Electronic Supplementary Material

New branched benign compounds including double antibiotic scaffolds: synthesis, simulation and adsorption for anticorrosion effect on mild steel

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Figs. S1-S16

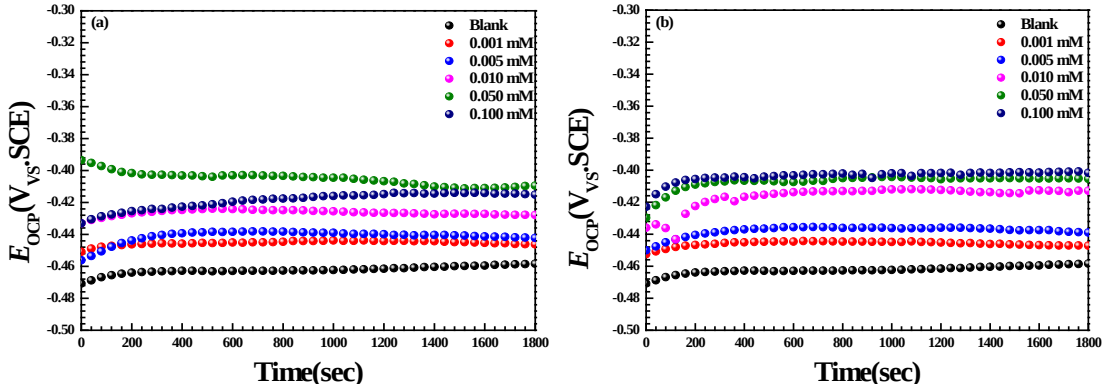


Fig. S1 OCP curves in 1M HCl solution for the blank mild steel and the mild steel eletrodes adsorbed by the **TCs** of various concentrations, (**a**) **TC1**, (**b**) **TC2** (the adsorption time: 8 h)

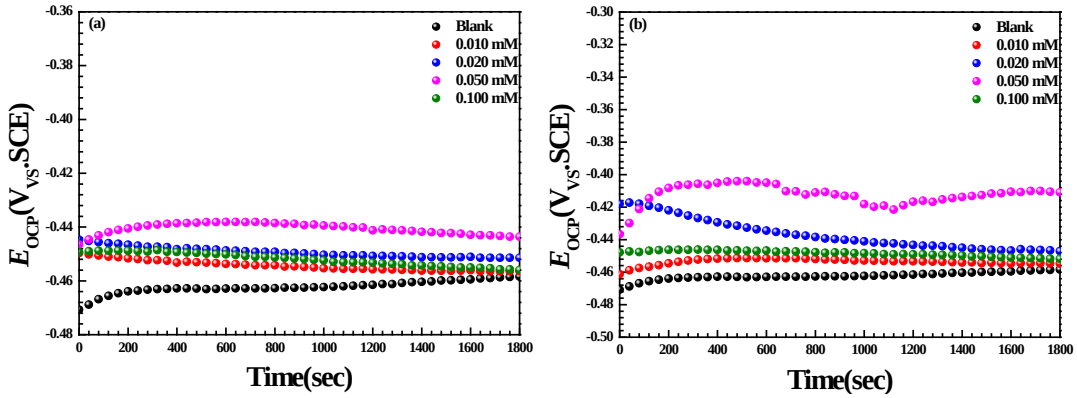


Fig. S2 OCP curves in 1M HCl solution for the blank mild steel and the mild steel eletrodes adsorbed by the **RCs** of various concentrations, (**a**) **RC1**, (**b**) **RC2** (the adsorption time: 8 h)

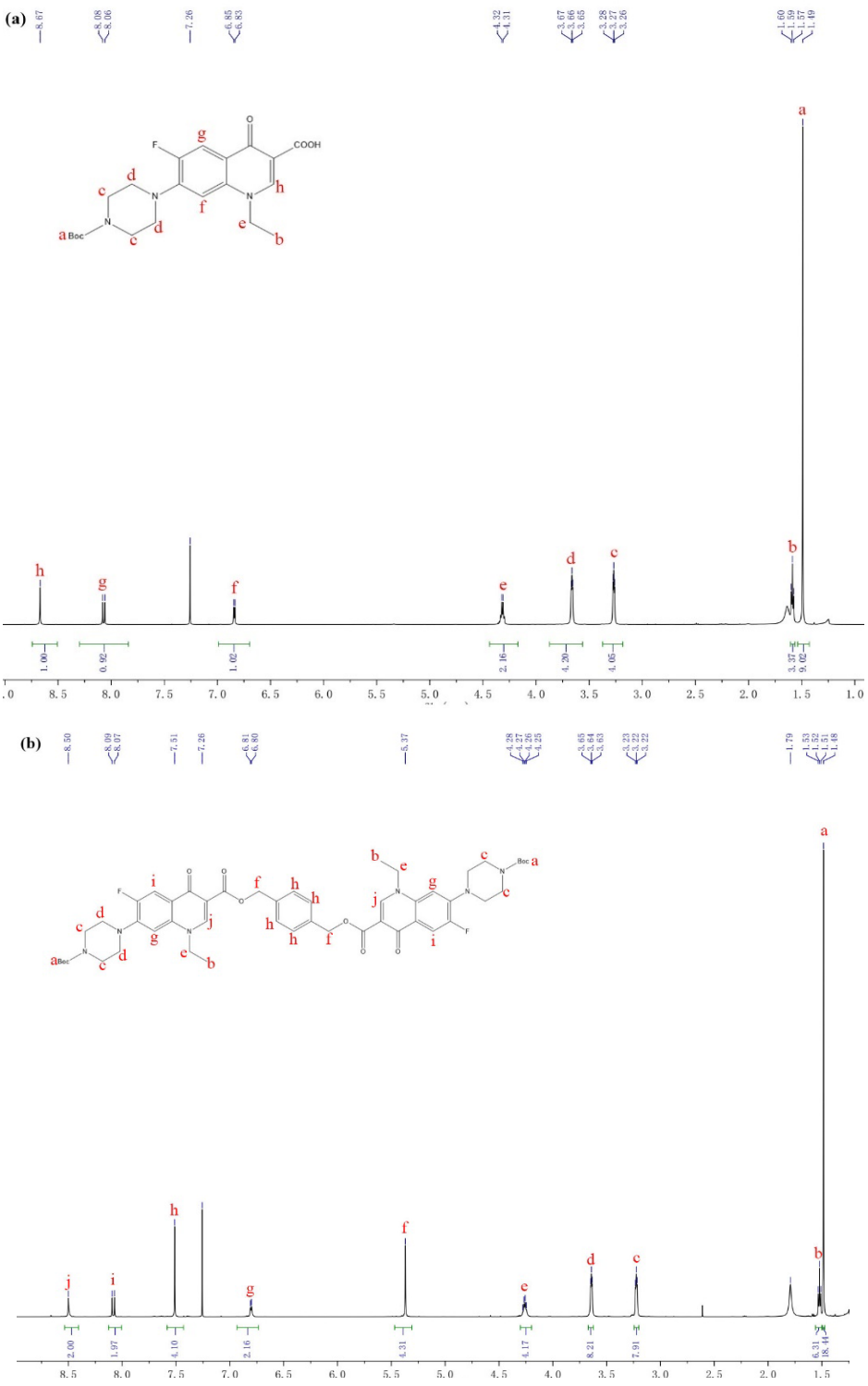


Fig. S3 ^{1}H-NMR (**a**) **I1** and (**b**) **I3**, respectively

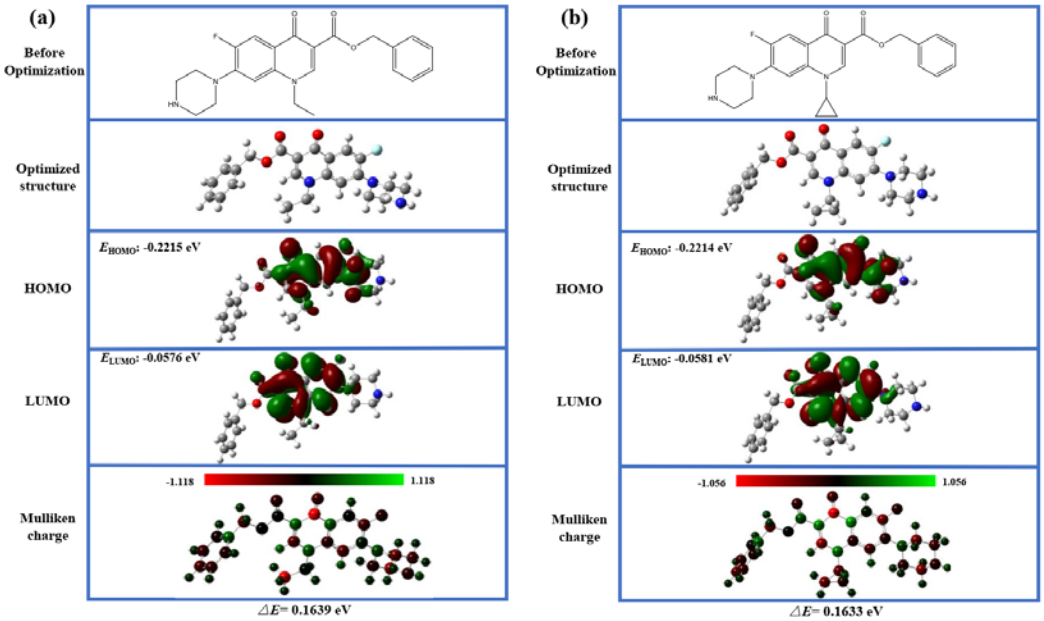


Fig. S4 The Optimized structures, frontier orbital density distributions, and Mulliken charge for the studied (**a**) **RC1** and (**b**) **RC2**, respectively

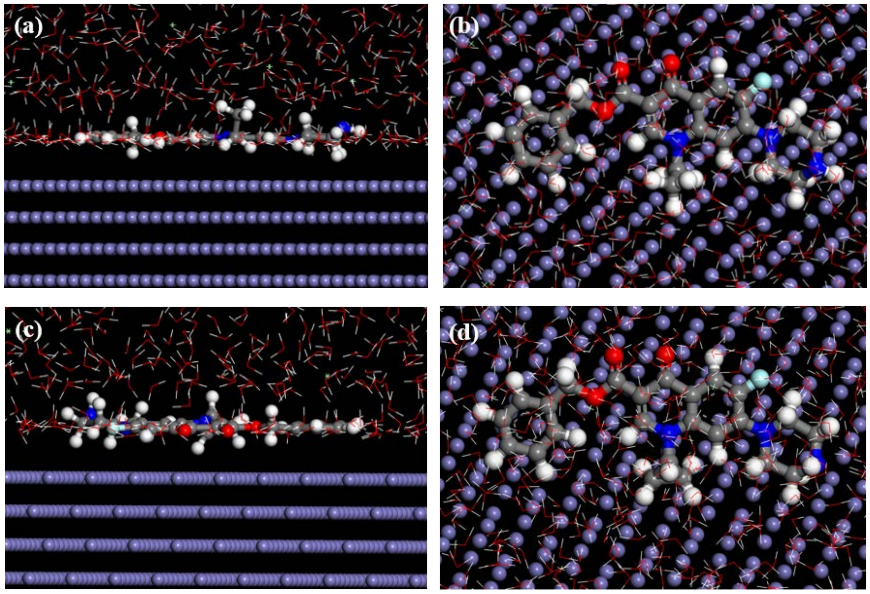
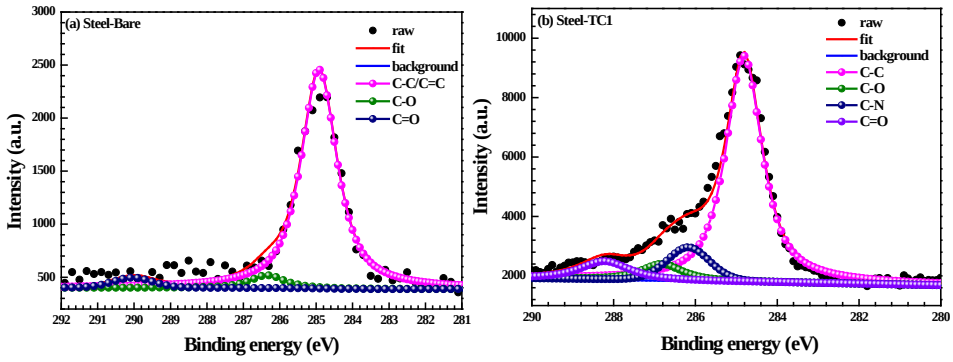


Fig. S5 Side (**a, c**) and top (**b, d**) views of the equilibrium configurations for the **RCs 1, 2** adsorbed on Fe (1 1 0) surface in 1 M HCl solution



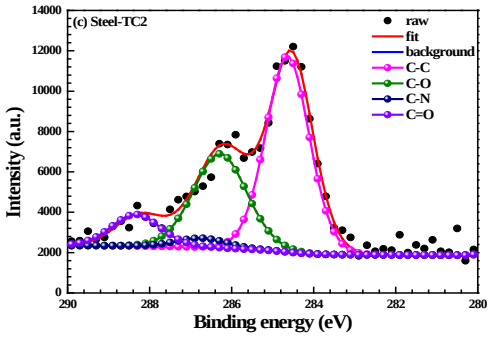


Fig. S6 (**a**) C 1s XPS spectra obtained from the investigated bare steel surface; (**b**) C 1s XPS spectra yielded from the studied mild steel specimens absorbed by the **TC1**; (**c**) C 1s XPS spectra yielded from the studied mild steel specimens absorbed by the **TC2,** after the metals were immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

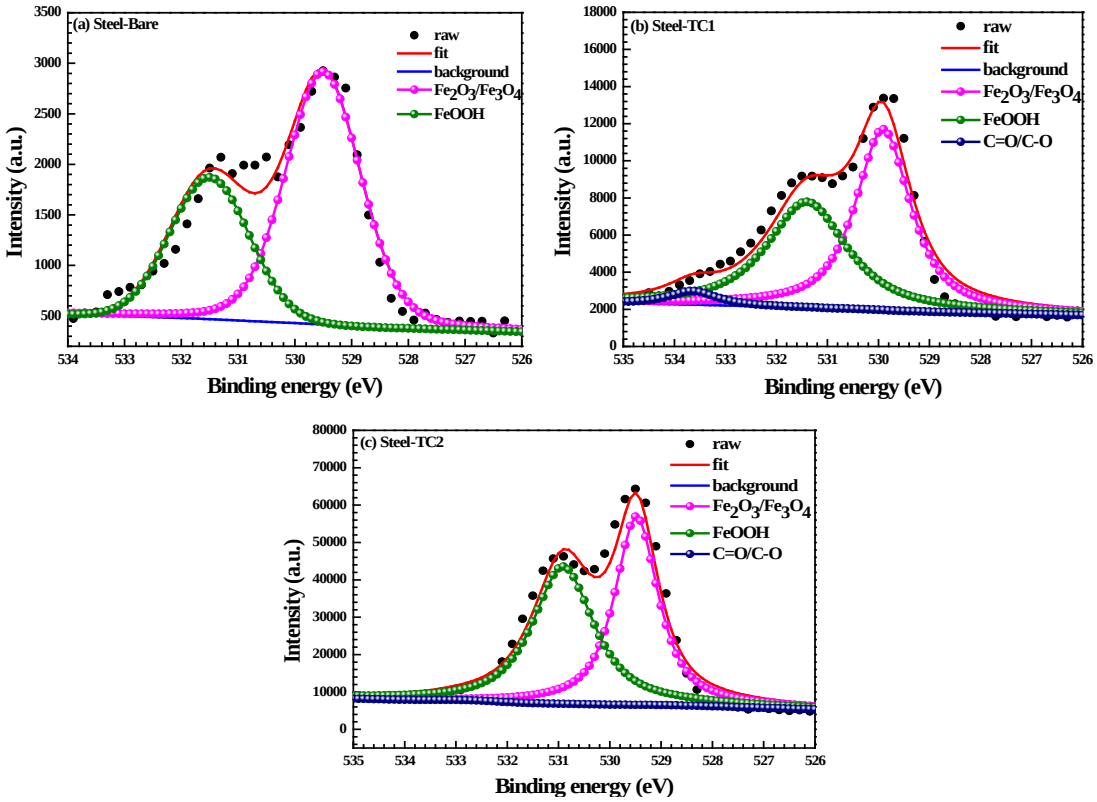


Fig. S7 (**a**) O 1s XPS spectra detected from investigated bare steel surface; (**b**) O 1s XPS spectra from surveyed steel specimen surface treated by the **TC1**; (**c**) O 1s XPS spectra from surveyed steel specimen surface treated by the **TC2,** after the metals were immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

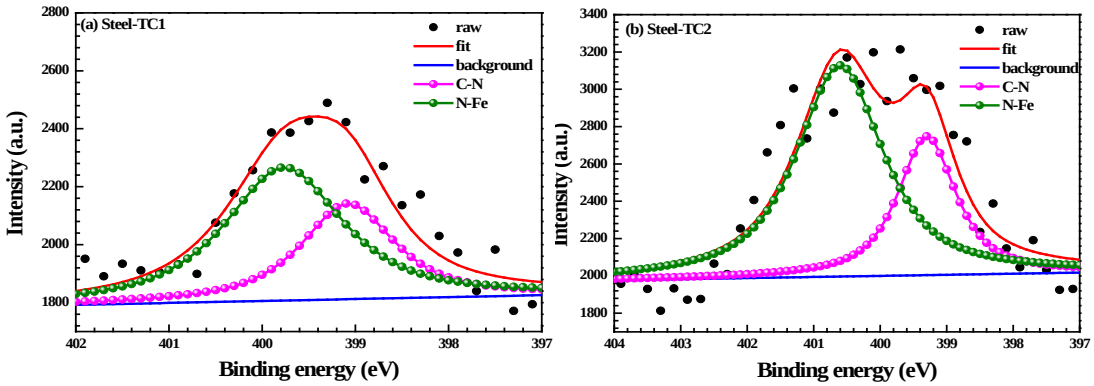


Fig. S8 (**a**) N 1s XPS spectra from surveyed steel specimen surface treated by the **TC1**; (**b**) N 1s XPS spectra from surveyed steel specimen surface treated by the **TC2**, after the metals were immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

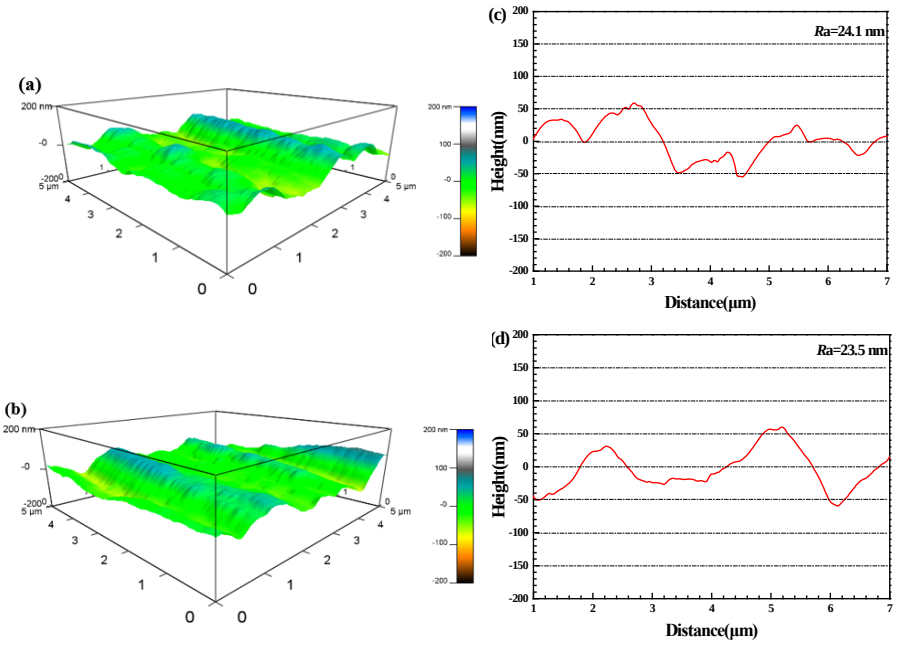


Fig. S9 (**a**) AFM micrographs of the studied polished mild steel specimen surface covered by the **RC1**; (**b**) AFM micrographs of the studied polished mild steel specimen surface covered by the **RC2** and (**c**)-(**d**) the corresponding height profile graphs of the studied mild steel specimen surfaces to (**a**)-(**b**), respectively. The metal was immersed in HCl solution for 1 h (the adsorption time: 8 h, at 0.05 mM)

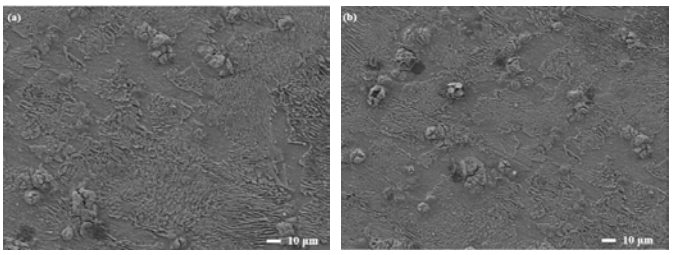
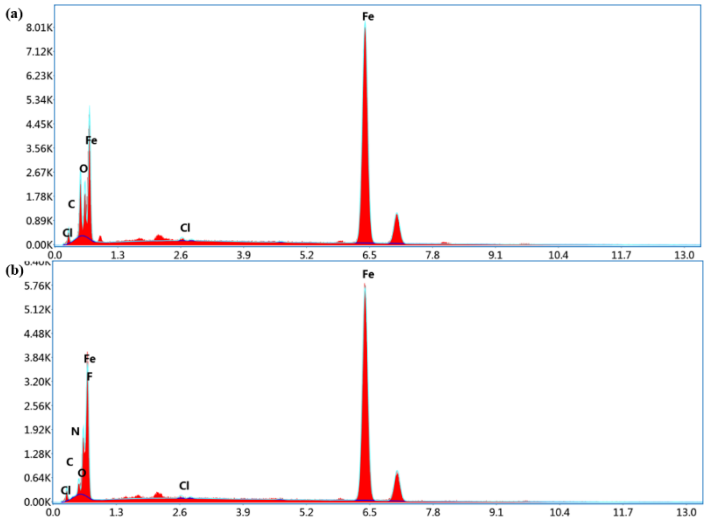


Fig. S10 (**a**) SEM micrograph of polished mild steel covered by stable the **RC1** of 0.05 mM; (**b**) SEM micrograph of polished mild steel covered by stable the **RC2** of 0.05 mM**.** The metal was incubated in 1 M HCl solution for 24 h (the adsorption time: 8 h)



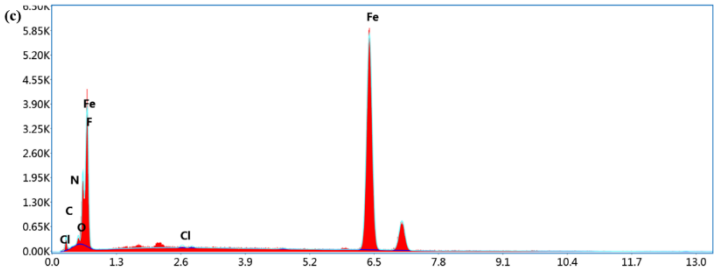


Fig. S11 EDS images for mild steel surface after immersion in 1 mol/L HCl solution, (**a**) blank and covered by (**b**) **TC1** and (**c**) **TC2** (the adsorption time: 8 h, at 0.05 mM)

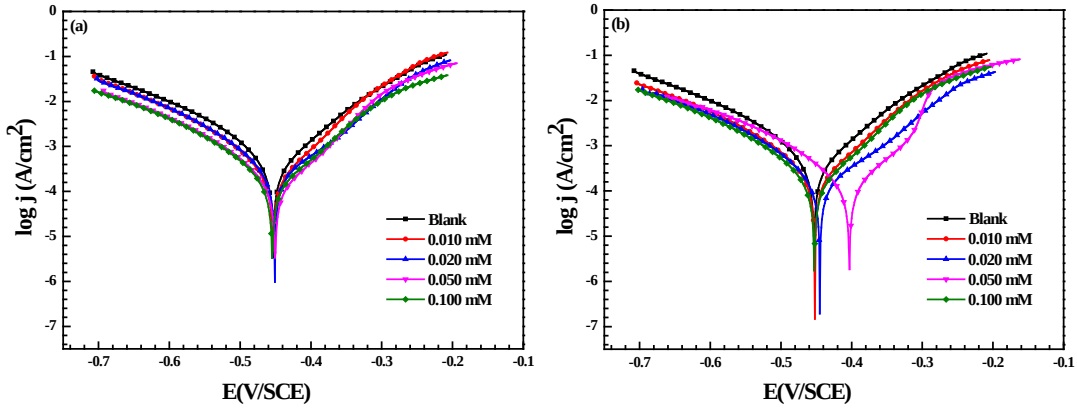


Fig. S12 (**a**) Tafel curves in 1 M HCl solutions for the investigated unmodified mild steel electrodes and the **RC1** of the different concentrations modified mild steel electrodes, (**b**) Tafel curves in 1 M HCl solutions for the investigated unmodified mild steel electrodes and the **RC2** of different concentrations modified mild steel electrodes, respectively (the adsorption time: 8 h)

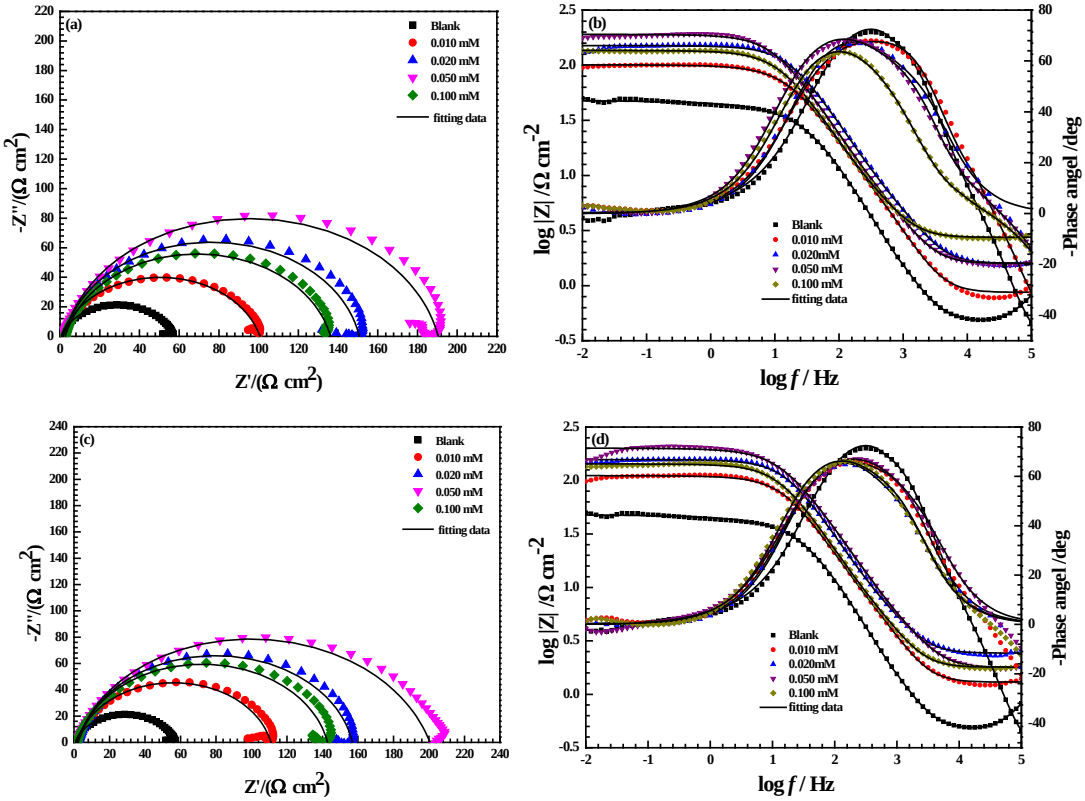


Fig. S13 Nyquist (**a, c**), Bode plots (**b, d**) in 1 M HCl solutions for the studied naked mild steel electrodes, and the metal surface covered by the **RC1** (**a, b**) and **RC2** (**c, d**) of different concentrations (the adsorption time: 8 h)

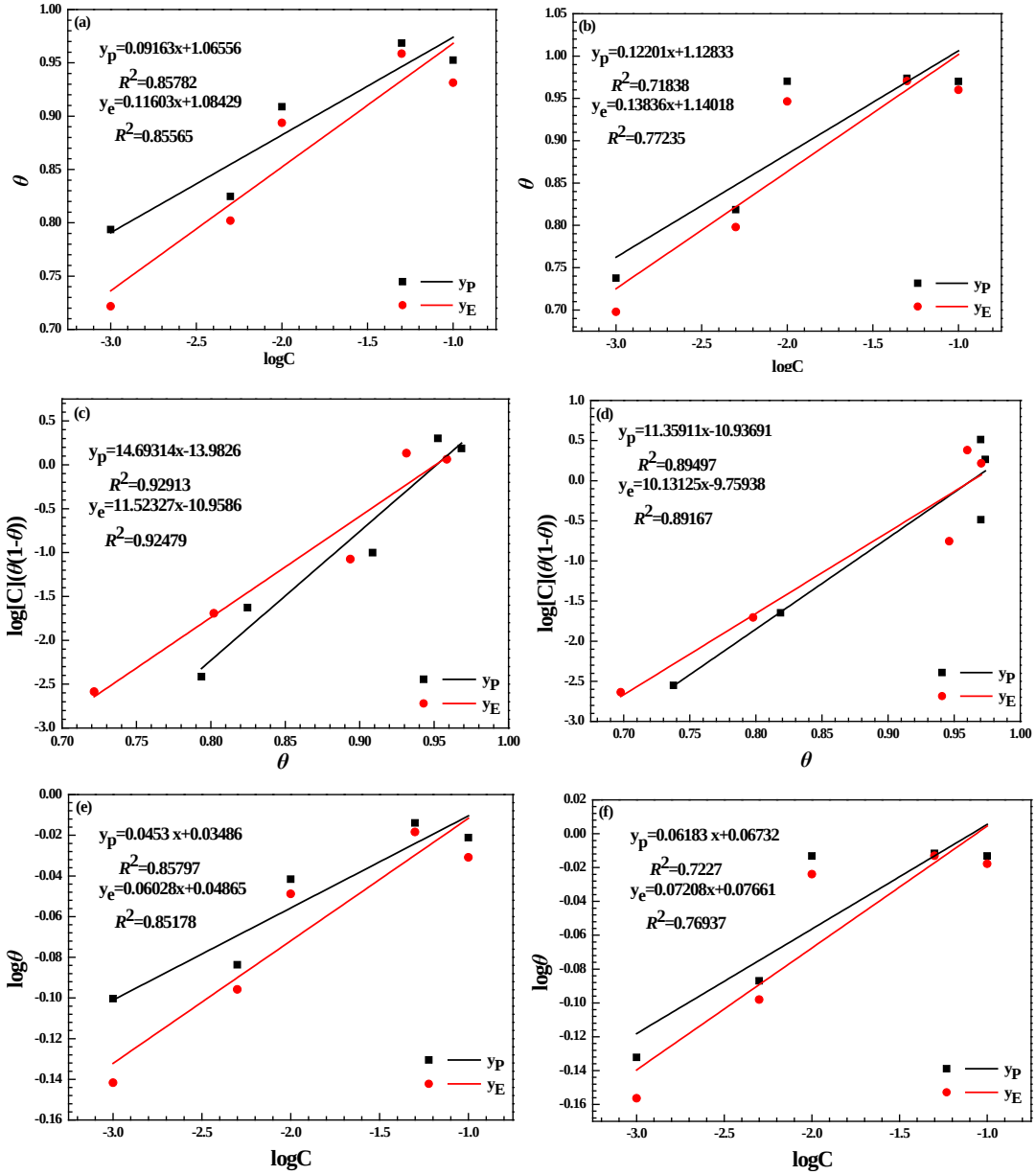


Fig. S14 Temkin (**a, b**), Frumkin (**c, d**) and Freundlich (**e, f**) adsorption isotherm of the **TC1** and **TC2** on the studied mild steel specimen surfaces in 1 M HCl solution at 298 K. (the adsorption time: 8 h)

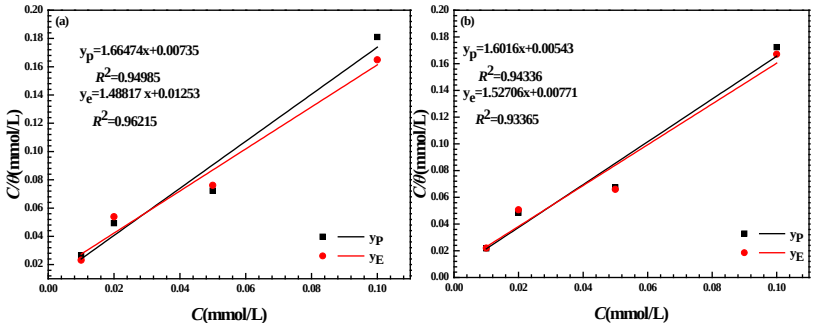


Fig. S15 Langmuir adsorption isotherm of the **RCs 1**, **2** on the studied mild steel specimen surfaces in 1 M HCl solution at 298 K. (the adsorption time: 8 h)

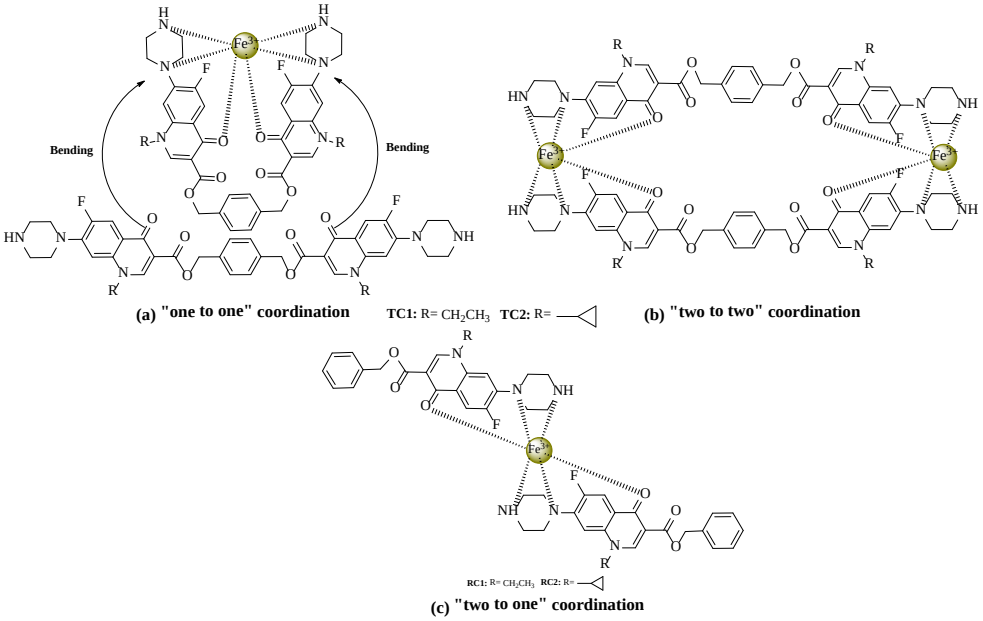


Fig. S16 Possible chemical coordination mechanisms between iron ions (Fe^{2+} or Fe^{3+}) and **TCs** (**a**), (**b**); or **RCs** (**c**).

Tables S1-S10

Table S1 Adsorption energies and the binding energies of the studied systems at equilibrated state (in kcal mol^{-1})

Compounds	E_{total}	$E_{surface+solution}$	$E_{inhibitor+solution}$	$E_{solution}$	$E_{adsorption}$	$E_{binding}$
RC1	-11773.67	-11551.63	-10868.02	-10868.85	-221.86	221.86
RC2	-11793.63	-11661.10	-10915.18	-11009.27	-226.62	226.62

Table S2 De-convolution parameters containing chemical states, binding energies and FWHMs of C 1s XPS spectra peaks detected from studied bare steel specimen surface and investigated mild steel specimens absorbed by the **TCs**, after the metal was immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

Samples	Chemical states	Binding energies(eV)	FWHMs (eV)
Steel-Bare	C-C/C=C	284.92	1.18
	C-O	286.34	1.12
	C=O	290.03	1.30
Steel-**TC1**	C-C/C=C	284.81	1.06
	C-O	286.17	1.21
	C-N	286.82	1.23
	C=O	288.21	1.43
Steel-**TC2**	C-C/C=C	284.54	1.25
	C-O	286.18	1.53
	C-N	286.63	1.44
	C=O	288.23	1.40

Table S3 De-convolution parameters containing the chemical states, the binding energies and FWHMs of O 1s XPS spectra peaks obtained from surfaces of studied bare mild steel, surveyed steel specimens covered by the **TCs,** after the metal was immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

Samples	**Chemical states**	**Binding energies(eV)**	**FWHMs (eV)**
Steel-Bare	Fe_2O_3/ Fe_3O_4	529.50	1.56
	FeOOH	531.50	1.64
Steel-**TC1**	Fe_2O_3/ Fe_3O_4	529.91	1.29
	FeOOH	531.40	1.85
	C=O/C-O	533.63	1.10
Steel-**TC2**	Fe_2O_3/ Fe_3O_4	529.48	1.01
	FeOOH	530.91	1.42
	C=O/C-O	532.77	1.60

Table S4 De-convolution parameters containing the chemical states, the binding energies and FWHMs of N 1s XPS spectra peaks obtained from surfaces of studied bare mild steel, surveyed steel specimens covered by the **TCs,** after the metal was immersed in HCl for 60 min, respectively (the adsorption time: 8 h, at 0.05 mM)

Samples	Chemical states	Binding energies(eV)	FWHMs (eV)
Steel-**TC1**	C-N	399.08	1.19
	N-Fe	399.77	1.50
Steel-**TC2**	C-N	399.30	1.04
	N-Fe	400.61	1.55

Table S5 Polarization parameters for investigated unmodified and modified mild steel specimens by the **TC1** and **TC2** of various concentrations in 1 M HCl solution (the adsorption time: 8 h)

Inhibitor	**Polarization parameters**					
	C (mM)	E_{corr} (V/SCE)	I_{corr} (μA/cm^2)	β_c (mV/dec)	β_a (mV/dec)	η_p (%)
Blank	—	-0.453	376.1	-111.074	77.640	—
TC1	0.001	-0.445	77.58	-105.753	50.282	79.37
	0.005	-0.448	65.93	-107.170	50.896	82.47
	0.010	-0.436	34.34	-109.337	43.798	90.87
	0.050	-0.435	11.87	-107.319	50.656	96.84
	0.100	-0.427	17.87	-101.719	42.660	95.25
TC2	0.001	-0.448	98.70	-117.440	69.633	73.76
	0.005	-0.442	68.24	-108.120	48.130	81.86
	0.010	-0.415	11.20	-107.078	32.292	97.02
	0.050	-0.415	9.93	-99.95	35.455	97.36
	0.100	-0.410	11.23	-106.963	32.581	97.01

Table S6 Polarization parameters for investigated unmodified and modified mild steel specimens by the corrosion inhibitor **RC1** and **RC2** of various concentrations in 1 M HCl solution (the adsorption time: 8 h)

Inhibitors	**Polarization parameters**					
	C (mM)	E_{corr} (V/SCE)	I_{corr} (μA/cm^2)	β_c (mV/dec)	β_a (mV/dec)	η_j (%)
Blank	—	-0.453	376.1	-111.074	77.640	—
RC1	0.010	-0.454	213.8	-106.191	63.963	43.15
	0.020	-0.454	166.5	-107.724	87.055	55.73
	0.050	-0.451	129.0	-106.338	60.024	65.70
	0.100	-0.455	148.0	-107.910	68.502	60.65
RC2	0.010	-0.452	205.0	-109.314	68.446	45.49
	0.020	-0.442	153.5	-105.630	80.431	59.18

	0.050	-0.403	90.9	-108.980	36.876	75.83
	0.100	-0.453	151.0	-110.108	64.454	59.85

Table S7 Electrochemical impedance parameters for investigated unmodified and modified mild steel specimens by the **TCs** of various concentrations in 1 M HCl solution (the adsorption time: 8 h)

Inhibitors	**Electrochemical impedance parameters**									
	C (mM)	R_s ($\Omega\cdot cm^2$)	R_{pore} ($\Omega\cdot cm^2$)	R_{ct} ($\Omega\cdot cm^2$)	C_f ($\mu F/cm^2$)	n	C_{dl} ($\mu F/cm^2$)	n	η_E (%)	X^2 ($\times 10^{-2}$)
Blank	—	0.92	—	54.68	—	—	101.20	0.88	—	1.78
TC1	0.001	0.94	16.41	196.4	45.90	1	54.17	0.81	72.16	1.59
	0.005	1.04	17.37	276.2	34.74	1	45.53	0.79	80.20	8.02
	0.010	1.35	18.79	514.5	27.89	1	45.85	0.77	89.37	0.40
	0.050	0.89	42.94	1320	19.15	1	37.50	0.73	95.86	1.67
	0.100	1.40	24.39	797.3	22.59	1	42.82	0.72	93.14	0.39
TC2	0.001	1.66	10.62	180.9	37.47	1	50.60	0.80	69.77	0.29
	0.005	1.09	17.48	270.5	30.00	1	46.17	0.79	79.79	0.88
	0.010	0.90	37.58	1016	17.97	1	36.09	0.73	94.63	0.40
	0.050	3.54	36.66	1854	15.42	1	35.76	0.70	97.05	0.14
	0.100	2.64	42.50	1368	18.82	1	40.51	0.70	96.00	0.42

Table S8 Electrochemical impedance parameters for investigated unmodified and modified mild steel specimens by the **RC1** and **RC2** of various concentrations in 1 M HCl solution (the adsorption time: 8 h)

Inhibitors	**Electrochemical impedance parameters**									
	C (mM)	R_s ($\Omega\cdot cm^2$)	R_{pore} ($\Omega\cdot cm^2$)	R_{ct} ($\Omega\cdot cm^2$)	C_f ($\mu F/cm^2$)	n	C_{dl} ($\mu F/cm^2$)	n	η_j (%)	X^2 ($\times 10^{-2}$)
Blank	—	0.92	—	54.68	—	—	101.20	0..88	—	0.78
RC1	0.010	0.87	12.18	87.73	50.43	1	68.61	0.76	37.67	1.74
	0.020	1.59	9.27	139.9	30.16	1	38.40	0.83	60.91	4.04
	0.050	1.60	11.20	177.7	41.37	1	51.91	0.81	69.23	0.37
	0.100	2.75	10.93	122.6	52.09	1	58.58	0.79	55.40	0.37
RC2	0.010	1.30	11.18	98.54	47.32	1	58.82	0.79	45.91	0.74
	0.02	2.43	10.62	143.9	30.16	1	38.07	0.83	62.00	4.28
	0.050	0.98	8.41	211.6	25.53	1	41.11	0.79	74.16	1.35
	0.100	1.80	10.93	130.2	43.63	1	52.99	0.81	58.00	0.32

Table S9 Thermodynamic parameters for the adsorption of **TC1** and **TC2** in 1 M HCl solution at 298 K

Inhibitors	**Methods**	**K_{ads}** (L/mol)	ΔG^0_{ads} (kJ/mol)
TC1	Polarization	2534.90	-36.53
	EIS	2849.63	-36.82
TC2	Polarization	2455.52	-36.45
	EIS	2145.97	-36.12

Table S10 Thermodynamic parameters for the adsorption of **TC1** and **TC2** in 1 M HCl solution at 298 K (the adsorption time: 8 h)

Inhibitors	**Methods**	**K_{ads}** (L/mol)	ΔG^0_{ads} (kJ/mol)
RC1	Polarization	136.05	-29.29
	EIS	79.81	-27.97
RC2	Polarization	184.16	-30.03
	EIS	129.70	-29.17

Synthesis and Characterization

Norfloxacin (0.964 g, 3.00 mmol) was dissolved in 1 M NaOH solution (10 ml) and THF (10 ml). Di-tert butyl dicarbonate (0.720 g, 3.30 mmol) was dissolved in THF (10 ml) and added to the above solution. The reaction was stirred at room temperature for 16 h to obtain a colorless transparent liquid. The solvent was removed under reduced pressure and neutralized with saturated NH_4Cl solution. Filter and dry to obtain a white solid, intermediate **I1**.

A mixture of **I1** (0.419 g, 1 mmol), K_2CO_3 (0.221 g, 1.6 mmol), α,α'-Dibromo-p-xylene (0.132 g, 0.5 mmol) and acetonitrile (20 mL) was stirred in a 100 mL flask, which was heated to 80℃ and overnight reflux. Extract with DCM (3×20 mL) and dry with anhydrous sodium sulfate. Filter and dry to obtain a white solid, intermediate **I3**.

A mixture of **I1** (0.210 g, 0.5 mmol), K_2CO_3 (0.083 g, 0.6 mmol), benzyl bromide (0.14 ml, 1 mmol) and acetonitrile (20 mL) was stirred in a 100 mL flask, which was heated to 80℃ and overnight reflux. Extract with DCM (3×20 mL) and dry with anhydrous sodium sulfate. After solvent removal under reduced pressure, add a large amount of ether to precipitate solid, filter and dry to obtain a white solid, intermediate **I5**.

I3 (0.094 g, 0.1 mmol) was dissolved in dichloromethane (10 mL) and TFA (2 mL) was added. The solvent was removed by rotary evaporation after stirring at room temperature for 1 h. Add methanol and filter. Dry to get the white solid **TC1**. The **RC1** was prepared based on similar route as the **TC1**, which used **I5** as the staring compounds.

The **TC2** and **RC2** were prepared based on similar route as the **TC1** and **RC1**, which used ciprofloxacin as the starting compounds.

I1, ^{1}H-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 8.668 (s, 1H, C=CH-N), 8.081-8.059 (d, 1H, *J*=13.2 Hz, C=CH-C), 6.846-6.834 (d, 1H, *J*=7.2 Hz, C-CH=C), 4.323-4.311 (q, 2H, *J*=2.4 Hz, N-CH_2-C), 3.670-3.654 (t, 4H, *J*=4.8 Hz, -CH_2-), 3.277-3.260 (t, 4H, *J*=5.1Hz, -CH_2-), 1.598-1.575 (t, 3H, *J*=6.9 Hz, -CH_3), 1.490 (s, 9H, -CH_3). ^{13}C-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm):179.632, 169.766, 157.177, 155.306, 149.851, 148.673, 139.707, 123.625, 115.707, 111.142, 106.669, 83.041,52.509, 52.400, 31.046, 17.136. FT-IR (cm^{-1}): 3421.56, 3077.81, 2968.98, 2876.19, 1732.45, 1685.91, 1628.96, 1560.46, 1520.86, 1484.02, 1426.84, 1382.12, 1287.86, 1246.84, 1169.26, 1130.15, 1107.45, 1071.87, 1035.74, 1003.48, 958.06, 926.31, 861.26, 822.15, 804.79, 750.72, 625.27. Elementary analysis, Anal. Calcd for $C_{21}H_{26}FN_3O_5$: C, 60.13, H, 6.25, N, 10.02. Found: C, 60.20, H, 6.21, F, 4.49, N, 9.96.

I2, ^{1}H-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 8.759 (s, 1H, C=CH-N), 8.033-8.011 (d, 1H, *J*=13.2 Hz, C=CH-C), 7.365-7.354 (d, 1H, *J*=6.6 Hz, C-CH=C), 3.673-3.658 (t, 4H, *J*=4.5 Hz, -CH_2-), 3.550-3.515 (hept, 1H, *J*=3.5 Hz, N-CH-C), 3.295-3.279 (t, 4H, *J*=4.8 Hz, -CH_2-), 1.493(s, 9H, -CH_3), 1.410-1.377 (q, 2H, *J*=6.6 Hz, -CH_2-), 1.218-1.190 (q, 2H, *J*=5.6 Hz, -CH_2-). ^{13}C-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 179.752, 169.580, 157.197, 155.457, 150.171, 148.447, 144.673, 122.854, 115.333, 110.889, 107.647, 83.026, 52.432, 37.946, 31.052, 10.917. FT-IR (cm^{-1}): 3448.02, 3062.91, 2969.46, 2874.44, 1733.54, 1693.96, 1628.93, 1504.49, 1471.19, 1420.82,

1384.33, 1384.33, 1339.08, 1287.08, 1248.22, 1217.61, 1170.11, 1125.68, 1083.40, 1037.39, 1003.39, 941.39, 890.96, 856.98, 829.28, 805.61, 770.90, 747.91, 710.86, 668.29, 627.73. Elementary analysis, Anal. Calcd for $C_{22}H_{268}FN_3O_5$: C, 61.24, H, 6.07, N, 9.74. Found: C, 61.31, H, 5.99, N, 9.69.

I3, ^{1}H-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 8.501 (s, 2H, C=CH-N), 8.094-8.072 (d, 2H, *J*=13.2 Hz, C=CH-C), 7.513(s, 4H, C=CH-C), 6.809-6.799 (d, 2H, *J*=6.0 Hz, C-CH=C), 5.370(s, 4H, O-CH_2-C), 4.280-4.245 (q, 4H, *J*=7 Hz, N-CH_2-C), 3.649-3.633(t, 8H, *J*=4.8 Hz, -CH_2-), 3.233-3.217 (t, 8H, *J*=4.8 Hz, -CH_2-), 1.534-1.544 (t, 6H, *J*=6.9 Hz, -CH_3), 1.484 (s, 18H, -CH_3). ^{13}C-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 175.349, 168.149, 157.223, 156.767, 155.113, 150.878, 138.919, 138.705, 131.130, 116.429, 112.333, 106.837, 82.906, 68.997, 52.668, 52.013, 31.054, 17.125. FT-IR (cm^{-1}): 3444.11, 2975.56, 2933.00, 2857.24, 1697.88, 1619.43, 1583.72, 1543.45, 1490.35, 1455.99, 1418.58, 1387.51, 1366.37, 1313.71, 1285.79, 1247.39, 1222.07, 1169.26, 1124.35, 1081.83, 1030.83, 999.84, 933.81, 896.50, 862.52, 802.70, 759.65, 706.85, 622.09. Elementary analysis, Anal. Calcd for $C_{50}H_{58}F_2N_6O_{10}$: C, 63.82, H, 6.21, N, 8.93. Found: C, 63.91, H, 6.16, N, 8.89.

I4, ^{1}H-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 8.484 (s, 1H, C=CH-N), 8.012-7.990 (d, 1H, *J*=14.4 Hz, C=CH-C), 7.491(s, 4H, C=CH-C), 7.245-7.233 (d, 1H, *J*=7.2 Hz, C-CH=C), 5.349(s, 4H, O-CH_2-C), 3.636 (s, 8H, -CH_2-), 3.408-3.372 (hept, 2H, *J*=3.6 Hz, N-CH-C), 3.204-3.188 (t, 8H, *J*=4.8 Hz, -CH_2-), 1.486(s, 18H, -CH_3), 1.285-1.274 (q, 4H, *J*=6.6 Hz, -CH_2-), 1.104-1.099 (q, 4H, *J*=3 Hz, -CH_2-). ^{13}C-NMR (600 MHz, $CDCl_3$-d_6) δ (ppm): 175.642, 167.944, 157.250, 155.169, 150.939, 147.077, 140.592, 138.818, 130.885, 116.120, 112.750, 107.659, 82.852, 68.729, 52.689, 37.191, 31.061, 10.823. FT-IR (cm^{-1}): 3470.31, 2973.48, 2928.97, 2859.59, 1730.15, 1696.15, 1622.58, 1588.04, 1546.42, 1493.87, 1477.19, 1423.66, 1391.13, 1365.64, 1329.25, 1311.47, 1285.60, 1248.02, 1209.29, 1164.02, 1121.78, 1079.73, 1035.08, 1000.13, 920.26, 890.55, 836.57, 802.95, 781.44. Elementary analysis, Anal. Calcd for $C_{52}H_{58}F_2N_6O_{10}$: C, 64.72, H, 6.06, N, 8.71. Found: C, 64.81, H, 6.11, N, 8.64.

I5: ^{1}H-NMR (400 MHz, $CDCl_3$-d_6) δ (ppm): 8.359 (s, 1H, C=CH-N), 8.055-8.022 (d, 1H, *J*=13.2 Hz, C=CH-C), 7.514-7.496 (d, 2H, *J*=7.2 Hz, C=CH-C), 7.383-7.346 (t, 2H, *J*=7.4 Hz, C=CH-C), 7.314-7.296 (d, 1H, *J*=7.2 Hz, C=CH-C), 6.702-6.68 (d, 1H, *J*=6.8 Hz, C-CH=C), 5.364 (s, 2H, O-CH_2-C), 4.154-4.100 (q, 2H, *J*=7.2 Hz, N-CH_2-C), 3.643-3.619 (t, 4H, *J*=4.8 Hz, -CH_2-), 3.186-3.162 (t, 4H, *J*=4.8 Hz, -CH_2-), 1.499-1.463 (t, 12H, *J*=7.2 Hz, -CH_3). ^{13}C-NMR (400 MHz, $CDCl_3$-d_6) δ (ppm): 172.999, 165.484, 154.603, 148.165, 144.696, 136.424, 135.977, 128.542, 128.096, 127.965, 124.095, 124.028, 113.872, 113.645, 110.158, 104.146, 80.223, 66.368, 49.977, 49.022, 28.425, 14.394. FT-IR (cm^{-1}): 3543.86, 3419.44, 2979.18, 1710.33, 1625.71, 1576.49, 1542.55, 1491.74, 1455.89, 1420399, 1390.81, 1366.36, 1315.59, 1287.17, 1246.40, 1226.60, 1169.18, 1126.02, 1100.33, 1033.24, 1000.32, 803.47, 758.55, 734.36, 697.01. Elementary analysis, Anal. Calcd for $C_{28}H_{32}FN_3O_5$: C, 66.00, H, 6.33, N, 8.25. Found: C, 66.08, H, 6.28, N, 8.19.

I6: ^{1}H-NMR (400 MHz, $CDCl_3$-d_6) δ (ppm): 8.476 (s, 1H, C=CH-N), 7.997-7.964 (d, 1H, *J*=13.2 Hz, C=CH-C), 7.511-7.493 (d, 2H, *J*=7.2 Hz, C=CH-C), 7.381-7.344 (t, 2H, *J*=7.4 Hz, C=CH-C), 7.311-7.292 (d, 1H, *J*=13.2 Hz, C=CH-C), 7.238-7.220 (d, 1H, *J*=7.2 Hz, C-CH=C), 5.364 (s, 2H, O-CH_2-C), 3.650-3.625 (t, 4H, *J*=10.0 Hz, -CH_2-), 3.416-3.362 (hept, 1H, *J*=3.6 Hz, N-CH-C), 3.208-3.183 (t, 4H, *J*=10.0 Hz, -CH_2-), 1.488 (s, 9H,-CH_3) 1.269-1.253 (q, 2H, *J*=6.4 Hz, -CH_2-), 1.095 (s, 2H, -CH_2-). ^{13}C-NMR (400 MHz, $CDCl_3$-d_6) δ (ppm): 172.983, 165.482, 154.623, 152.116, 148.344, 144.450, 144.247, 137.939, 136.458, 128.825, 127.973, 127.914, 123.291, 123.221, 113.451, 110.093, 105.053, 80.210, 66.356, 49.933, 34.548, 28.432, 8.144. FT-IR (cm^{-1}): 3434.24, 1726.46, 1700.64, 1622.18, 1589.73, 1492.22, 1472.18, 1453.85, 1404.12, 1365.22, 1344.32, 1327.66, 1309.93, 1250.12, 1226.51, 1205.79, 1155.91, 1133.70, 1110.02, 1074.27, 1035.91, 1018.60, 10006.50, 892.61, 804.01, 783.04, 696.11. Elementary analysis, Anal. Calcd for $C_{52}H_{58}F_2N_6O_{10}$: C, 64.72, H, 6.06, F, 3.94, N, 8.71, O, 16.58. Elementary analysis, Anal. Calcd for $C_{29}H_{32}FN_3O_5$: C, 66.78, H, 6.18, N, 8.06. Found: C, 66.81, H, 6.12, N, 7.99.

TC1, ^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm): 8.670 (s, 2H, C=CH-N), 7.854-7.832 (d, 2H, *J*=13.2 Hz, C=CH-C), 7.502(s, 4H, C=CH-C), 7.108-7.097 (d, 2H, *J*=6.6 Hz, C-CH=C), 5.268(s, 4H, O-CH_2-C), 4.444-4.408 (q, 4H, *J*=7.2 Hz, N-CH_2-C), 3.439-3.423(t, 8H, *J*=4.8 Hz, -CH_2-), 3.299-3.283 (t, 8H, *J*=4.8 Hz, -CH_2-), 1.360-1.337 (t, 6H, *J*=6.9 Hz, -CH_3), 1.210 (s, 2H, -NH-).^{13}C-NMR (600 MHz,DMSO-d_6) δ (ppm): 174.604, 167.808, 154.589, 152.242, 146.195, 139.309, 139.275, 130.767, 126.439, 115.344, 112.289, 109.510, 68.129, 51.251, 49.831, 45.868, 17.447. FT-IR (cm^{-1}): 3421.51, 2993.09, 2851.02, 2769.39, 1684.87, 1628.74, 1573.49, 1543.69, 1491.62, 1456.65, 1399.10, 1317.65, 1273.28, 1226.41, 1203.19, 1175.65, 1127.86, 1087.78, 1033.35, 933.99, 897.18, 834.43, 804.68, 720.96, 620.75. Elementary analysis, Anal. Calcd for $C_{40}H_{42}F_2N_6O_6$: C, 64.85, H, 5.71, N, 11.34. Found: C, 64.91, H, 5.68, N, 11.40.

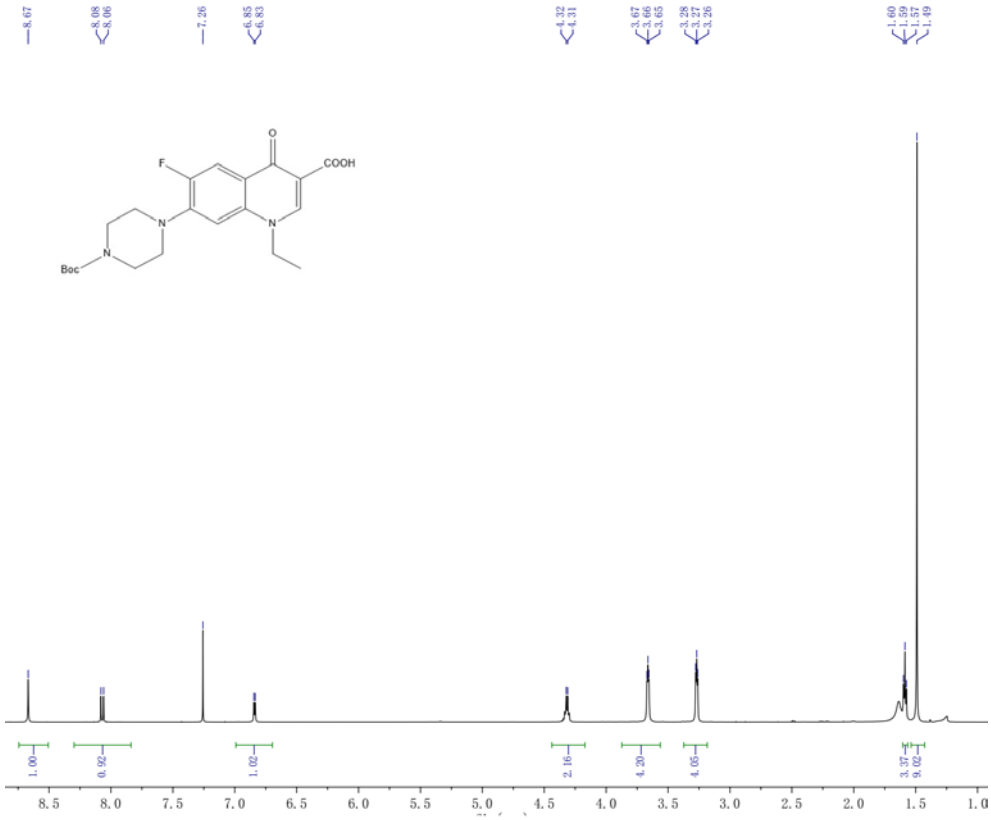
TC2 ^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm): 8.467 (s, 2H, C=CH-N), 7.798-7.776 (d, 2H, *J*=13.2 Hz, C=CH-C), 7.490(s, 4H, C=CH-C), 7.443-7.430 (d, 2H, *J*=7.9 Hz, C-CH=C), 5.260(s, 4H, O-CH_2-C), 1.235-1.211 (t, 6H, *J*=7.2 Hz, -CH_3), 1.089-1.063 (q, 4H, *J*=5.2 Hz, -CH_2-).^{13}C-NMR (600 MHz,DMSO-d_6) δ (ppm): 174.604, 167.808, 154.589, 152.242, 146.195, 139.309, 139.275, 130.767, 126.439, 115.344, 112.289, 109.510, 68.129, 51.251, 49.831, 45.868, 17.447. FT-IR (cm^{-1}): 3436.16, 3016.43, 2849.07, 1690.26, 1624.45, 1545.89, 1494.05, 1457.44, 1399.61, 1383.61, 1348.16, 1312.36, 1271.30, 1223.52, 1203.75, 1169.84, 1128.59, 1087.10, 1020.45, 898.21, 834.70, 800.85, 781.56, 721.24. Elementary analysis, Anal. Calcd for $C_{42}H_{42}F_2N_6O_6$: C, 65.96, H, 5.54, N, 10.99. Found: C, 66.01, H, 5.49, N, 11.03.

RC1: ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.690 (s, 1H, C=CH-N), 7.857-7.824 (d, 1H, *J*=13.2 Hz, C=CH-C), 7.506-7.488 (d, 2H, *J*=7.2 Hz, C=CH-C), 7.407-7.370 (t, 2H, *J*=7.4 Hz, C=CH-C), 7.339-7.321 (d, 1H, *J*=7.2 Hz, C=CH-C), 7.128-7.110 (d, 1H, *J*=7.2 Hz, C-CH=C), 5.280 (s, 2H, O-CH_2-C), 4.467-4.419 (q, 2H, *J*=6.4 Hz, N-CH_2-C), 3.459 (s, 4H, -CH_2-), 3.320 (s, 4H, -CH_2-), 1.382-1.347 (t, 6H, *J*=7.0 Hz, -CH_3). ^{13}C-NMR (400 MHz,DMSO-d_6) δ (ppm): 172.010, 165.152, 151.552, 149.063, 143.606, 143.504, 137.135, 136.629, 128.831, 128.211,

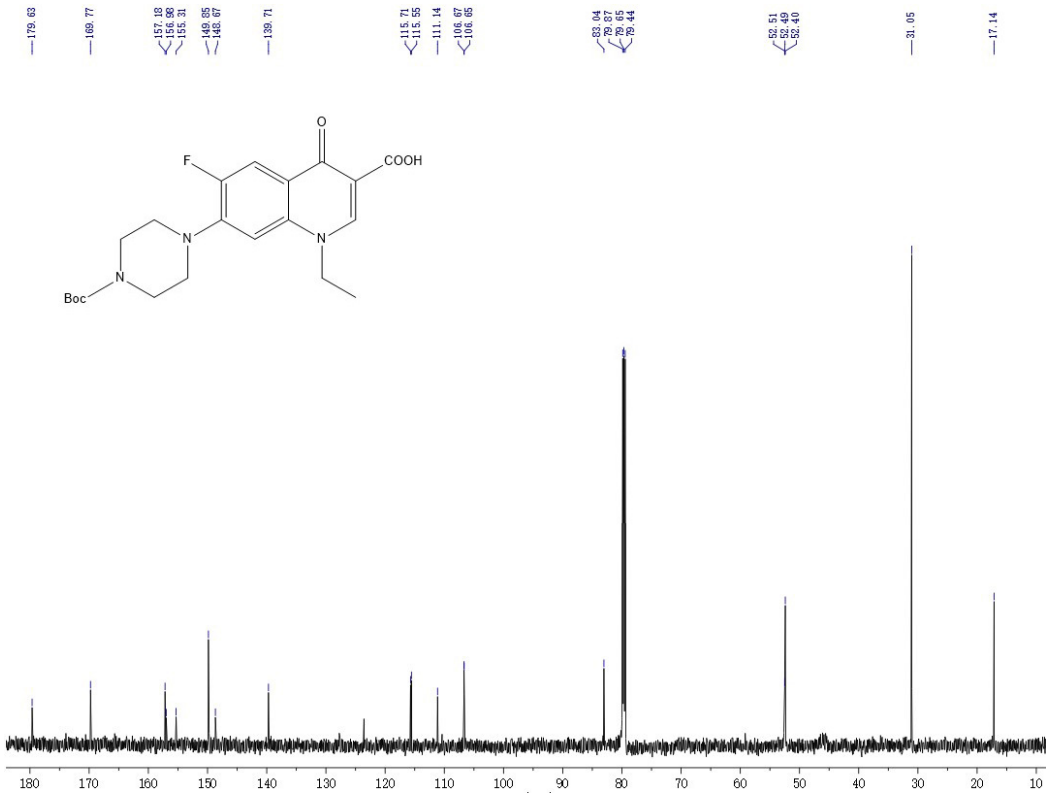
128.094, 123.805, 112.478, 109.588, 106.857, 65.675, 48.634, 47.189, 47.144, 14.802. FT-IR (cm^{-1}): 3450.80, 1709.18, 1688.10, 1627.34, 1577.23, 1543.60, 1492.96, 1455.60, 1317.95, 1274.88, 1257.00, 1225.46, 1204.01, 1175.41, 1130.36, 1087.01, 1033.22, 910.27, 829.46, 804.62. Elementary analysis, Anal. Calcd for $C_{23}H_{24}FN_3O_3$: C, 67.47, H, 5.91, N, 10.26. Found: C, 67.52, H, 5.86, N, 10.30.

RC2: ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.485 (s, 1H, C=CH-N), 7.817-7.783 (d, 1H, *J*=13.6 Hz, C=CH-C), 7.504-7.484 (t, 3H, *J*=4.0 Hz, C=CH-C), 7.419-7.382 (t, 2H, *J*=7.4 Hz, C=CH-C), 7.352-7.334 (d, 1H, *J*=7.2 Hz, C=CH-C), 7.128-7.110 (d, 1H, *J*=7.2 Hz, C-CH=C), 5.278 (s, 2H, O-CH_2-C), 3.704-3.650 (hept, 1H, *J*=3.6 Hz, N-CH-C), 3.464 (s, 4H, -CH_2-), 3.356 (s, 4H, -CH_2-), 1.262-1.246 (q, 2H, *J*=6.4 Hz, -CH_2-), 1.105 (s, 2H, -CH_2-). ^{13}C-NMR (400 MHz,DMSO-d_6) δ (ppm): 172.050, 164.933, 151.705, 149.054, 143.277, 138.463, 137.092, 128.855, 128.253, 128.090, 123.076, 112.387, 109.380, 107.249, 65.738, 47.074, 43.164, 35.376, 8.023. FT-IR (cm^{-1}): 3483.22, 2969.13, 2846.50, 2744.64, 1709.66, 1691.44, 1625.83, 1579.14, 1544.58, 1494.58, 1480.08, 1456.45, 1399.32, 1348.60, 1314.54, 1273.60, 1232.94, 1203.52, 1172.04, 1128.42, 1089.03, 1022.56, 909.22, 830.64, 804.46. Elementary analysis, Anal. Calcd for $C_{24}H_{24}FN_3O_3$: C, 68.39, H, 5.74, N, 9.97. Found: C, 68.44, H, 5.69, N, 10.01.

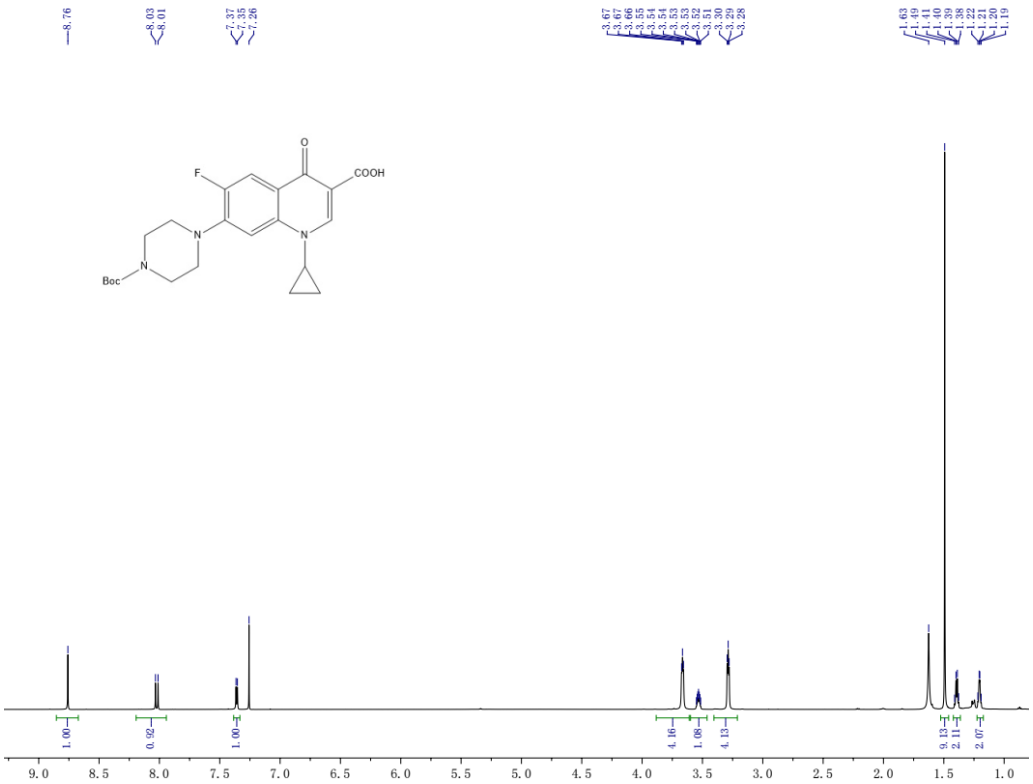
^{1}H-NMR ($CDCl_3$- d_6) of I1:



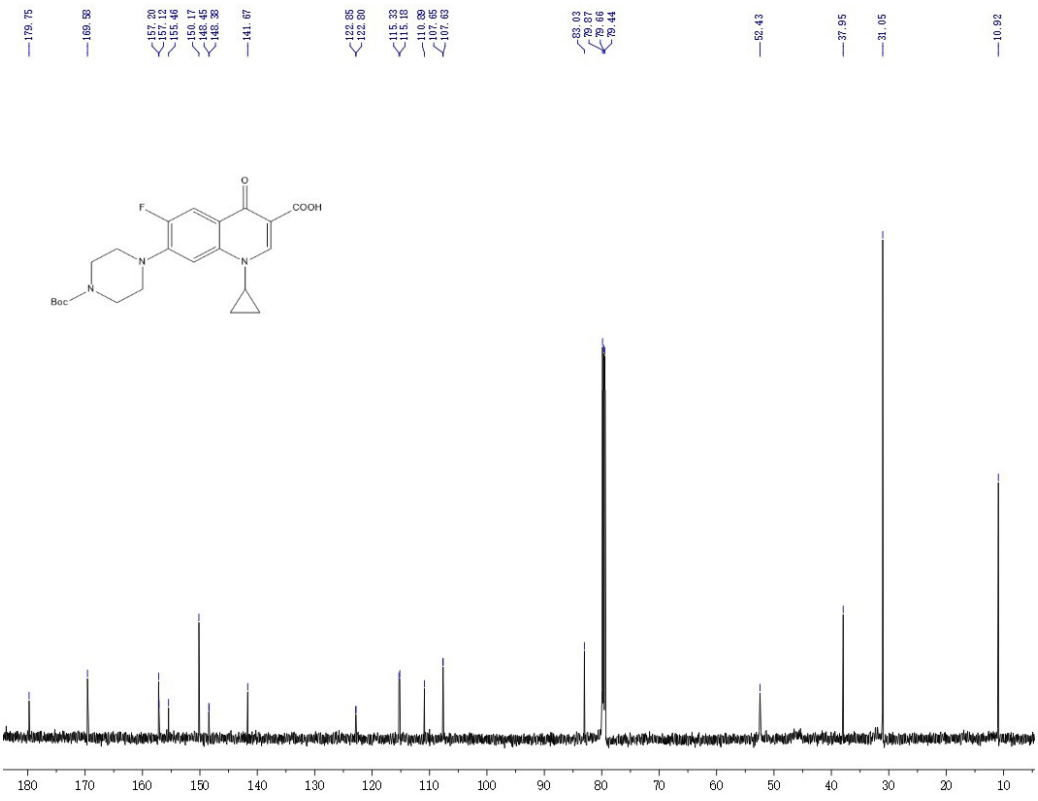
^{13}C-NMR ($CDCl_3$-d_6) of I1:



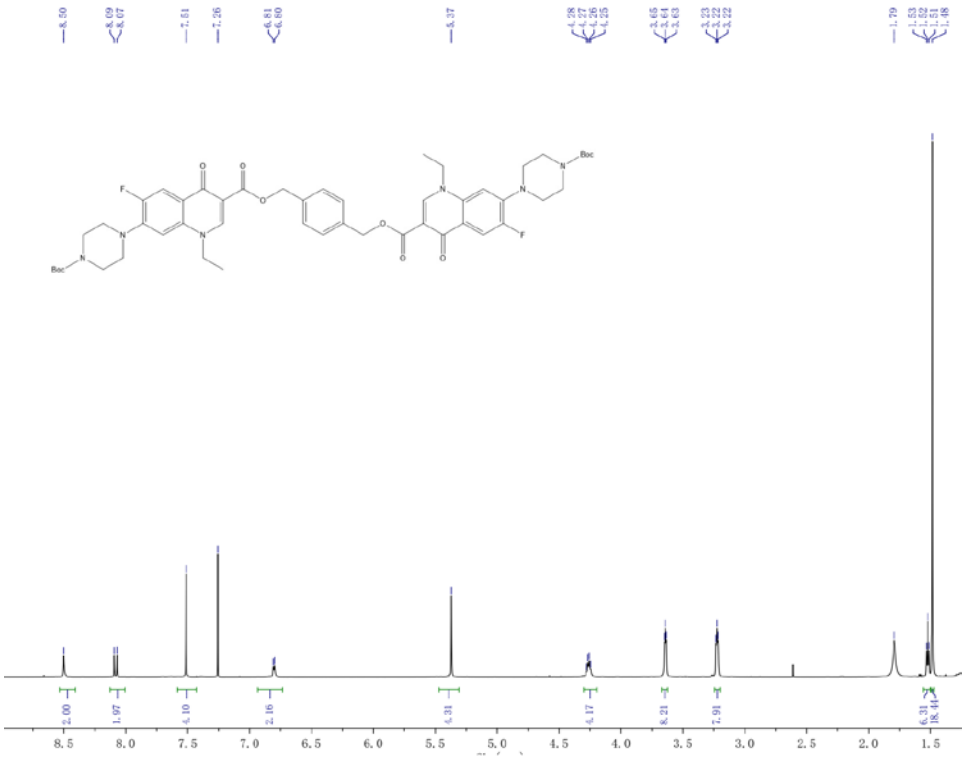
^{1}H-NMR ($CDCl_3$-d_6) of I2:



^{13}C-NMR ($CDCl_3$-d_6) of I2:

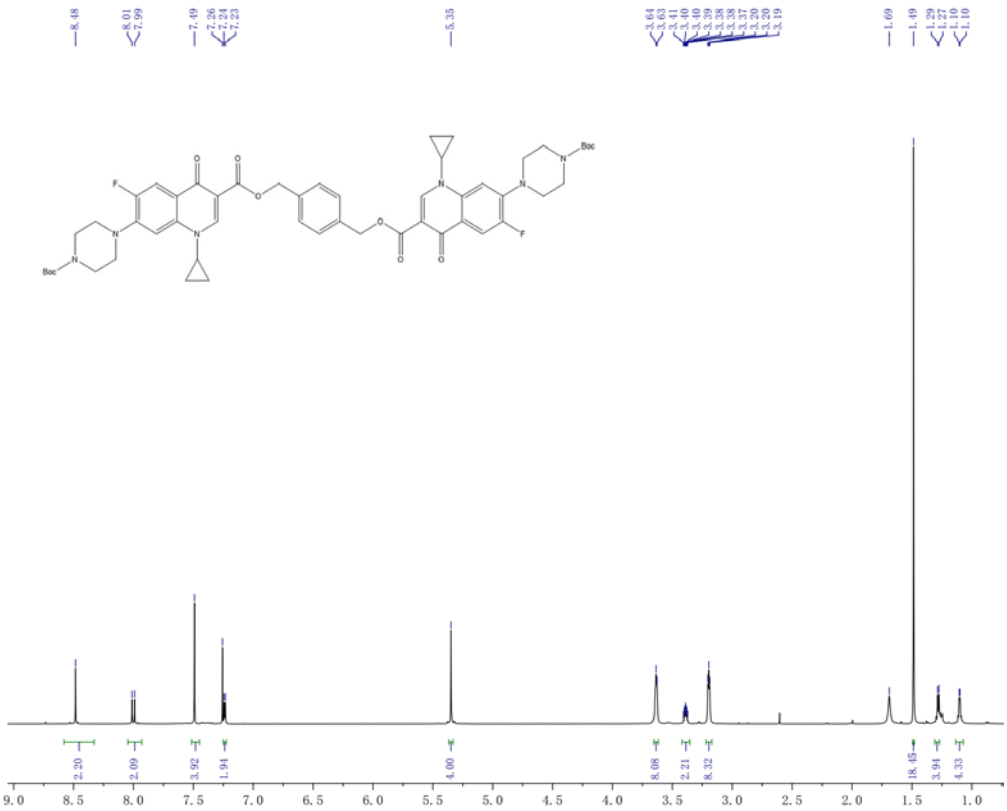


^{1}H-NMR ($CDCl_3$-d_6) of I3:

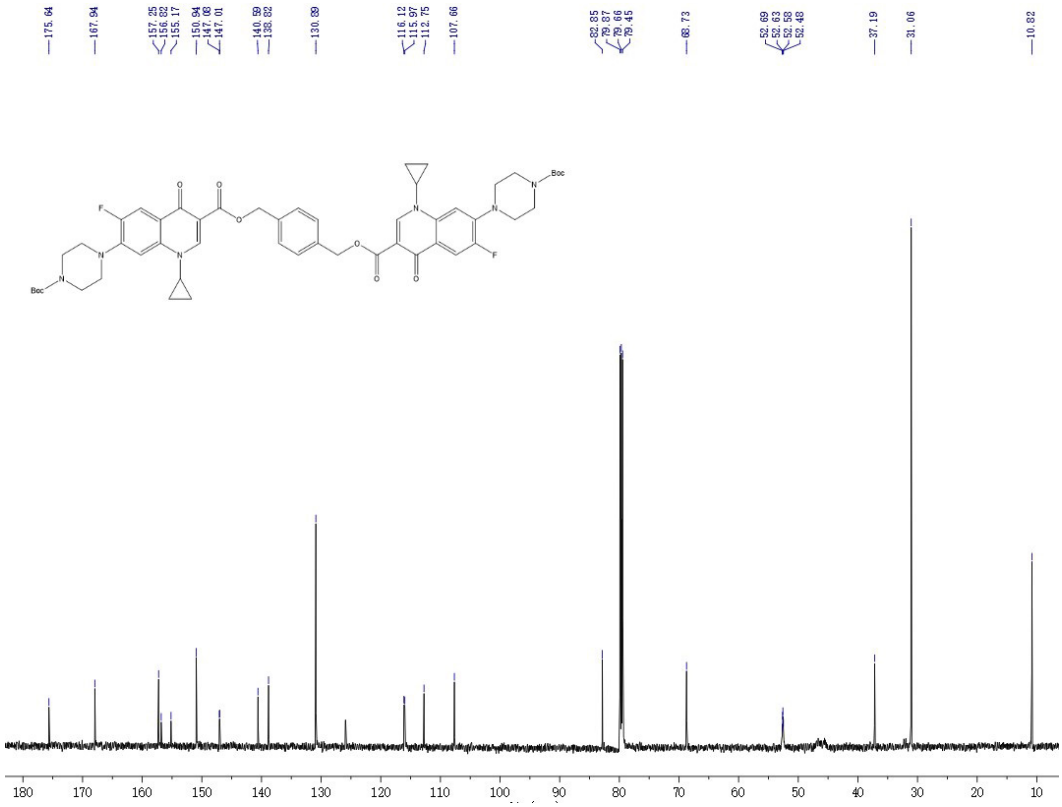


^{13}C-NMR ($CDCl_3$-d_6) of I3:

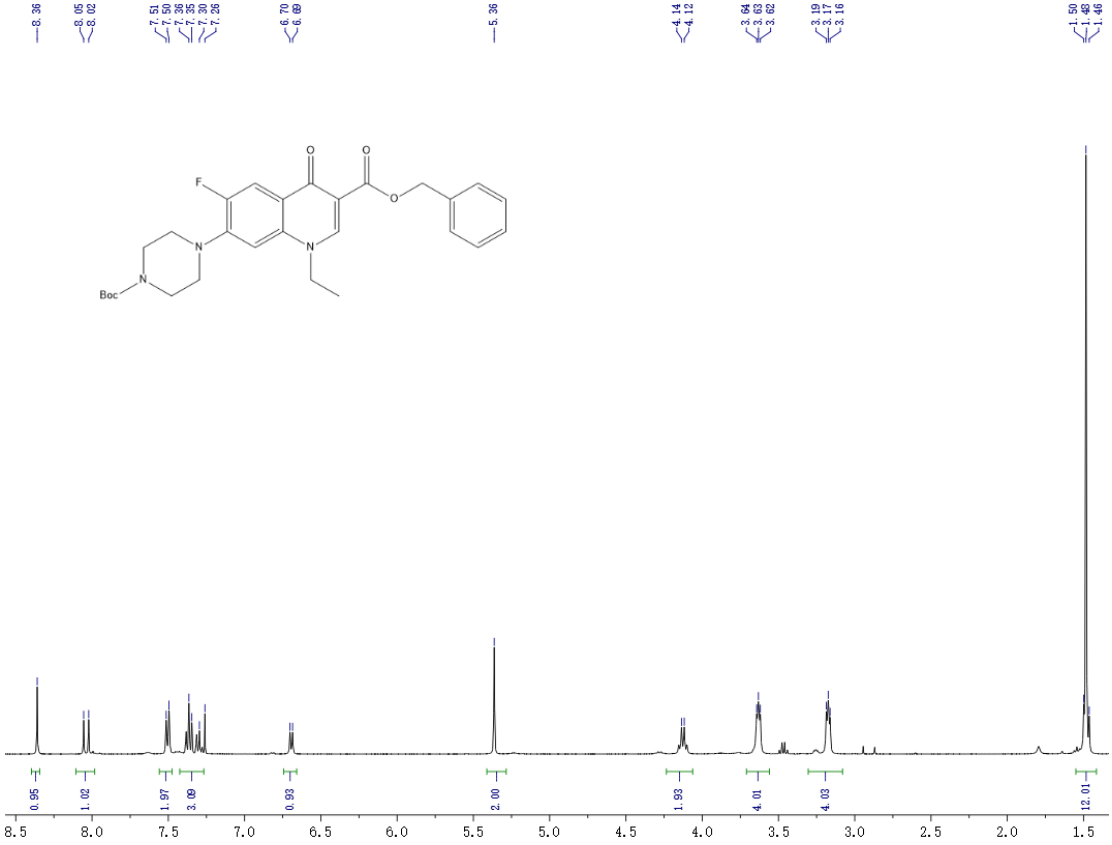
^{1}H-NMR ($CDCl_3$-d_6) of I4:



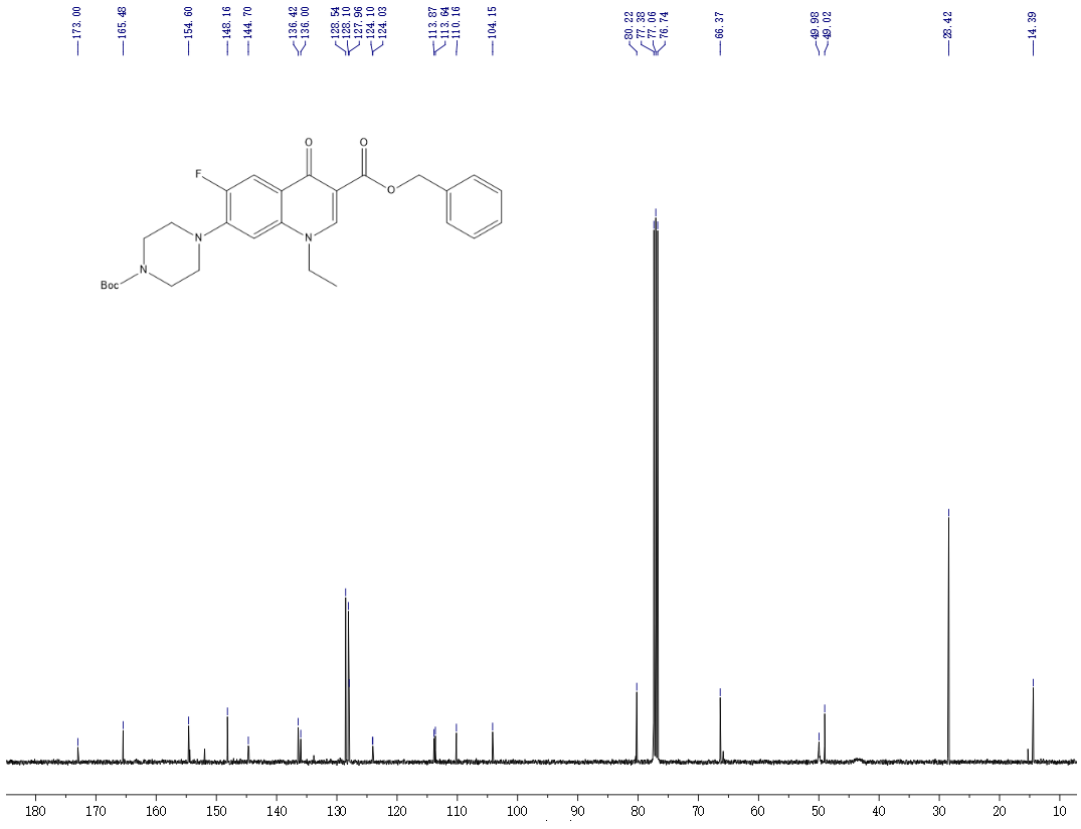
^{13}C-NMR ($CDCl_3$-d_6) of I4:



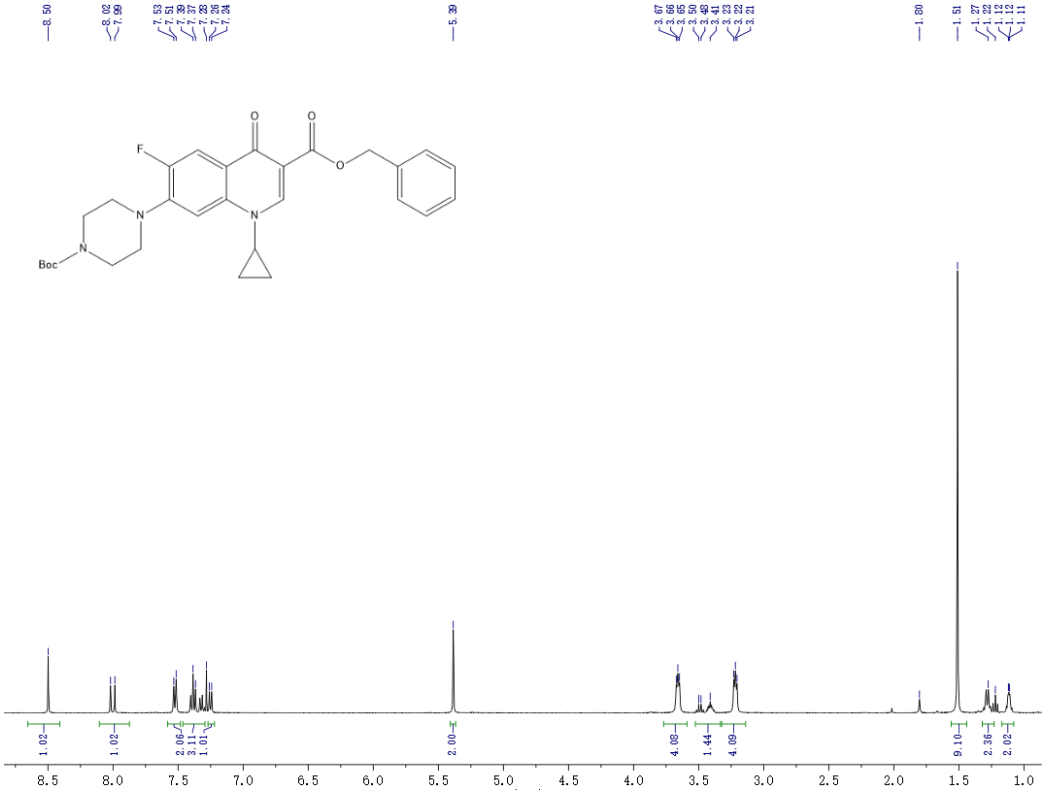
^{1}H-NMR ($CDCl_3$-d_6) of I5:



^{13}C-NMR ($CDCl_3$-d_6) of I5:

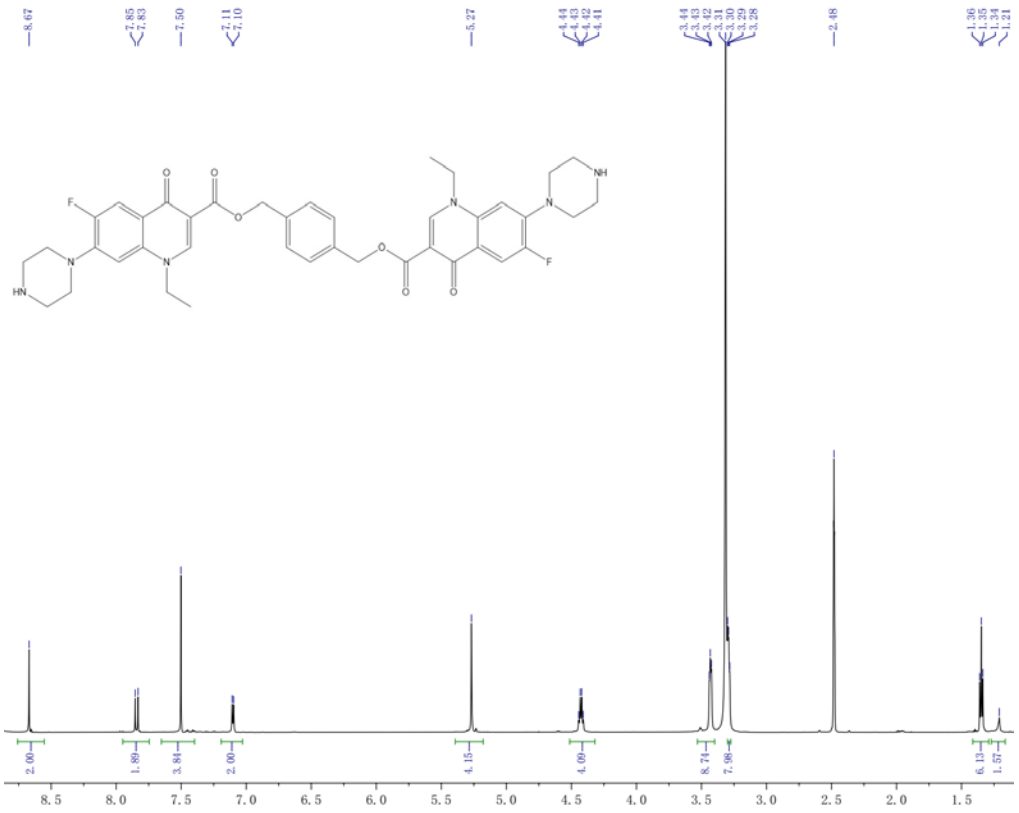


^{1}H-NMR ($CDCl_3$-d_6) of I6:

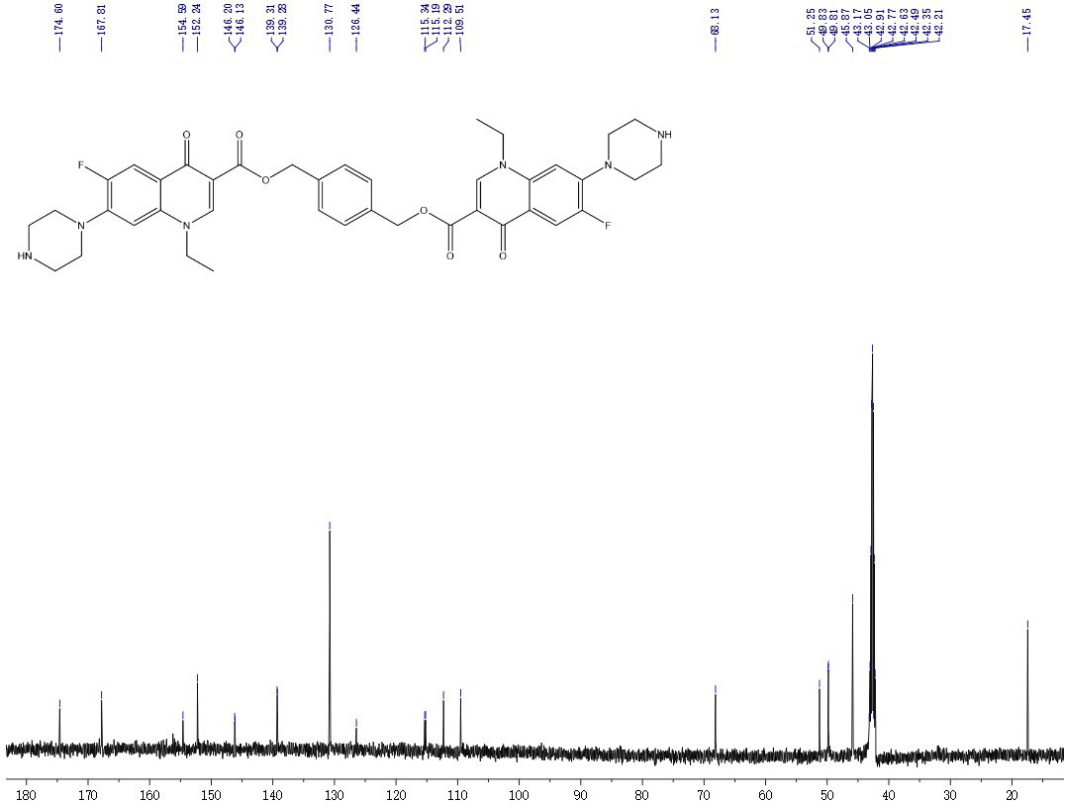


^{13}C-NMR ($CDCl_3$-d_6) of I6:

^{1}H-NMR (DMSO-d_6) of TC1:

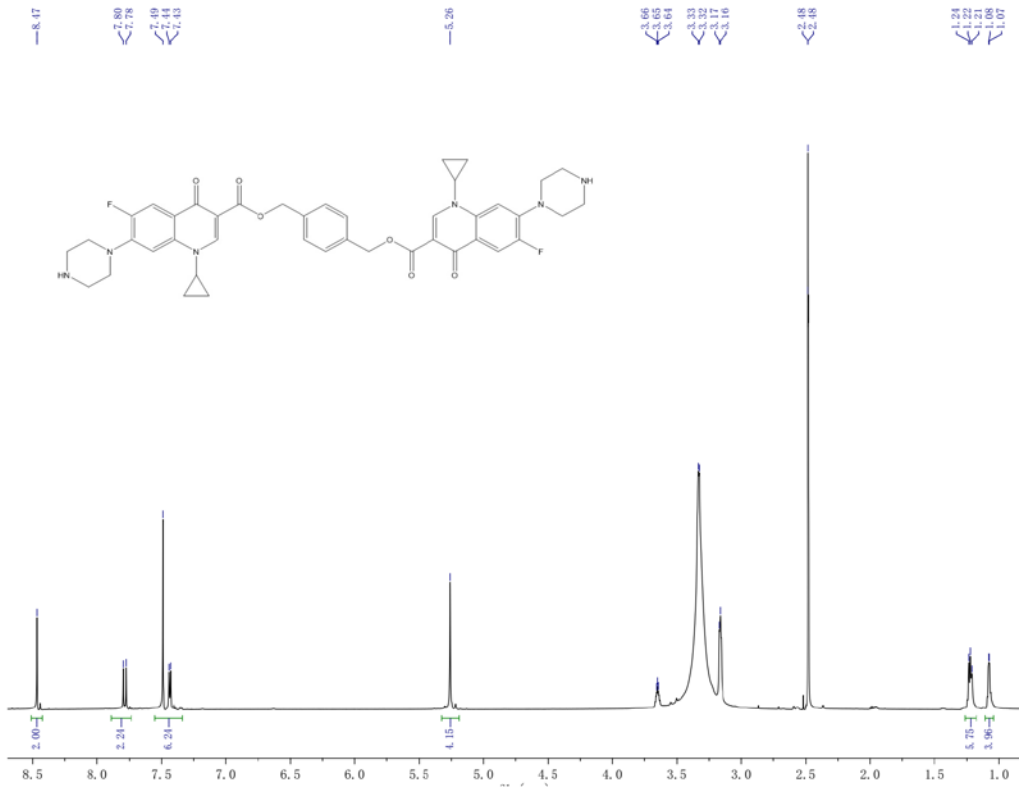


^{13}C-NMR (DMSO-d_6) of TC1:

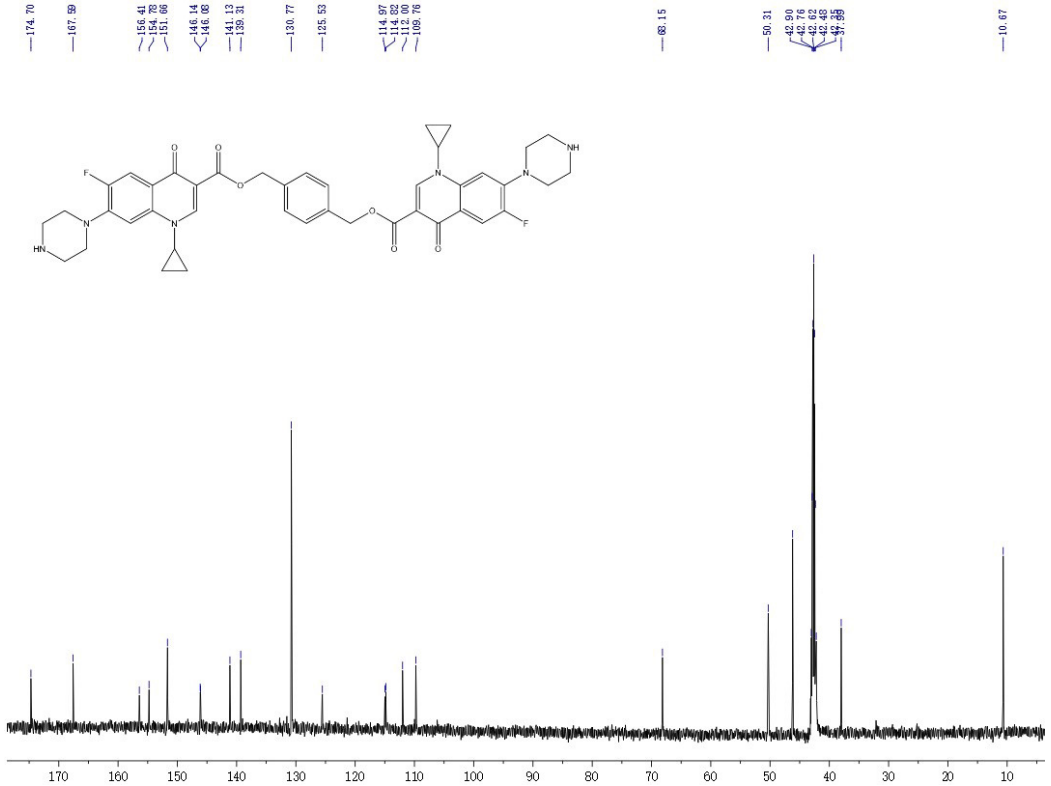


^{19}F-NMR (DMSO-d_6) of TC1:

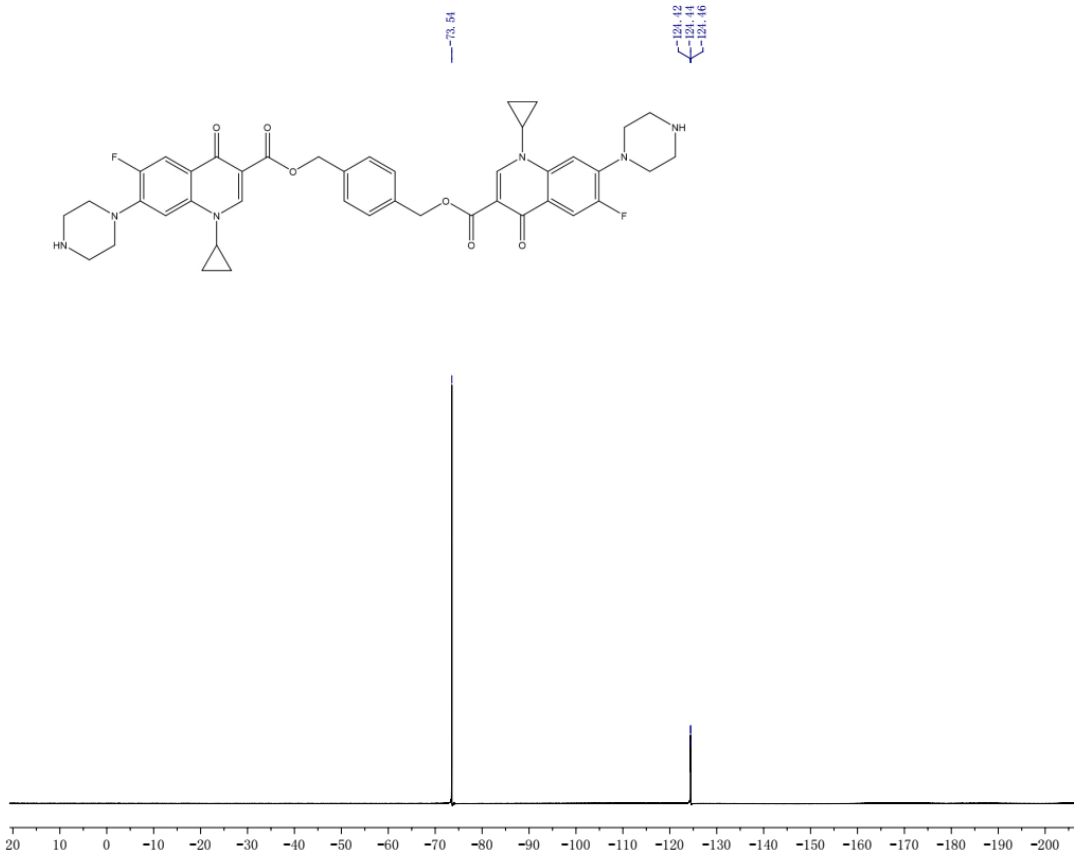
^{1}H-NMR (DMSO-d_6) of TC2:



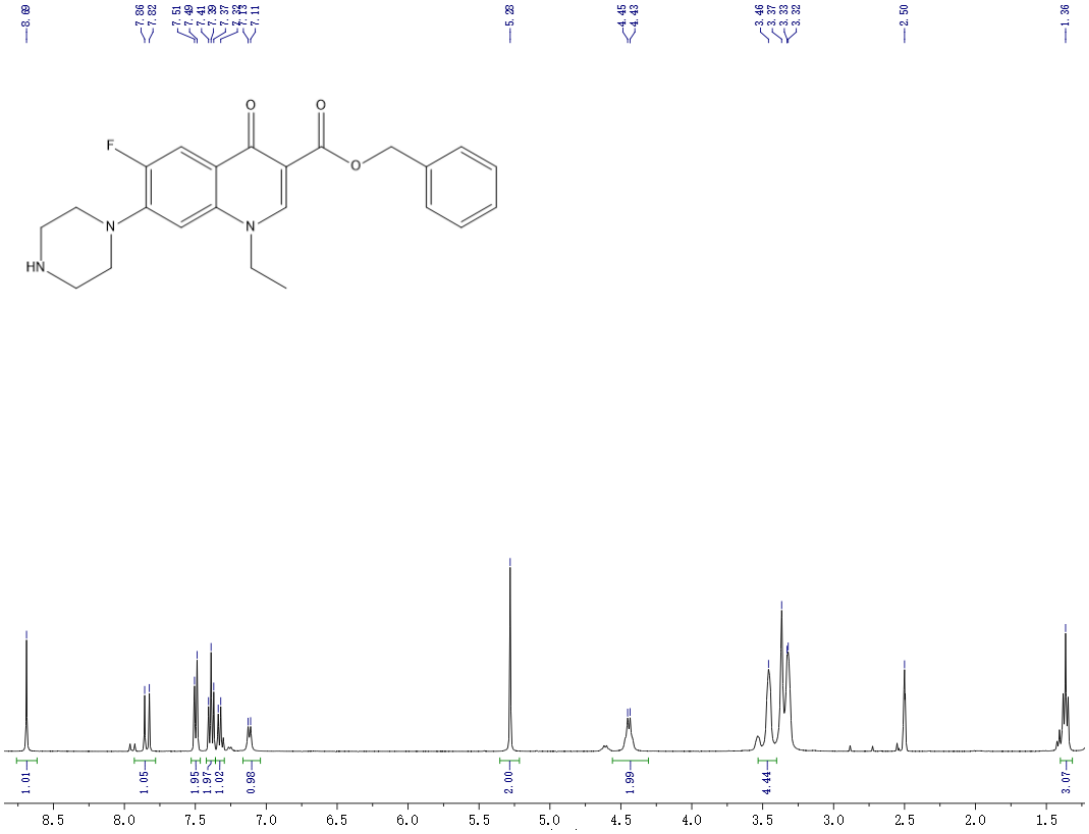
^{13}C-NMR (DMSO-d_6) of TC2:



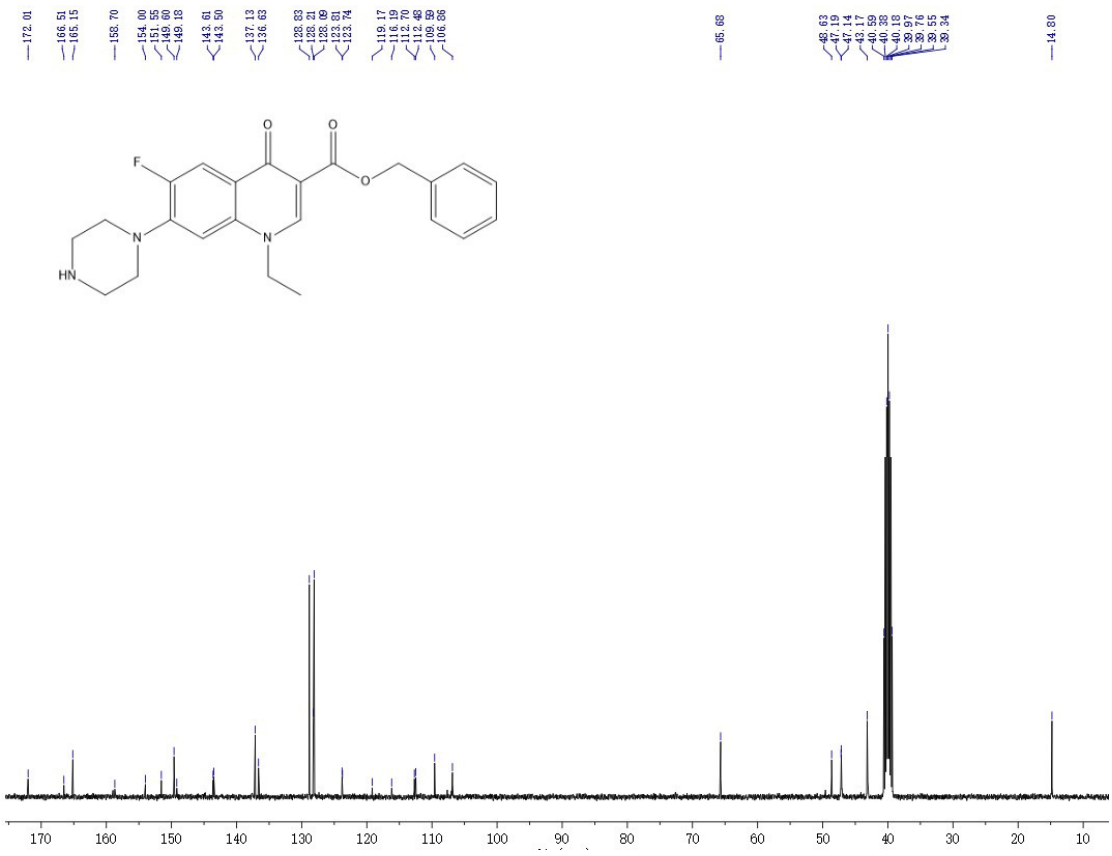
^{19}F-NMR (DMSO-d_6) of TC2:



^{1}H-NMR (DMSO-d_6) of RC1:

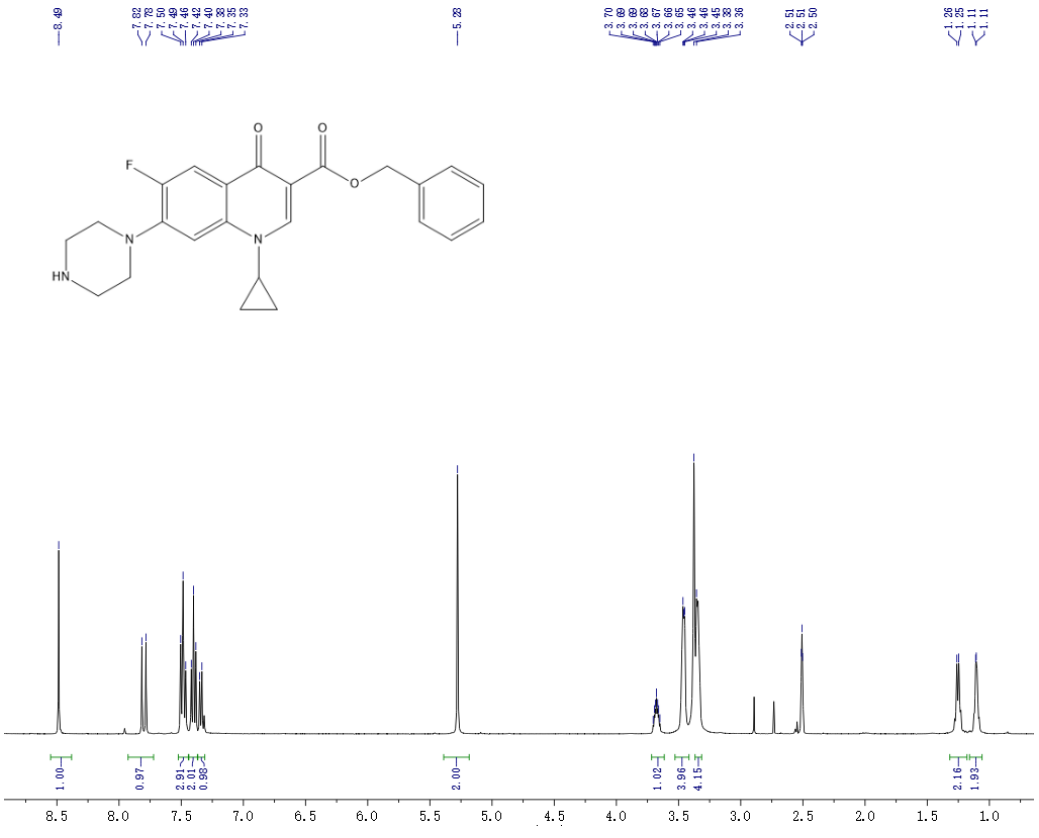


^{13}C-NMR (DMSO-d_6) of RC1:

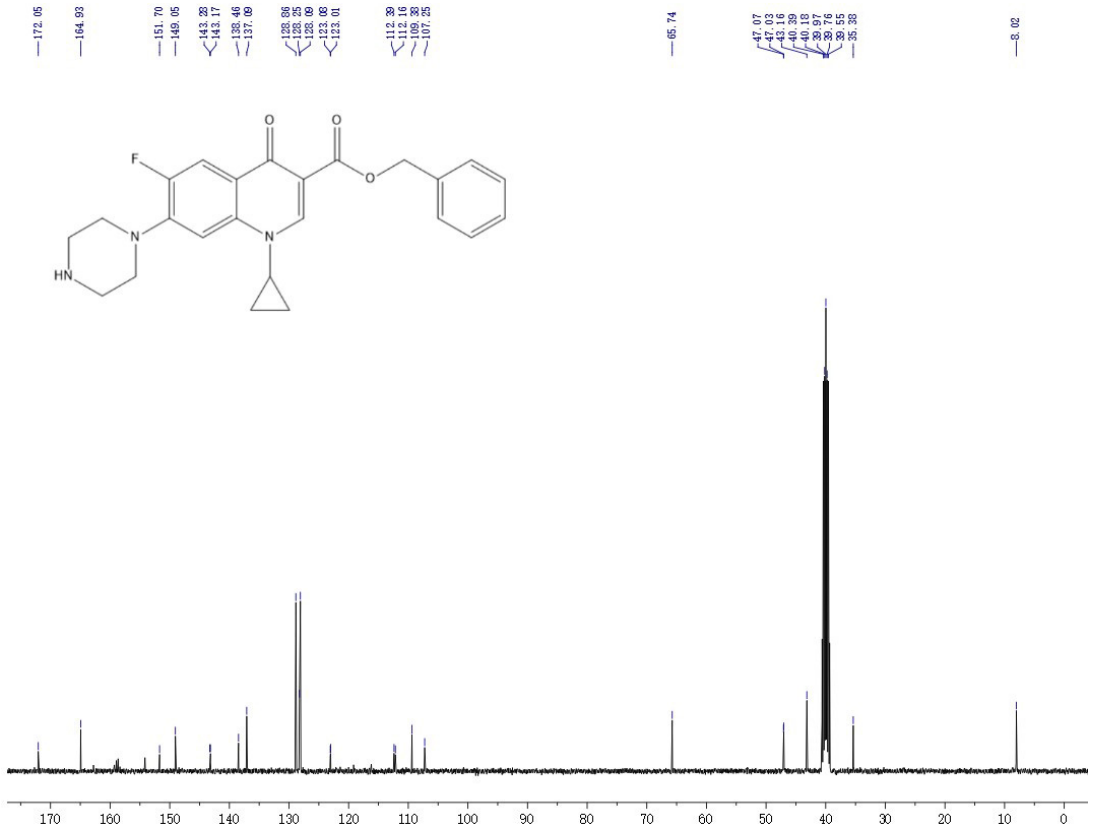


^{19}F-NMR (DMSO-d_6) of RC1:

^{1}H-NMR (DMSO-d_6) of RC2:

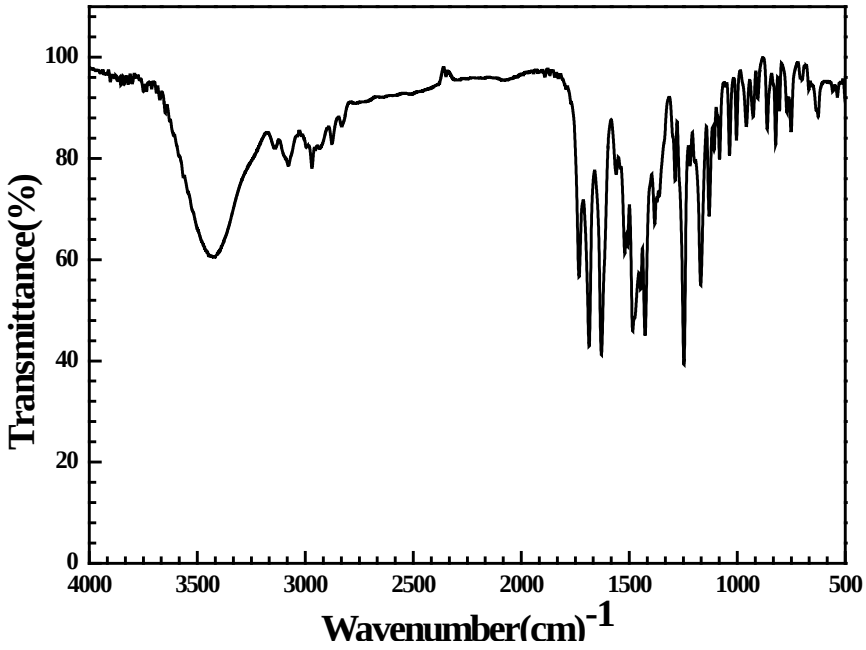


^{13}C-NMR (DMSO-d_6) of RC2:

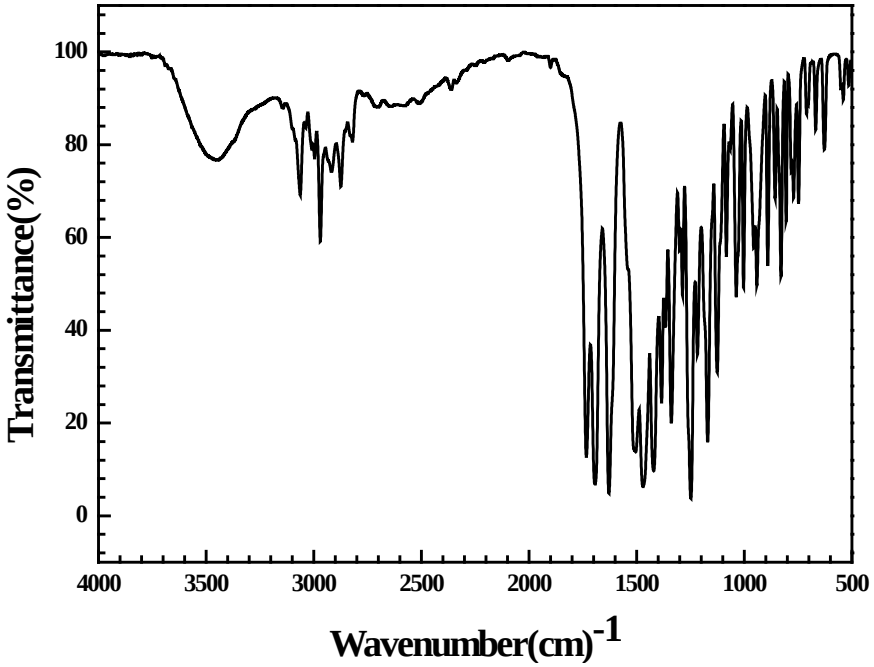


^{19}F-NMR (DMSO-d_6) of RC2:

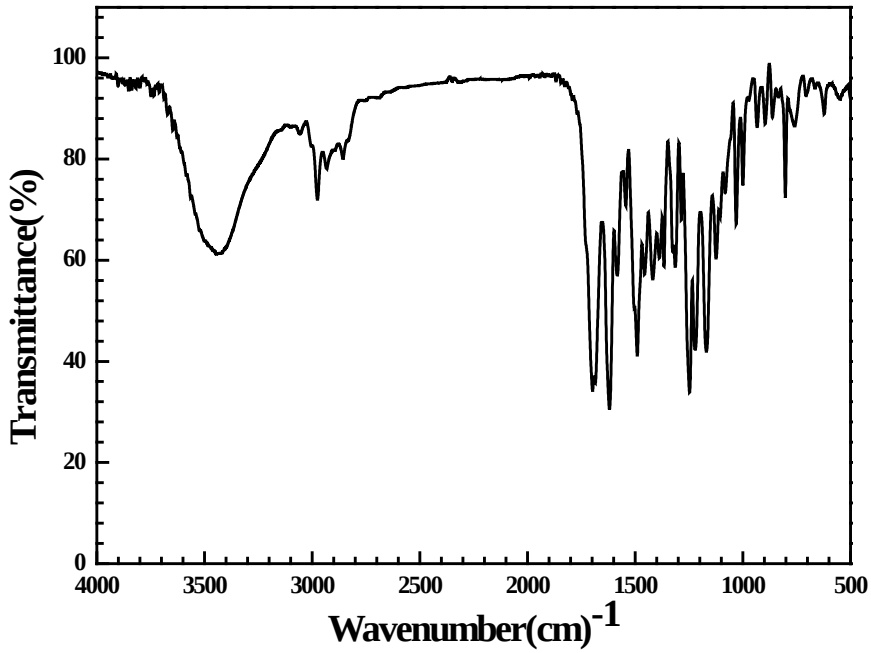
FT-IR of I1:



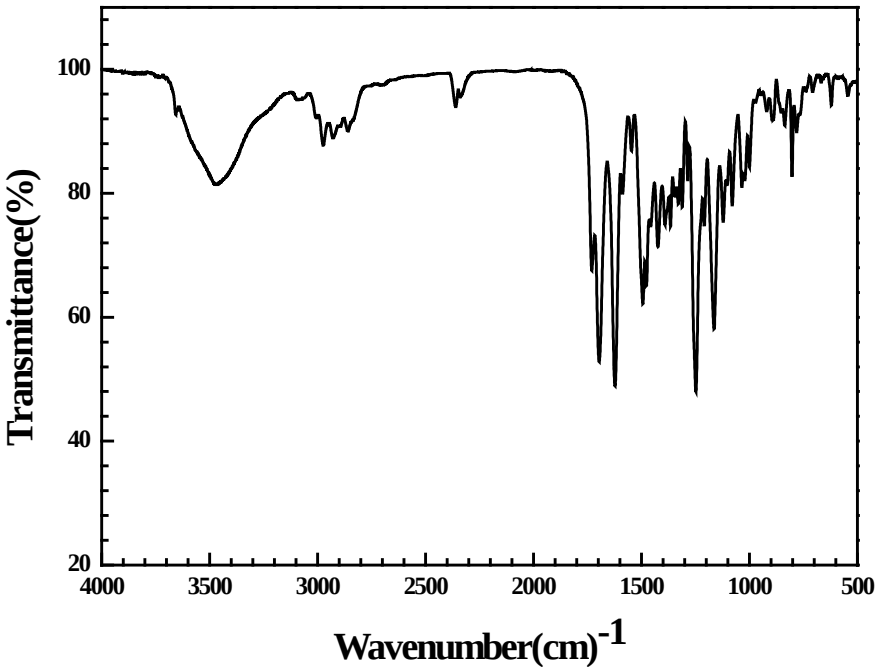
FT-IR of I2:



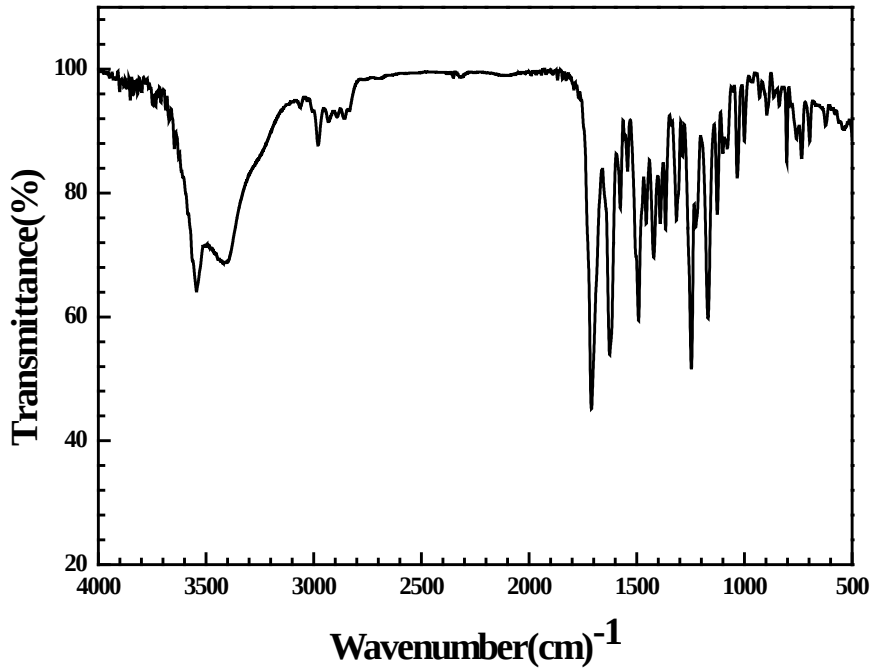
FT-IR of I3:



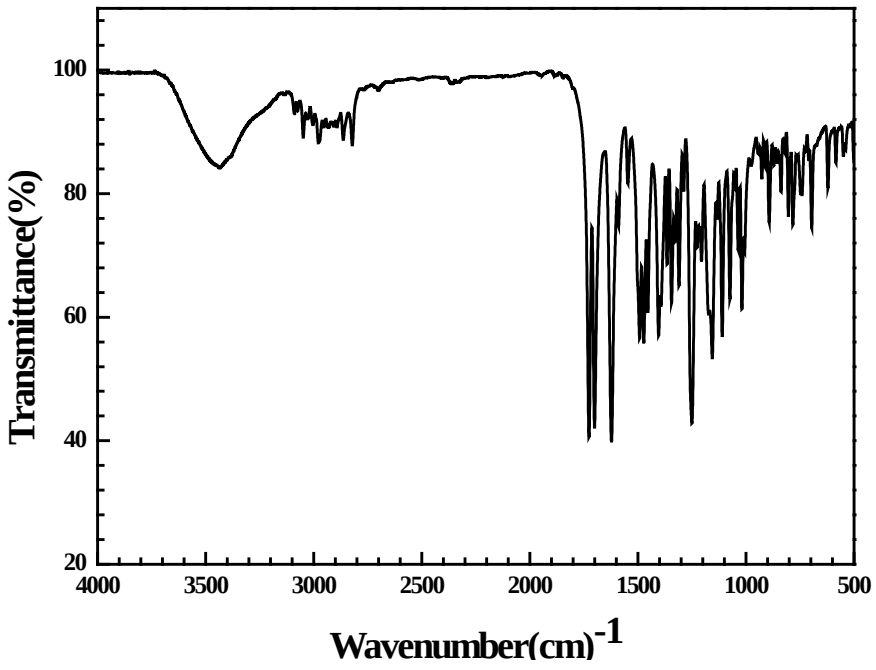
FT-IR of I4:



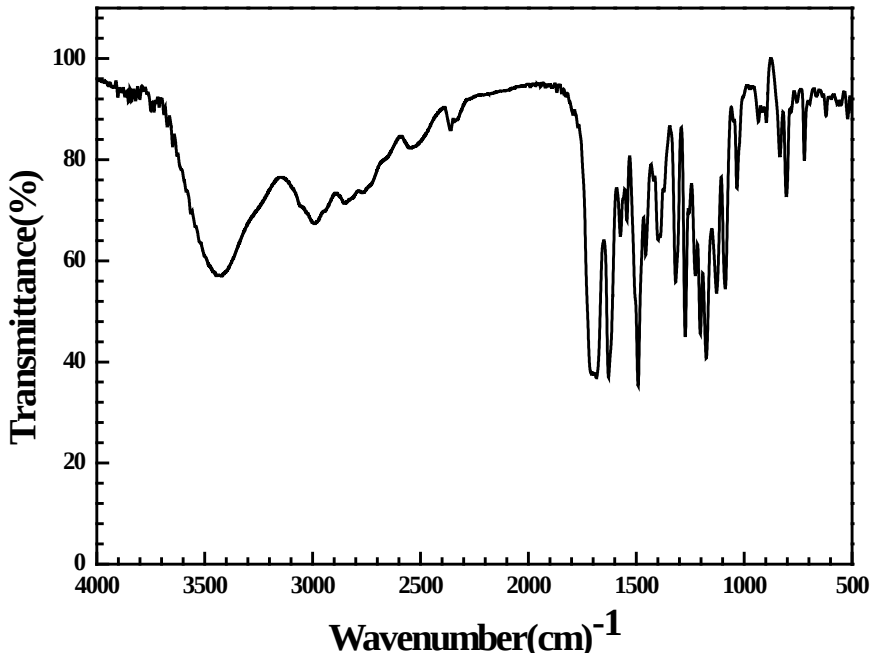
FTIR of I5:



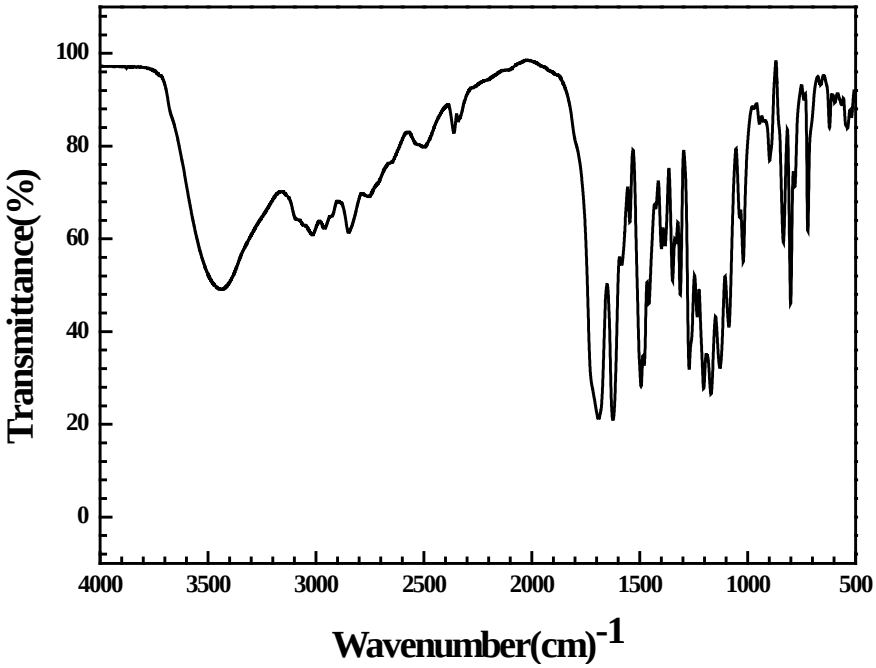
FTIR of I6:



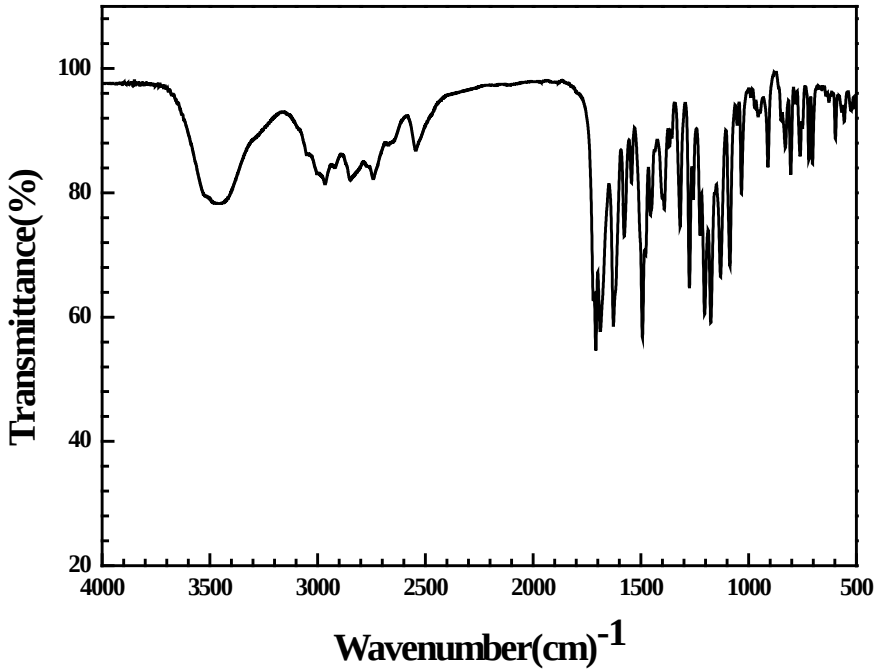
FT-IR of TC1:



FT-IR of TC2:



FT-IR of RC1:



FT-IR of RC2: