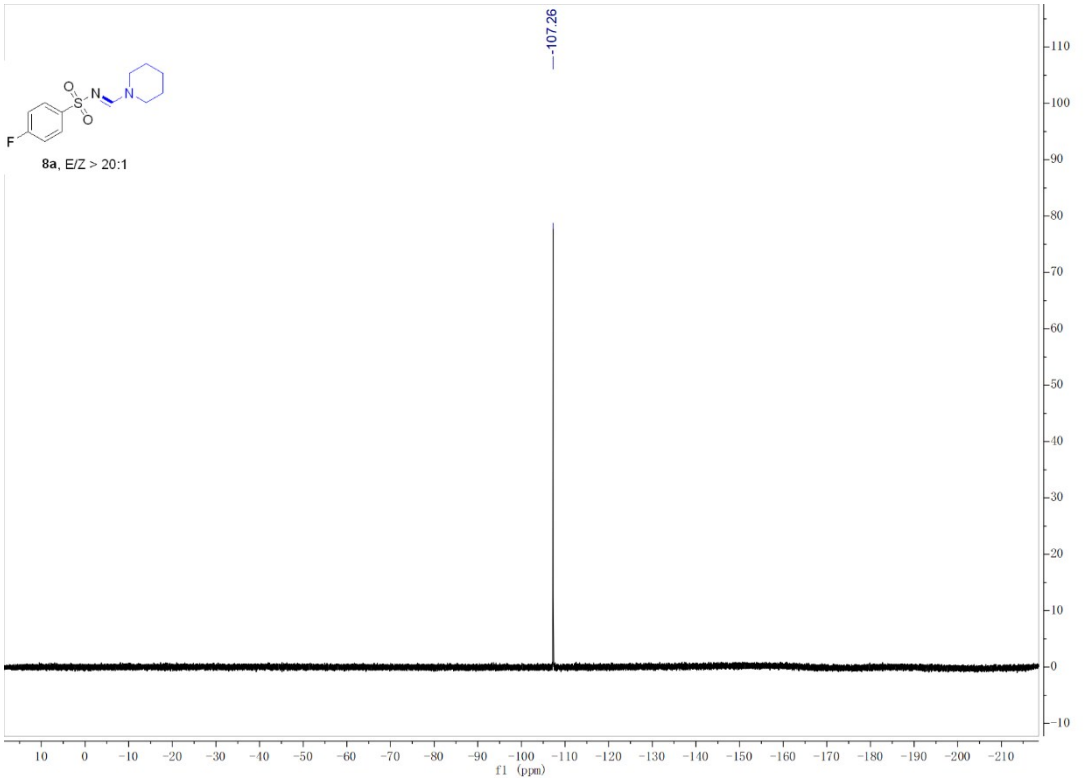




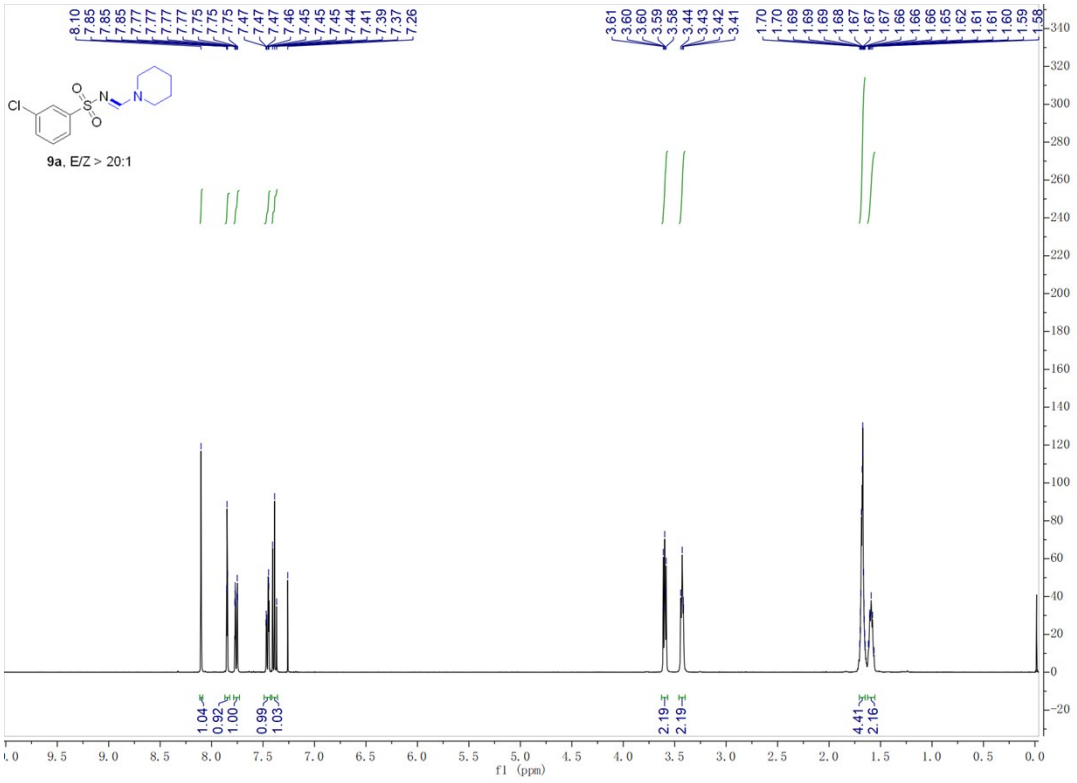
8a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

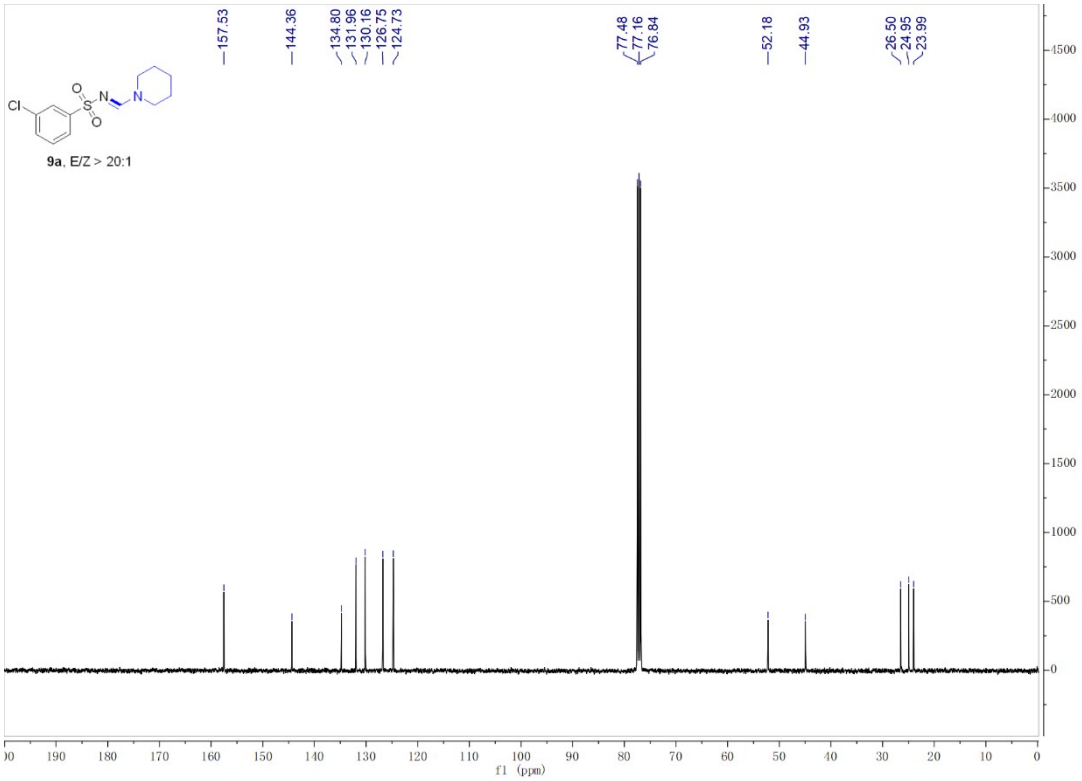



165.89
163.38
157.34
138.82
138.79
129.20
129.11
115.99
115.77
77.48
77.16
76.84
52.08
44.81
26.49
24.93
23.98
8a, E/Z > 20:1
f1 (ppm)

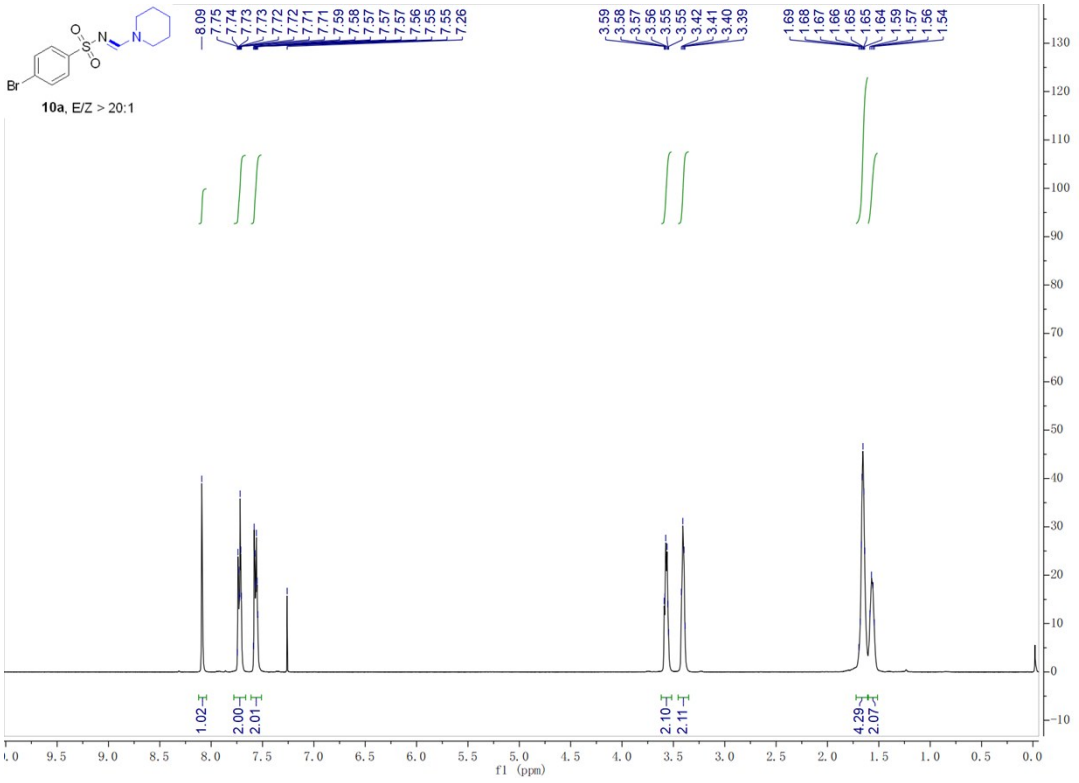

-107.26
8a, E/Z > 20:1
f1 (ppm)

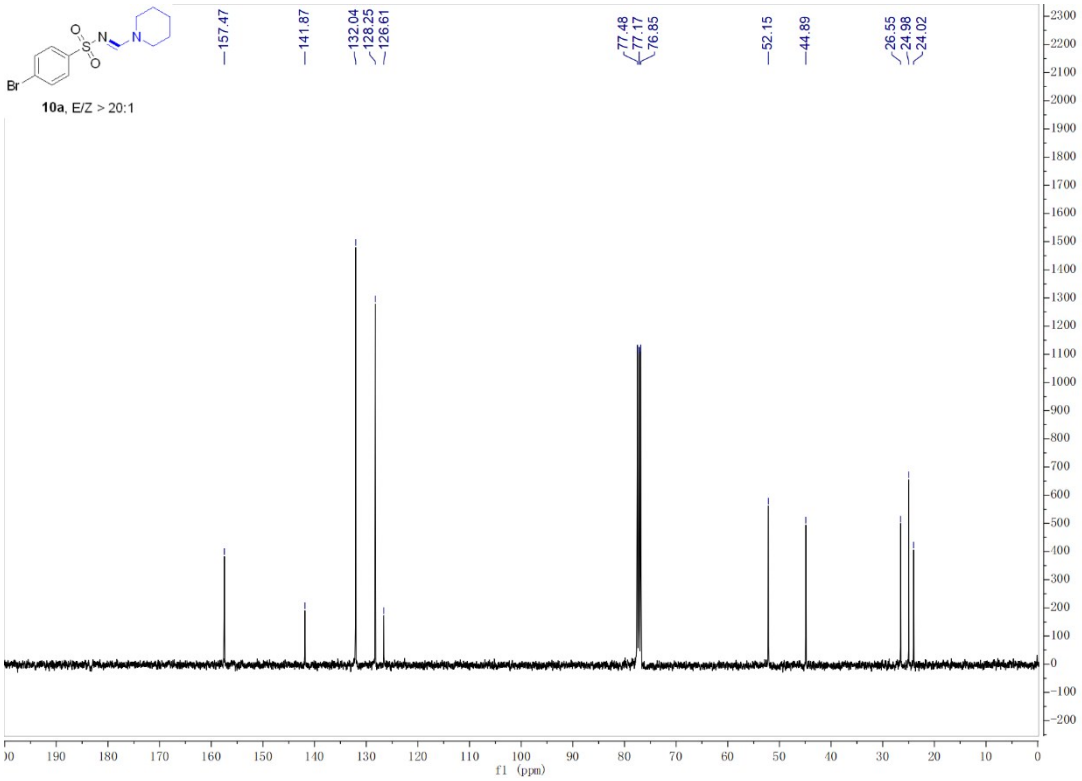
9a ^{1}H, ^{13}C, $CDCl_3$



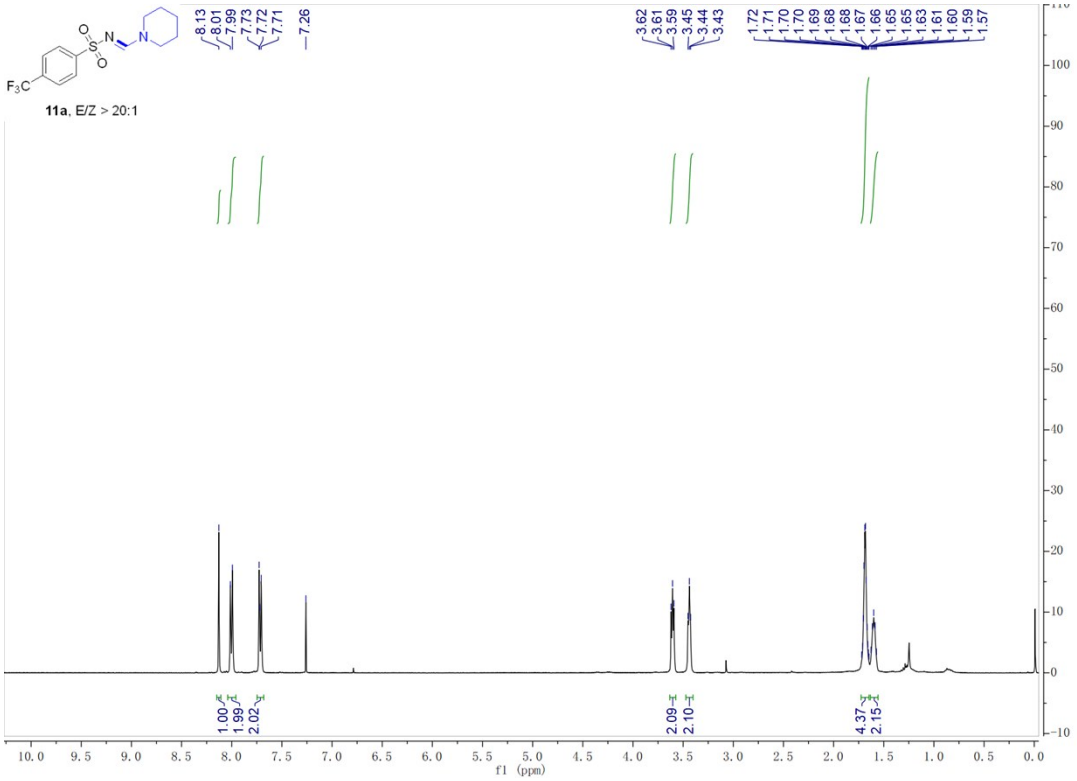


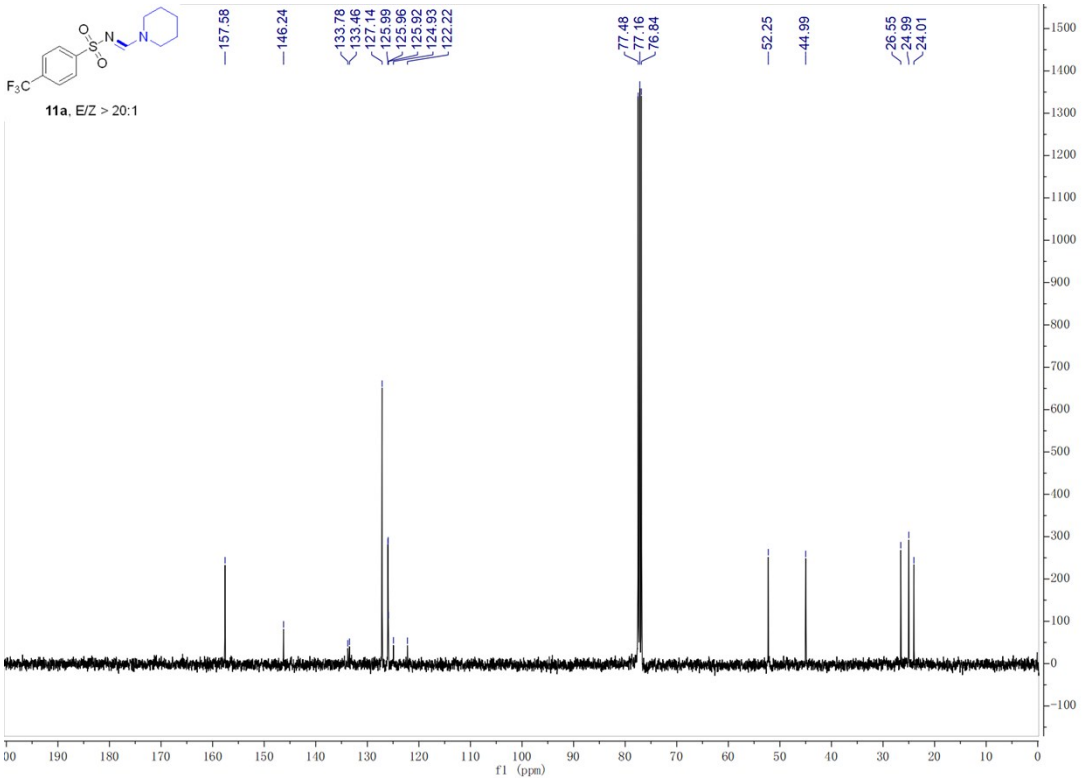
10a ^{1}H, ^{13}C, $CDCl_3$

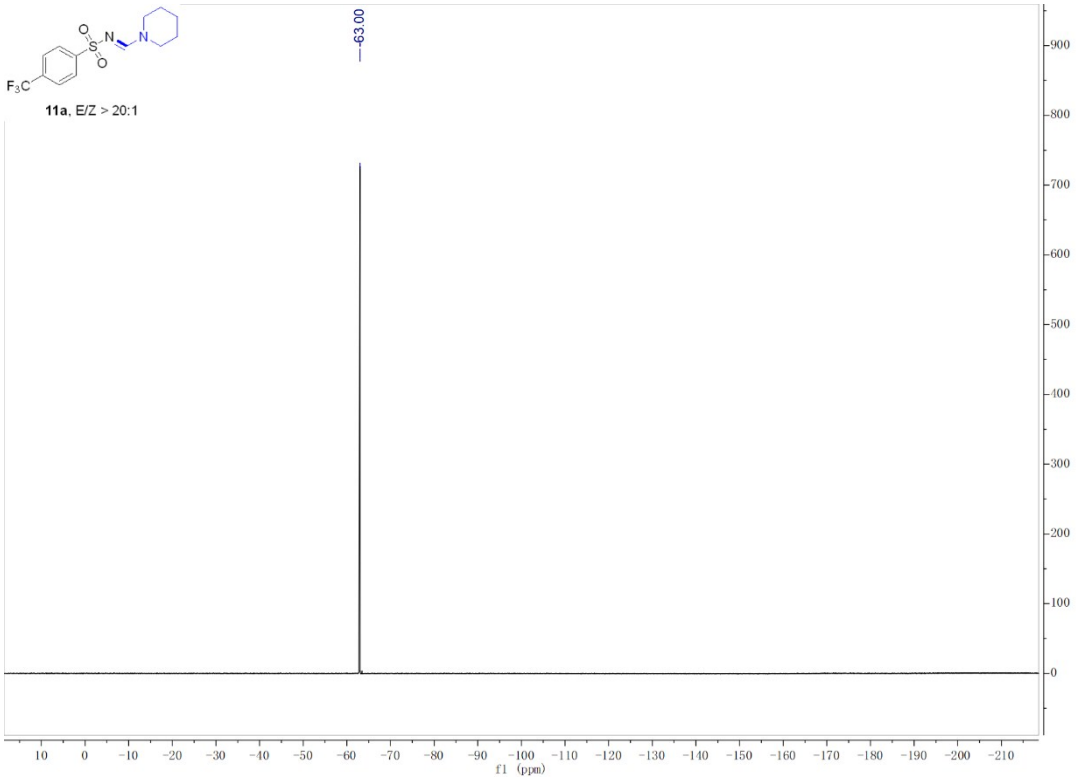




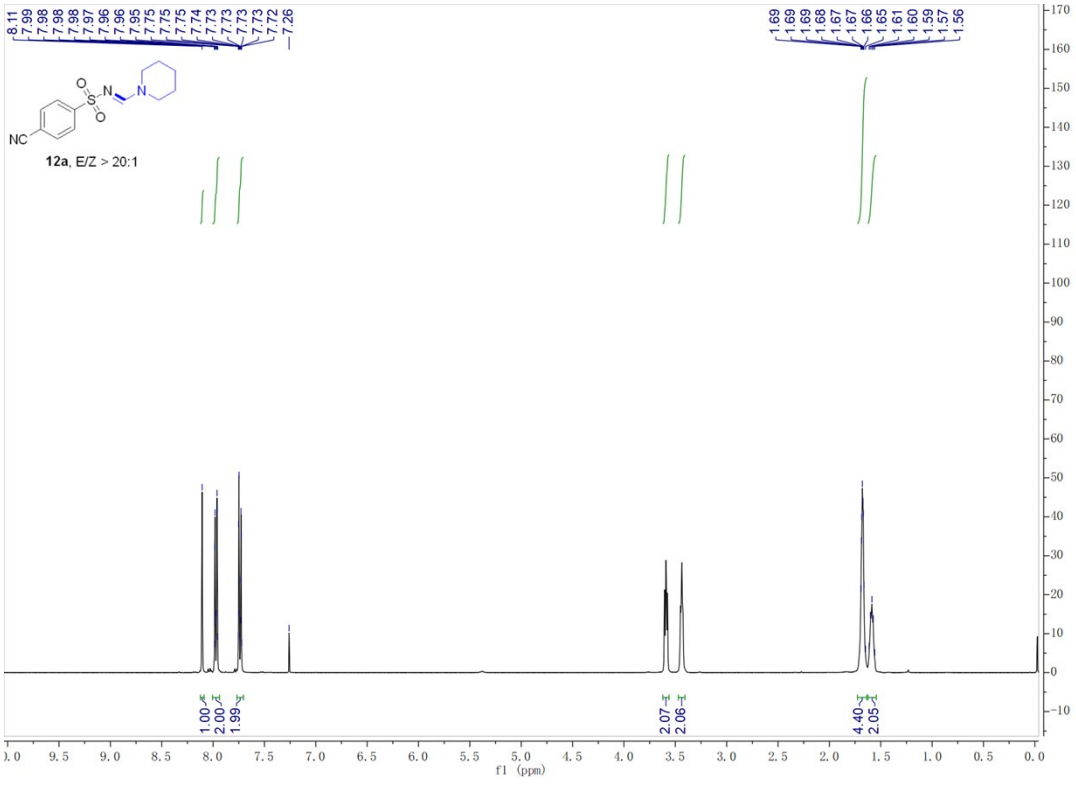
11a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

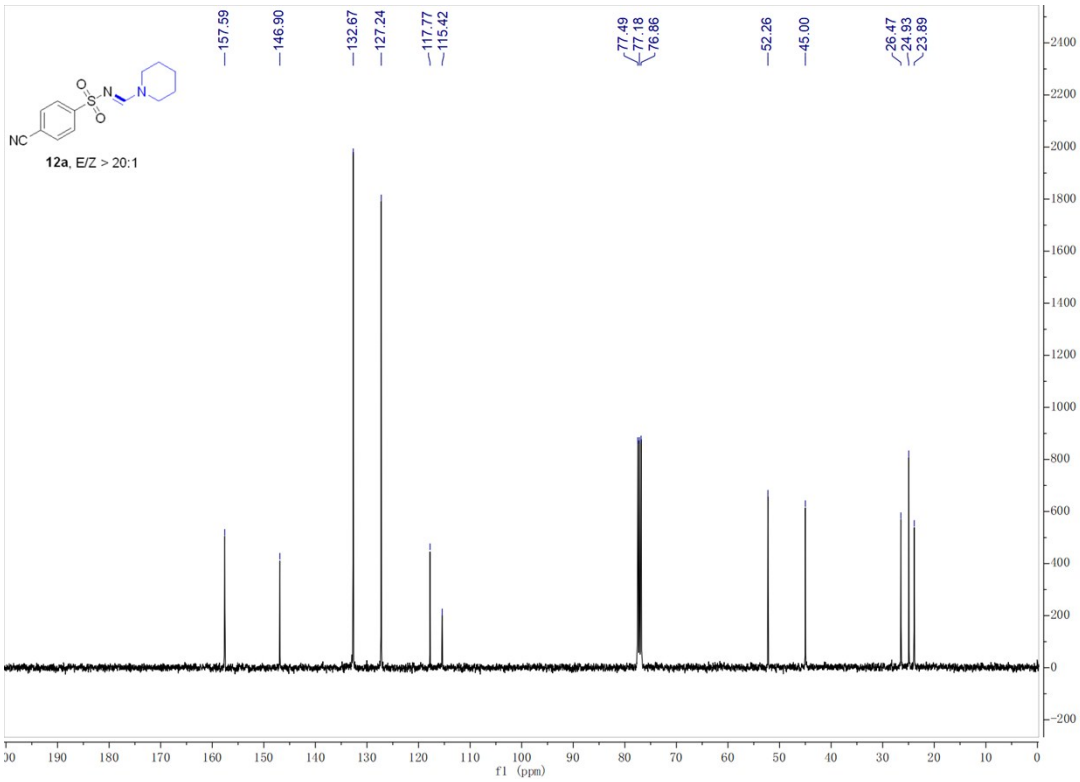




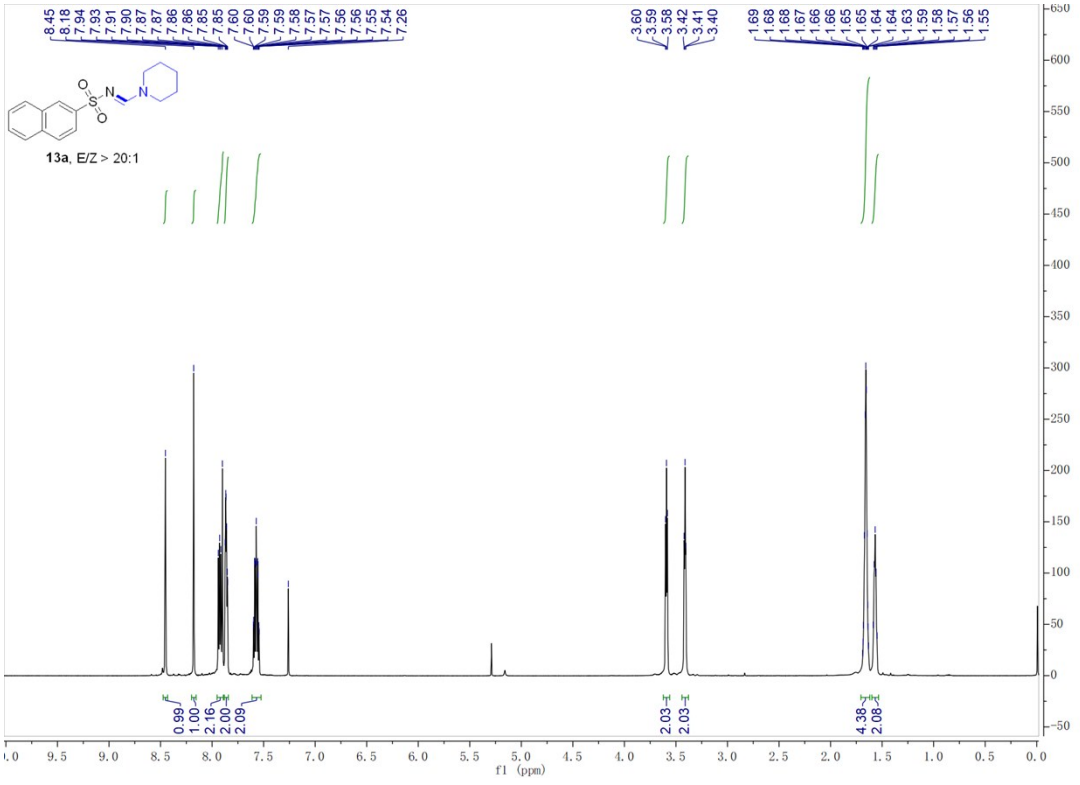


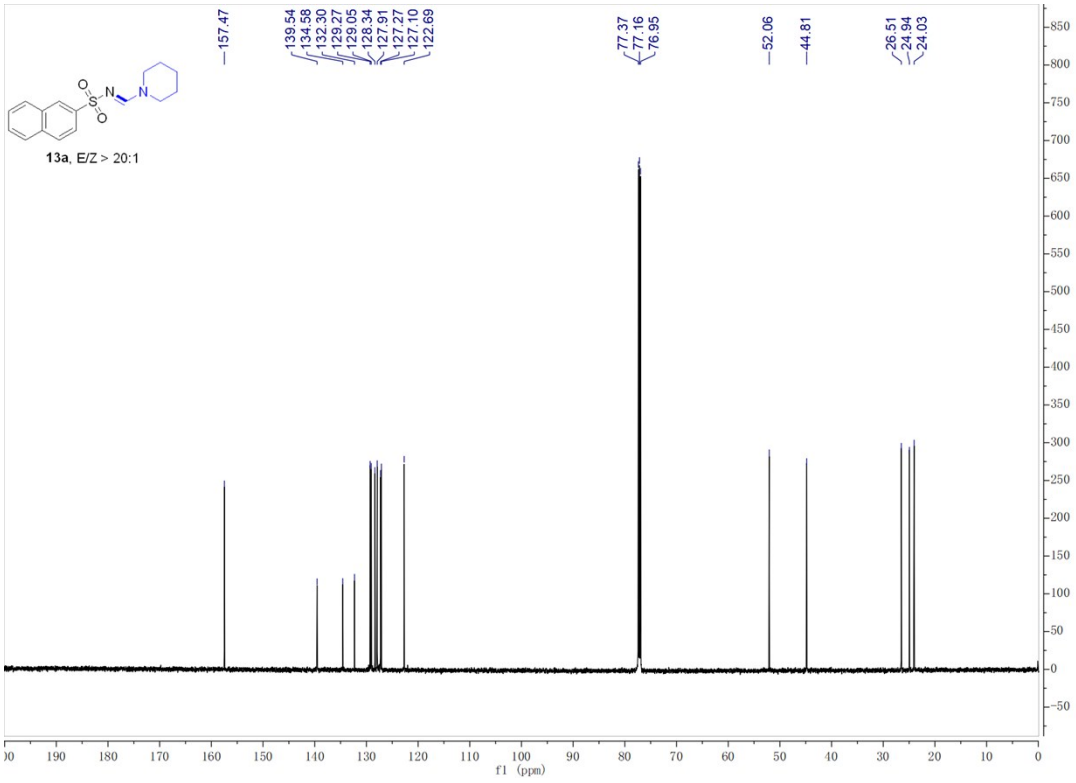
12a ^{1}H, ^{13}C, $CDCl_3$



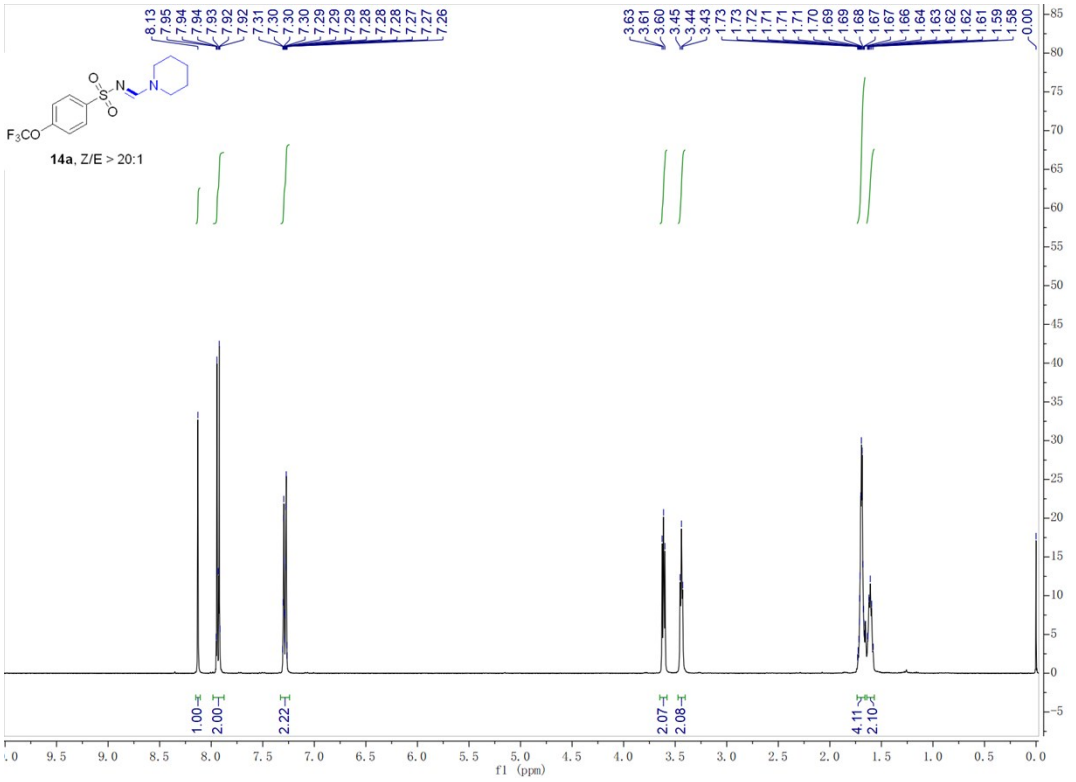


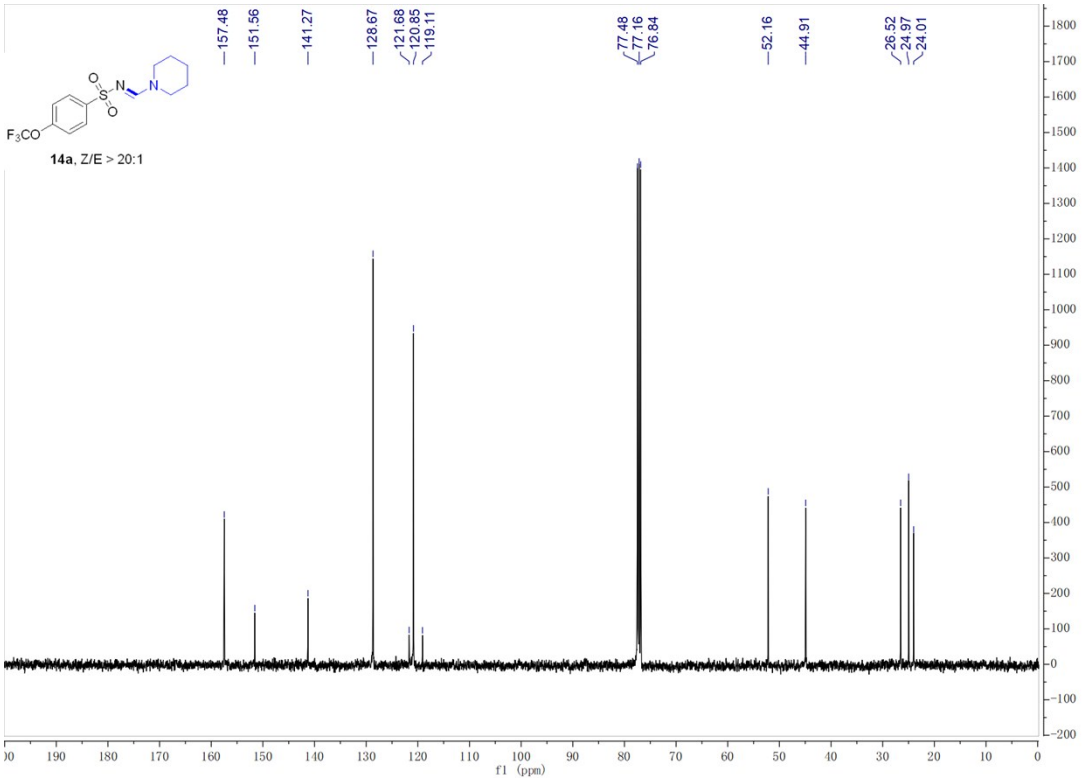
13a ^{1}H, ^{13}C, $CDCl_3$

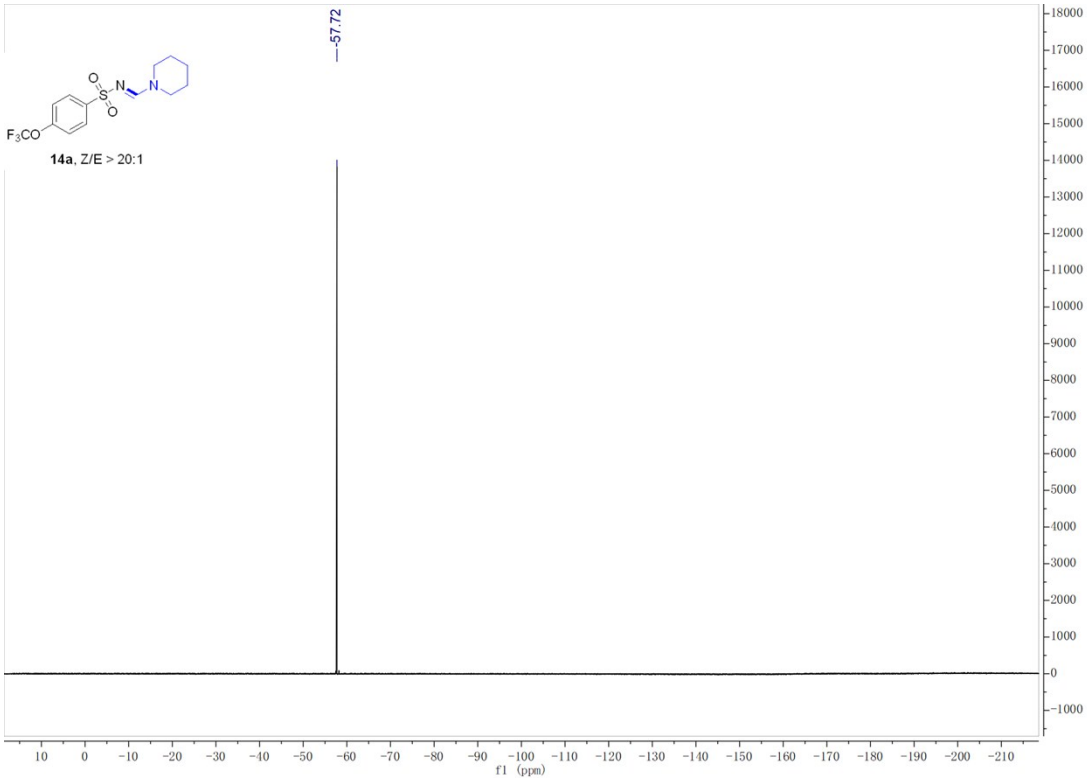




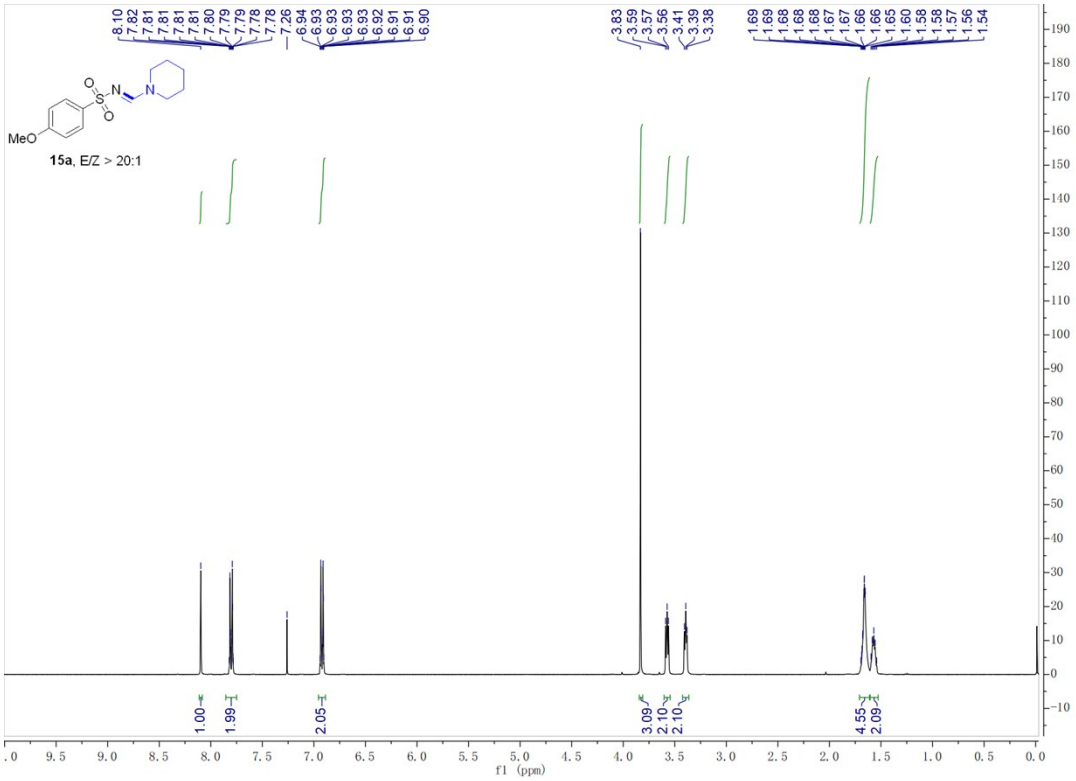
14a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

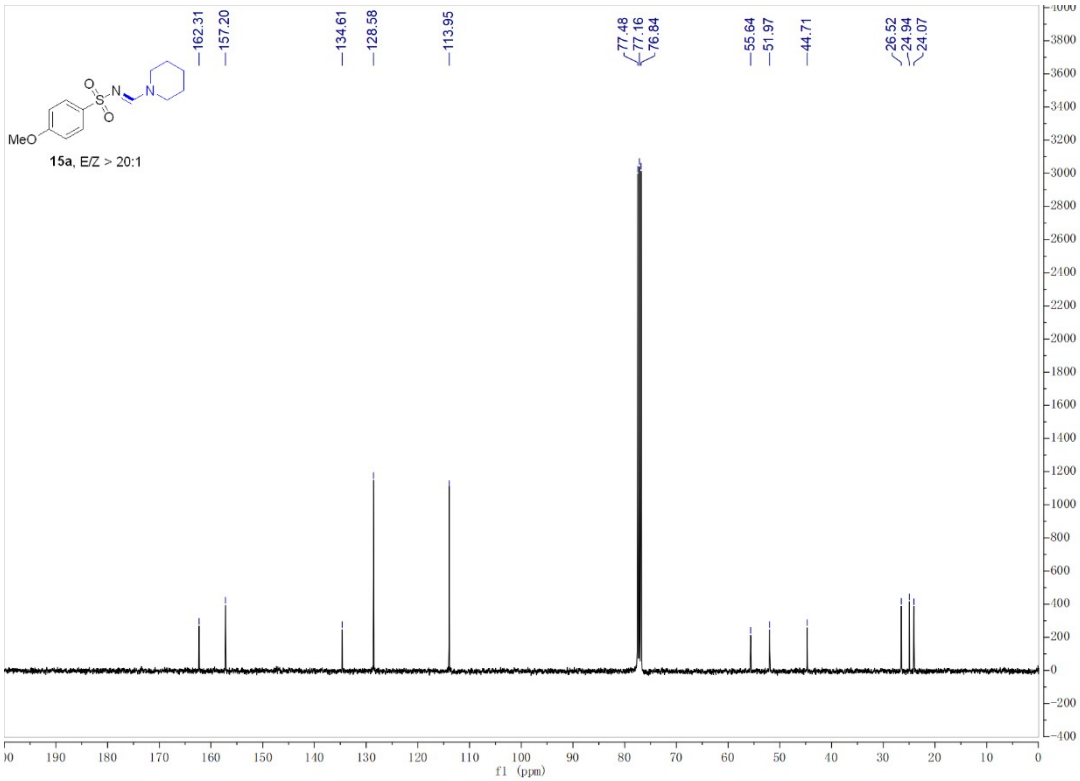



157.48
151.56
141.27
128.67
121.68
120.85
119.11
77.48
77.16
76.84
52.16
44.91
26.52
24.97
24.01
F3CO
14a, Z/E > 20:1
f1 (ppm)

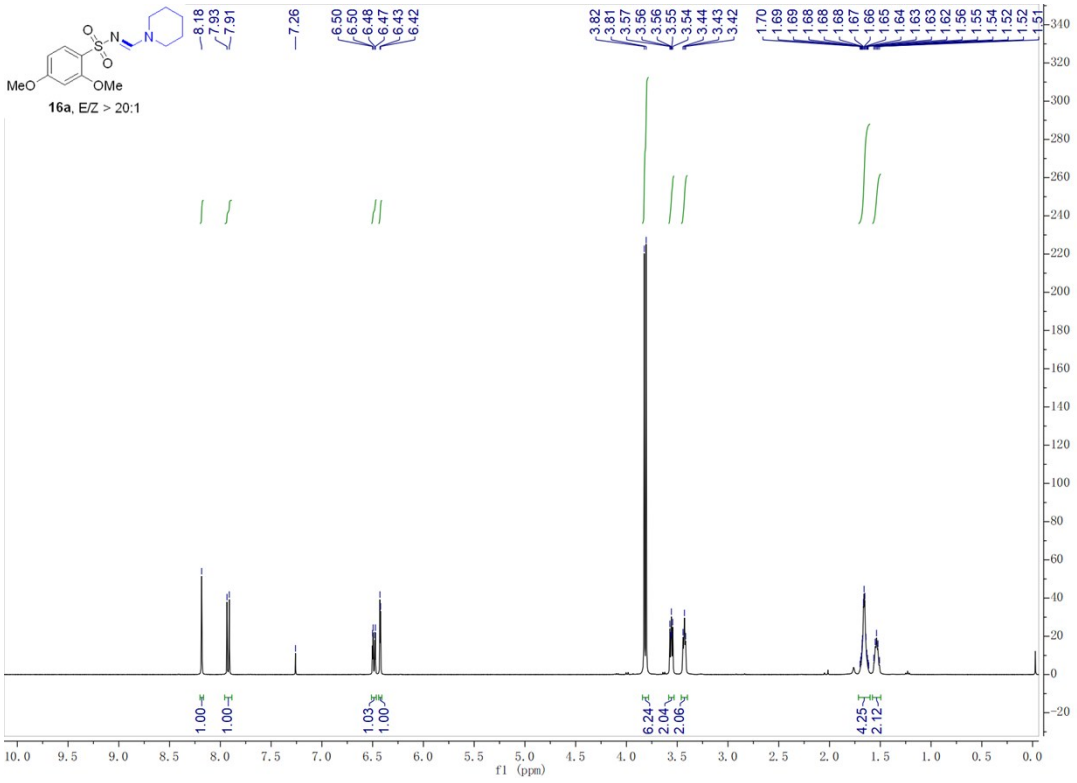

-57.72
F3CO
14a, Z/E > 20:1
f1 (ppm)

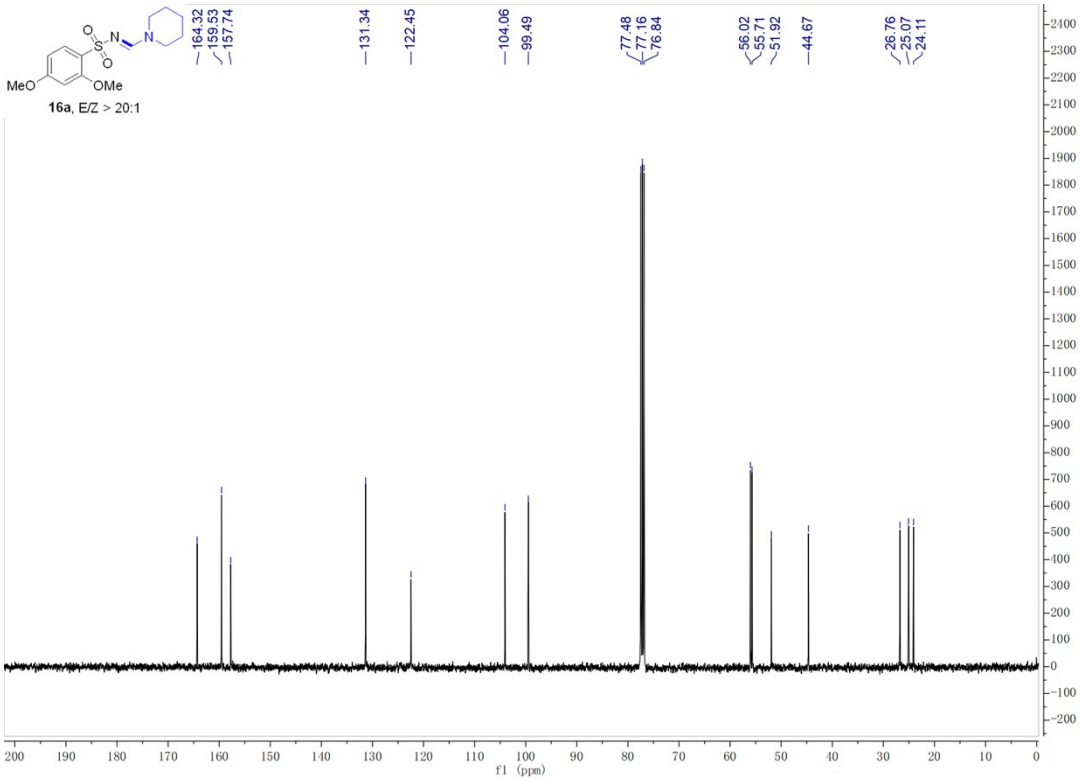
15a ^{1}H, ^{13}C, $CDCl_3$



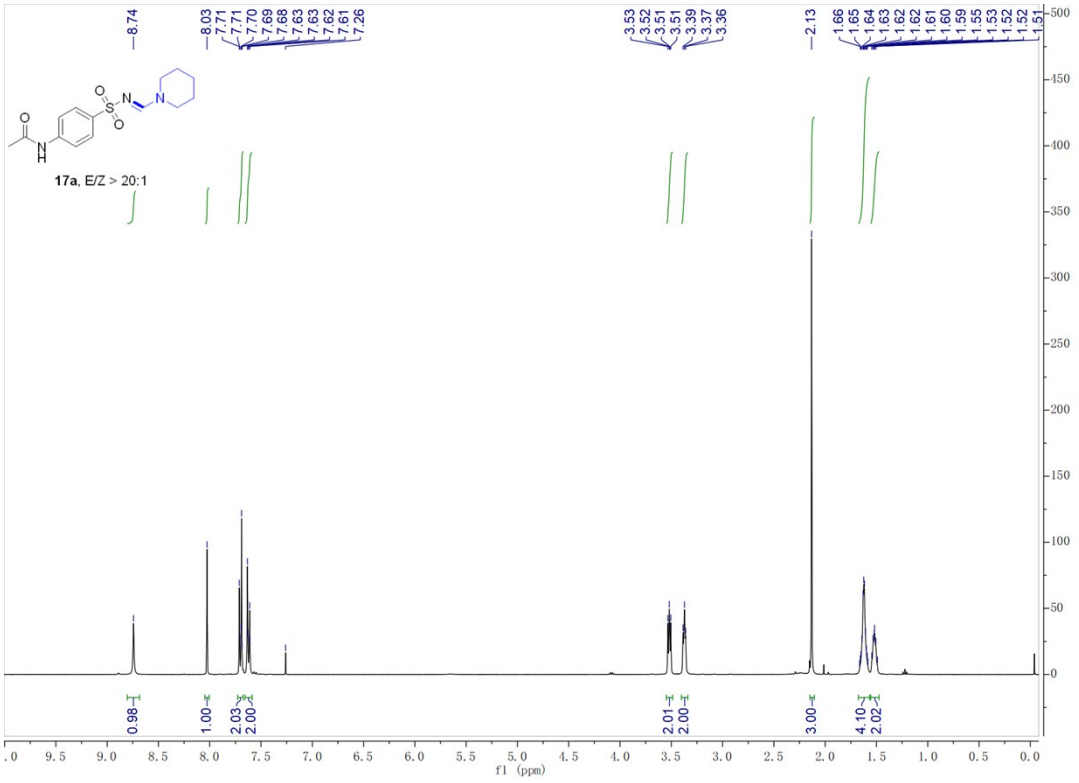


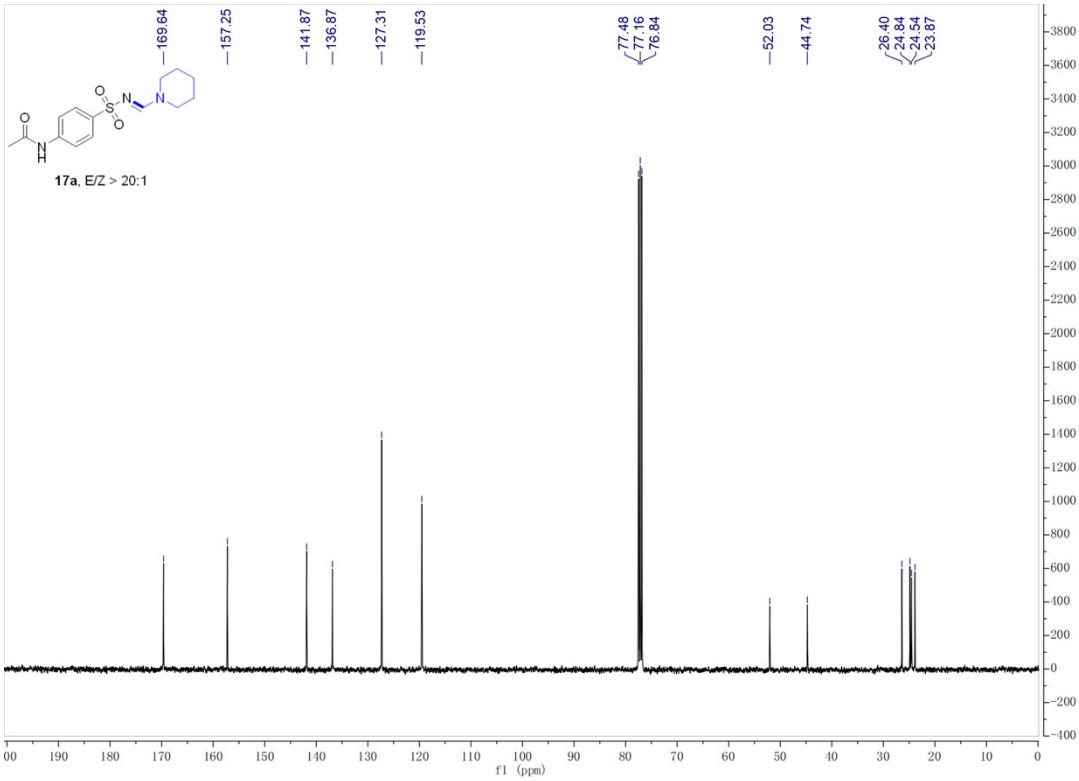
16a ^{1}H, ^{13}C, $CDCl_3$



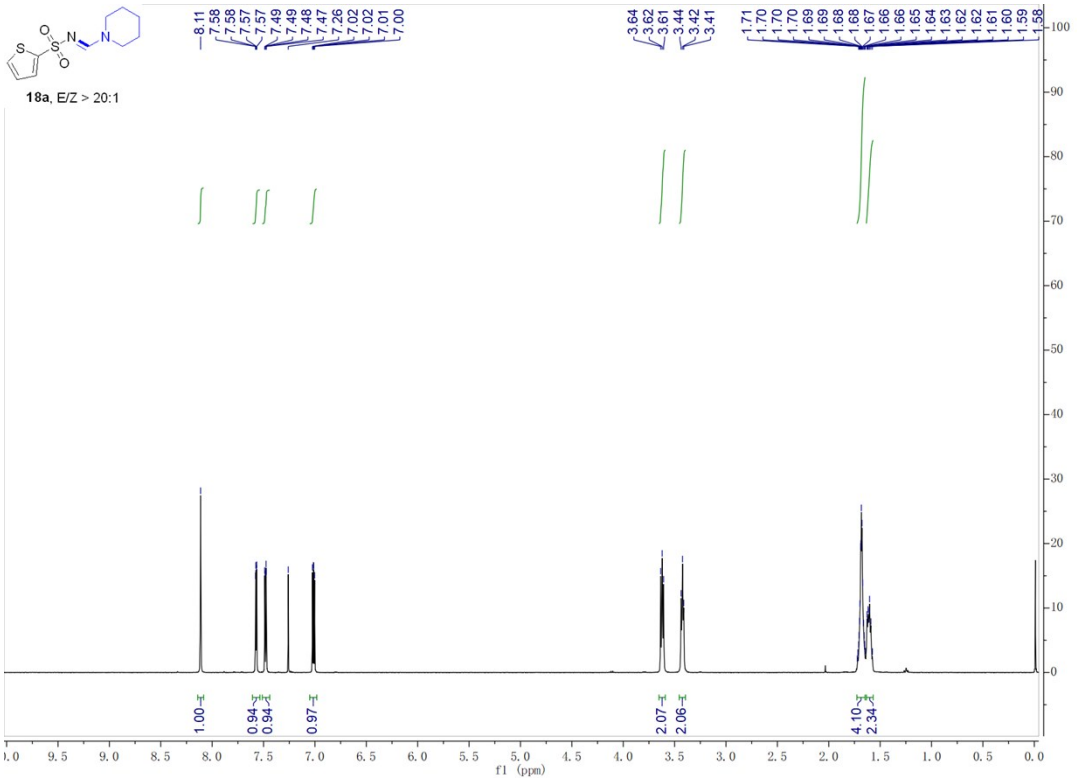


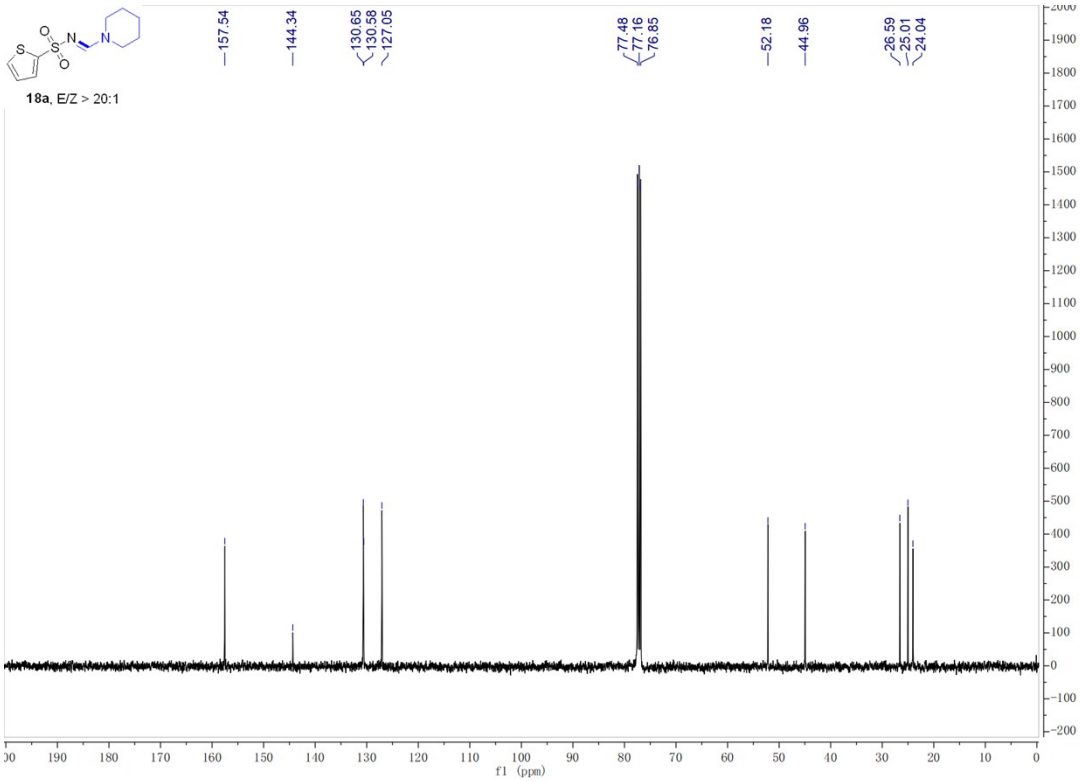
17a ^{1}H, ^{13}C, $CDCl_3$



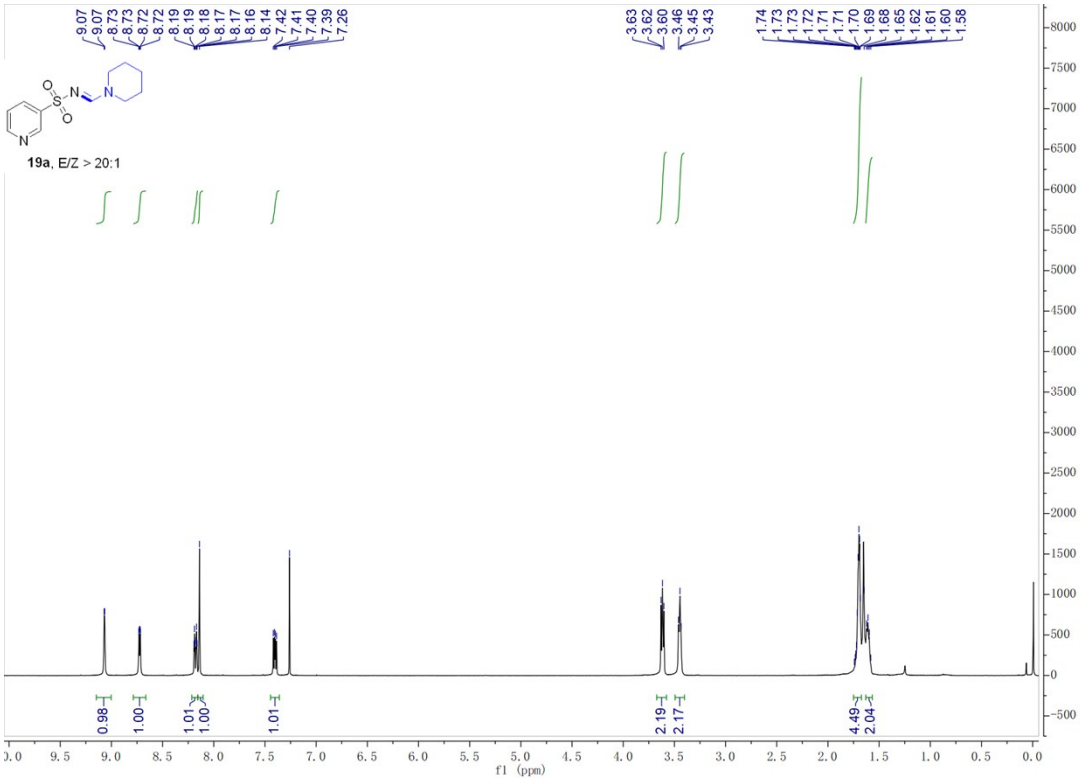


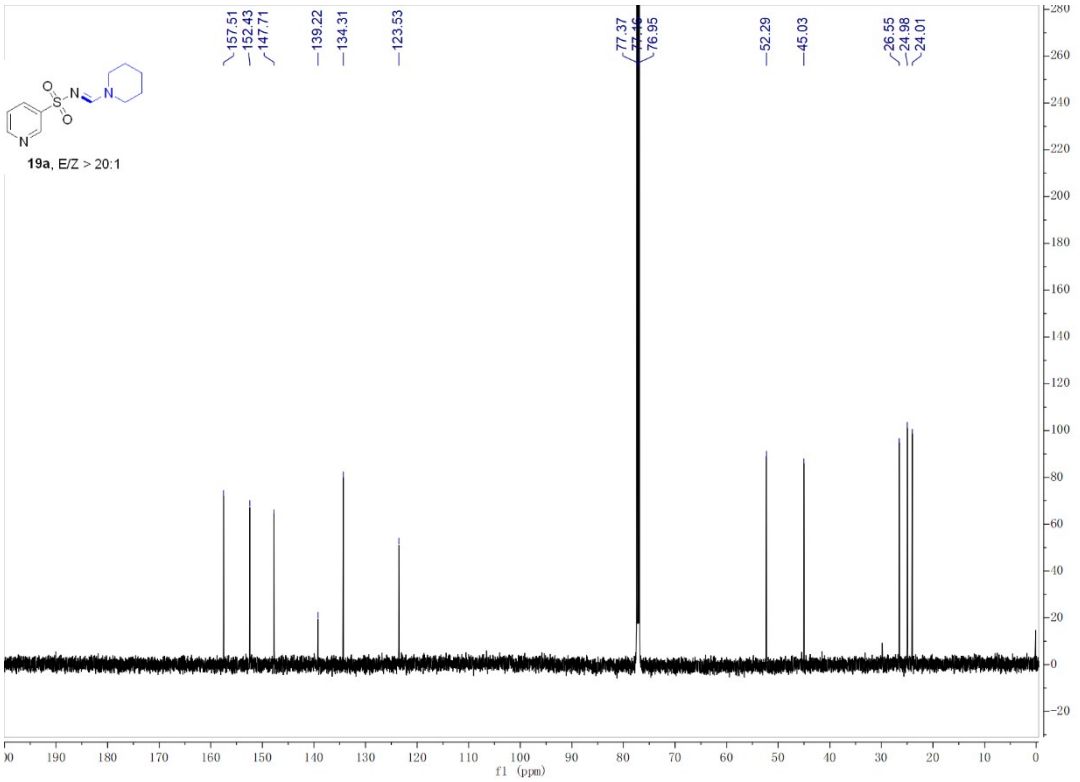
18a ^{1}H, ^{13}C, $CDCl_3$



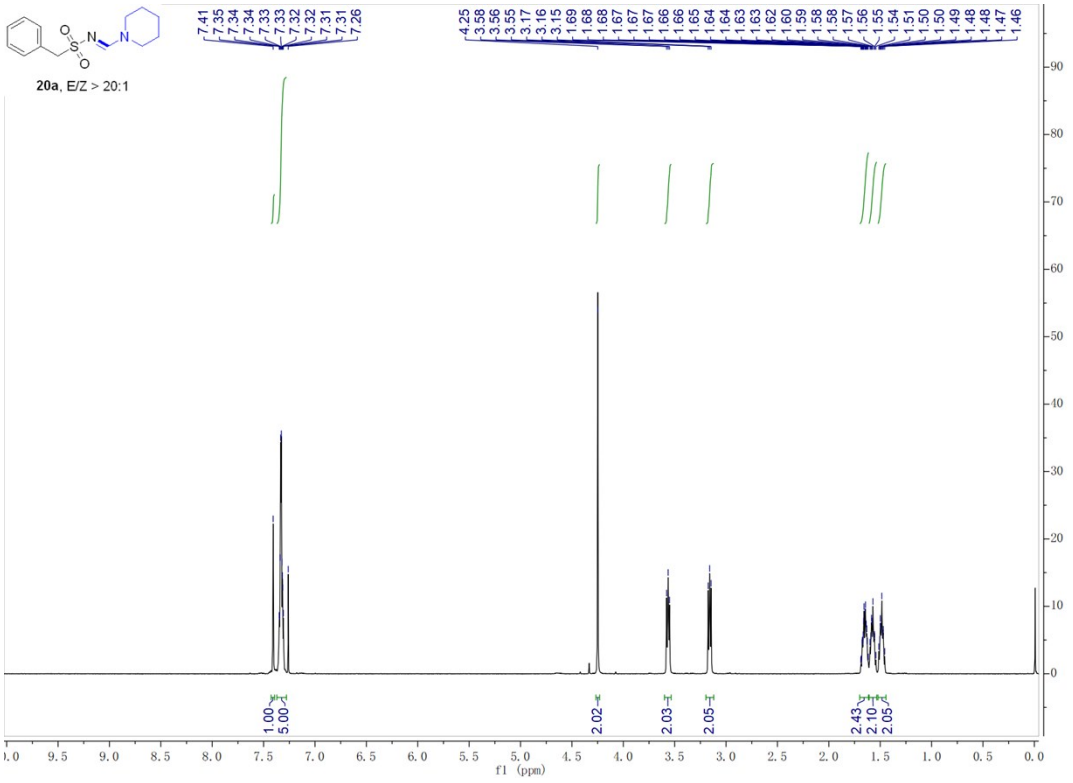


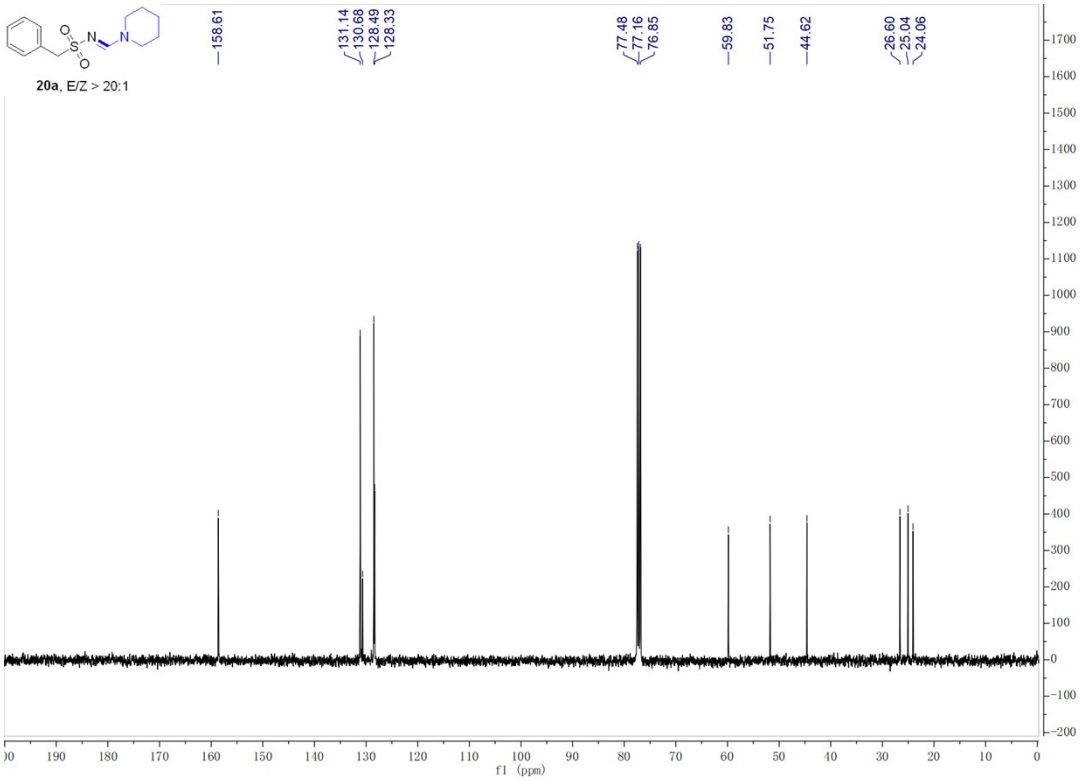
19a ^{1}H, ^{13}C, $CDCl_3$



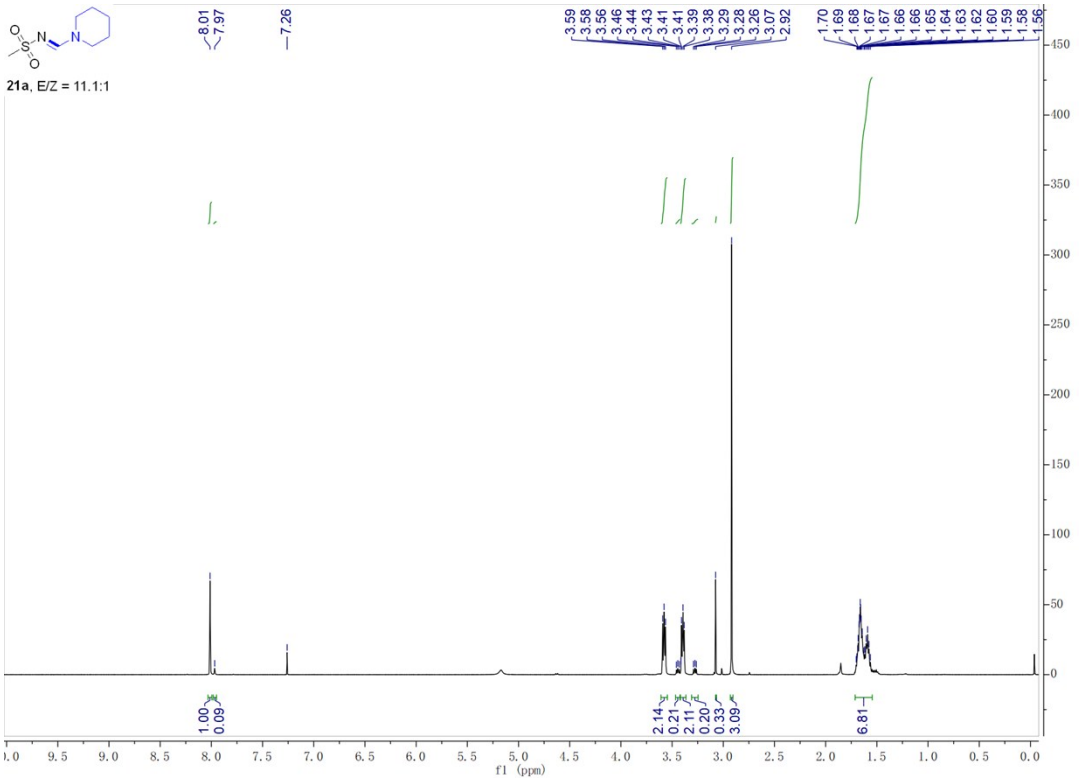


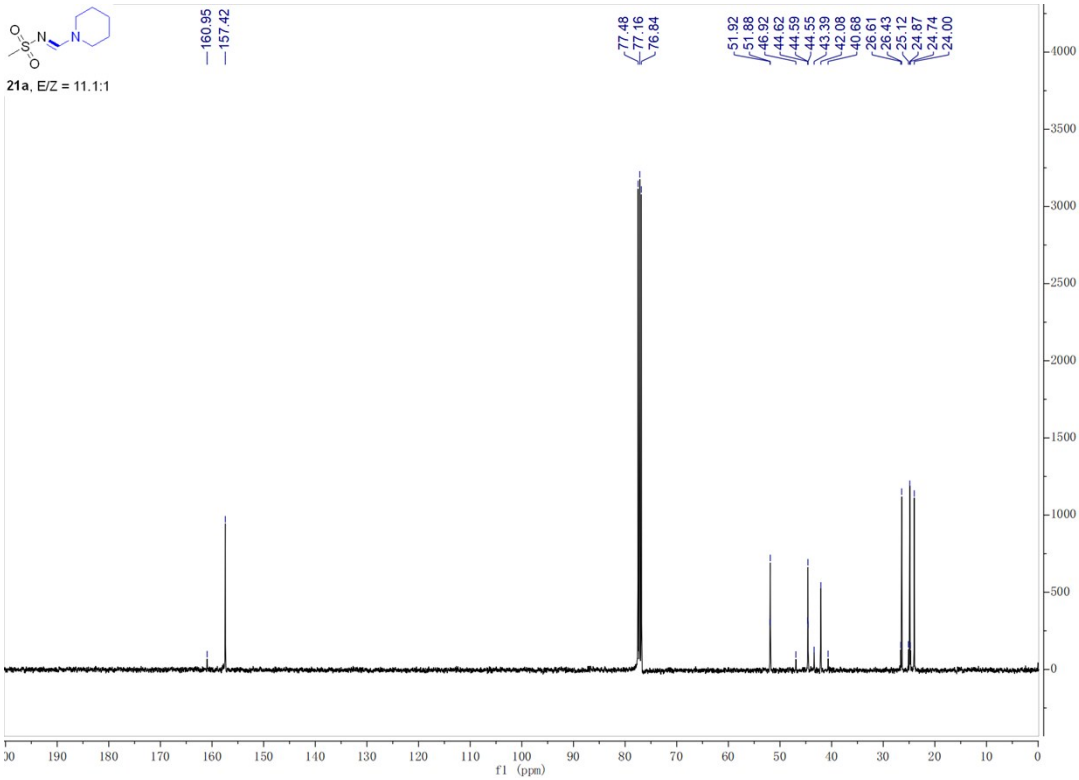
20a ^{1}H, ^{13}C, $CDCl_3$



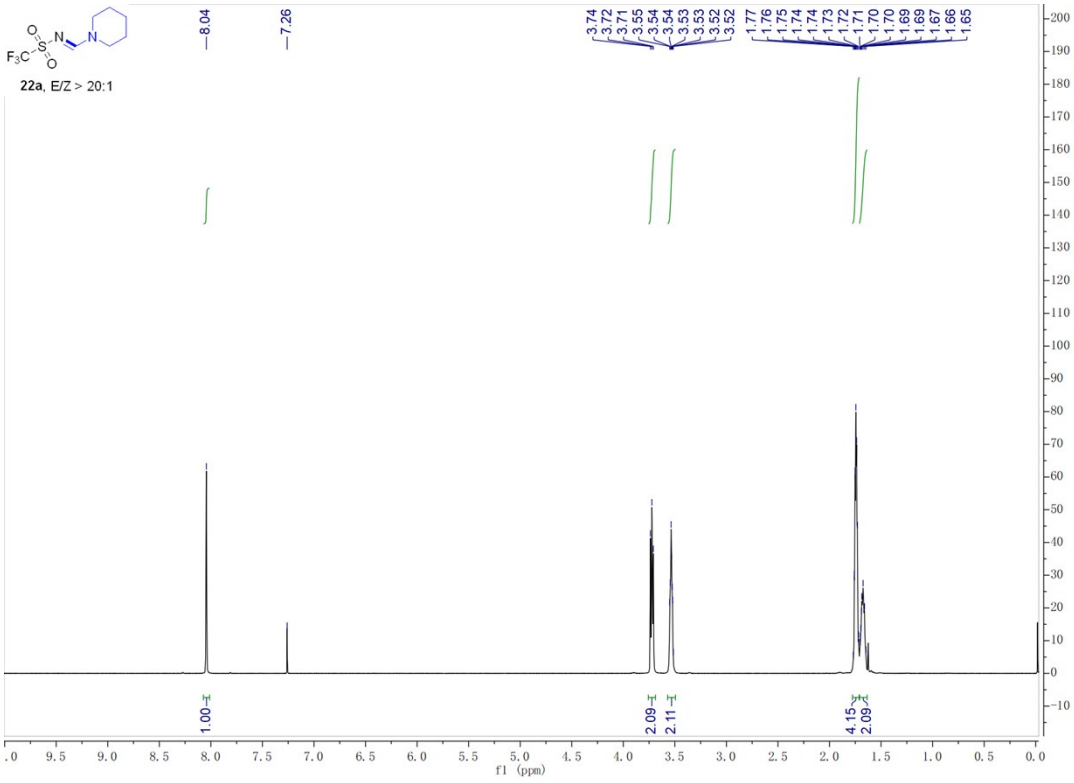


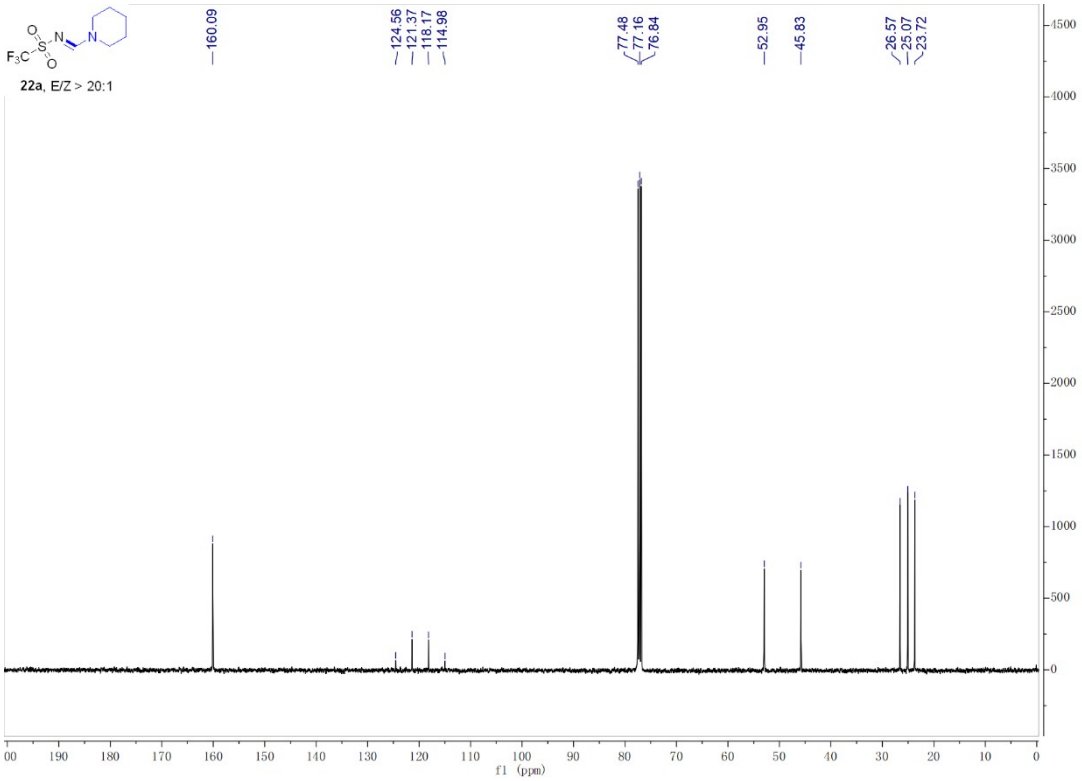
21a ^{1}H, ^{13}C, $CDCl_3$

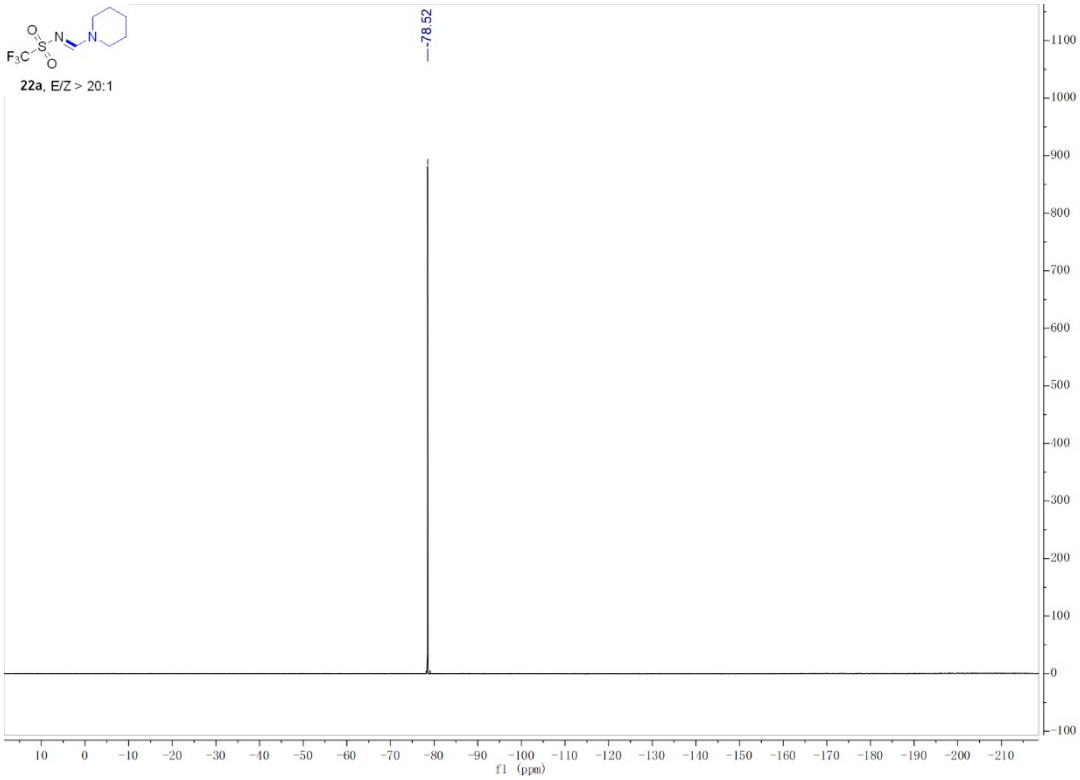




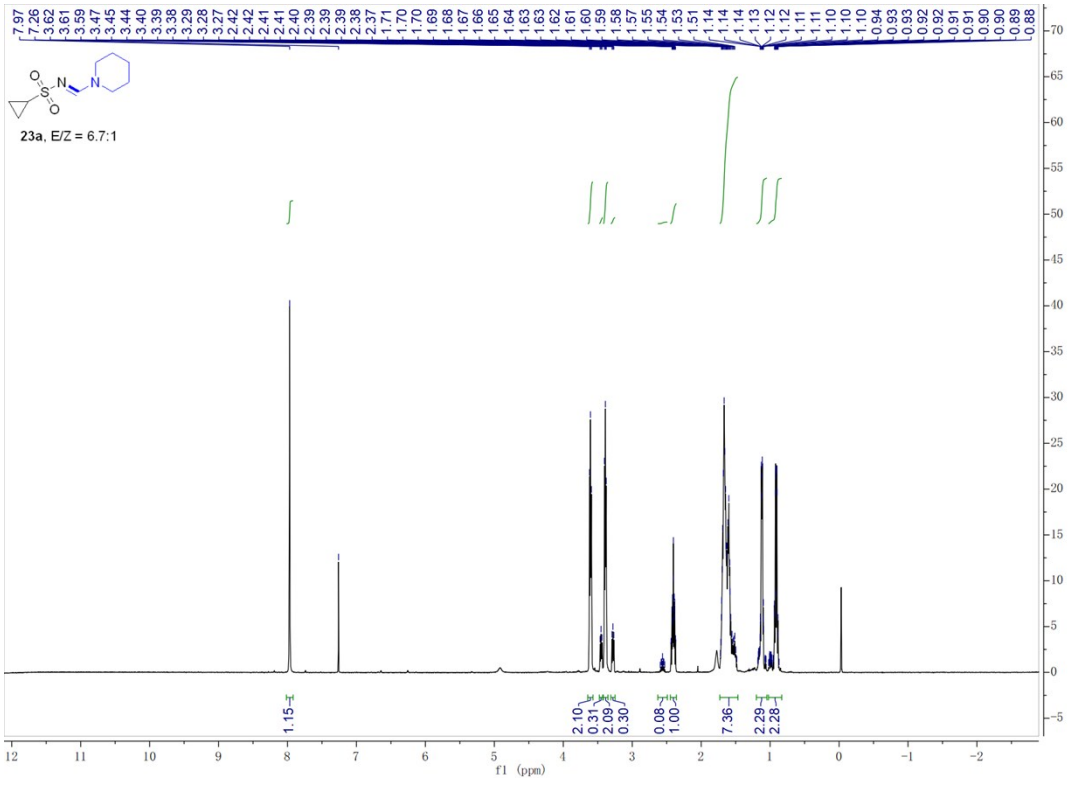
22a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

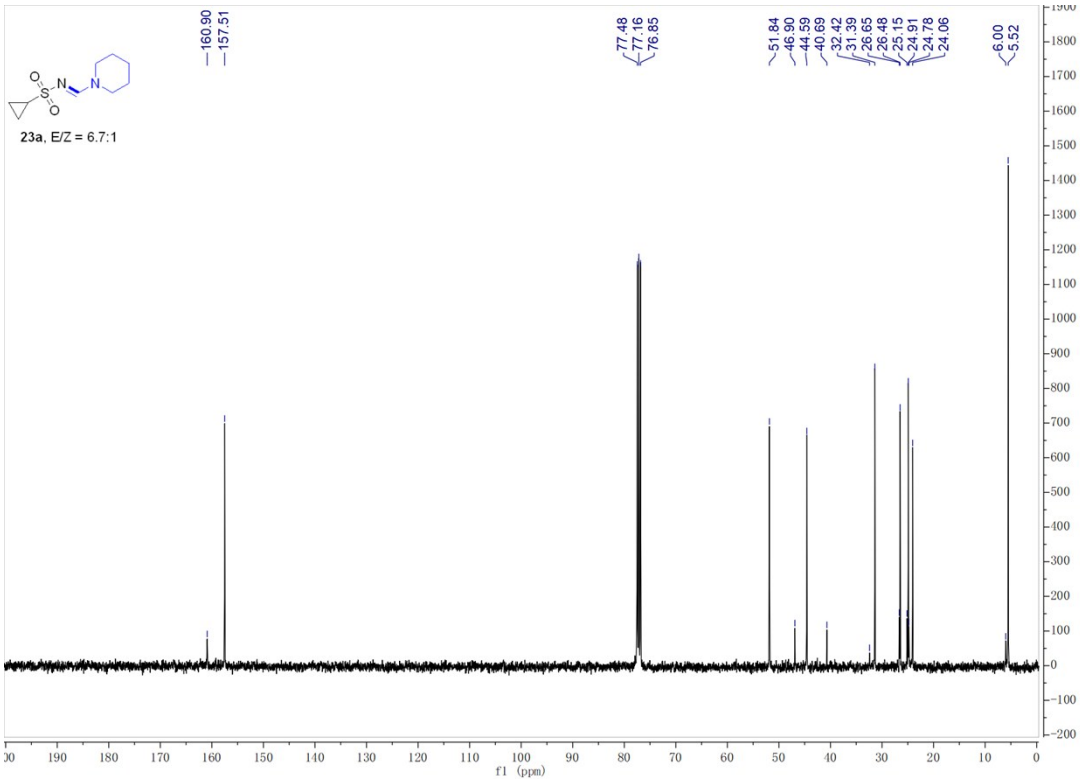




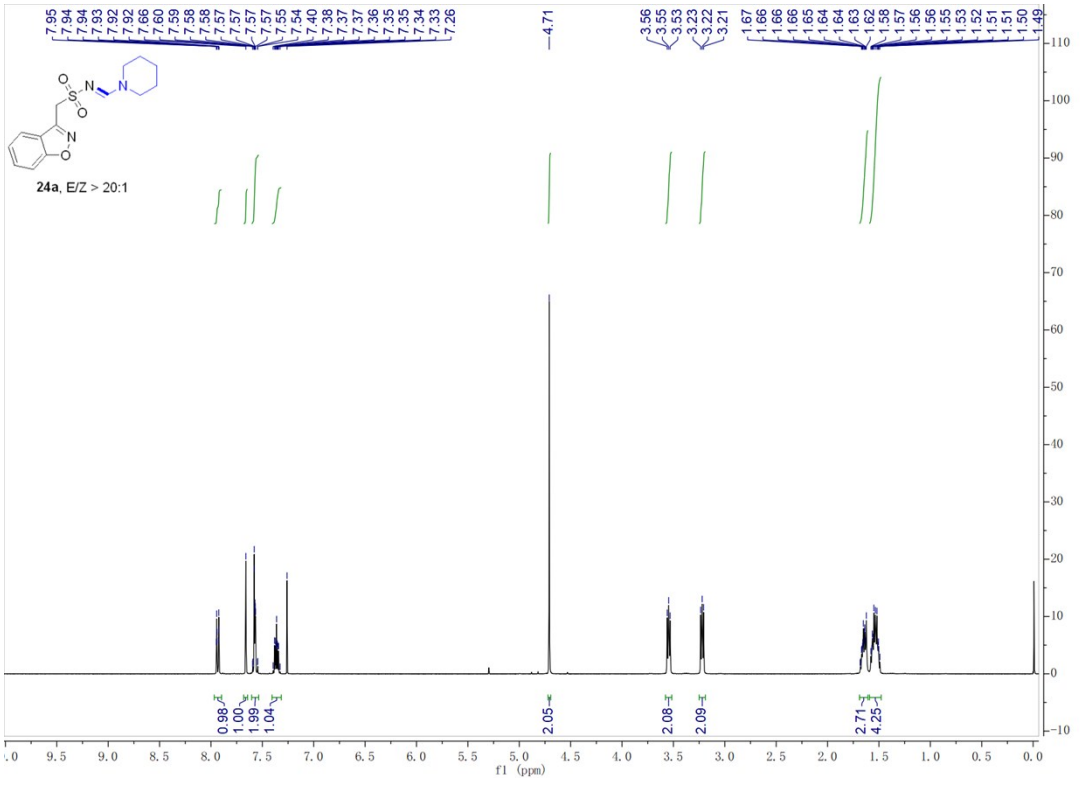


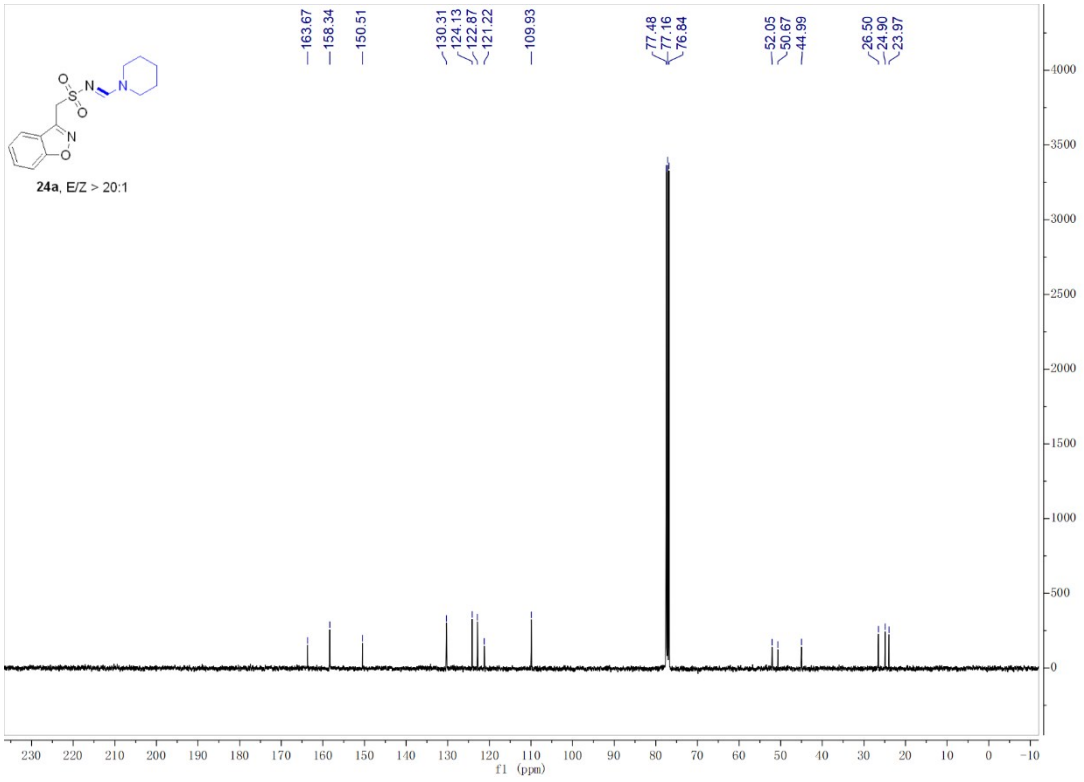
23a ^{1}H, ^{13}C, $CDCl_3$



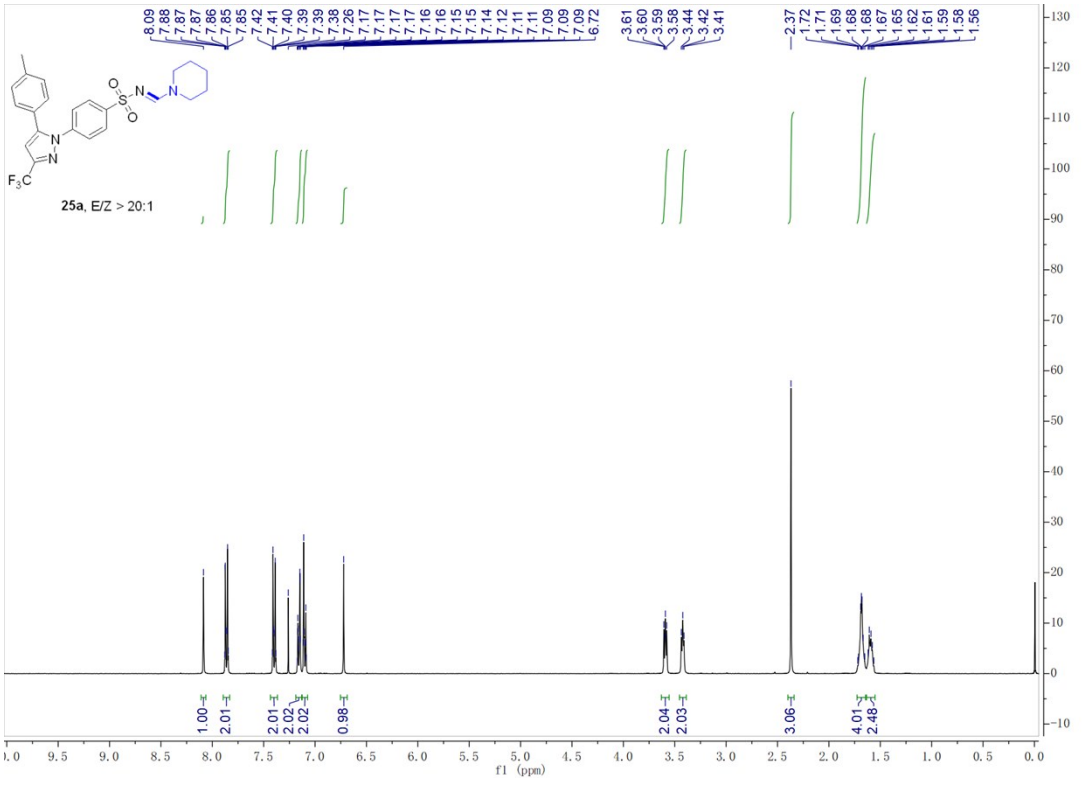


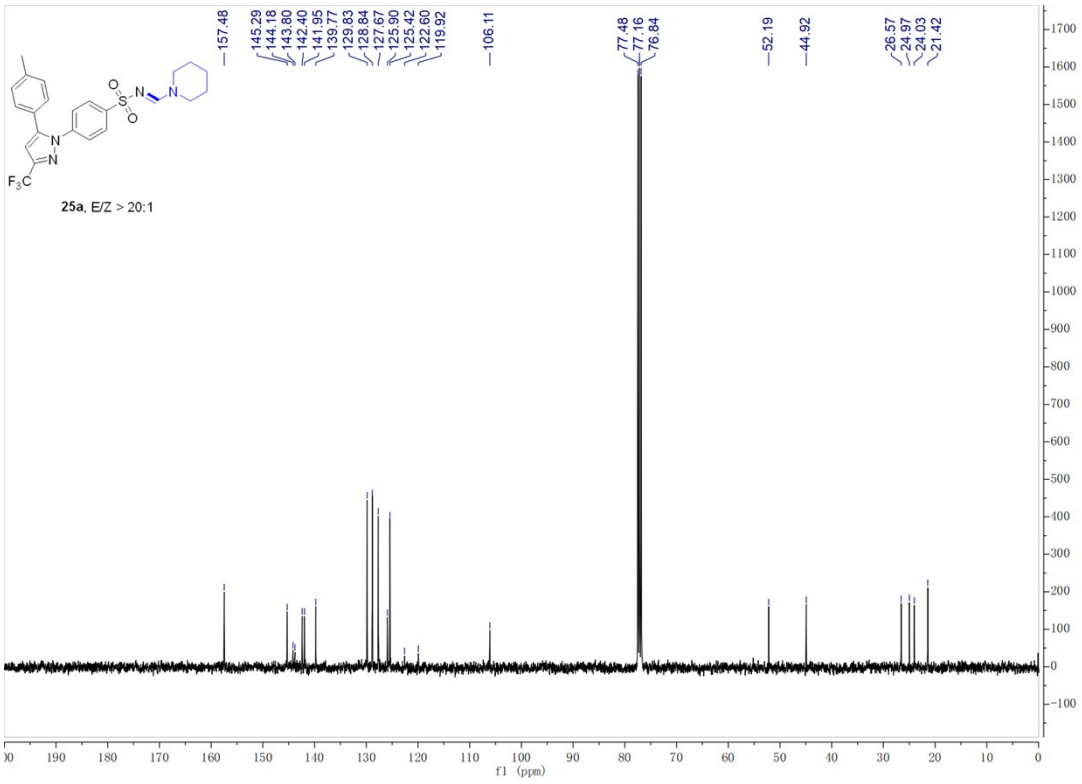
24a ^{1}H, ^{13}C, $CDCl_3$





25a ^{1}H, ^{13}C, ^{19}F, $CDCl_3$

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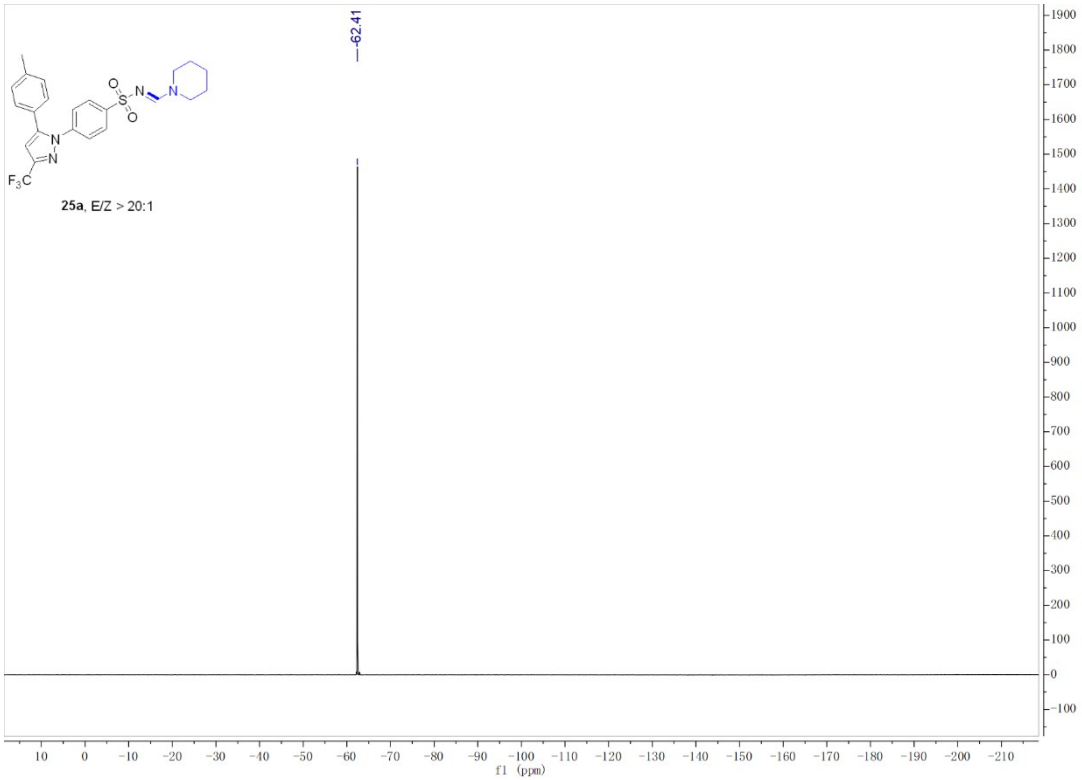
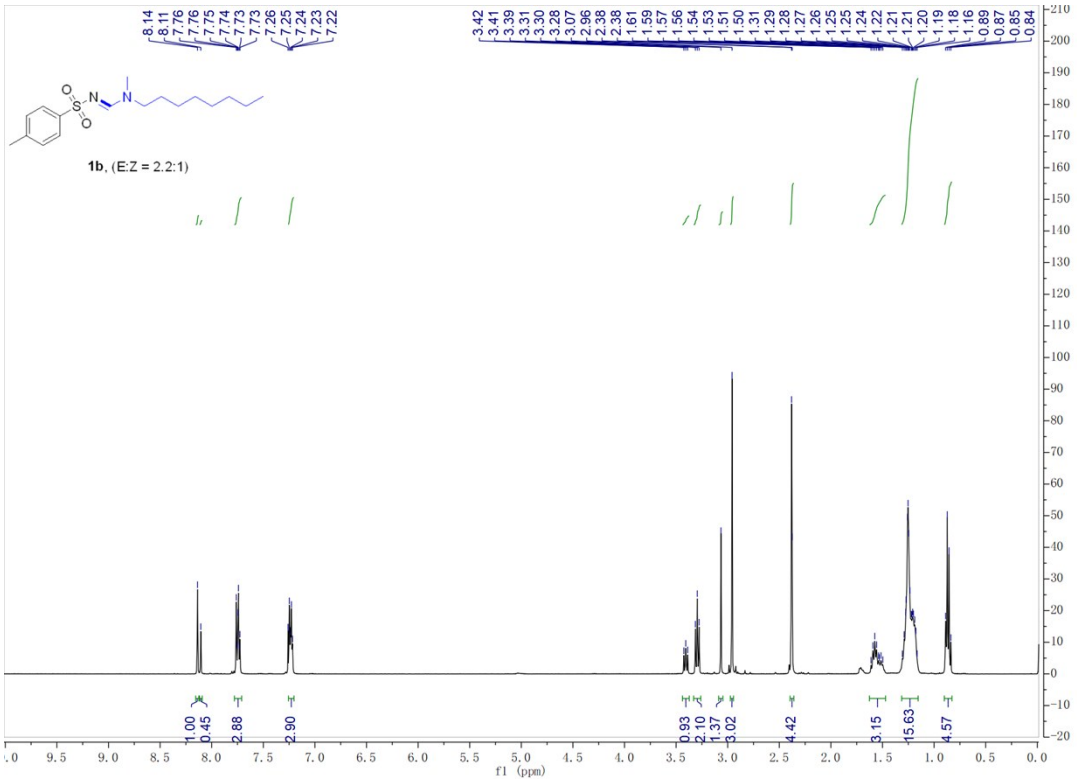
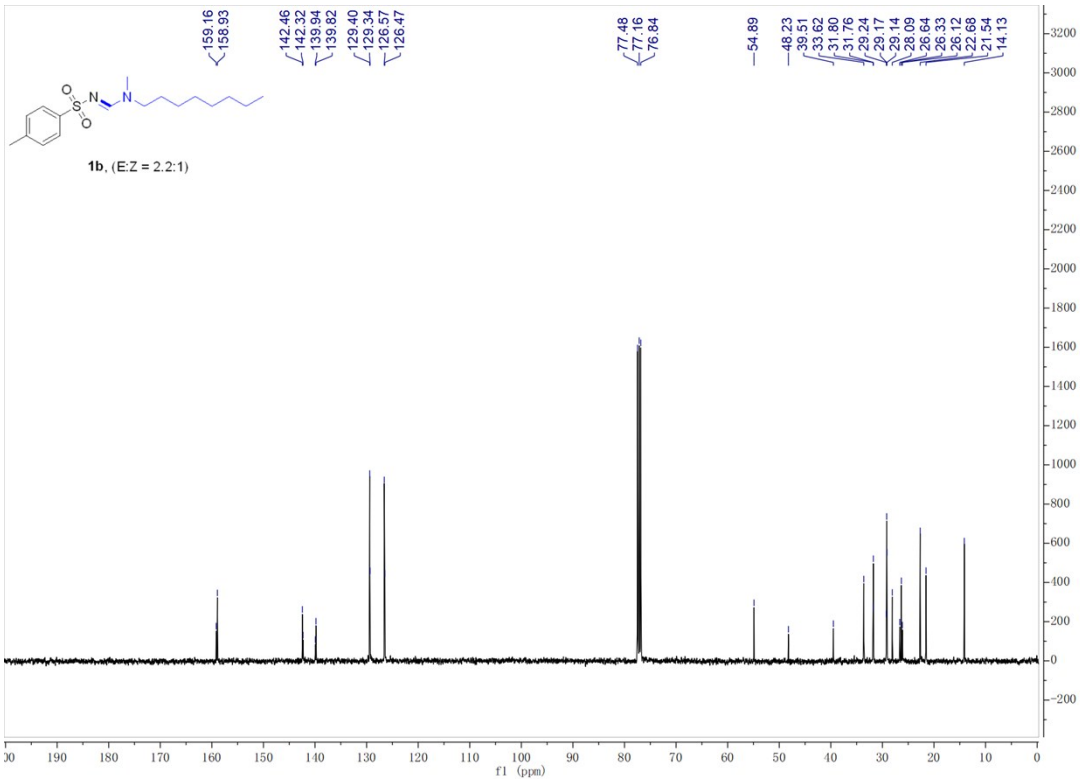
106.11
77.48
77.16
76.84
52.19
44.92
26.57
24.97
24.03
21.42
25a, E/Z > 20:1
f1 (ppm)

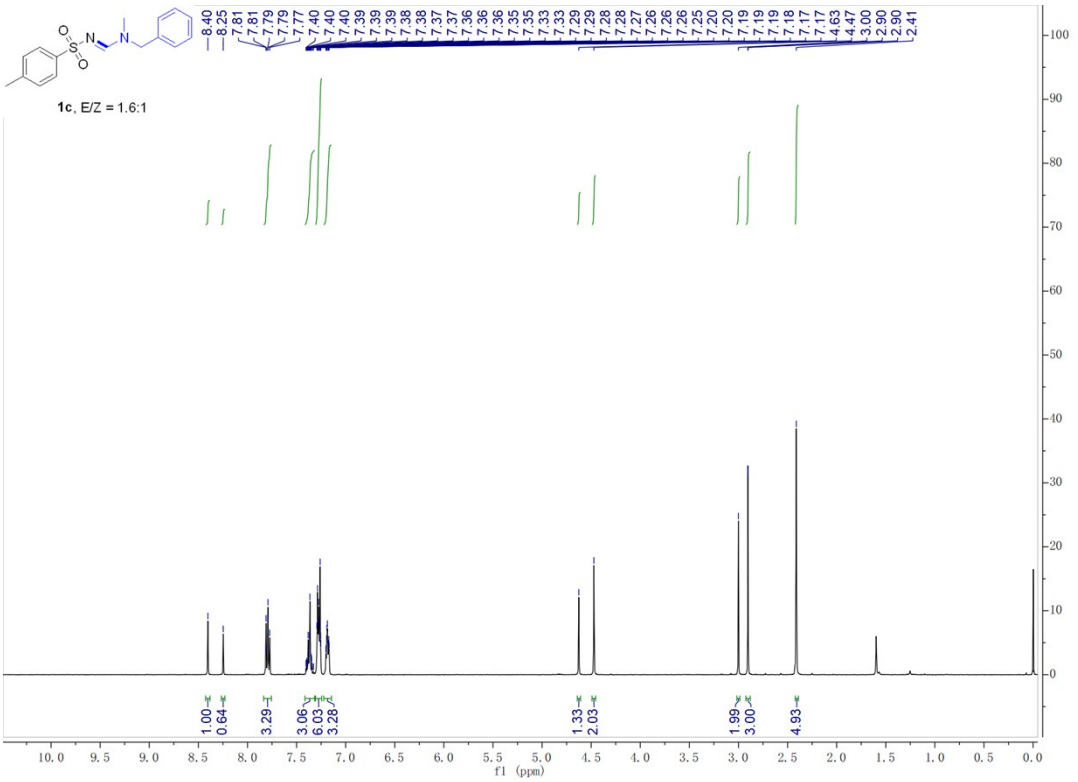

-62.41
25a, E/Z > 20:1
f1 (ppm)

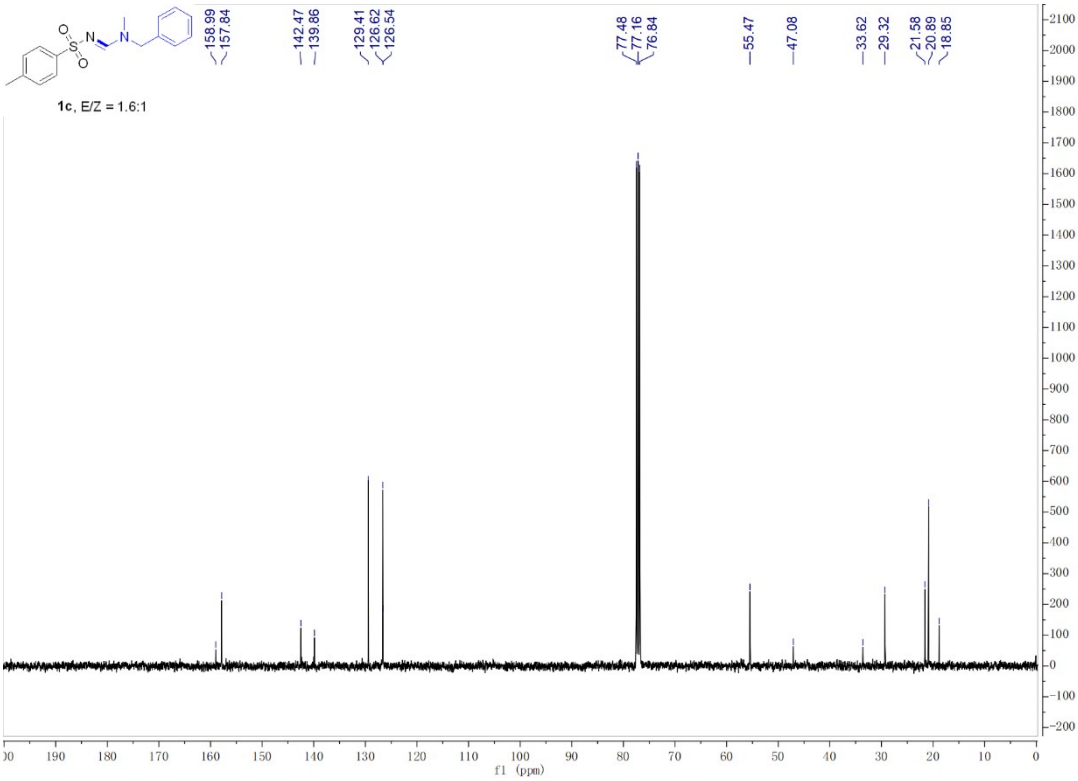
1b ^{1}H, ^{13}C, $CDCl_3$



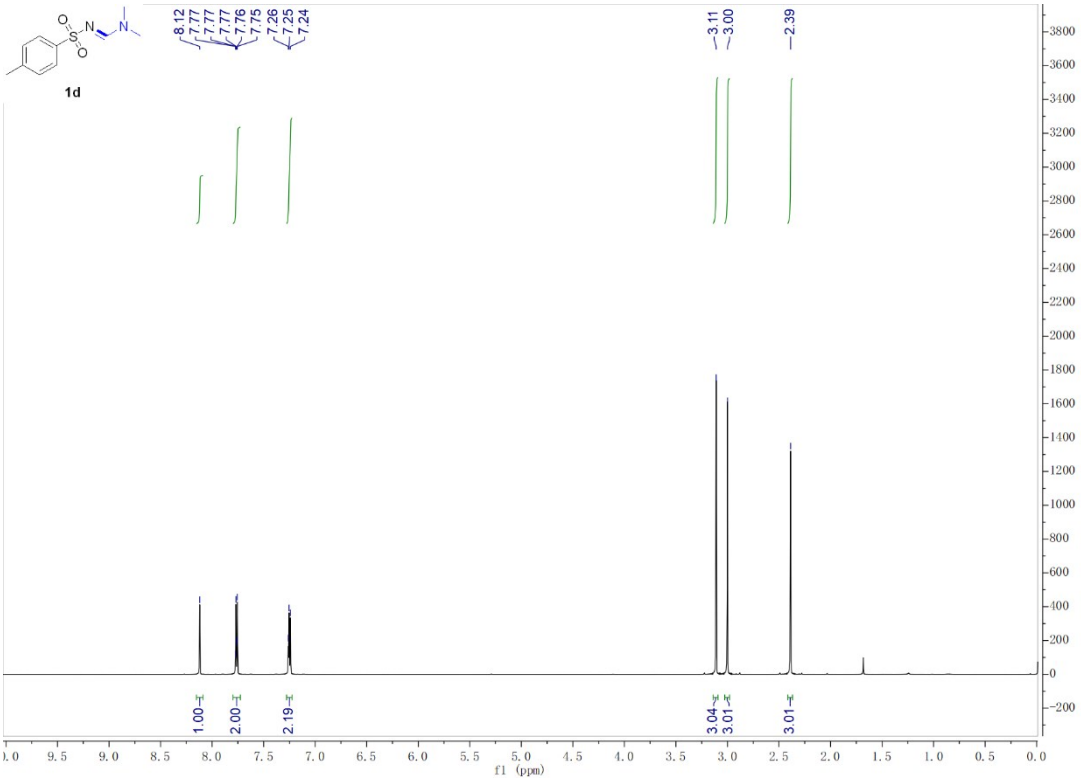


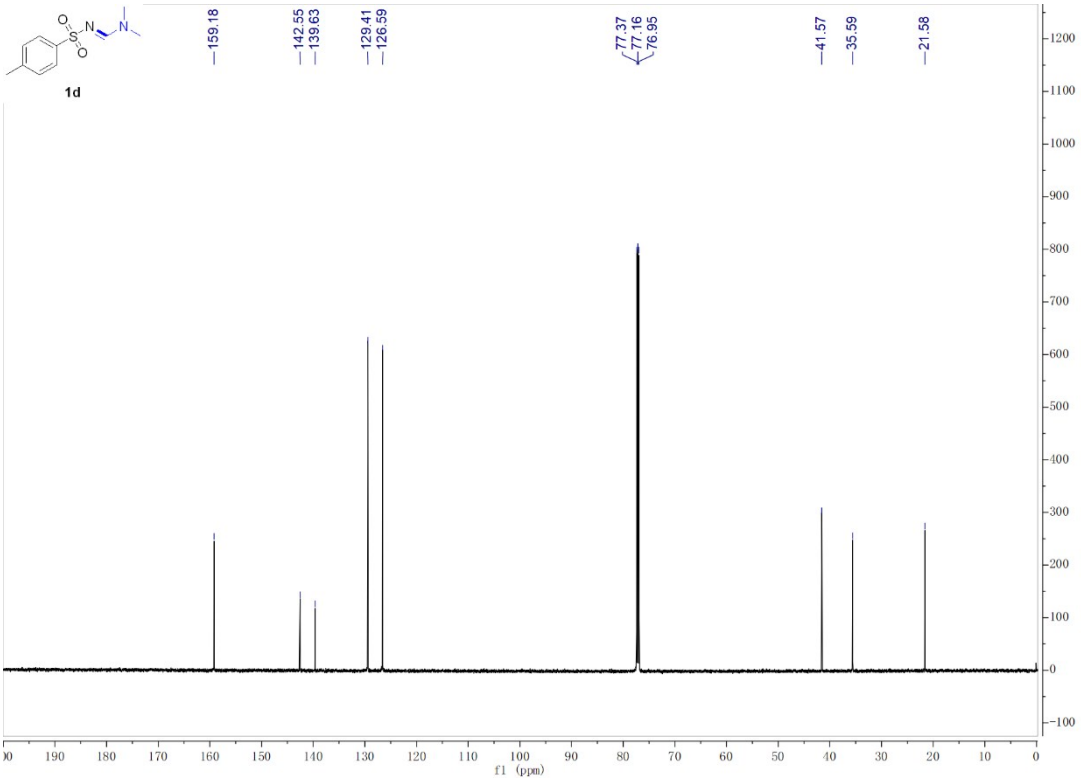
1c ^{1}H, ^{13}C, $CDCl_3$



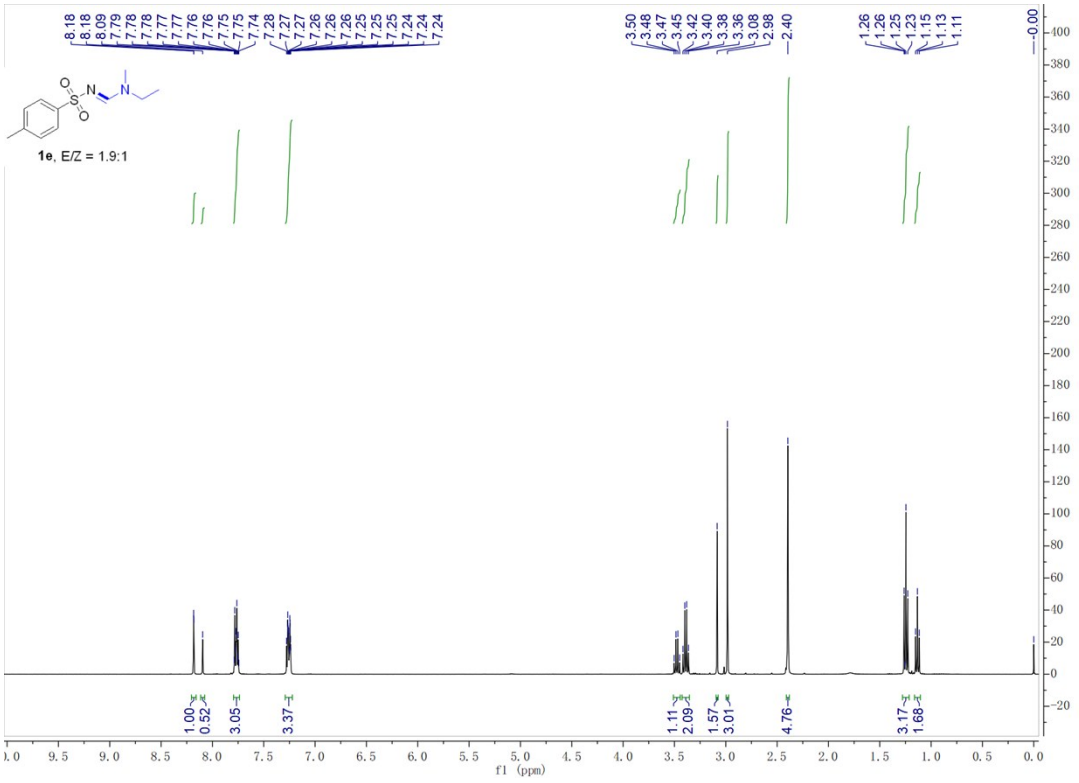


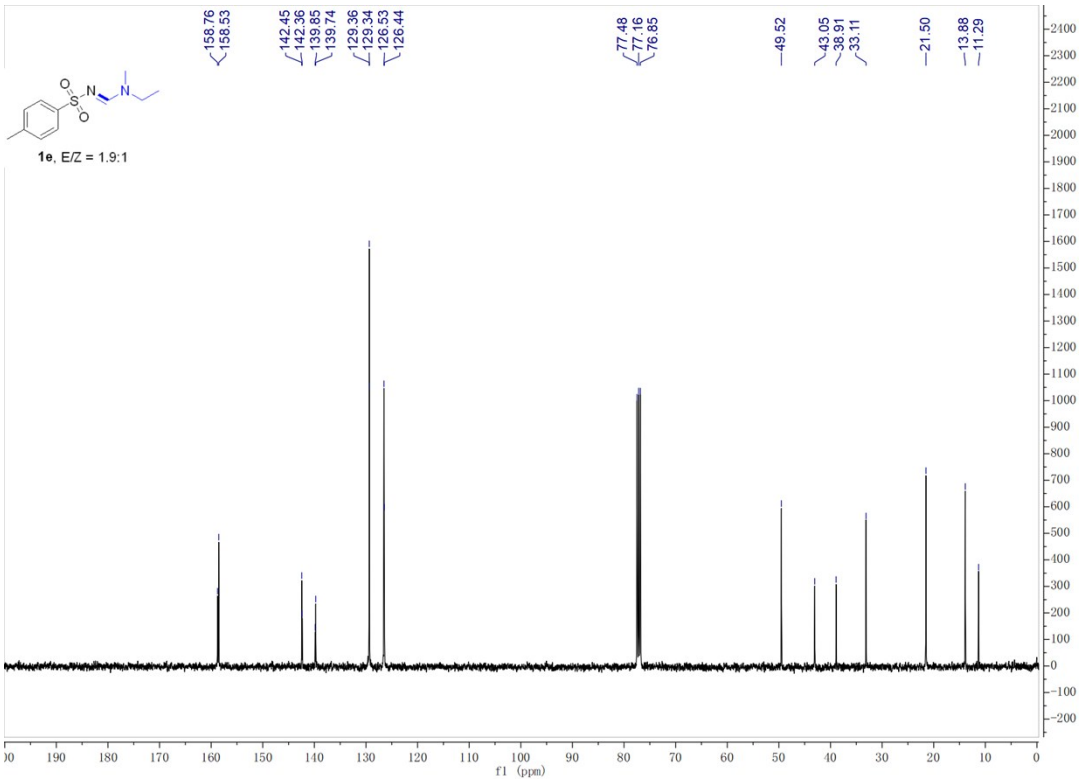
1d ^{1}H, ^{13}C, $CDCl_3$



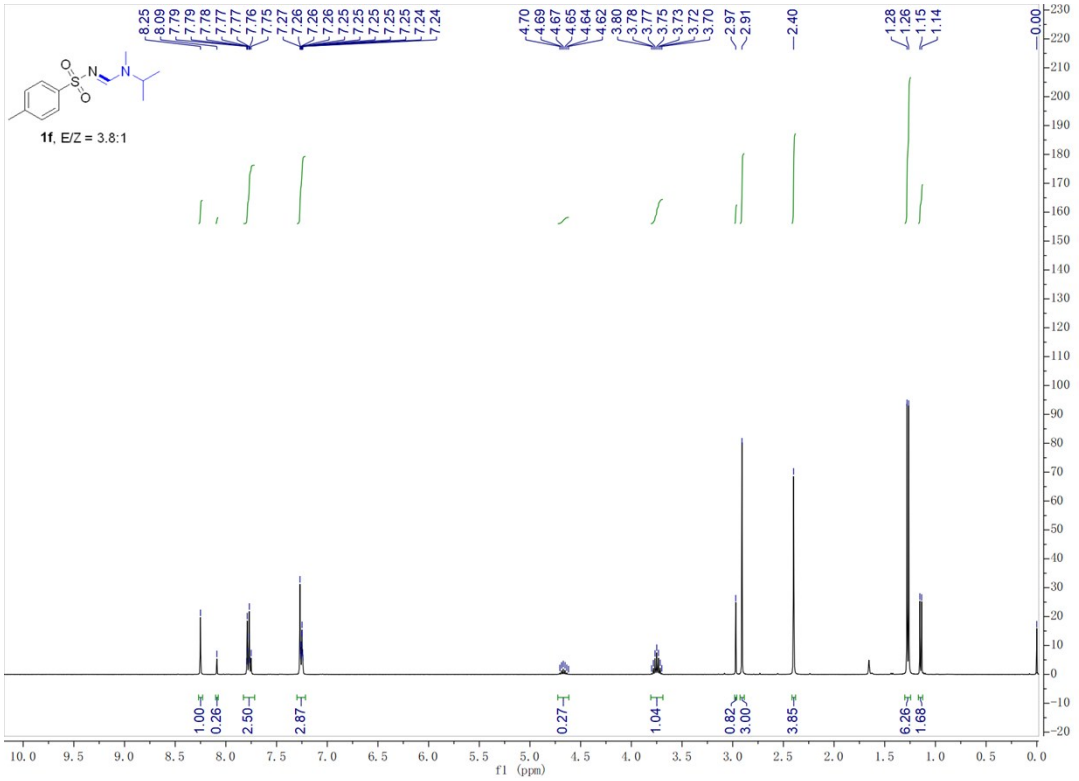


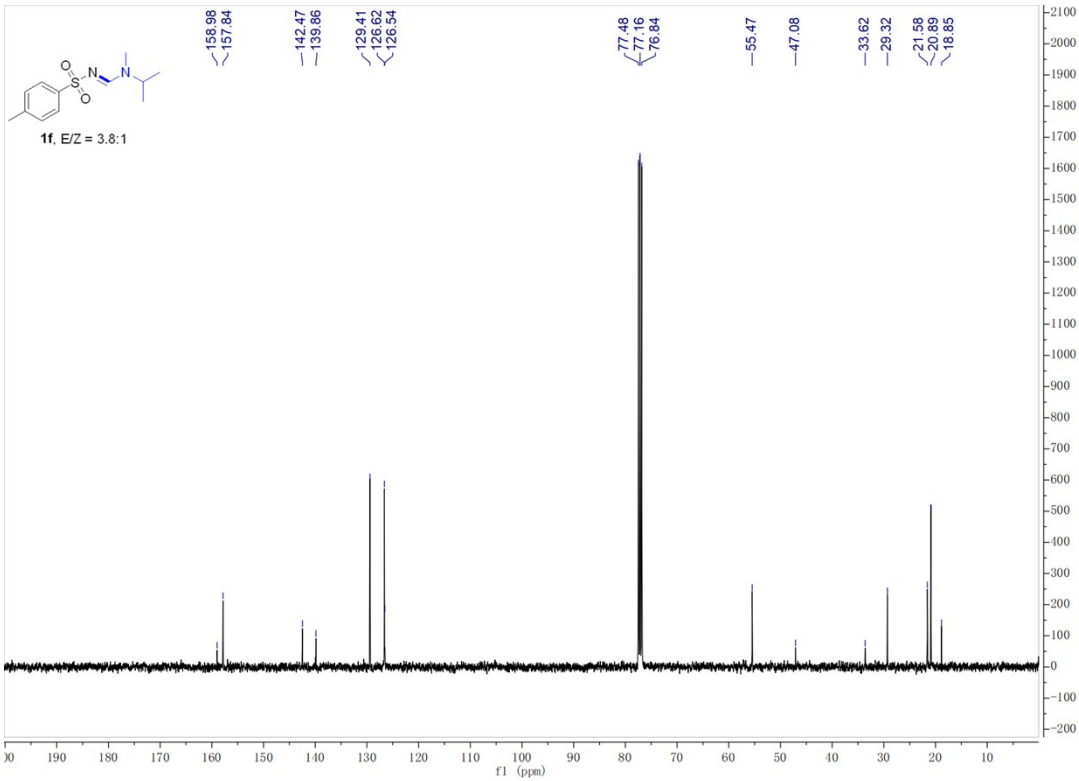
1e ^{1}H, ^{13}C, $CDCl_3$



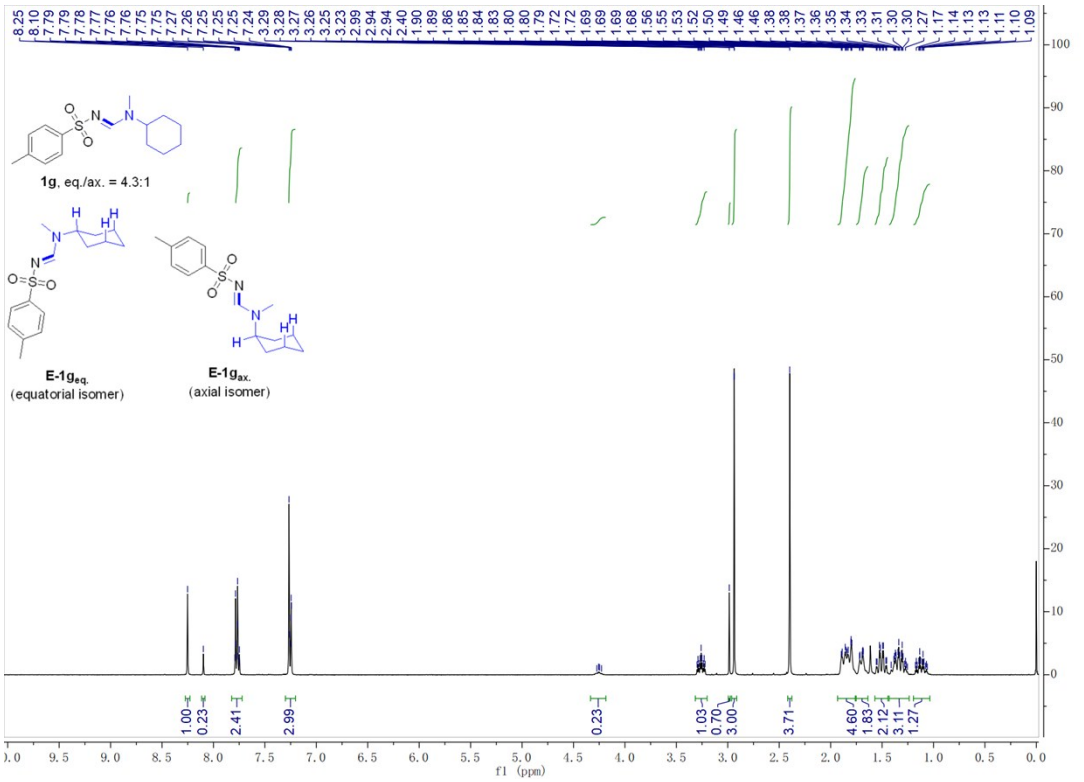


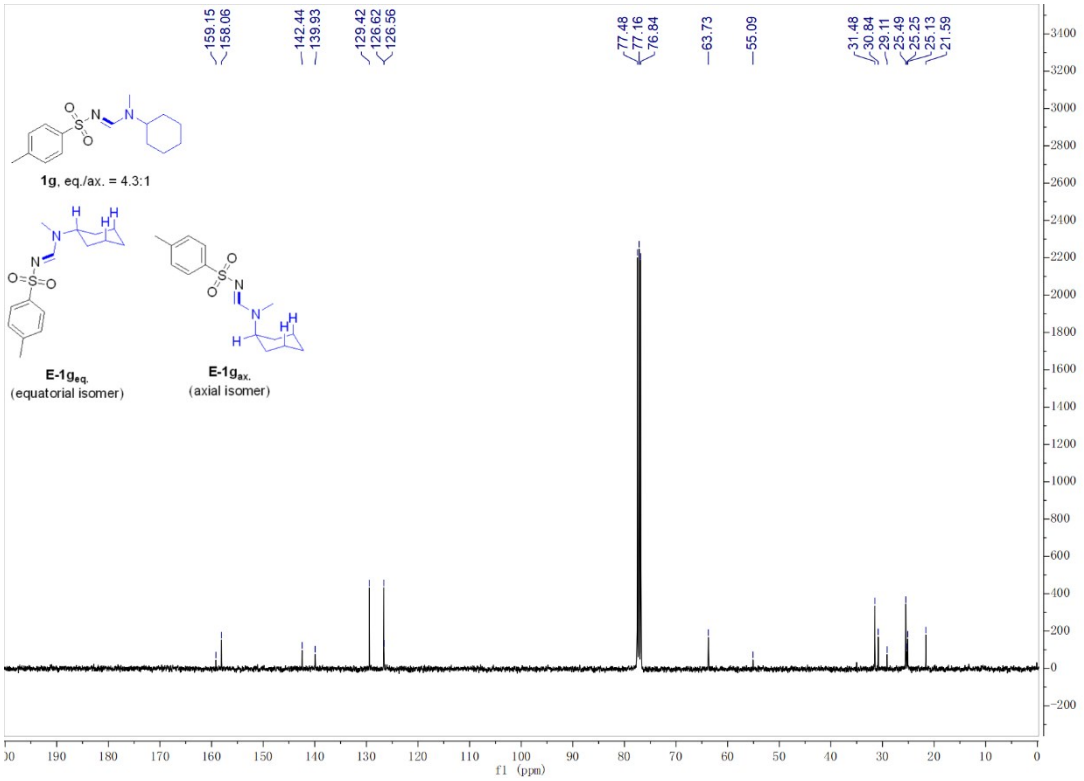
1f ^{1}H, ^{13}C, $CDCl_3$



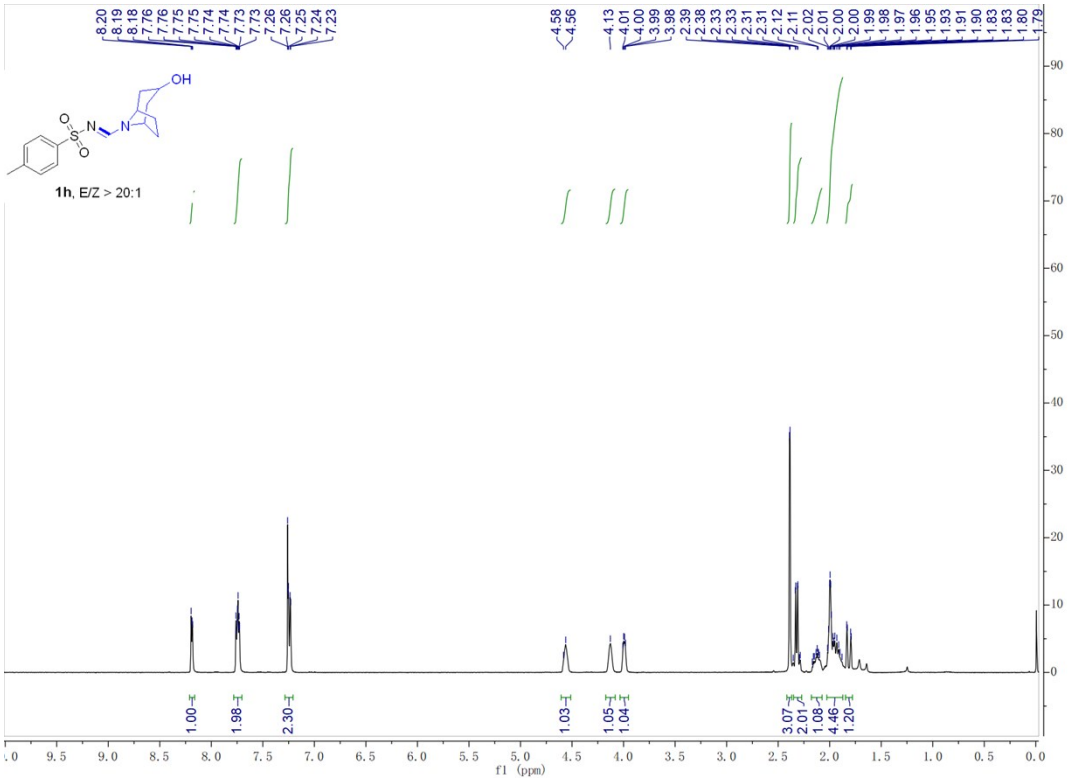


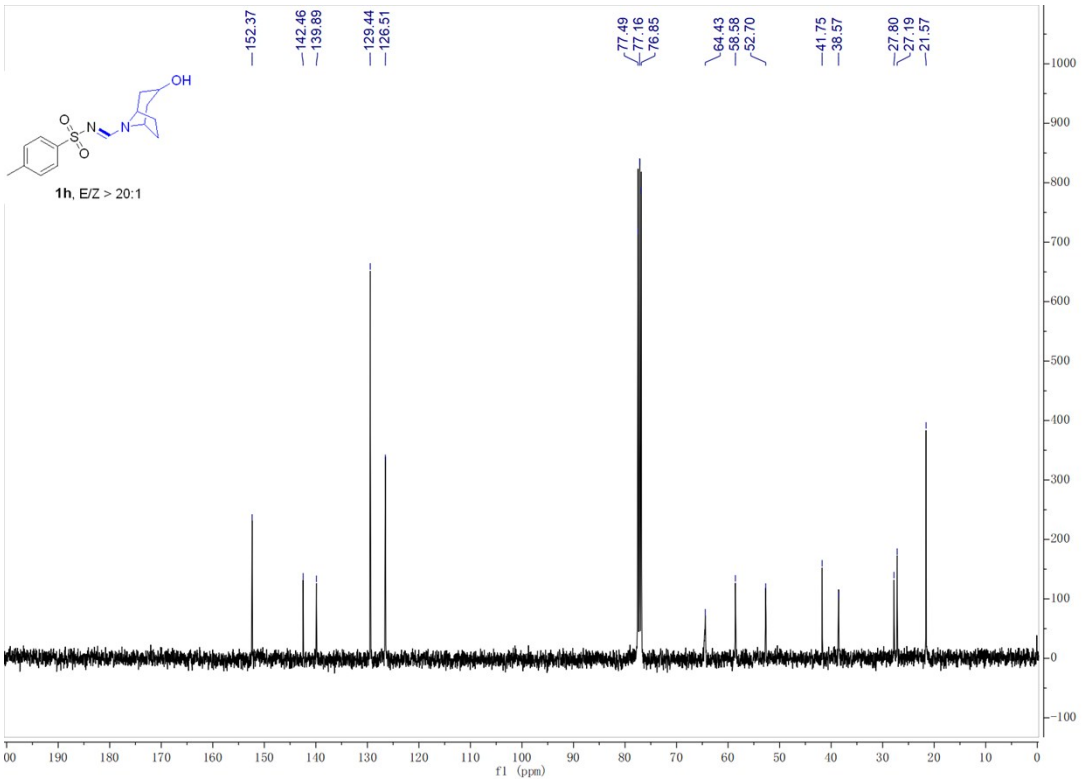
1g ^{1}H, ^{13}C, $CDCl_3$



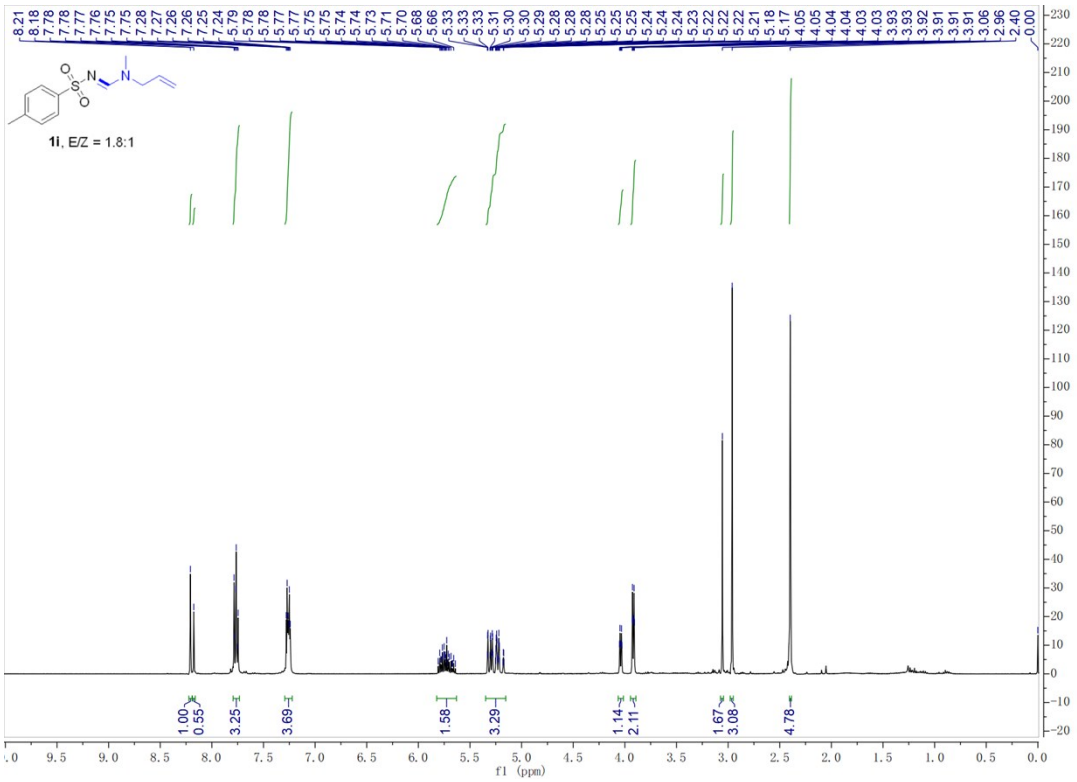


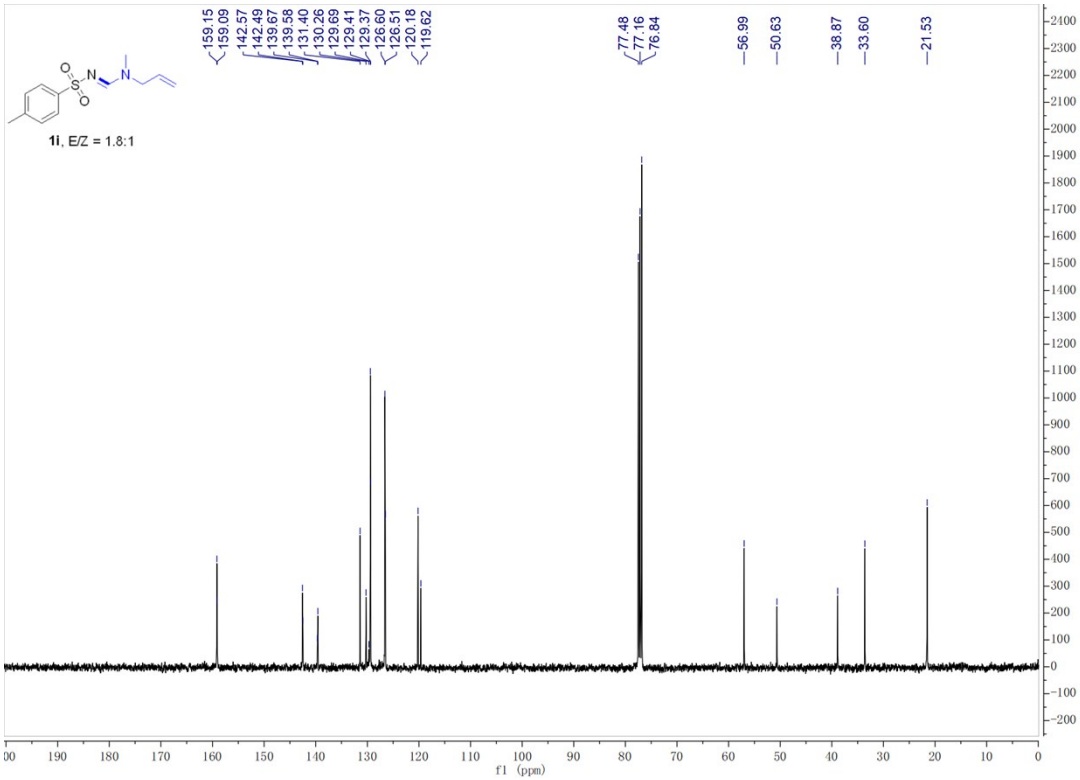
1h ^{1}H, ^{13}C, $CDCl_3$



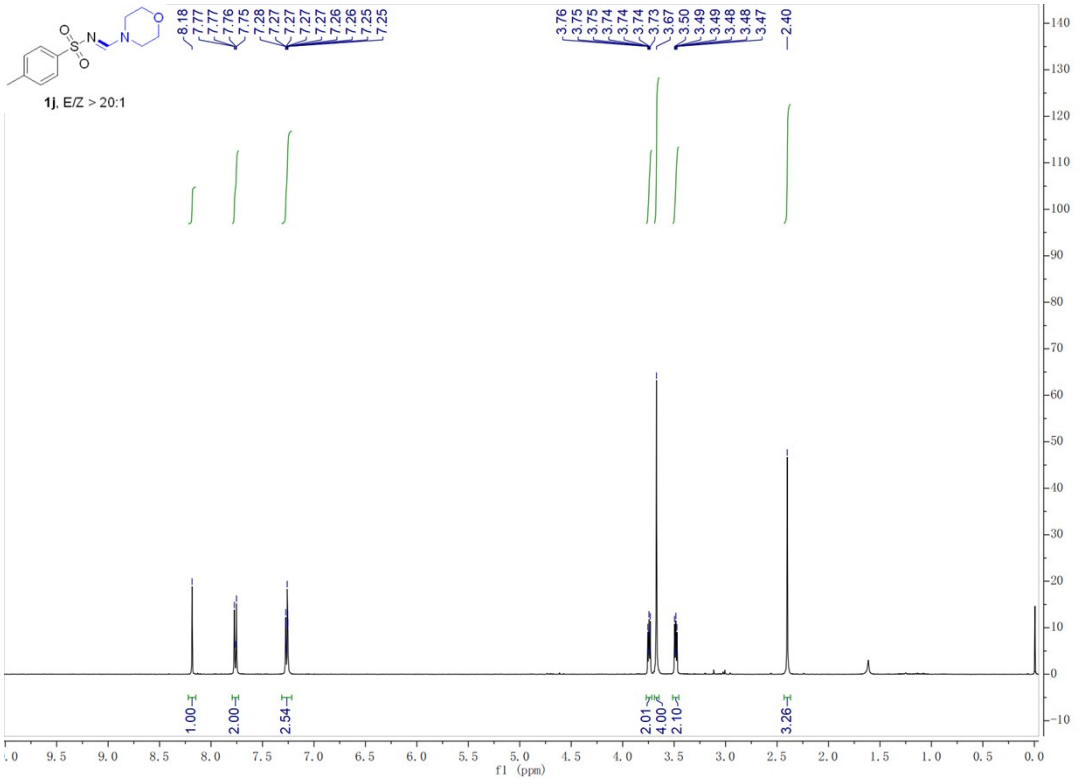


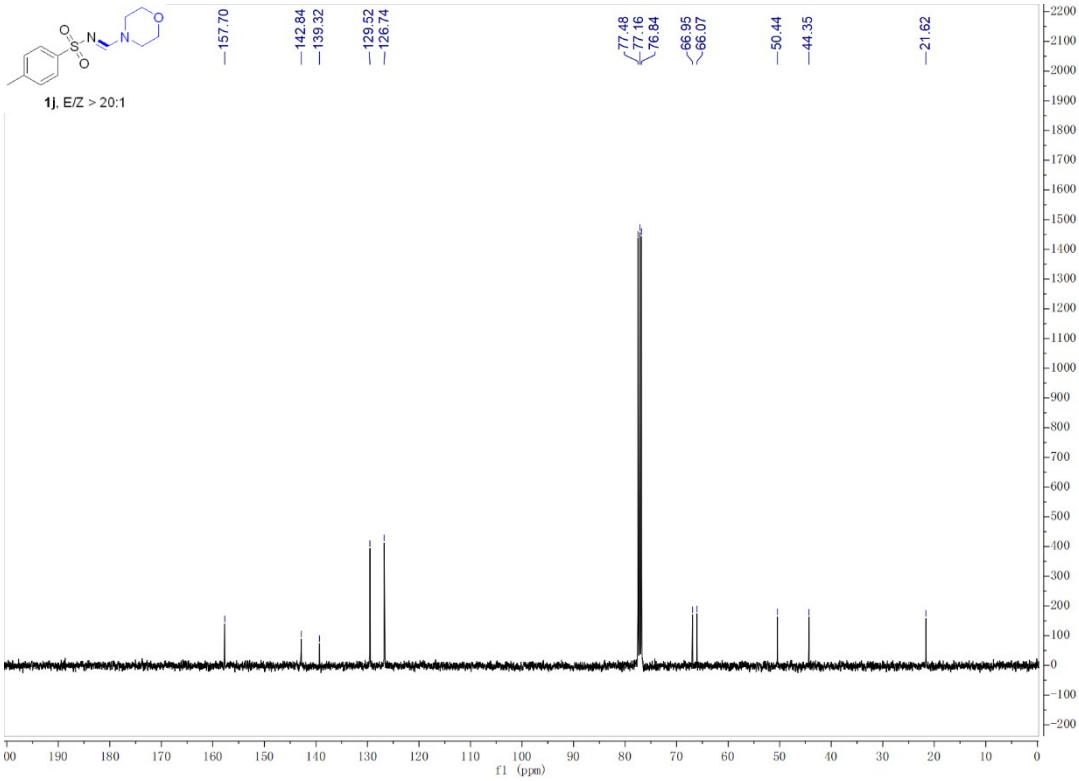
1i ^{1}H, ^{13}C, $CDCl_3$



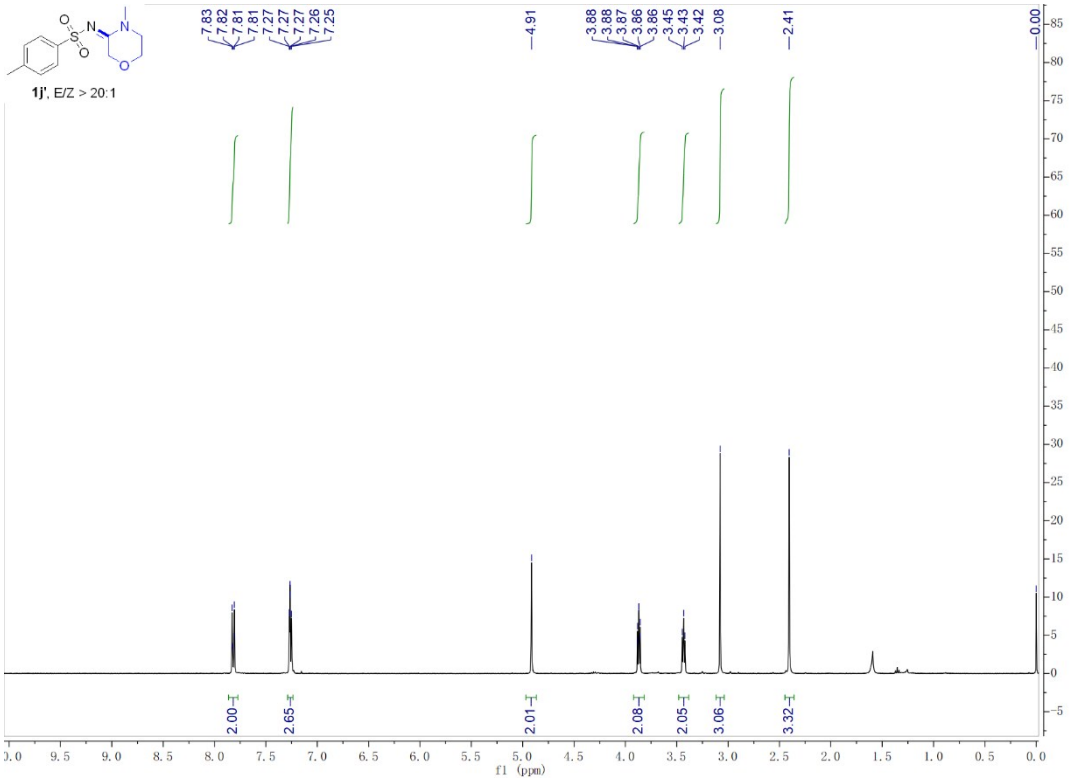


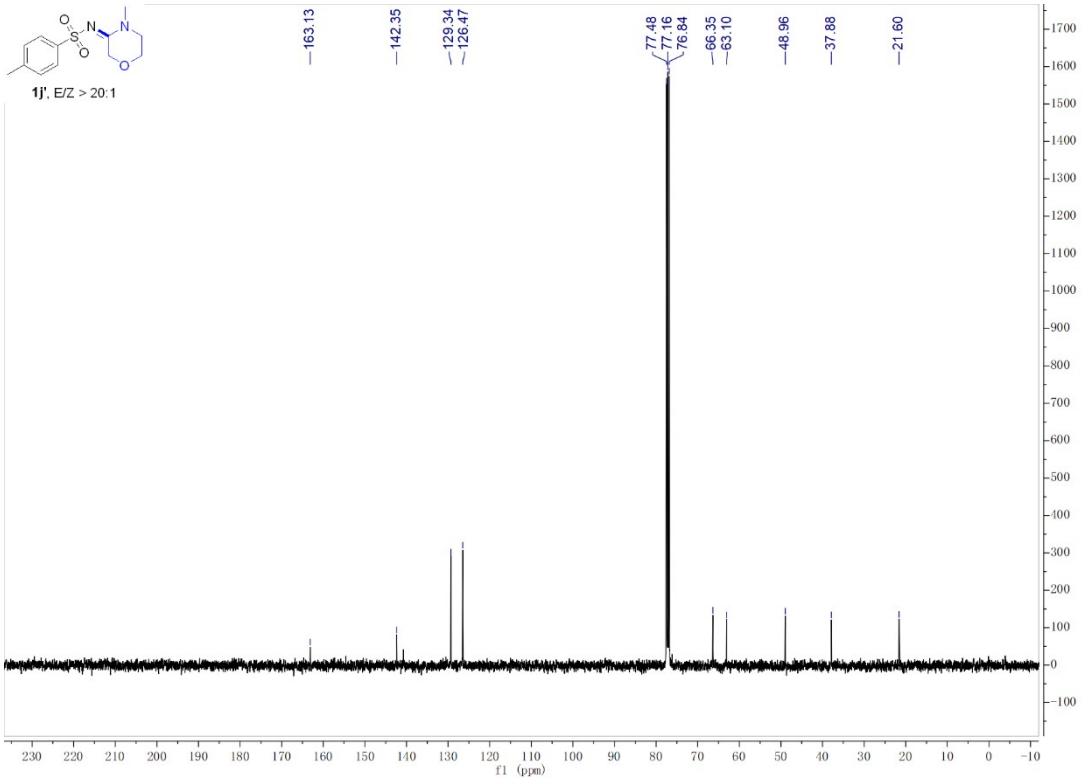
1j ^{1}H, ^{13}C, $CDCl_3$



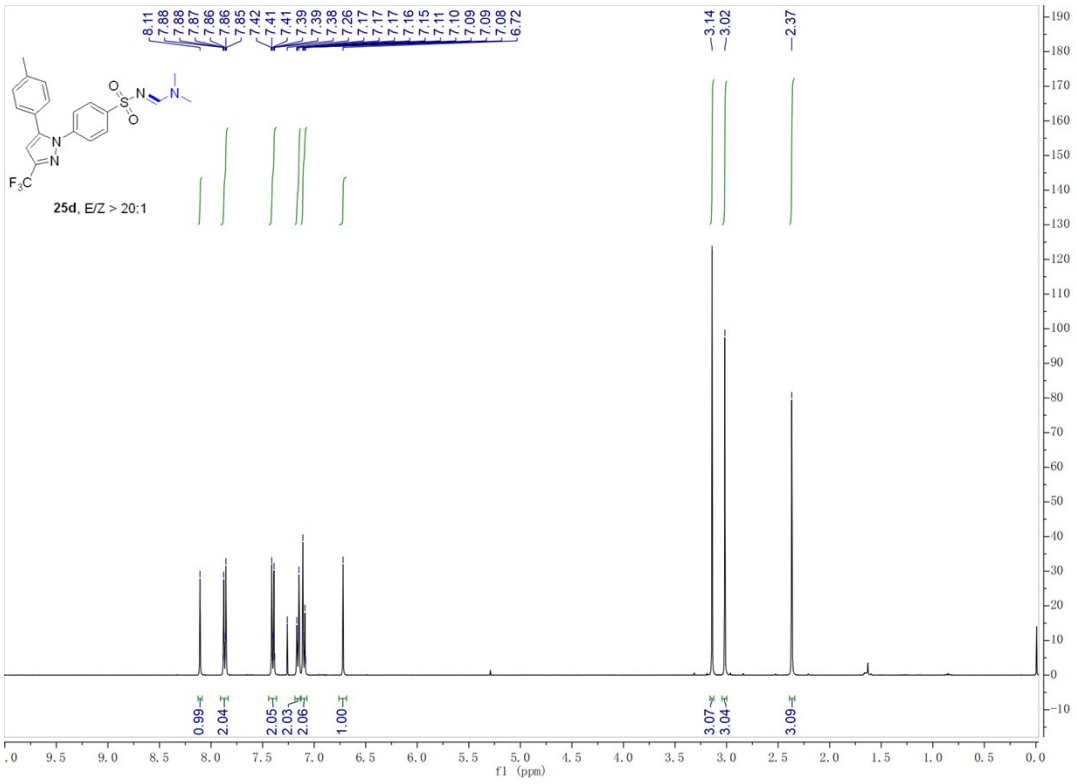


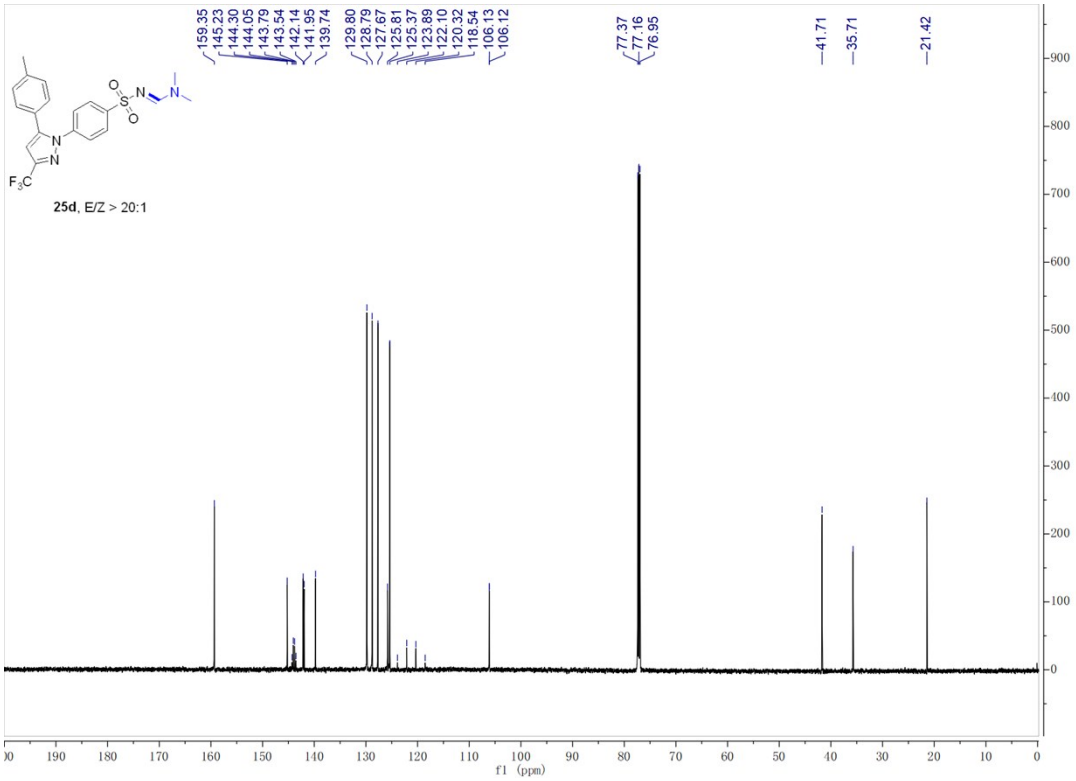
1j' ^{1}H, ^{13}C, $CDCl_3$

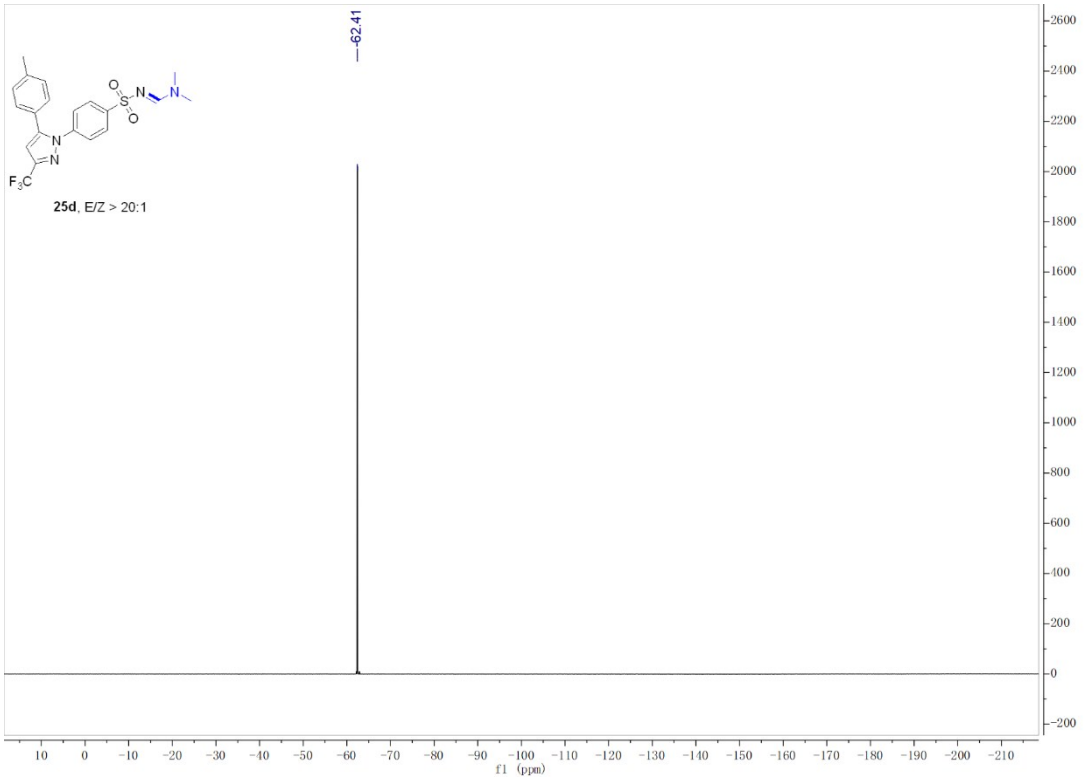




25d ^{1}H, ^{13}C, $CDCl_3$






-62.41
25d, E/Z > 20:1
f1 (ppm)