Supplementary Information

for

An efficient and green synthesis of ferrocenyl-quinoline conjugates *via* a TsOH-catalyzed three-component reaction in water

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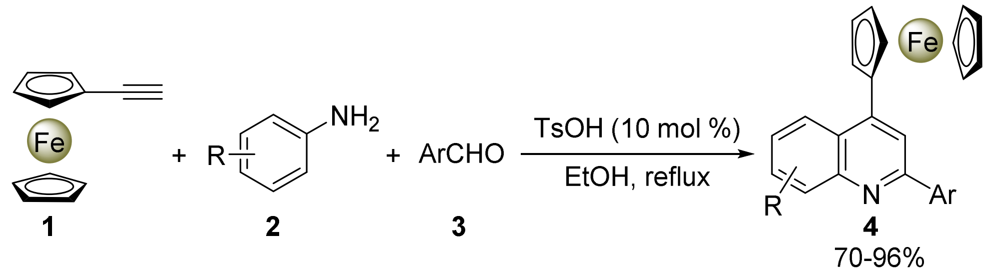
1. Synthesis of **4** in EtOH



General procedure:

A solution of aldehyde (1.0 mmol), amine (1.0 mmol), ferrocenylacetylene (1.1 mmol) and TsOH (0.1 mmol) in EtOH (1.0 mL) was stirred at refluxing under air. When the reaction completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The organic phase was washed with saturated sodium bicarbonate solution and brine, and then dried over anhydrous $MgSO_4$. The volatile was evaporated under reduced pressure, and the residue was subjected to the flash column chromatography (silica-gel), to afford products **4a-4t**. The results are summarized in Table S1.

Table S1 Synthetic results of **4** in EtOH

Compd.	T/^{o}C	t/h	Yield/%	Compd.	T/^{o}C	t/h	Yield/%
4a	78	2	93	**4k'**	78	2	55
4b	78	2	96	**4l**	78	2	80
4c	78	2	93	**4m**	78	2	93
4d	78	2	81	**4n**	78	2	89
4e	78	2	88	**4o**	78	2	85
4f	78	3	70	**4p**	78	3	72
4g	78	2.5	81	**4q**	78	2	90
4h	78	2.5	82	**4r**	78	2	89
4i	78	2.5	75	**4s**	78	2	82
4j	78	2	93	**4t**	78	2.5	80
4k	78	2	37				

2. Crystallographic data of **4a** and **4k**

Table S2 Crystallographic and refinement data of **4a** and **4k**

Code	**4a**	**4k**
Empirical formula	$C_{25}H_{19}FeN$	$C_{26}H_{21}FeN$
Formula weight	389.26	403.29
Temperature (K)	100 K	100 K
Wavelength (Å)	0.71073	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	*P21/n*	*P21/n*
a (Å)	7.3370 (3)	8.36603(17)
b (Å)	10.4908(4)	20.5582(4)
c (Å)	23.2831(9)	11.3490(2)
β (°)	95.626(3)	107.835
Volume (Å^3)	1783.49 (12)	1858.12(6)
Z	4	4
Density (mg/m^3)	1.450	1.442
μ (mm^{-1})	0.85	6.57
F(000)	808	840
Crystal size (mm)	0.38×0.16×0.12	0.24×0.17×0.09
θ range (°)	3.9 to 28.7	4.3 to 71.0
Collected reflections	7550	6994
Independent reflections	3375	3490
Observed reflections [I>2σ (I)]	2978	3136
Goodness-of-fit on F^2	1.055	1.015
Final R indices [I>2σ (I)]	R = 0.0336, wR = 0.0840	R = 0.0365, wR = 0.0899
R indices (all data)	R = 0.0388, wR = 0.0878	R = 0.0420, wR = 0.0928
($\Delta\rho$)max, ($\Delta\rho$)min (e. Å^{-3})	0.27, -0.44	0.44, -0.65

Table S3 Bond lengths (Å), bond angles (°) and torsion angles (°) for **4a**

C1—H1	0.9800	C10—Fe1	2.041 (2)
C1—C2	1.422 (3)	C11—C12	1.377 (3)
C1—C5	1.438 (3)	C11—C25	1.431 (3)
C1—Fe1	2.046 (2)	C12—H12	0.9300
C2—H2	0.9800	C12—C13	1.416 (3)
C2—C3	1.420 (3)	C13—C14	1.494 (3)
C2—Fe1	2.045 (2)	C13—N1	1.329 (3)
C3—H3	0.9800	C14—C15	1.396 (3)
C3—C4	1.421 (3)	C14—C19	1.397 (3)
C3—Fe1	2.043 (2)	C15—H15	0.9300
C4—H4	0.9800	C15—C16	1.390 (3)
C4—C5	1.438 (3)	C16—H16	0.9300
C4—Fe1	2.043 (2)	C16—C17	1.385 (3)
C5—C11	1.478 (3)	C17—H17	0.9300
C5—Fe1	2.0544 (19)	C17—C18	1.387 (3)
C6—H6	0.9800	C18—H18	0.9300
C6—C7	1.419 (3)	C18—C19	1.385 (3)
C6—C10	1.421 (3)	C19—H19	0.9300
C6—Fe1	2.042 (2)	C20—C21	1.419 (3)
C7—H7	0.9800	C20—C25	1.429 (3)
C7—C8	1.421 (3)	C20—N1	1.366 (3)
C7—Fe1	2.049 (2)	C21—H21	0.9300
C8—H8	0.9800	C21—C22	1.364 (3)
C8—C9	1.421 (3)	C22—H22	0.9300
C8—Fe1	2.051 (2)	C22—C23	1.410 (3)
C9—H9	0.9800	C23—H23	0.9300
C9—C10	1.421 (3)	C23—C24	1.369 (3)
C9—Fe1	2.042 (2)	C24—H24	0.9300
C10—H10	0.9800	C24—C25	1.418 (3)
C2—C1—H1	125.8	C17—C16—C15	120.0 (2)
C2—C1—C5	108.39 (19)	C17—C16—H16	120.0
C2—C1—Fe1	69.64 (12)	C16—C17—H17	120.1
C5—C1—H1	125.8	C16—C17—C18	119.7 (2)
C5—C1—Fe1	69.80 (12)	C18—C17—H17	120.1
Fe1—C1—H1	125.8	C17—C18—H18	119.9
C1—C2—H2	125.9	C19—C18—C17	120.2 (2)
C1—C2—Fe1	69.69 (12)	C19—C18—H18	119.9
C3—C2—C1	108.27 (19)	C14—C19—H19	119.5
C3—C2—H2	125.9	C18—C19—C14	120.9 (2)
C3—C2—Fe1	69.59 (12)	C18—C19—H19	119.5
Fe1—C2—H2	125.9	C21—C20—C25	119.14 (19)

C2—C3—H3	125.9	N1—C20—C21	117.19 (18)
C2—C3—C4	108.11 (19)	N1—C20—C25	123.67 (19)
C2—C3—Fe1	69.77 (12)	C20—C21—H21	119.5
C4—C3—H3	125.9	C22—C21—C20	120.92 (19)
C4—C3—Fe1	69.65 (12)	C22—C21—H21	119.5
Fe1—C3—H3	125.9	C21—C22—H22	119.9
C3—C4—H4	125.7	C21—C22—C23	120.3 (2)
C3—C4—C5	108.52 (19)	C23—C22—H22	119.9
C3—C4—Fe1	69.65 (12)	C22—C23—H23	119.9
C5—C4—H4	125.7	C24—C23—C22	120.3 (2)
C5—C4—Fe1	69.89 (11)	C24—C23—H23	119.9
Fe1—C4—H4	125.7	C23—C24—H24	119.3
C1—C5—C4	106.71 (18)	C23—C24—C25	121.33 (19)
C1—C5—C11	128.99 (19)	C25—C24—H24	119.3
C1—C5—Fe1	69.15 (11)	C20—C25—C11	117.20 (18)
C4—C5—C11	124.11 (18)	C24—C25—C11	124.71 (18)
C4—C5—Fe1	69.02 (11)	C24—C25—C20	118.06 (18)
C11—C5—Fe1	130.54 (14)	C1—Fe1—C5	41.05 (8)
C7—C6—H6	125.8	C1—Fe1—C7	124.99 (9)
C7—C6—C10	108.4 (2)	C1—Fe1—C8	109.34 (9)
C7—C6—Fe1	69.98 (13)	C2—Fe1—C1	40.67 (8)
C10—C6—H6	125.8	C2—Fe1—C5	68.89 (8)
C10—C6—Fe1	69.59 (12)	C2—Fe1—C7	107.42 (9)
Fe1—C6—H6	125.8	C2—Fe1—C8	122.56 (9)
C6—C7—H7	126.0	C3—Fe1—C1	68.55 (9)
C6—C7—C8	107.9 (2)	C3—Fe1—C2	40.64 (9)
C6—C7—Fe1	69.44 (13)	C3—Fe1—C5	68.99 (8)
C8—C7—H7	126.0	C3—Fe1—C7	120.30 (9)
C8—C7—Fe1	69.77 (12)	C3—Fe1—C8	156.75 (9)
Fe1—C7—H7	126.0	C4—Fe1—C1	68.70 (9)
C7—C8—H8	126.1	C4—Fe1—C2	68.46 (9)
C7—C8—Fe1	69.66 (12)	C4—Fe1—C3	40.70 (8)
C9—C8—C7	107.8 (2)	C4—Fe1—C5	41.09 (8)
C9—C8—H8	126.1	C4—Fe1—C7	155.35 (9)
C9—C8—Fe1	69.38 (12)	C4—Fe1—C8	161.97 (9)
Fe1—C8—H8	126.1	C6—Fe1—C1	160.48 (9)
C8—C9—H9	125.8	C6—Fe1—C2	122.98 (9)
C8—C9—C10	108.35 (19)	C6—Fe1—C3	105.59 (9)
C8—C9—Fe1	69.99 (12)	C6—Fe1—C4	119.79 (9)
C10—C9—H9	125.8	C6—Fe1—C5	156.12 (10)
C10—C9—Fe1	69.58 (12)	C6—Fe1—C7	40.58 (10)
Fe1—C9—H9	125.8	C6—Fe1—C8	68.27 (9)
C6—C10—C9	107.5 (2)	C6—Fe1—C9	68.29 (9)

C6—C10—H10	126.2	C7—Fe1—C5	162.22 (9)
C6—C10—Fe1	69.67 (13)	C7—Fe1—C8	40.57 (9)
C9—C10—H10	126.2	C8—Fe1—C5	125.65 (8)
C9—C10—Fe1	69.69 (12)	C9—Fe1—C1	123.41 (9)
Fe1—C10—H10	126.2	C9—Fe1—C2	158.63 (9)
C12—C11—C5	117.87 (18)	C9—Fe1—C3	159.94 (9)
C12—C11—C25	117.43 (18)	C9—Fe1—C4	124.35 (8)
C25—C11—C5	124.69 (18)	C9—Fe1—C5	108.42 (8)
C11—C12—H12	119.1	C9—Fe1—C7	68.29 (9)
C11—C12—C13	121.72 (19)	C9—Fe1—C8	40.63 (8)
C13—C12—H12	119.1	C10—Fe1—C1	158.12 (9)
C12—C13—C14	121.03 (19)	C10—Fe1—C2	159.14 (9)
N1—C13—C12	121.98 (19)	C10—Fe1—C3	122.31 (9)
N1—C13—C14	116.99 (18)	C10—Fe1—C4	106.21 (9)
C15—C14—C13	122.01 (18)	C10—Fe1—C5	121.20 (9)
C15—C14—C19	118.21 (19)	C10—Fe1—C6	40.74 (9)
C19—C14—C13	119.77 (19)	C10—Fe1—C7	68.54 (9)
C14—C15—H15	119.5	C10—Fe1—C8	68.56 (9)
C16—C15—C14	120.9 (2)	C10—Fe1—C9	40.74 (9)
C16—C15—H15	119.5	C13—N1—C20	117.97 (17)
C15—C16—H16	120.0		

C1—C2—C3—C4	0.2 (2)	C7—C6—Fe1—C4	160.31 (13)
C1—C2—C3—Fe1	−59.14 (14)	C7—C6—Fe1—C5	−168.16 (18)
C1—C2—Fe1—C3	119.64 (17)	C7—C6—Fe1—C8	−37.65 (13)
C1—C2—Fe1—C4	81.96 (13)	C7—C6—Fe1—C9	−81.54 (14)
C1—C2—Fe1—C5	37.71 (12)	C7—C6—Fe1—C10	−119.59 (19)
C1—C2—Fe1—C6	−165.67 (13)	C7—C8—C9—C10	−0.1 (2)
C1—C2—Fe1—C7	−123.85 (13)	C7—C8—C9—Fe1	−59.27 (15)
C1—C2—Fe1—C8	−81.95 (14)	C7—C8—Fe1—C1	−121.64 (14)
C1—C2—Fe1—C9	−49.0 (3)	C7—C8—Fe1—C2	−78.49 (16)
C1—C2—Fe1—C10	160.8 (2)	C7—C8—Fe1—C3	−41.1 (3)
C1—C5—C11—C12	142.1 (2)	C7—C8—Fe1—C4	157.9 (3)
C1—C5—C11—C25	−37.2 (3)	C7—C8—Fe1—C5	−164.60 (13)
C1—C5—Fe1—C2	−37.37 (12)	C7—C8—Fe1—C6	37.66 (14)
C1—C5—Fe1—C3	−81.06 (13)	C7—C8—Fe1—C9	119.21 (19)
C1—C5—Fe1—C4	−118.39 (17)	C7—C8—Fe1—C10	81.62 (15)
C1—C5—Fe1—C6	−162.1 (2)	C8—C7—Fe1—C1	78.69 (15)
C1—C5—Fe1—C7	43.8 (3)	C8—C7—Fe1—C2	120.04 (14)
C1—C5—Fe1—C8	78.29 (14)	C8—C7—Fe1—C3	162.50 (13)
C1—C5—Fe1—C9	120.09 (12)	C8—C7—Fe1—C4	−163.77 (19)
C1—C5—Fe1—C10	163.04 (12)	C8—C7—Fe1—C5	45.0 (3)
C2—C1—C5—C4	0.1 (2)	C8—C7—Fe1—C6	−119.25 (19)

C2—C1—C5—C11	−174.9 (2)	C8—C7—Fe1—C9	−37.72 (13)
C2—C1—C5—Fe1	59.14 (14)	C8—C7—Fe1—C10	−81.68 (14)
C2—C1—Fe1—C3	−37.46 (12)	C8—C9—C10—C6	0.2 (2)
C2—C1—Fe1—C4	−81.32 (13)	C8—C9—C10—Fe1	−59.46 (15)
C2—C1—Fe1—C5	−119.67 (17)	C8—C9—Fe1—C1	−80.82 (15)
C2—C1—Fe1—C6	38.4 (3)	C8—C9—Fe1—C2	−44.7 (3)
C2—C1—Fe1—C7	75.29 (15)	C8—C9—Fe1—C3	157.2 (2)
C2—C1—Fe1—C8	117.81 (13)	C8—C9—Fe1—C4	−166.45 (13)
C2—C1—Fe1—C9	160.76 (12)	C8—C9—Fe1—C5	−123.72 (13)
C2—C1—Fe1—C10	−161.7 (2)	C8—C9—Fe1—C6	81.49 (14)
C2—C3—C4—C5	−0.1 (2)	C8—C9—Fe1—C7	37.66 (13)
C2—C3—C4—Fe1	−59.38 (15)	C8—C9—Fe1—C10	119.54 (18)
C2—C3—Fe1—C1	37.49 (12)	C9—C8—Fe1—C1	119.15 (13)
C2—C3—Fe1—C4	119.34 (18)	C9—C8—Fe1—C2	162.30 (12)
C2—C3—Fe1—C5	81.67 (13)	C9—C8—Fe1—C3	−160.3 (2)
C2—C3—Fe1—C6	−122.86 (13)	C9—C8—Fe1—C4	38.7 (3)
C2—C3—Fe1—C7	−81.46 (15)	C9—C8—Fe1—C5	76.19 (15)
C2—C3—Fe1—C8	−51.8 (3)	C9—C8—Fe1—C6	−81.55 (14)
C2—C3—Fe1—C9	168.0 (2)	C9—C8—Fe1—C7	−119.21 (19)
C2—C3—Fe1—C10	−163.89 (12)	C9—C8—Fe1—C10	−37.59 (13)
C3—C2—Fe1—C1	−119.64 (17)	C9—C10—Fe1—C1	−51.2 (3)
C3—C2—Fe1—C4	−37.67 (12)	C9—C10—Fe1—C2	163.9 (2)
C3—C2—Fe1—C5	−81.93 (13)	C9—C10—Fe1—C3	−165.64 (12)
C3—C2—Fe1—C6	74.69 (15)	C9—C10—Fe1—C4	−124.26 (13)
C3—C2—Fe1—C7	116.51 (13)	C9—C10—Fe1—C5	−82.12 (14)
C3—C2—Fe1—C8	158.42 (13)	C9—C10—Fe1—C6	118.66 (19)
C3—C2—Fe1—C9	−168.7 (2)	C9—C10—Fe1—C7	81.23 (14)
C3—C2—Fe1—C10	41.2 (3)	C9—C10—Fe1—C8	37.49 (13)
C3—C4—C5—C1	0.0 (2)	C10—C6—C7—C8	0.2 (3)
C3—C4—C5—C11	175.35 (19)	C10—C6—C7—Fe1	−59.19 (15)
C3—C4—C5—Fe1	−59.12 (14)	C10—C6—Fe1—C1	168.7 (2)
C3—C4—Fe1—C1	81.46 (14)	C10—C6—Fe1—C2	−162.47 (13)
C3—C4—Fe1—C2	37.62 (13)	C10—C6—Fe1—C3	−121.76 (14)
C3—C4—Fe1—C5	119.78 (18)	C10—C6—Fe1—C4	−80.11 (15)
C3—C4—Fe1—C6	−79.02 (15)	C10—C6—Fe1—C5	−48.6 (3)
C3—C4—Fe1—C7	−47.3 (3)	C10—C6—Fe1—C7	119.59 (19)
C3—C4—Fe1—C8	168.6 (3)	C10—C6—Fe1—C8	81.94 (14)
C3—C4—Fe1—C9	−161.84 (13)	C10—C6—Fe1—C9	38.05 (13)
C3—C4—Fe1—C10	−121.04 (14)	C10—C9—Fe1—C1	159.64 (13)
C4—C3—Fe1—C1	−81.85 (13)	C10—C9—Fe1—C2	−164.2 (2)
C4—C3—Fe1—C2	−119.34 (18)	C10—C9—Fe1—C3	37.7 (3)
C4—C3—Fe1—C5	−37.67 (13)	C10—C9—Fe1—C4	74.01 (15)
C4—C3—Fe1—C6	117.81 (14)	C10—C9—Fe1—C5	116.74 (13)

C4—C3—Fe1—C7	159.20 (13)	C10—C9—Fe1—C6	−38.05 (13)
C4—C3—Fe1—C8	−171.1 (2)	C10—C9—Fe1—C7	−81.88 (14)
C4—C3—Fe1—C9	48.6 (3)	C10—C9—Fe1—C8	−119.54 (18)
C4—C3—Fe1—C10	76.77 (15)	C11—C5—Fe1—C1	−124.1 (2)
C4—C5—C11—C12	−32.2 (3)	C11—C5—Fe1—C2	−161.4 (2)
C4—C5—C11—C25	148.5 (2)	C11—C5—Fe1—C3	154.9 (2)
C4—C5—Fe1—C1	118.39 (17)	C11—C5—Fe1—C4	117.5 (2)
C4—C5—Fe1—C2	81.02 (13)	C11—C5—Fe1—C6	73.9 (3)
C4—C5—Fe1—C3	37.32 (13)	C11—C5—Fe1—C7	−80.2 (3)
C4—C5—Fe1—C6	−43.7 (3)	C11—C5—Fe1—C8	−45.8 (2)
C4—C5—Fe1—C7	162.2 (3)	C11—C5—Fe1—C9	−4.0 (2)
C4—C5—Fe1—C8	−163.33 (13)	C11—C5—Fe1—C10	39.0 (2)
C4—C5—Fe1—C9	−121.53 (13)	C11—C12—C13—C14	177.64 (19)
C4—C5—Fe1—C10	−78.58 (14)	C11—C12—C13—N1	−1.9 (3)
C5—C1—C2—C3	−0.2 (2)	C12—C11—C25—C20	0.1 (3)
C5—C1—C2—Fe1	−59.24 (14)	C12—C11—C25—C24	178.30 (19)
C5—C1—Fe1—C2	119.67 (17)	C12—C13—C14—C15	−12.4 (3)
C5—C1—Fe1—C3	82.21 (13)	C12—C13—C14—C19	167.90 (19)

Table S4 Bond lengths (Å), bond angles (°) and torsion angles (°) for **4k**

C1—H1	0.9800	C11—C20	1.373 (3)
C1—C2	1.423 (3)	C12—C13	1.440 (3)
C1—C5	1.428 (3)	C12—C18	1.432 (3)
C1—Fe1	2.056 (2)	C13—C14	1.509 (3)
C2—H2	0.9800	C13—C15	1.370 (3)
C2—C3	1.423 (3)	C14—H14A	0.9600
C2—Fe1	2.042 (2)	C14—H14B	0.9600
C3—H3	0.9800	C14—H14C	0.9600
C3—C4	1.424 (3)	C15—H15	0.9300
C3—Fe1	2.031 (2)	C15—C16	1.404 (3)
C4—H4	0.9800	C16—H16	0.9300
C4—C5	1.431 (3)	C16—C17	1.360 (3)
C4—Fe1	2.044 (2)	C17—H17	0.9300
C5—C11	1.488 (3)	C17—C18	1.415 (3)
C5—Fe1	2.0800 (19)	C18—N1	1.369 (3)
C6—H6	0.9800	C19—C20	1.413 (3)
C6—C7	1.416 (3)	C19—C21	1.486 (3)
C6—C10	1.418 (4)	C19—N1	1.320 (3)
C6—Fe1	2.060 (2)	C20—H20	0.9300
C7—H7	0.9800	C21—C22	1.395 (3)
C7—C8	1.417 (3)	C21—C26	1.396 (3)
C7—Fe1	2.058 (2)	C22—H22	0.9300

C8—H8	0.9800	C22—C23	1.387 (3)
C8—C9	1.420 (4)	C23—H23	0.9300
C8—Fe1	2.037 (2)	C23—C24	1.387 (3)
C9—H9	0.9800	C24—H24	0.9300
C9—C10	1.407 (4)	C24—C25	1.385 (3)
C9—Fe1	2.034 (2)	C25—H25	0.9300
C10—H10	0.9800	C25—C26	1.388 (3)
C10—Fe1	2.049 (2)	C26—H26	0.9300
C11—C12	1.439 (3)		

C2—C1—H1	125.9	C17—C16—C15	119.7 (2)
C2—C1—C5	108.30 (18)	C17—C16—H16	120.2
C2—C1—Fe1	69.14 (12)	C16—C17—H17	119.8
C5—C1—H1	125.9	C16—C17—C18	120.4 (2)
C5—C1—Fe1	70.73 (11)	C18—C17—H17	119.8
Fe1—C1—H1	125.9	C17—C18—C12	120.50 (19)
C1—C2—H2	125.9	N1—C18—C12	124.17 (18)
C1—C2—Fe1	70.20 (12)	N1—C18—C17	115.32 (19)
C3—C2—C1	108.15 (18)	C20—C19—C21	120.66 (17)
C3—C2—H2	125.9	N1—C19—C20	121.82 (19)
C3—C2—Fe1	69.14 (12)	N1—C19—C21	117.42 (18)
Fe1—C2—H2	125.9	C11—C20—C19	121.58 (18)
C2—C3—H3	126.1	C11—C20—H20	119.2
C2—C3—C4	107.84 (18)	C19—C20—H20	119.2
C2—C3—Fe1	69.96 (12)	C22—C21—C19	119.50 (17)
C4—C3—H3	126.1	C22—C21—C26	118.19 (19)
C4—C3—Fe1	70.07 (12)	C26—C21—C19	122.16 (19)
Fe1—C3—H3	126.1	C21—C22—H22	119.5
C3—C4—H4	125.8	C23—C22—C21	121.00 (18)
C3—C4—C5	108.38 (18)	C23—C22—H22	119.5
C3—C4—Fe1	69.04 (12)	C22—C23—H23	119.9
C5—C4—H4	125.8	C22—C23—C24	120.1 (2)
C5—C4—Fe1	71.04 (12)	C24—C23—H23	119.9
Fe1—C4—H4	125.8	C23—C24—H24	120.3
C1—C5—C4	107.31 (18)	C25—C24—C23	119.5 (2)
C1—C5—C11	127.15 (18)	C25—C24—H24	120.3
C1—C5—Fe1	68.89 (11)	C24—C25—H25	119.8
C4—C5—C11	125.36 (18)	C24—C25—C26	120.37 (19)
C4—C5—Fe1	68.36 (11)	C26—C25—H25	119.8
C11—C5—Fe1	131.73 (14)	C21—C26—H26	119.6
C7—C6—H6	126.0	C25—C26—C21	120.78 (19)
C7—C6—C10	108.1 (2)	C25—C26—H26	119.6
C7—C6—Fe1	69.81 (13)	C1—Fe1—C5	40.38 (8)

C10—C6—H6	126.0	C1—Fe1—C6	120.40 (9)
C10—C6—Fe1	69.40 (14)	C1—Fe1—C7	110.45 (9)
Fe1—C6—H6	126.0	C2—Fe1—C1	40.66 (8)
C6—C7—H7	126.0	C2—Fe1—C4	68.53 (8)
C6—C7—C8	107.9 (2)	C2—Fe1—C5	68.20 (8)
C6—C7—Fe1	69.97 (13)	C2—Fe1—C6	149.73 (10)
C8—C7—H7	126.0	C2—Fe1—C7	115.14 (9)
C8—C7—Fe1	68.97 (13)	C2—Fe1—C10	166.10 (11)
Fe1—C7—H7	126.0	C3—Fe1—C1	68.67 (8)
C7—C8—H8	126.1	C3—Fe1—C2	40.90 (8)
C7—C8—C9	107.8 (2)	C3—Fe1—C4	40.89 (8)
C7—C8—Fe1	70.55 (12)	C3—Fe1—C5	68.54 (8)
C9—C8—H8	126.1	C3—Fe1—C6	169.28 (9)
C9—C8—Fe1	69.49 (13)	C3—Fe1—C7	145.41 (9)
Fe1—C8—H8	126.1	C3—Fe1—C8	111.59 (9)
C8—C9—H9	125.9	C3—Fe1—C9	104.47 (10)
C8—C9—Fe1	69.69 (13)	C3—Fe1—C10	129.00 (10)
C10—C9—C8	108.3 (2)	C4—Fe1—C1	68.33 (8)
C10—C9—H9	125.9	C4—Fe1—C5	40.60 (8)
C10—C9—Fe1	70.39 (14)	C4—Fe1—C6	134.20 (9)
Fe1—C9—H9	125.9	C4—Fe1—C7	173.35 (9)
C6—C10—H10	126.0	C4—Fe1—C10	109.98 (9)
C6—C10—Fe1	70.24 (13)	C6—Fe1—C5	113.96 (9)
C9—C10—C6	108.0 (2)	C7—Fe1—C5	134.39 (9)
C9—C10—H10	126.0	C7—Fe1—C6	40.22 (9)
C9—C10—Fe1	69.28 (15)	C8—Fe1—C1	129.38 (10)
Fe1—C10—H10	126.0	C8—Fe1—C2	104.75 (10)
C12—C11—C5	123.41 (18)	C8—Fe1—C4	145.42 (9)
C20—C11—C5	118.07 (18)	C8—Fe1—C5	169.60 (10)
C20—C11—C12	118.43 (18)	C8—Fe1—C6	67.98 (10)
C11—C12—C13	126.66 (19)	C8—Fe1—C7	40.49 (9)
C18—C12—C11	115.67 (18)	C8—Fe1—C10	68.21 (11)
C18—C12—C13	117.63 (18)	C9—Fe1—C1	166.44 (12)
C12—C13—C14	**124.39 (19)**	C9—Fe1—C2	126.71 (11)
C15—C13—C12	119.1 (2)	C9—Fe1—C4	114.70 (9)
C15—C13—C14	**116.55 (19)**	C9—Fe1—C5	149.55 (10)
C13—C14—H14A	109.5	C9—Fe1—C6	67.86 (11)
C13—C14—H14B	109.5	C9—Fe1—C7	68.10 (10)
C13—C14—H14C	109.5	C9—Fe1—C8	40.82 (11)
H14A—C14—H14B	109.5	C9—Fe1—C10	40.32 (12)
H14A—C14—H14C	109.5	C10—Fe1—C1	152.79 (11)
H14B—C14—H14C	109.5	C10—Fe1—C5	120.33 (10)
C13—C15—H15	118.6	C10—Fe1—C6	40.37 (10)

C13—C15—C16	122.7 (2)	C10—Fe1—C7	67.89 (10)
C16—C15—H15	118.6	C19—N1—C18	118.32 (18)
C15—C16—H16	120.2		

C1—C2—C3—C4	−0.5 (2)	C7—C6—Fe1—C8	−37.60 (14)
C1—C2—C3—Fe1	59.58 (14)	C7—C6—Fe1—C9	−81.81 (16)
C1—C2—Fe1—C3	−119.44 (18)	C7—C6—Fe1—C10	−119.4 (2)
C1—C2—Fe1—C4	−81.31 (13)	C7—C8—C9—C10	−0.4 (3)
C1—C2—Fe1—C5	−37.49 (12)	C7—C8—C9—Fe1	−60.45 (16)
C1—C2—Fe1—C6	63.0 (2)	C7—C8—Fe1—C1	−74.62 (18)
C1—C2—Fe1—C7	92.64 (13)	C7—C8—Fe1—C2	−111.61 (15)
C1—C2—Fe1—C8	134.46 (13)	C7—C8—Fe1—C3	−154.18 (14)
C1—C2—Fe1—C9	173.20 (13)	C7—C8—Fe1—C4	174.95 (15)
C1—C2—Fe1—C10	−167.8 (4)	C7—C8—Fe1—C5	−65.5 (5)
C1—C5—C11—C12	−78.2 (3)	C7—C8—Fe1—C6	37.36 (14)
C1—C5—C11—C20	105.2 (2)	C7—C8—Fe1—C9	118.5 (2)
C1—C5—Fe1—C2	37.74 (12)	C7—C8—Fe1—C10	81.02 (16)
C1—C5—Fe1—C3	81.89 (13)	C8—C7—Fe1—C1	127.30 (16)
C1—C5—Fe1—C4	119.75 (17)	C8—C7—Fe1—C2	83.30 (17)
C1—C5—Fe1—C6	−109.41 (14)	C8—C7—Fe1—C3	45.5 (2)
C1—C5—Fe1—C7	−66.66 (16)	C8—C7—Fe1—C4	−154.5 (7)
C1—C5—Fe1—C8	−10.9 (5)	C8—C7—Fe1—C5	166.71 (15)
C1—C5—Fe1—C9	163.9 (2)	C8—C7—Fe1—C6	−119.4 (2)
C1—C5—Fe1—C10	−154.50 (14)	C8—C7—Fe1—C9	−38.24 (17)
C2—C1—C5—C4	−1.4 (2)	C8—C7—Fe1—C10	−81.89 (17)
C2—C1—C5—C11	173.80 (19)	C8—C9—C10—C6	0.2 (3)
C2—C1—C5—Fe1	−59.14 (14)	C8—C9—C10—Fe1	−59.63 (17)
C2—C1—Fe1—C3	37.74 (13)	C8—C9—Fe1—C1	−48.6 (4)
C2—C1—Fe1—C4	81.84 (13)	C8—C9—Fe1—C2	−67.81 (18)
C2—C1—Fe1—C5	119.28 (18)	C8—C9—Fe1—C3	−106.42 (16)
C2—C1—Fe1—C6	−148.61 (13)	C8—C9—Fe1—C4	−148.63 (14)
C2—C1—Fe1—C7	−105.16 (13)	C8—C9—Fe1—C5	−178.56 (17)
C2—C1—Fe1—C8	−63.24 (16)	C8—C9—Fe1—C6	81.48 (16)
C2—C1—Fe1—C9	−23.9 (4)	C8—C9—Fe1—C7	37.94 (15)
C2—C1—Fe1—C10	173.65 (19)	C8—C9—Fe1—C10	119.1 (2)
C2—C3—C4—C5	−0.4 (2)	C9—C8—Fe1—C1	166.85 (16)
C2—C3—C4—Fe1	60.02 (14)	C9—C8—Fe1—C2	129.87 (17)
C2—C3—Fe1—C1	−37.53 (12)	C9—C8—Fe1—C3	87.30 (18)
C2—C3—Fe1—C4	−118.64 (17)	C9—C8—Fe1—C4	56.4 (2)
C2—C3—Fe1—C5	−81.04 (13)	C9—C8—Fe1—C5	175.9 (5)
C2—C3—Fe1—C6	173.3 (4)	C9—C8—Fe1—C6	−81.17 (18)
C2—C3—Fe1—C7	57.9 (2)	C9—C8—Fe1—C7	−118.5 (2)
C2—C3—Fe1—C8	87.78 (14)	C9—C8—Fe1—C10	−37.51 (17)

C2—C3—Fe1—C9	130.18 (14)	C9—C10—Fe1—C1	173.74 (17)
C2—C3—Fe1—C10	166.64 (14)	C9—C10—Fe1—C2	−23.7 (5)
C3—C2—Fe1—C1	119.44 (17)	C9—C10—Fe1—C3	−62.78 (18)
C3—C2—Fe1—C4	38.13 (12)	C9—C10—Fe1—C4	−105.00 (15)
C3—C2—Fe1—C5	81.95 (13)	C9—C10—Fe1—C5	−148.67 (14)
C3—C2—Fe1—C6	−177.55 (16)	C9—C10—Fe1—C6	119.1 (2)
C3—C2—Fe1—C7	−147.92 (12)	C9—C10—Fe1—C7	81.75 (16)
C3—C2—Fe1—C8	−106.10 (14)	C9—C10—Fe1—C8	37.95 (15)
C3—C2—Fe1—C9	−67.36 (16)	C10—C6—C7—C8	−0.3 (2)
C3—C2—Fe1—C10	−48.4 (4)	C10—C6—C7—Fe1	−59.06 (15)
C3—C4—C5—C1	1.1 (2)	C10—C6—Fe1—C1	−154.40 (15)
C3—C4—C5—C11	−174.22 (18)	C10—C6—Fe1—C2	163.29 (18)
C3—C4—C5—Fe1	59.16 (14)	C10—C6—Fe1—C3	−8.0 (5)
C3—C4—Fe1—C1	−82.00 (13)	C10—C6—Fe1—C4	−65.92 (19)
C3—C4—Fe1—C2	−38.13 (12)	C10—C6—Fe1—C5	−109.29 (16)
C3—C4—Fe1—C5	−119.25 (17)	C10—C6—Fe1—C7	119.4 (2)
C3—C4—Fe1—C6	166.08 (14)	C10—C6—Fe1—C8	81.81 (17)
C3—C4—Fe1—C7	−162.8 (7)	C10—C6—Fe1—C9	37.60 (16)
C3—C4—Fe1—C8	46.8 (2)	C10—C9—Fe1—C1	−167.7 (3)
C3—C4—Fe1—C9	83.62 (16)	C10—C9—Fe1—C2	173.08 (14)
C3—C4—Fe1—C10	127.09 (15)	C10—C9—Fe1—C3	134.47 (15)
C4—C3—Fe1—C1	81.11 (13)	C10—C9—Fe1—C4	92.25 (16)
C4—C3—Fe1—C2	118.64 (17)	C10—C9—Fe1—C5	62.3 (2)
C4—C3—Fe1—C5	37.59 (12)	C10—C9—Fe1—C6	−37.64 (15)
C4—C3—Fe1—C6	−68.0 (5)	C10—C9—Fe1—C7	−81.18 (15)
C4—C3—Fe1—C7	176.53 (14)	C10—C9—Fe1—C8	−119.1 (2)
C4—C3—Fe1—C8	−153.58 (13)	C11—C5—Fe1—C1	121.5 (2)
C4—C3—Fe1—C9	−111.19 (14)	C11—C5—Fe1—C2	159.3 (2)
C4—C3—Fe1—C10	−74.72 (17)	C11—C5—Fe1—C3	−156.6 (2)
C4—C5—C11—C12	96.2 (2)	C11—C5—Fe1—C4	−118.7 (2)
C4—C5—C11—C20	−80.3 (3)	C11—C5—Fe1—C6	12.1 (2)
C4—C5—Fe1—C1	−119.75 (17)	C11—C5—Fe1—C7	54.9 (2)
C4—C5—Fe1—C2	−82.01 (13)	C11—C5—Fe1—C8	110.7 (5)
C4—C5—Fe1—C3	−37.86 (12)	C11—C5—Fe1—C9	−74.6 (3)
C4—C5—Fe1—C6	130.84 (13)	C11—C5—Fe1—C10	−33.0 (2)
C4—C5—Fe1—C7	173.59 (13)	C11—C12—C13—C14	1.5 (3)
C4—C5—Fe1—C8	−130.6 (5)	C11—C12—C13—C15	−178.4 (2)
C4—C5—Fe1—C9	44.1 (3)	C11—C12—C18—C17	178.69 (18)
C4—C5—Fe1—C10	85.75 (15)	C11—C12—C18—N1	−0.3 (3)
C5—C1—C2—C3	1.2 (2)	C12—C11—C20—C19	0.7 (3)
C5—C1—C2—Fe1	60.13 (14)	C12—C13—C15—C16	0.5 (3)
C5—C1—Fe1—C2	−119.28 (18)	C12—C18—N1—C19	0.5 (3)
C5—C1—Fe1—C3	−81.54 (13)	C13—C12—C18—C17	0.8 (3)

C5—C1—Fe1—C4	−37.44 (12)	C13—C12—C18—N1	−178.17 (19)
C5—C1—Fe1—C6	92.11 (14)	C13—C15—C16—C17	−0.2 (4)
C5—C1—Fe1—C7	135.55 (12)	C14—C13—C15—C16	−179.4 (2)
C5—C1—Fe1—C8	177.48 (13)	C15—C16—C17—C18	0.2 (3)
C5—C1—Fe1—C9	−143.2 (4)	C16—C17—C18—C12	−0.5 (3)
C5—C1—Fe1—C10	54.4 (2)	C16—C17—C18—N1	178.6 (2)
C5—C4—Fe1—C1	37.25 (12)	C17—C18—N1—C19	−178.56 (18)
C5—C4—Fe1—C2	81.12 (13)	C18—C12—C13—C14	179.1 (2)
C5—C4—Fe1—C3	119.25 (17)	C18—C12—C13—C15	−0.8 (3)
C5—C4—Fe1—C6	−74.67 (16)	C19—C21—C22—C23	−174.44 (19)
C5—C4—Fe1—C7	−43.5 (8)	C19—C21—C26—C25	174.19 (18)
C5—C4—Fe1—C8	166.03 (17)	C20—C11—C12—C13	177.36 (19)
C5—C4—Fe1—C9	−157.13 (15)	C20—C11—C12—C18	−0.3 (3)
C5—C4—Fe1—C10	−113.66 (14)	C20—C19—C21—C22	152.1 (2)
C5—C11—C12—C13	0.8 (3)	C20—C19—C21—C26	−23.4 (3)
C5—C11—C12—C18	−176.85 (18)	C20—C19—N1—C18	−0.1 (3)
C5—C11—C20—C19	177.45 (18)	C21—C19—C20—C11	−176.83 (18)
C6—C7—C8—C9	0.4 (3)	C21—C19—N1—C18	176.34 (17)
C6—C7—C8—Fe1	−59.34 (15)	C21—C22—C23—C24	0.1 (3)
C6—C7—Fe1—C1	−113.30 (14)	C22—C21—C26—C25	−1.4 (3)
C6—C7—Fe1—C2	−157.29 (14)	C22—C23—C24—C25	−1.4 (3)
C6—C7—Fe1—C3	164.93 (15)	C23—C24—C25—C26	1.2 (3)
C6—C7—Fe1—C4	−35.1 (8)	C24—C25—C26—C21	0.2 (3)
C6—C7—Fe1—C5	−73.89 (18)	C26—C21—C22—C23	1.3 (3)
C6—C7—Fe1—C8	119.4 (2)	Fe1—C1—C2—C3	−58.92 (14)
C6—C7—Fe1—C9	81.17 (17)	Fe1—C1—C5—C4	57.70 (13)
C6—C7—Fe1—C10	37.52 (15)	Fe1—C1—C5—C11	−127.1 (2)
C6—C10—Fe1—C1	54.6 (3)	Fe1—C2—C3—C4	−60.09 (14)
C6—C10—Fe1—C2	−142.9 (4)	Fe1—C3—C4—C5	−60.41 (14)
C6—C10—Fe1—C3	178.08 (13)	Fe1—C4—C5—C1	−58.03 (14)
C6—C10—Fe1—C4	135.86 (14)	Fe1—C4—C5—C11	126.6 (2)
C6—C10—Fe1—C5	92.19 (15)	Fe1—C5—C11—C12	−172.22 (15)
C6—C10—Fe1—C7	−37.39 (13)	Fe1—C5—C11—C20	11.2 (3)
C6—C10—Fe1—C8	−81.19 (15)	Fe1—C6—C7—C8	58.71 (15)
C6—C10—Fe1—C9	−119.1 (2)	Fe1—C6—C10—C9	−59.20 (17)
C7—C6—C10—C9	0.1 (3)	Fe1—C7—C8—C9	59.78 (16)
C7—C6—C10—Fe1	59.31 (15)	Fe1—C8—C9—C10	60.07 (17)
C7—C6—Fe1—C1	86.19 (15)	Fe1—C9—C10—C6	59.80 (16)
C7—C6—Fe1—C2	43.9 (2)	N1—C19—C20—C11	−0.6 (3)
C7—C6—Fe1—C3	−127.5 (4)	N1—C19—C21—C22	−24.3 (3)
C7—C6—Fe1—C4	174.68 (13)	N1—C19—C21—C26	160.14 (19)
C7—C6—Fe1—C5	131.30 (13)		

Table S5 Hydrogen bond geometry (Å, °) for **4a** and **4k**

Compd.	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
4a	C1–H1···*Cg*1^{i}	0.98	2.593	3.498(1)	153.6
	C17–H17···*Cg*2^{ii}	0.93	2.925	3.792(3)	155.7
	C4–H4···*Cg*3^{iii}	0.98	2.612	3.567(1)	164.9
	C10–H10···*Cg*4^{iii}	0.98	2.812	3.752(2)	160.9
4k	C1–H1···*Cg*1^{i}	0.98	2.881	3.724(2)	144.7
	C23–H23···*Cg*2^{i}	0.93	3.039	3.745(1)	134.0
	C9–H9···*Cg*3^{ii}	0.98	2.847	3.780(2)	159.3
	C16–H16···*Cg*4^{iii}	0.93	3.226	3.885(3)	129.5

Symmetry codes: **4a**: (i) 3/2 − x, 1/2 + y, 1/2 − z; (ii) −1/2 + x, 1/2 − y, 1/2 + z; (iii) 3/2 − x, −1/2 + y, 1/2 − z. *Cg*1 is the centroid of C13–C14 bond; *Cg*2, *Cg*3 and *Cg*4 are the centroid of C6–C10, C20–C25 and pyridine rings, respectively. **4k**: (i) −x, 1 − y, 2 − z; (ii) −x, 1 − y, 1 − z; (iii) 1 + x, y, 1 + z. *Cg*1 and *Cg*2 are the centroid of C18–N1–C19 and C2–C3–C4 bonds, *Cg*3 and *Cg*4 are the centroid of C21–C26 and C6–C10 rings, respectively.

3. Hirshfeld surface analysis of **4a** and **4k**

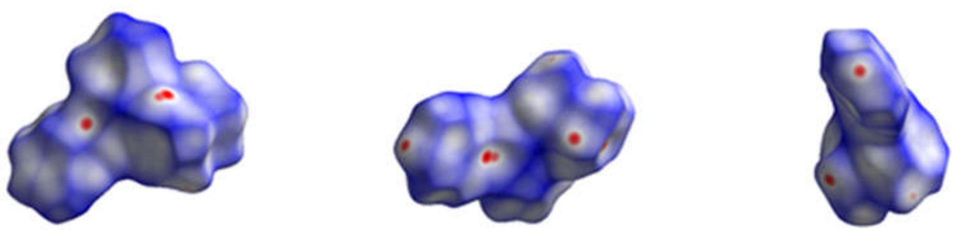


Fig. S1 Hirshfeld surfaces for **4a** are shown in different orientations.

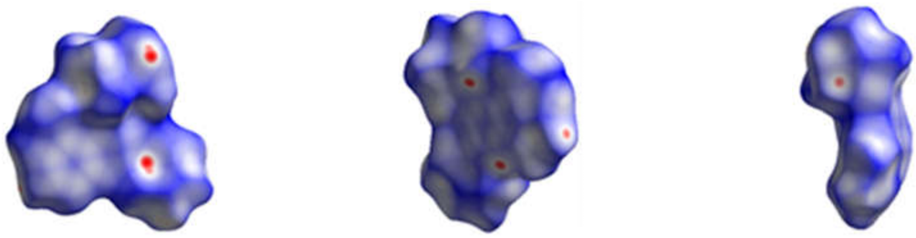
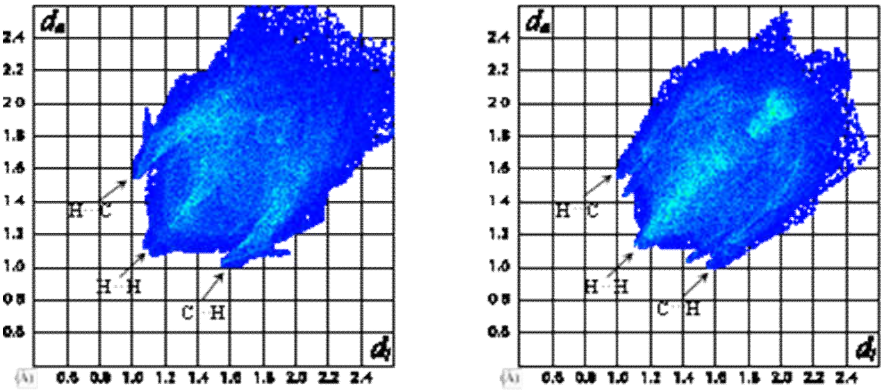


Fig. S2 Hirshfeld surfaces for **4k** are shown in different orientations.



4a **4k**

Fig. S3 Fingerprint plots of **4a** and **4k**.

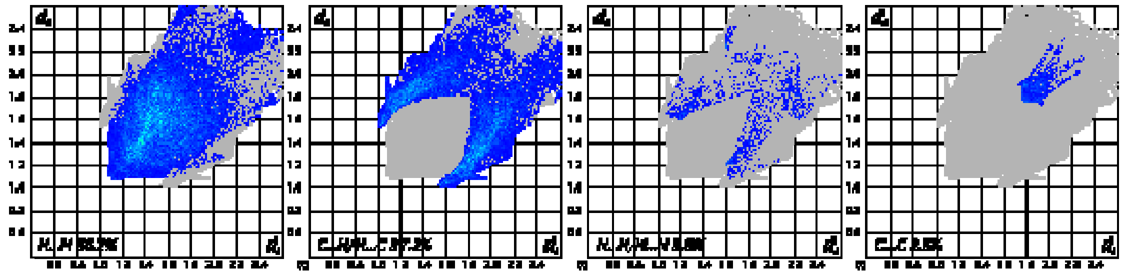


Fig. S4 Fingerprint plots of **4a** resolved into the indicated intermolecular contacts.

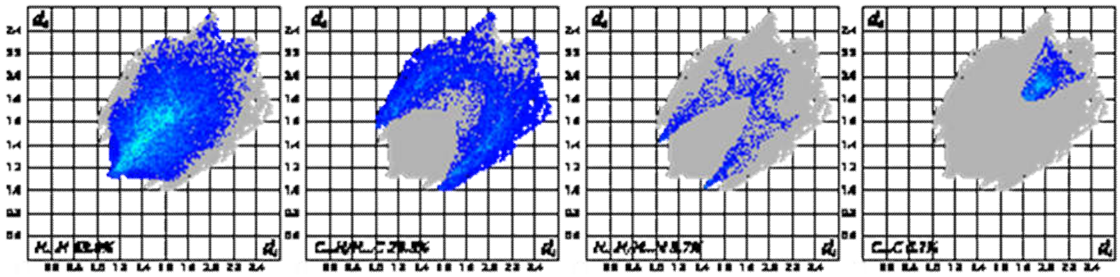


Fig. S5 Fingerprint plots of **4k** resolved into the indicated intermolecular contacts.

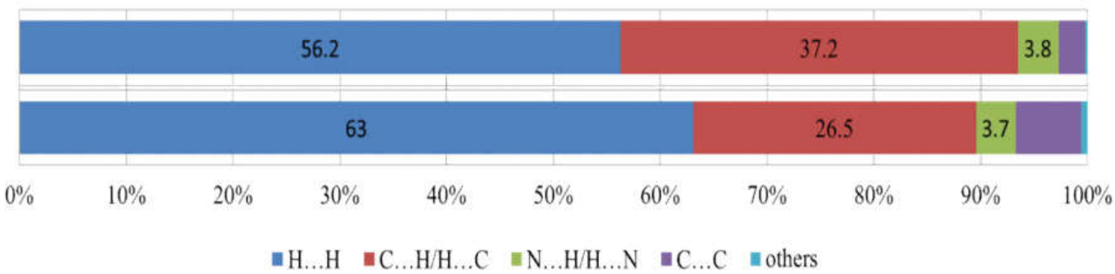


Fig. S6 Distribution of intermolecular contacts from Hirshfeld surface analysis (%) for **4a** (top) and **4k** (bottom).

4. Electrochemistry of **4**

Cyclic voltametry measurements were performed using a solution of compounds **4** (7.0 × 10^{-4} M) in CH_3CN with 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte, Hg/Hg_2Cl_2 as the reference electrode, along with platinum working and auxiliary electrodes, and a scan rate of 100 mVs^{-1}. Fig S7 showed the CV curves of **4**.

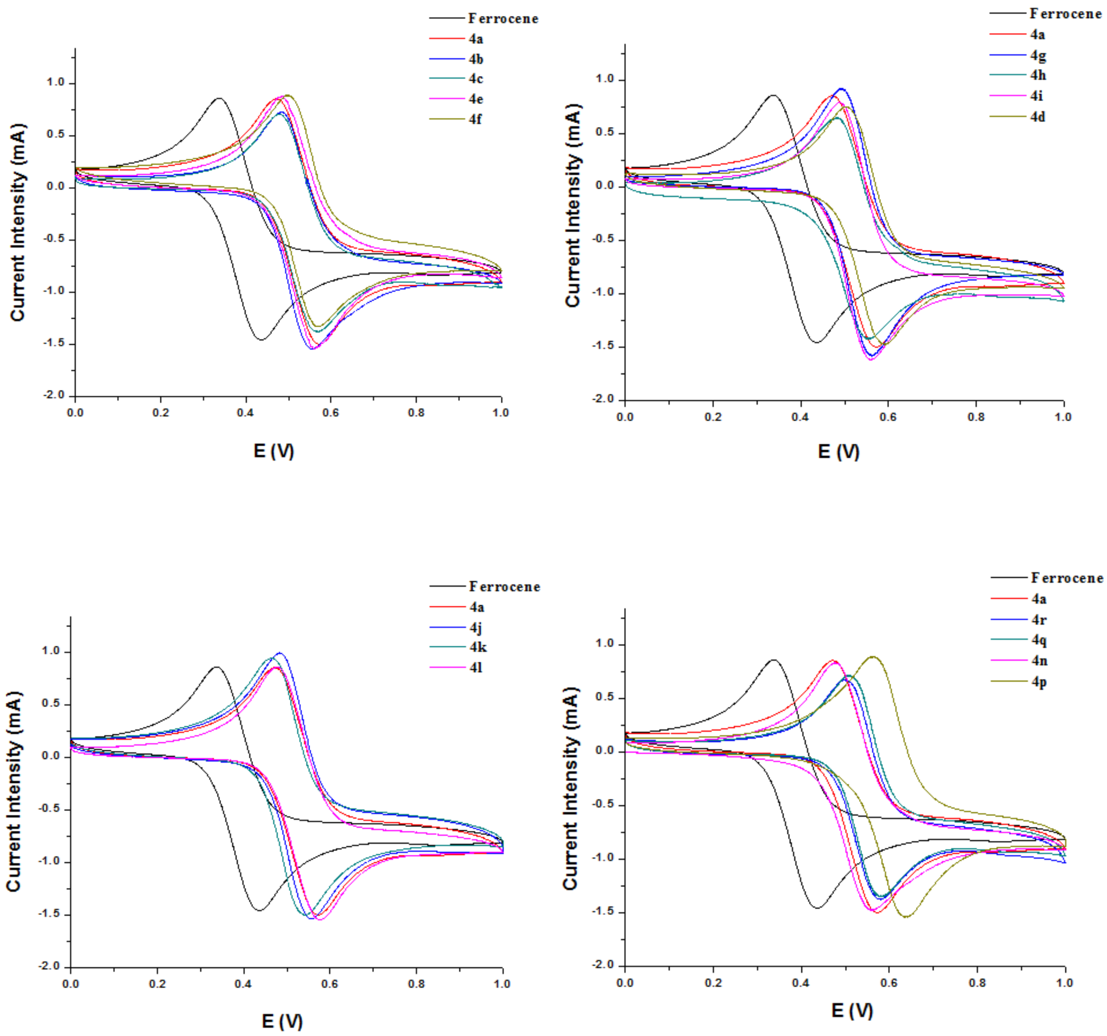


Fig. S7 CV curves of compounds **4**.

5. UV-vis properties of **4**

UV-vis spectra were carried out using two different concentrations of **4** (3.0 × 10^{-5} M and 7.0 × 10^{-4} M) in anhydrous MeOH. The results are summarized in Table S6 and shown Fig. S8.

Table S6 UV-vis spectral data for **4a-4t**

Compd.	λ_1/nm	A_1 ^{a}	λ_2/nm	A_2 ^{a}	λ_3/nm	A_3 ^{a}	λ_4/nm	A_4 ^{b}	λ_5/nm	A_5 ^{b}
4a	211	3.287	257	2.423	314	0.811	386	1.099	466	0.792
4b	204	2.919	264	1.717	314	0.720	382	1.237	465	0.714
4c	203	2.598	275	1.328	320	0.703	393	1.203	465	0.653
4d	202	2.422	263	1.736	313	0.724			468	0.847
4e	203	2.496	276	1.219	286	1.200	385	1.101	469	0.686
4f	203	2.821	300	1.402	330	1.156			483	0.812
4g	203	2.692	256	2.176	317	0.672	394	0.986	475	0.852
4h	203	2.152	275	1.121	324	0.625	393	1.232	469	0.798
4i	204	2.478	276	1.208	325	0.729	393	1.203	468	0.798
4j	203	2.700	263	1.958	314	0.527	385	1.015	466	0.571
4k	204	2.848	259	2.114	316	0.617	383	1.174	464	0.689
4l	204	2.932	260	2.207	316	0.651	383.5	1.089	464	0.656
4m	205	2.770	263	1.939	315	0.416	382	0.951	460	0.385
4n	203	2.386	274	1.809	328	0.272	329	3.677	468	0.723
4o	204	2.489	258	1.737	310	0.395	395	1.100	465	0.681
4p	204	2.391	262	1.326	323	0.506	404	1.111	486	0.888
4q	204	2.520	265	1.696	320	0.506	392	0.810	476	0.662
4r	204	2.489	266	1.761	321	0.526	393	0.884	477	0.722
4s	203	1.998	263	1.553	318	0.525	394	0.731	469	0.621
4t	205	3.154	287	1.033	310	0.820	381	2.862	459	1.598

^{a} Data obtained in 3.0×10^{-5} M of **4** in anhydrous MeOH;

^{b} Data obtained in 7.0×10^{-4} M of **4** in anhydrous MeOH.

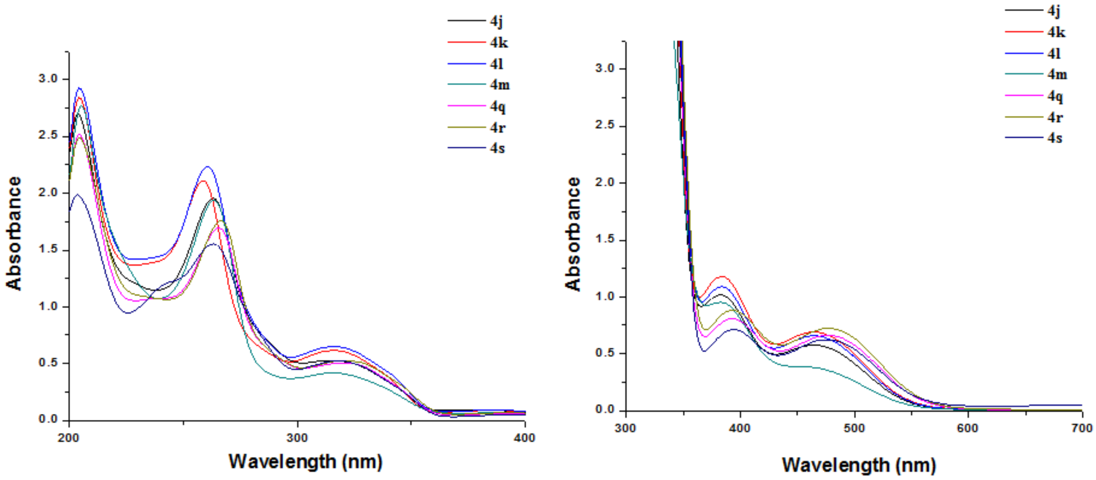
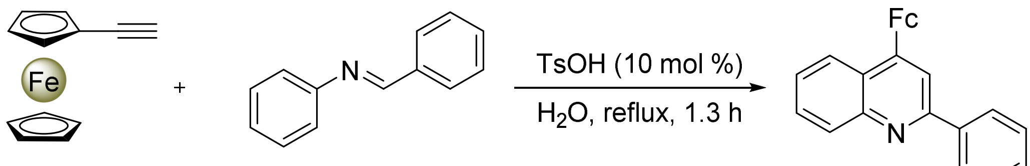


Fig. S8 UV-vis spectra of **4j**, **4k**, **4l**, **4m**, **4q**, **4r** and **4s** (3.0×10^{-5} M, left) and (7.0×10^{-4} M, right) in anhydrous MeOH.

6. Supplementary experiments for the mechanism

6.1 Synthesis of **4a** using aldimine **Ia** instead of **2a** and **3a**

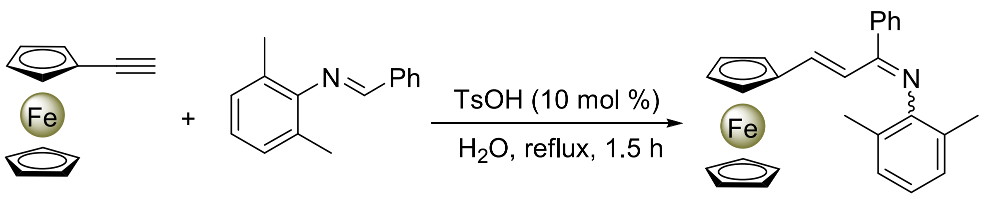


1 **Ia** **4a**

Synthetic procedure:

A suspension of ferrocenylacetylene **1** (0.210 g, 1.0 mmol), aldimine **Ia** (0.182 g, 1.0 mmol), and TsOH (0.017 g, 0.1 mmol) in water (1.0 mL) was stirred at 100 °C for 1.3 h. The reaction mixture was cooled to room temperature and then extracted with ethyl acetate. The organic phase was washed with saturated sodium bicarbonate solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:20, v/v, $R_f = 0.3$), to give **4a** in 91% yield (while no **4a** was formed in the absence of TsOH).

6.2 Synthesis of **6** using aldimine **5** and ferrocenylacetylene **1**



1 **5** **6**, 46% yield

Synthetic procedure:

A suspension of aldimine **5** (0.210 g, 1.0 mmol), ferrocenylacetylene **1** (0.210 g, 1.0 mmol) and TsOH (0.017 g, 0.1 mmol) in H_2O (1.0 mL) was stirred at 100 °C for 1.5 h. The reaction mixture was cooled to room temperature and then extracted with ethyl acetate. The organic phase was washed with saturated sodium bicarbonate solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:20, v/v, R_f = 0.6), to give **6** in 46% as a red solid, m.p. 103-106 ^oC.

Characterization:

^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 15.5 Hz, 0.6H), 7.65 (d, *J* = 7.5 Hz, 1.2H), 7.45-7.41 (m, 2.4H), 7.37 (d, *J* = 7.2 Hz, 0.6H), 7.34-7.26 (m, 6H), 7.03-6.98 (m, 3H), 6.90 (t, *J* = 7.8 Hz, 1.8H), 6.51 (d, *J* = 16.6 Hz, 1H), 4.91 (s, 2H), 4.49 (s, 2H), 4.30 (s, 5H), 4.24 (s, 1.2H), 4.20 (s, 3H), 4.08 (s, 1.2H), 2.09 (s, 6H), 2.02 (s, 3.6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 137.9, 136.5, 136.1, 134.9, 129.1, 128.9, 128.8, 127.9, 127.5, 127.2, 126.78, 125.7, 122.7, 122.4, 121.8, 82.7, 70.5, 70.3, 69.7, 69.6, 69.4, 18.3, 18.0. HR-MS (ESI): Calcd for $C_{27}H_{25}FeN$ $[M+H]^+$: 420.1415; Found: 420.1404.

Note: Aldimine **1** and **5** were prepared by the literature methods[1,2].

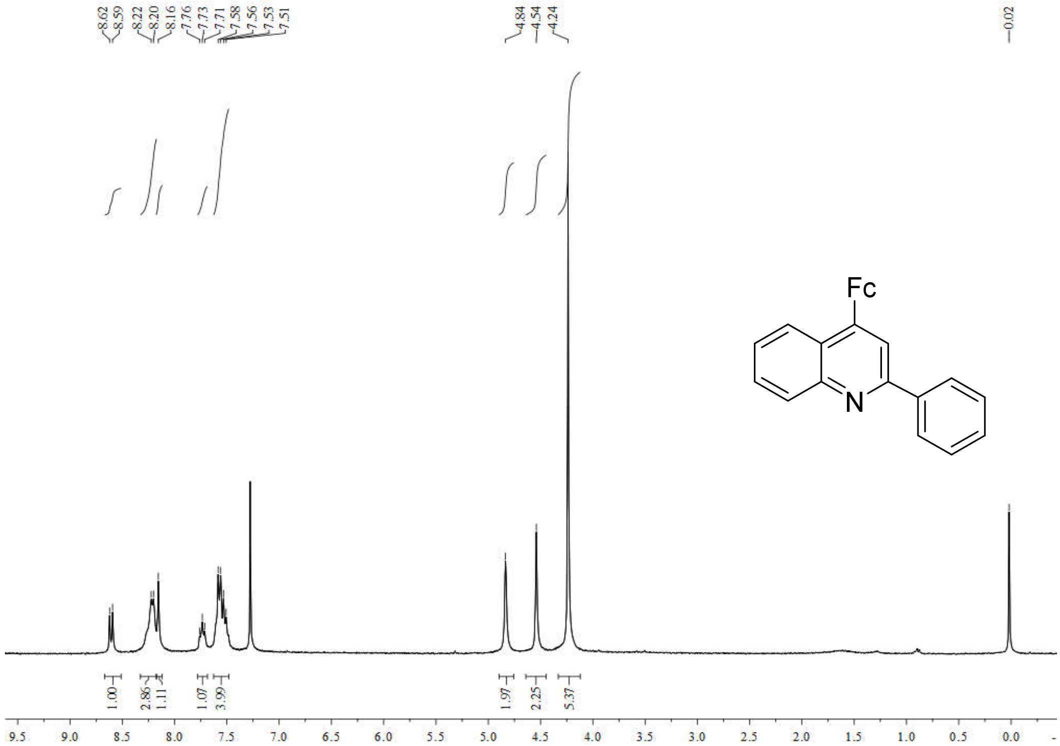
Reference:

[1] N. S. Khrushcheva, N. M. Loim and V. L Sokoiov, *Russ. Chem. Bull.,* 1997, **46**. 1952-1953;

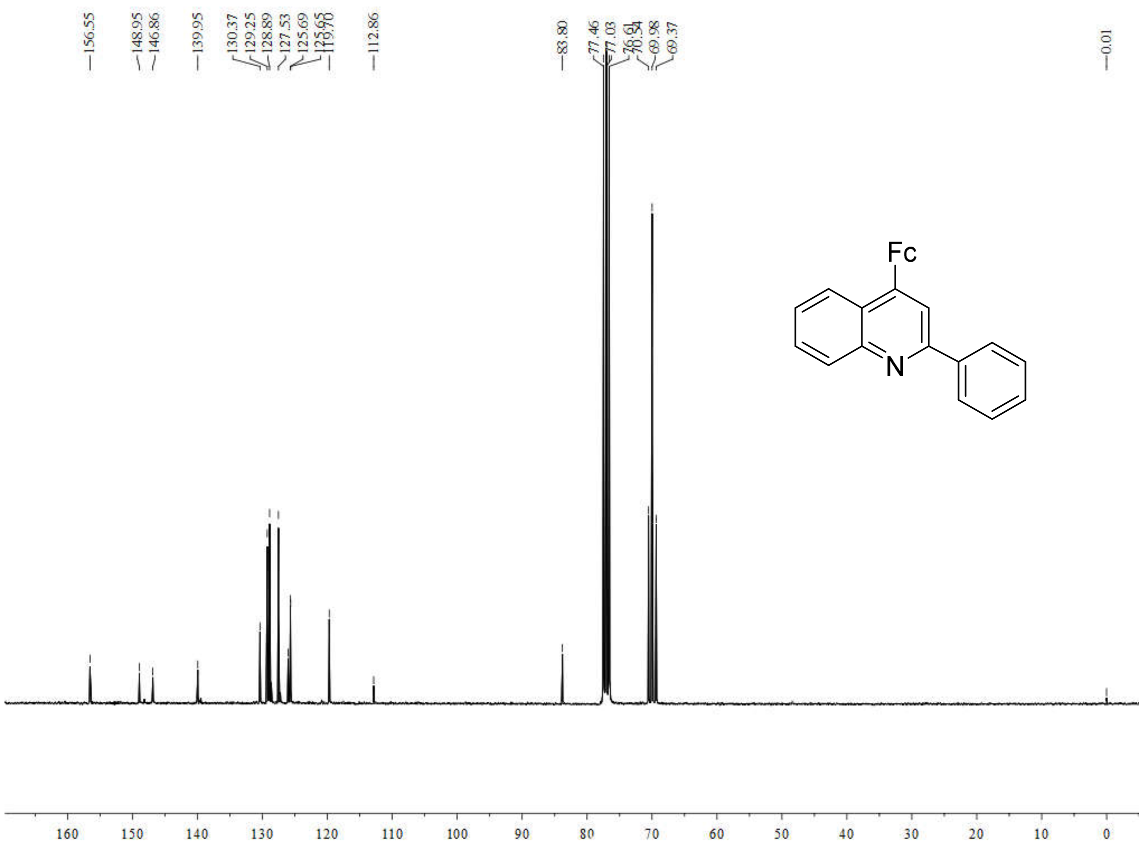
[2] I. Iovel, L. Golomba, M. Fleisher, J. Popelis, S. Grinberga and E. Lukevics, *Chem. Heterocycl. Compd.*, 2004, **40**, 701-714.

7 NMR spectra of **4a-4t** and **6** (where Fc refers to the ferrocenyl group).

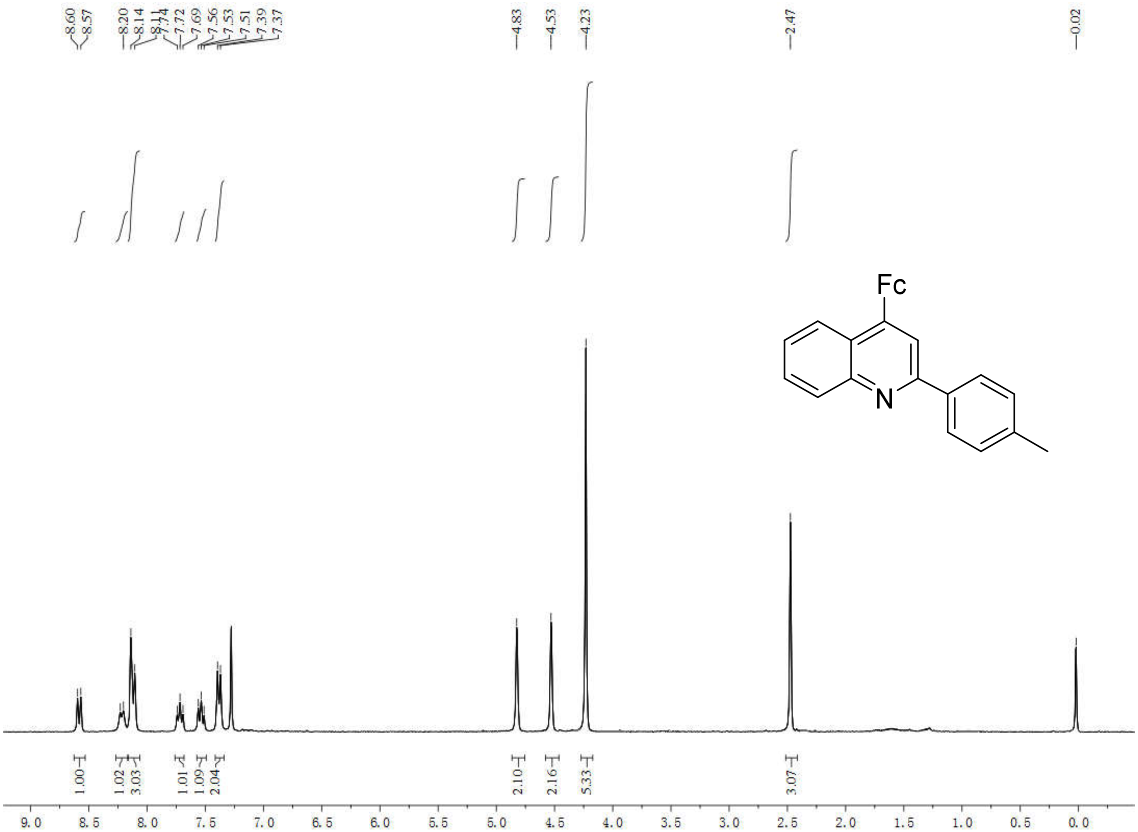
The ^{1}H NMR of **4a**.



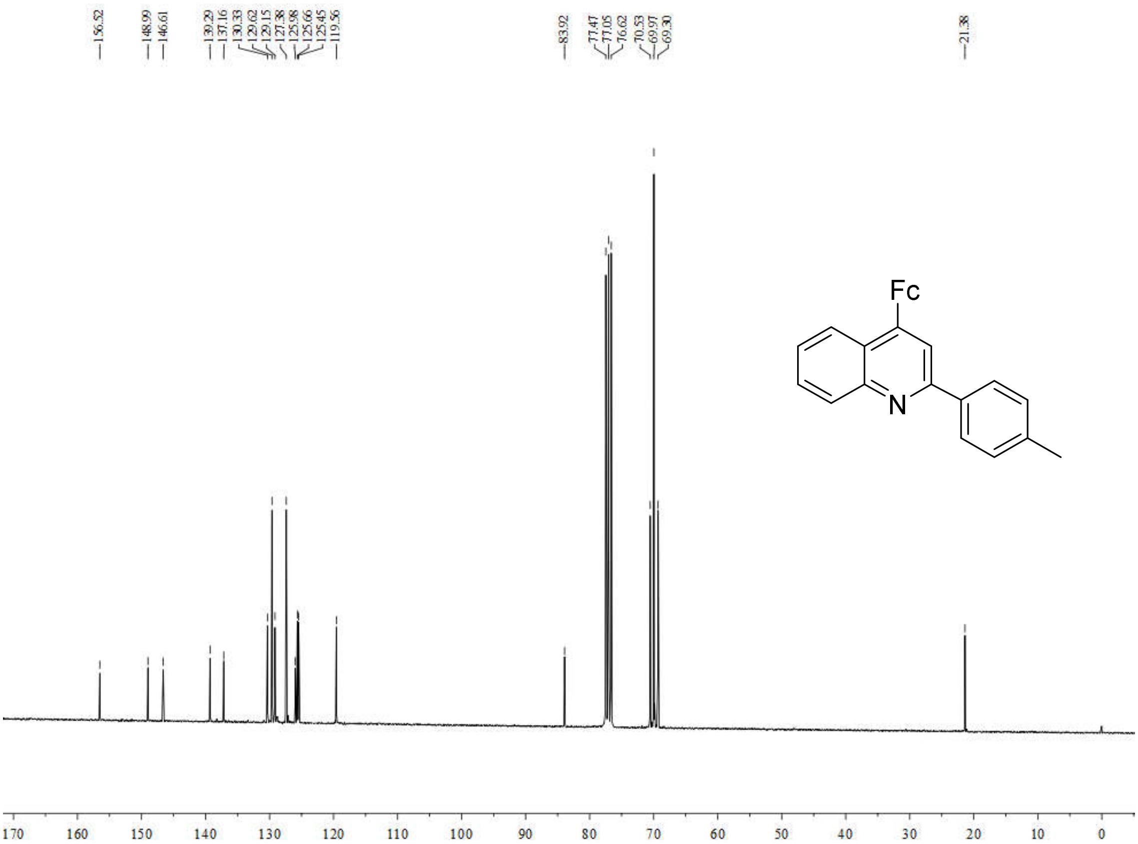
The ^{13}C NMR of **4a**.



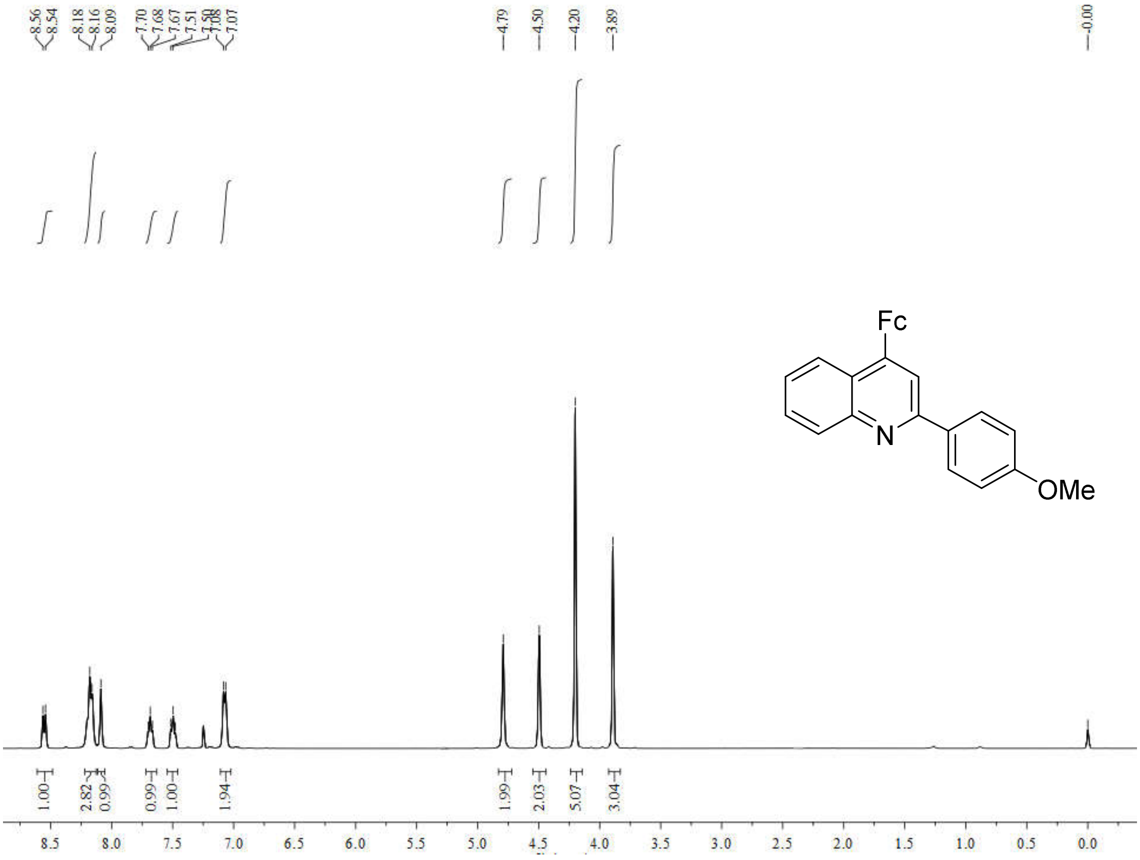
The ^{1}H NMR of **4b**.



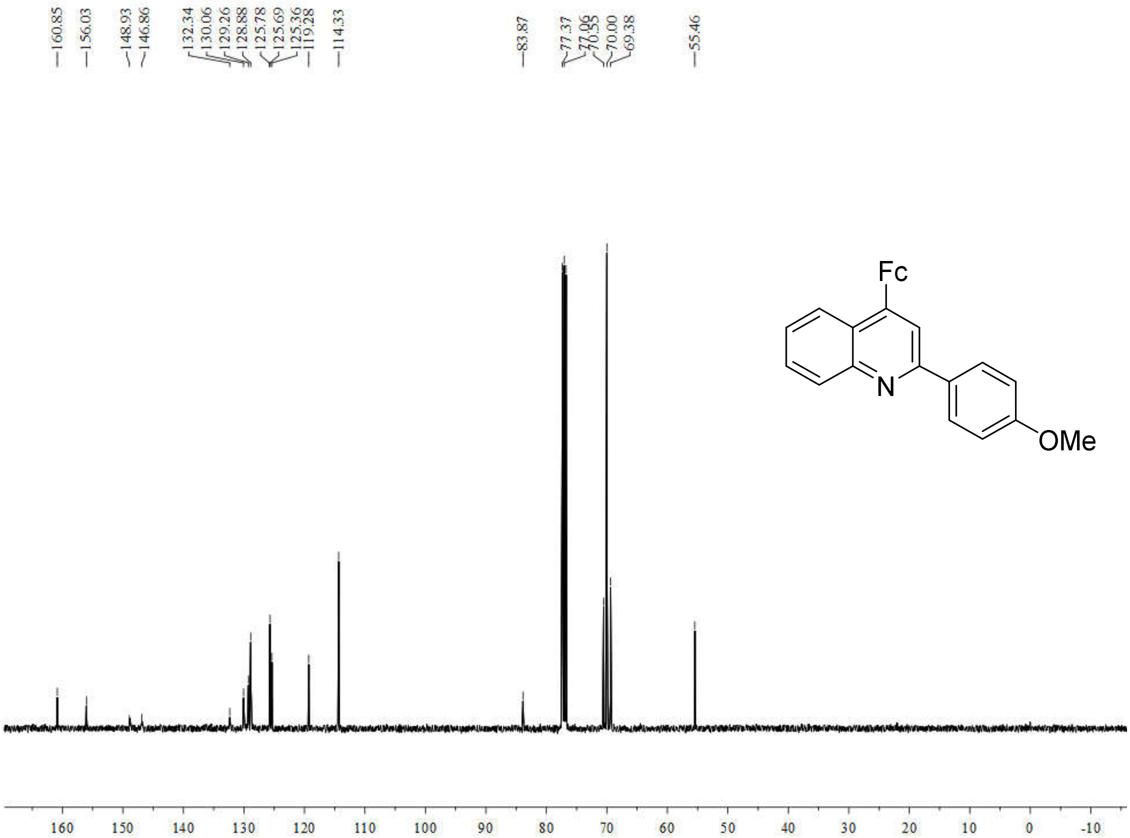
The ^{13}C NMR of **4b**.



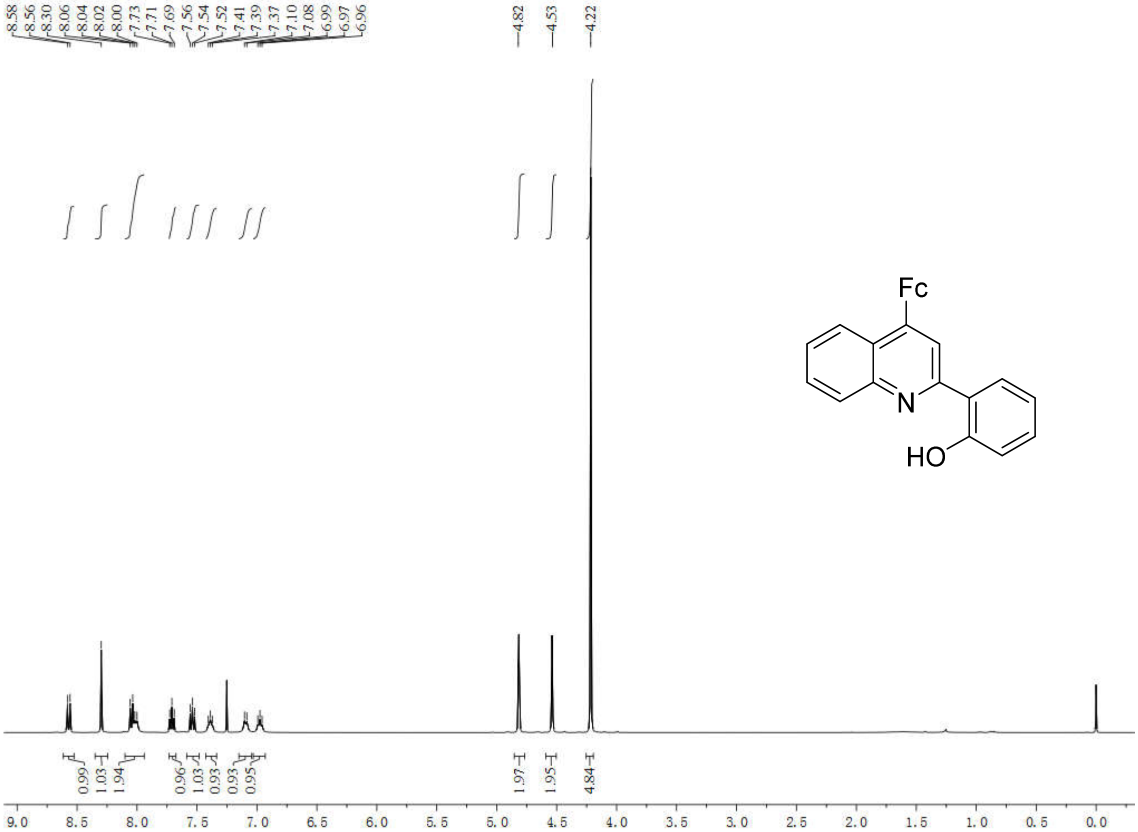
The ^{1}H NMR of **4c**.



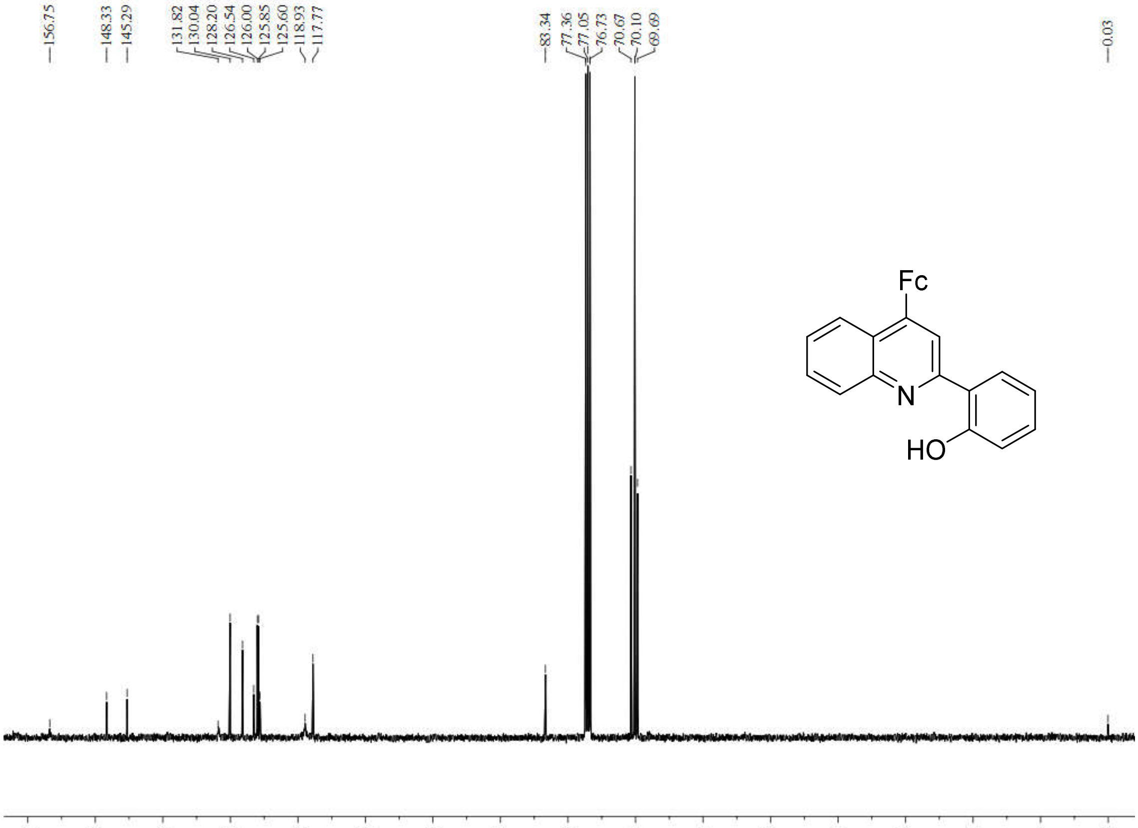
The ^{13}C NMR of **4c**.



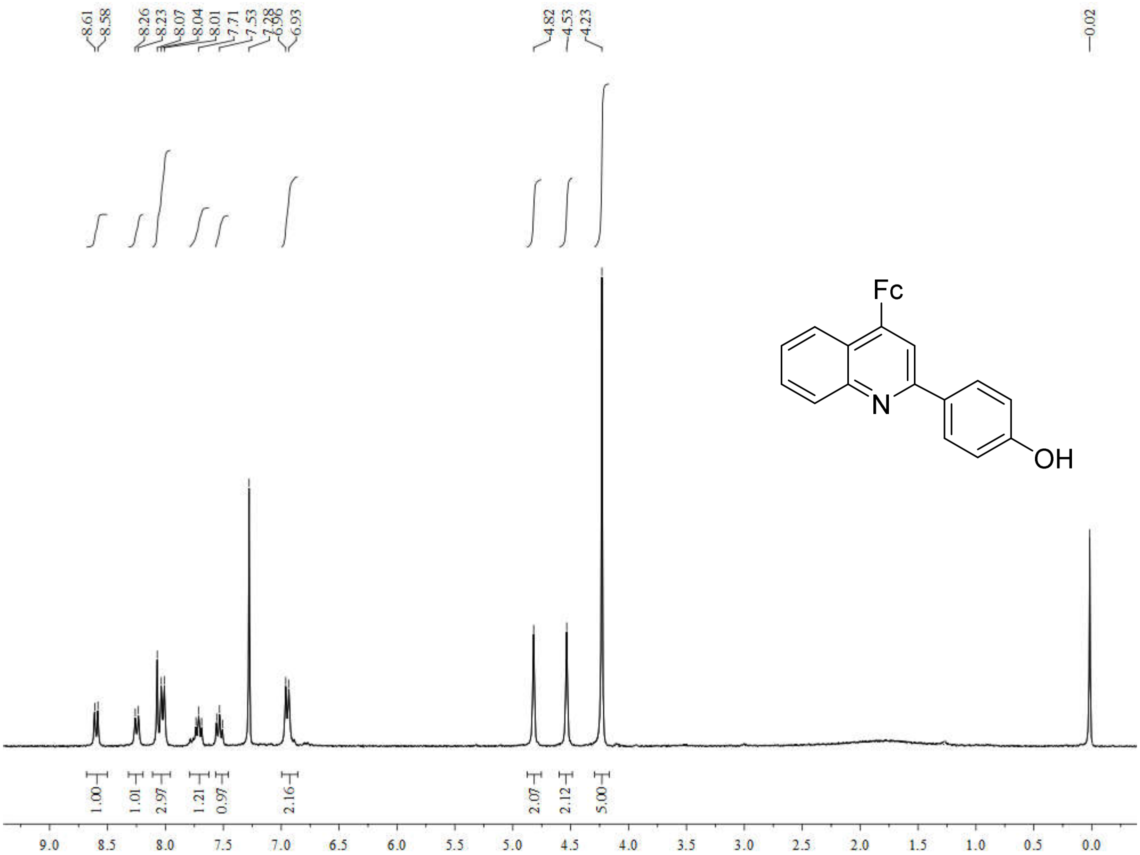
The [1]H NMR of **4d**.



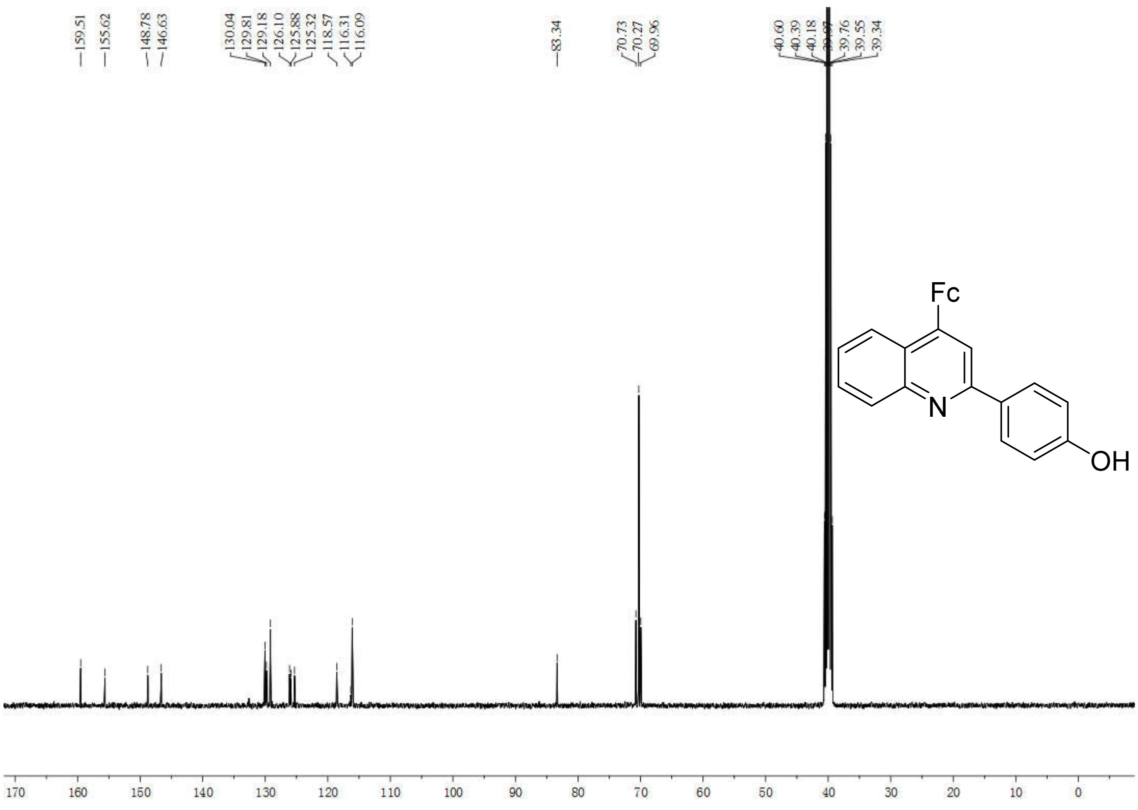
The [13]C NMR of **4d**.



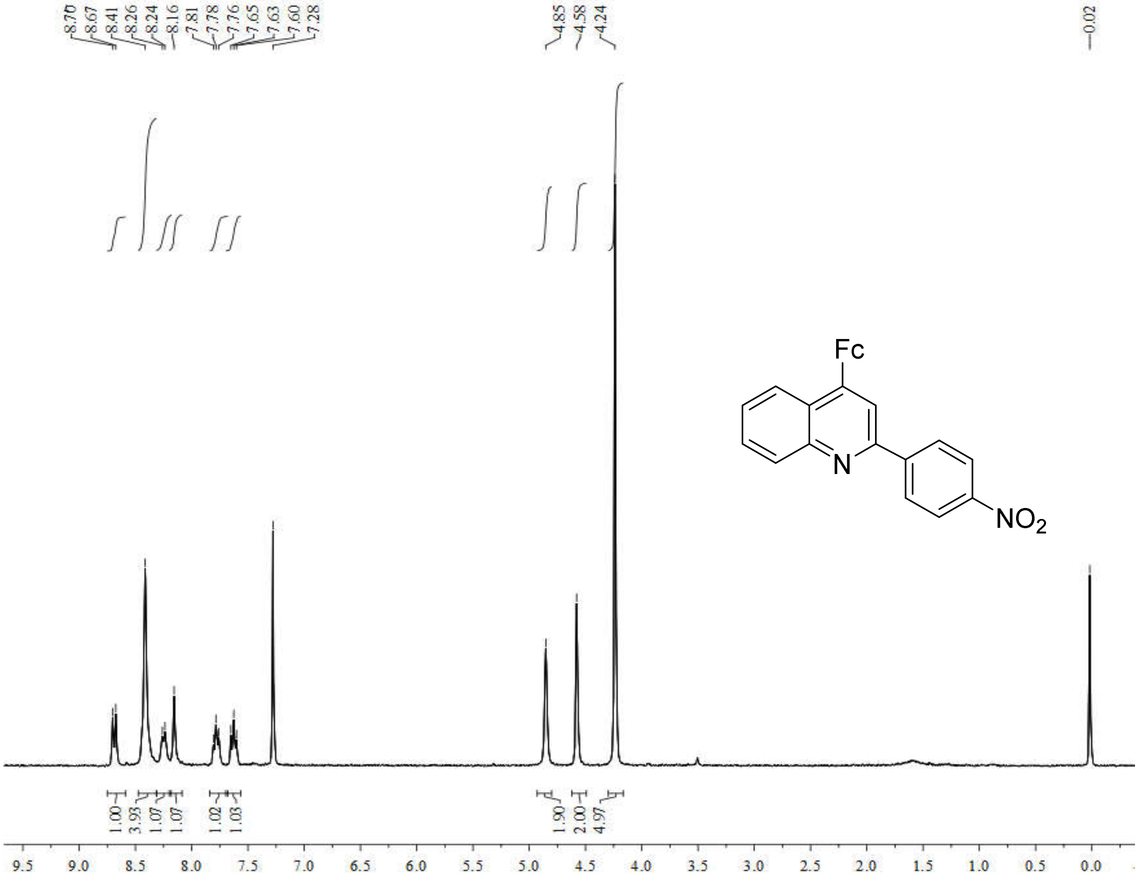
The ^{1}H NMR of **4e**.



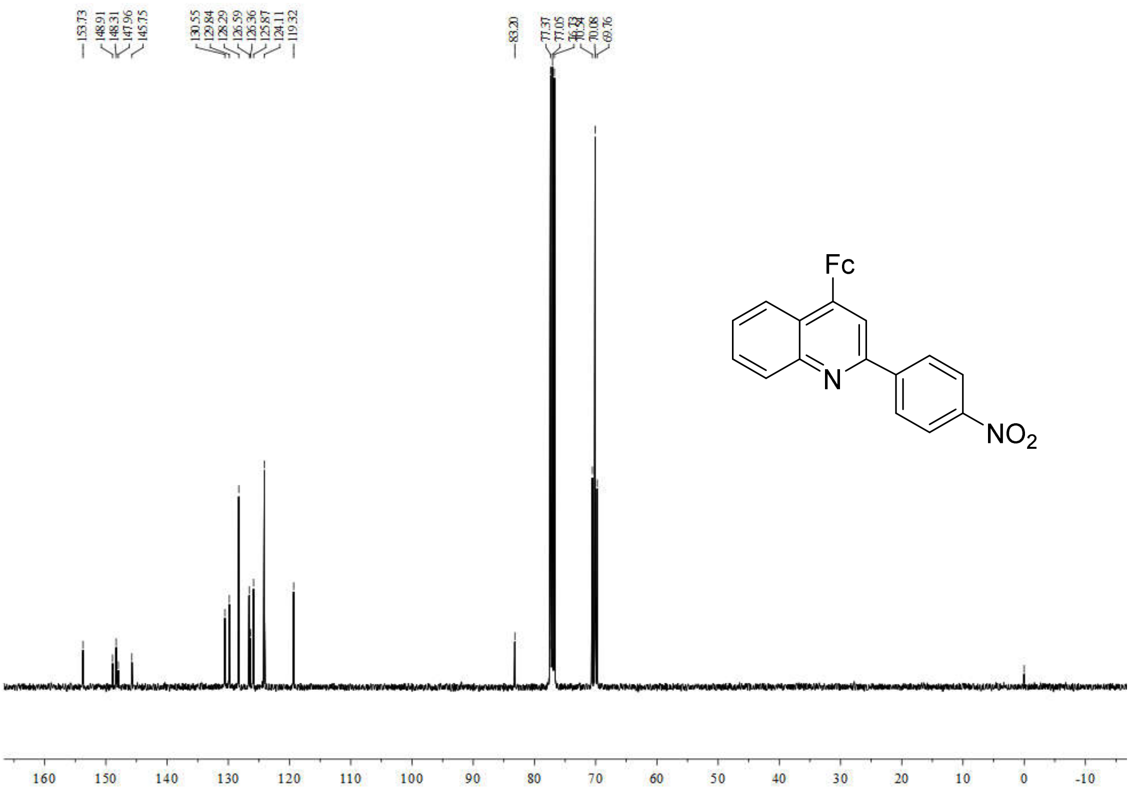
The ^{13}C NMR of **4e**.



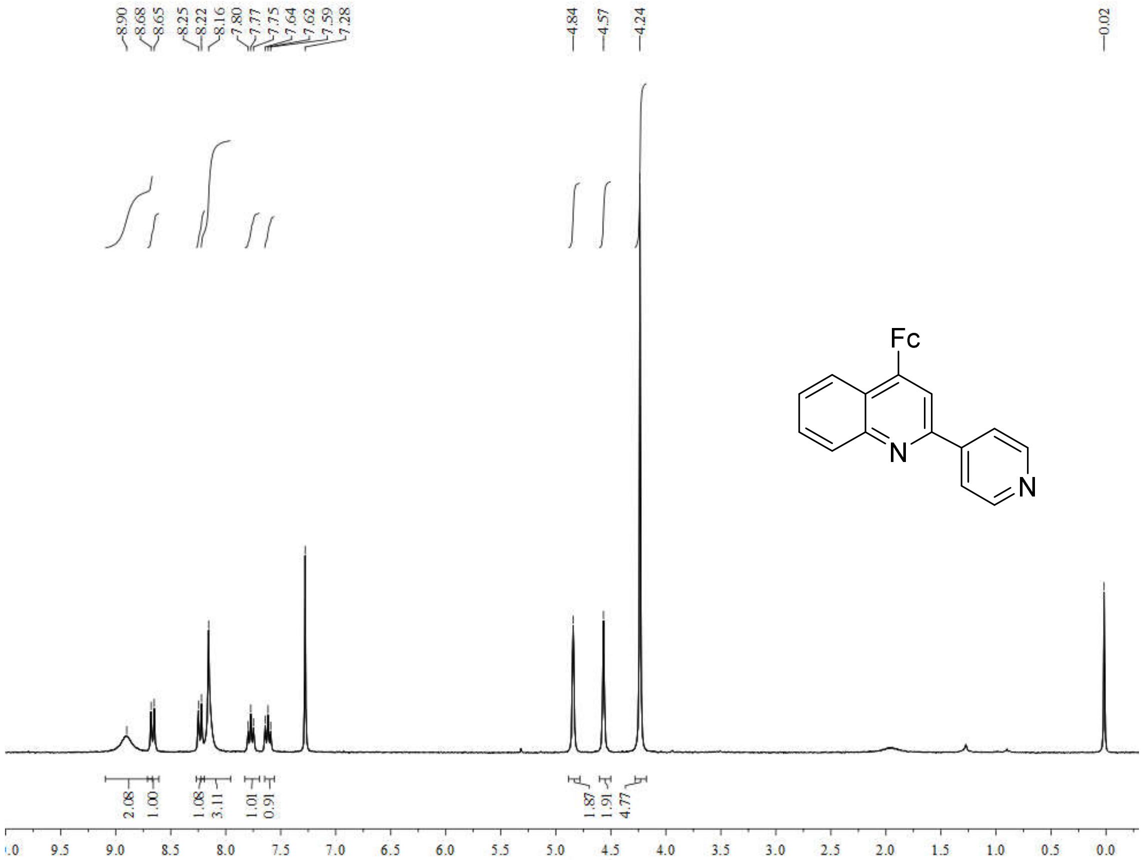
The ^{1}H NMR of **4f**.



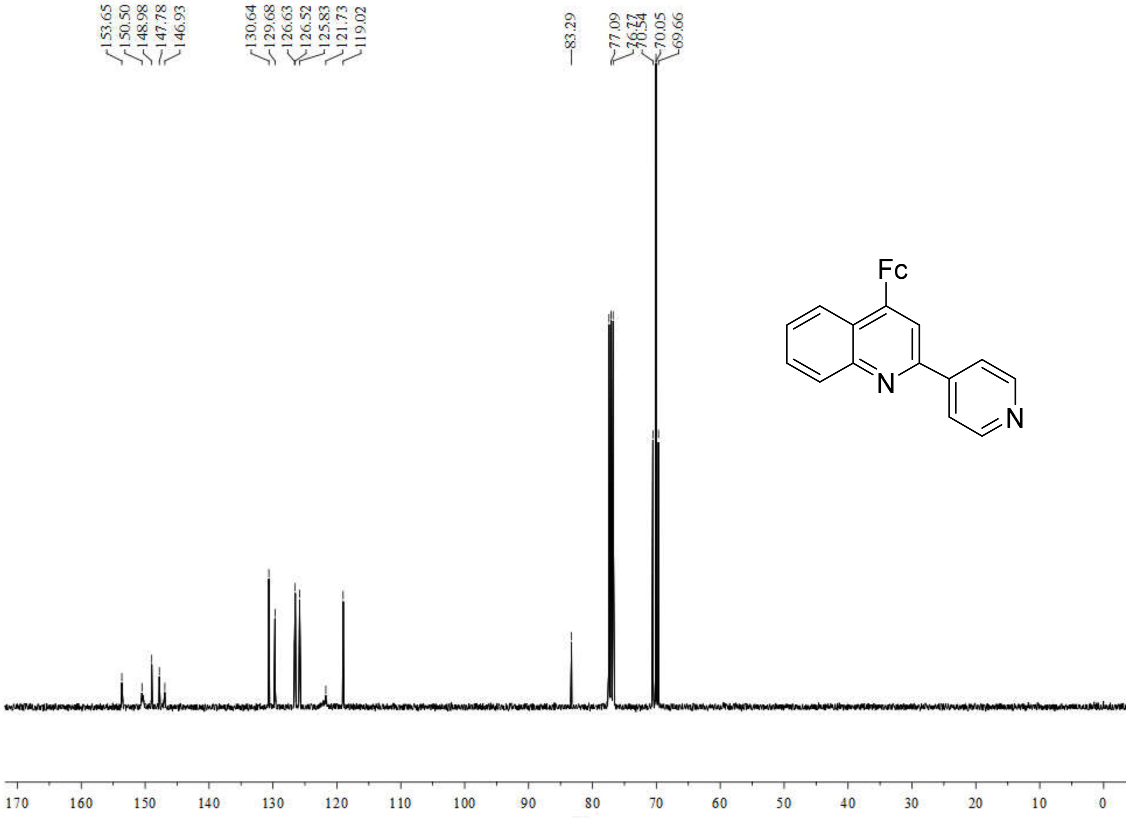
The ^{13}C NMR of **4f**.



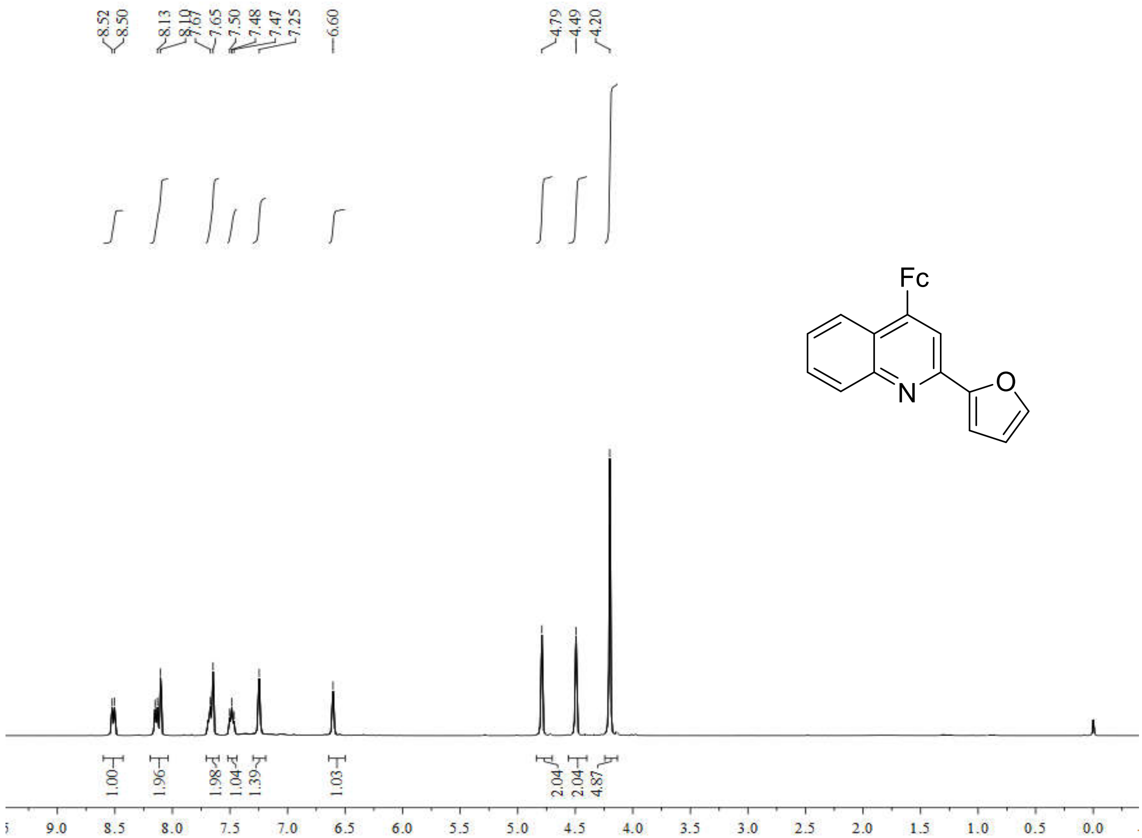
The ^{1}H NMR of **4g**.



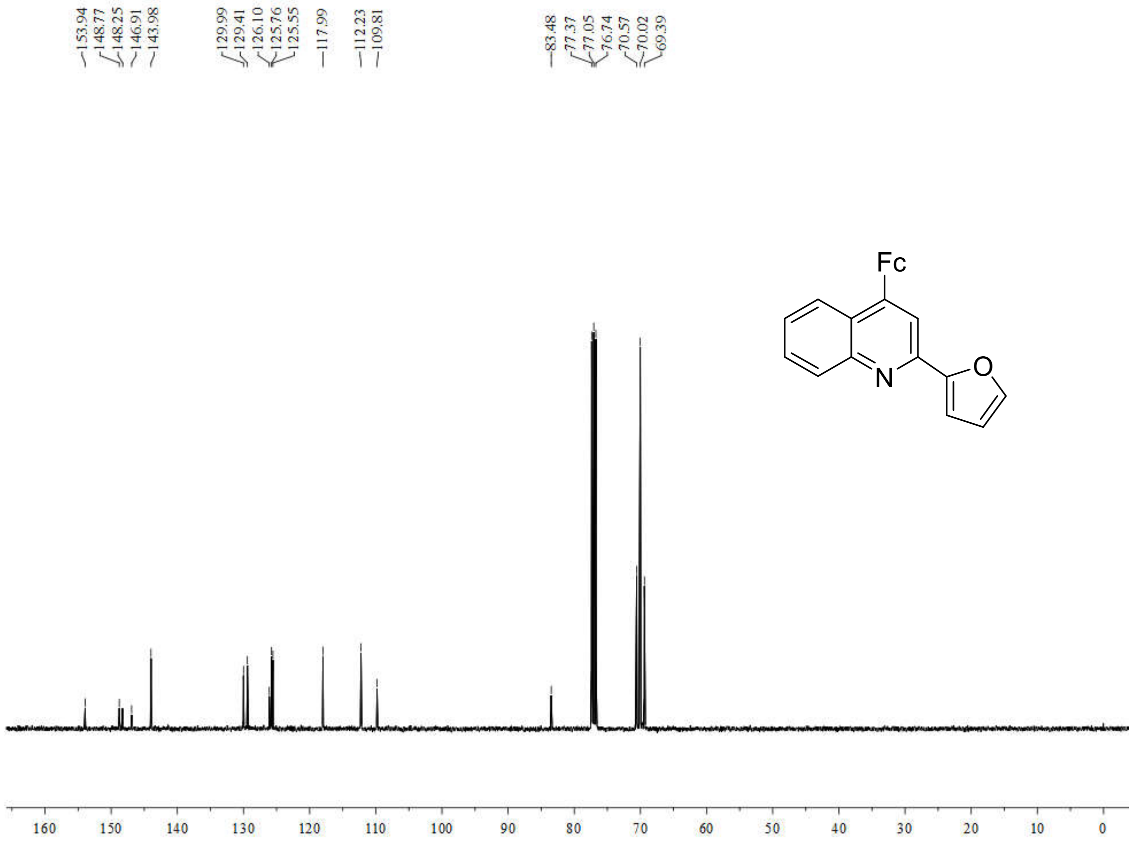
The ^{13}C NMR of **4g.**



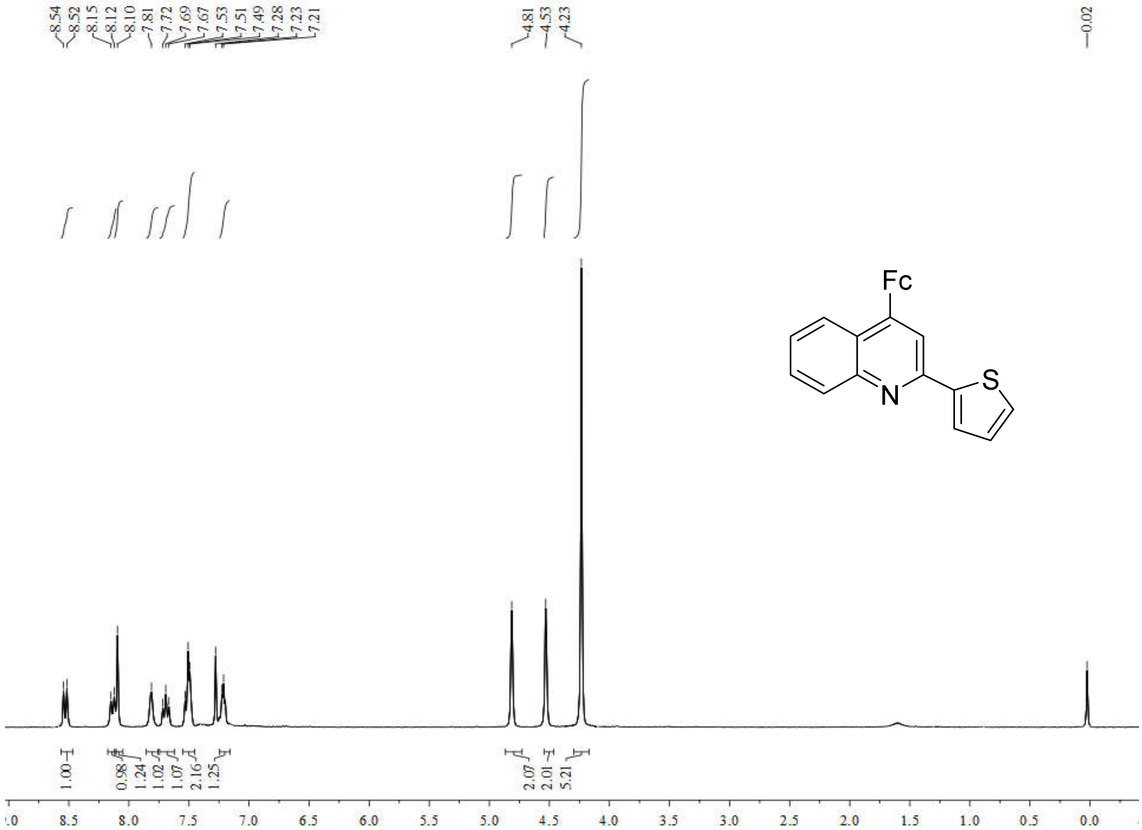
The ^{1}H NMR of **4h**.



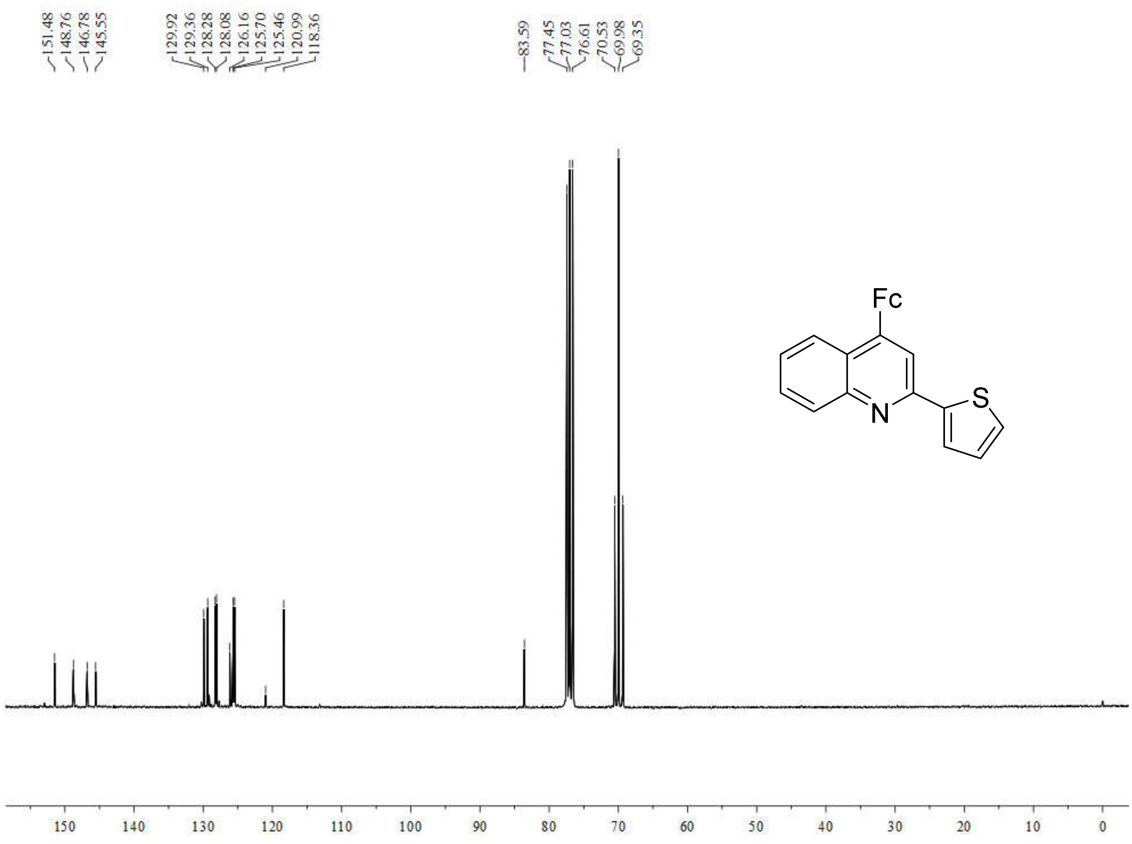
The ^{13}C NMR of **4h**.



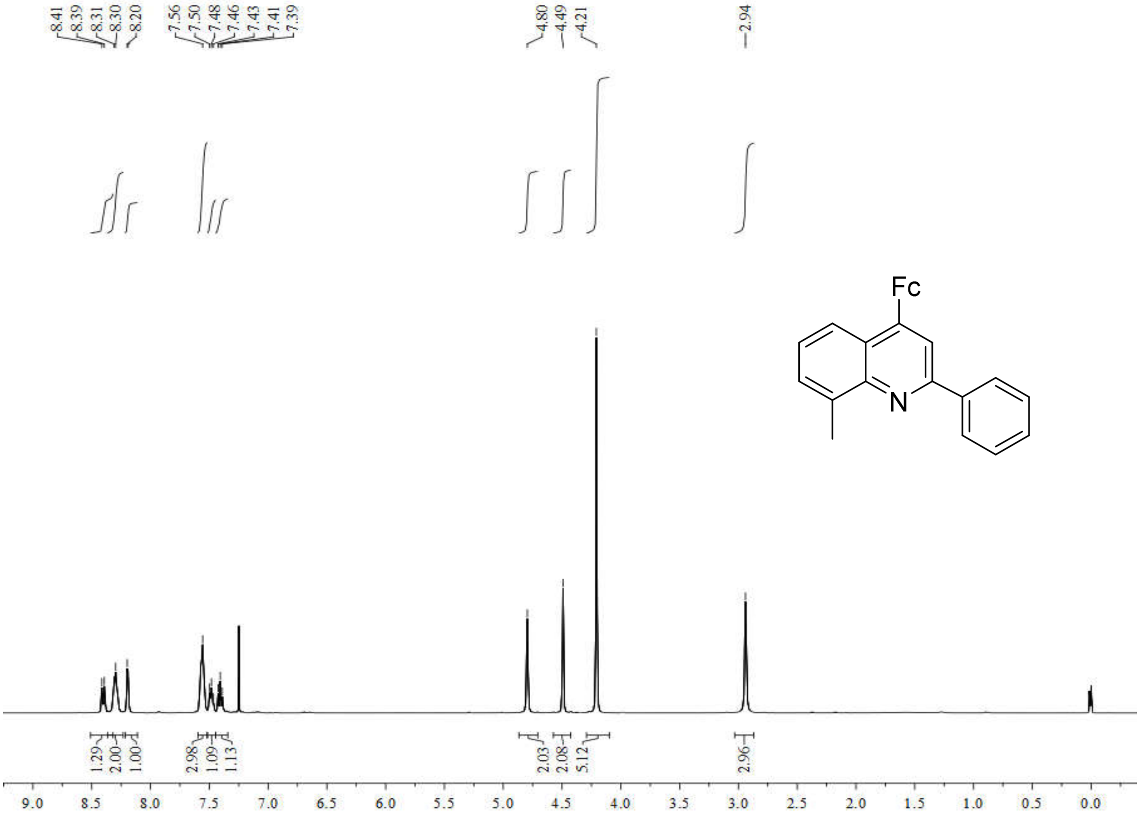
The ^{1}H NMR of **4i**.



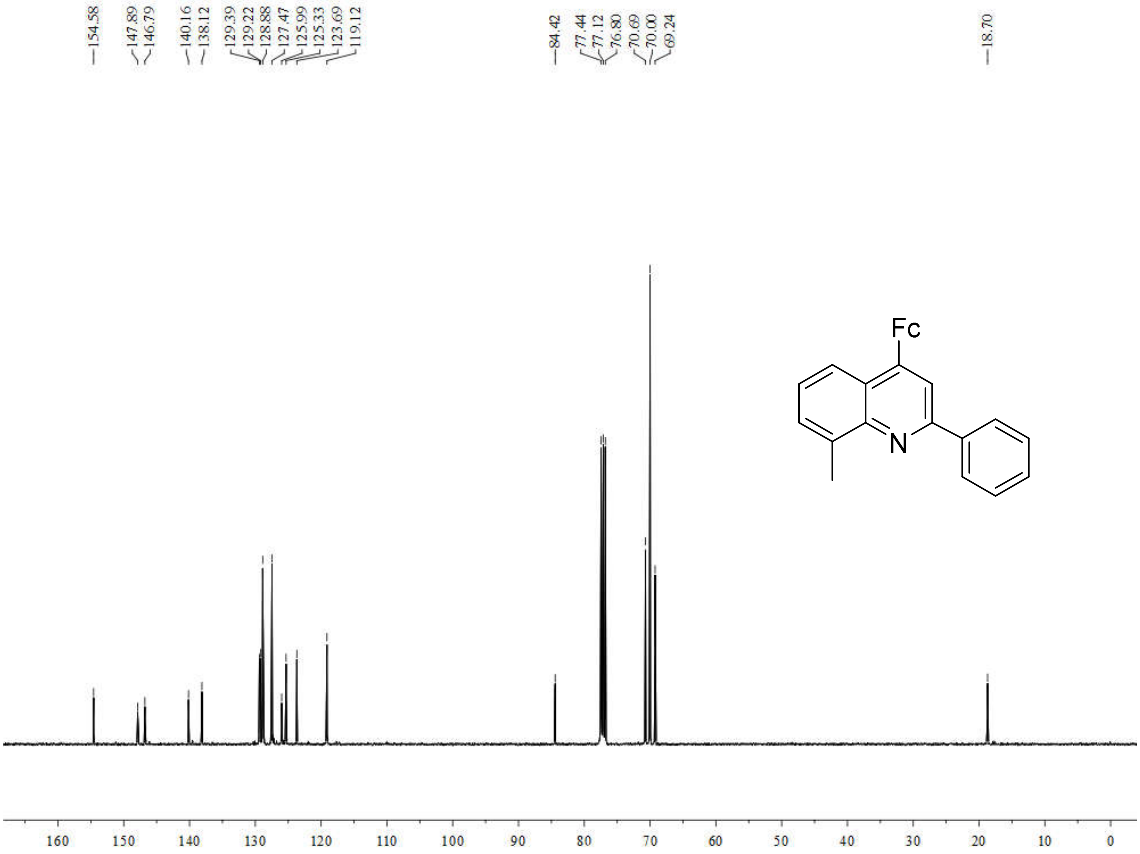
The ^{13}C NMR of **4i**.



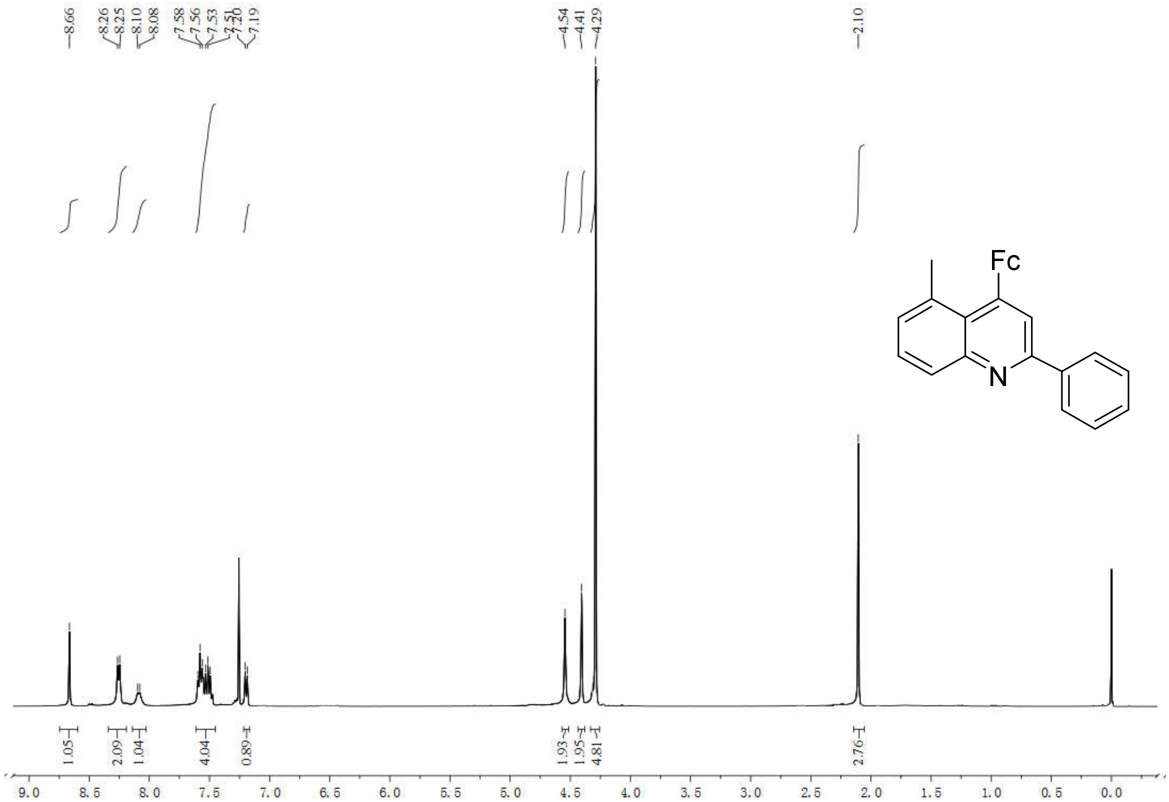
The ^{1}H NMR of **4j**.



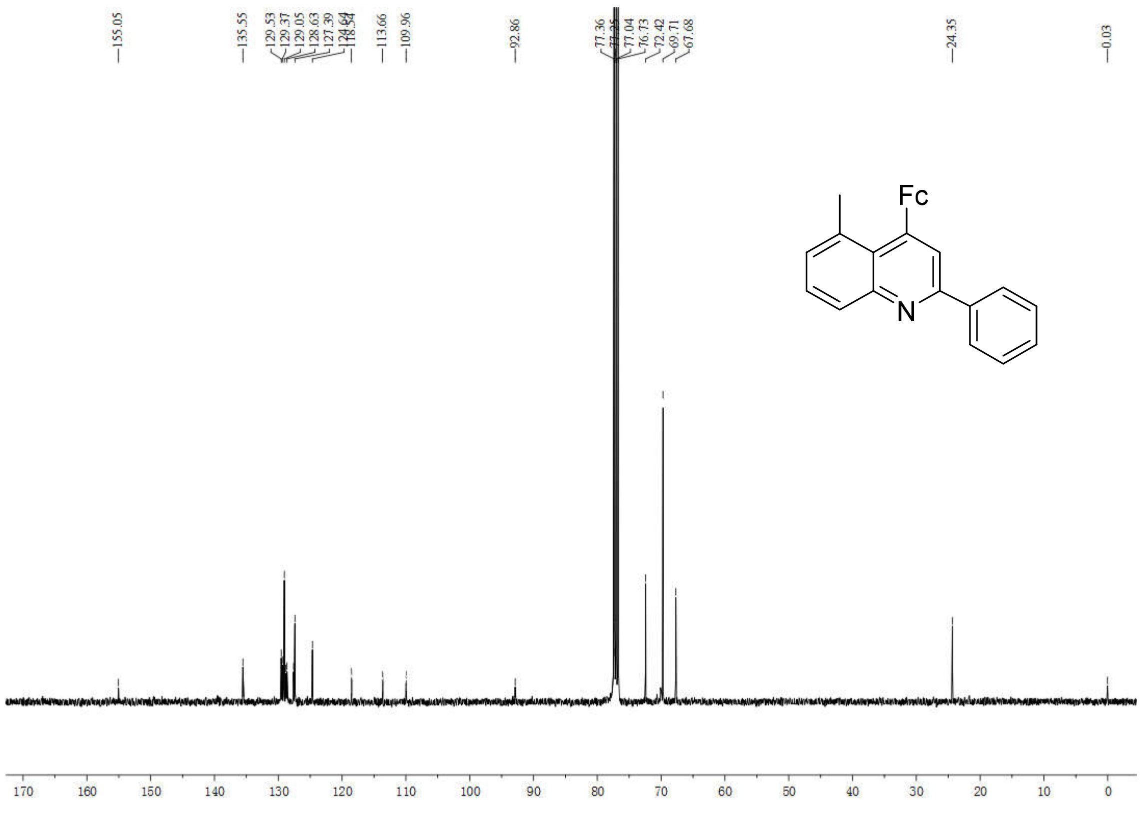
The ^{13}C NMR of **4j**.



The [1]H NMR of **4k**.

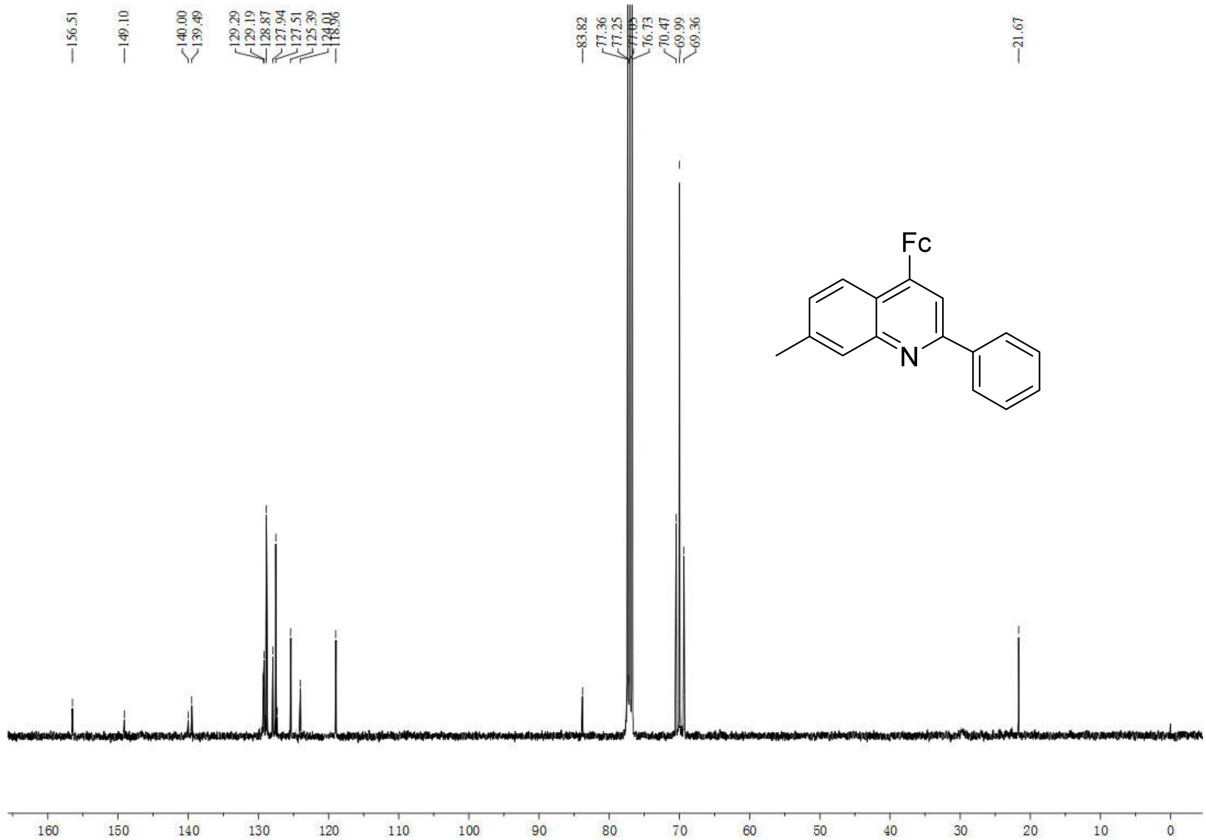


The [13]C NMR of **4k**.

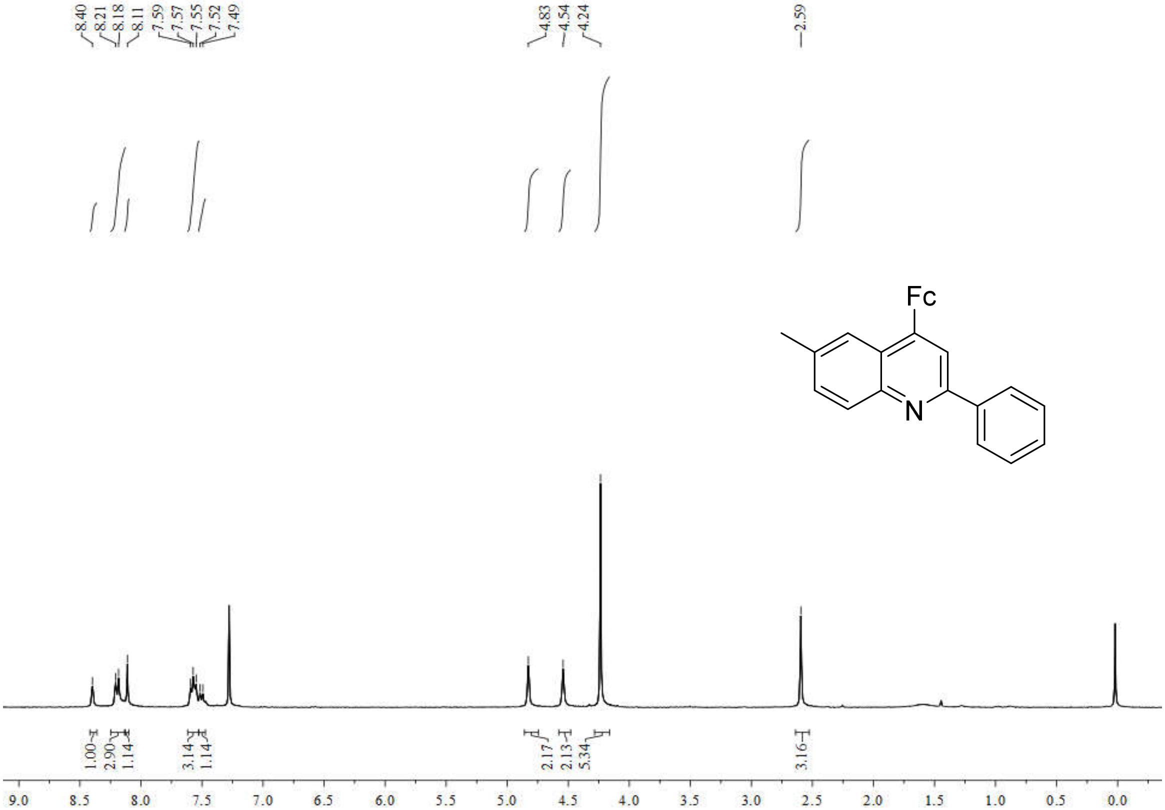


The ^{1}H NMR of **4k'**.

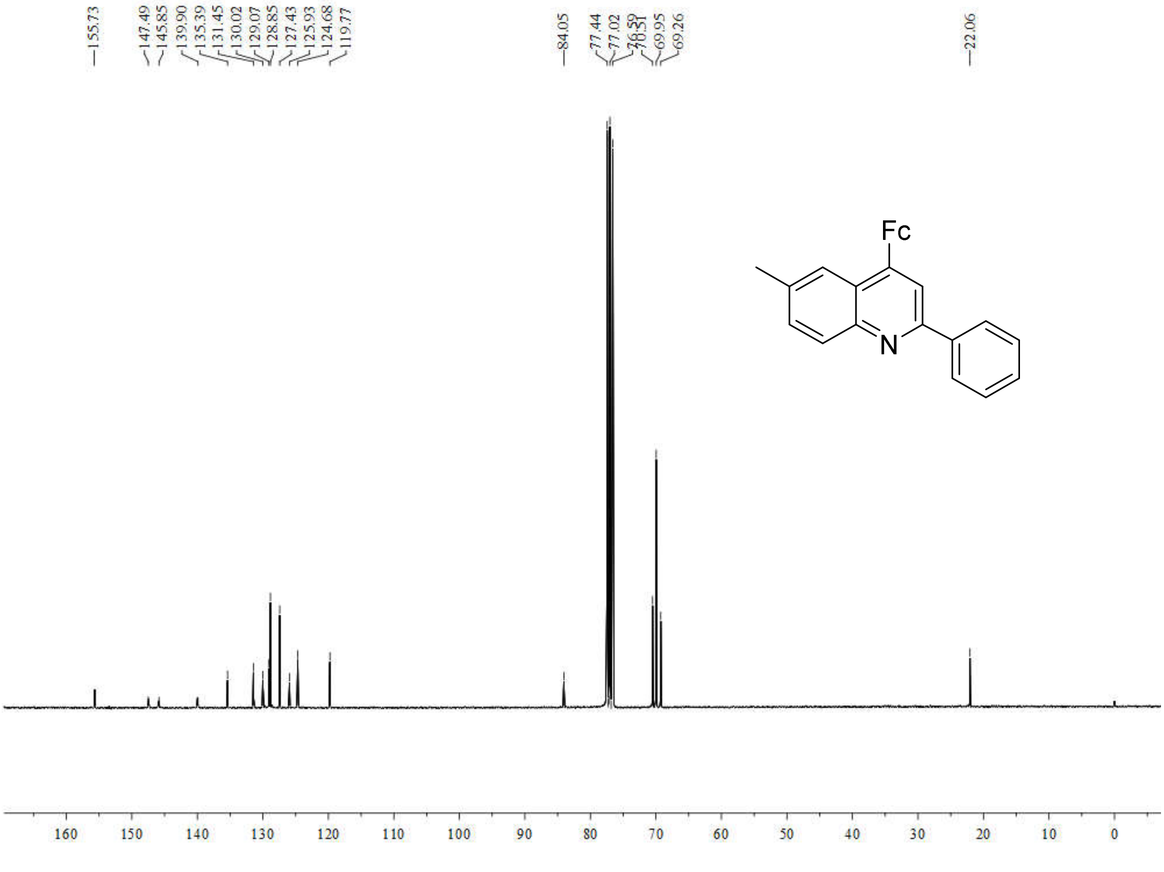
The ^{13}C NMR of **4k'**.



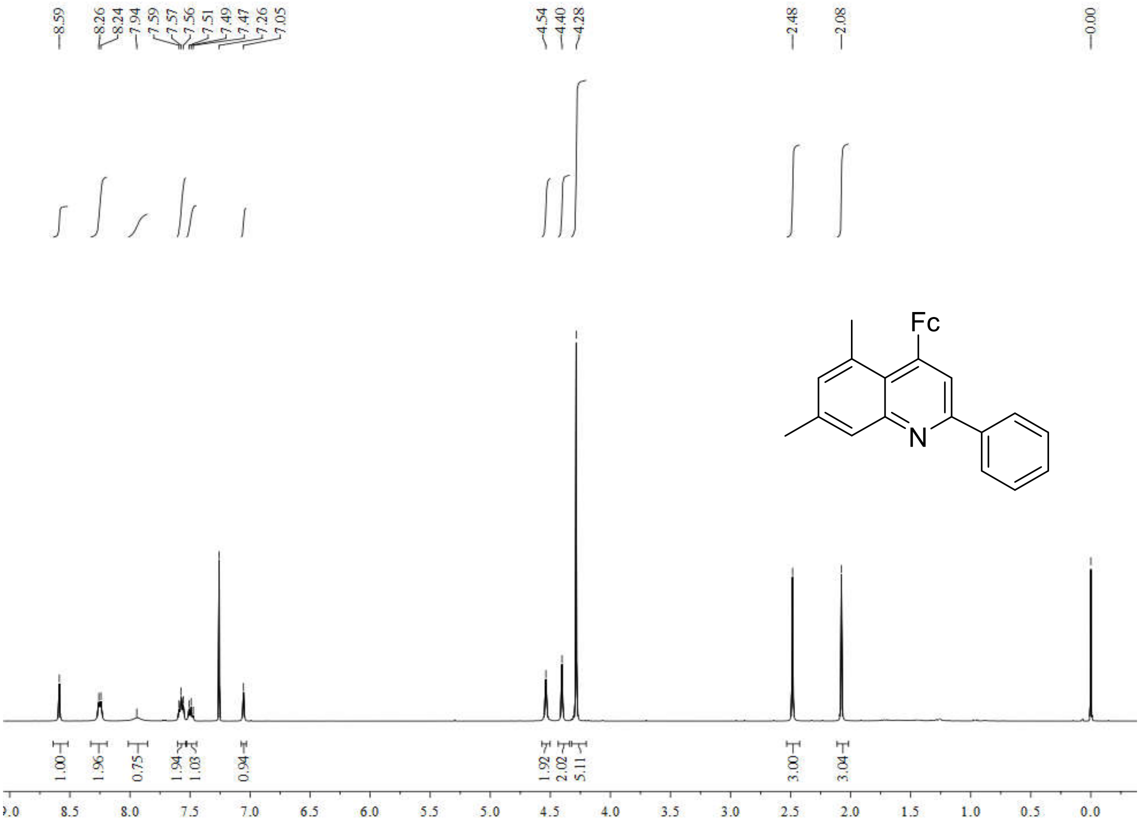
The [1]H NMR of **4l**.



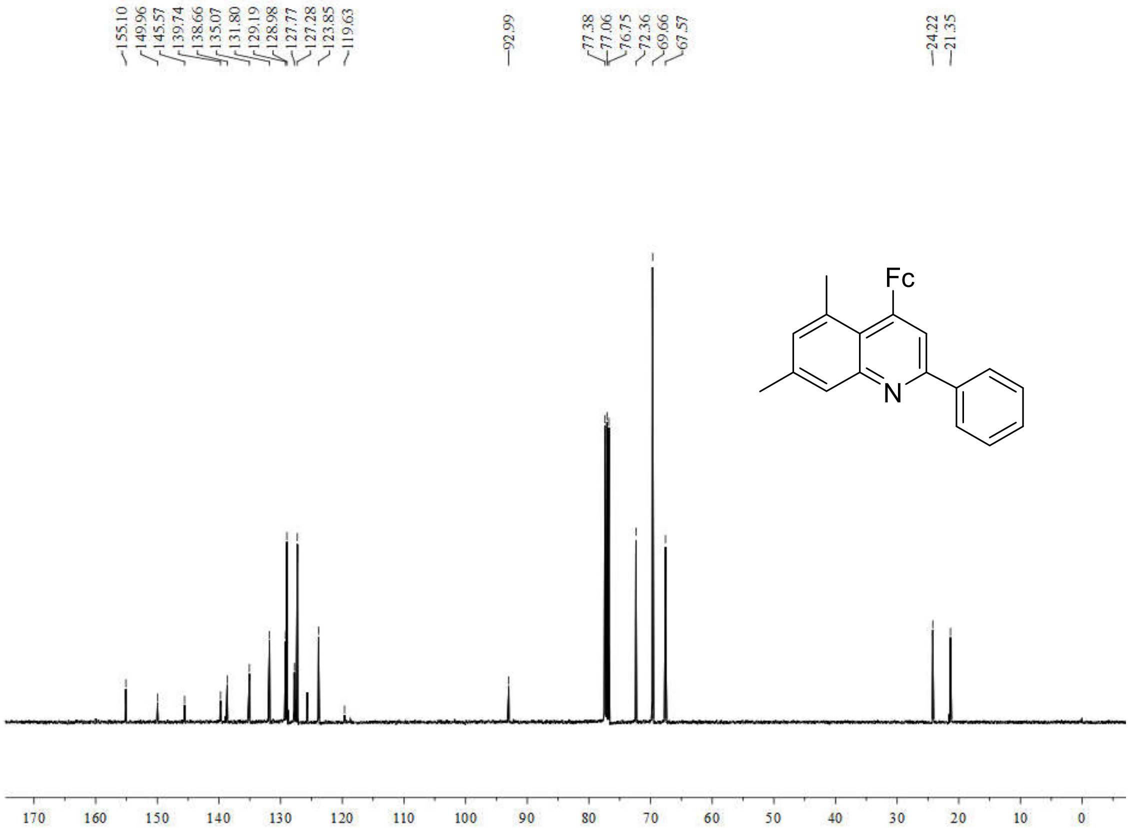
The [13]C NMR of **4l**.



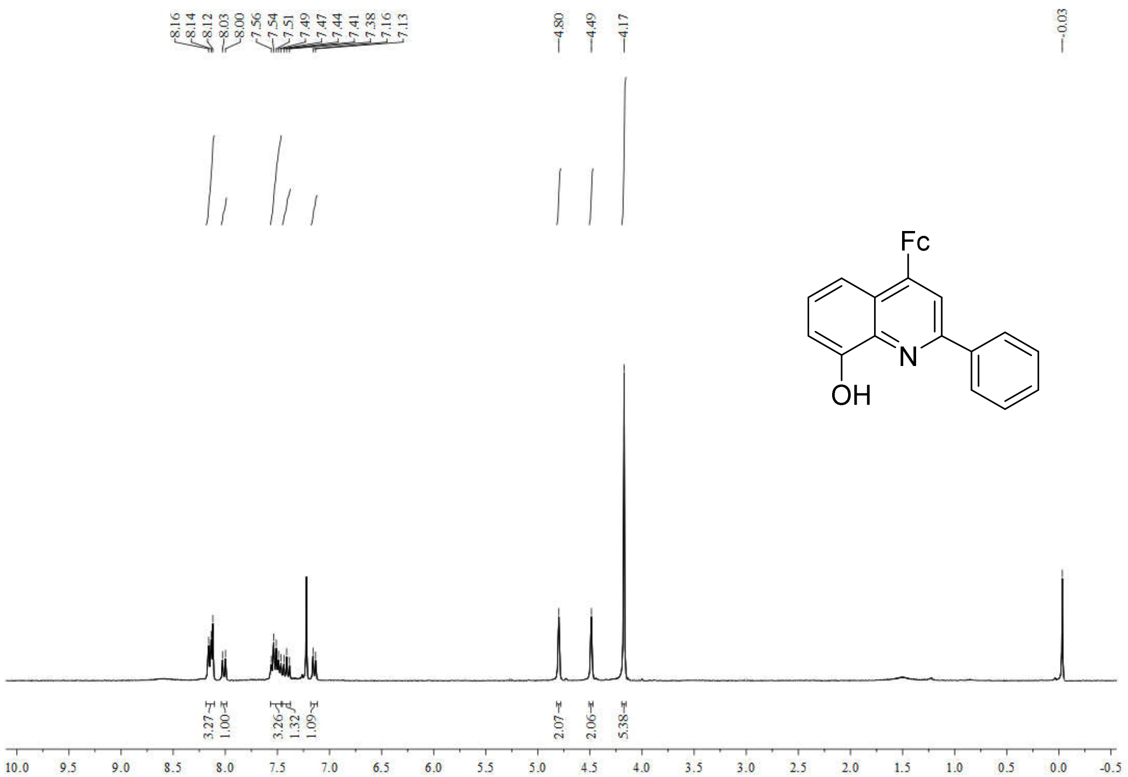
The ^{1}H NMR of **4m**.



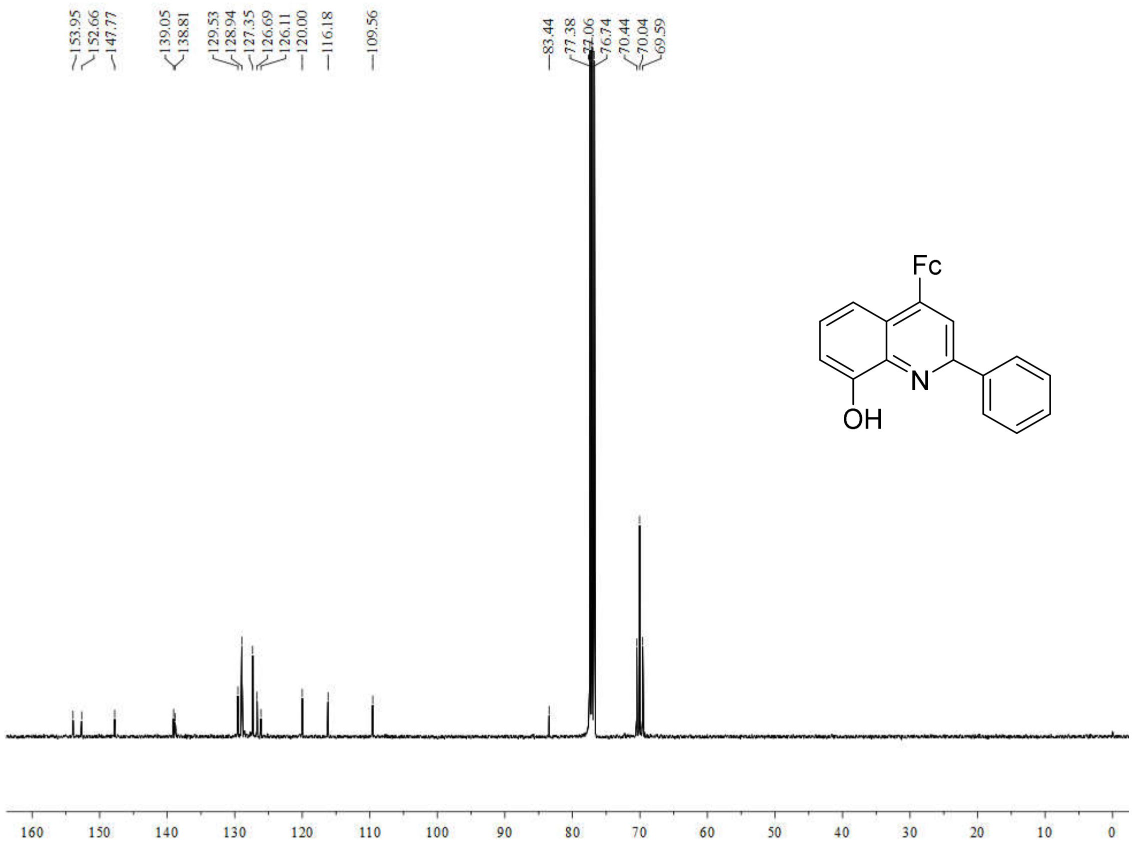
The ^{13}C NMR of **4m**.



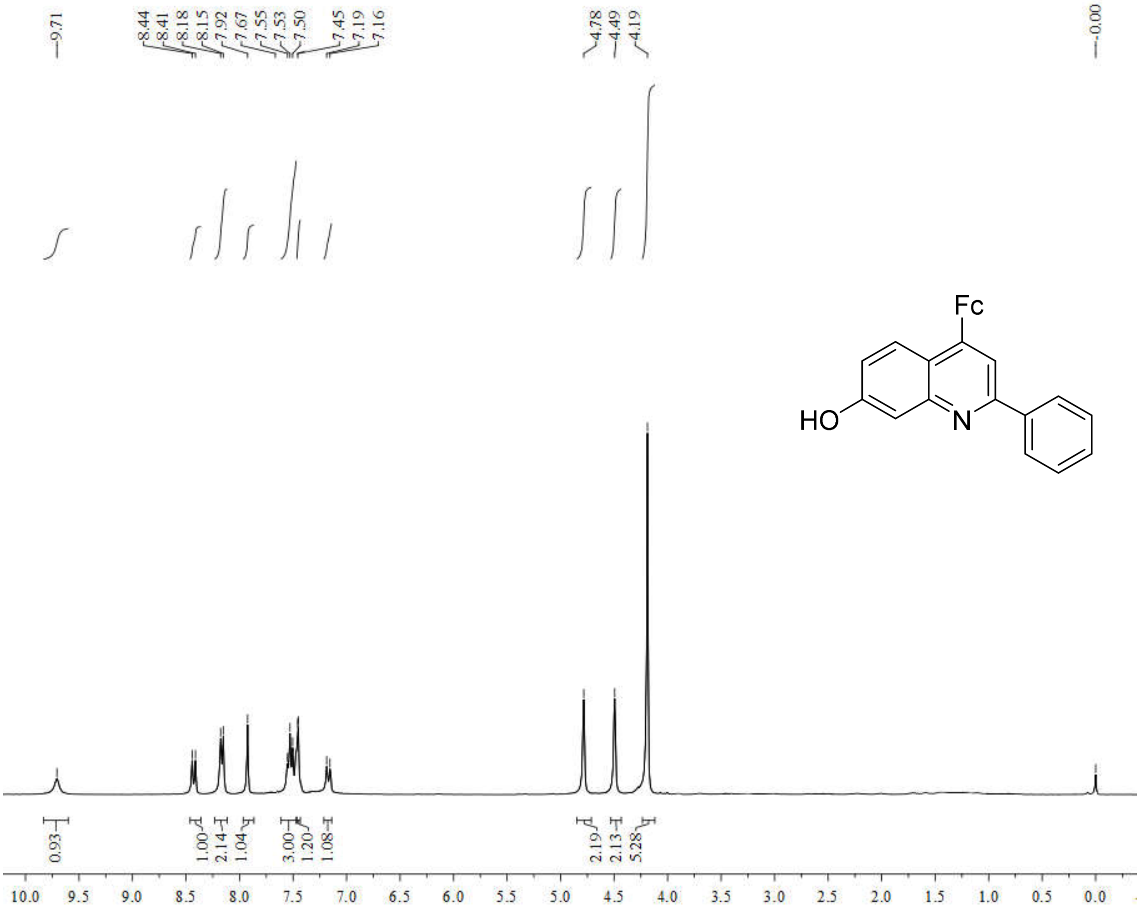
The [1]H NMR of **4n**.



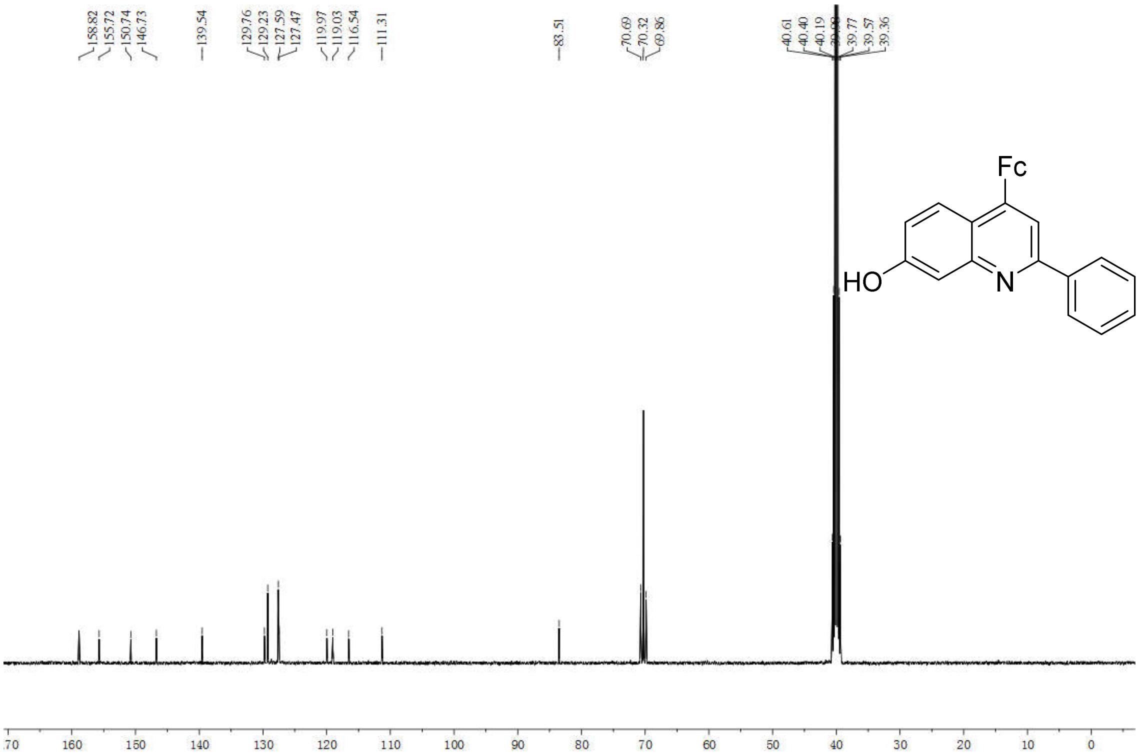
The [13]C NMR of **4n**.



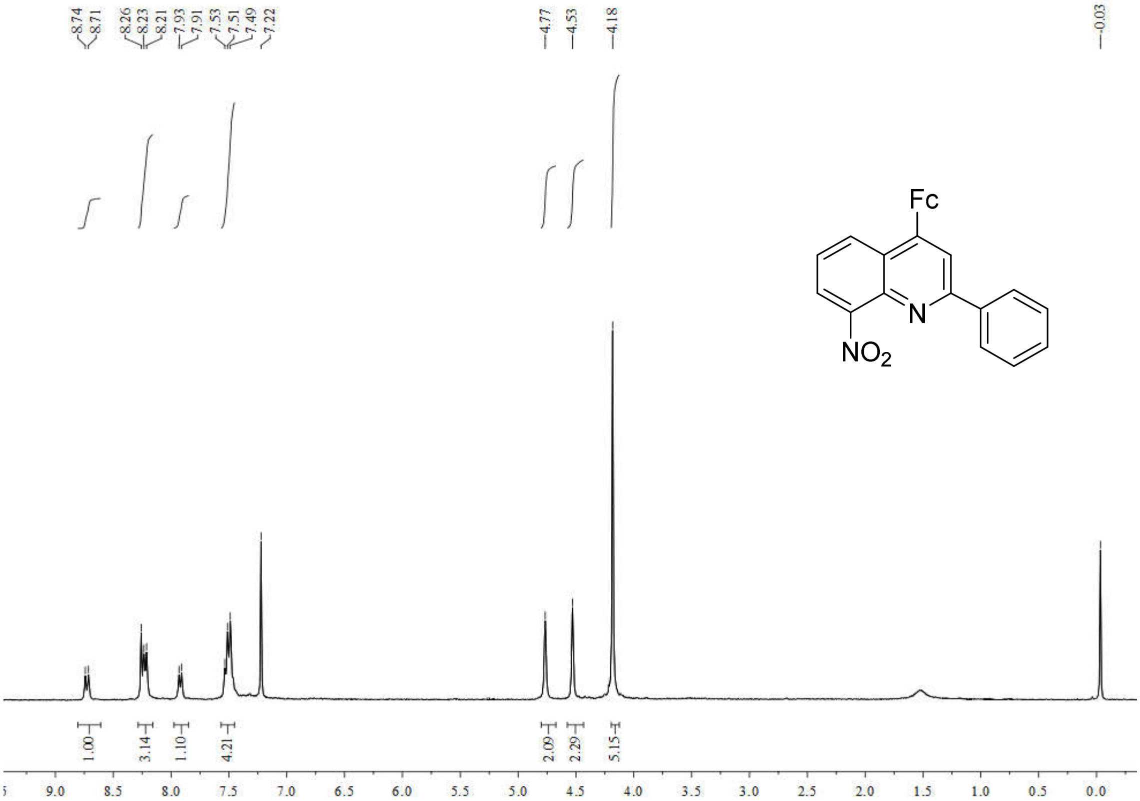
The ^{1}H NMR of **4o**.



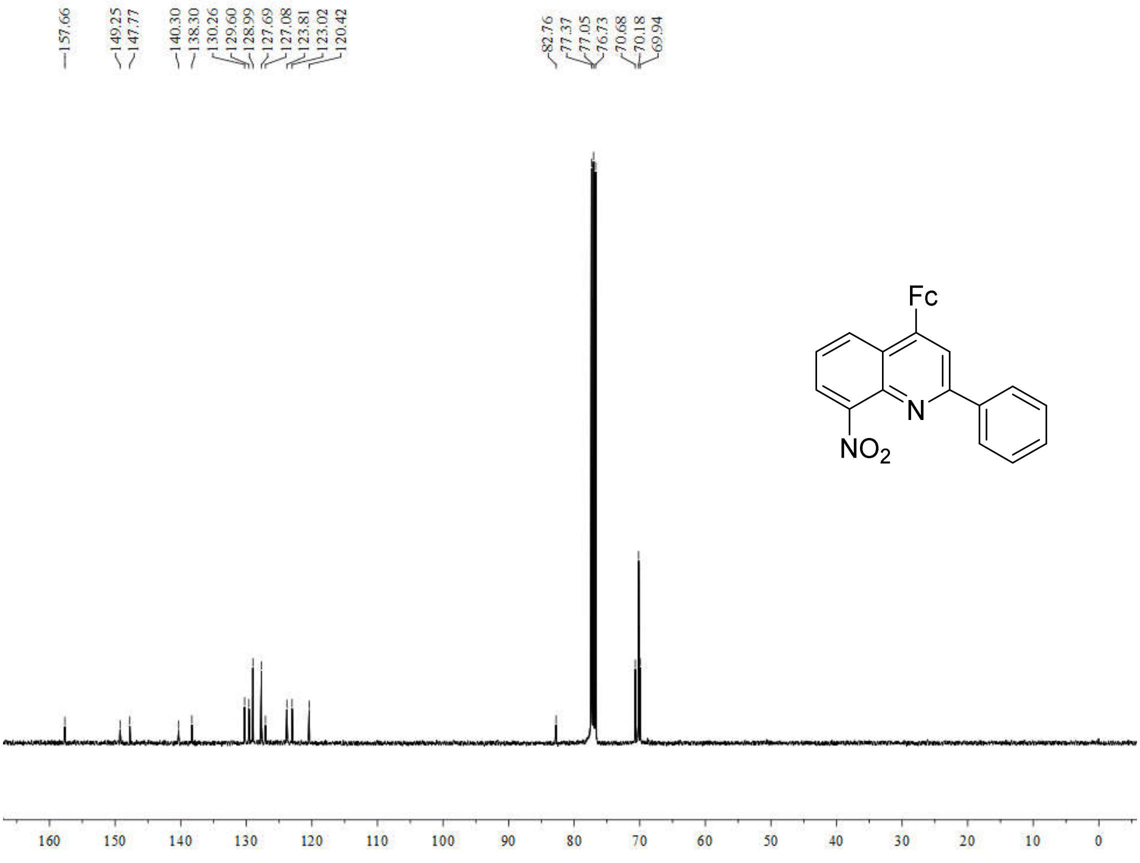
The ^{13}C NMR of **4o**.



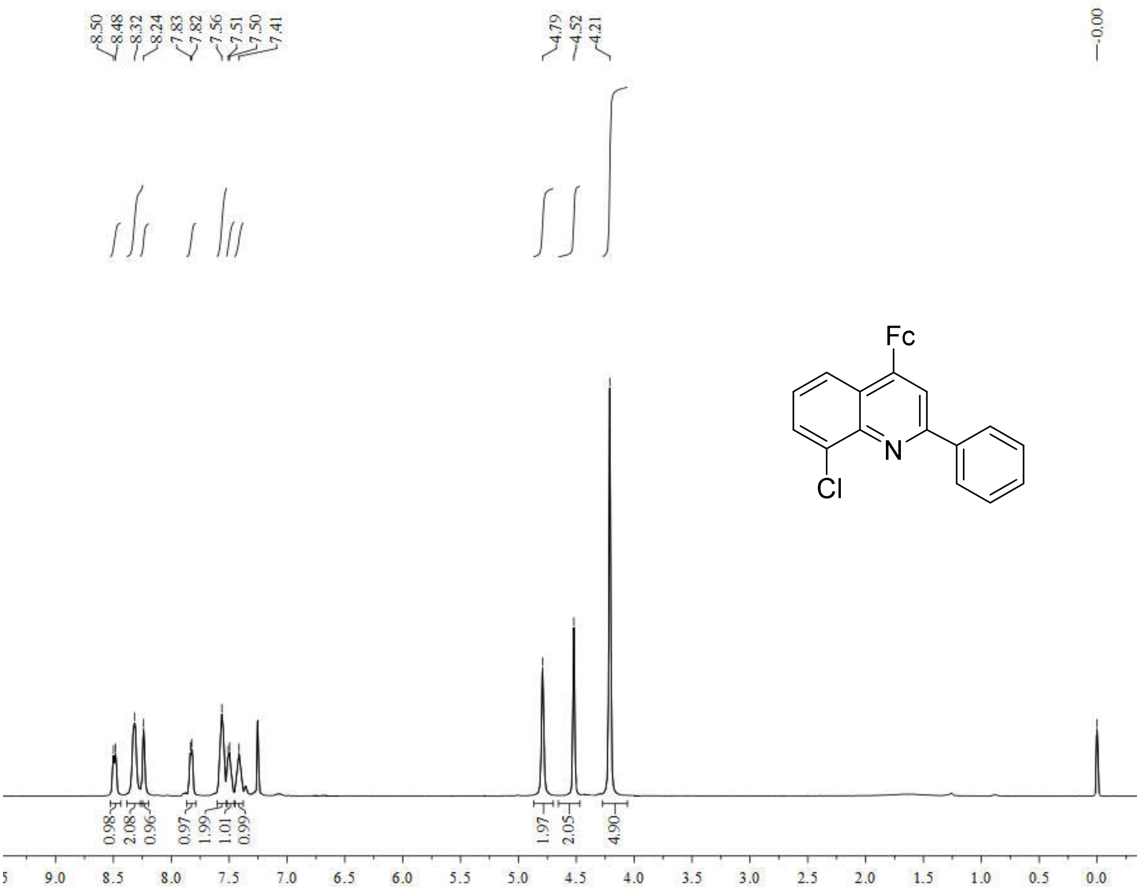
The ^{1}H NMR of **4p**.



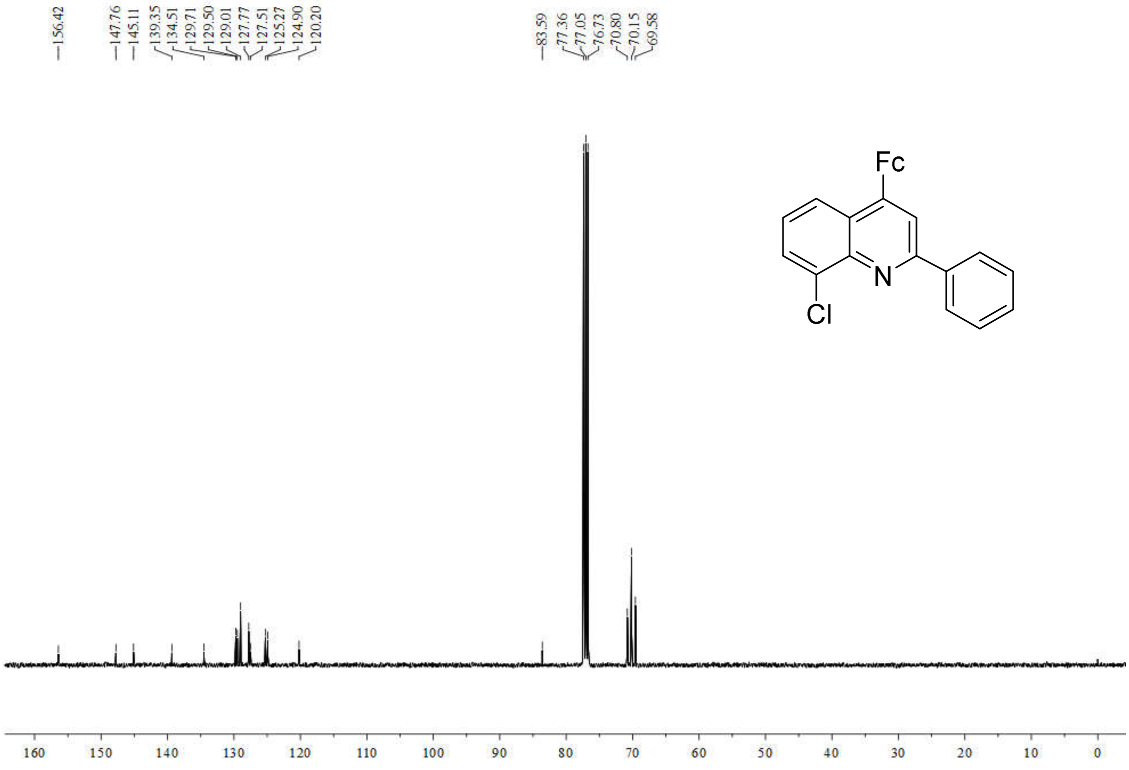
The ^{13}C NMR of **4p**.



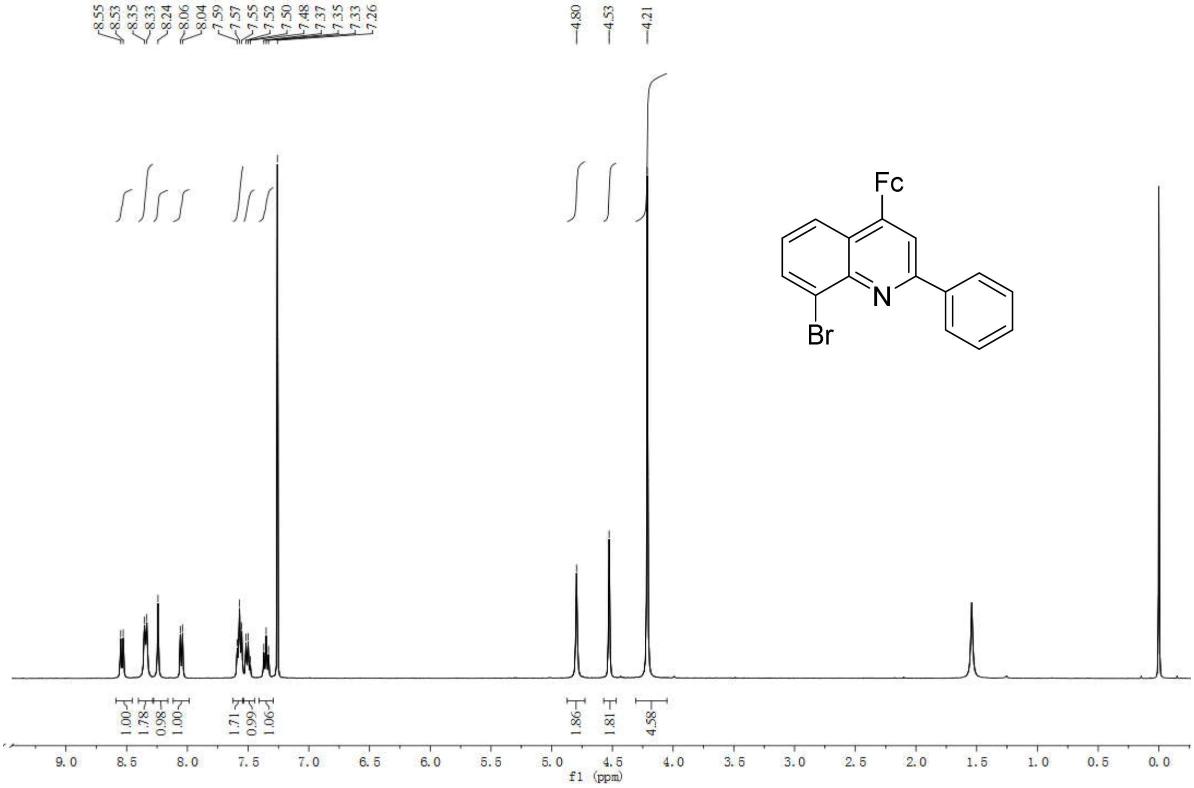
The ^{1}H NMR of **4q**.



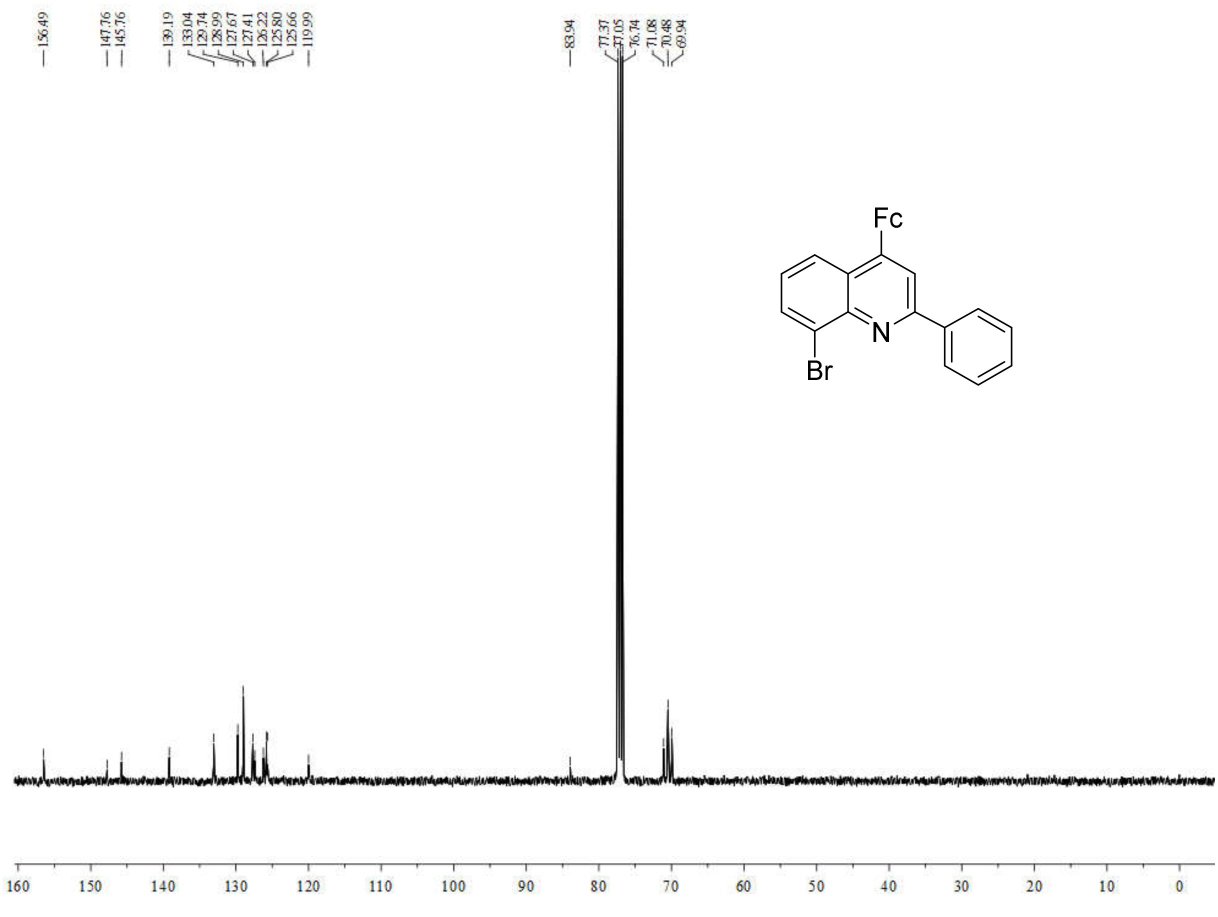
The ^{13}C NMR of **4q**.



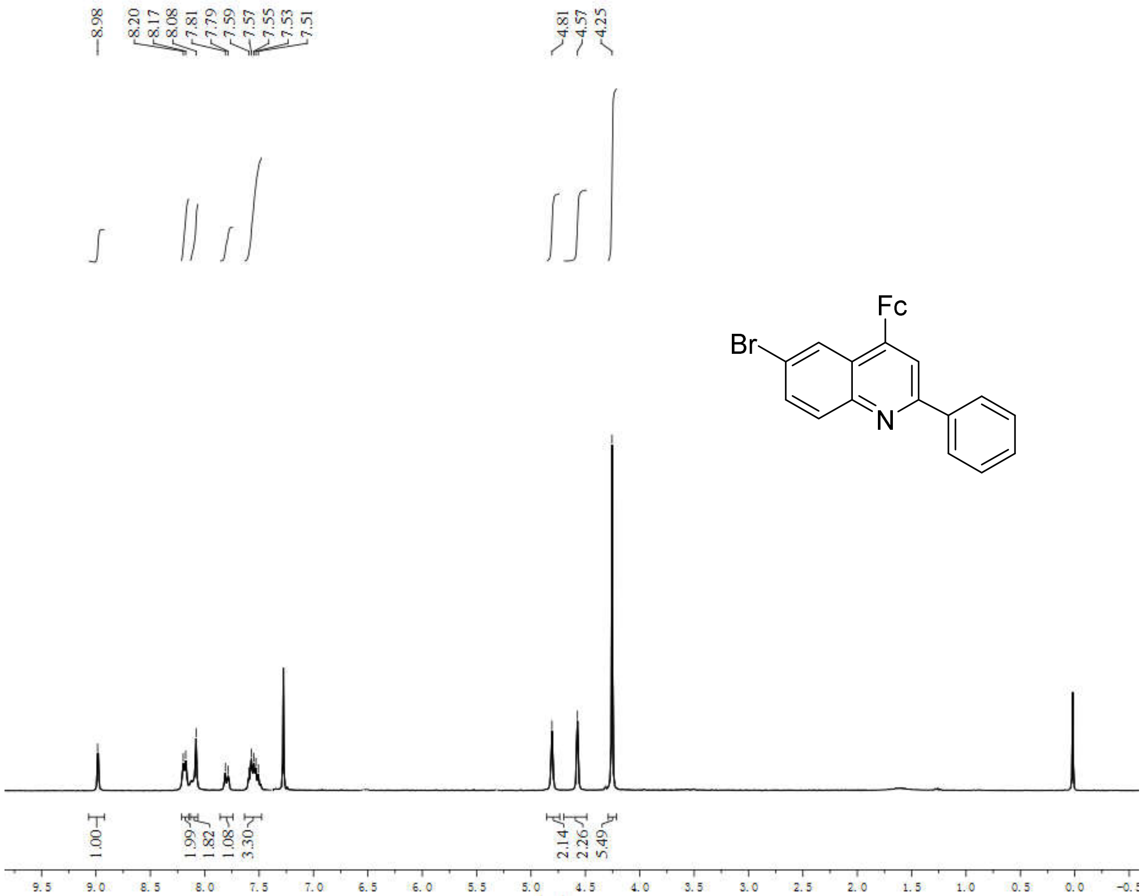
The ^{1}H NMR of **4r**.



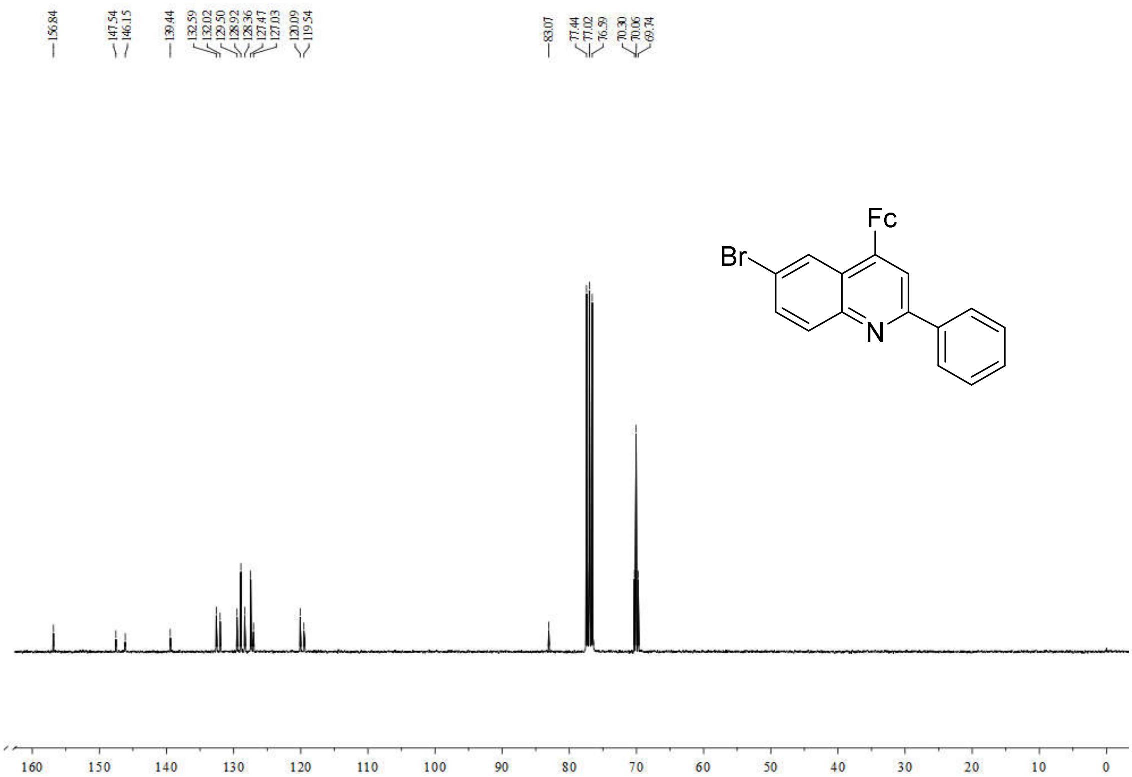
The ^{13}C NMR of **4r**.



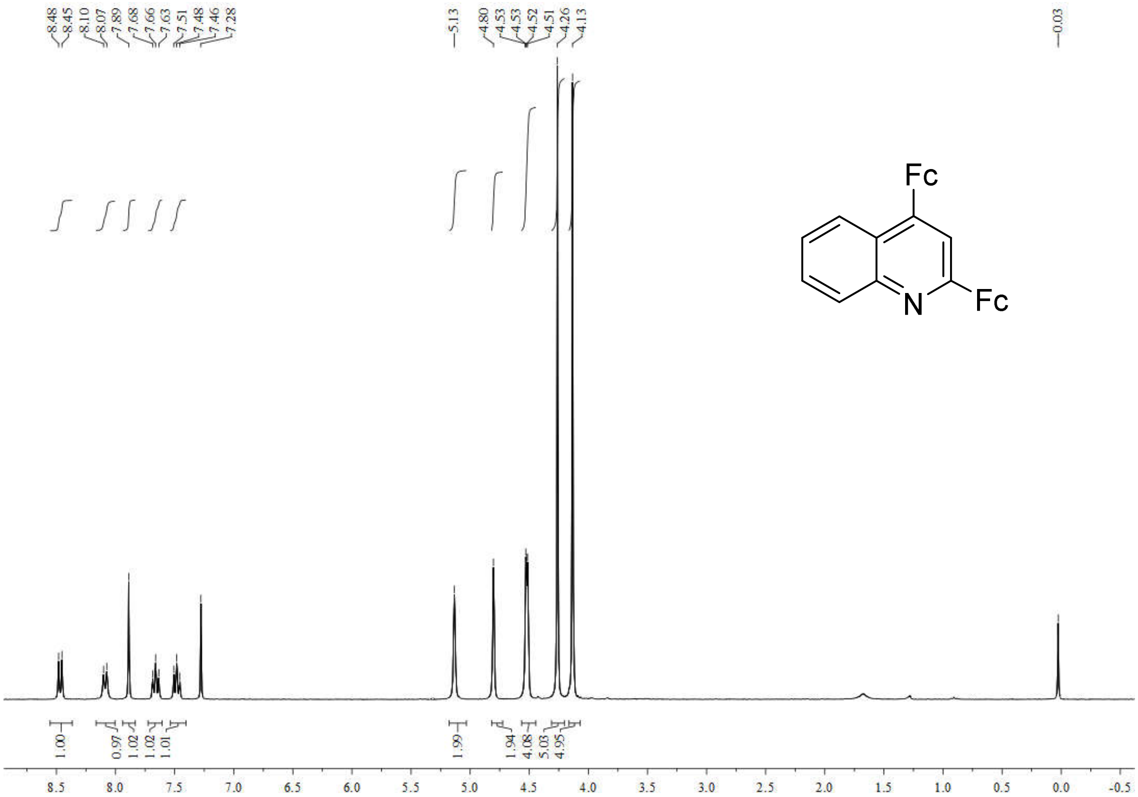
The ^{1}H NMR of **4s**.



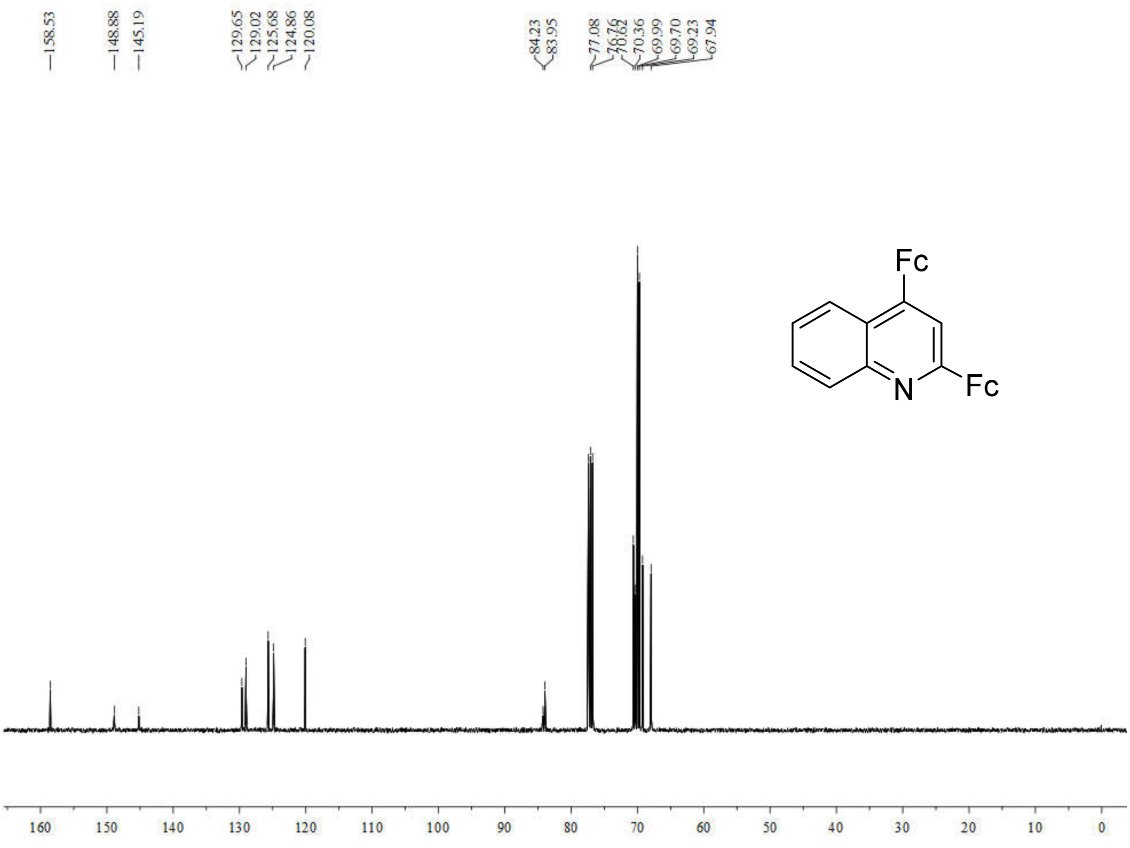
The ^{13}C NMR of **4s**.



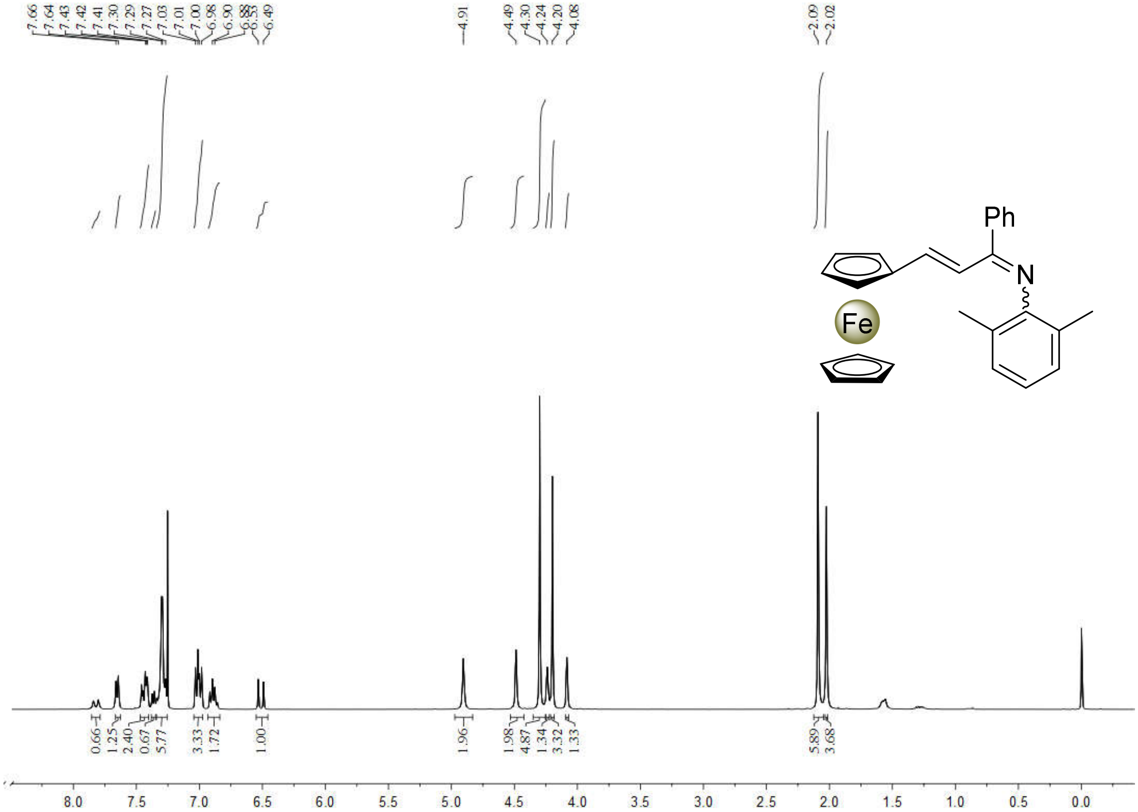
The ^{1}H NMR of **4t**.



The ^{13}C NMR of **4t**.



The ^{1}H NMR of **6**.



The ^{13}C NMR of **6**.