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Supporting Information

Photocatalytic synthesis of azaheterocycle-fused piperidines and pyrrolidines via tandem difunctionalization of unactivated alkenes

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Contents

1. General information

All solvents and reagents were purchased from the suppliers and used without further purification unless otherwise noted. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 NMR spectrometers. The chemical-shift scale is based on internal TMS. High-solution mass spectra were acquired on Agilent 6230 TOF LC/MS. The melting points were recorded on an X-4 microscope melting point apparatus and are uncorrected. The model used for the infrared spectrometer is Nicolet iS20. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100 - 200 mesh). LEDs (25 W) used for light irradiation were purchased from Xuzhou Ai Jia Electronic Technology, Co. LTD. The wavelength of peak intensity (λ_p) for the selected LED source 460-470 nm is 465.4 nm with the half-intensity width ($\Delta\lambda$) of 18.6 nm. Fans were used to maintain the reaction temperature at room temperature. Borosilicate vessels were used for LED irradiation without filters, approximately 2 cm away from the light source.

2. General procedure

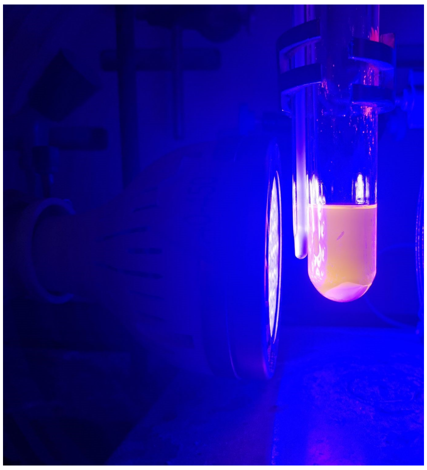
2.1 A 0.2 mmol-scale synthesis

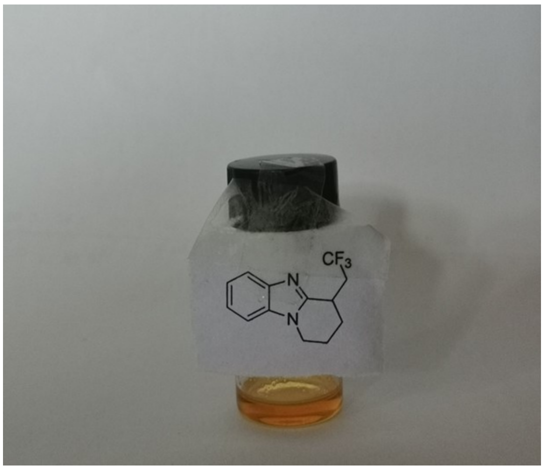
1-(pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (**1a**) (0.2 mmol, 0.0372g), CF_3SO_2Na (0.6mmol, 0.0936g) (**2a**), Eosin Y-Na_2 (5 mol%), CH_3CN (2 mL) were placed in a 10 mL silica borate glass tube. The reaction system was stirred rapidly under the irradiation with 25 W blue LED lamp (about 2 cm away from the light source) at 62°C (no fan). TLC monitored the reaction process until the reaction was completed (6 h). After completion, ethyl acetate and water were added and extracted for three times. Organic phase was combined and dried over anhydrous sodium sulfate. The crude product underwent purification by column chromatography (petroleum ether: ethyl acetate = 3:1, v/v) to give product **3aa**~**3ua**.

If CF_3SO_2Na was replaced by CHF_2SO_2Na, the product **3cb** was obtained. If 1- (pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (**1a**) was replaced by 1-allyl-2-phenyl -1*H* - benzo[*d*]imidazole (**4**), the product **5** was obtained.

2.2 A 1 mmol-scale synthesis

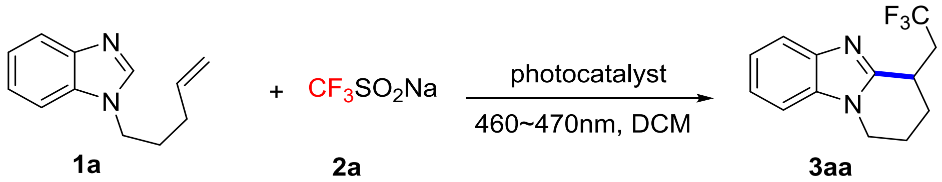
To a 25 mL borosilicate glass vial was added **1a** (1.0 mmol, 186.1 mg), **2a** (468 mg, 3.0 mmol), Eosin Y-Na_2 (5 mol%), and 10 mL of CH_3CN. The reaction mixture was sealed with a rubber stopper and then stirred rapidly under irradiation with a 25 W blue LED (approximately 2 cm away from the light source) without fan (62 °C) for 12 h. Work-up as described in 0.2-mmol scale synthesis gave product **3aa** in 80 % yield (203.2 mg).





3. Screening parameters

Table S1 Screening of Photocatalyst [a]



Entry	Photocatalyst	Isolated yield (%)
1	Eosin Y-H_2	32
2	Eosin Y-Na_2	57
3	$[Ir(dtbbpy)(ppy)_2]PF_6$	49
4	$[Ir(dFppy)_2(dtbbpy)]PF_6$	43
5	fac-$Ir(ppy)_3$	23
6	$Ru(BPY)_3{\cdot}6H_2O$	36
7	Rhodamine 6G	14
8	4CzIPN	Trace
9	Methylene blue	31
10	Riboflavin	24
11	Phenothiazine	27
12	Rhodamine B	12

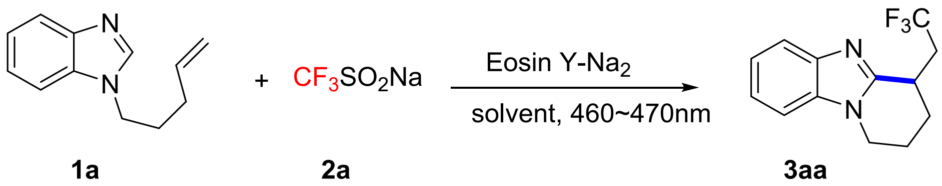
13[b]	Eosin Y-Na_2	52
14[c]	Eosin Y-Na_2	56

a) Reaction condition: **1a** (0.2 mmol), **2a** (0.6 mmol), photocatalyst (5 mol%), solvents (2 mL), rt, 4 h.

b) Photocatalyst (3 mol%).

c) Photocatalyst (10 mol%).

Table S2 Screening of Solvent [a]



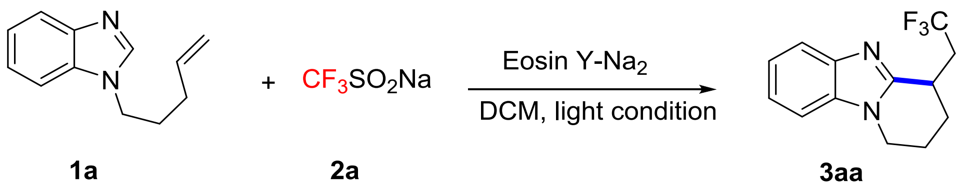
Entry	Solvents	Isolated yield (%)
1	DCM	57
2	DCE	50
3	CH_3CN	55
4	Dioxane	Trace
5	EtOH	15
6	EtOAc	21
7	DMF	Trace
8[b]	DCM	54
9[c]	DCM	48

a) Reaction condition: **1a** (0.2 mmol), **2a** (0.6 mmol), Eosin Y-Na_2 (5 mol%), solvent (2 mL), rt, 4 h.

b) 1 mL of DCM

c) 4 mL of DCM

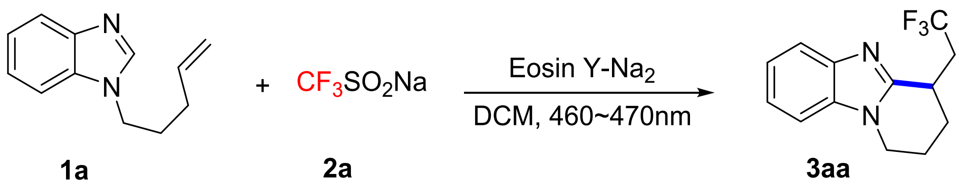
Table S3 Screening of light source [a]



Entry	Light source	Isolated yield (%)
1	Natural light	15
2	420 – 430 nm	33
3	440 – 450 nm	44
4	450 – 460 nm	51
5	460 – 470 nm	57
6	510 – 520 nm	23

a) Reaction condition: **1a** (0.2 mmol), **2a** (0.6 mmol), Eosin Y-Na_2(5 mol%), DCM (2 mL), rt, 4 h.

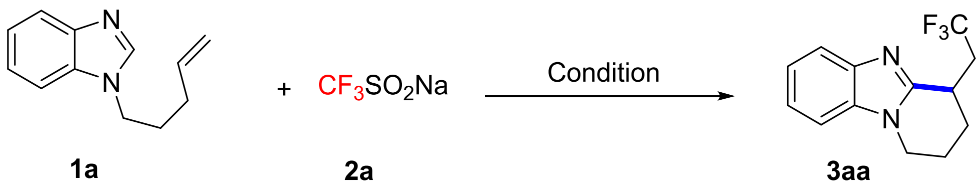
Table S4 Screening of reaction time [a]



Entry	Time (h)	Isolated yield (%)
1	4	57
2	5	58
3	6	67
4	7	67

a) Reaction condition: **1a** (0.2 mmol), **2a** (0.6 mmol), Eosin Y-Na_2 (5 mol%), DCM (2 mL), 460–470 nm, rt.

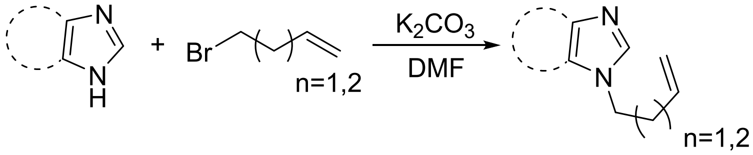
Table S5 Control experiments

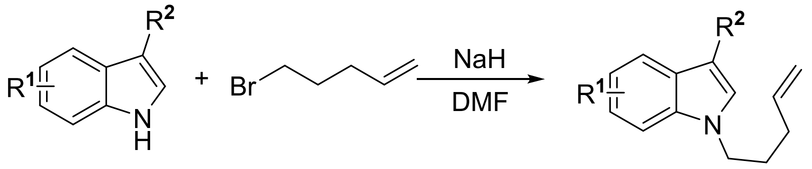


Entry	Condition Control	Isolated yield (%)
1	standard condition [a]	67
2	in dark	N.R.
3	w/o photocatalyst	N.R.
4	N_2	N.R.
5	no fan (ca. 62 °C)	88

a) Standard condition: **1a** (0.2 mmol), **2a** (0.6 mmol), Eosin Y-Na_2 (5 mol%), DCM (2 mL), 460–470 nm, rt, 6h.

4. Preparation of azaheterocycle-anchored alkenes





Synthesis of N-(but-3-en-1-yl)imidazoles and N-(pent-4-en-1-yl)imidazoles

Imidazole (5 mmol), 5-bromo-1-pentene or 4-bromo-butene (7.5 mmol), anhydrous potassium carbonate (7.5 mmol) and dry DMF solvent were successively added to a 50 mL round-bottom flask for 4-6 h of reaction at 40°C (TLC monitoring the reaction until completion). At the end of the reaction, ethyl acetate and deionized water were added to extract the mixture three times, and the organic phase was combined. Anhydrous sodium sulfate was used to dry the mixture, and the concentration was performed under reduced pressure. Silica gel column was loaded with solid samples, and the of eluent petroleum ether: ethyl acetate = 10:1 (V/V) was used to separate and purify the products **1a**~**1l**. If 5-bromopent-1-ene was replaced with 4-bromobut-1-ene (7.5 mmol), the products **1p**~**1v** were obtained. Precursor **4** was synthesized according to this method.

Synthesis of N-(pent-4-en-1-yl)indoles

The indole (3 mmol) and 20 mL dry DMF solvent were added into a 50 mL dry round-bottom flask and stirred in an ice bath at 0°C. Afterwards, NaH (2 equiv, 60%) was quickly weighed and added into the flask in batches, and the bottle was sealed with balloon for about 30 min of reaction. After no bubbles were generated, 5-bromo-1-pentene (4.5 mmol) was added to the flask, and the reaction was continued for 4 h at room temperature (TLC monitoring the reaction until completion). At the end of the reaction, ethyl acetate and deionized water were added to extract the mixture three times, and the organic phase was combined. Anhydrous sodium sulfate was used to dry the mixture, and the concentration was performed under reduced pressure. Silica gel column chromatography using petroleum ether as eluent delivered products **1m**,**1n** and **1o**. Precursor **1w** was synthesized according to this method.

5. Control experiments regarding TEMPO, BHT and 1,1-diphenylethylene

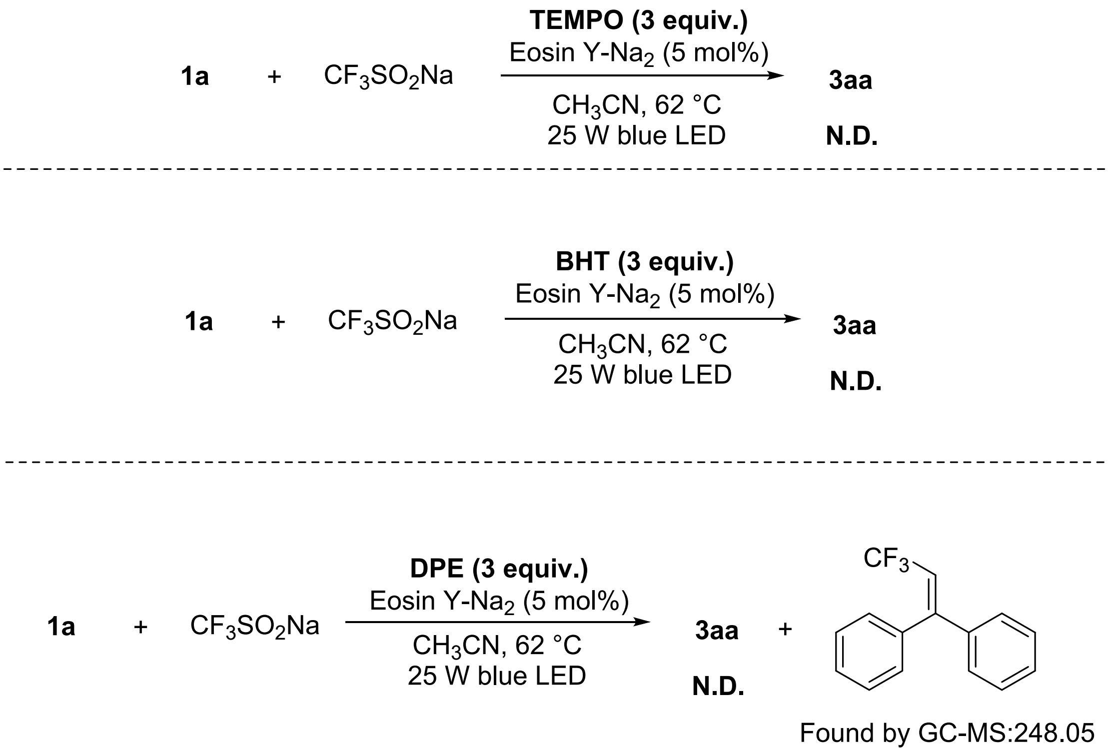


Figure S-1 Radical trapping experiment

Free radical capture reagent 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO, 3 equiv.) and free radical inhibitor 2,6-bis-(tert-butyl)-4-methylphenol (BHT, 3 equiv.) were added under standard reaction conditions for **3aa**, respectively. The reaction mixture was for TLC and GC-MS monitoring. No product **3aa** was observed.

Three equivalents of 1,1-stilbene (DPE) were added under standard reaction conditions for **3aa**. A small amount of the trifluoromethyl-DPE adduct was detected by GC-MS (Figure S-2). This suggest that the photoreaction may be a radical reaction.

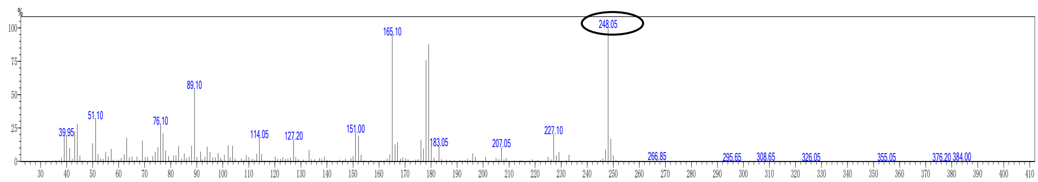


Figure S-2 The GC-MS spectra using 1,1-diphenylethylene as radical trapper

6. On/off blue light irradiation experiments

Eight standard reactions were run under 25 W blue LED irradiation at 62°C (no fan). After 1.5 hours, the blue LED was turned off and a reaction tube was removed from the light source for GC-MS analysis. The remaining 7 tubes were stirred for 1.5 hours with the blue LED light off. Another tube was then removed for analysis. The remaining 6 tubes continued to be irradiated under the blue LED for 1.5 hours. The above experimental operations were cycled, and the reaction yields were analyzed and detected in GC-MS, respectively. The results were drawn as Figure S-3.

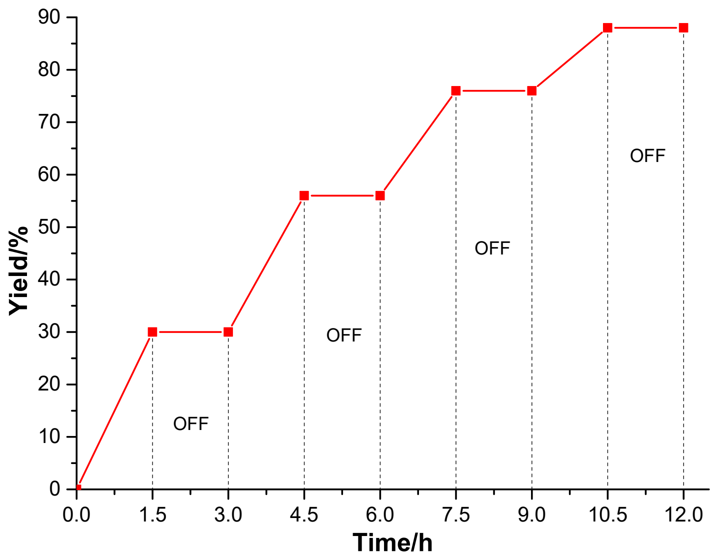


Figure S-3 ON-OFF experiments

7. Fluorescence quenching experiments

Fluorescence F7000 was used to record the fluorescence quenching curve of photosensitizer Eosin Y-Na_2 (CH_3CN, 0.3 μM) titrated with CF_3SO_2Na (CH_3CN, 5 μM), and the Stern-Volmer equation was calculated, as shown in Figure S-4.

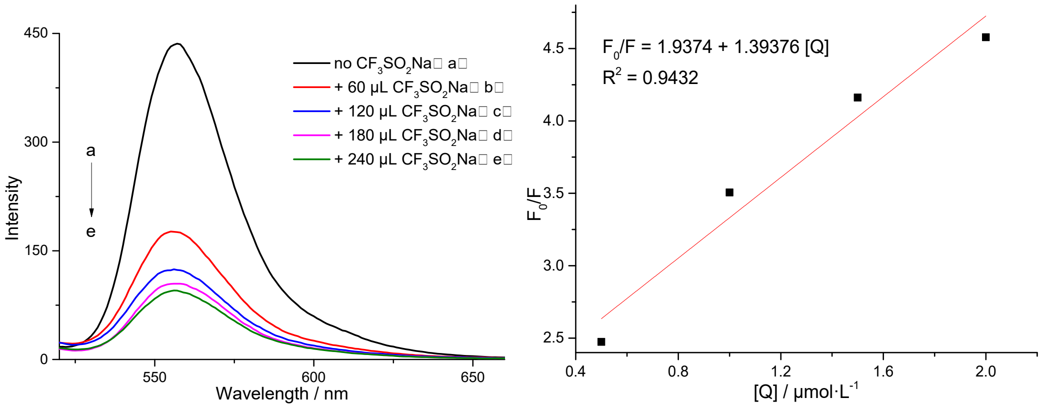
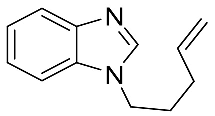


Figure S-4 Fluorescence quenching experiments (left) and Stern-Volmer equation (right)

8. Characterization data of all compounds

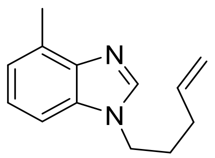
1-(Pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (1a)



735.7 mg, yield 79%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.87 – 7.81 (m, 1H), 7.44 – 7.38 (m, 1H), 7.36 – 7.28 (m, 2H), 5.88 – 5.74 (m, 1H), 5.13 – 5.04 (m, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.06 (m, 2H), 2.06 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.0, 136.7, 133.8, 122.8, 122.1, 120.4, 116.3, 109.6, 44.2, 30.6, 28.7. HRMS (ESI): Calcd. for $C_{12}H_{14}N_2Na$ ($[M+Na]^+$): 209.1049; Found 209.1057. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3064, 3021, 2983, 2973, 2923, 2854, 1701, 1635, 1540, 1532, 1483, 1472, 1301, 891, 743, 710.

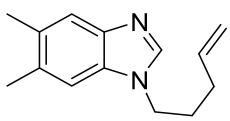
4-Methyl-1-(pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (1b)



556.5 mg, yield 67%, brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.25 – 7.17 (m, 2H), 7.13 – 7.05 (m, 1H), 5.86 – 5.71 (m, 1H), 5.12 – 4.99 (m, 2H), 4.16 (t, *J* = 6.9 Hz, 2H), 2.68 (s, 3H), 2.14 – 2.04 (m, 2H), 2.04 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.1, 136.7, 133.4, 130.3, 122.8, 122.4, 116.2, 107.2, 44.3, 30.6, 28.7, 16.7. HRMS (ESI): Calcd. for $C_{13}H_{16}N_2Na$ ($[M+Na]^+$): 223.1206; Found 223.1213. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3067, 3017, 2973, 2887, 2850, 1696, 1631, 1547, 1532, 1480, 1471, 1317, 893, 792, 713.

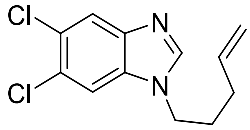
5,6-Dimethyl-1-(pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (1c)



674.0 mg, yield 74%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.56 (s, 1H), 7.15 (s, 1H), 5.86 – 5.71 (m, 1H), 5.07 (d, *J* = 5.8 Hz, 1H), 5.04 (s, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 2.12 – 2.04 (m, 2H), 2.02 – 1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 142.2, 136.8, 132.3, 131.9, 130.9, 120.4, 116.1, 109.8, 44.2, 30.6, 28.7, 20.6, 20.2. HRMS (ESI): Calcd. for $C_{14}H_{18}N_2Na$ ($[M+Na]^+$): 237.1362; Found 237.1372. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3063, 3017, 2970, 2884, 2855, 1692, 1632, 1544, 1530, 1487, 1463, 1308, 883, 719.

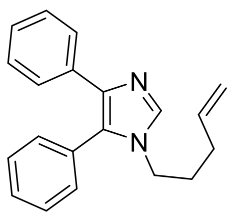
5,6-Dichloro-1-(pent-4-en-1-yl)-1*H*-benzo[*d*]imidazole (1d)



762.4 mg, yield 72%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.48 (s, 1H), 5.84 – 5.71 (m, 1H), 5.09 (s, 1H), 5.06 (d, J = 7.0 Hz, 1H), 4.13 (t, J = 7.0 Hz, 2H), 2.13 – 2.05 (m, 2H), 2.02 –1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.2, 136.3, 133.0, 127.0, 126.3, 121.6, 116.6, 111.1, 44.5, 30.5, 28.5. HRMS (ESI): Calcd. for $C_{12}H_{12}Cl_2N_2Na$ ($[M+Na]^+$): 277.0270; Found 277.0287. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 3010, 2983, 2852, 1692, 1632, 1544, 1530, 1487, 1463, 1308, 897, 717, 670.

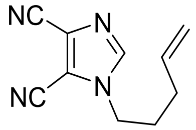
1-(Pent-4-en-1-yl)-4,5-diphenyl-1*H*-imidazole (1e)



614.3 mg, yield 71%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, J = 7.6 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.22 – 7.15 (m, 2H), 7.15 – 7.05 (m, 1H), 5.67 – 5.54 (m, 1H), 4.98 – 4.87 (m, 2H), 3.77 (t, J = 7.3 Hz, 2H), 1.99 – 1.87 (m, 2H), 1.69 – 1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.7 (2C), 134.7, 130.9, 130.8 (2C), 129.1 (2C), 128.7, 128.4, 128.1 (2C), 126.5 (2C), 126.2, 115.8, 44.5, 30.3, 29.7. HRMS (ESI): Calcd. for $C_{20}H_{20}N_2Na$ ($[M+Na]^+$): 289.1699; Found 289.1713. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3036, 3017, 2981, 2858, 1697, 1637, 1540, 1530, 1477, 1461, 1302, 899, 752, 717.

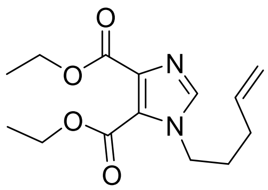
1-(Pent-4-en-1-yl)-1*H*-imidazole-4,5-dicarbonitrile (1f)



413.4 mg, yield 74%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 5.84 – 5.70 (m, 1H), 5.15 – 5.06 (m, 2H), 4.17 (t, *J* = 7.2 Hz, 2H), 2.20 – 2.09 (m, 2H), 2.08 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 135.3, 123.1, 117.3, 112.1, 111.5, 107.9, 47.3, 30.1, 29.1. HRMS (ESI): Calcd. for $C_{10}H_{10}N_4Na$ ($[M+Na]^+$): 209.0798; Found 209.0807. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3036, 3017, 2981, 2237, 1697, 1637, 1477, 1461, 1302, 891, 717.

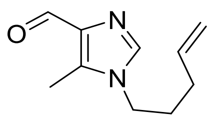
Diethyl 1-(pent-4-en-1-yl)-1*H*-imidazole-4,5-dicarboxylate (1g)



487.8 mg, yield 58%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 5.83 – 5.70 (m, 1H), 5.12 – 5.00 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 4H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.03 (m, 2H), 1.94 – 1.83 (m, 2H), 1.43 – 1.39 (m, 3H), 1.39 – 1.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 160.1, 139.4, 137.5, 136.5, 124.6, 116.2, 61.7, 61.3, 46.4, 30.3, 29.9, 14.2, 14.0. HRMS (ESI): Calcd. for $C_{14}H_{20}N_2O_4Na$ ($[M+Na]^+$): 303.1315; Found 303.1327. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3042, 3021, 2961, 2230, 1722, 1687, 1623, 1477, 1460, 1382, 1297, 1277, 1110, 894, 710.

5-Methyl-1-(pent-4-en-1-yl)-1*H*-imidazole-4-carbaldehyde (1h)

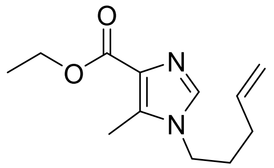


326.2 mg, yield 61%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.53 (s, 1H), 5.85 – 5.72 (m, 1H), 5.10 – 5.00 (m, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.07 (q, *J* = 6.9 Hz, 2H), 1.91 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 153.6, 142.0, 136.9, 126.3, 115.9, 46.5, 30.3, 29.6, 13.3. HRMS (ESI): Calcd. for $C_{10}H_{14}N_2ONa$ ($[M+Na]^+$): 201.0998;

Found 201.1010. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3040, 3018, 2960, 2823, 2727, 2233, 1721, 1687, 1620, 1477, 1462, 1382, 1297, 897, 715.

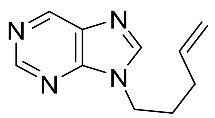
Ethyl 5-methyl-1-(pent-4-en-1-yl)-1*H*-imidazole-4-carboxylate (1i)



420.1 mg, yield 63%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 5.85 – 5.72 (m, 1H), 5.10 – 4.98 (m, 2H), 4.33 (q, J = 7.1 Hz, 2H), 4.24 (t, J = 7.1 Hz, 2H), 2.48 (s, 3H), 2.06 (q, J = 7.0 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 148.6, 140.2, 137.0, 118.3, 115.7, 60.2, 46.8, 30.4, 30.0, 16.0, 14.3. HRMS (ESI): Calcd. for $C_{12}H_{18}N_2O_2Na$ ([M+Na]$^+$): 245.1260; Found 245.1276. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3040, 3023, 2960, 2225, 1723, 1680, 1620, 1480, 1453, 1385, 1305, 1270, 1115, 895, 712.

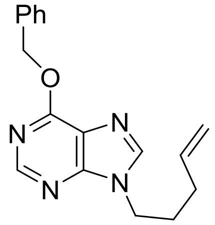
9-(Pent-4-en-1-yl)-9*H*-purine (1j)



265.4 mg, yield 47%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 9.00 (s, 1H), 8.10 (s, 1H), 5.87 – 5.72 (m, 1H), 5.12 – 5.00 (m, 2H), 4.32 (t, J = 6.9 Hz, 2H), 2.18 – 2.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 151.4, 148.6, 145.2, 136.4, 134.1, 116.3, 43.2, 30.5, 28.7. HRMS (ESI): Calcd. for $C_{10}H_{12}N_4H$ ([M+H]$^+$): 189.1135; Found 189.1143. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 3017, 2973, 1697, 1637, 1477, 1461, 1302, 892, 717.

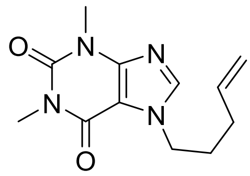
6-(Benzyloxy)-9-(pent-4-en-1-yl)-9*H*-purine (1k)



370.9 mg, yield 42%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.90 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.29 (m, 3H), 5.85 – 5.72 (m, 1H), 5.68 (s, 2H), 5.10 – 4.98 (m, 2H), 4.24 (t, *J* = 7.0 Hz, 2H), 2.15 – 2.06 (m, 2H), 2.06 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 152.3, 151.9, 142.1, 136.5, 136.2, 128.4 (2C), 128.3 (2C),128.1, 121.6, 116.2, 68.3, 43.4, 30.5, 28.9. HRMS (ESI): Calcd. for $C_{17}H_{18}N_4ONa$ ($[M+Na]^+$): 317.1373; Found 317.1390. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3027, 3012, 2970, 1697, 1637, 1477, 1462, 1307, 1273, 892, 715.

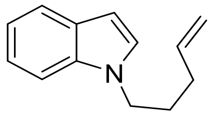
1,3-Dimethyl-7-(pent-4-en-1-yl)-3,7-dihydro-1*H*-purine-2,6-dione (1l)



610.8 mg, yield 82%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 5.86 – 5.71 (m, 1H), 5.12 – 5.00 (m, 2H), 4.29 (t, *J* = 7.0 Hz, 2H), 3.59 (s, 3H), 3.42 (s, 3H), 2.16 – 2.05 (m, 2H), 2.06 – 1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.7, 149.0, 140.9, 136.6, 116.1, 106.9, 46.5, 30.2, 29.8, 29.7, 28.0. HRMS (ESI): Calcd. for $C_{12}H_{16}N_4O_2Na$ ($[M+Na]^+$): 271.1165; Found 271.1178. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3054, 2989, 2883, 2360, 1710, 1675, 1655, 1379, 1324, 890, 743.

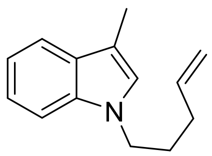
1-(Pent-4-en-1-yl)-1*H*-indole (1m)



416.8 mg, yield 75%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2, 1H), 7.22 – 7.16 (m, 1H), 7.12 – 7.03 (m, 2H), 6.50 – 6.44 (m, 1H), 5.85 – 5.71 (m, 1H), 5.07 – 4.96 (m, 2H), 4.08 (t, *J* = 7.0 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.95 – 1.85 (m, 2H). HRMS (ESI): Calcd. for $C_{13}H_{16}N$ ($[M+H]^+$): 186.1278; Found 186.1293. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3060, 3017, 2981, 2971, 2920, 2850, 1634, 1541, 1531, 1480, 1471, 1301, 890, 740, 712.

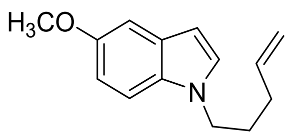
3-Methyl-1-(pent-4-en-1-yl)-1*H*-indole (1n)



430.5 mg, yield 72%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H, overlap with CDCl3), 7.24 – 7.14 (m, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 5.86 – 5.72 (m, 1H), 5.09 – 4.95 (m, 2H), 4.05 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.12 – 2.00 (m, 2H), 1.96 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.3, 128.7, 125.4, 121.3, 119.0, 118.5, 115.5, 110.2, 109.2, 45.3, 30.9, 29.4, 9.6. HRMS (ESI): Calcd. for $C_{14}H_{17}NNa$ ($[M+Na]^+$): 222.1254; Found 222.1264. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3037, 3012, 2977, 2971, 2920, 2862, 1630, 1543, 1530, 1482, 1470, 1297, 897, 743, 722.

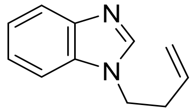
5-Methoxy-1-(pent-4-en-1-yl)-1*H*-indole (1o)



438.9 mg, yield 68%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$)δ7.32 – 7.25 (m, 1H, overlap with CDCl3), 7.19 – 7.09 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.46 (d, *J* = 2.6 Hz, 1H), 5.92 – 5.79 (m, 1H), 5.16 – 5.04 (m, 2H), 4.14 (t, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 2.17–2.05 (m, 2H), 2.03–1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$)δ 153.9, 137.4, 131.3, 128.9, 128.3, 115.7, 111.8, 110.1, 102.6, 100.5, 55.9, 45.8, 30.9, 29.3. HRMS (ESI): Calcd. for $C_{14}H_{17}NONa$ ($[M+Na]^+$): 238.1203; Found 238.1207. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3060, 3017, 2981, 2971, 2920, 2850, 1634, 1541, 1531, 1480, 1471, 1301, 1234, 1042, 890,850, 740, 712.

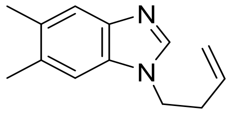
1-(But-3-en-1-yl)-1*H*-benzo[*d*]imidazole (1p)



382.3 mg, yield 74%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.85 - 7.78 (m, 1H), 7.41 (d, *J* = 7.1 Hz, 1H), 7.34 - 7.27 (m, 2H), 5.84 - 5.70 (m, 1H), 5.14 - 5.00 (m, 2H), 4.23 (t, *J* = 7.0 Hz, 2H), 2.62 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.9, 133.7, 133.5, 122.8, 122.1, 120.4, 118.4, 109.6, 44.6, 34.0. HRMS (ESI): Calcd. for $C_{11}H_{12}N_2Na$ ([M+Na]$^+$): 195.0893; Found 195.0904. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3062, 3021, 2980, 2969, 2922, 2855, 1707, 1634, 1546, 1533, 1480, 1470, 1301, 897, 746, 712.

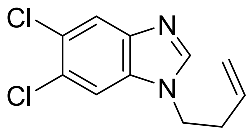
1-(But-3-en-1-yl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1q)



372.8 mg, yield 73%, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.58 (s, 1H), 7.18 (s, 1H), 5.84 – 5.70 (m, 1H), 5.13 – 5.03 (m, 2H), 4.19 (t, *J* = 7.1 Hz, 2H), 2.62 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 142.2, 133.7, 132.2, 131.9, 130. 9, 120.4, 118.2, 109.8, 44.5, 34.0, 20.6, 20.2. HRMS (ESI): Calcd. for $C_{13}H_{16}N_2Na$ ([M+Na]$^+$): 223.1206; Found 223.1218. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3064, 3012, 2977, 2885, 2855, 1695, 1631, 1545, 1537, 1485, 1460, 1302, 880, 719.

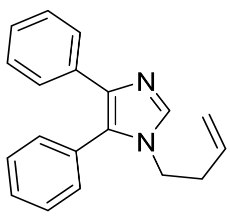
1-(But-3-en-1-yl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (1r)



467.3 mg, yield 76%, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.51 (s, 1H), 5.81 – 5.67 (m, 1H), 5.14 – 5.00 (m, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 2.61 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (2C), 143.2, 133.0, 127.1, 126.4, 121.6, 119.0, 111.1, 44.8, 33.9. HRMS (ESI): Calcd. for $C_{11}H_{10}Cl_2N_2Na$ ([M+Na]$^+$): 263.0113; Found 263.0127. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 3007, 2927, 2855, 1690, 1630, 1550, 1541, 1477, 1460, 1303, 895, 717, 676.

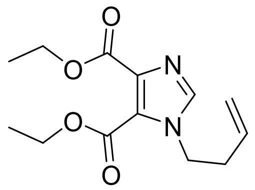
1-(But-3-en-1-yl)-4,5-diphenyl-1*H*-imidazole (1s)



543.2 mg, yield 66%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.49 – 7.43 (m, 5H), 7.51 – 7.42 (m, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 5.70 – 5.55 (m, 1H), 5.07 – 4.93 (m, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 2.30 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.7 (2C), 134.6, 133.5, 130.9 (2C), 129.1 (2C), 128.7, 128.3, 128.1 (2C), 126.5 (2C), 126.3, 118.1, 44.7, 35.0. HRMS (ESI): Calcd. for $C_{19}H_{18}N_2Na$ ($[M+Na]^+$): 297.1362; Found 297.1381. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3030, 3015, 2982, 2850, 1695, 1640, 1540, 1520, 1472, 1460, 1302, 900, 750, 710.

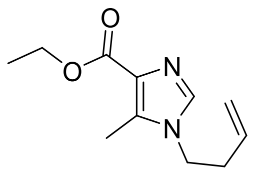
Diethyl 1-(but-3-en-1-yl)-1*H*-imidazole-4,5-dicarboxylate (1t)



519.3 mg, yield 65%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 5.70 – 5.53 (m, 1H), 5.04 – 4.88 (m, 2H), 4.35 – 4.23 (m, 4H), 4.19 (t, *J* = 7.0 Hz, 2H), 2.42 (q, *J* = 6.9 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.0, 139.4, 137.3, 132.8, 124.4, 118.6, 61.5, 61.1, 46.4, 35.0, 14.1, 13.9. HRMS (ESI): Calcd. for $C_{13}H_{18}N_2O_4Na$ ($[M+Na]^+$): 289.1159; Found 289.1178. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3041 3020, 2959, 2233, 1720, 1680, 1620, 1470, 1466, 1380, 1292, 1277, 1111, 890, 715.

Ethyl 1-(but-3-en-1-yl)-5-methyl-1*H*-imidazole-4-carboxylate (1u)

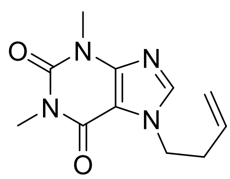


449.8 mg, yield 72%, yellow oil

^{1}H NMR (400 MHz, CDCl3) δ 7.33 (s, 1H), 5.69 – 5.52 (m, 1H), 5.00 – 4.84 (m, 2H), 4.31 – 4.08 (m, 4H), 2.44 – 2.30 (m, 5H), 1.35 – 1.20 (m, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 160.9, 148.4, 140.2, 133.6, 118.1, 117.8, 60.1, 46.8, 35.2, 15.9, 14.2. HRMS (ESI): Calcd. for $C_{11}H_{16}N_2O_2Na$ ($[M+Na]^+$): 231.1104; Found 231.1118. FTIR ($CHCl_3$)

ν_{max}/cm^{-1} 3044, 3020, 2963, 2222, 1720, 1683, 1626, 1488, 1450, 1380, 1306, 1271, 1117, 896, 716.

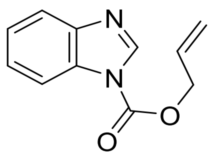
7-(But-3-en-1-yl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (1v)



548.2 mg, yield 78%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 5.85 – 5.64 (m, 1H), 5.16 – 4.97 (m, 2H), 4.36 (t, *J* = 5.8 Hz, 2H), 3.59 (s, 3H), 3.42 (s, 3H), 2.71 – 2.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.7, 148.9, 141.0, 133.1, 118.7, 106.8, 46.6, 35.0, 29.8, 28.0. HRMS (ESI): Calcd. for $C_{11}H_{14}N_4O_2Na$ ([M+Na]$^+$): 257.1009; Found 257.1024. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3050, 2999, 2873, 2357, 1721, 1669, 1651, 1380, 1330, 889, 730.

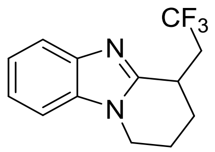
Allyl 1*H*-benzo[*d*]imidazole-1-carboxylate(1w)



388.2 mg, yield 64%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.06–8.00 (m, 1H), 7.83–7.77 (m, 1H), 7.44–7.34 (m, 2H), 6.15–6.02 (m, 1H), 5.55–5.47 (m, 1H), 5.44–5.39 (m, 1H), 4.98 (dt, *J* = 6.0, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$)δ149.2, 144.0, 141.6, 131.3, 130.6, 125.5, 124.6, 120.7, 120.5, 114.4, 68.4. HRMS (ESI): Calcd. for $C_{11}H_{10}N_2O_2Na$ ([M+Na]$^+$): 225.0635; Found 225.0649. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3052, 3025, 2980, 2970, 2922, 2854, 1744, 1692, 1652, 1630, 1540, 1527, 1480, 1471, 1298,1162, 891, 740, 712.

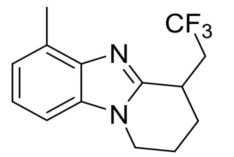
4-(2,2,2-Trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine(3aa)



44.8 mg, yield 88%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 1H), 7.34 – 7.24 (m, 3H), 4.28 – 4.19 (m, 1H), 3.98 (td, J = 11.5, 5.0 Hz, 1H), 3.57 – 3.35 (m, 2H), 2.55 – 2.41 (m, 1H), 2.41 – 2.24 (m, 2H), 2.2 – 2.1 (m, 1H), 1.74 (td, J = 13.1, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 142.4, 134.8, 126.8 (q, $^{1}J_{C\text{-}F(CF3)}$ = 275 Hz), 122.5, 122.4, 119.1, 109.1, 42.4, 37.2 (q, $^{2}J_{C\text{-}F(CF3)}$ = 28.1 Hz), 31.5 (q,$^{3}J_{C\text{-}F\ (CF3)}$ = 2.8 Hz), 26.7, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{13}H_{13}F_3N_2Na$ ($[M+Na]^+$): 277.0923; Found 277.0928. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3020, 2998, 2923, 2850, 1701,, 1540, 1532, 1483, 1472, 1301, 891, 743, 710.

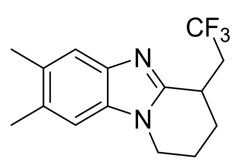
6-Methyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (3ba)



46.1 mg, yield 86%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.10 (m, 2H), 7.09–7.02 (m, 1H), 4.23 –4.14 (m, 1H), 3.94 (td, J = 11.4, 5.1 Hz, 1H), 3.61–3.38 (m, 2H), 2.65 (s, 3H), 2.50–2.39 (m, 1H), 2.38–2.22 (m, 2H), 2.13–2.00 (m, 1H), 1.73 (td, J = 13.1, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)δ 151.3, 141.9, 134.5, 129.3, 126.9(q, $^{1}J_{C\text{-}F(CF3)}$ = 276 Hz), 122.8, 122.2, 106.5, 42.5, 37.3 (q, $^{2}J_{C\text{-}F(CF3)}$ = 27.9 Hz), 31.5 (q, $^{3}J_{C\text{-}F(CF3)}$ = 2.7 Hz), 26.6, 21.5, 16.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. HRMS (ESI): Calcd. for $C_{14}H_{15}F_3N_2Na$ ($[M+Na]^+$): 291.1080; Found 291.1087. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3018, 2892, 2862, 1670, 1555, 1534, 1484, 1463, 1310, 890, 792, 707.

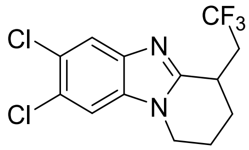
7,8-Dimethyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine(3ca)



40.0 mg, yield 71%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.05 (s, 1H), 4.21 – 4.11 (m, 1H), 3.90 (td, J = 11.5, 5.0 Hz, 1H), 3.53 – 3.31 (m, 2H), 2.47 – 2.40 (m, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 2.34 – 2.21 (m, 2H), 2.12 – 1.97 (m, 1H), 1.69 (td, J = 13.2, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 141.1, 133.4, 131.3, 131.1, 126.9(q, $^{1}J_{C\text{-}F(CF3)}$ = 276 Hz), 119.3, 109.3, 42.3, 37.2 (q, $^{2}J_{C\text{-}F(CF3)}$ = 27.9 Hz), 31.4 (q, $^{3}J_{C\text{-}F(CF3)}$ = 2.8 Hz), 26.7, 21.7, 20.5, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{15}H_{17}F_3N_2Na$ ([M+Na]$^+$): 305.1236; Found 305.1242. FTIRν_{max}($CHCl_3$)/cm^{-1} 3010, 2884, 2852, 1694, 1540, 1560, 1469, 1463, 1317, 875, 709.

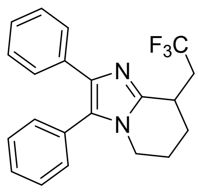
7,8-Dichloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (3da)



54.2 mg, yield 84%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.31 (s, 1H), 4.16–4.08 (m, 1H), 3.91 (td, J = 11.6, 5.1 Hz, 1H), 3.49–3.31 (m, 2H), 2.51–2.40 (m, 1H), 2.39–2.25 (m, 2H), 2.16–2.01 (m, 1H), 1.73 (td, J = 13.2, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.8, 134.1, 126.6 (q, $^{1}J_{C\text{-}F(CF3)}$ = 275 Hz), 126.2, 126.1, 120.3, 110.4, 42.6, 36.9 (q, $^{2}J_{C\text{-}F(CF3)}$ = 28.3 Hz), 31.5 (q, $^{3}J_{C\text{-}F(CF3)}$ = 2.8 Hz), 26.4, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS (ESI): Calcd. for $C_{13}H_{11}Cl_2F_3N_2Na$ ([M+Na]$^+$): 345.0144; Found 345.0148. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3010, 2884, 2852, 1694, 1540, 1560, 1469, 1464, 1317, 875, 709.

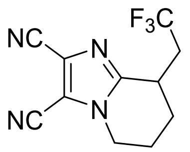
2,3-Diphenyl-8-(2,2,2-trifluoroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (3ea)



45.6 mg, yield 64%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 5H), 7.35–7.31 (m, 2H), 7.22–7.17 (m, 2H), 7.15–7.10 (m, 1H), 3.77–3.72 (m, 1H), 3.70–3.62 (m, 1H), 3.56–3.42 (m, 1H), 3.39–3.31 (m, 1H), 2.44–2.28 (m, 2H), 2.13–2.00 (m, 1H), 1.98–1.87 (m, 1H), 1.73–1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 136.9, 134.5, 130.8, 130.6 (2C), 128.9 (2C), 128.4, 128.1 (2C), 127.9, 127.0 (q, $^{1}J_{C\text{-}F(CF3)}$ = 276 Hz), 126.8 (2C), 126.3, 43.8, 37.6 (q, $^{2}J_{C\text{-}F(CF3)}$ = 27.5 Hz), 30.9 (q, $^{3}J_{C\text{-}F(CF3)}$ = 2.7 Hz), 26.7, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3. HRMS (ESI): Calcd. for $C_{21}H_{20}F_3N_2$ ($[M+H]^+$): 357.1573; Found 357.1586. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3035, 3014, 2987, 2850, 1692, 1541, 1532, 1477, 1459, 1297, 892, 750, 710.

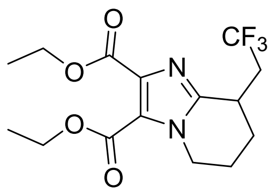
8-(2,2,2-Trifluoroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2,3-dicarbonitrile (3fa)



40.6 mg, yield 80%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (ddd, J = 12.9, 5.6, 2.6 Hz, 1H), 4.03 (td, J = 11.9, 5.0 Hz, 1H), 3.30-3.13 (m, 2H), 2.52 – 2.39 (m, 1H), 2.35 – 2.23 (m, 2H), 2.07 (dtdd, J = 14.3, 11.4, 5.7, 2.7 Hz, 1H), 1.71 (td, J = 13.4, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 127.6, 126.2 (q, $^{1}J_{C\text{-}F(CF3)}$=277.2 Hz), 122.0, 111.7, 111.6, 45.3, 36.6 (q, J$^{2}J_{C\text{-}F(CF3)}$ = 29.0 Hz), 31.2 (q, J = 2.9 Hz), 25.7, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS (ESI): Calcd. for $C_{11}H_9F_3N_4Na$ ($[M+Na]^+$): 277.0672; Found 277.0691. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 3017, 2992, 2232, 1690, 1635, 1475, 1460, 1307, 890, 712.

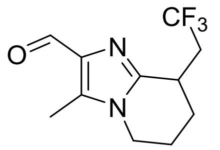
Diethyl 8-(2,2,2-trifluoroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2,3-dicarboxylate (3ga)



44.6 mg, yield 64%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 – 4.32 (m, 5H), 4.08 – 3.97 (m, 1H), 3.45 – 3.31 (m, 1H), 3.31 – 3.18 (m, 1H), 2.42 – 2.30 (m, 1H), 2.29 – 2.12 (m, 2H), 2.01 – 1.88 (m, 1H), 1.65 (td, *J* = 13.0, 2.5 Hz, 1H), 1.37 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.9, 148.3, 136.7, 126.5(q, $^{1}J_{C\text{-}F(CF3)}$ = 276 Hz), 123.9, 61.42 , 61.40, 45.4, 37.1 (q, ${}^{2}J_{C-F(CF3)}$ = 28.1 Hz), 31.0 (q, ${}^{3}J_{C-F(CF3)}$ = 2.9 Hz), 25.7, 21.6, 14.2, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{15}H_{19}F_3N_2O_4Na$ ([M+Na]$^+$): 371.1189; Found 371.1199. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3031, 3017, 2952, 2237, 1728, 1688, 1624, 1470, 1460, 1373, 1291, 1275, 1117, 898, 714.

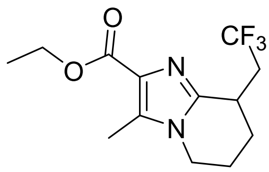
3-Methyl-8-(2,2,2-trifluoroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2-carbaldehyde (3ha)



36.9 mg, yield 75%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 4.58 – 4.47 (m, 1H), 4.13 – 4.01 (m, 1H), 3.34 – 3.16 (m, 2H), 2.46 (s, 3H), 2.38 – 2.27 (m, 1H), 2.28 – 2.09 (m, 2H), 2.00 – 1.86 (m, 1H), 1.65 (td, *J* = 12.6, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 152.2, 150.7, 127.0, 126.6(q, ${}^{1}J_{C-F(CF3)}$ = 275 Hz), 45.2, 37.0 (q, ${}^{2}J_{C-F(CF3)}$ = 28.2 Hz), 30.8 (q, ${}^{3}J_{C-F(CF3)}$ = 2.8 Hz), 25.6, 21.5, 13.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63. 6. HRMS (ESI): Calcd. for $C_{11}H_{14}F_3N_2$ ([M+H]$^+$): 247.1053; Found 247.1052. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3038, 3012, 2960, 2820, 2717, 2234, 1723, 1680, 1623, 1470, 1461, 1380, 1295, 899, 720.

Ethyl 3-methyl -8- (2,2,2-trifluoroethyl) -5,6,7,8- tetrahydroimidazo [1,2-*a*] pyridine-2-carboxylate (3ia)

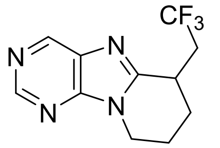


44.7 mg, yield 77%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 – 4.42 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.08 – 3.96 (m, 1H), 3.36 – 3.15 (m, 2H), 2.46 (s, 3H), 2.37 – 2.26 (m, 1H), 2.25 – 2.08 (m, 2H), 1.98 – 1.83 (m, *J* = 8.6, 5.5, 2.4 Hz, 1H), 1.68 – 1.55 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 148.4, 147.0, 126.7 (q, ${}^{1}J_{C-F(CF3)}$ = 276 Hz), 118.7, 60.0, 45.5, 37.2 (q, ${}^{2}J_{C-F(CF3)}$ = 27.9 Hz), 31.0 (q, ${}^{3}J_{C-F(CF3)}$ = 2.8 Hz), 25.8, 21.8, 15.6, 14.3. ^{19}F NMR (376 MHz, CDCl3) δ -63.5. HRMS (ESI): Calcd. for

$C_{13}H_{18}F_3N_2O_2$ ([M+H]$^+$): 291.1315; Found 291.1322. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3049, 3021, 2964, 2227, 1722, 1683, 1622, 1480, 1455, 1380, 1301, 1273, 1112, 895, 731.

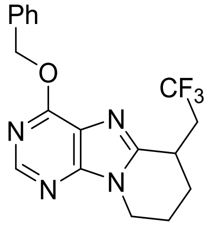
6-(2,2,2-Trifluoroethyl)-6,7,8,9-tetrahydropyrido[1,2-*e*]purine (3ja)



33.3 mg, yield 65%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.89 (s, 1H), 4.50 – 4.39 (m, 1H), 3.98 (td, J = 12.1, 5.0 Hz, 1H), 3.43–3.30 (m, 2H), 2.47–2.40 (m, 1H), 2.38 – 2.25 (m, 2H), 2.08–1.97 (m, 1H), 1.77–1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 152.2, 152.1, 147.0, 133.4, 126.5 (q, $^1J_{C\text{-}F(CF3)}$ = 275.4 Hz), 41.7, 36.7 (q, $^2J_{C\text{-}F(CF3)}$ = 28.6 Hz), 31.93 (q, $^3J_{C\text{-}F(CF3)}$ = 2.7 Hz), 26.5, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS (ESI): Calcd. for $C_{11}H_{12}F_3N_4$ ([M+H]$^+$): 257.1009; Found 257.1026. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3031, 3015, 2970, 1712, 1634, 1470, 1462, 1300, 895, 711.

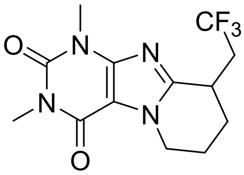
4-(Benzyloxy)-6-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydropyrido[1,2-*e*]purine (3ka)



44.9 mg, yield 62%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.56 – 7.51 (m, 2H), 7.38 – 7.29 (m, 3H), 5.69 (q, J = 12.2 Hz, 2H), 4.46 – 4.37 (m, 1H), 4.03 – 3.93 (m, 1H), 3.59 – 3.44 (m, 1H), 3.44 – 3.33 (m, 1H), 2.54 – 2.44 (m, 1H), 2.37 – 2.26 (m, 2H), 2.10 – 1.98 (m, 1H), 1.74 (td, J = 13.3, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 152.9, 152.0, 151.3, 136.3, 128.5, 128.4, 128.1, 126.6 (q, $^1J_{C\text{-}F(CF3)}$ = 275 Hz), 120.7, 68.4, 42.0, 36.9 (q, $^2J_{C\text{-}F(CF3)}$ = 28.4 Hz), 31.7 (q, $^3J_{C\text{-}F(CF3)}$ = 2.9 Hz), 26.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{18}H_{17}F_3N_4ONa$ ([M+Na]$^+$): 385.1247; Found 385.1264. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3042, 3013, 2972, 1690, 1630, 1474, 1466, 1306, 1274, 891, 710.

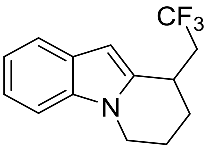
1,3-Dimethyl-9-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydropyrido[2,1-*f*]purine-2,4(1*H*,3*H*)-dione (3la)



51.9 mg, yield 82%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 – 4.53 (m, 1H), 4.15 – 4.08 (m, 1H), 3.53 (s, 3H), 3.36 (s, 3H), 3.30 – 3.18 (m, 2H), 2.40 – 2.34 (m, 1H), 2.31 – 2.18 (m, 2H), 2.05 – 1.95 (m, 1H), 1.69 (td, *J* = 12.6, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.7, 150.6, 148.1, 126.5 (q, $^1J_{C\text{-}F(CF3)}$ = 277.3 Hz), 107.1, 44.7, 36.9 (q, $^2J_{C\text{-}F(CF3)}$ = 28.5 Hz), 31.0 (q, $^3J_{C\text{-}F(CF3)}$ = 2.6 Hz), 29.7, 27.8, 25.9, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{13}H_{15}F_3N_4O_2Na$ ([M+Na]$^+$): 277.0923; Found 277.0928. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3057, 2980, 2880, 2363, 1710, 1675, 1655, 1377, 1325, 893, 741.

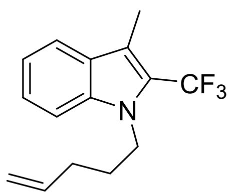
9-(2,2,2-Trifluoroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (3ma)



23.8 mg, yield 47%, green oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.29 (s, 1H), 4.25 – 4.16 (m, 1H), 3.89 (td, *J* = 11.2, 5.0 Hz, 1H), 3.43 – 3.31 (m, 1H), 2.92 – 2.75 (m, 1H), 2.41 – 2.17 (m, 3H), 2.10 – 1.97 (m, 1H), 1.62 (td, *J* = 12.7, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 136.4, 127.8, 126.7(q, $^1J_{C\text{-}F(CF3)}$ = 276 Hz), 121.0, 120.01, 119.98, 108.8, 97.5, 42.1, 39.1 (q, $^2J_{C\text{-}F(CF3)}$ = 27.5 Hz), 29.91 (q, $^3J_{C\text{-}F(CF3)}$ = 2.7 Hz), 27.2, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{14}H_{15}F_3N$ ([M+H]$^+$): 254.1152; Found 254.1151. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3023, 2981, 2923, 2854, 1541, 1531, 1483, 1472, 1290, 893, 741, 717.

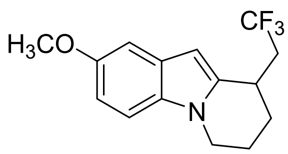
3-Methyl-1-(pent-4-en-1-yl)-2-(trifluoromethyl)-1*H*-indole (3na)



14.4 mg, yield 27%, grass green oil

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.19 – 7.13 (m, 1H), 5.90 – 5.74 (m, 1H), 5.12 – 5.00 (m, 2H), 4.24 – 4.11 (m, 2H), 2.45 (q, *J* = 2.6 Hz, 3H), 2.19 – 2.08 (m, 2H), 1.95 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.2, 137.0, 127.2, 124.5, 122.8(q, $^1J_{C-F(CF3)}$ = 268 Hz), 122.2 (q, $^2J_{C-F(CF3)}$ = 34.8 Hz), 120.3, 119.8, 115.6, 114.40 (q, $^3J_{C-F(CF3)}$ = 2.8 Hz), 109.9, 44.4 (q, $^4J_{C-F(CF3)}$ = 2.1 Hz), 31.0, 29.0, 8.9 (q, $^4J_{C-F(CF3)}$ = 2.3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -55.4. HRMS (ESI): Calcd. for $C_{15}H_{17}F_3N$ ([M+H]$^+$): 268.1308; Found 268.1307. FTIR (CHCl$_3$) ν_{max}/cm^{-1} 3032, 3017, 2970, 2973, 2923, 2862, 1627, 1553, 1537, 1477, 1472, 1288, 1136, 877, 763, 721.

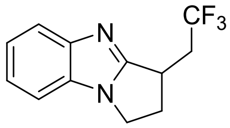
2-Methoxy-9-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (3oa)



27.8 mg, yield 49%, yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.21 (s, 1H), 4.19 – 4.08 (m, 1H), 3.94 – 3.79 (m, 4H), 3.40 – 3.28 (m, 1H), 2.90 – 2.73 (m, 1H), 2.42 – 2.14 (m, 3H), 2.08 – 1.94 (m, 1H), 1.63 – 1.51 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.5, 139.0, 131.8, 128.2, 126.7 (q, $^1J_{C-F(CF3)}$ = 275.8 Hz), 111.1, 109.5, 102.1, 97.2, 55.9, 42.2, 39.0 (q, $^2J_{C-F(CF3)}$ = 28.0 Hz), 29.9 (q, $^3J_{C-F(CF3)}$ = 2.8 Hz), 27.1, 22.0. ^{19}F NMR (376 MHz, CDCl$_3$) δ -63.4. HRMS (ESI): Calcd. for $C_{15}H_{16}F_3NO$ ([M+H]$^+$): 284.1257; Found 284.1271. FTIR (CHCl$_3$) ν_{max}/cm^{-1} 3015, 2983, 2923, 2854, 1543, 1537, 1484, 1471, 1321, 1237, 1040, 893, 854, 742, 714.

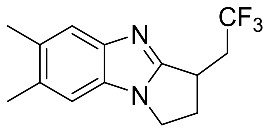
3-(2,2,2-Trifluoroethyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (3pa)



23.1 mg, yield 48%, yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.21 (m, 2H), 4.21 – 4.13 (m, 1H), 4.07 – 3.97 (m, 1H), 3.63 – 3.51 (m, 1H), 3.23 – 3.06 (m, 1H), 3.05 – 2.94 (m, 1H), 2.58 – 2.42 (m, 1H), 2.37 – 2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 148.4, 132.4, 126.4(q, $^{1}J_{C\text{-}F(CF3)}$ = 275 Hz), 122.4, 122.1, 119.9, 109.7, 42.0, 36.8 (q, $^{2}J_{C\text{-}F(CF3)}$ = 28.6 Hz), 33. 7, 30.8 (q, $^{3}J_{C\text{-}F(CF3)}$ = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0. HRMS (ESI): Calcd. for $C_{12}H_{11}F_3N_2Na$ ($[M+Na]^+$): 263.0767; Found 263.0777. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 2994, 2923, 2855, 1711, 1544, 1533, 1480, 1477, 1297, 892, 741, 714.

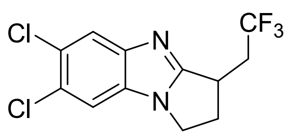
6,7-Dimethyl-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (3qa)



22.0 mg, yield 41%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.10 (s, 1H), 4.18 – 4.09 (m, 1H), 4.04 – 3.94 (m, 1H), 3.62 – 3.50 (m, 1H), 3.22 – 3.05 (m, 1H), 3.05 – 2.93 (m, 1H), 2.57 – 2.42 (m, 1H), 2.36 (d, J = 2.3 Hz, 6H), 2.30 – 2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 147.0, 131.4, 130.9, 130.8, 126.5 (q, $^{1}J_{C\text{-}F(CF3)}$ = 277.0 Hz), 119.9, 110.0, 41.9, 36.9 (q, $^{2}J_{C\text{-}F(CF3)}$ = 28.7 Hz), 33.7， 30.8 (q, $^{3}J_{C\text{-}F(CF3)}$ = 2.9 Hz), 20.4, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0. HRMS (ESI): Calcd. for $C_{14}H_{15}F_3N_2Na$ ($[M+Na]^+$): 291.1080; Found 291.1091. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3023, 2886, 2850, 1698, 1540, 1560, 1470, 1464, 1315, 870, 708.

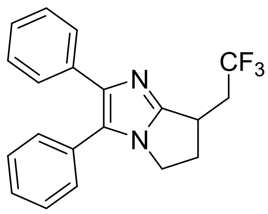
6,7-Dichloro-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (3ra)



35.7 mg, yield 58%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.43 (s, 1H), 4.23 – 4.14 (m, 1H), 4.10 – 4.00 (m, 1H), 3.66 – 3.55 (m, 1H), 3.20 – 2.99 (m, 2H), 2.62 – 2.49 (m, 1H), 2.38 – 2.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.7, 131.5, 126.5, 126.3, 126.2 (q, $^{1}J_{C-F(CF3)}$ = 275.2 Hz), 121.1, 111.1, 42.3, 36.6 (q, $^{2}J_{C-F(CF3)}$ = 29.1 Hz), 33.6, 30.9 (q, $^{3}J_{C-F(CF3)}$ = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9. HRMS (ESI): Calcd. for $C_{12}H_{10}Cl_2F_3N_2$ ($[M+H]^+$): 309.0168; Found 309.0180. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3023, 2890, 2850, 1691, 1543, 1563, 1470, 1460, 1316, 860, 710.

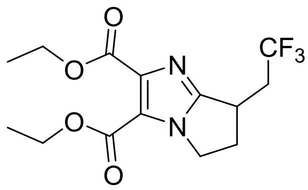
2,3-Diphenyl-7-(2,2,2-trifluoroethyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole (3sa)



37.7 mg, yield 55%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.30 (m, 5H), 7.28 – 7.21 (m, 2H, overlap with $CDCl_3$), 7.21 – 7.14 (m, 1H), 4.05 – 3.96 (m, 1H), 3.96 – 3.86 (m, 1H), 3.59 – 3.48 (m, 1H), 3.22 – 3.07 (m, 1H), 2.98 – 2.84 (m, 1H), 2.50 – 2.35 (m, 1H), 2.36 – 2.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 142.2, 135.0, 130.7, 128.9 (2C), 128.8 (2C), 128.2 (2C), 127.9, 127.3 (2C), 126.64, 126.58 (q, $^{1}J_{C-F(CF3)}$ = 275 Hz), 125.7, 43.5, 37.2 (q, $^{2}J_{C-F(CF3)}$ = 28.1 Hz), 33.5, 31.0 (q, $^{3}J_{C-F(CF3)}$ = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9. HRMS (ESI): Calcd. for $C_{20}H_{17}F_3N_2Na$ ($[M+Na]^+$): 365.1237; Found 365.1251. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3032, 3012, 2993, 2853, 1683, 1531, 1470, 1453, 1290, 892, 753, 710.

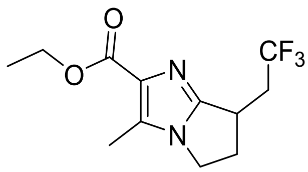
Diethyl 7-(2,2,2-trifluoroethyl)-6,7-dihydro-5*H*-pyrrolo [1,2-*a*]imidazole-2,3-dicarboxylate (3ta)



32.1 mg, yield 48%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 – 4.33 (m, 5H), 4.20 – 4.10 (m, 1H), 3.53 – 3.42 (m, 1H), 3.17 – 3.01 (m, 1H), 2.99 – 2.87 (m, 1H), 2.51 – 2.40 (m, 1H), 2.30 – 2.14 (m, 1H), 1.39 (q, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.1, 155.7, 141.0, 126.2 (q, $^1J_{C\text{-}F(CF3)}$ = 275.4 Hz), 122.6, 61.45, 61.42, 45.9, 36.7 (q, $^2J_{C\text{-}F(CF3)}$ = 28.5 Hz), 33.3, 30.8 (q, $^3J_{C\text{-}F(CF3)}$ = 3.1 Hz), 14.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.07. HRMS (ESI): Calcd. for $C_{14}H_{17}F_3N_2O_4Na$ ($[M+Na]^+$): 357.1033; Found 357.1059. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3037 3017, 2957, 2214, 1730, 1620, 1630, 1454, 1441, 1364, 1280, 1270, 1117, 887, 710.

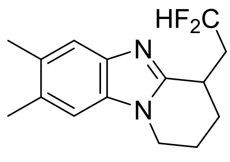
Ethyl 3-methyl-7-(2,2,2-trifluoroethyl)-6,7-dihydro-5*H*-pyrrolo [1,2-*a*]imidazole-2-carboxylate (3ua)



32.0 mg, yield 58%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 – 4.28 (m, 3H), 4.14 – 4.02 (m, 1H), 3.48 – 3.35 (m, 1H), 3.07 – 2.83 (m, 2H), 2.49 (s, 3H), 2.44 – 2.33 (m, 1H), 2.29 – 2.13 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.6, 151.7, 126.3(q, $^1J_{C\text{-}F(CF3)}$ = 275.4 Hz), 117.4, 60.2, 45.7, 36.8 (q, $^2J_{C\text{-}F(CF3)}$ = 28.4 Hz), 33.1, 30.96 (q, $^3J_{C\text{-}F(CF3)}$ = 3.1 Hz), 15.5, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.07. HRMS (ESI): Calcd. for $C_{12}H_{15}F_3N_3O_2Na$ ($[M+Na]^+$): 299.0978; Found 299.0978. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3049, 3021, 2964, 2227, 1722, 1683, 1622, 1480, 1455, 1380, 1301, 1273, 1112, 895, 731.

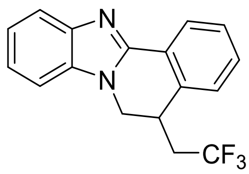
4-(2,2-Difluoroethyl)-7,8-dimethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (3cb)



27.0 mg, yield 51%, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.04 (s, 1H), 6.36 (tdd, J = 56.9, 5.2, 4.1 Hz, 1H), 4.16–4.06 (m, 1H), 3.31–3.20 (m, 1H), 2.81–2.62 (m, 1H), 2.85–2.63 (m, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 2.29–1.99 (m, 4H), 1.77–1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 141.2, 133.2, 131.1, 131.0, 119.3 116.9 (t, $^1J_{C\text{-}F\ (CF2)}$ = 237.5 Hz, overlap withδ119.3), 109.3, 42.3, 38.1 (t,$^2J_{C\text{-}F\ (CF2)}$ = 21.2 Hz), 31.3 (t, $^3J_{C\text{-}F(CF2)}$ = 4.8 Hz), 27.6, 21.8, 20.4, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0–118.1. HRMS (ESI): Calcd. for $C_{14}H_{16}F_2N_2Na$ ($[M+Na]^+$): 273.1174; Found 273.1189. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3012, 2876, 2854, 1692, 1546, 1563, 1460, 1464, 1316, 875, 684.

5-(2,2,2-Trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5)



22.9 mg, yield 76%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.34 (m, 1H), 7.89 – 7.87 (m, 1H), 7.54 – 7.47 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 4.59 (dd, J = 13.0, 2.2 Hz, 1H), 4.30 (dd, J = 13.0, 4.1 Hz, 1H), 3.68 – 3.65 (m, 1H), 2.47 –‘ 2.33 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 143.9, 136.3, 134.8, 130.8, 128.8, 127.7, 126.2, 126.1 (q, $^1J_{C\text{-}F(CF3)}$= 276 Hz), 125.8, 123.2, 122.9, 119.9, 109.1, 43.7, 37.5 (q, $^2J_{C\text{-}F(CF3)}$= 28 Hz), 33.3 (q, $^3J_{C\text{-}F(CF3)}$= 2 Hz), 29.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS (ESI): Calcd. for $C_{17}H_{13}F_3N_2$ ($[M + Na]^+$):325.0923; Found 325.0925. FTIR ($CHCl_3$) ν_{max}/cm^{-1} 3027, 2987, 2920, 2851, 1700, 1543, 1537, 1480, 1475, 1301, 893, 749, 712.

9. Copies of NMR spectra of all compounds

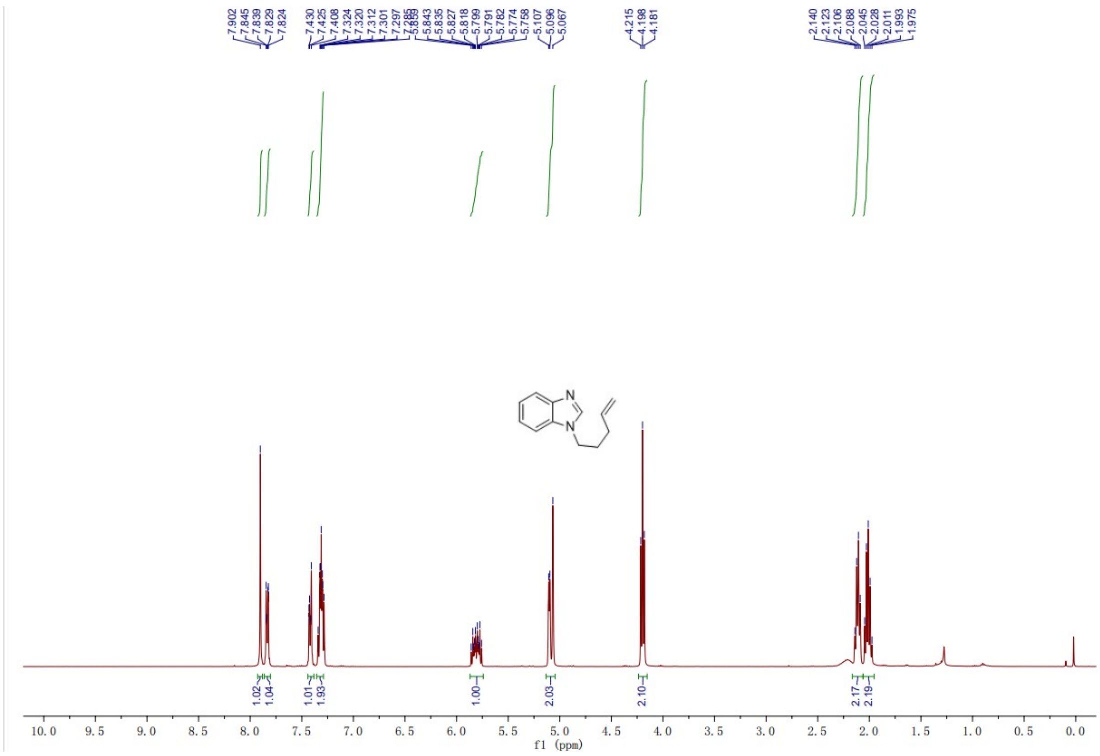


Figure S-5 [1]H NMR spectrum of **1a**

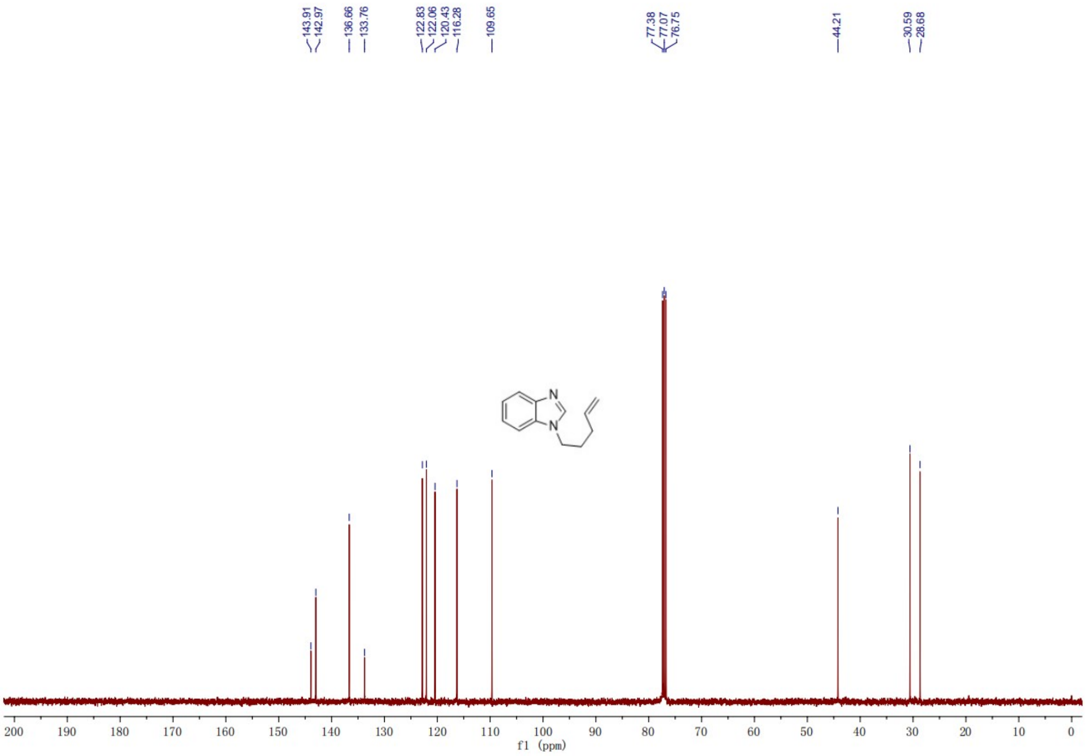


Figure S-6 [13]C NMR spectrum of **1a**

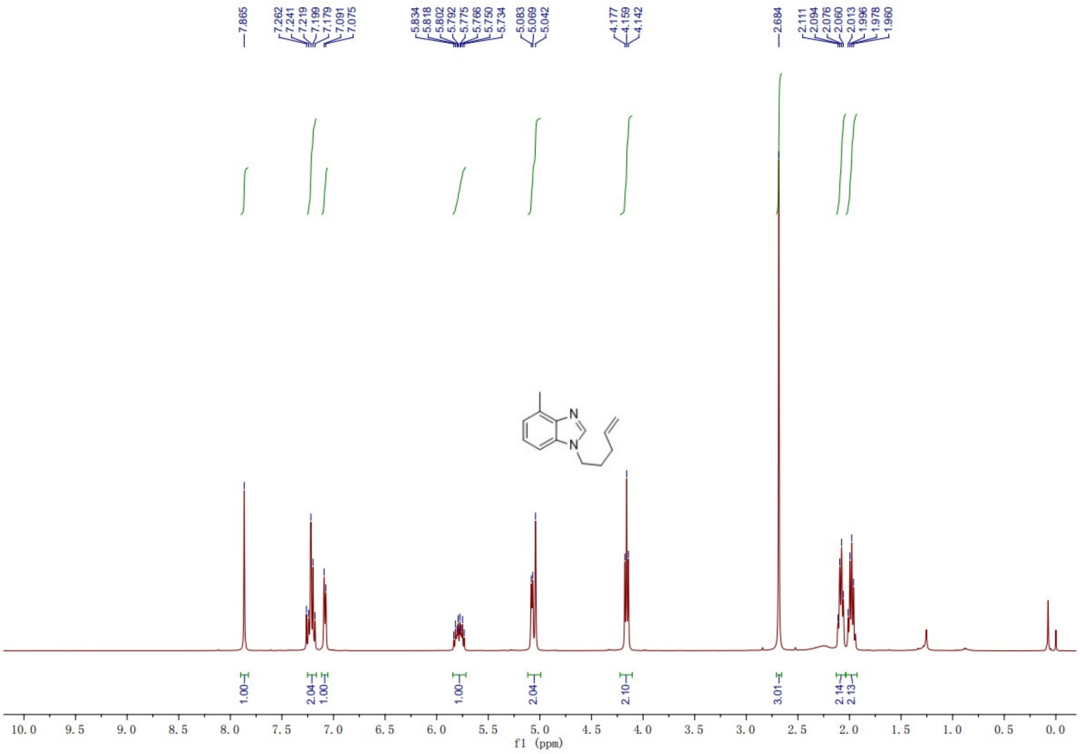


Figure S-7 ^{1}H NMR spectrum of **1b**

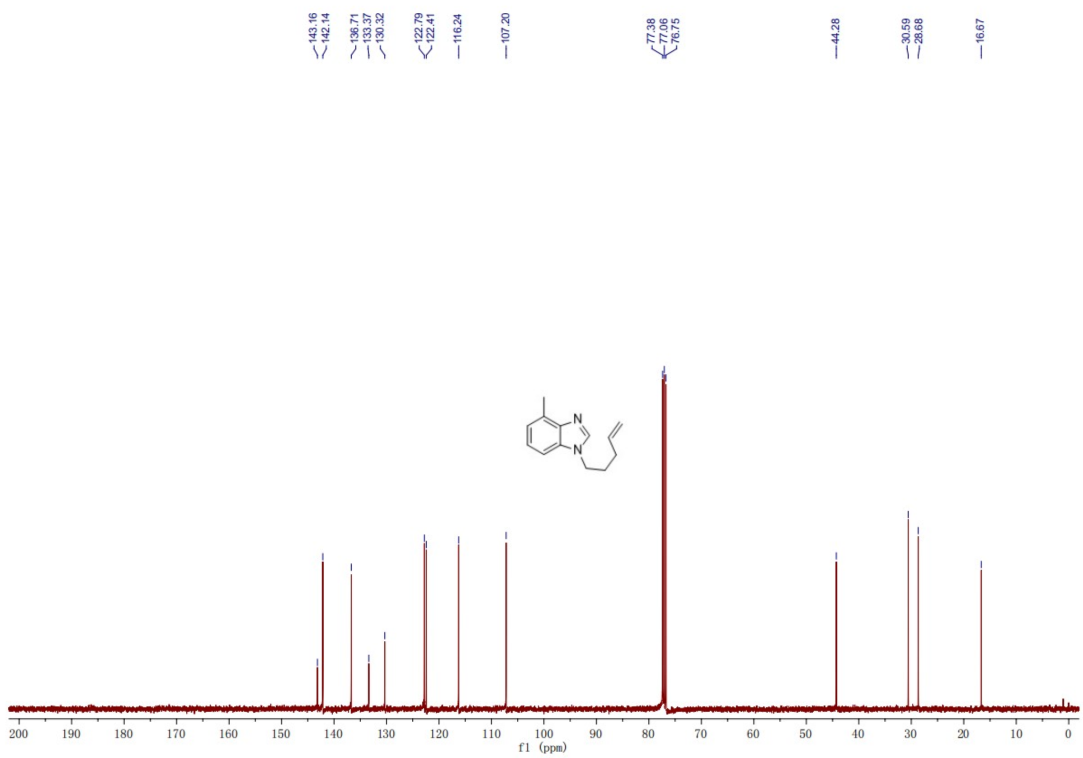


Figure S-8 ^{13}C NMR spectrum of **1b**

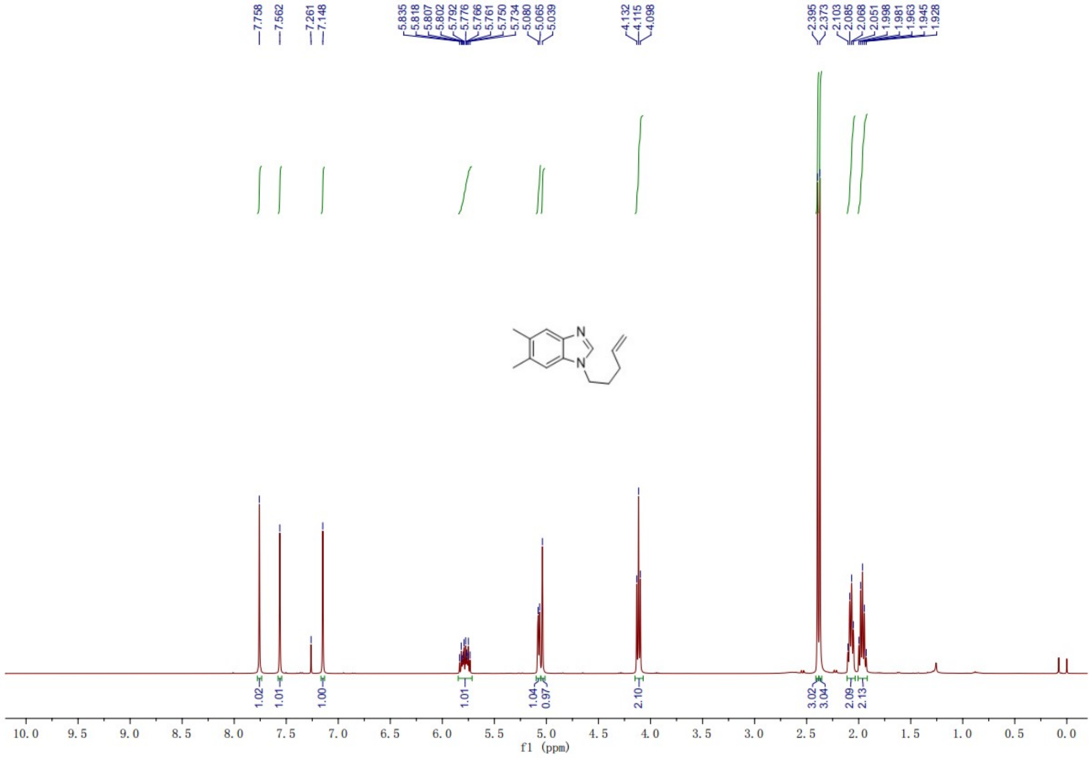


Figure S-9 ^{1}H NMR spectrum of **1c**

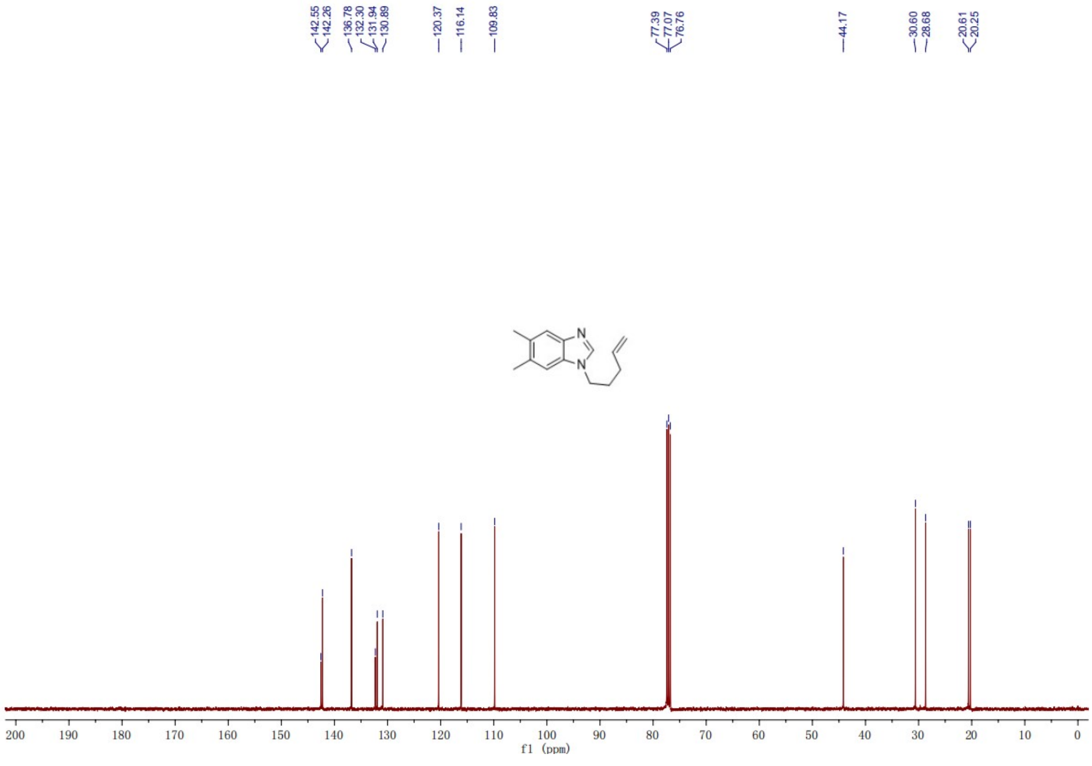


Figure S-10 ^{13}C NMR spectrum of **1c**

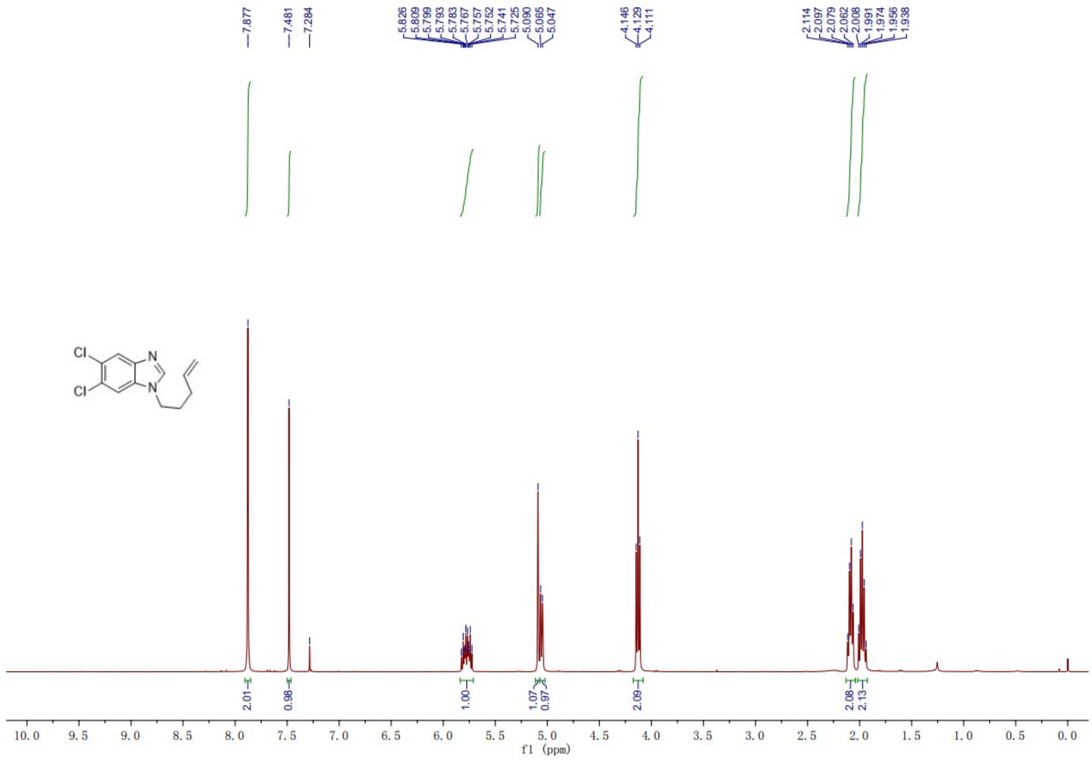


Figure S-11 ^{1}H NMR spectrum of **1d**

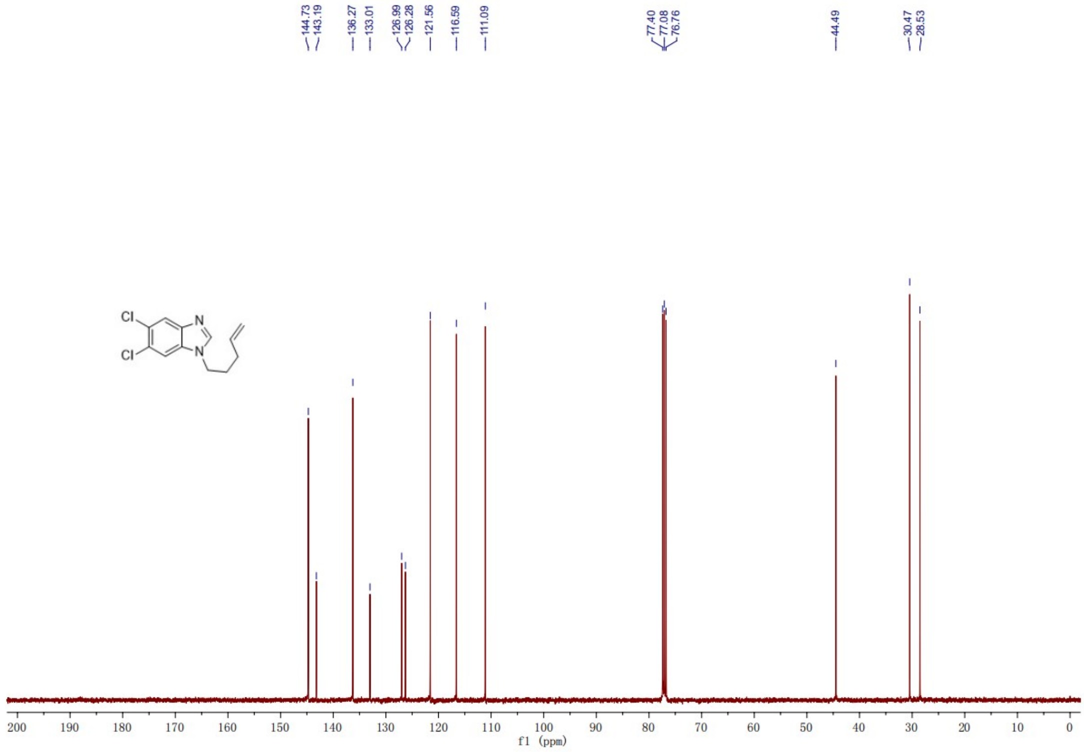


Figure S-12 ^{13}C NMR spectrum of **1d**

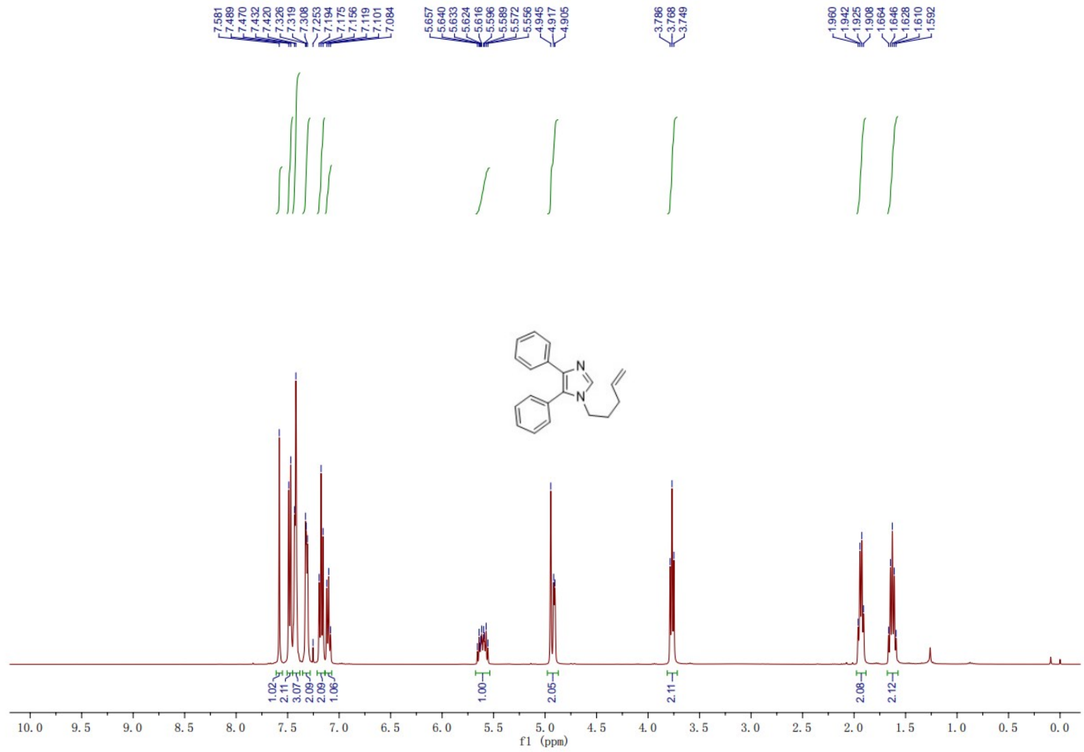


Figure S-13 ^{1}H NMR spectrum of **1e**

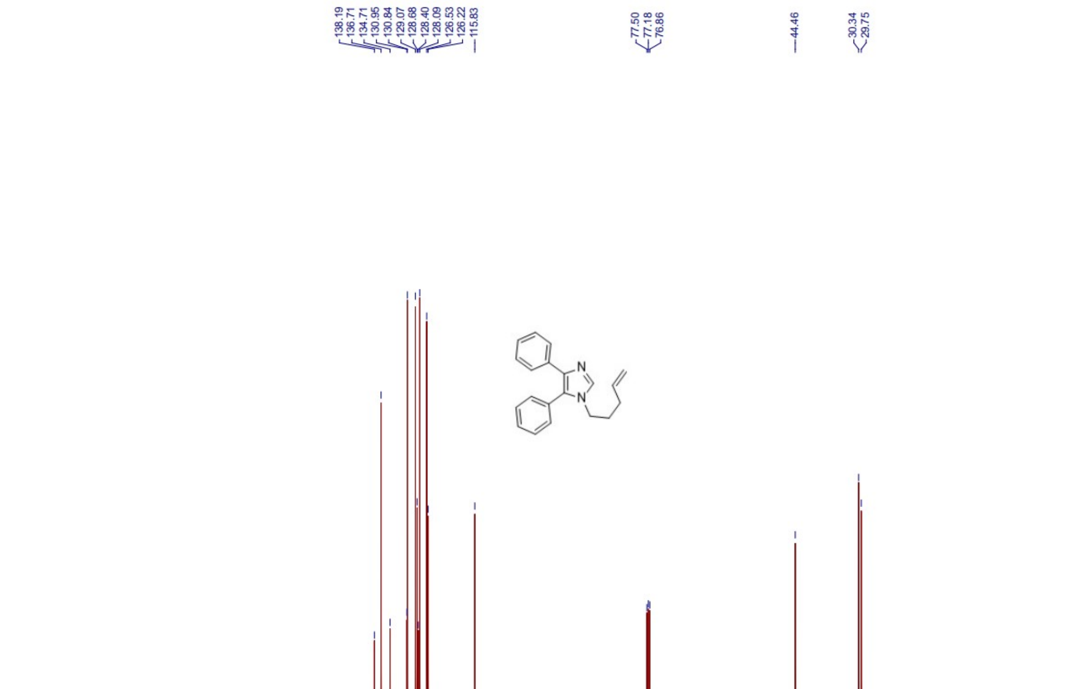


Figure S-14 ^{13}C NMR spectrum of **1e**

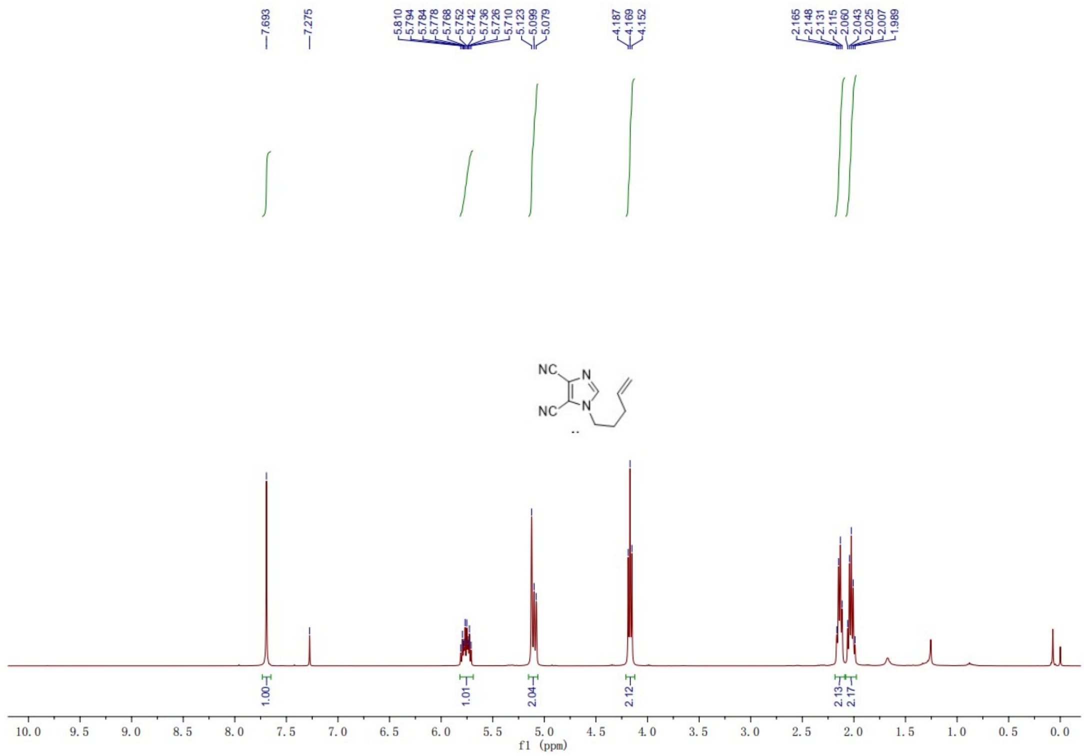


Figure S-15 ^{1}H NMR spectrum of **1f**

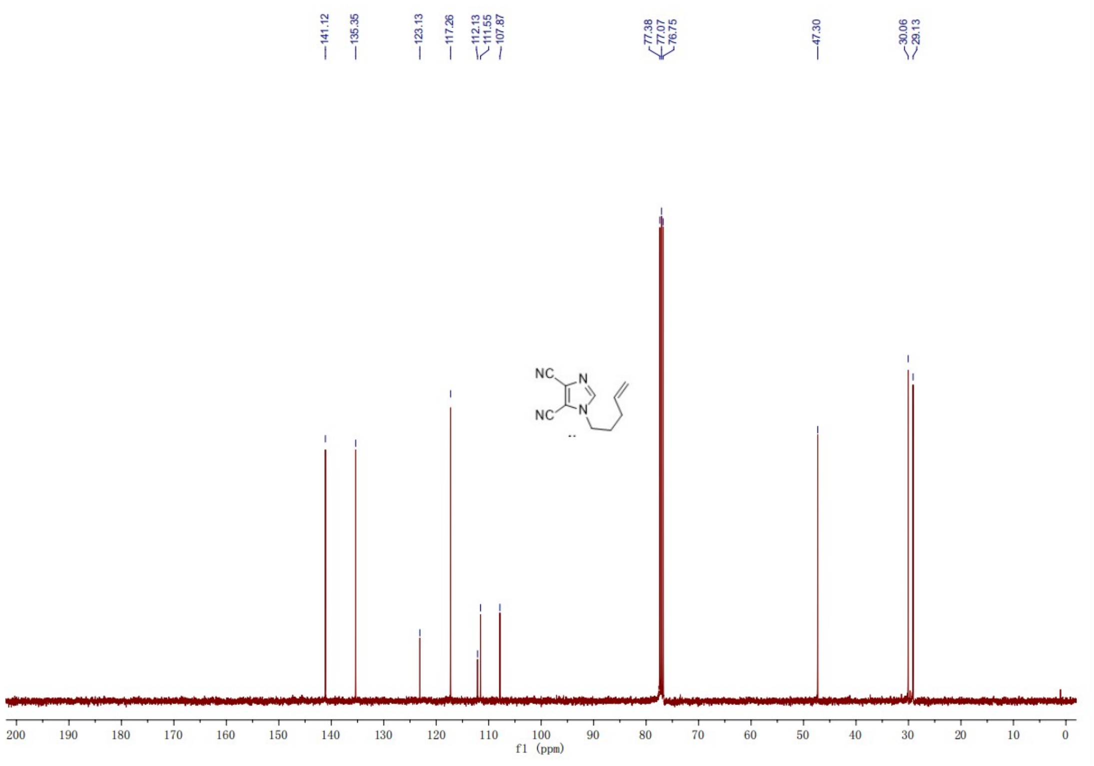


Figure S-16 ^{13}C NMR spectrum of **1f**

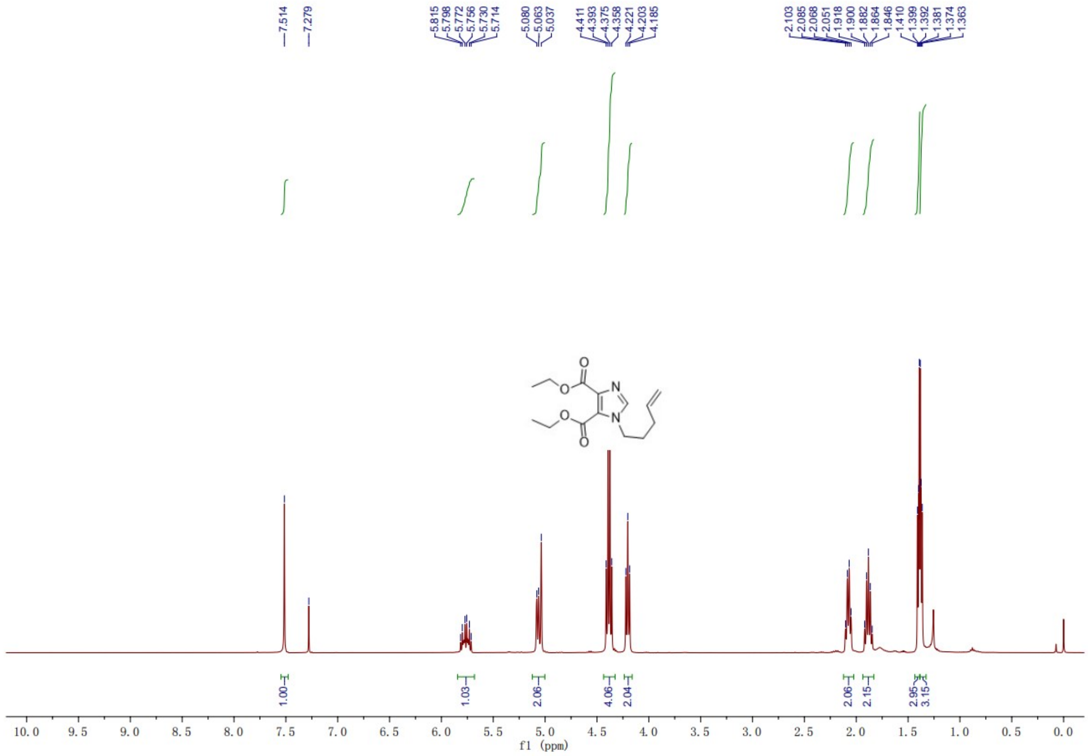


Figure S-17 ^{1}H NMR spectrum of **1g**

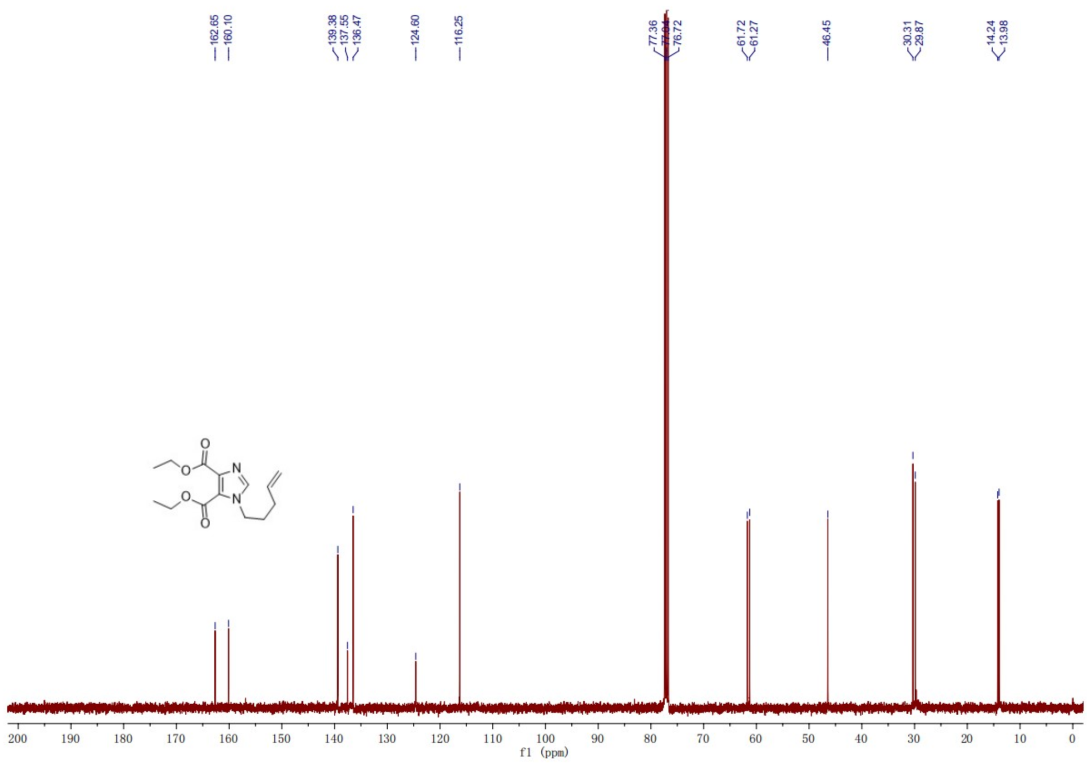


Figure S-18 ^{13}C NMR spectrum of **1g**

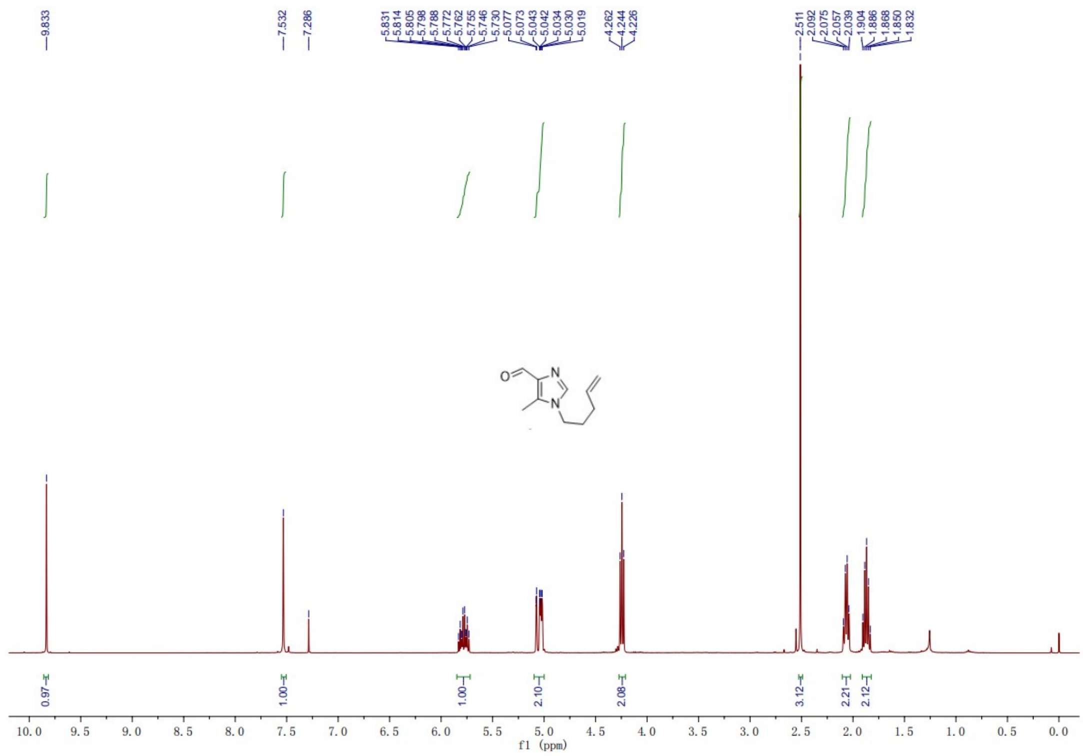


Figure S-19 ^{1}H NMR spectrum of **1h**

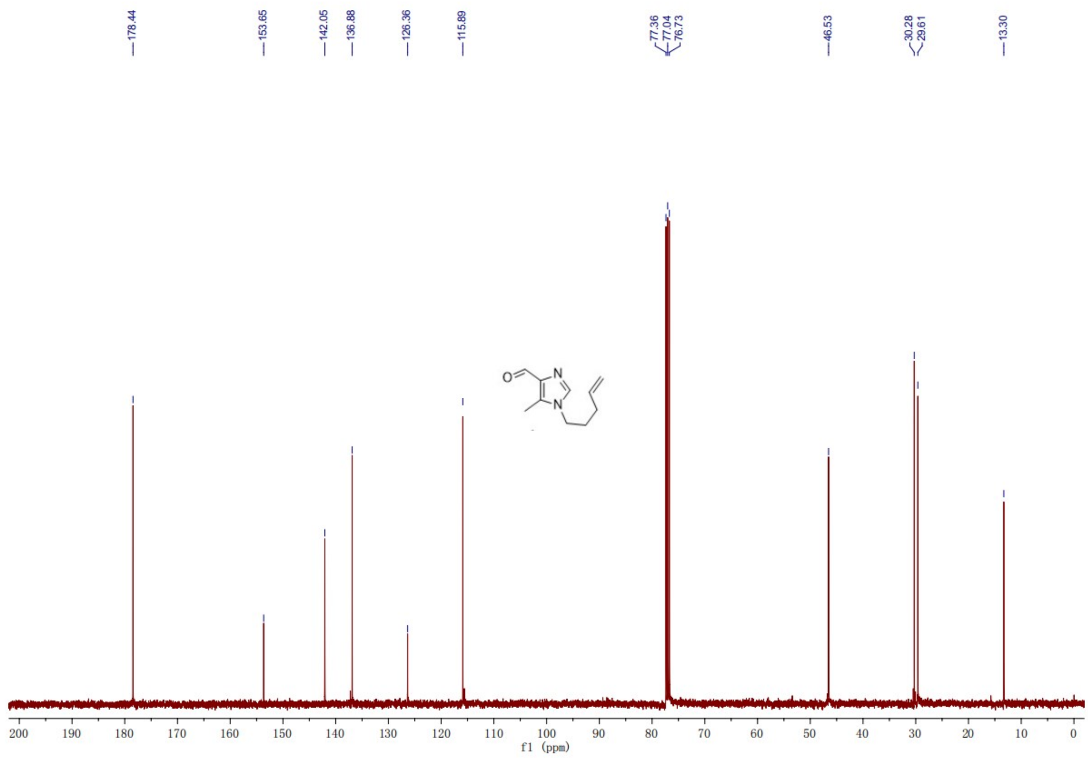


Figure S-20 ^{13}C NMR spectrum of **1h**

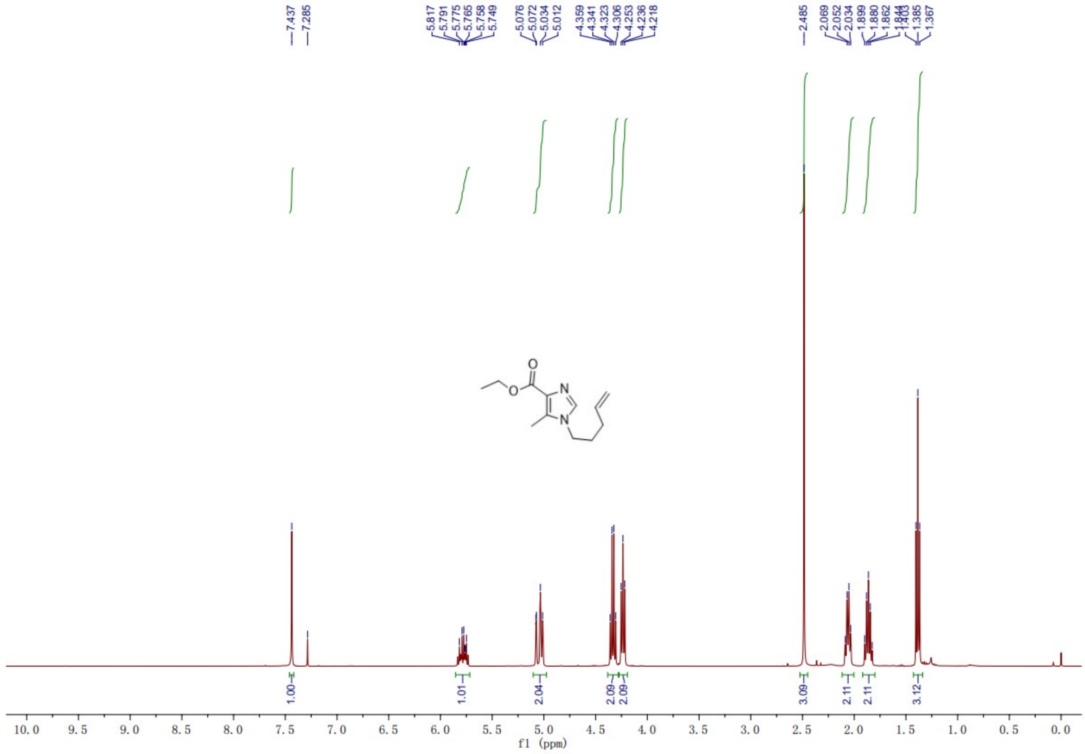


Figure S-21 ^{1}H NMR spectrum of **1i**

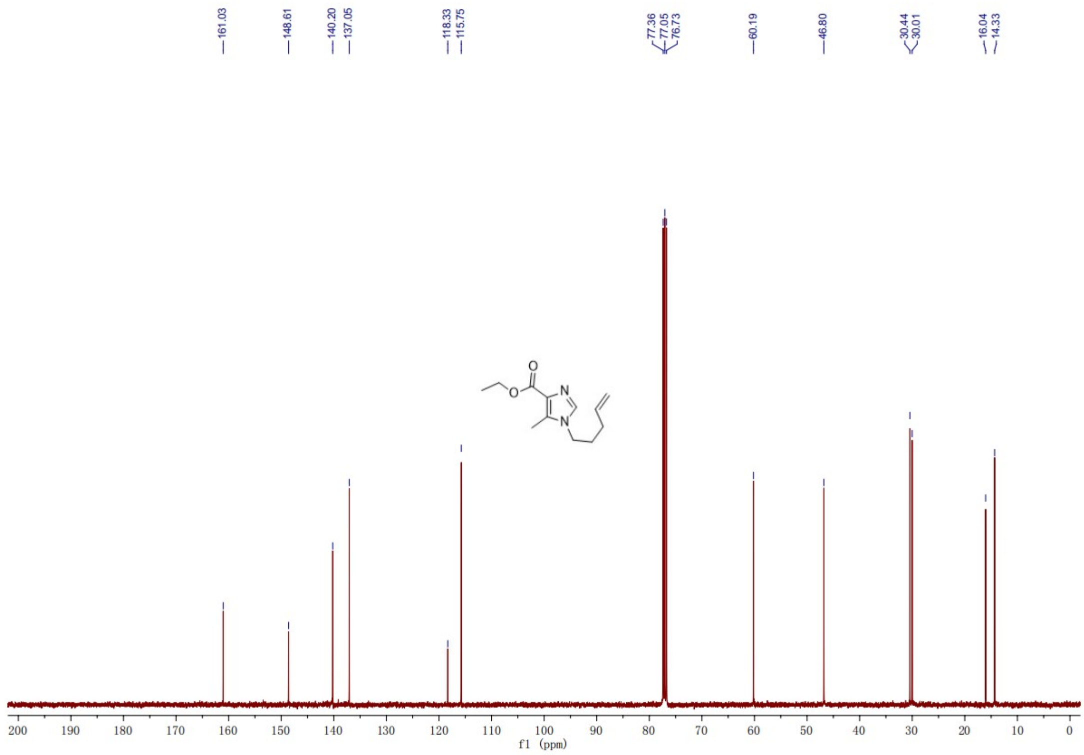


Figure S-22 ^{13}C NMR spectrum of **1i**

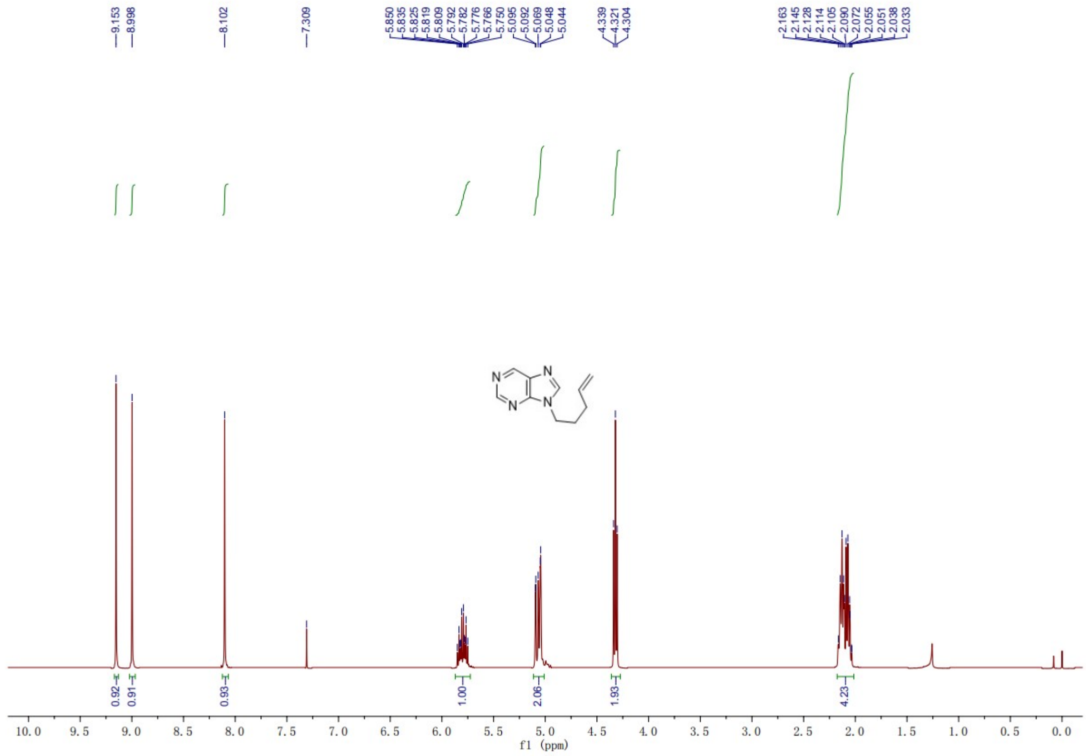


Figure S-23 ^{1}H NMR spectrum of **1j**

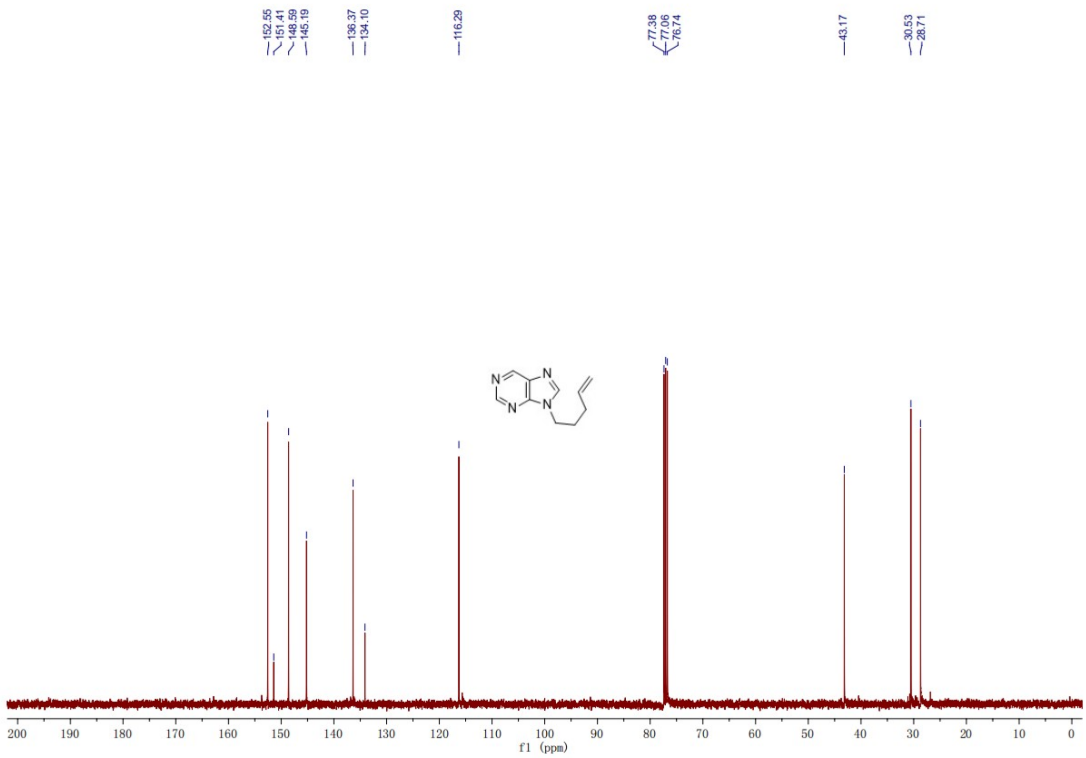


Figure S-24 ^{13}C NMR spectrum of **1j**

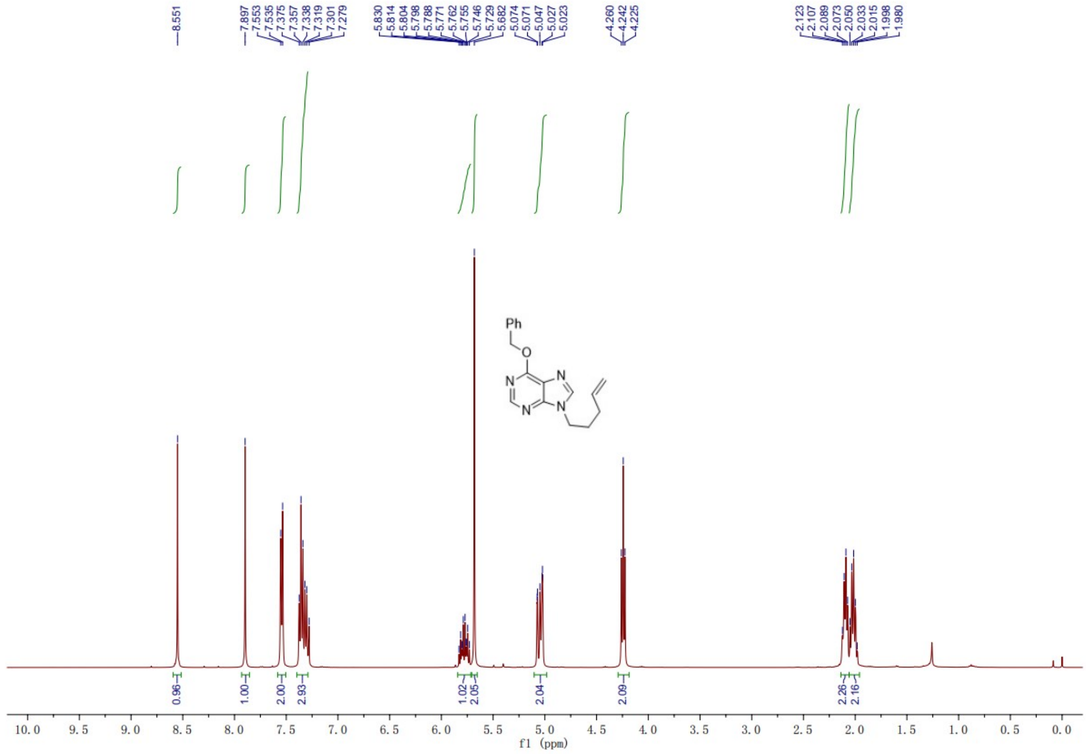


Figure S-25 ¹H NMR spectrum of **1k**

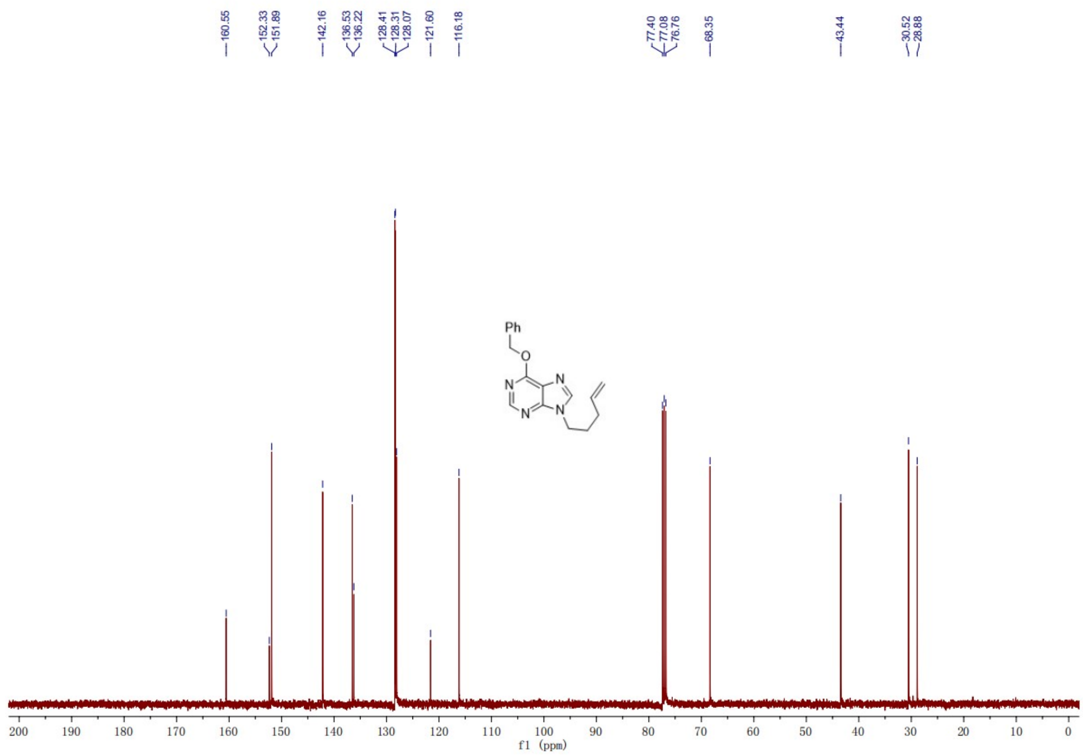


Figure S-26 ¹³C NMR spectrum of **1k**

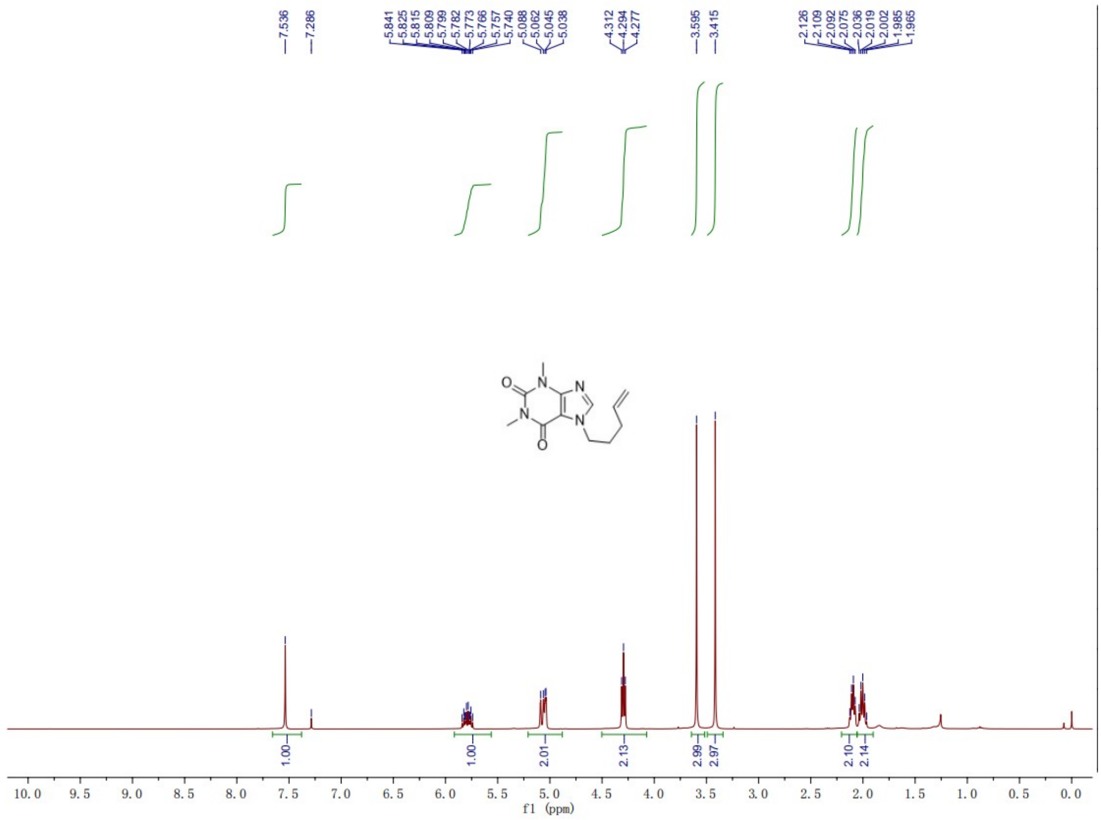


Figure S-27 ^{1}H NMR spectrum of **1l**

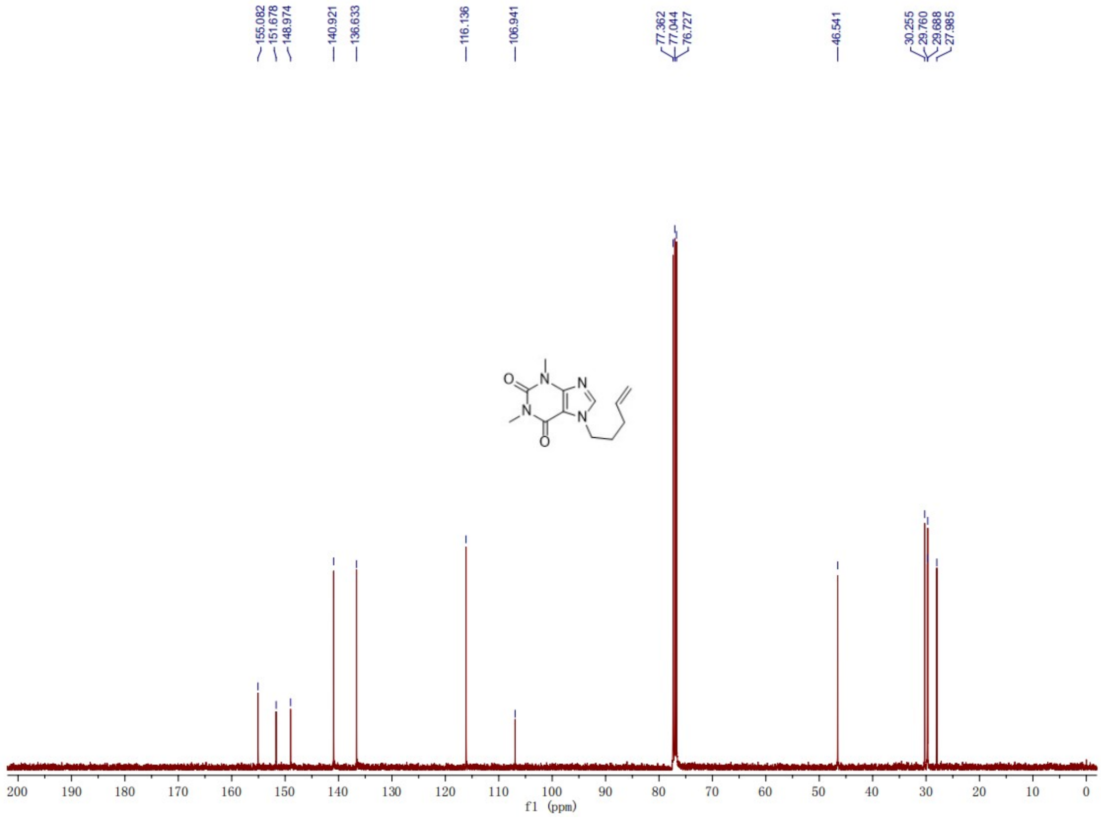


Figure S-28 ^{13}C NMR spectrum of **1l**

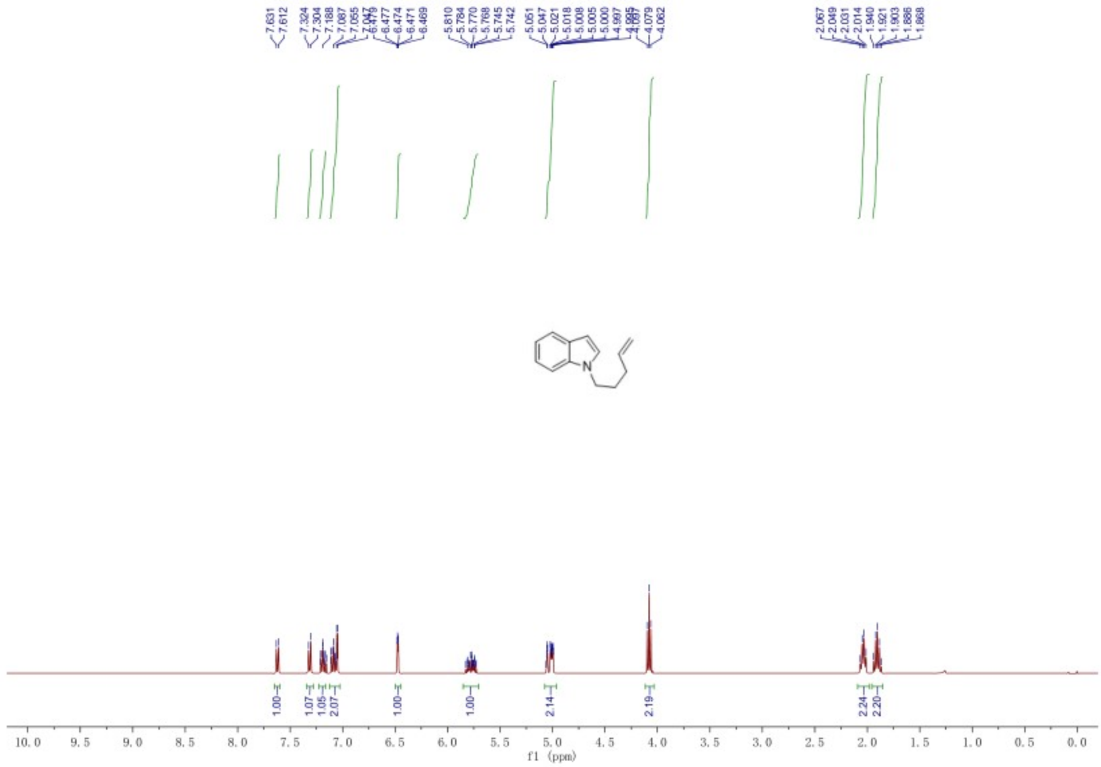


Figure S-29 ^{1}H NMR spectrum of **1m**

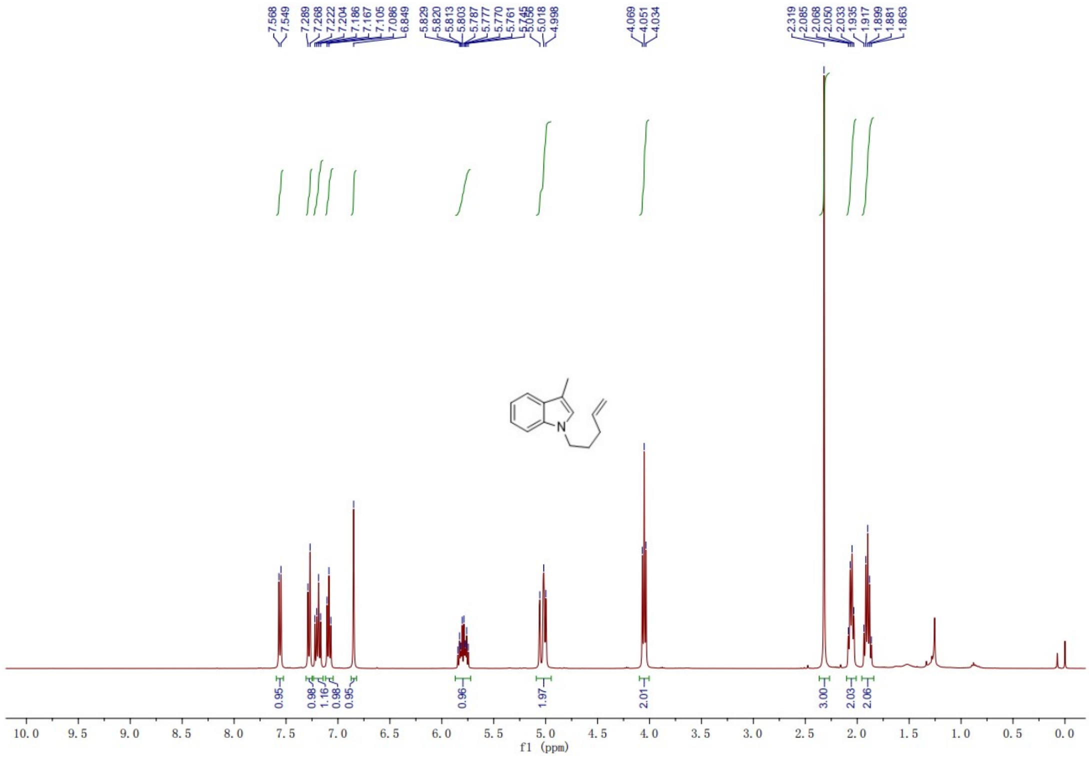


Figure S-30 ^{1}H NMR spectrum of **1n**

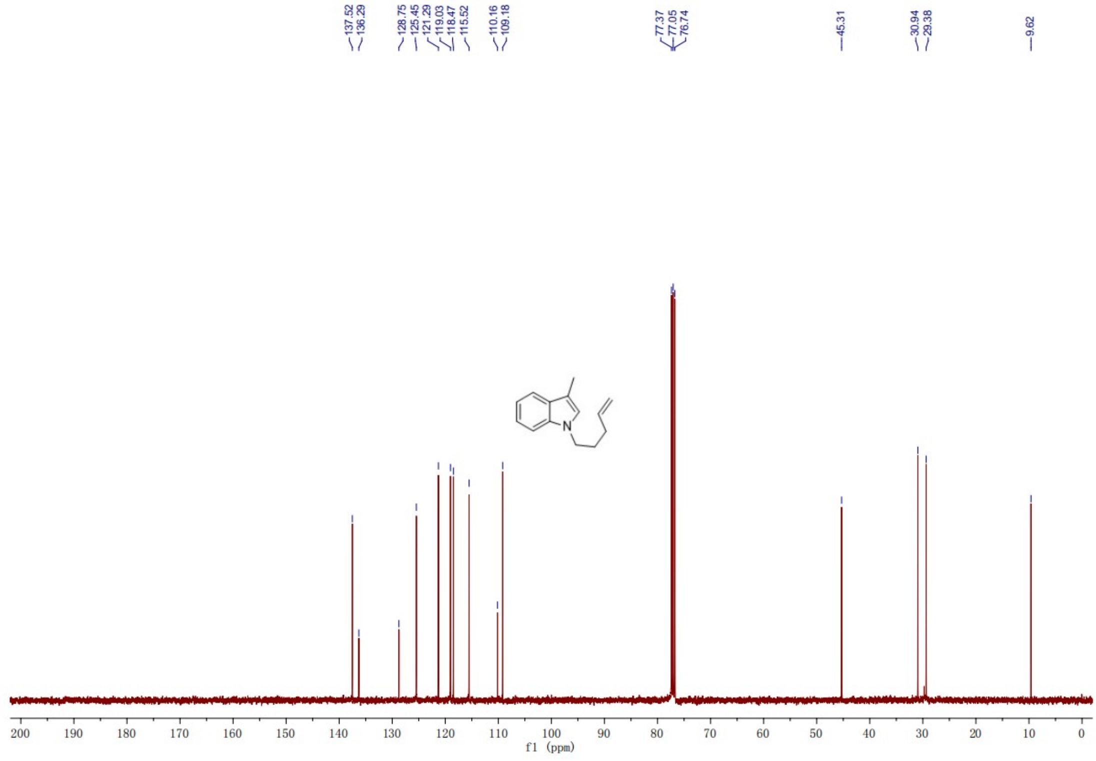


Figure S-31 ^{13}C NMR spectrum of **1n**

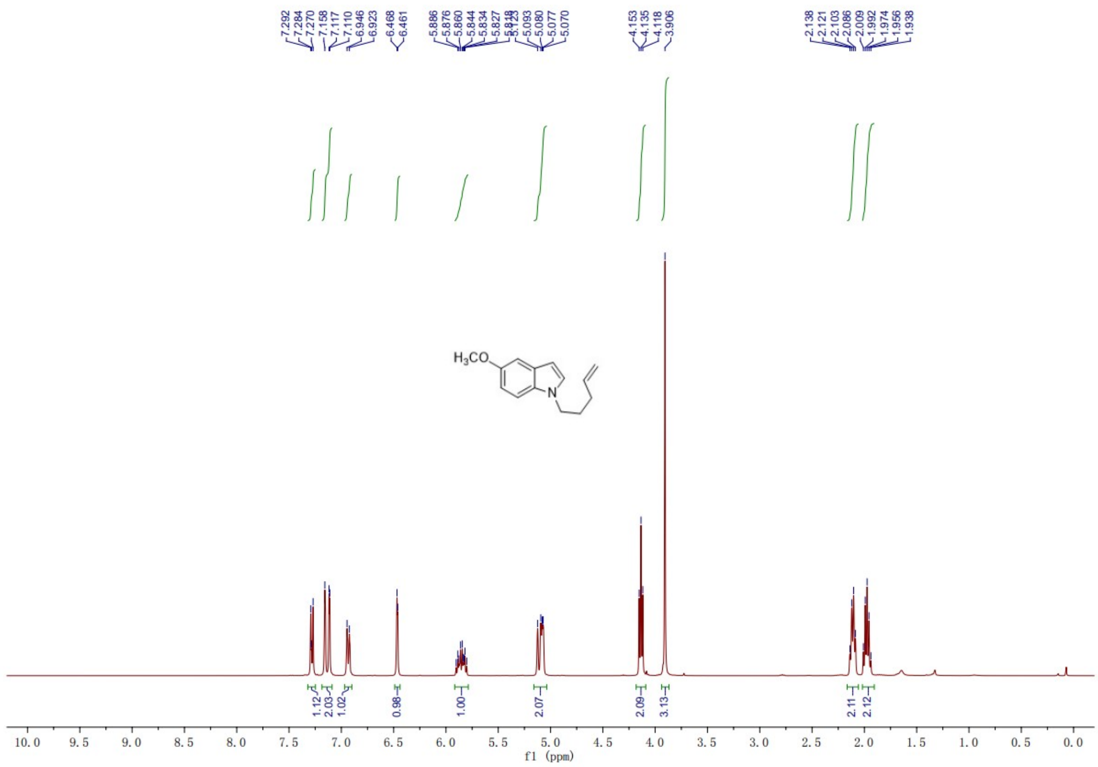


Figure S-32 ^{1}H NMR spectrum of **1o**

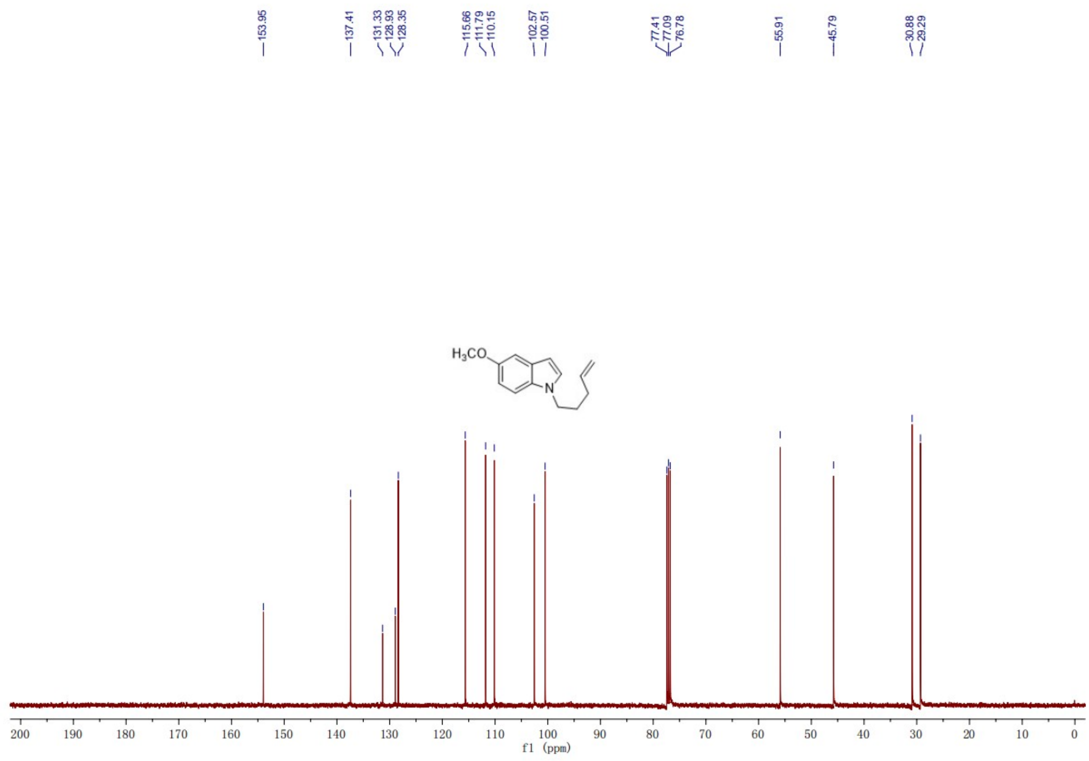


Figure S-33 ^{13}C NMR spectrum of **1o**

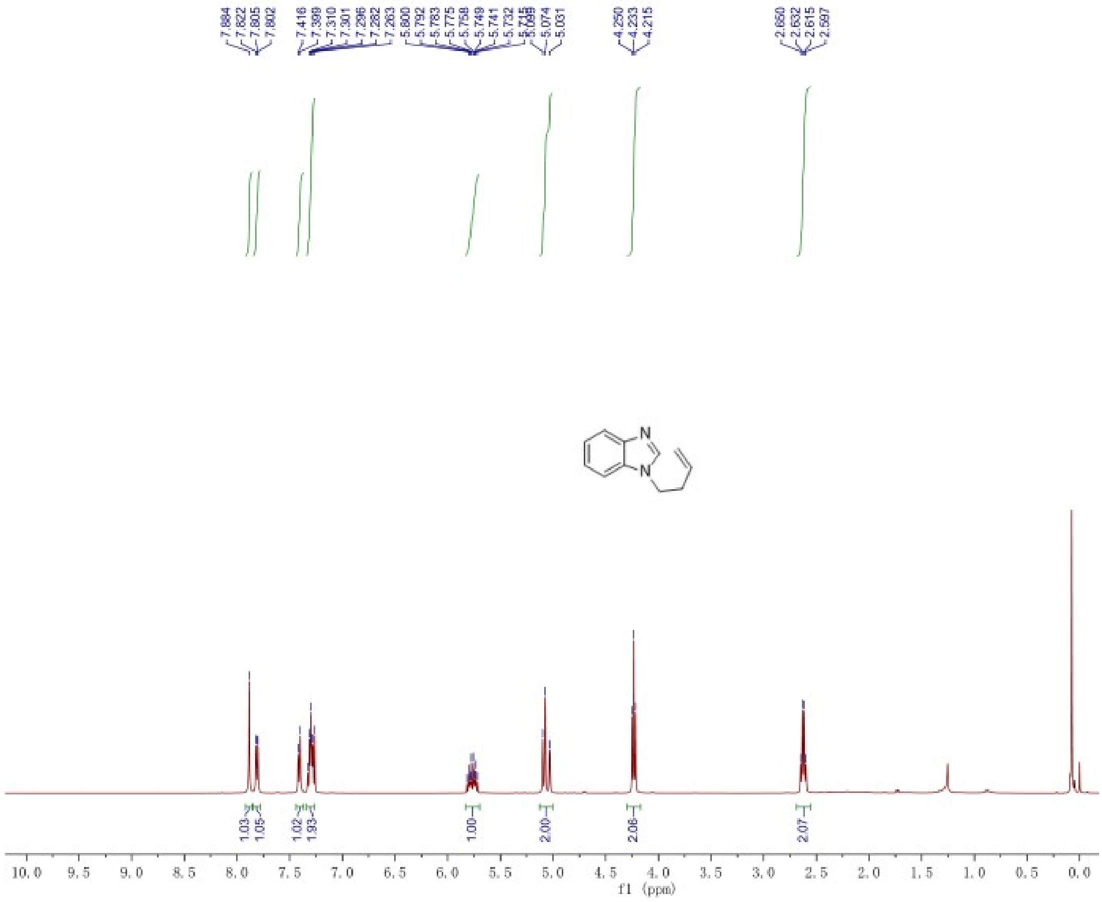


Figure S-34 ^{1}H NMR spectrum of **1p**

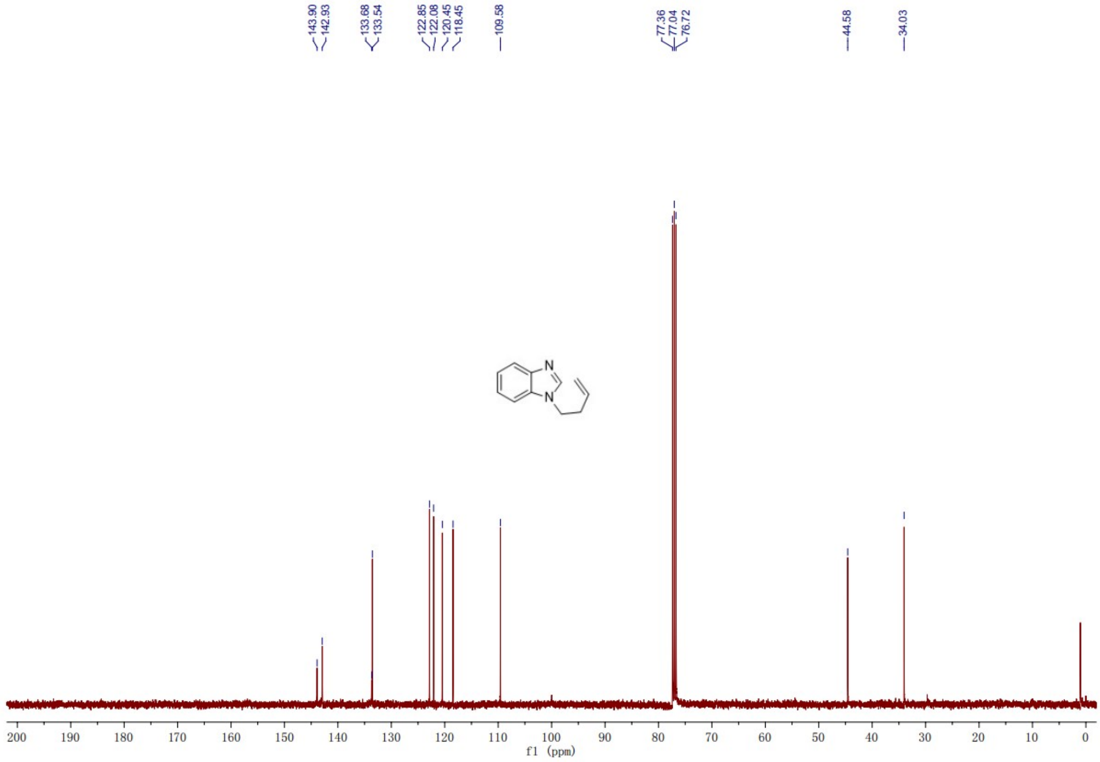


Figure S-35 ^{13}C NMR spectrum of **1p**

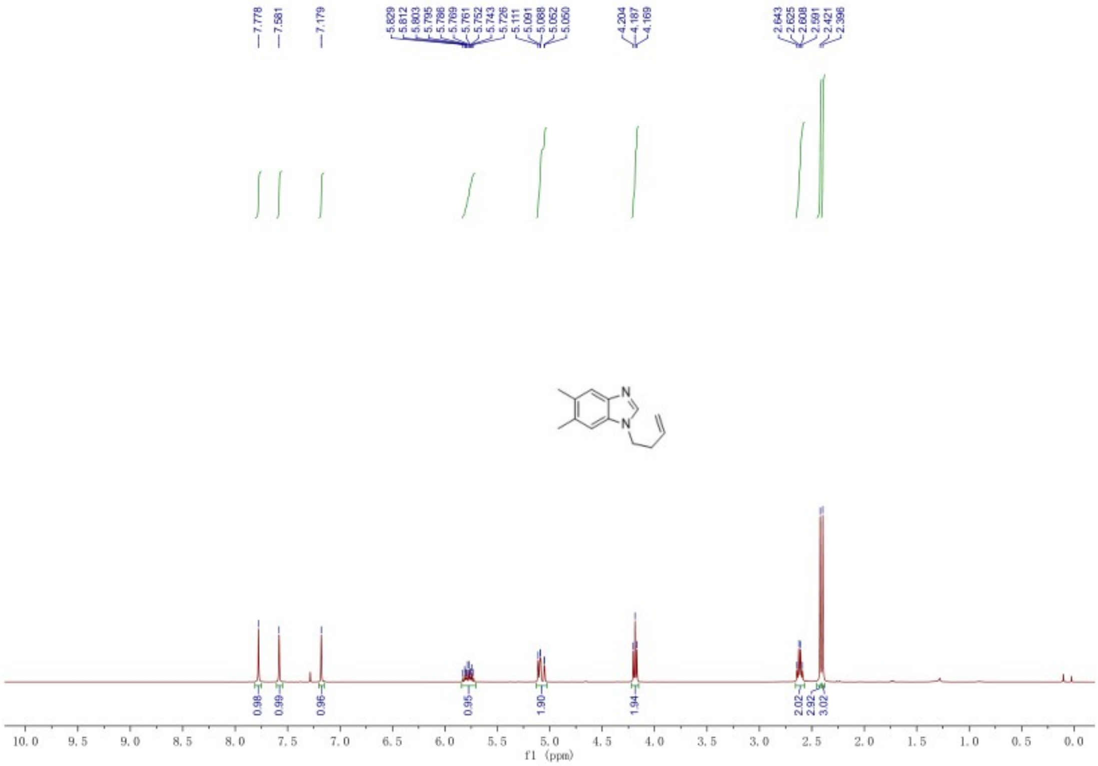


Figure S-36 ^{1}H NMR spectrum of **1q**

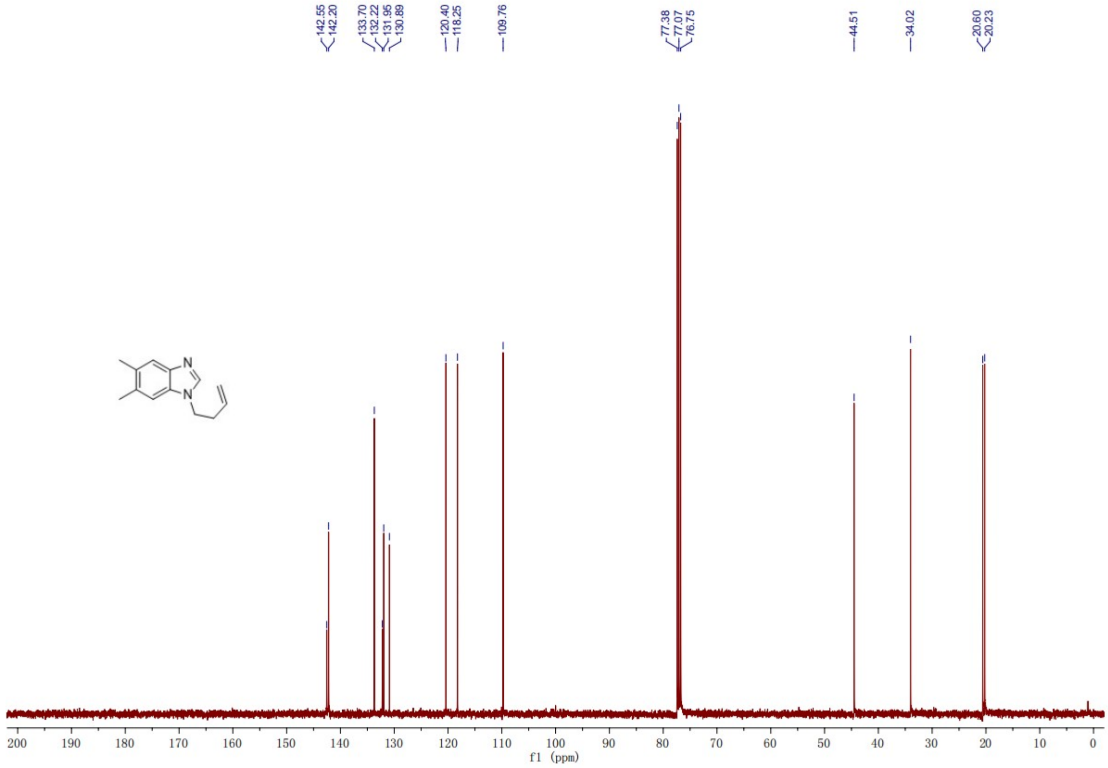


Figure S-37 ^{13}C NMR spectrum of **1q**

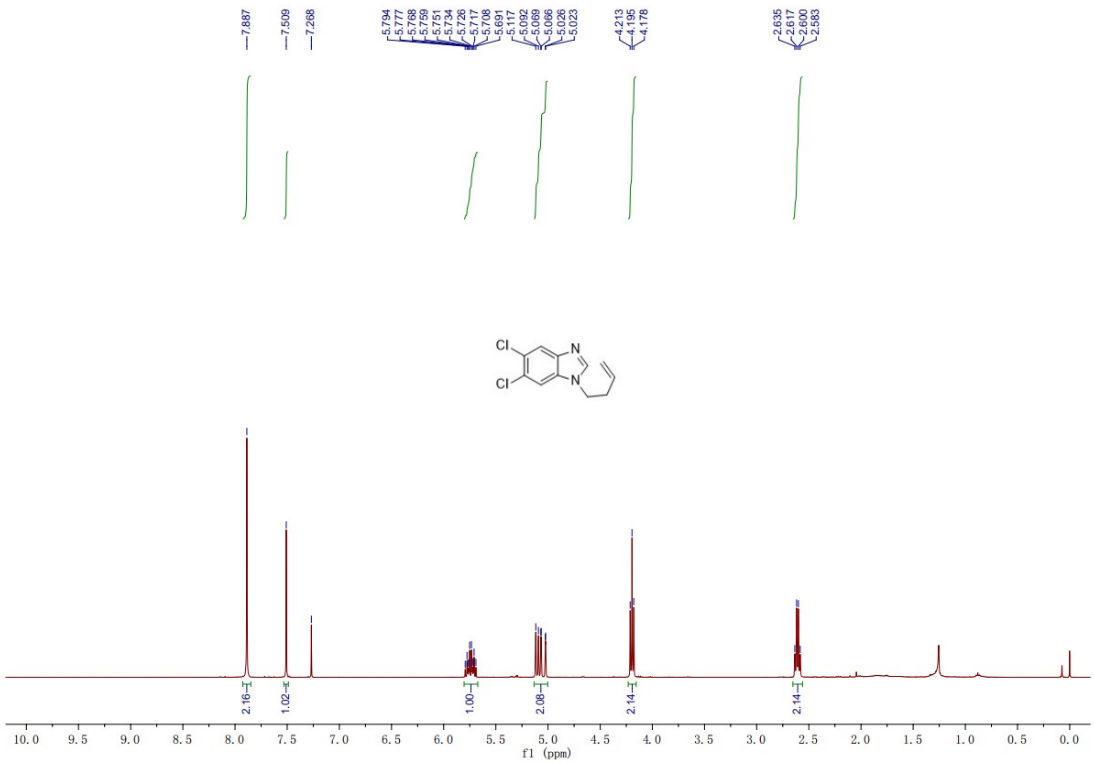


Figure S-38 ^{1}H NMR spectrum of **1r**

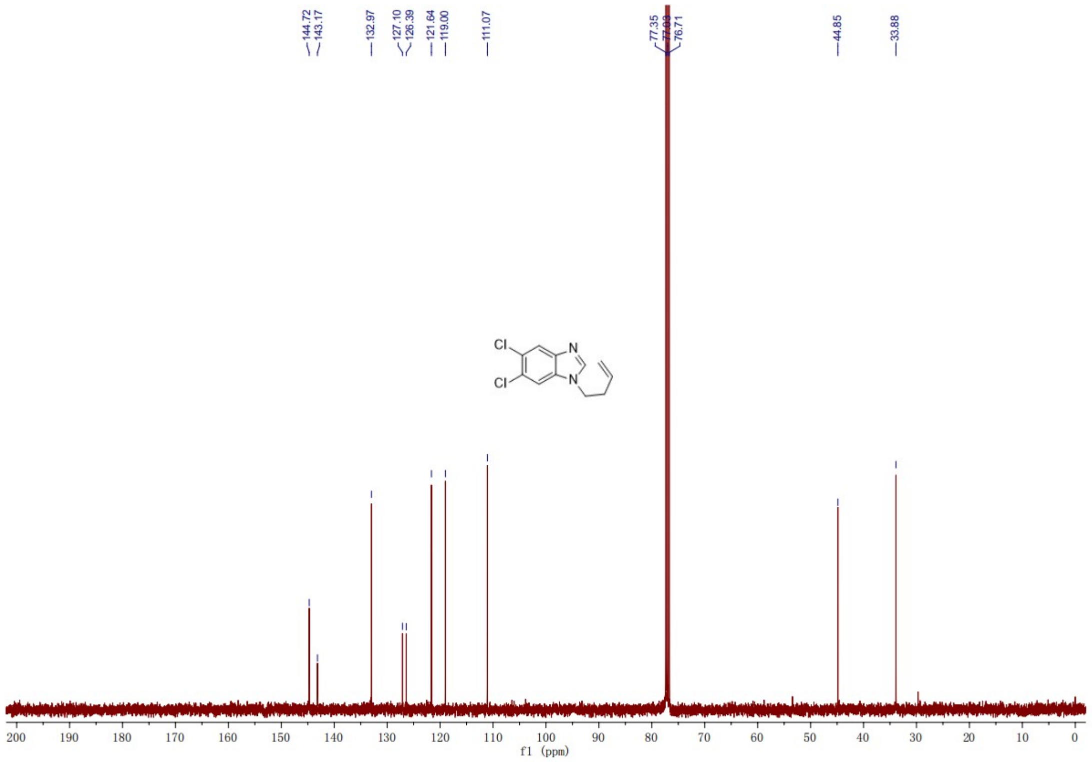


Figure S-39 ^{13}C NMR spectrum of **1r**

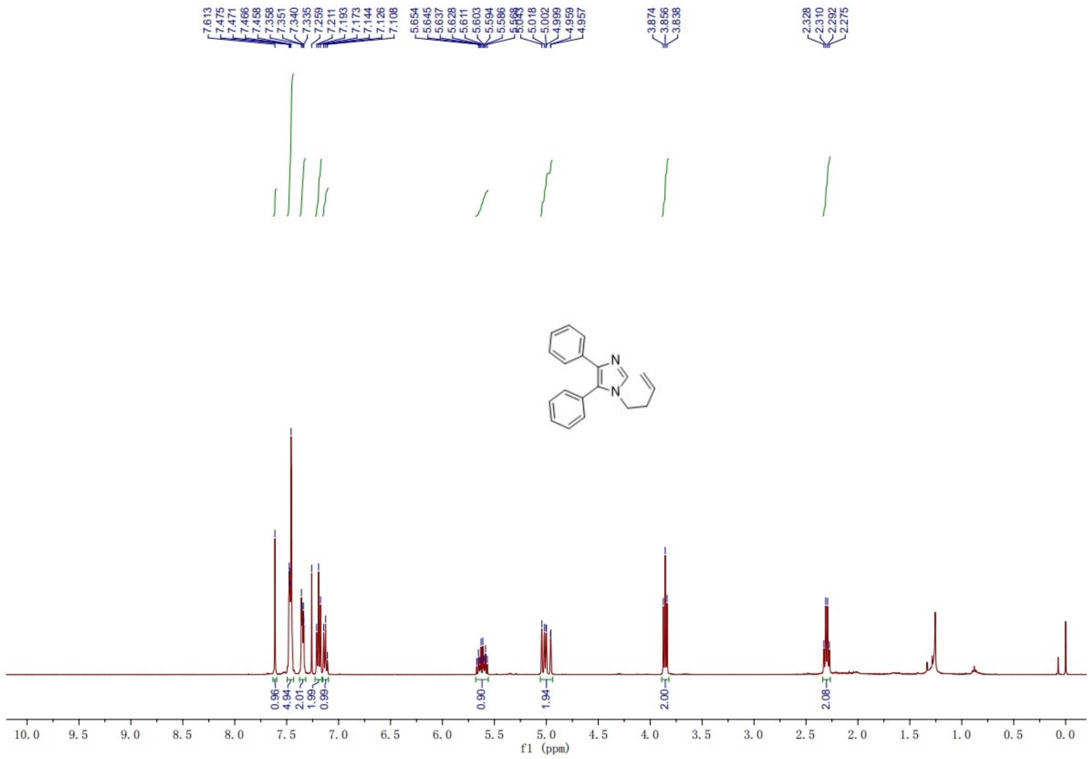


Figure S-40 ^{1}H NMR spectrum of **1s**

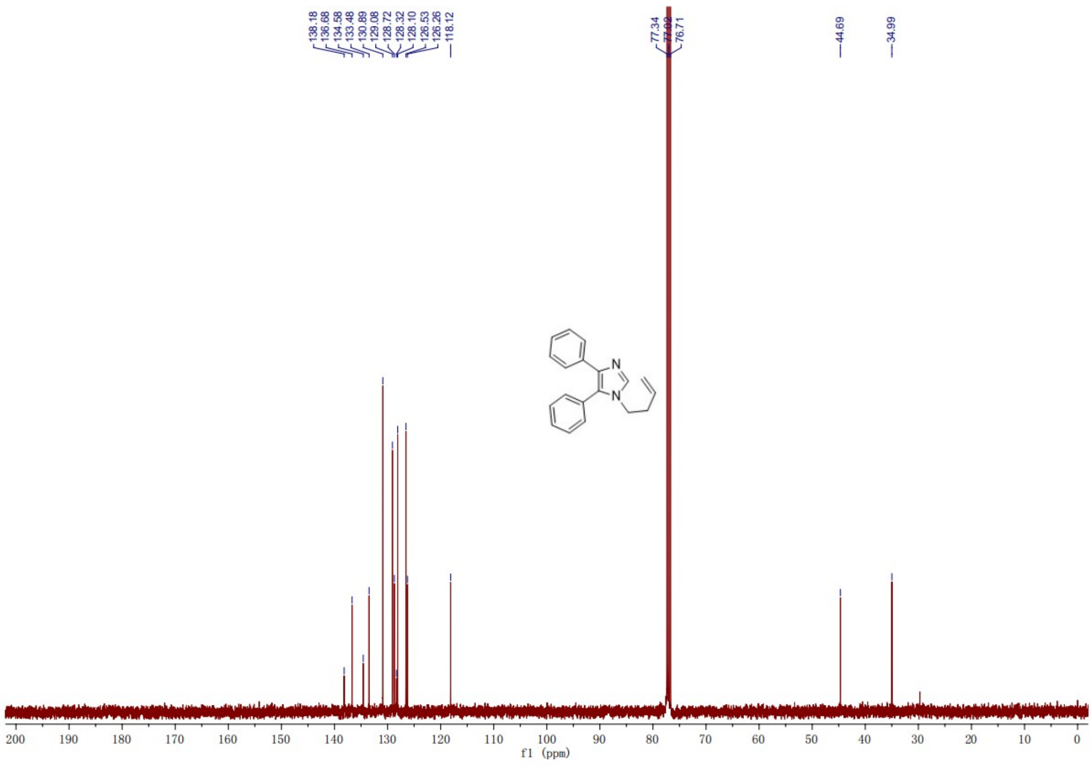


Figure S-41 ^{13}C NMR spectrum of **1s**

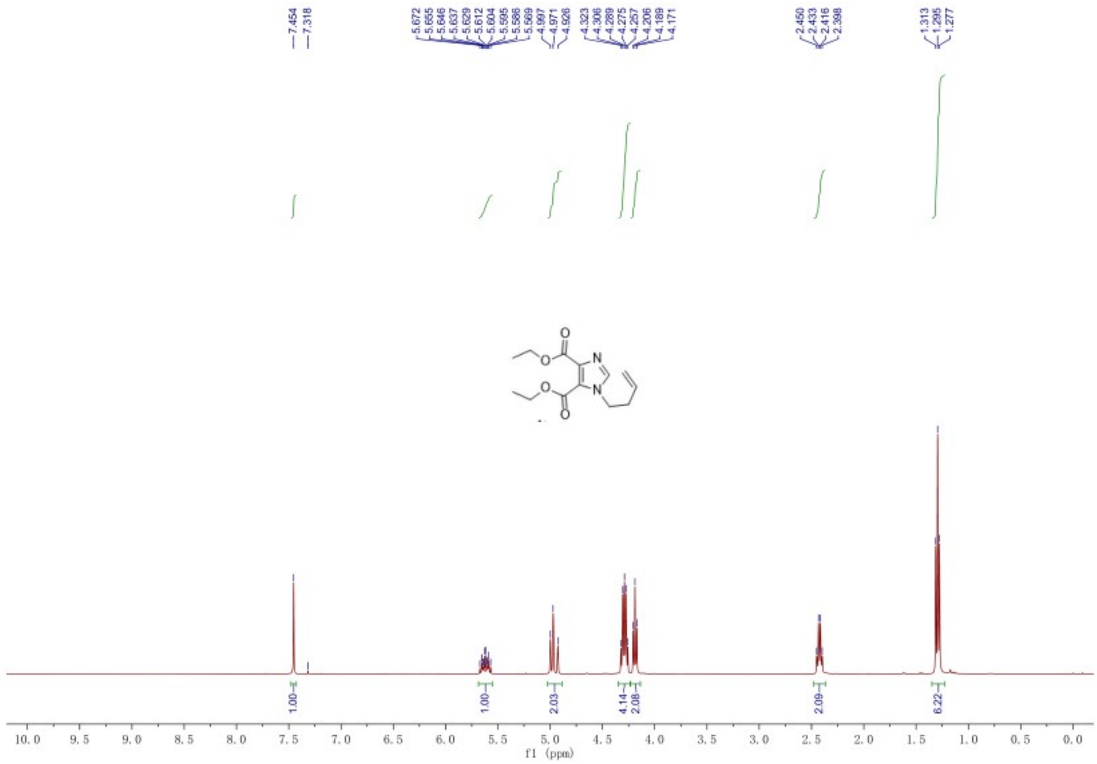


Figure S-42 ^{1}H NMR spectrum of **1t**

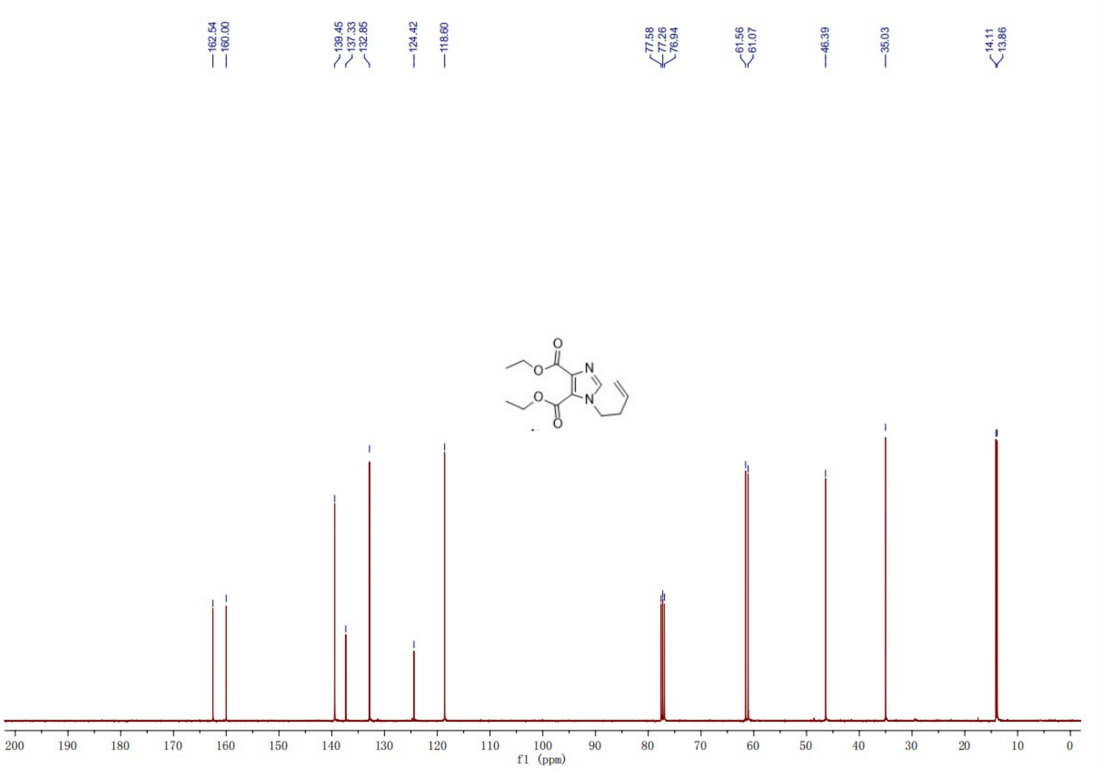


Figure S-43 ^{13}C NMR spectrum of **1t**

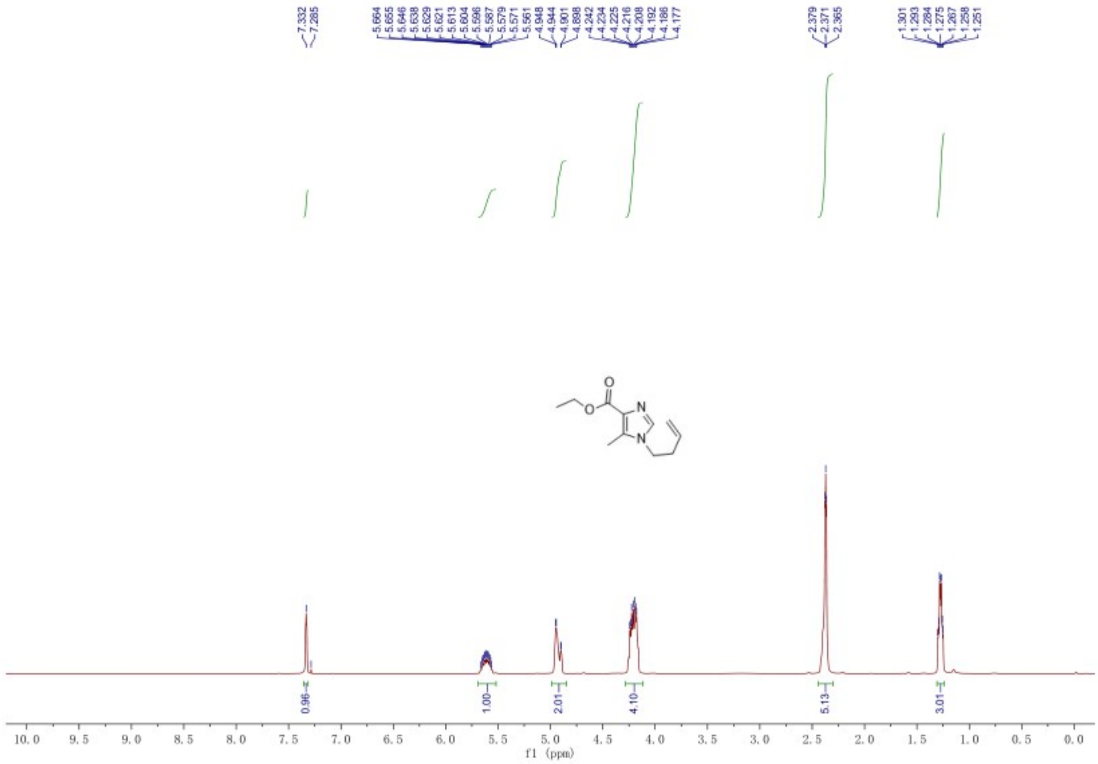


Figure S-44 ^{1}H NMR spectrum of **1u**

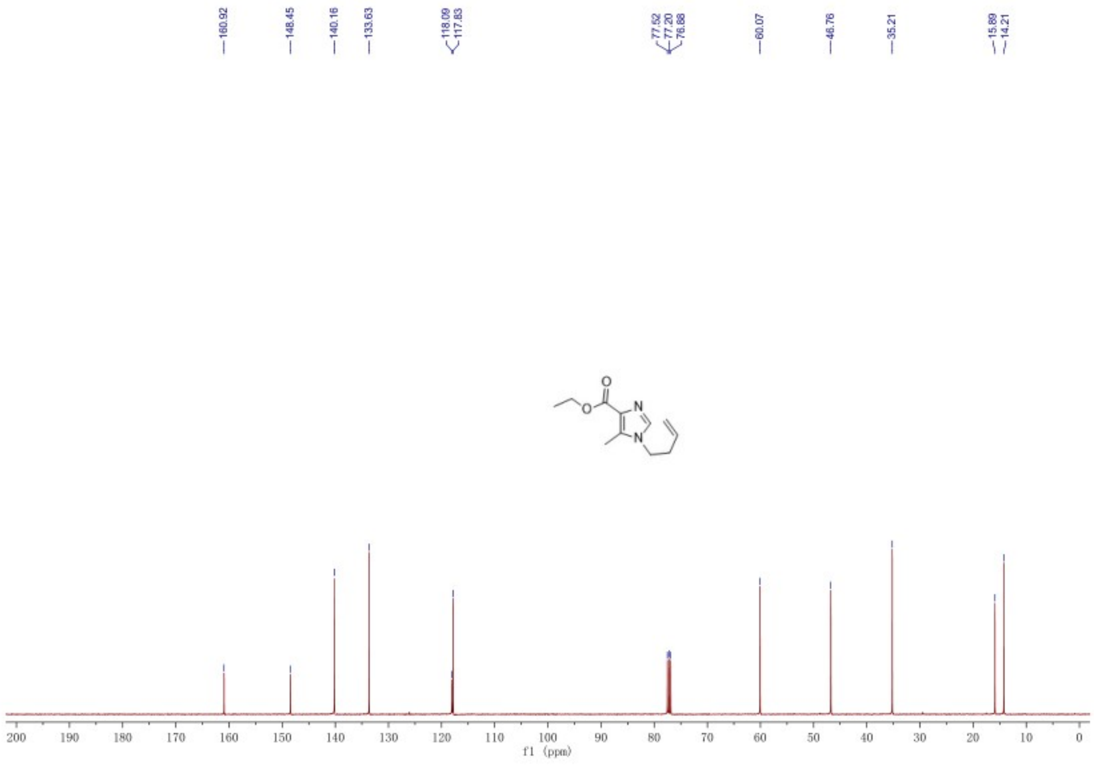


Figure S-45 ^{13}C NMR spectrum of **1u**

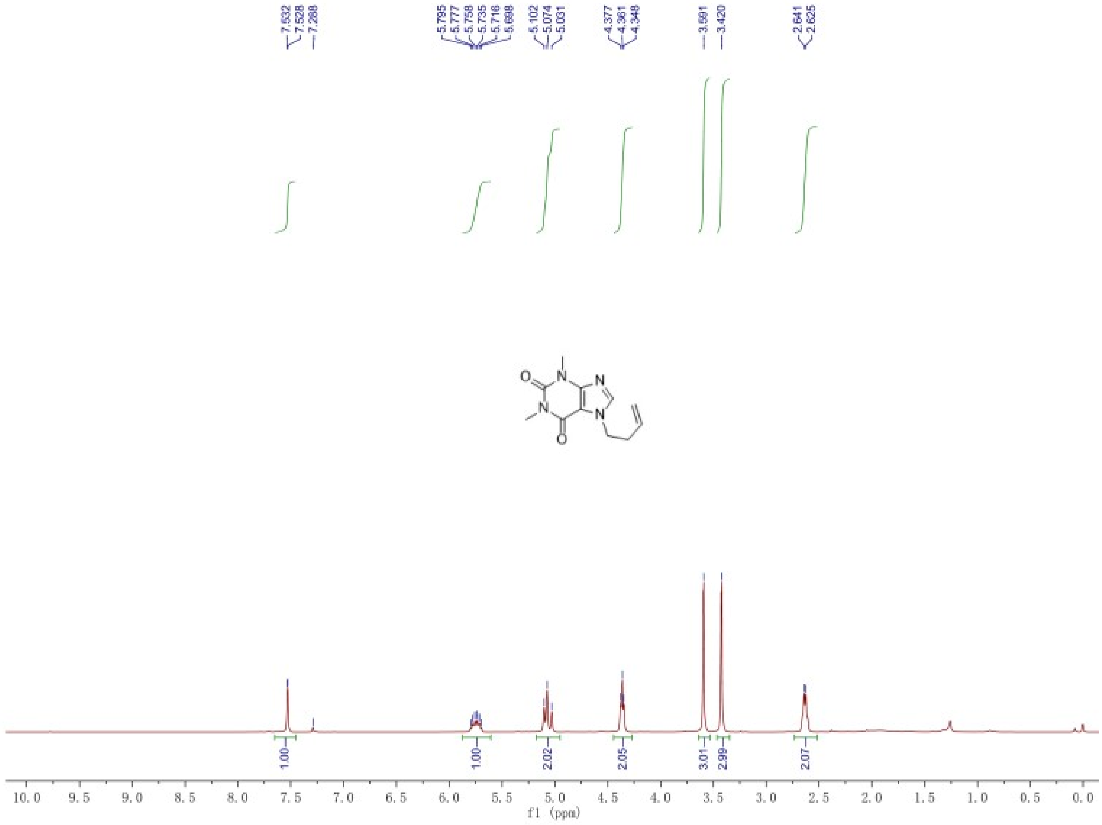


Figure S-46 [1]H NMR spectrum of **1v**

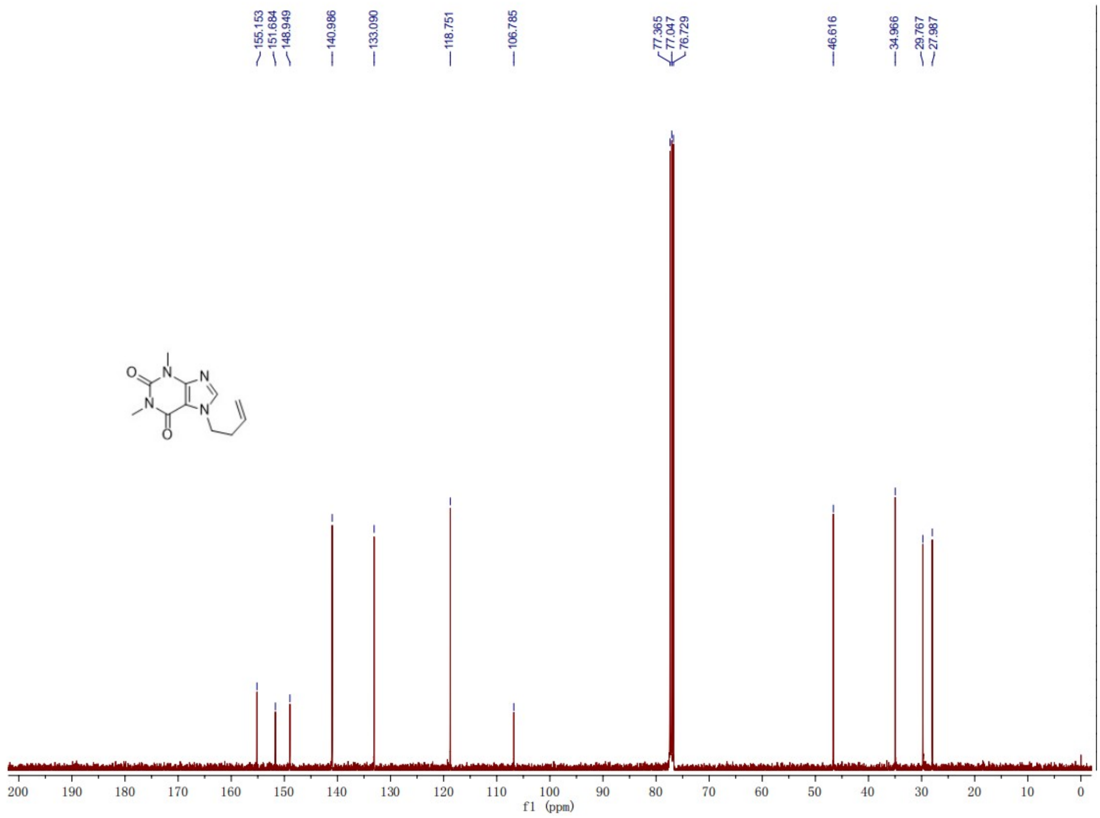


Figure S-47 [13]C NMR spectrum of **1v**

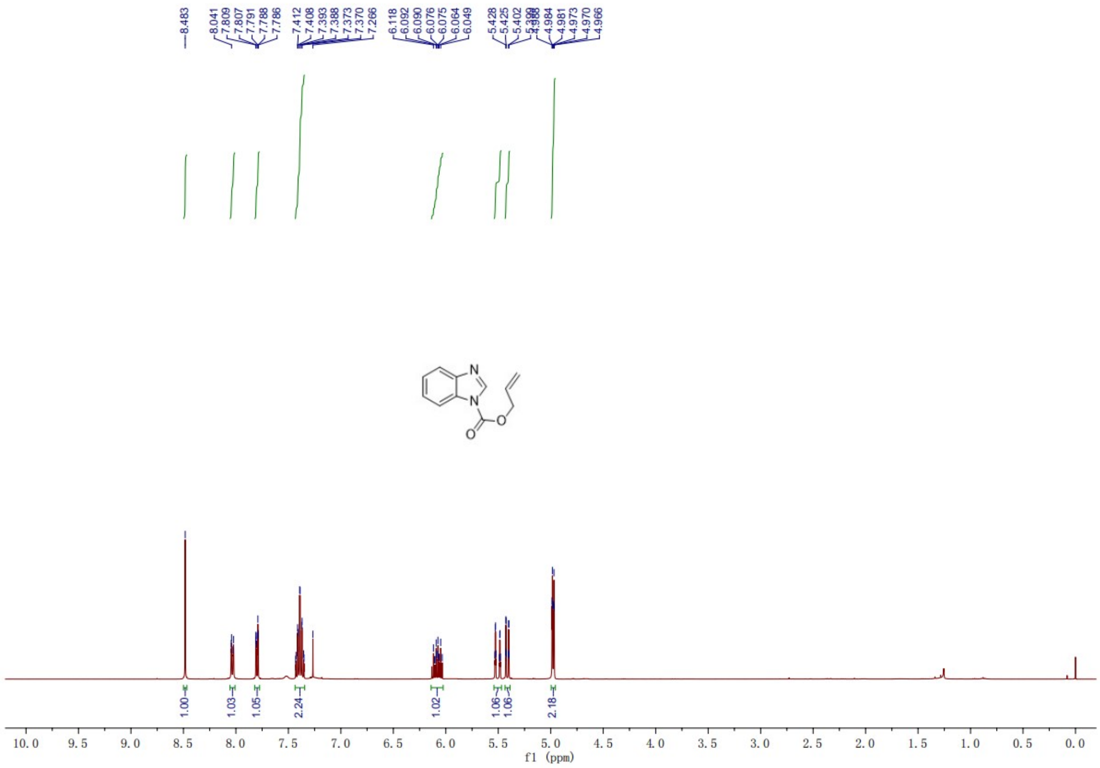


Figure S-48 ^{1}H NMR spectrum of **1w**

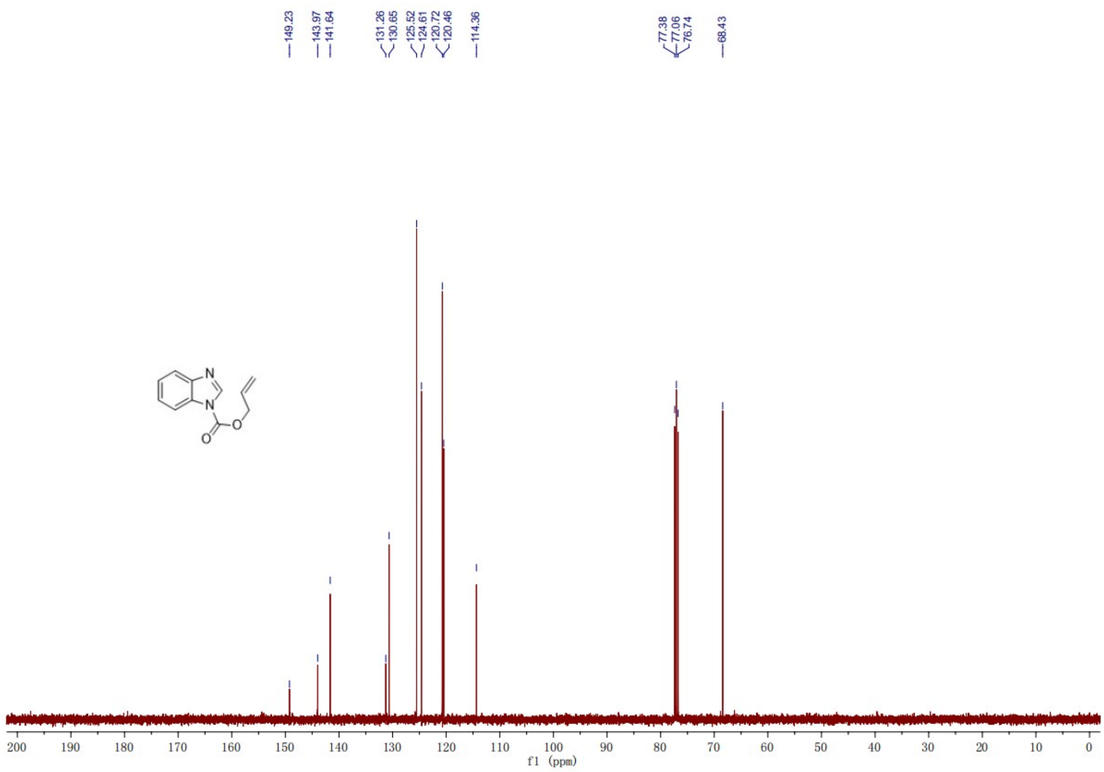


Figure S-49 ^{13}C NMR spectrum of **1w**

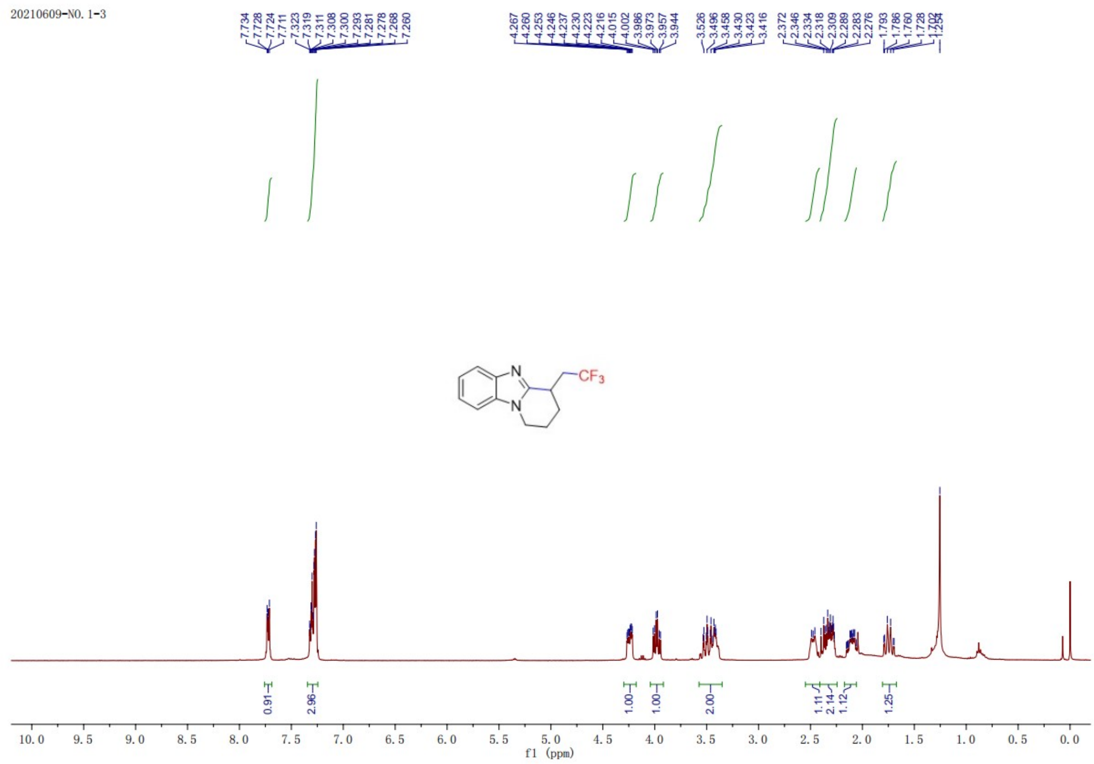


Figure S-50 ^{1}H NMR spectrum of **3aa**

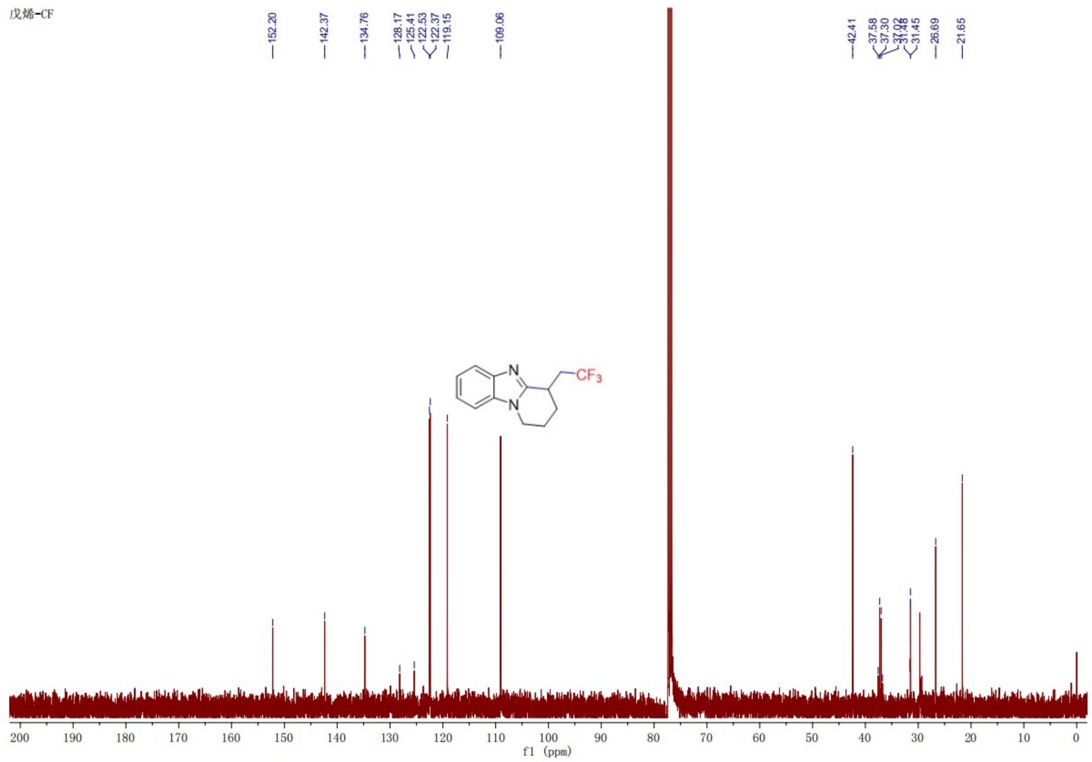


Figure S-51 ^{13}C NMR spectrum of **3aa**

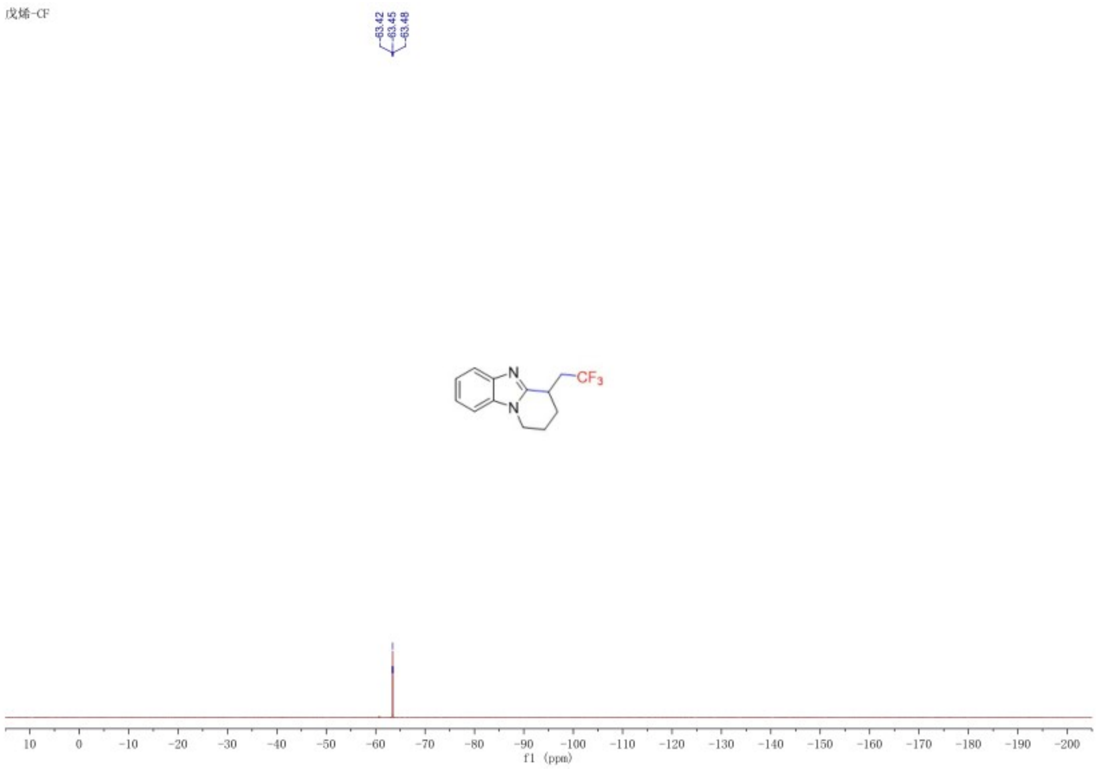


Figure S-52 ^{19}F NMR spectrum of **3aa**

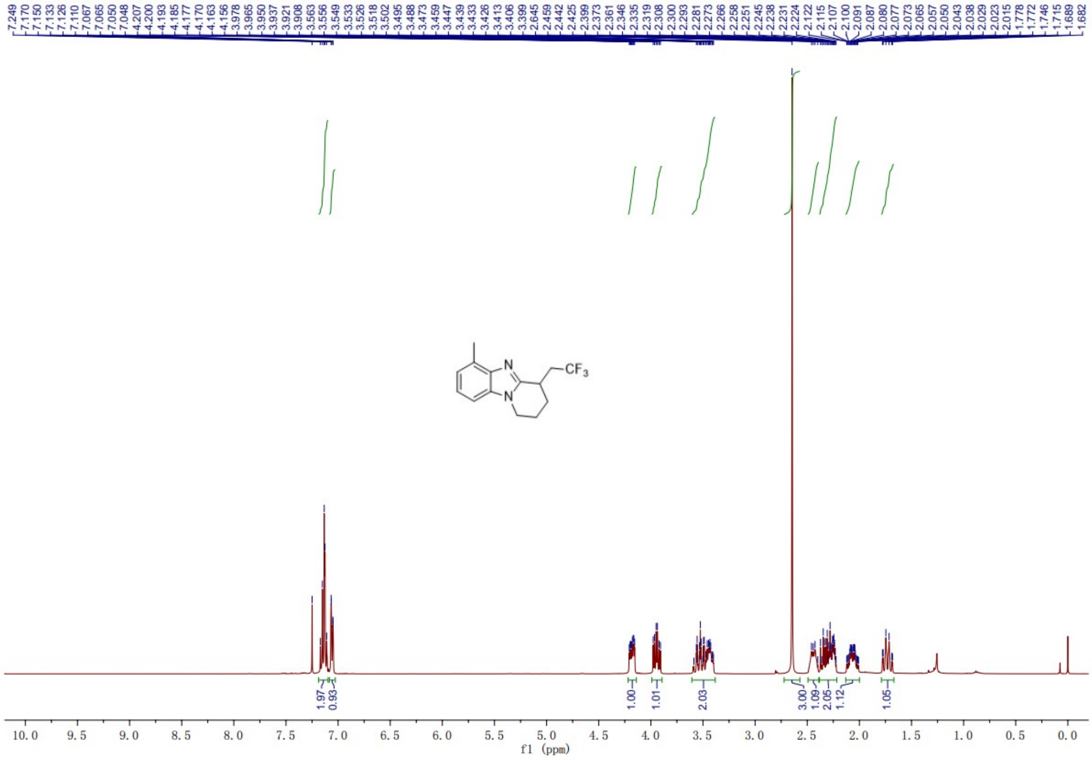


Figure S-53 ^{1}H NMR spectrum of **3ba**

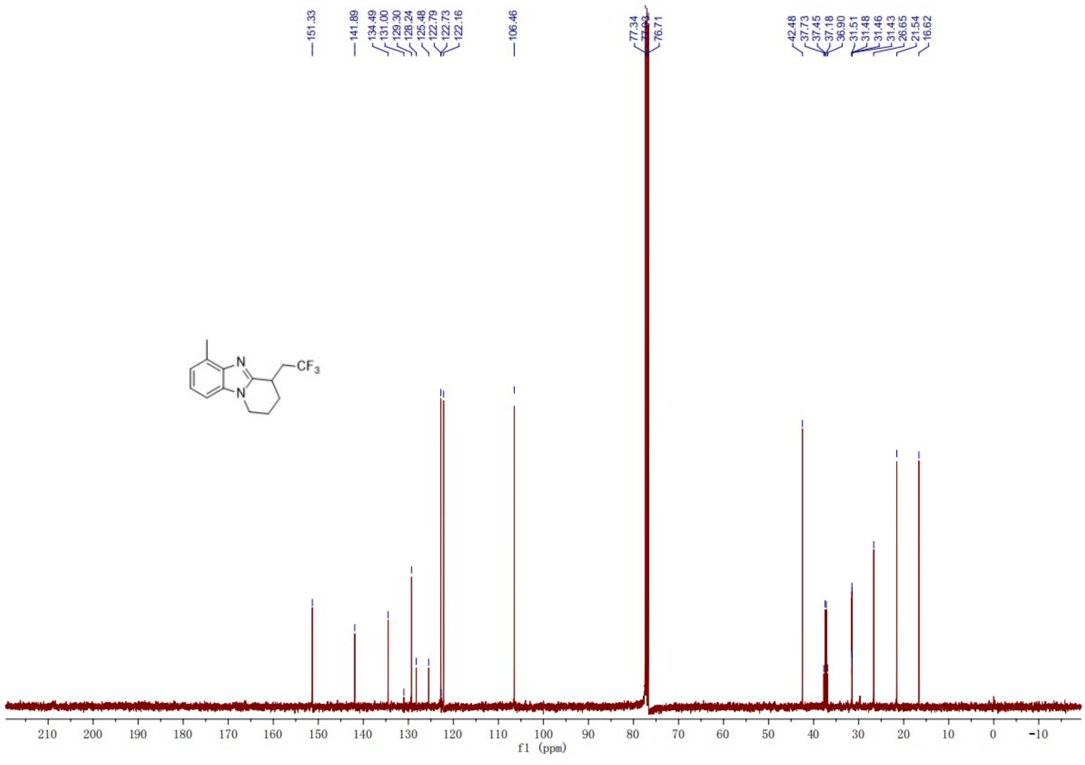


Figure S-54 ^{13}C NMR spectrum of **3ba**

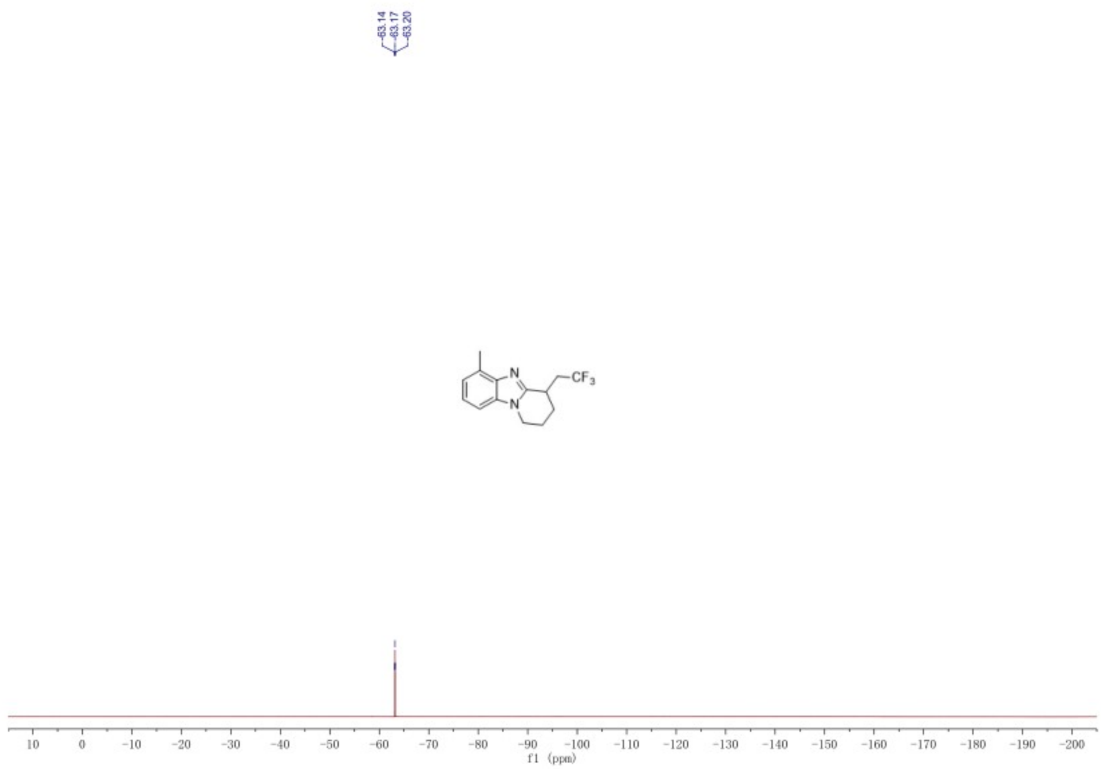


Figure S-55 ^{19}F NMR spectrum of **3ba**

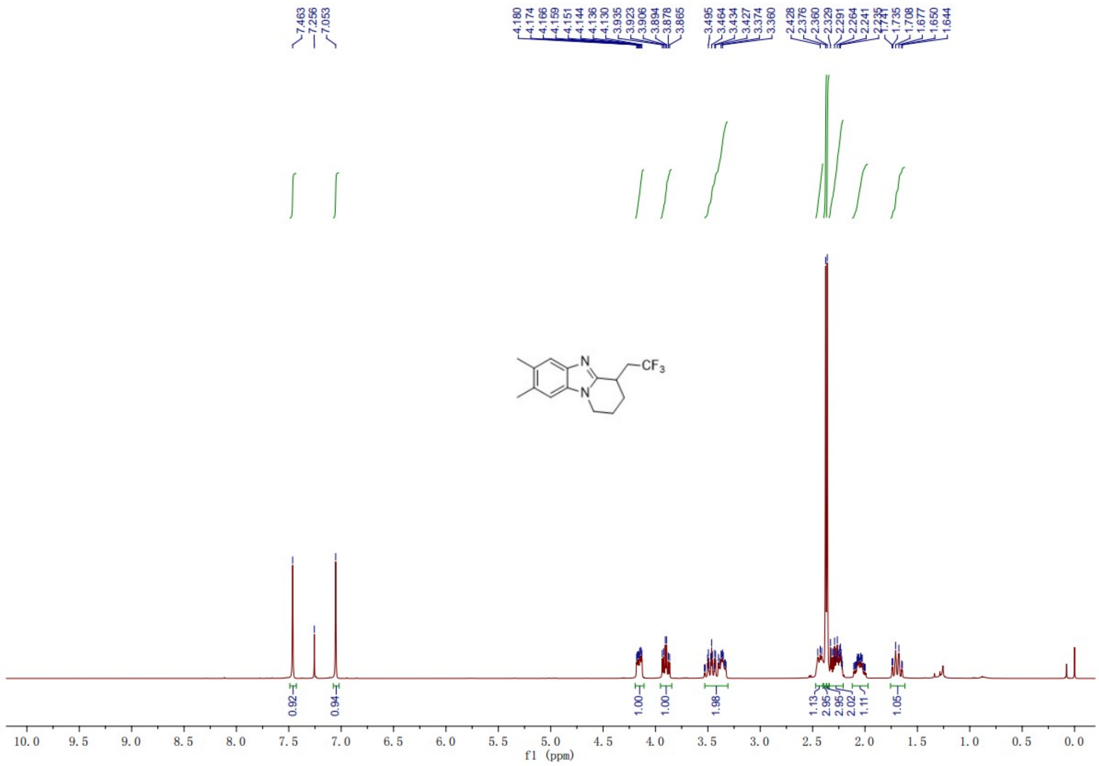


Figure S-56 ^{1}H NMR spectrum of **3ca**

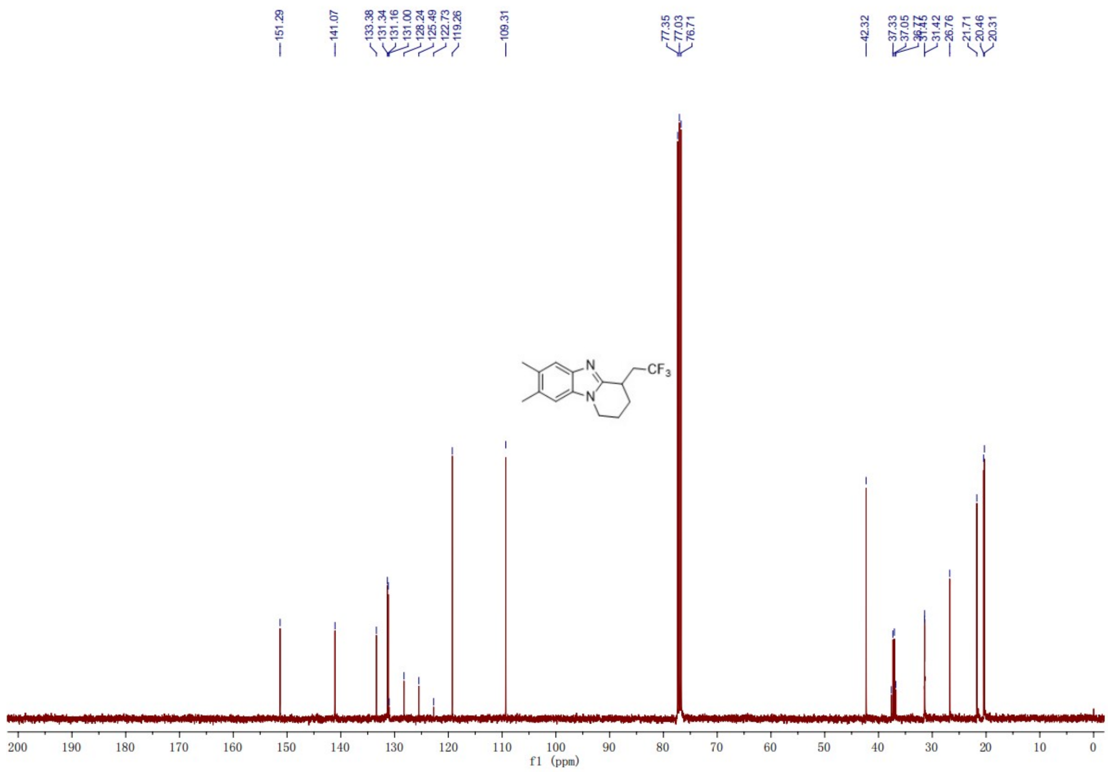


Figure S-57 ^{13}C NMR spectrum of **3ca**

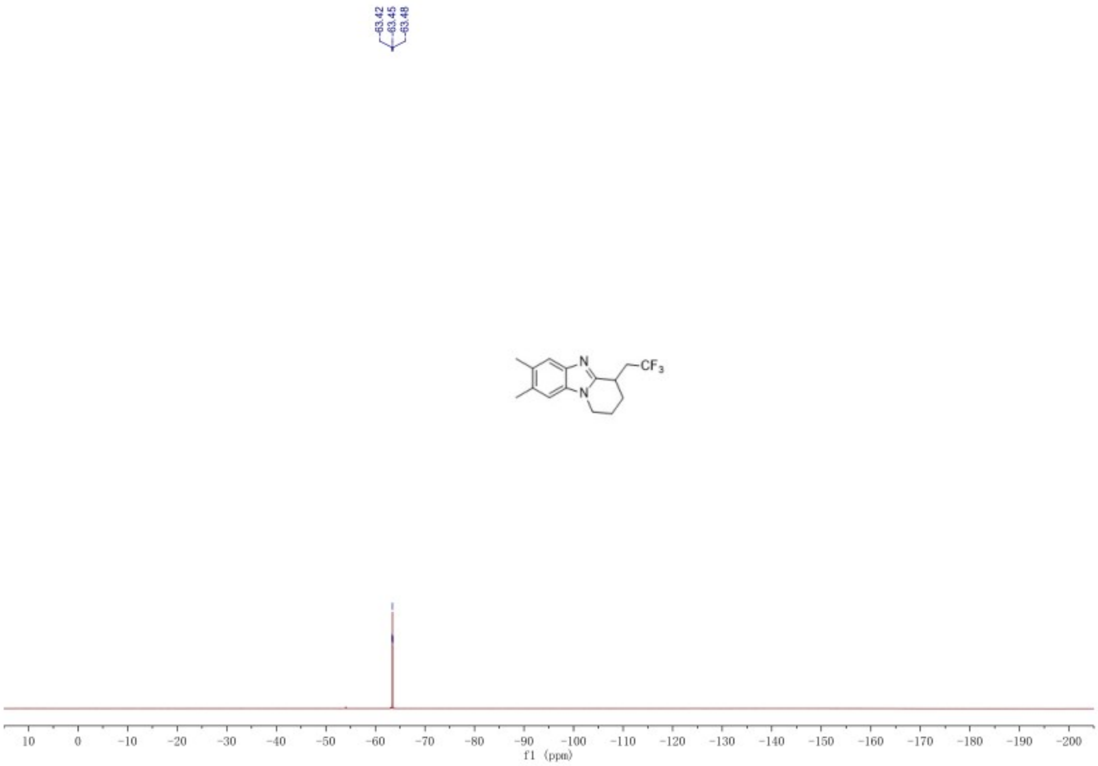


Figure S-58 ^{19}F NMR spectrum of **3ca**

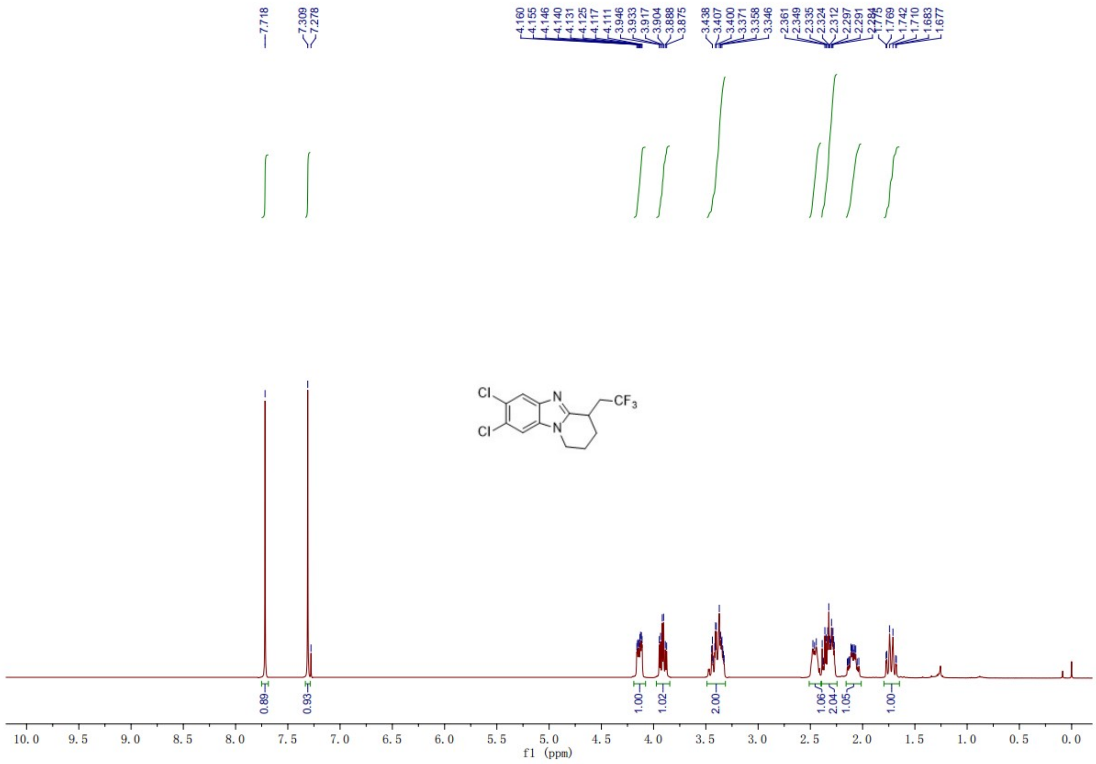


Figure S-59 ^{1}H NMR spectrum of **3da**

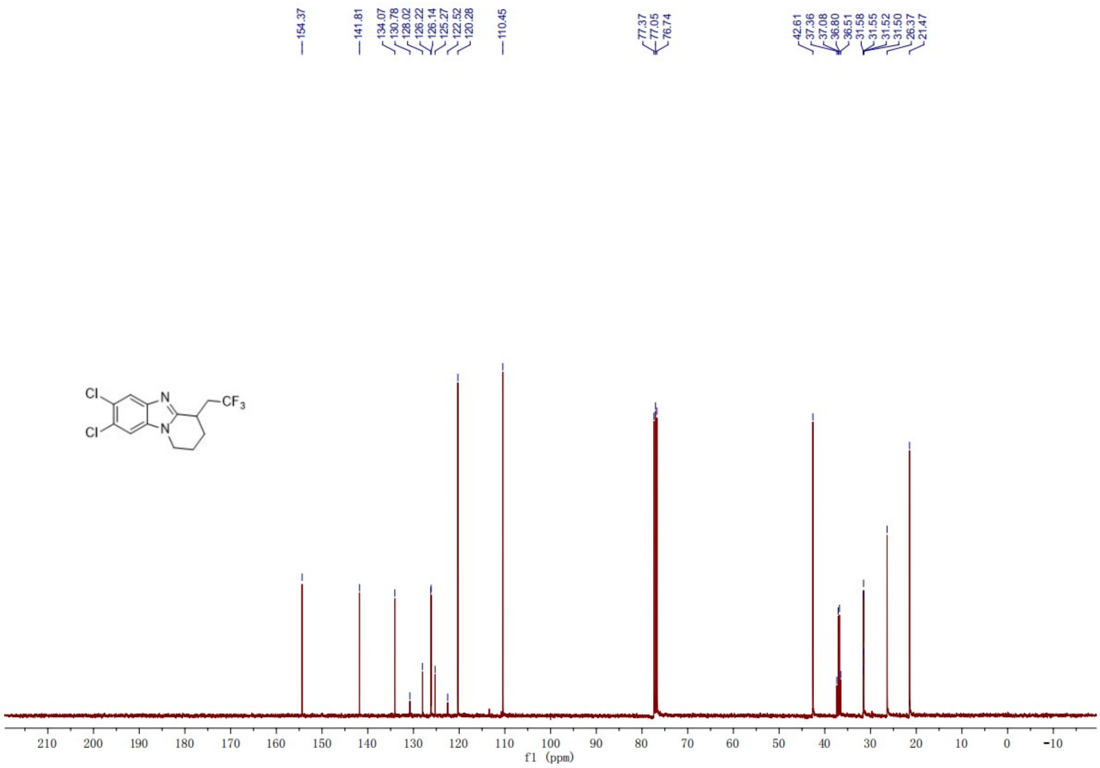


Figure S-60 ^{13}C NMR spectrum of **3da**

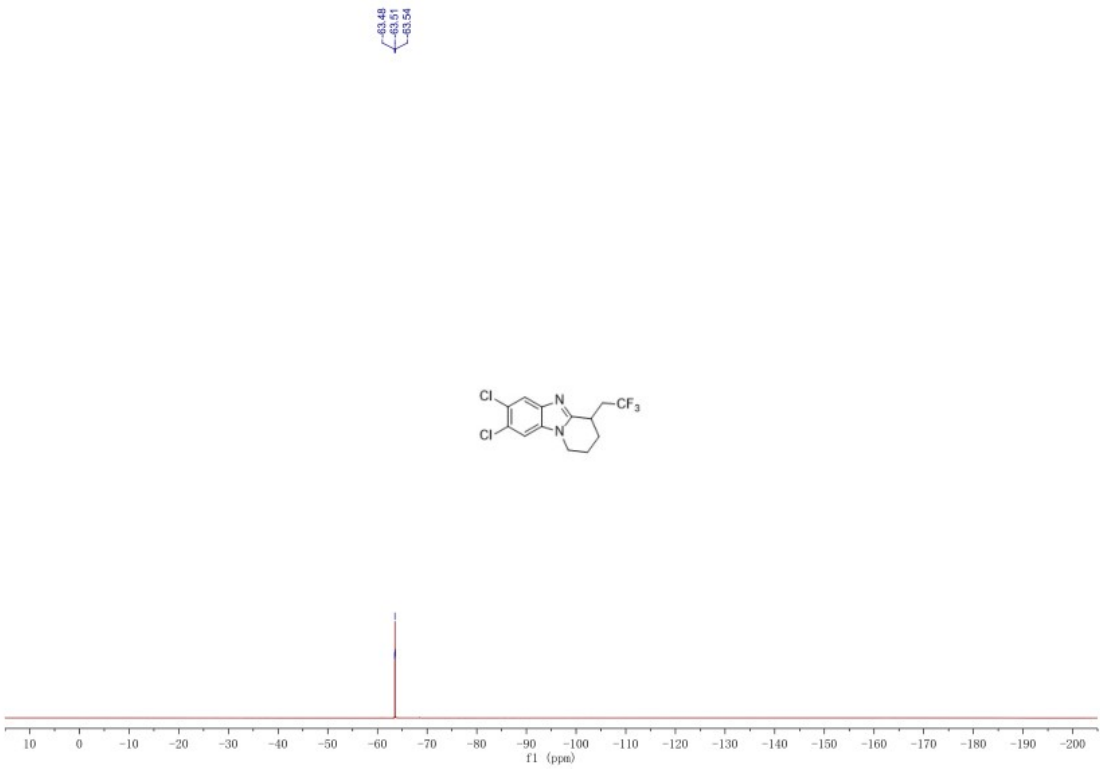


Figure S-61 ^{19}F NMR spectrum of **3da**

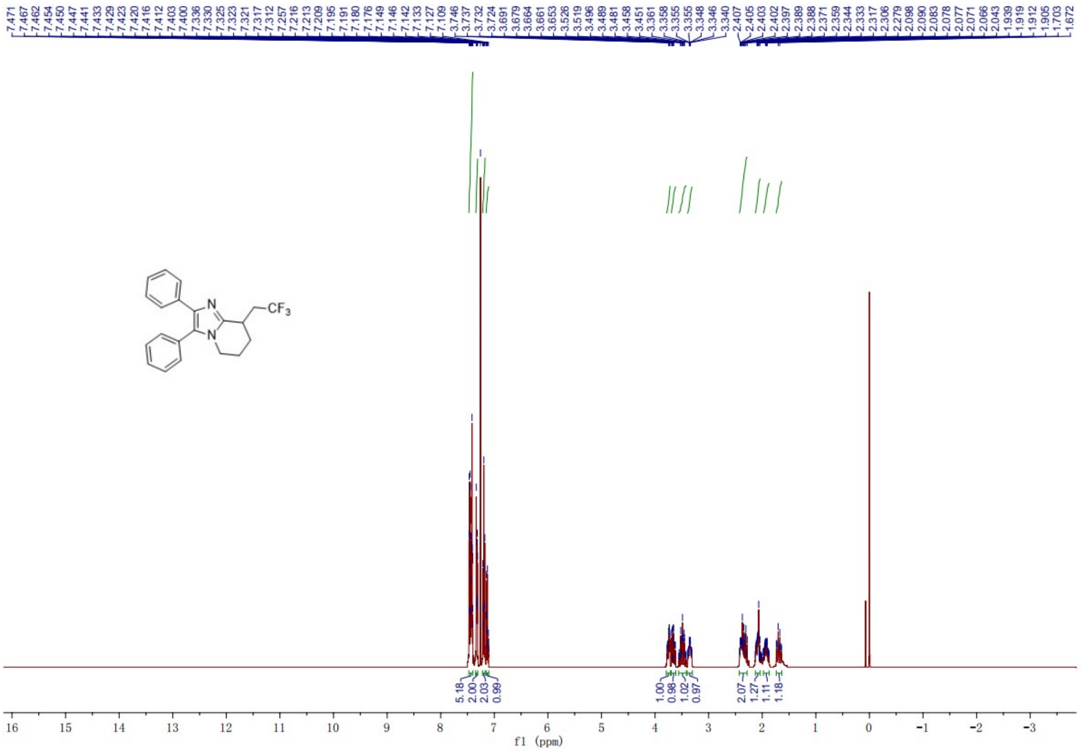


Figure S-62 ^{1}H NMR spectrum of **3ea**

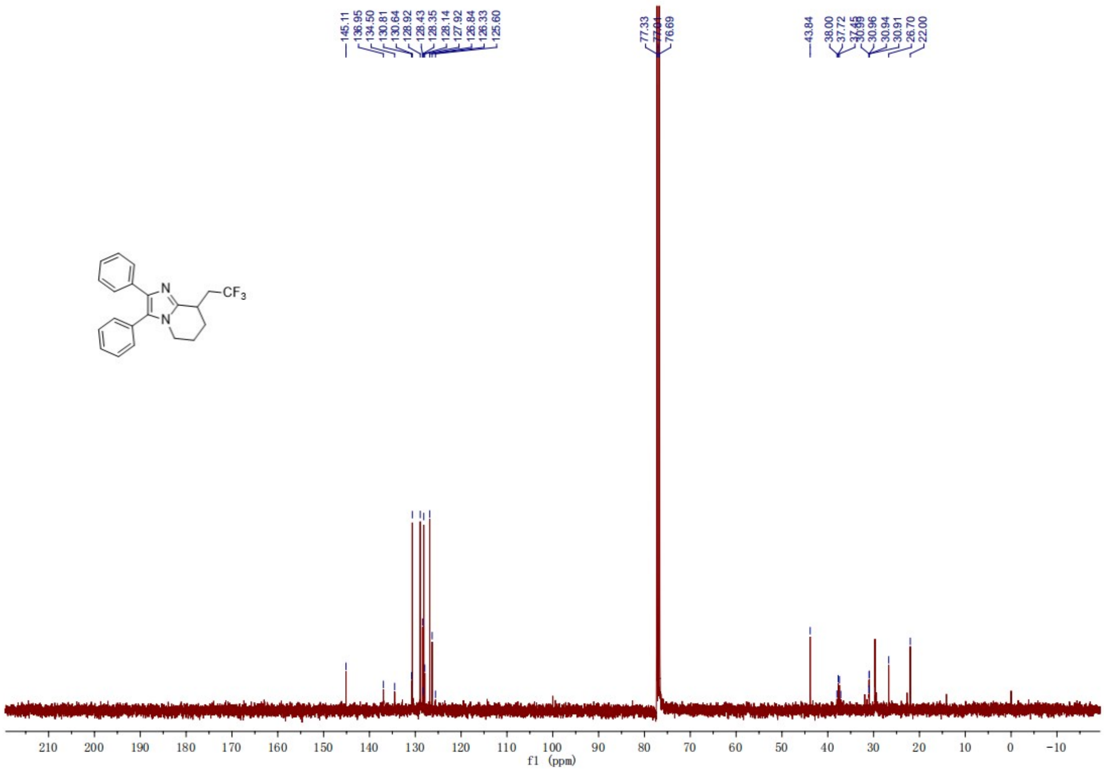


Figure S-63 ^{13}C NMR spectrum of **3ea**

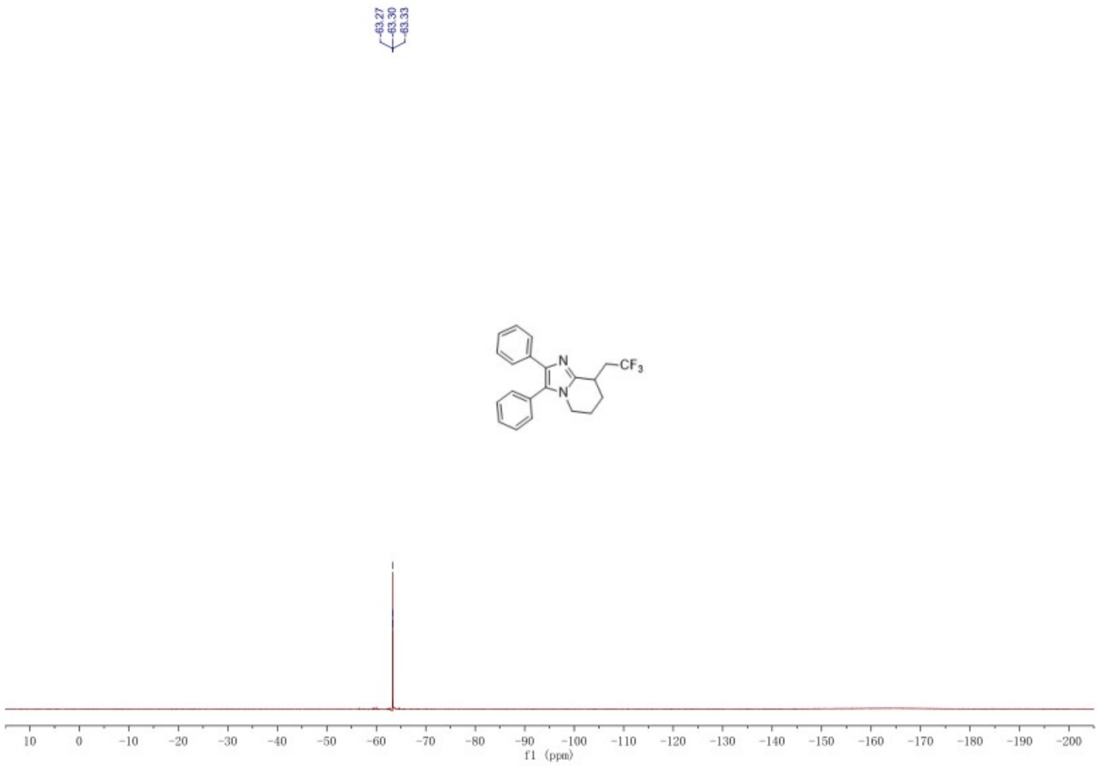


Figure S-64 ^{19}F NMR spectrum of **3ea**

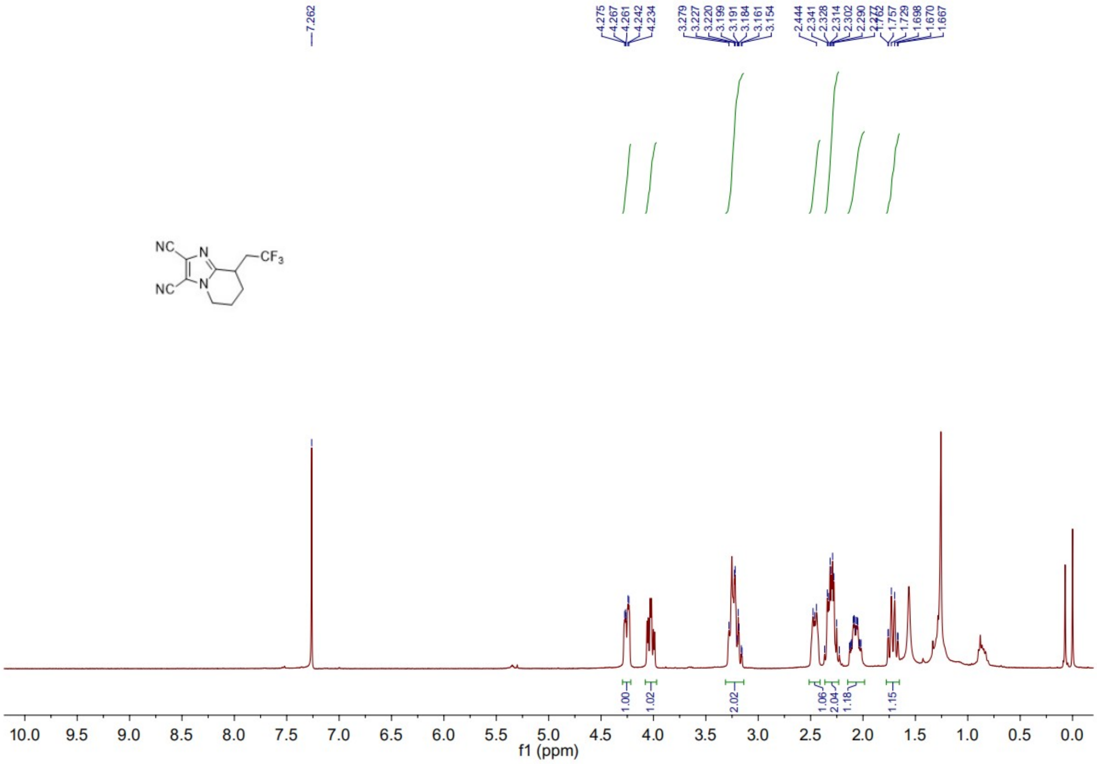


Figure S-65 ^{1}H NMR spectrum of **3fa**

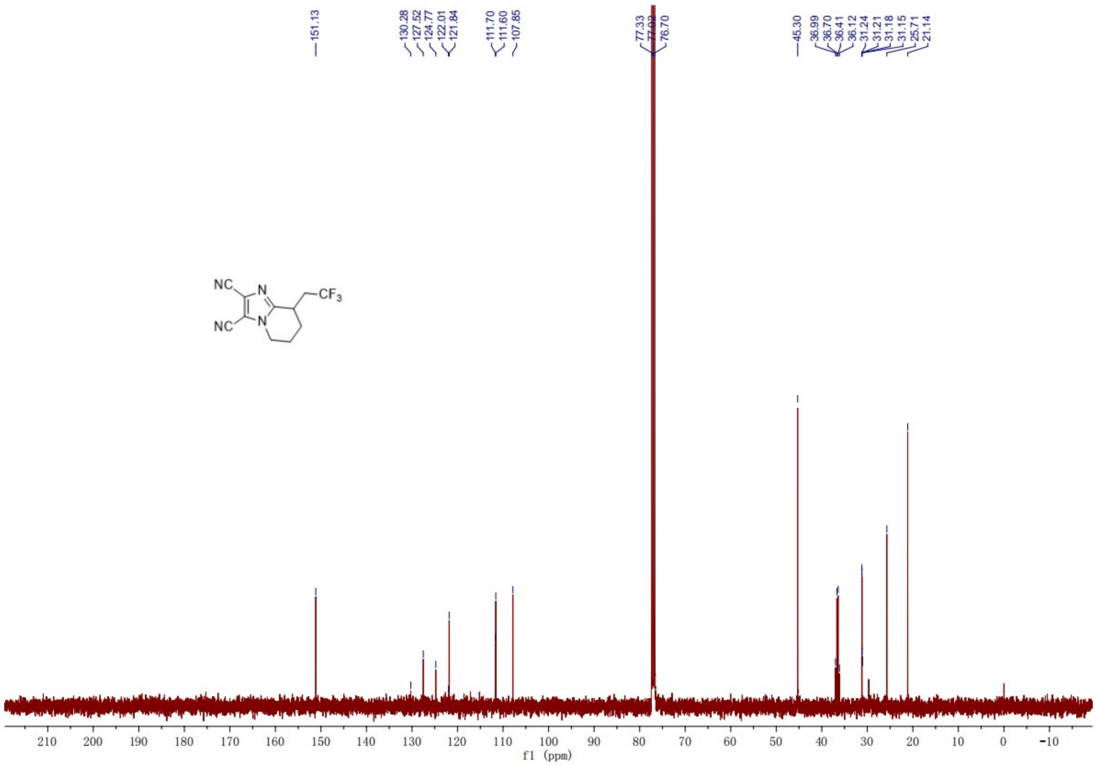


Figure S-66 ^{13}C NMR spectrum of **3fa**

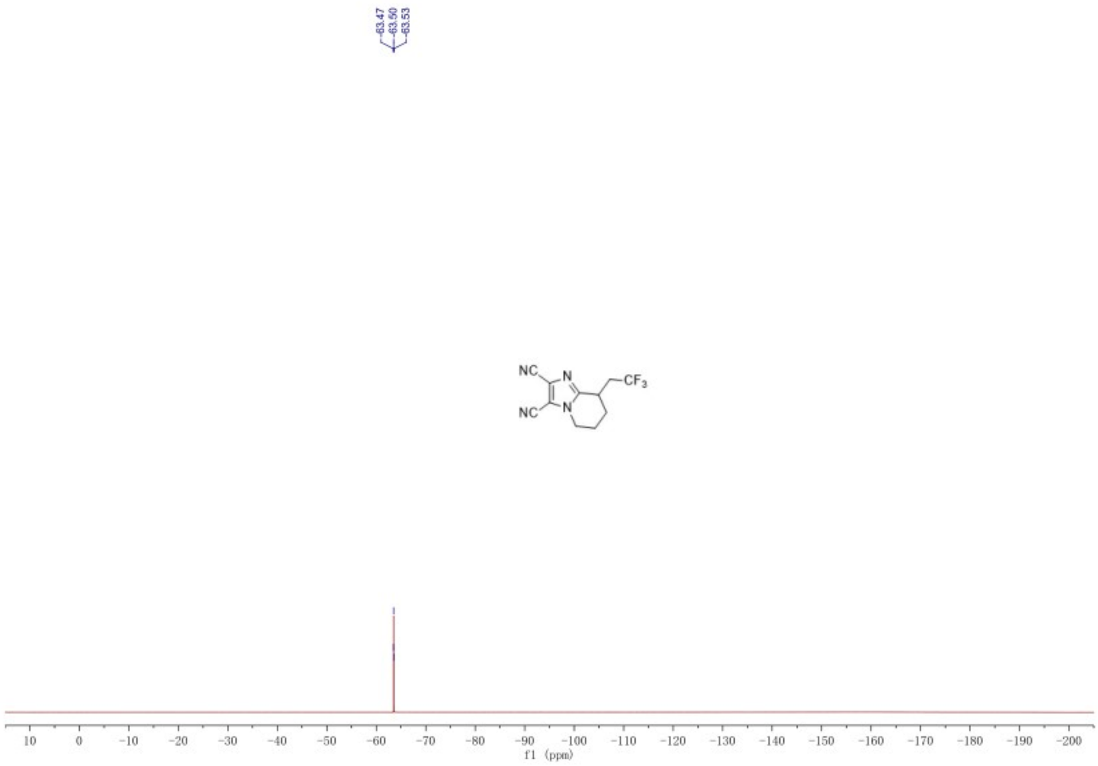


Figure S-67 [19]F NMR spectrum of **3fa**

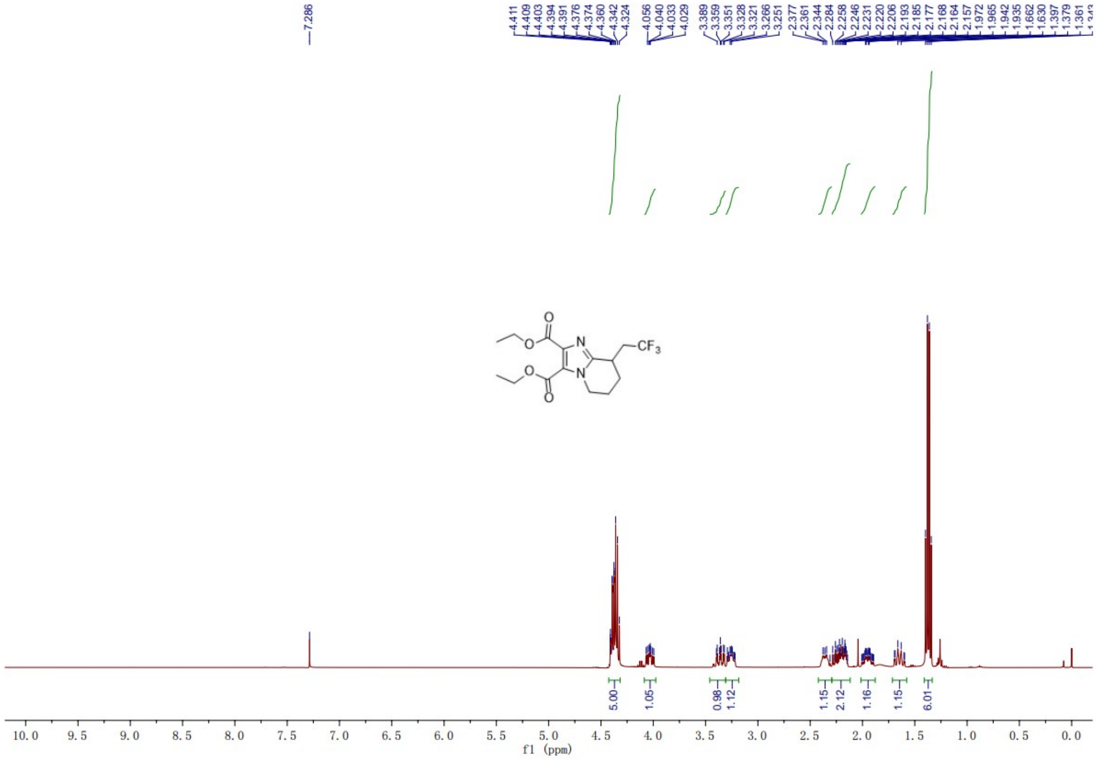


Figure S-68 ^{1}H NMR spectrum of **3ga**

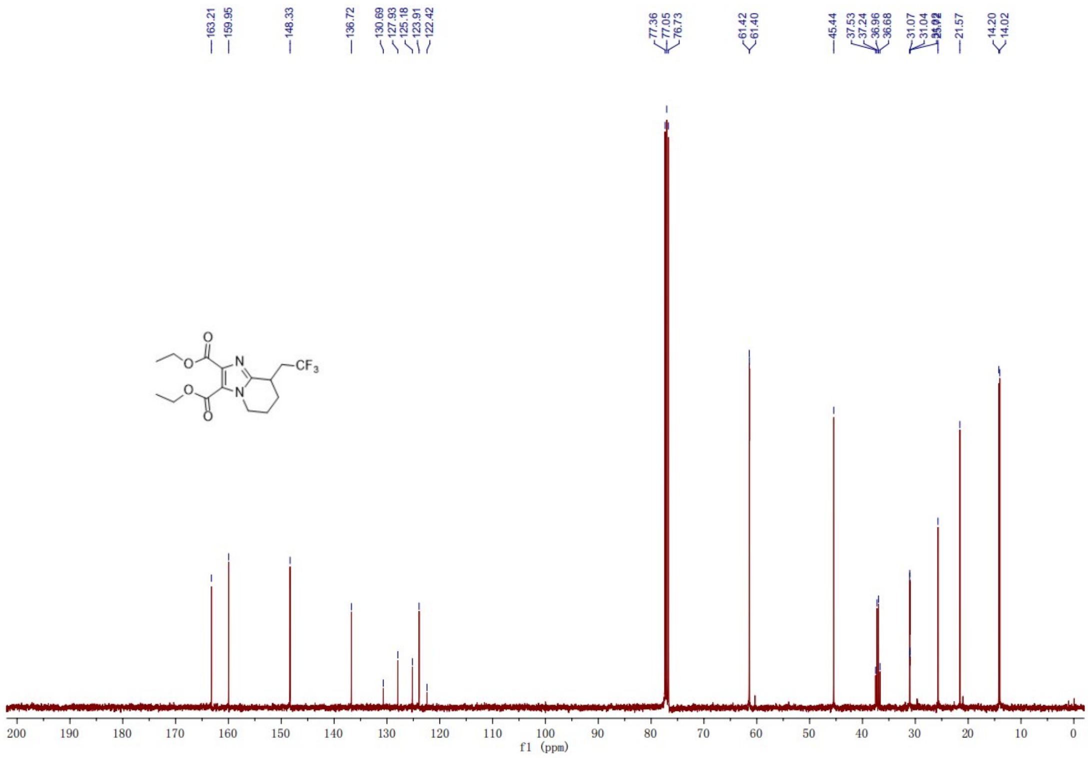


Figure S-69 ^{13}C NMR spectrum of **3ga**

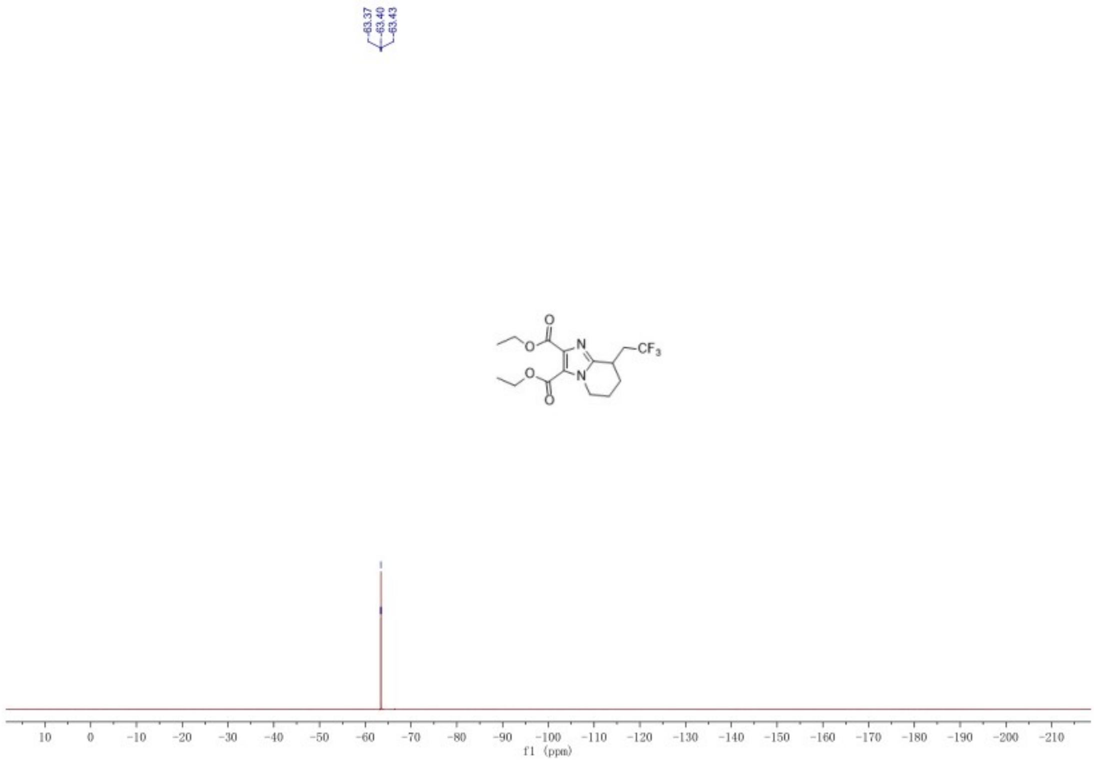


Figure S-70 ^{19}F NMR spectrum of **3ga**

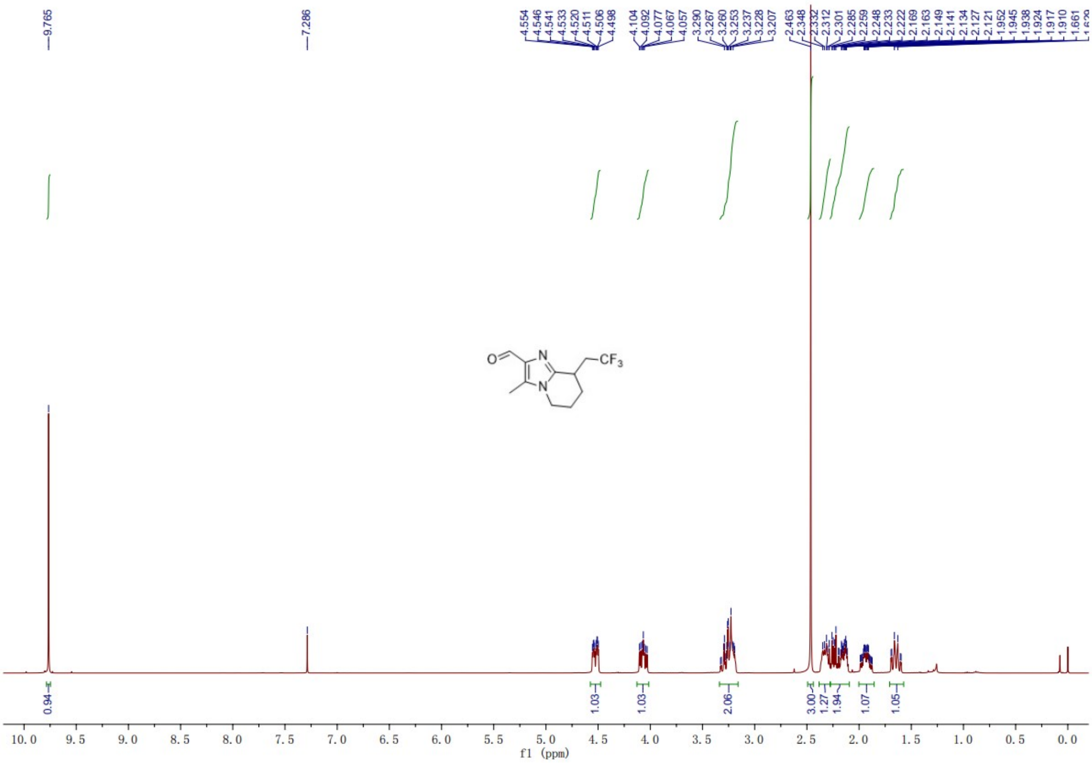


Figure S-71 ^{1}H NMR spectrum of **3ha**

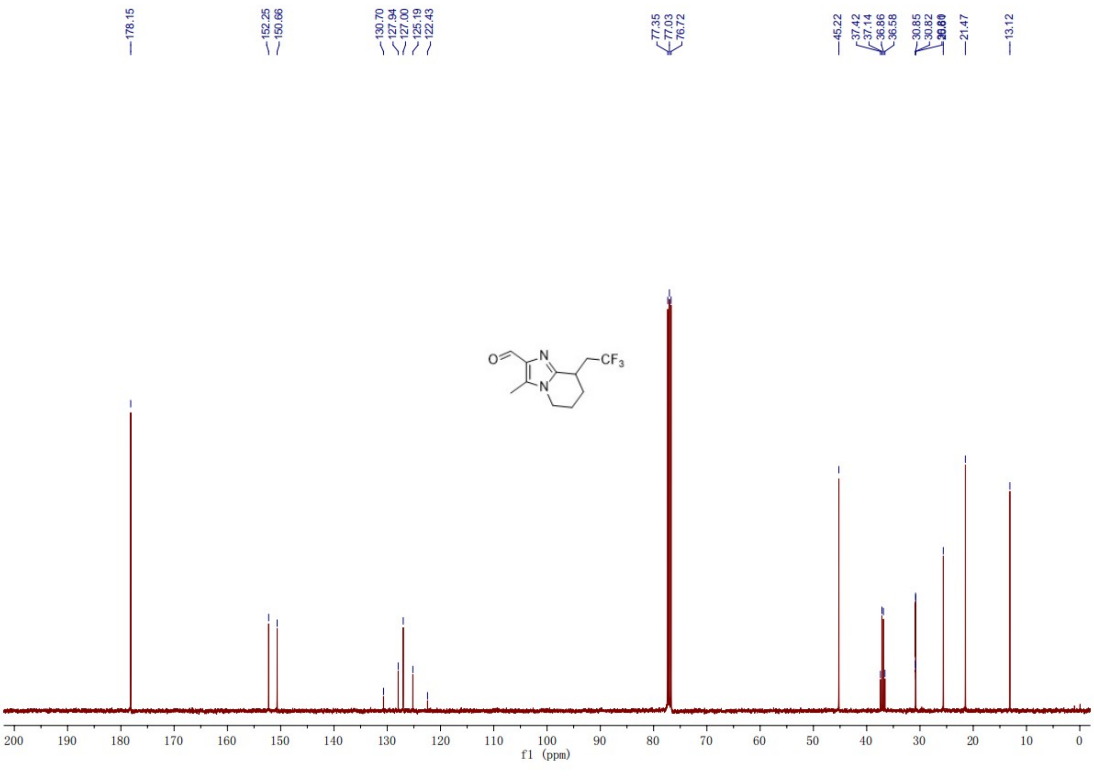


Figure S-72 ^{13}C NMR spectrum of **3ha**

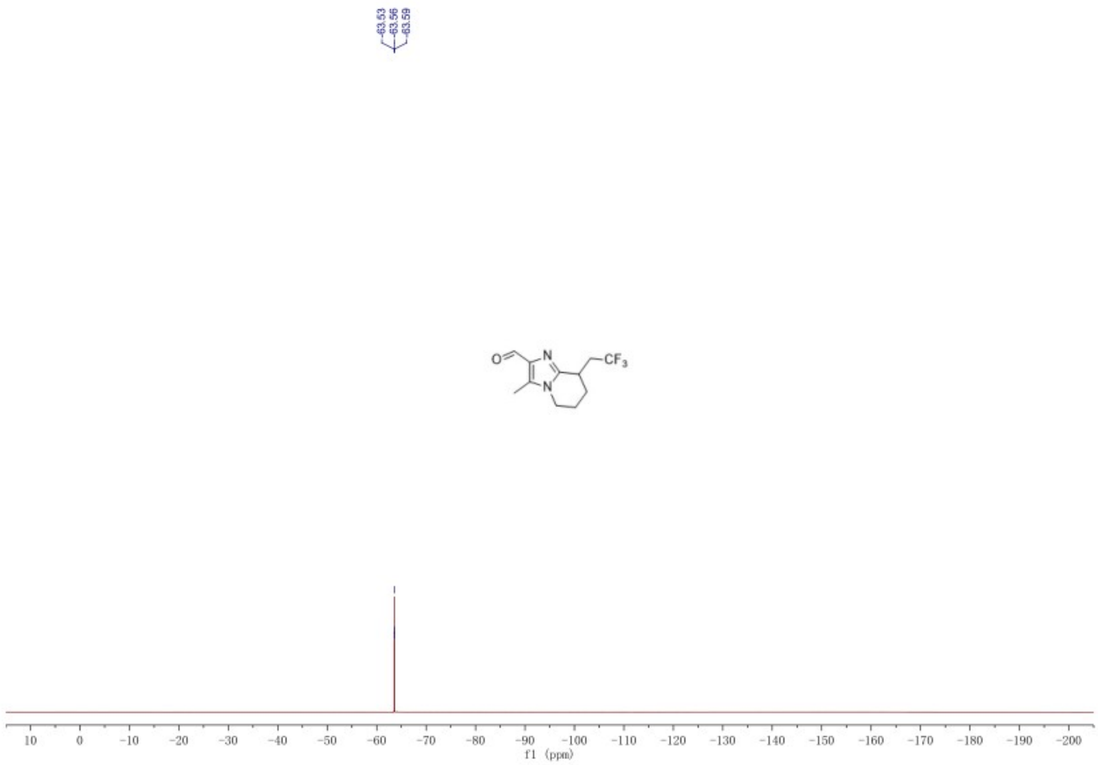


Figure S-73 ^{19}F NMR spectrum of **3ha**

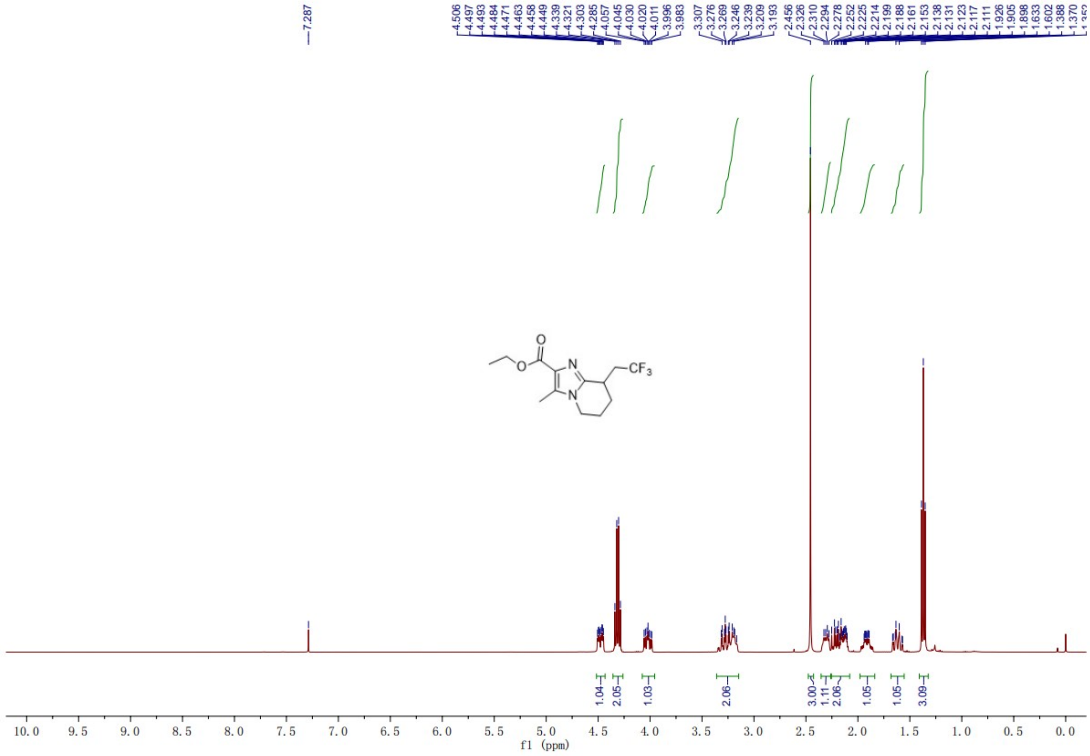


Figure S-74 ^{1}H NMR spectrum of **3ia**

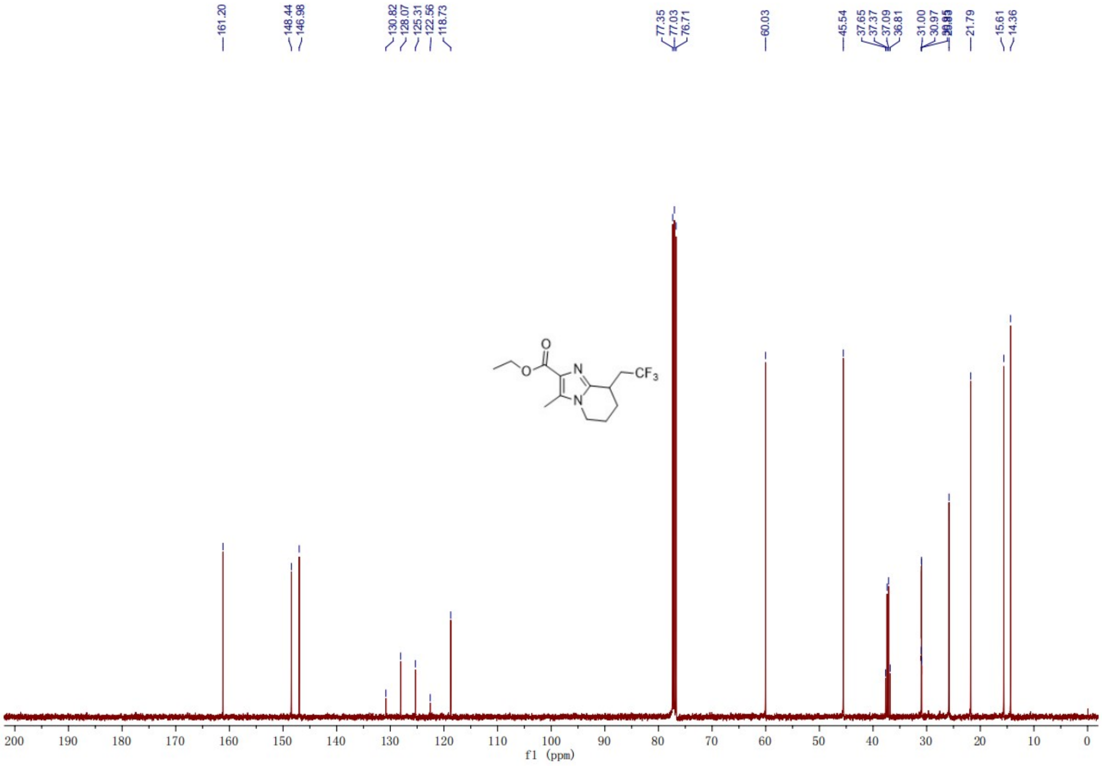


Figure S-75 ^{13}C NMR spectrum of **3ia**

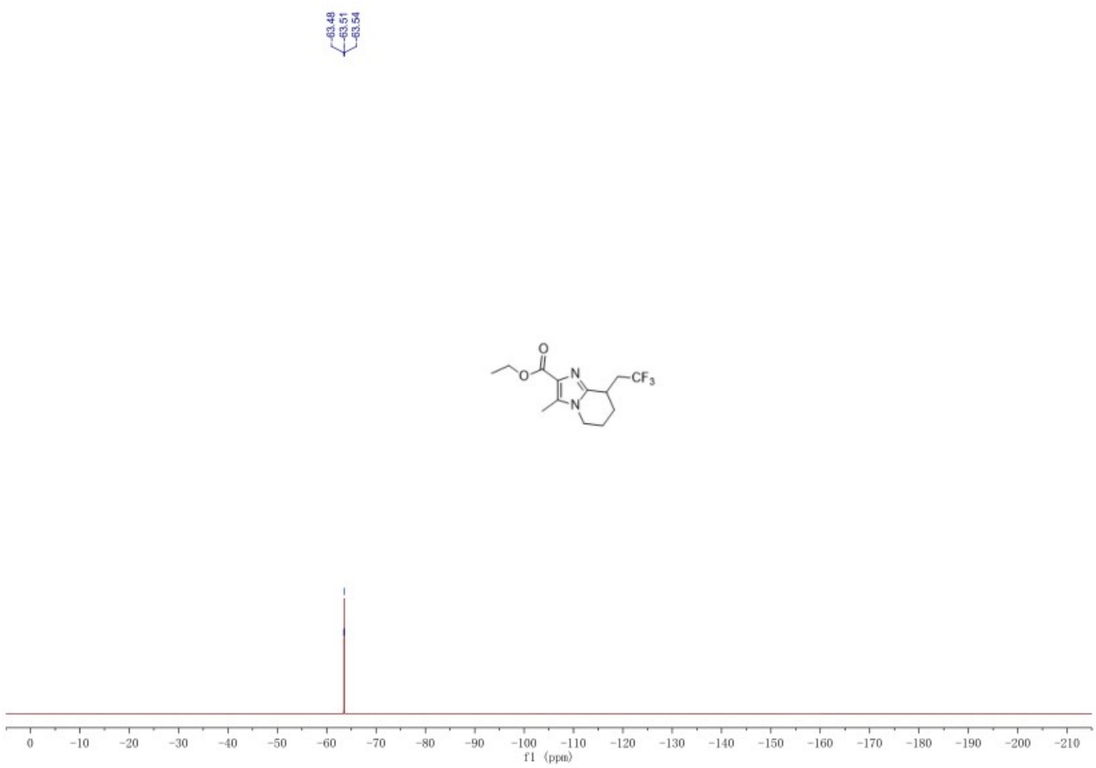


Figure S-76 [19]F NMR spectrum of **3ia**

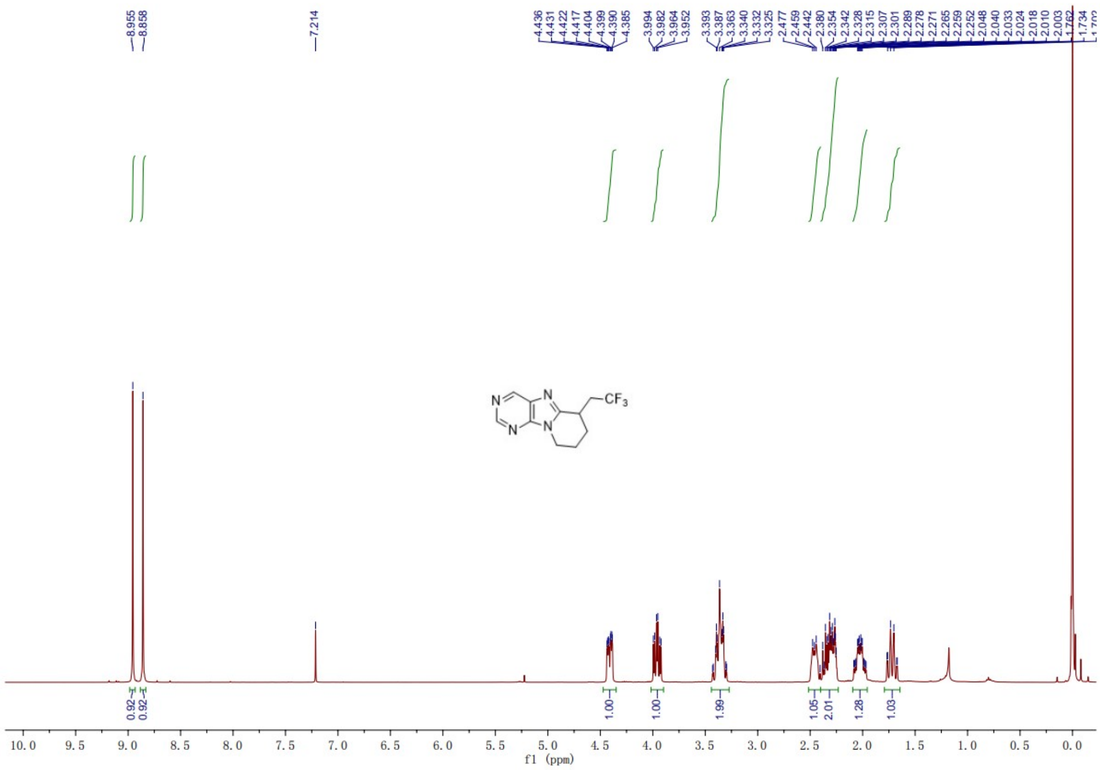


Figure S-77 ^{1}H NMR spectrum of **3ja**

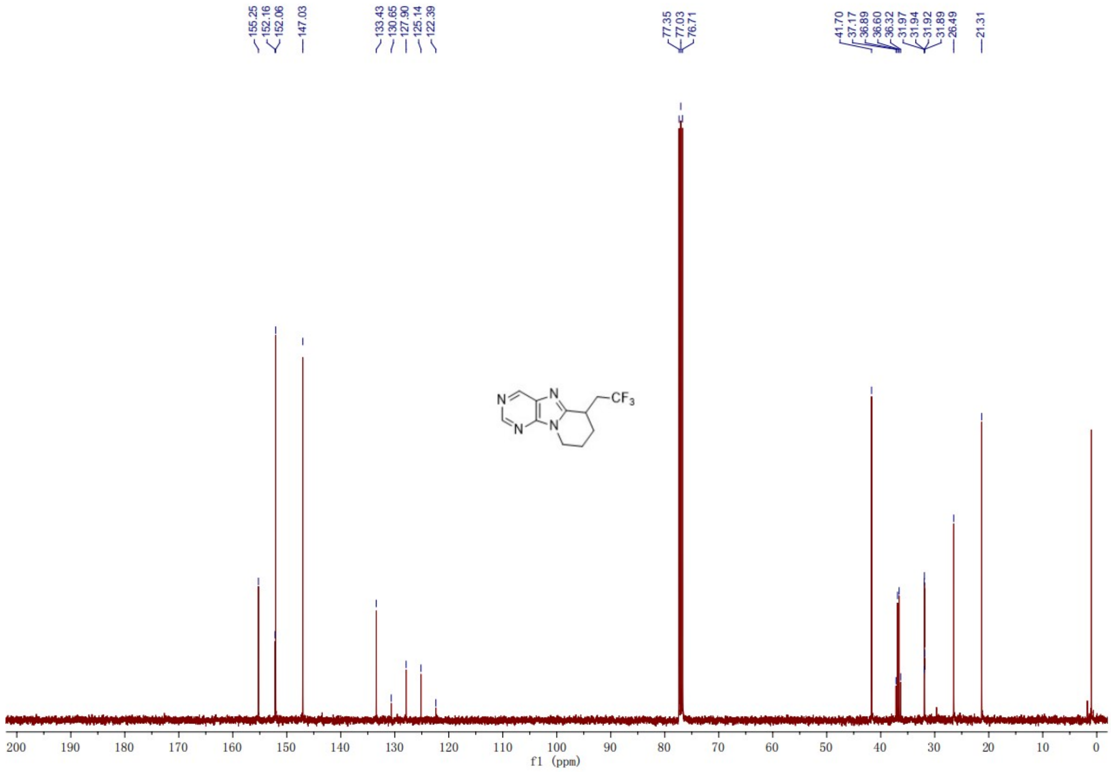


Figure S-78 ^{13}C NMR spectrum of **3ja**

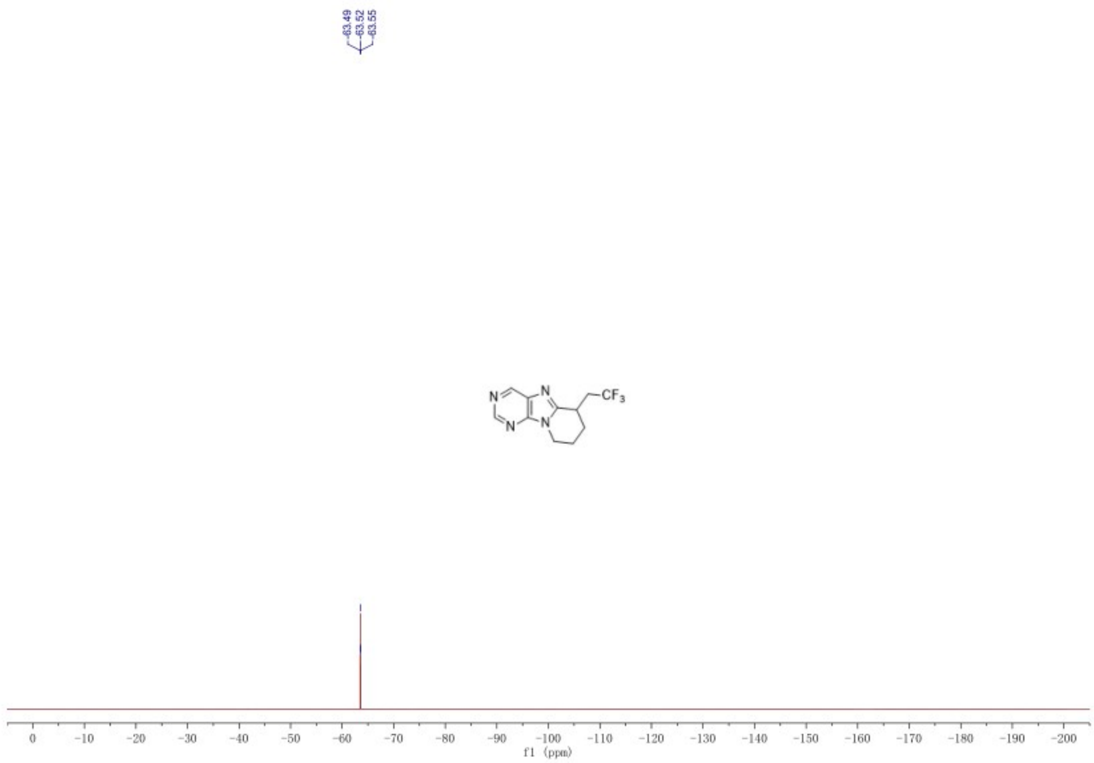


Figure S-79 [19]F NMR spectrum of **3ja**

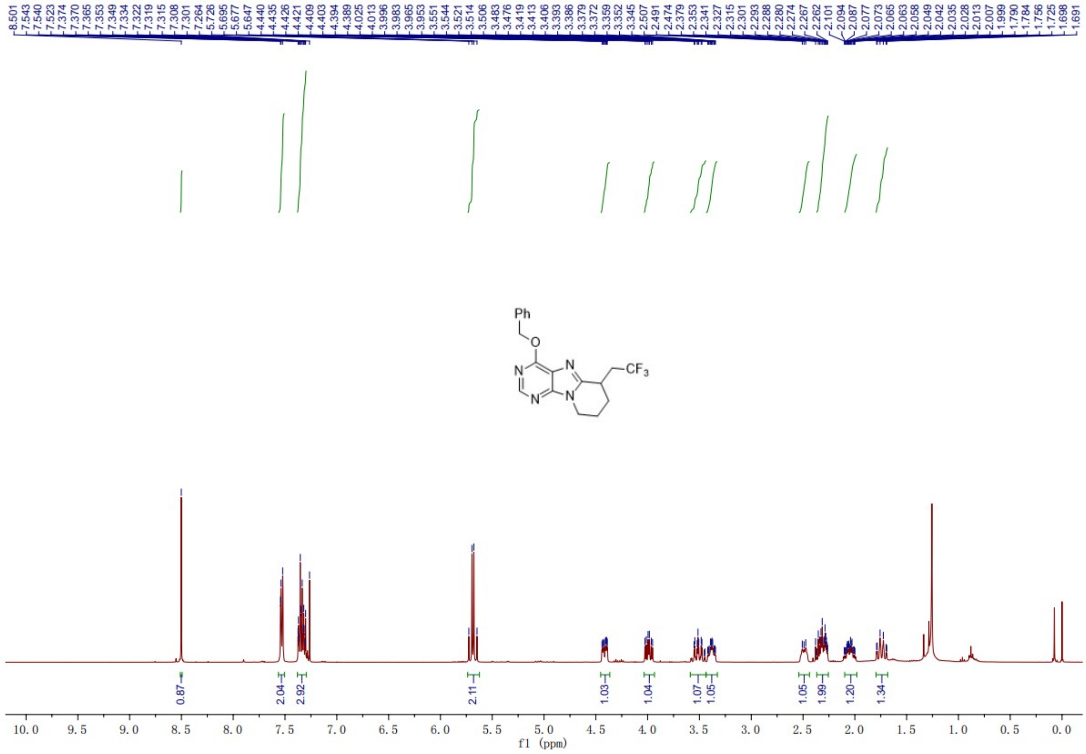


Figure S-80 ^{1}H NMR spectrum of **3ka**

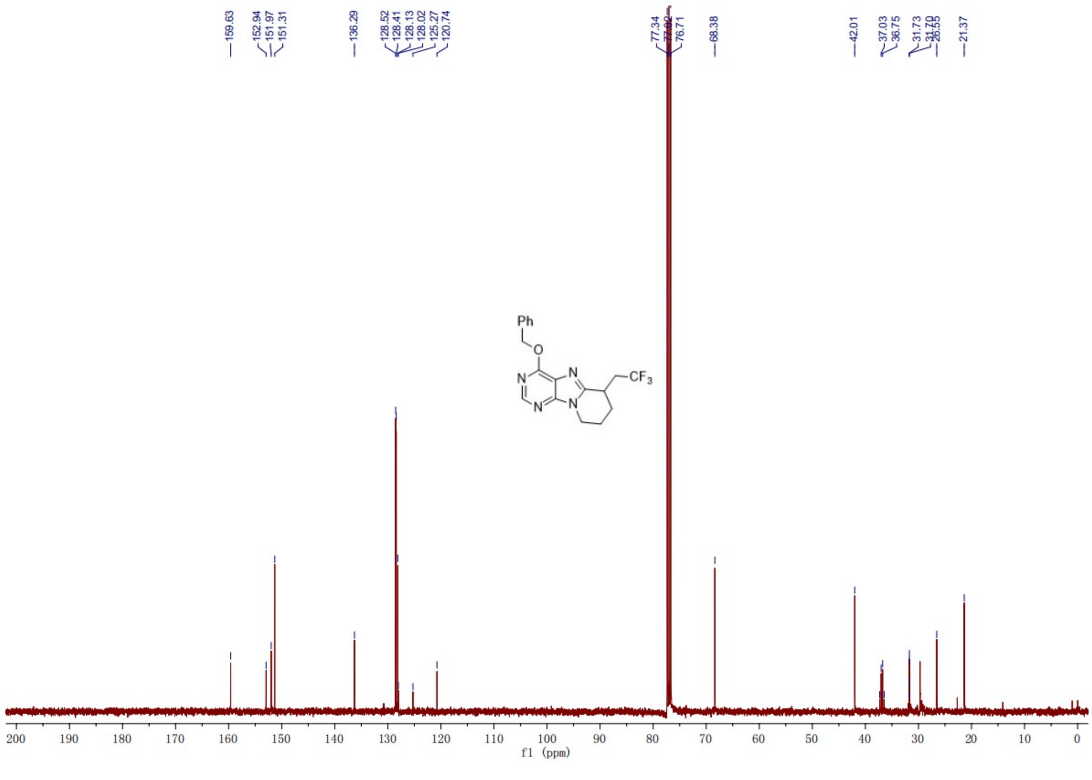


Figure S-81 ^{13}C NMR spectrum of **3ka**

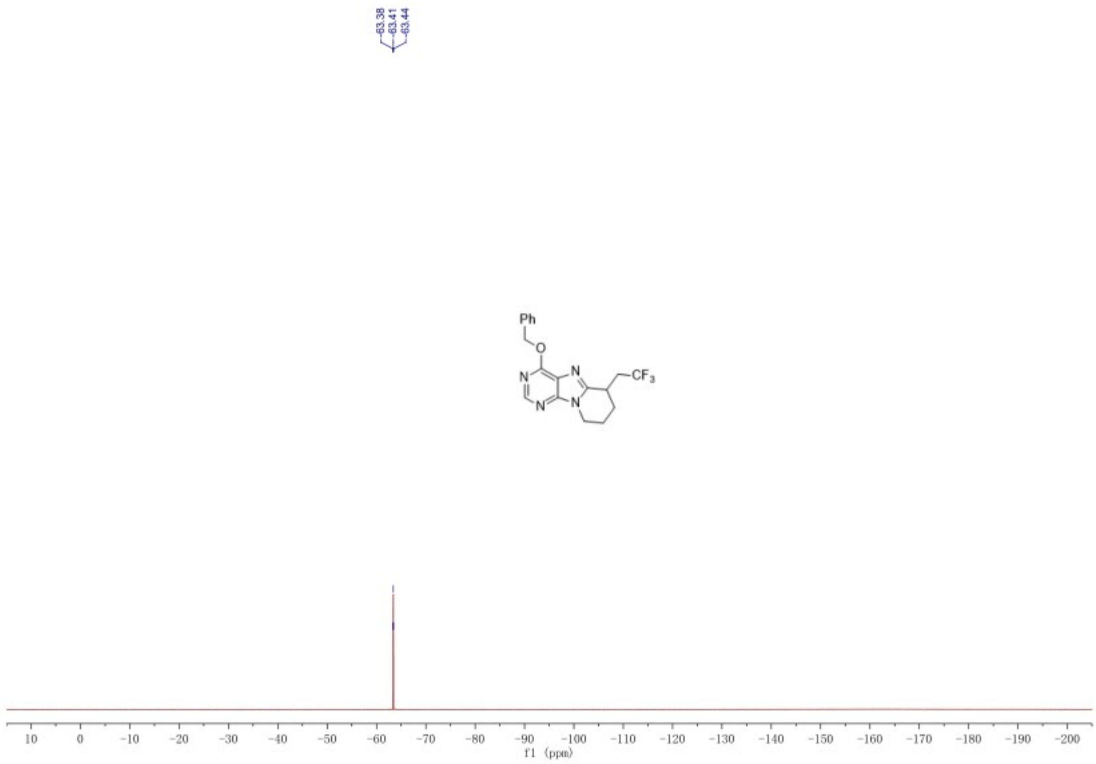


Figure S-82 ^{19}F NMR spectrum of **3ka**

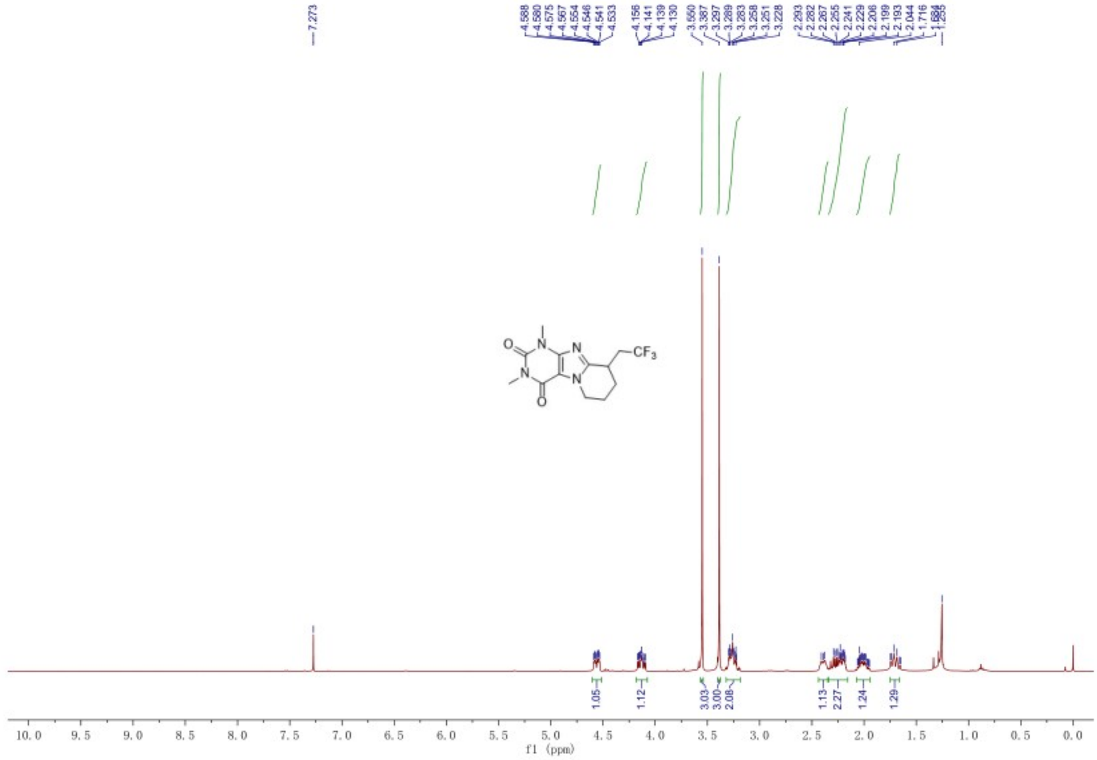


Figure S-83 ^{1}H NMR spectrum of **3la**

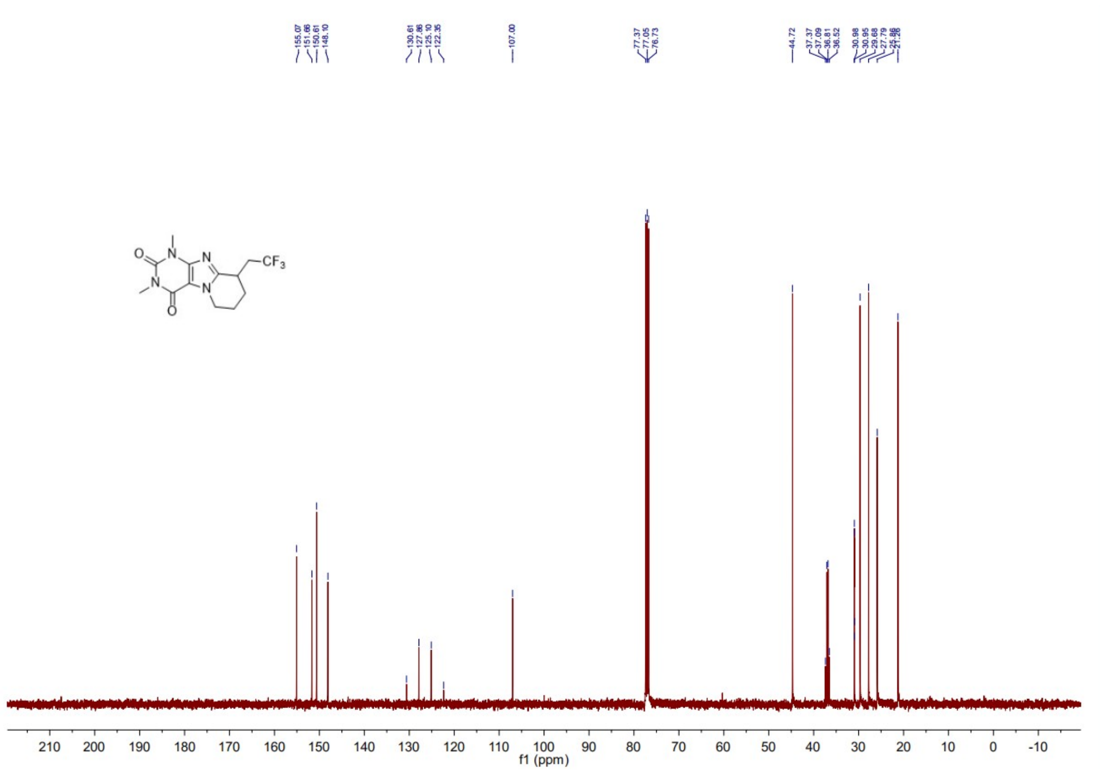


Figure S-84 ^{13}C NMR spectrum of **3la**

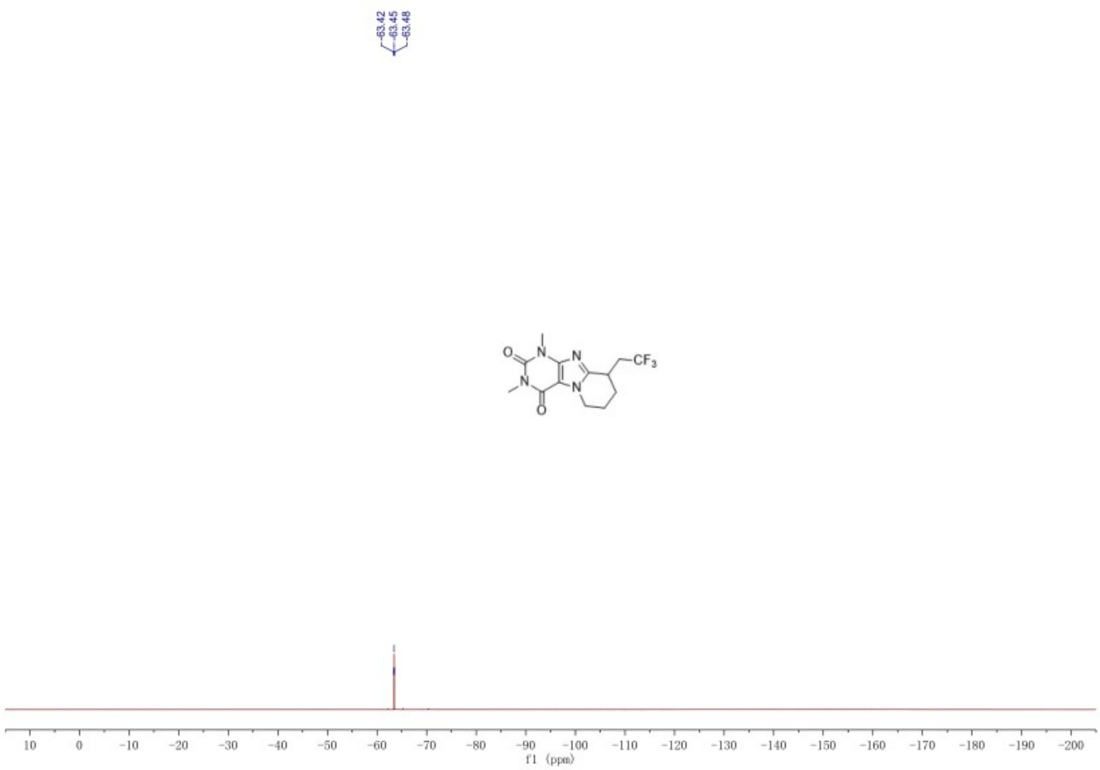


Figure S-85 ^{19}F NMR spectrum of **3la**

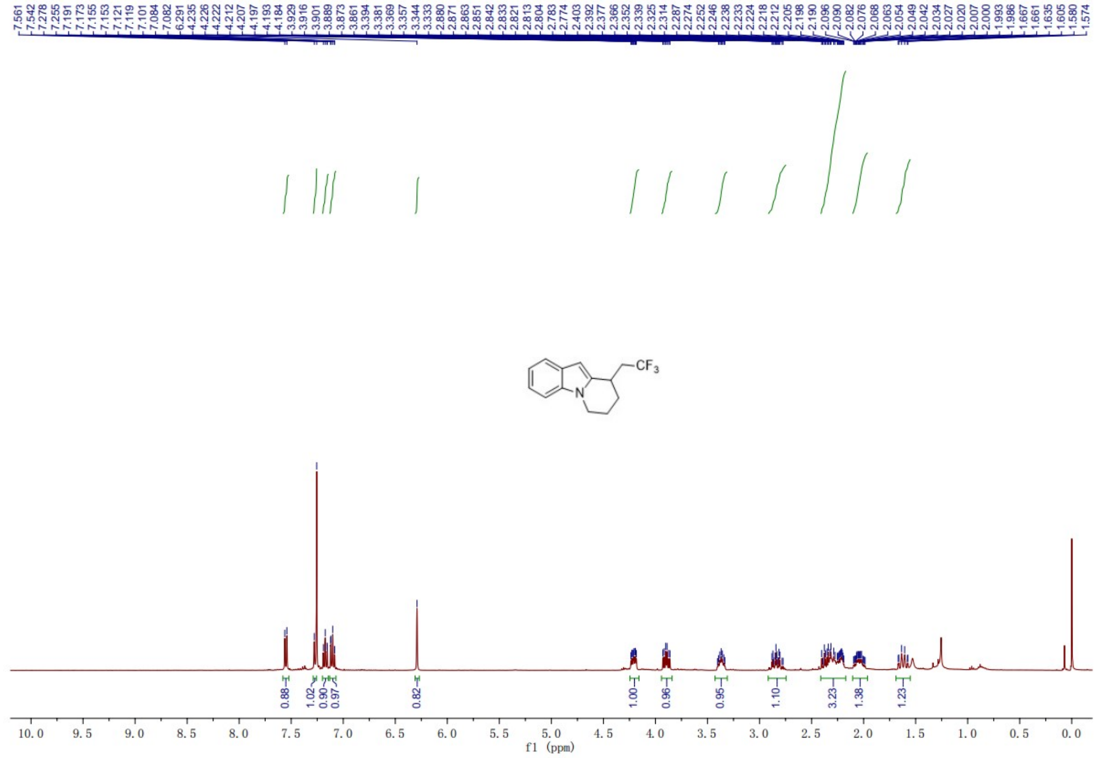


Figure S-86 ^{1}H NMR spectrum of **3ma**

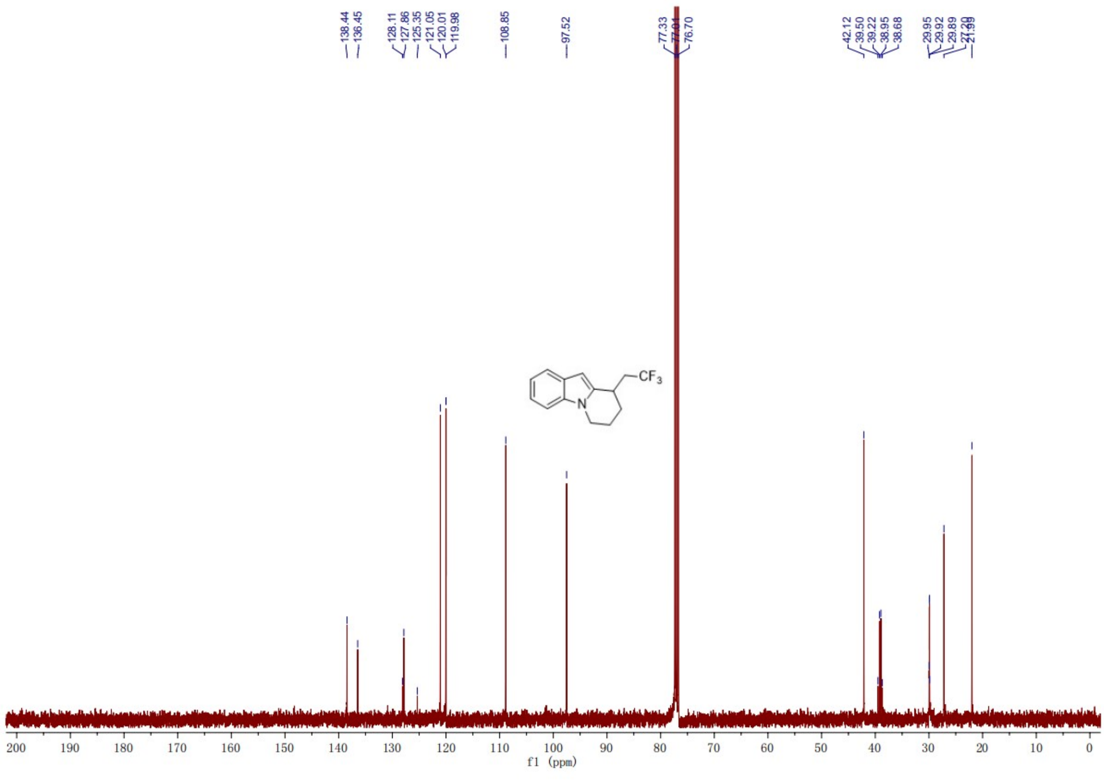


Figure S-87 ^{13}C NMR spectrum of **3ma**

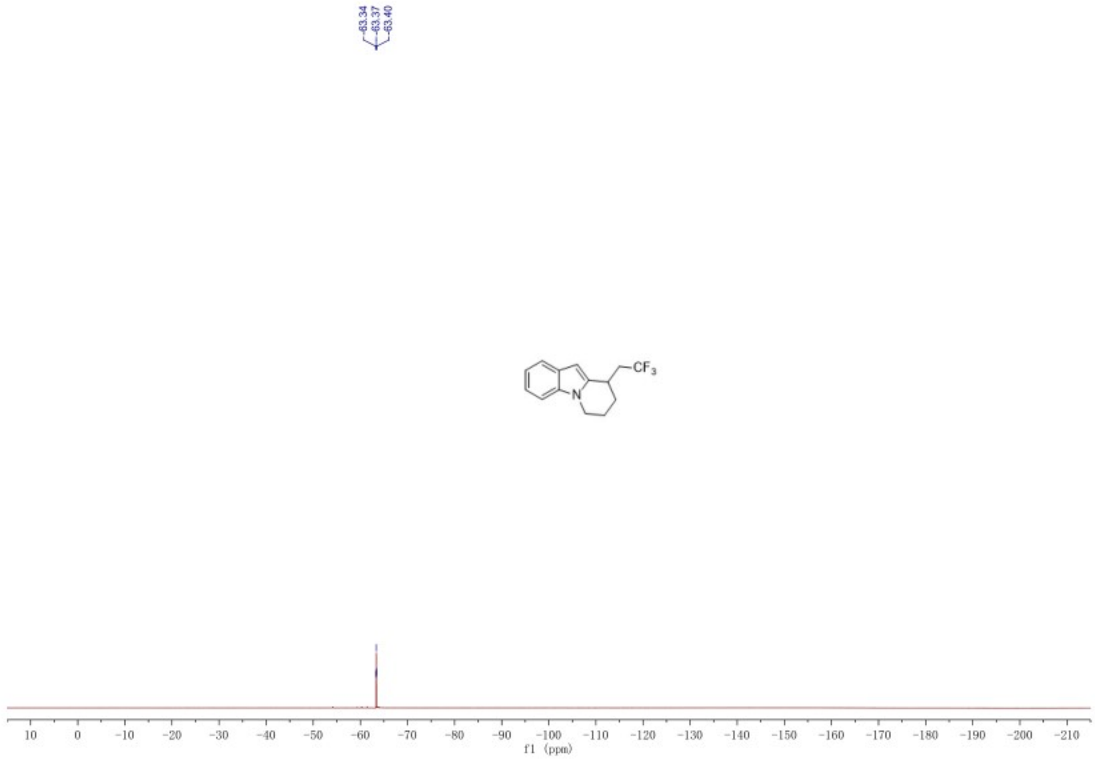


Figure S-88 [19]F NMR spectrum of **3ma**

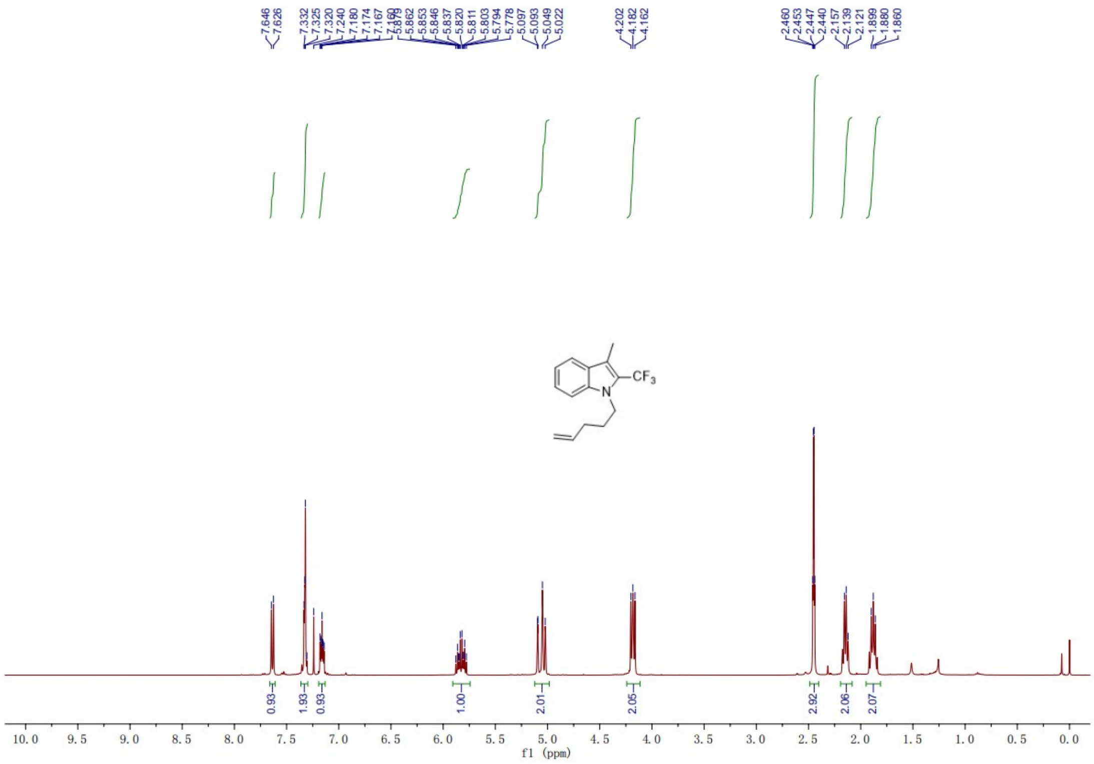


Figure S-89 ^{1}H NMR spectrum of **3na**

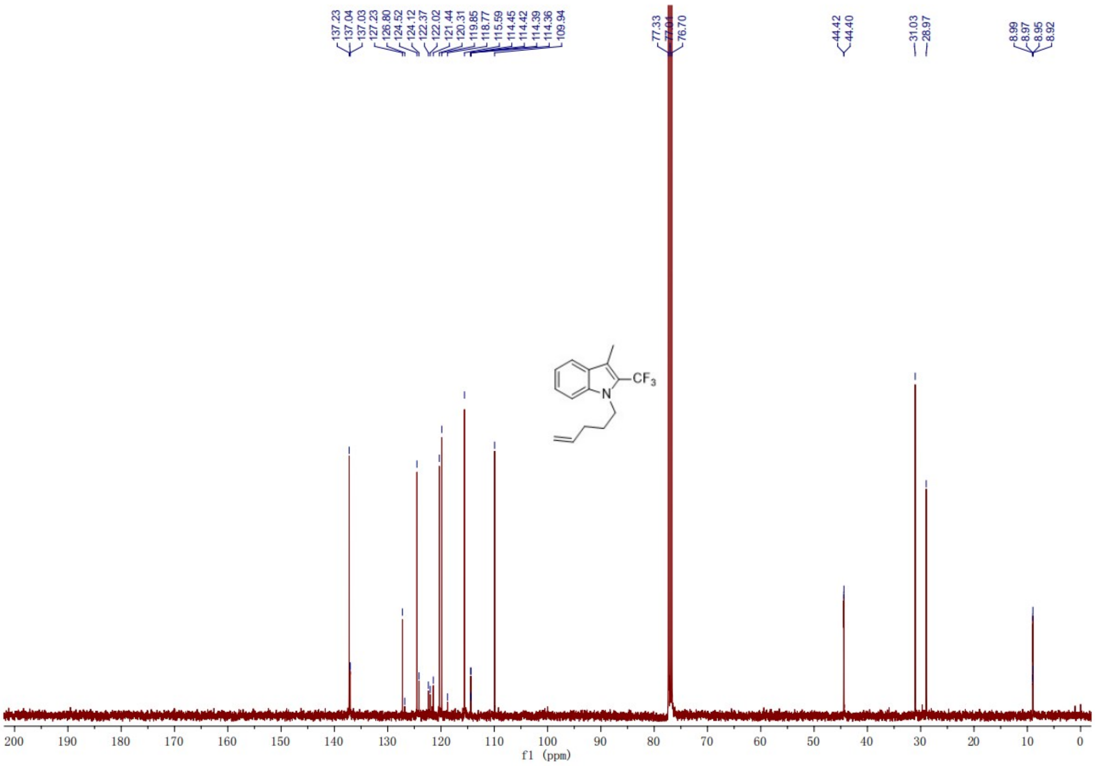


Figure S-90 ^{13}C NMR spectrum of **3na**

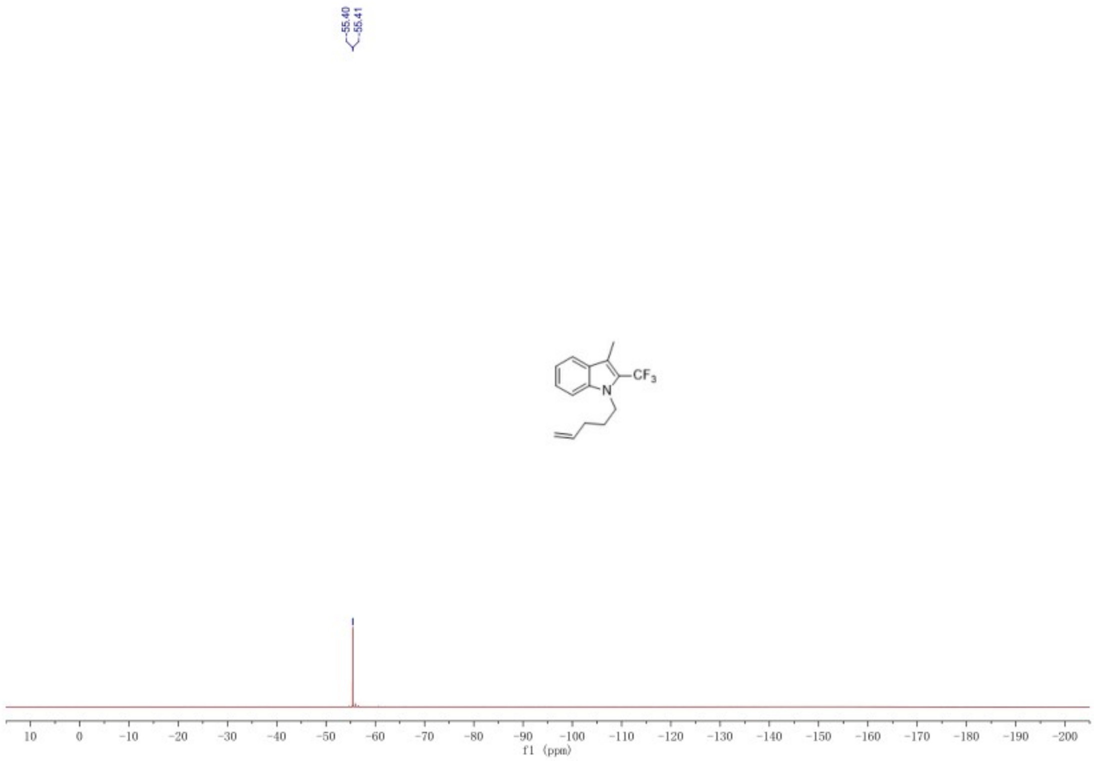


Figure S-91 ^{19}F NMR spectrum of **3na**

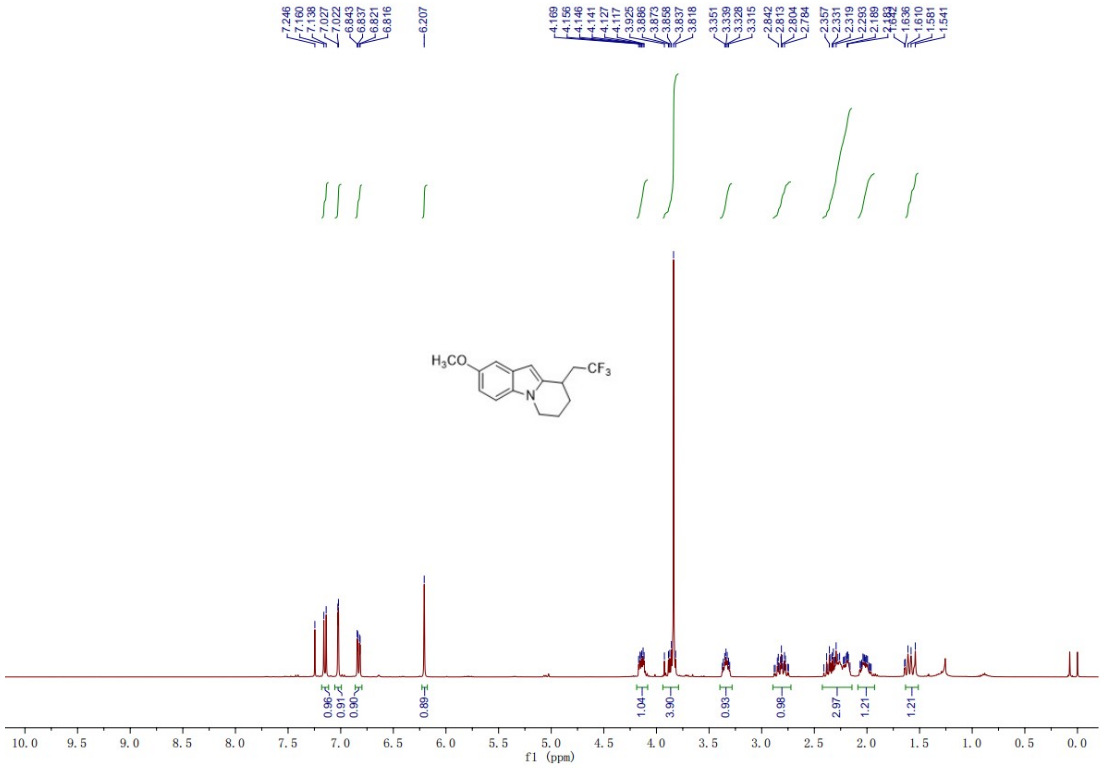


Figure S-92 ^{1}H NMR spectrum of **3oa**

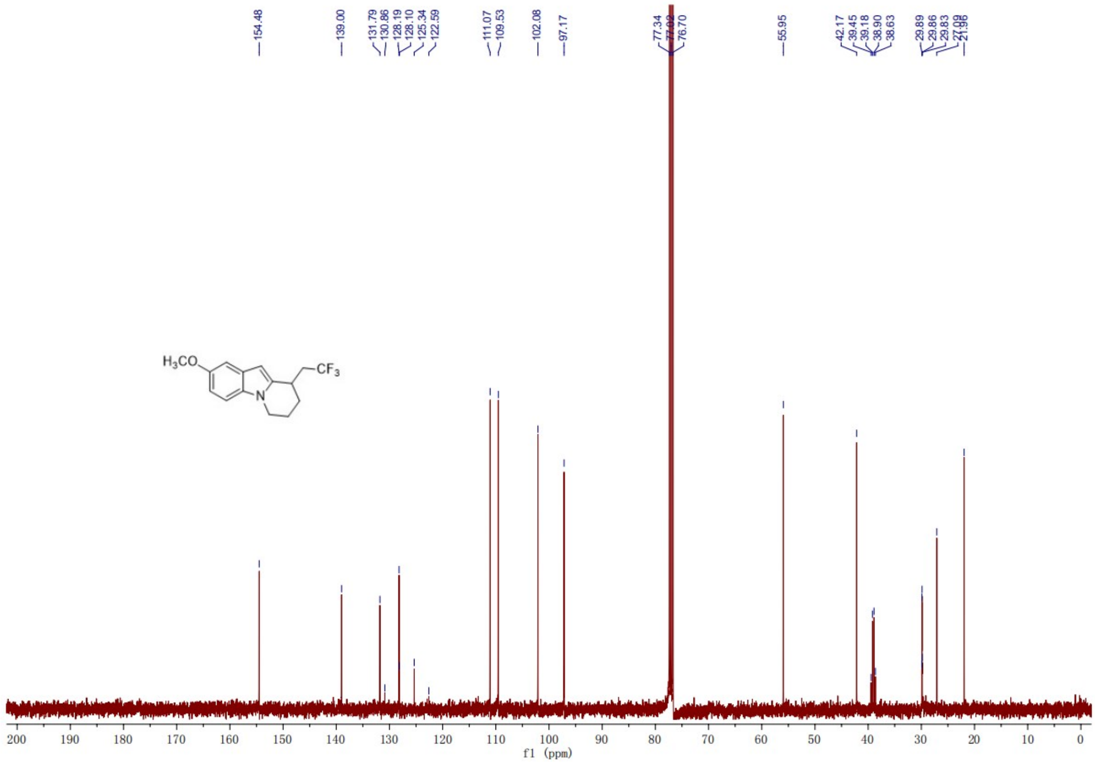


Figure S-93 ^{13}C NMR spectrum of **3oa**

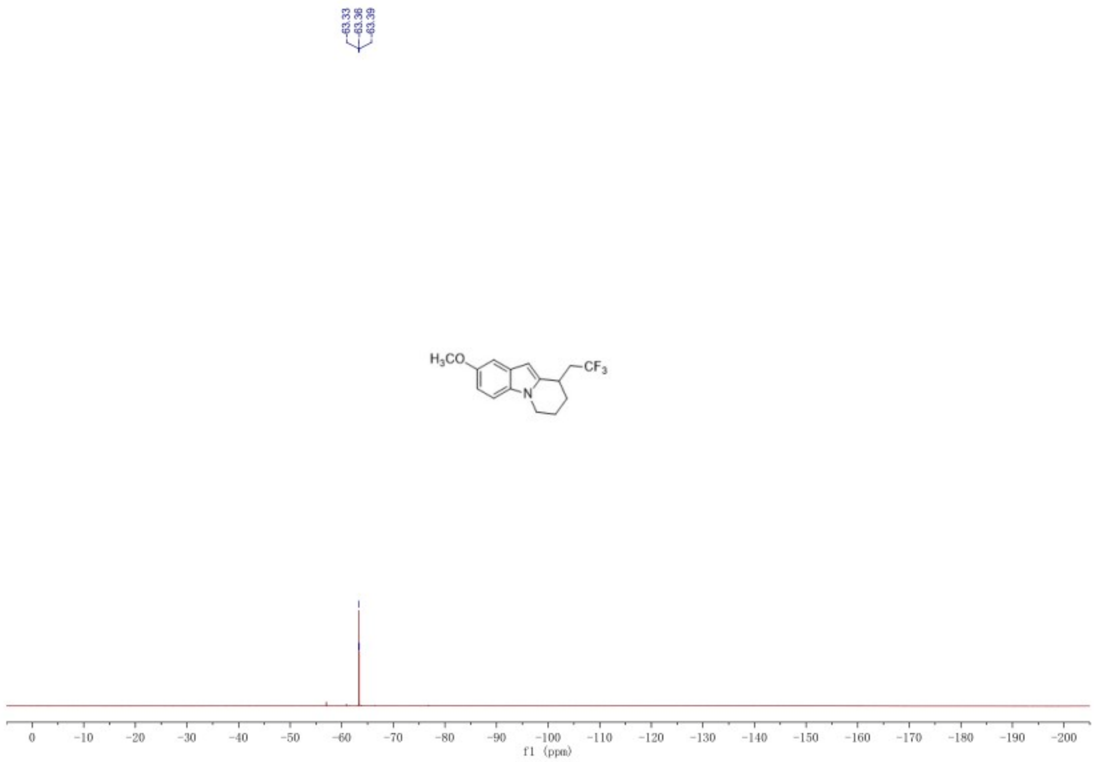


Figure S-94 ^{19}F NMR spectrum of **3oa**

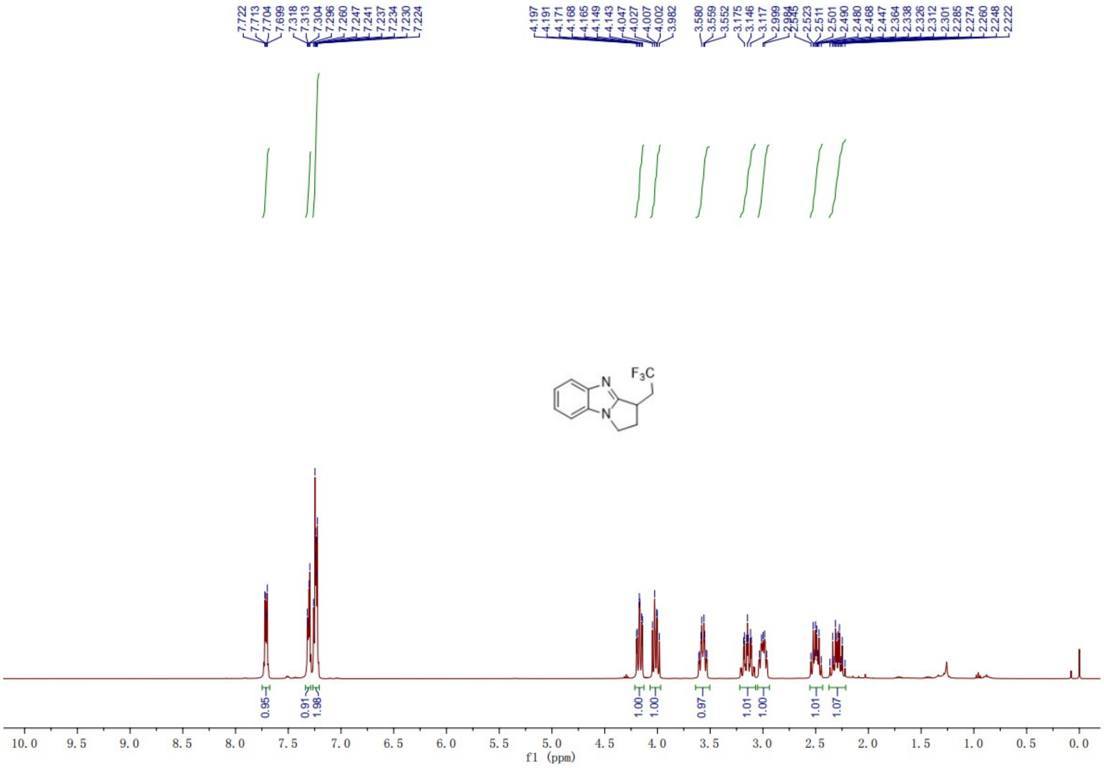


Figure S-95 ^{1}H NMR spectrum of **3pa**

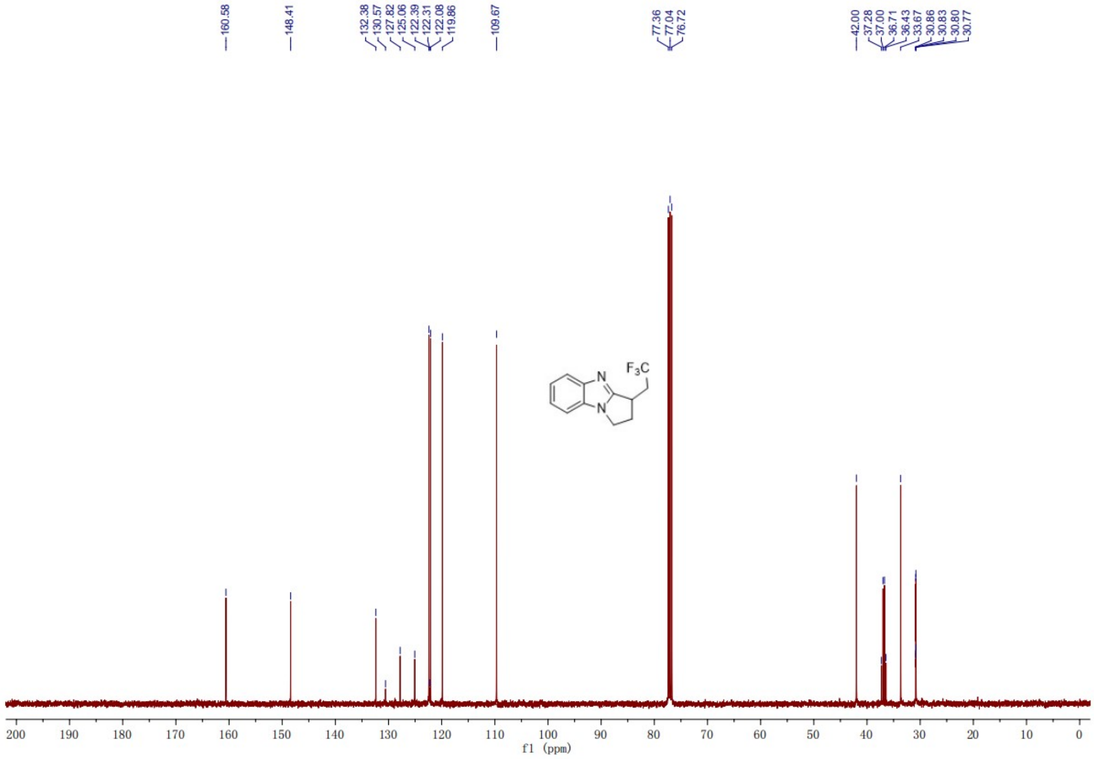


Figure S-96 ^{13}C NMR spectrum of **3pa**

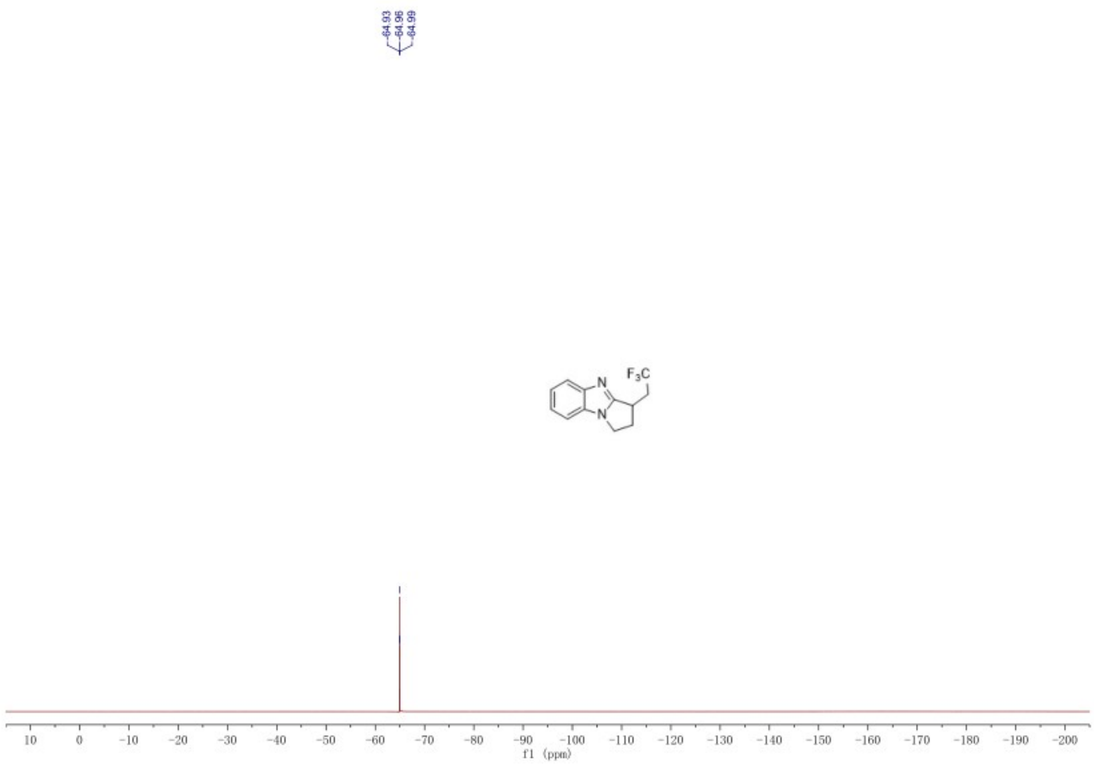


Figure S-97 19F NMR spectrum of **3pa**

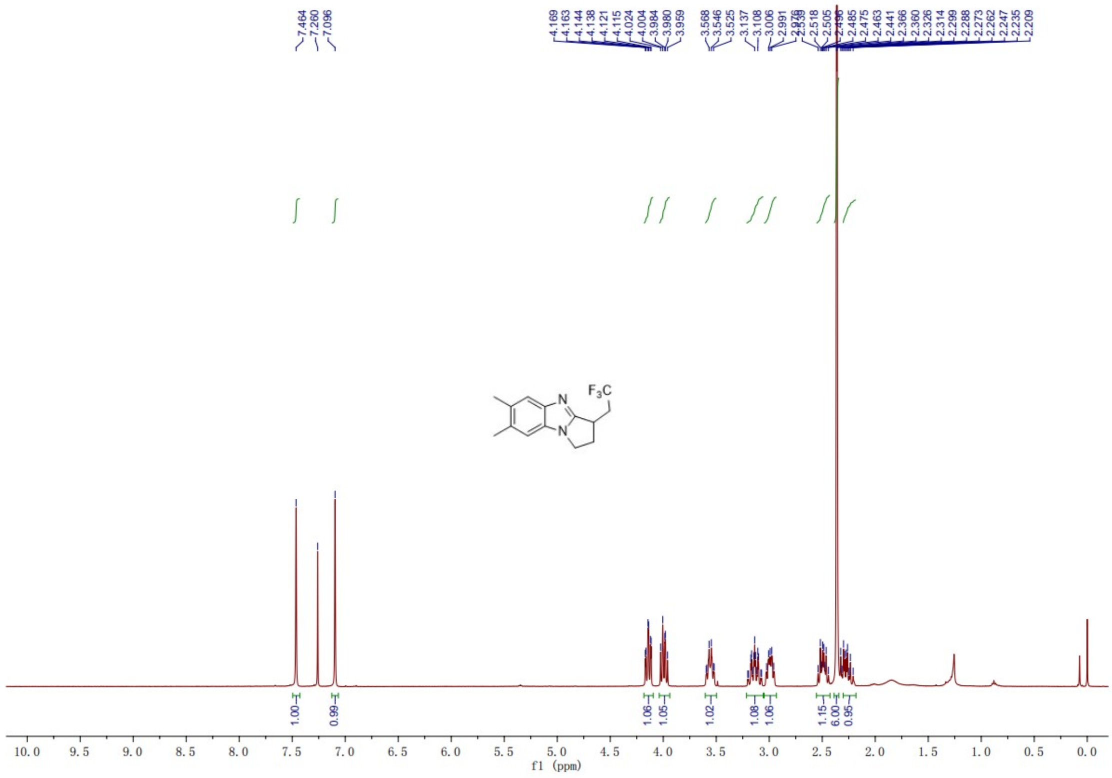


Figure S-98 ^{1}H NMR spectrum of **3qa**

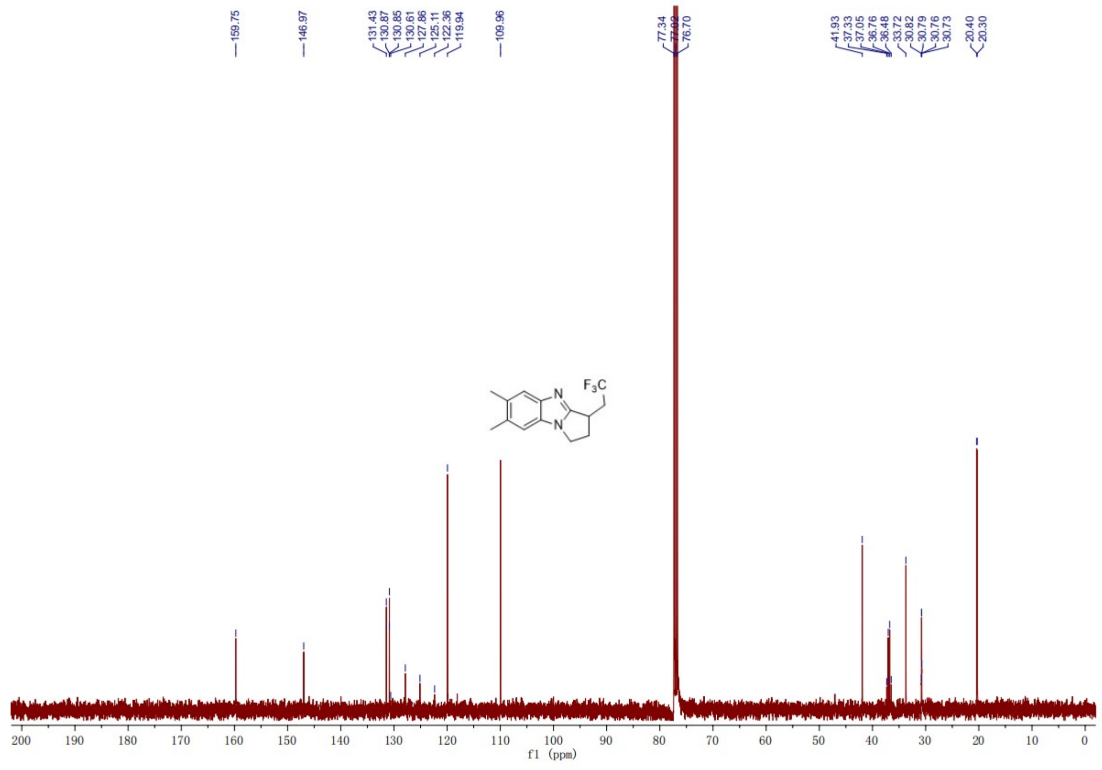


Figure S-99 ^{13}C NMR spectrum of **3qa**

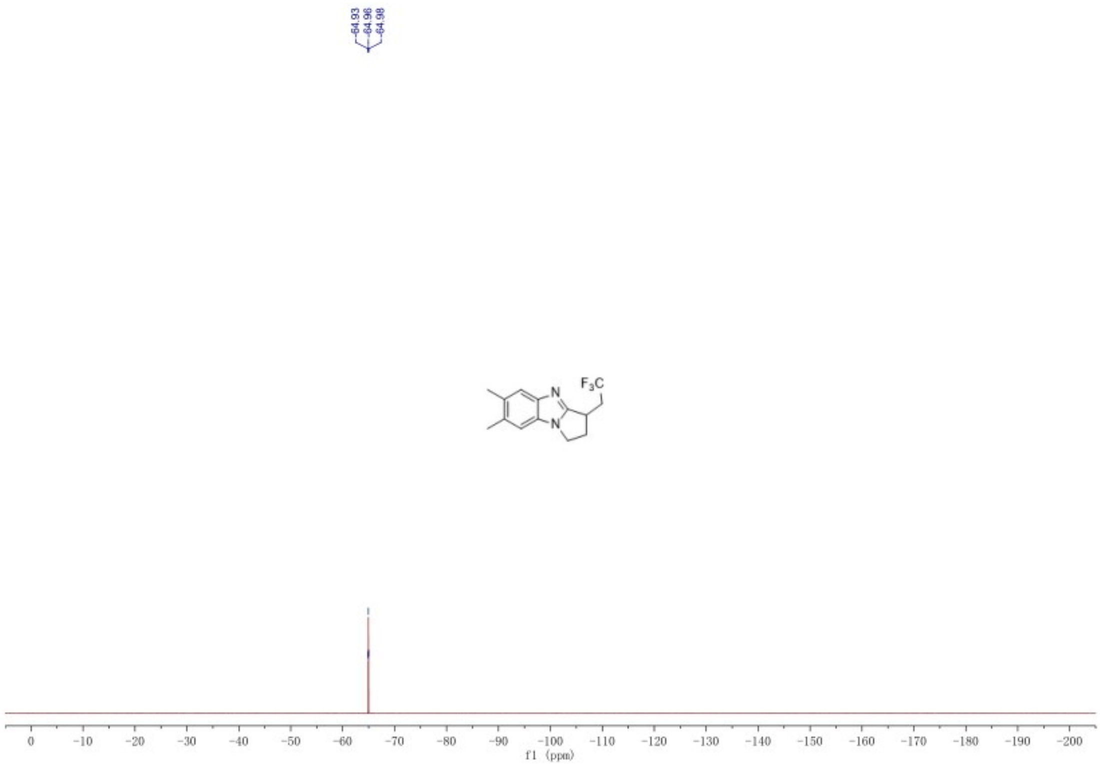


Figure S-100 [19]F NMR spectrum of **3qa**

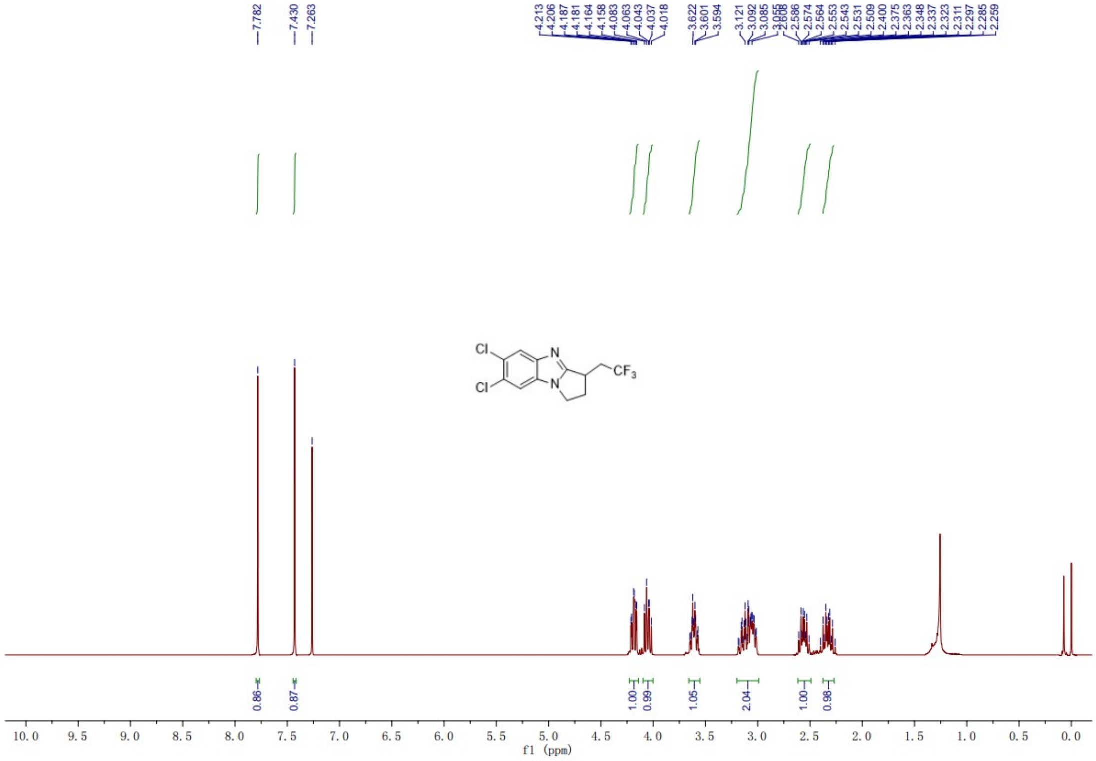


Figure S-101 ^{1}H NMR spectrum of **3ra**

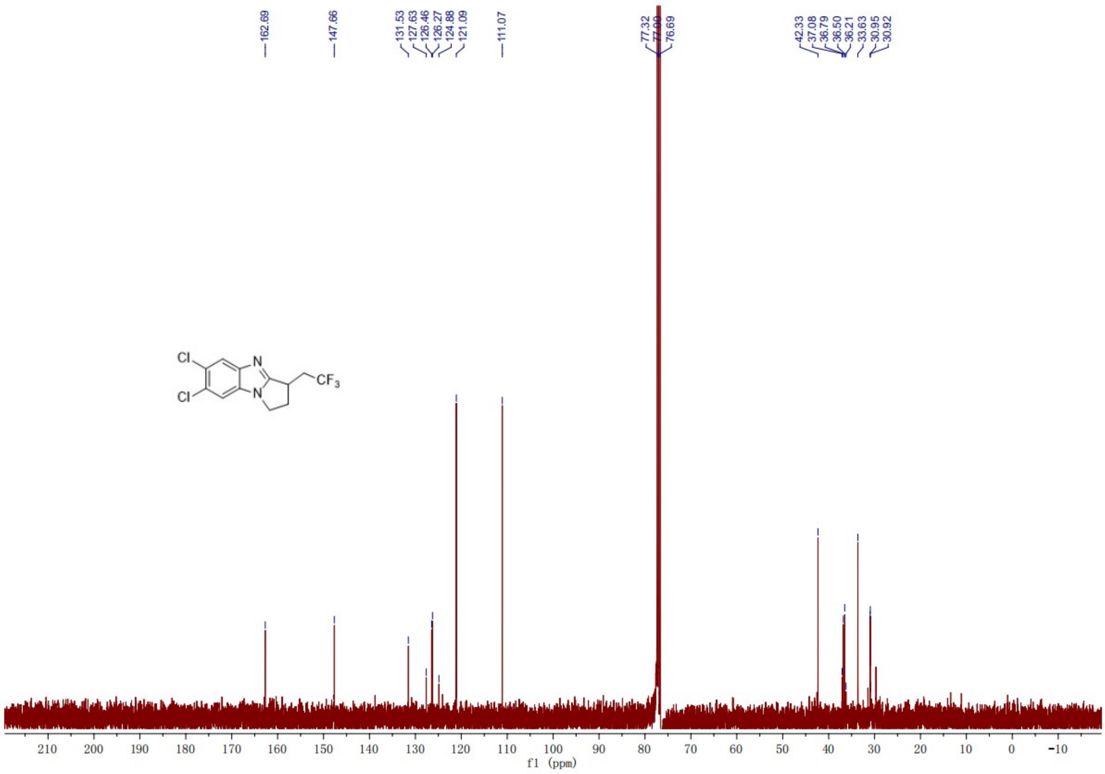


Figure S-102 ^{13}C NMR spectrum of **3ra**

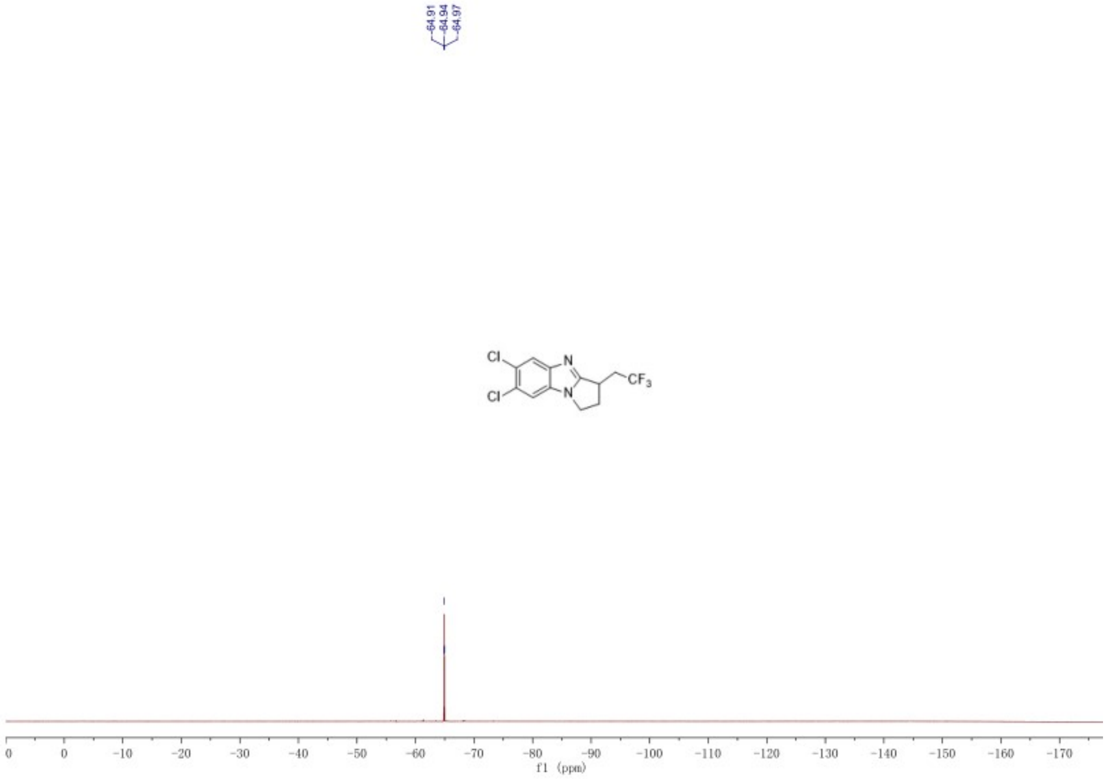


Figure S-103 ^{19}F NMR spectrum of **3ra**

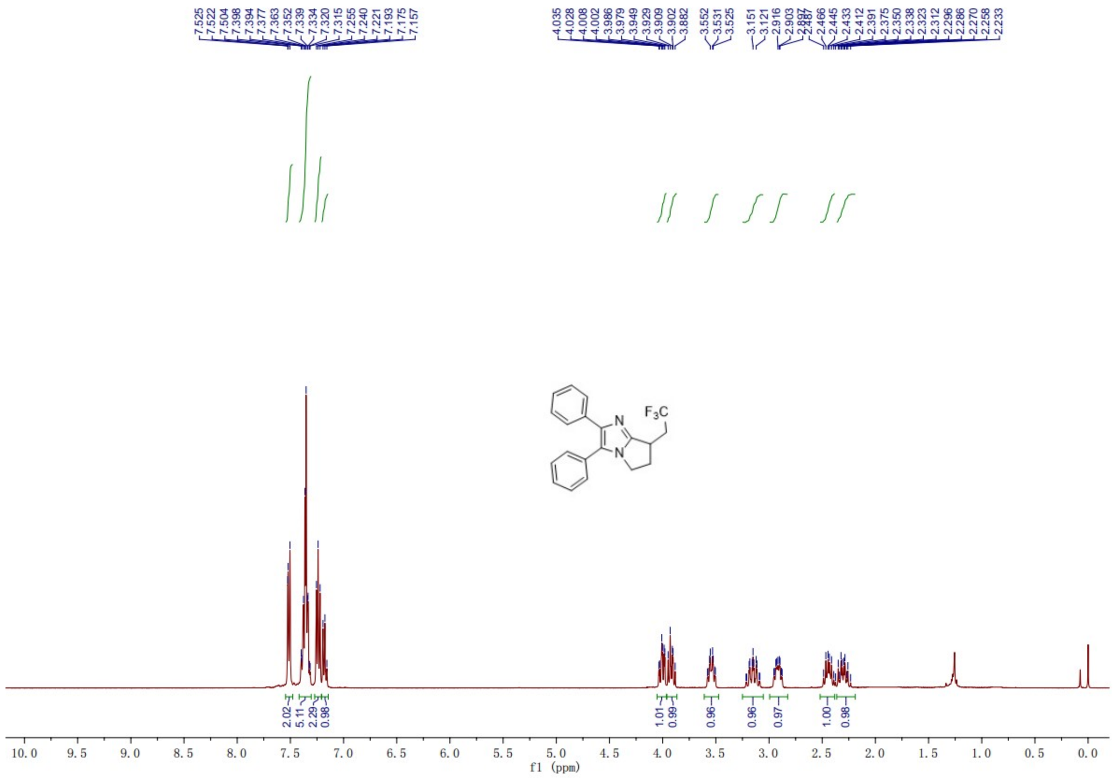


Figure S-104 ^{1}H NMR spectrum of **3sa**

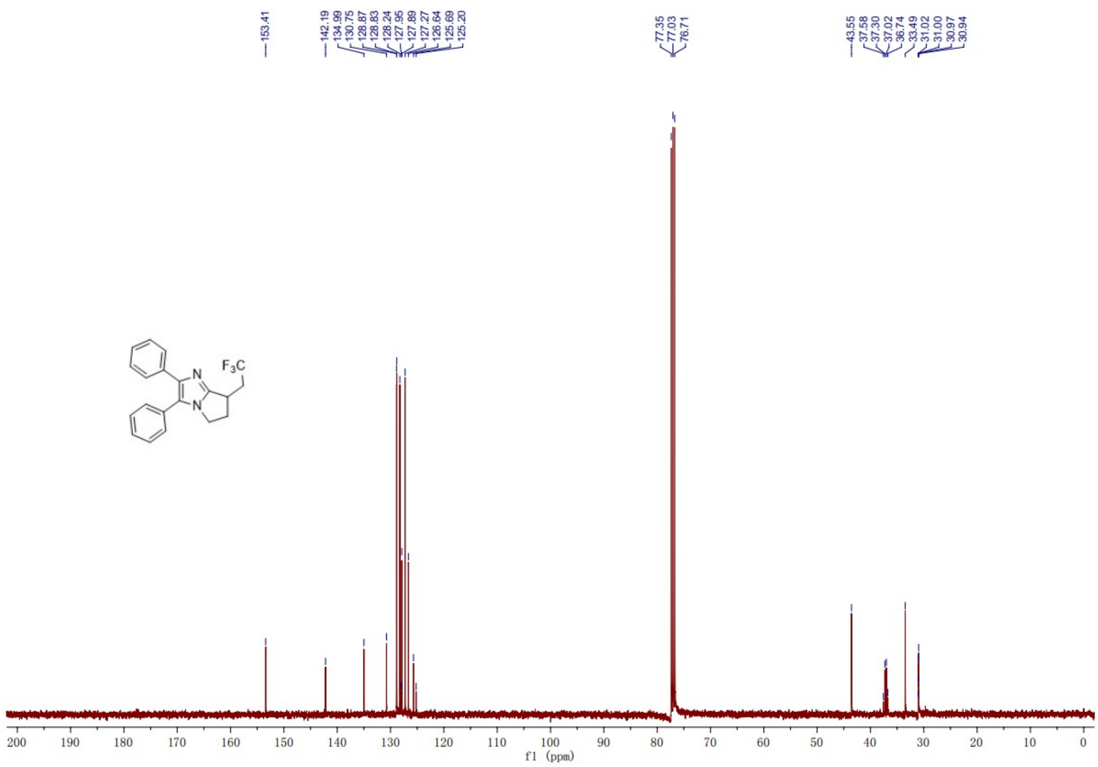


Figure S-105 ^{13}C NMR spectrum of **3sa**

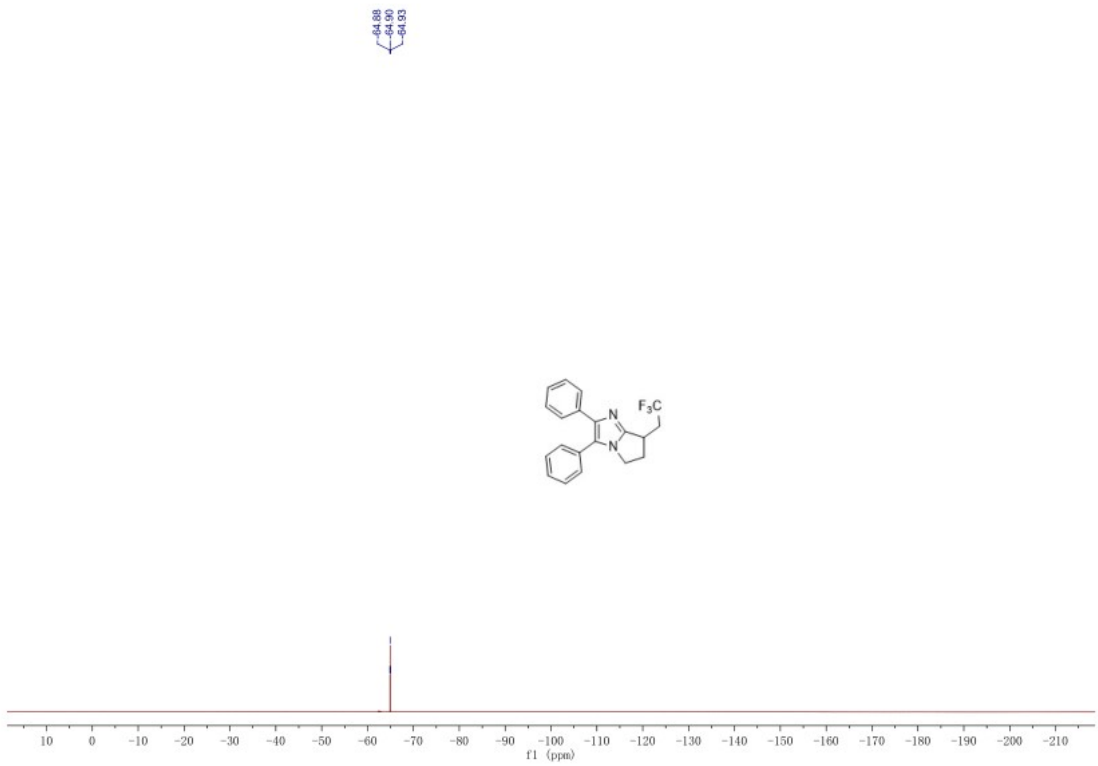


Figure S-106 ^{19}F NMR spectrum of **3sa**

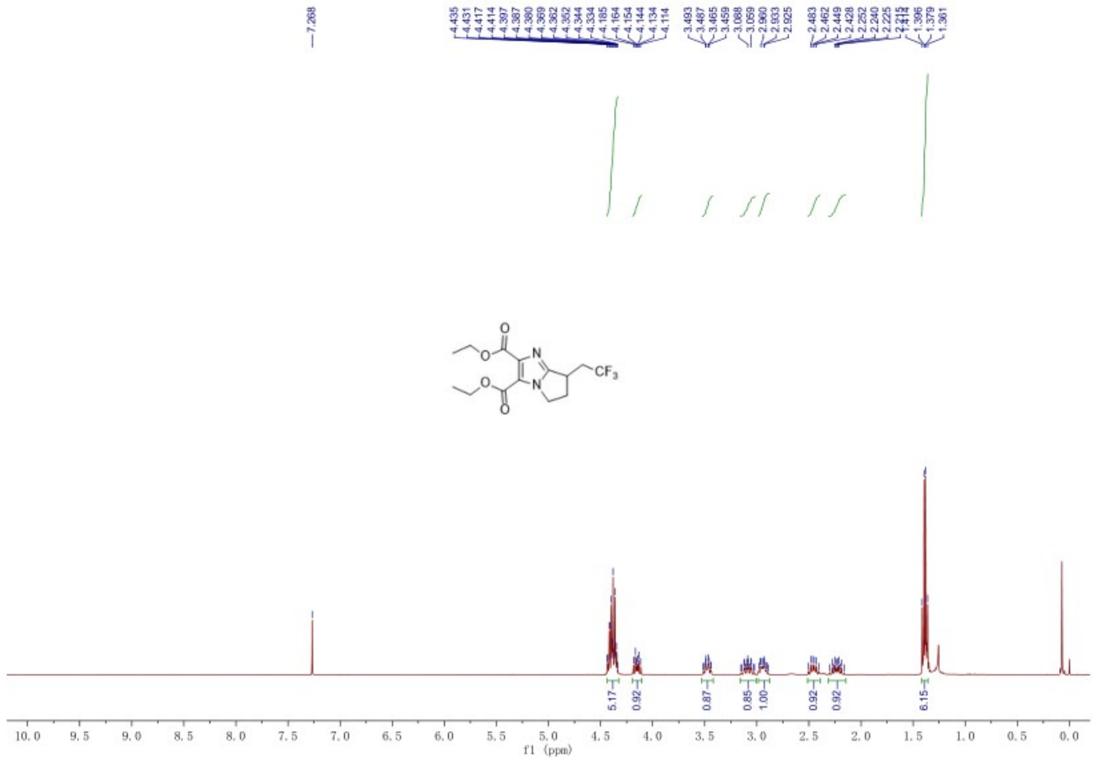


Figure S-107 ^{1}H NMR spectrum of **3ta**

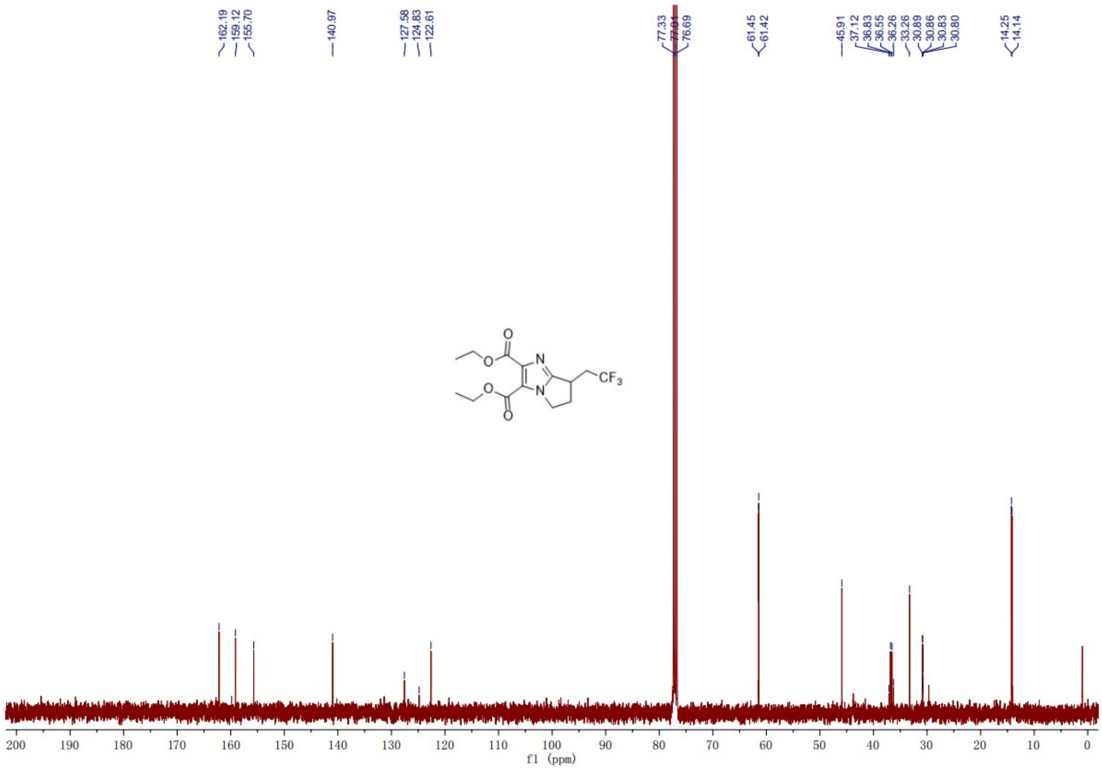


Figure S-108 ^{13}C NMR spectrum of **3ta**

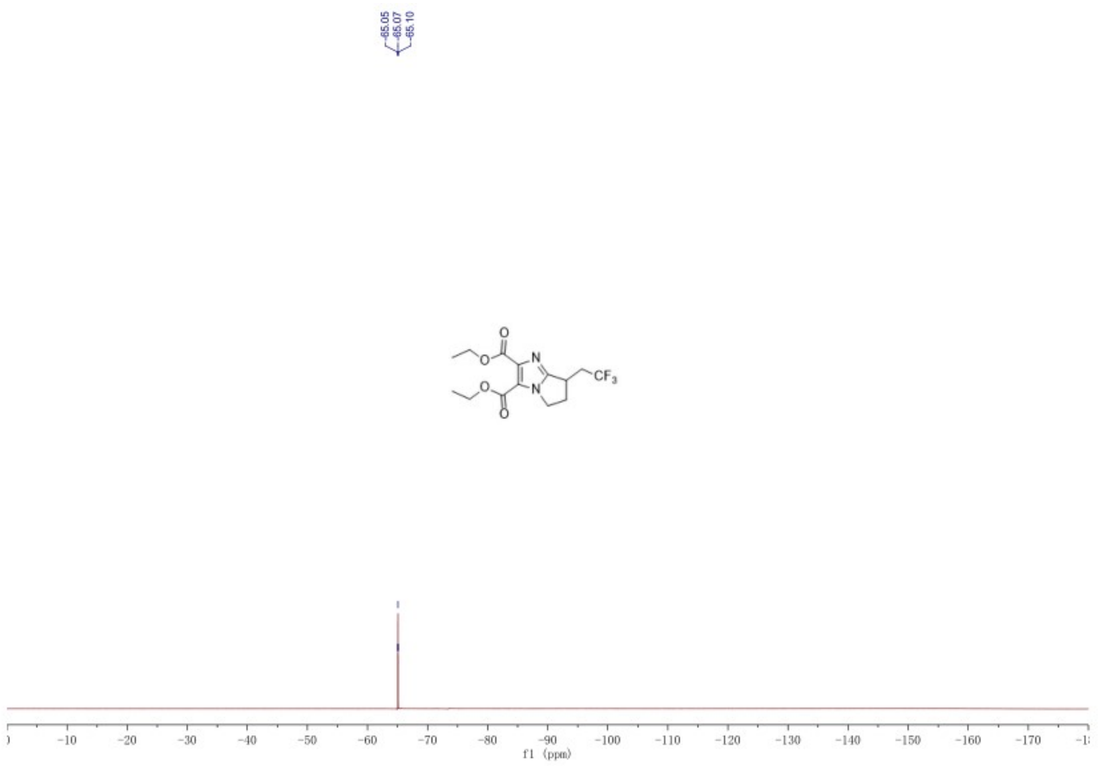


Figure S-109 ^{19}F NMR spectrum of **3ta**

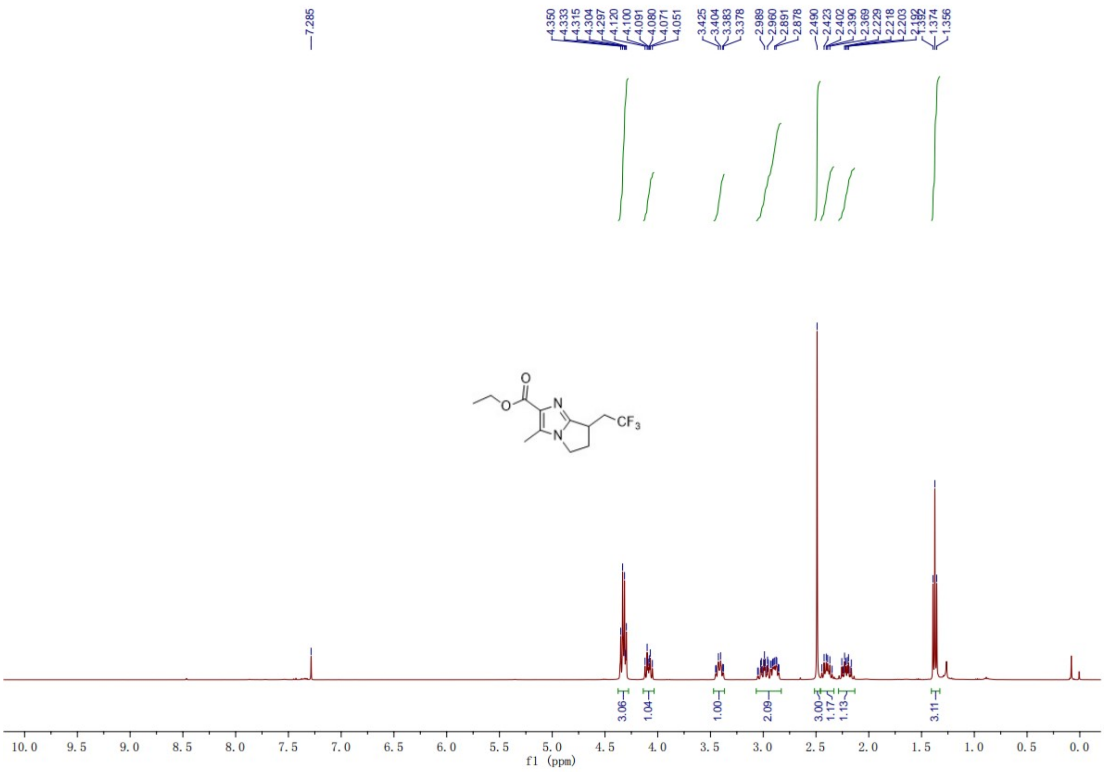


Figure S-110 ^{1}H NMR spectrum of **3ua**

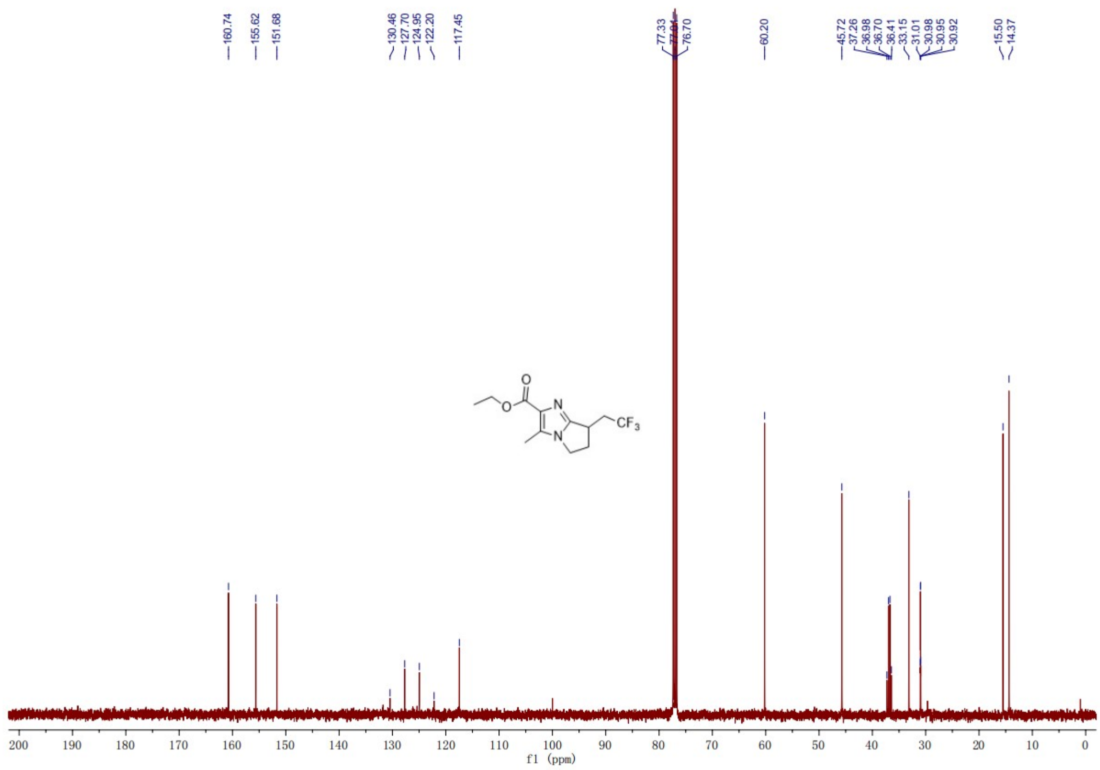


Figure S-111 ^{13}C NMR spectrum of **3ua**

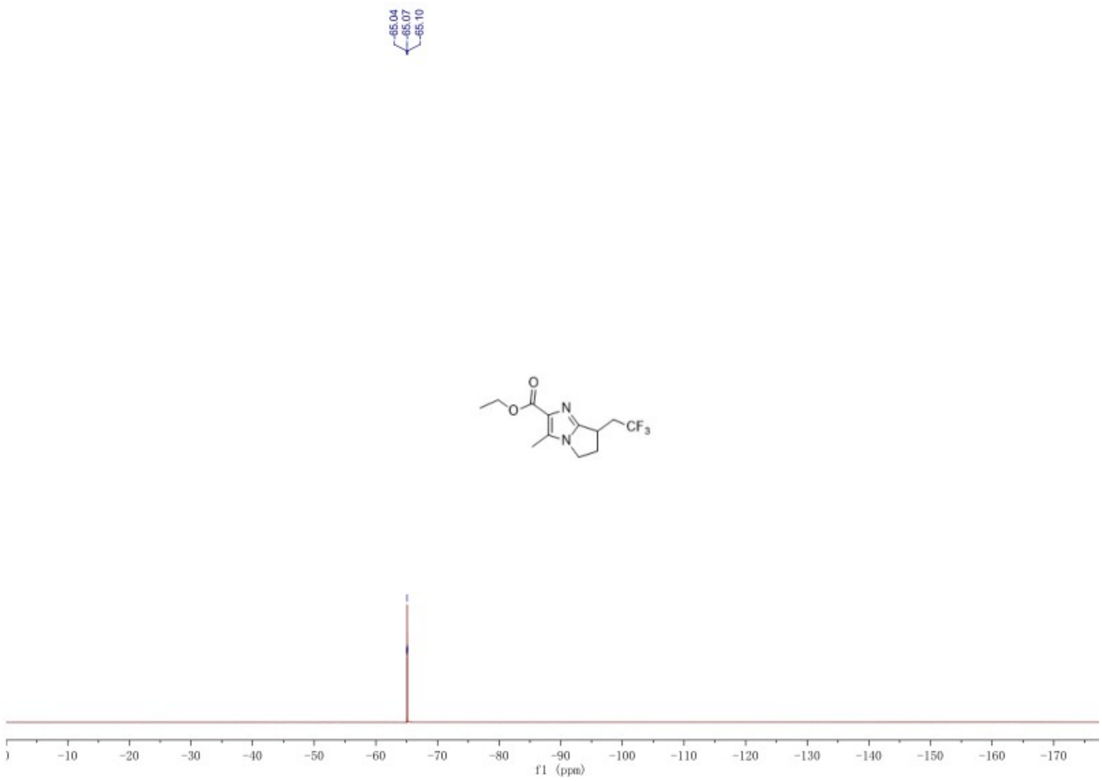


Figure S-112 ^{19}F NMR spectrum of **3ua**

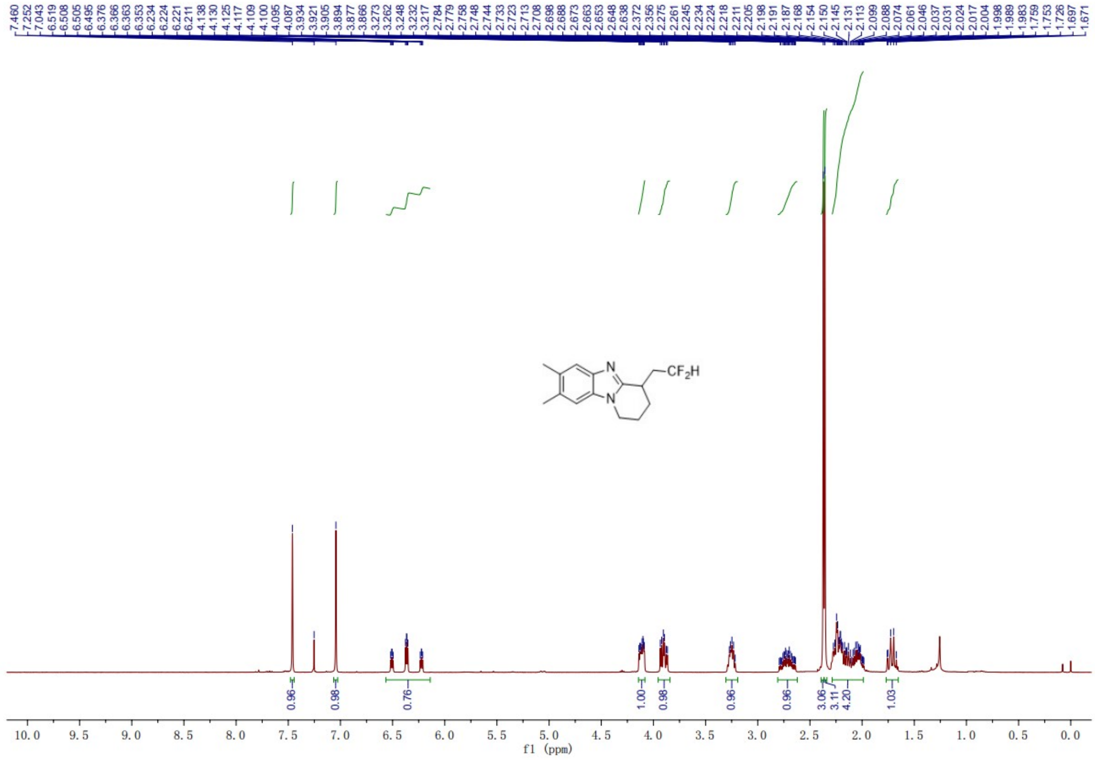


Figure S-113 ^{1}H NMR spectrum of **3cb**

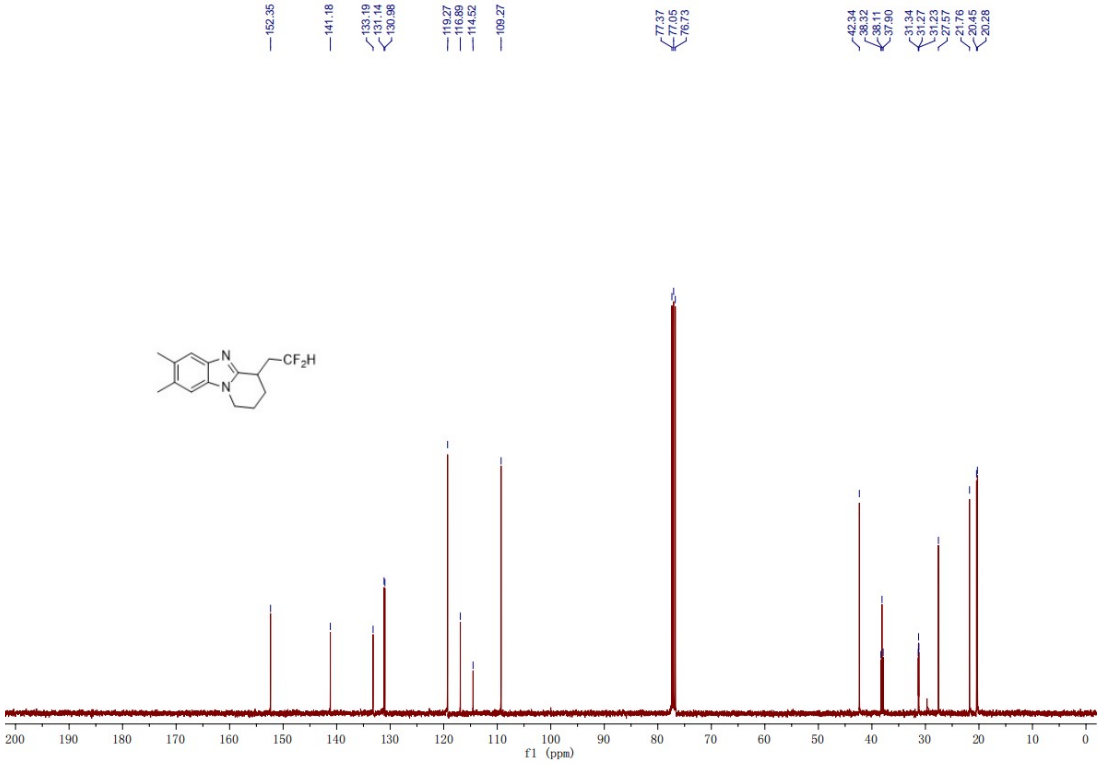


Figure S-114 ^{13}C NMR spectrum of **3cb**

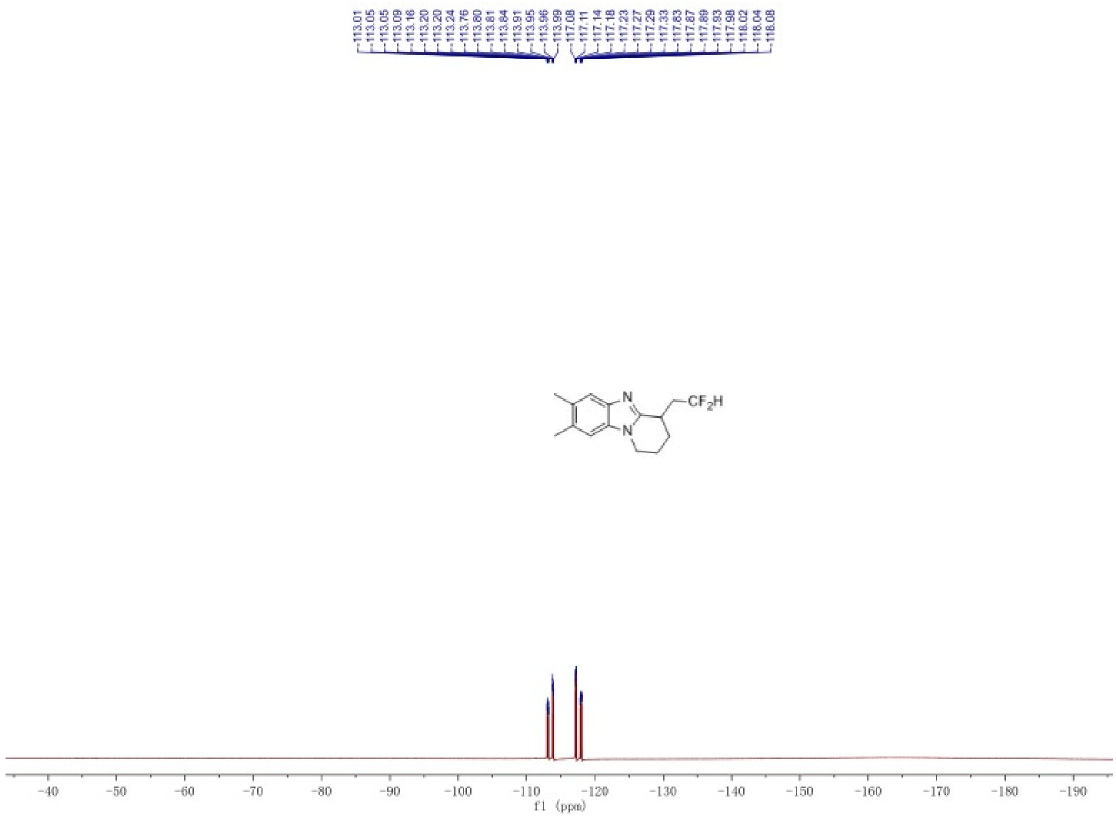


Figure S-115 ^{19}F NMR spectrum of **3cb**

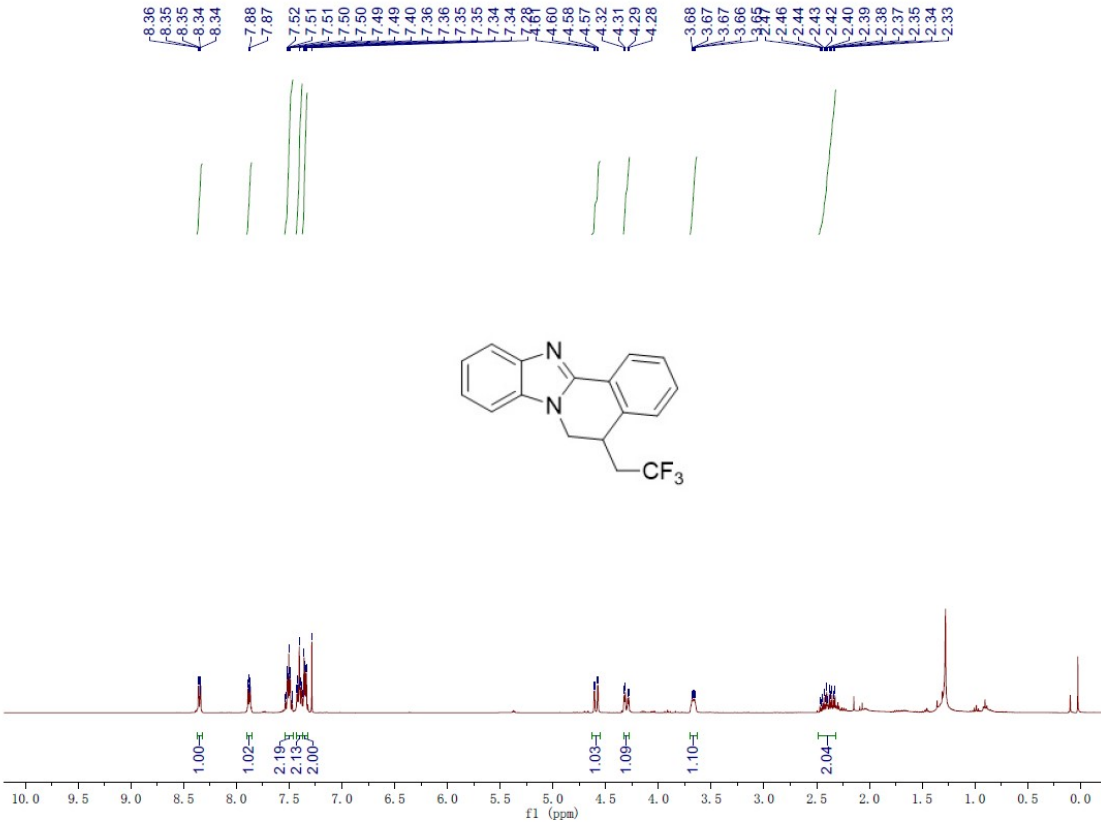


Figure S-116 ^{1}H NMR spectrum of **5**

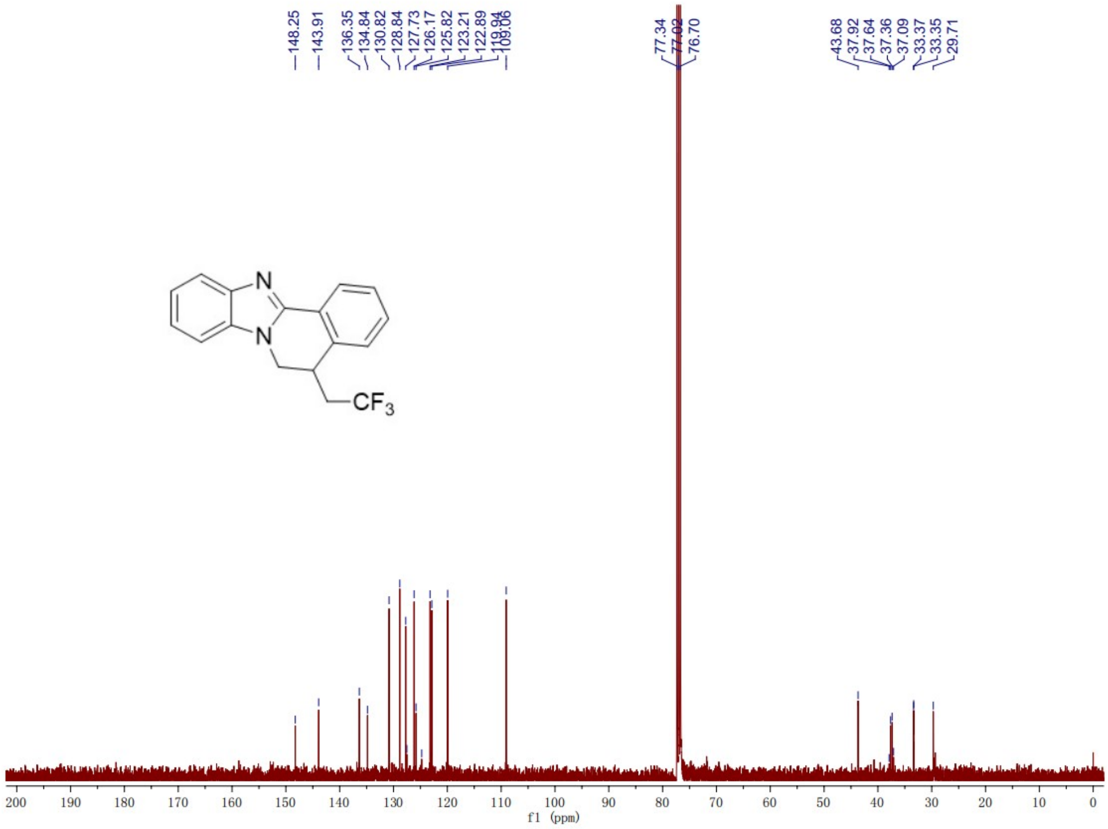


Figure S-117 ^{13}C NMR spectrum of **5**

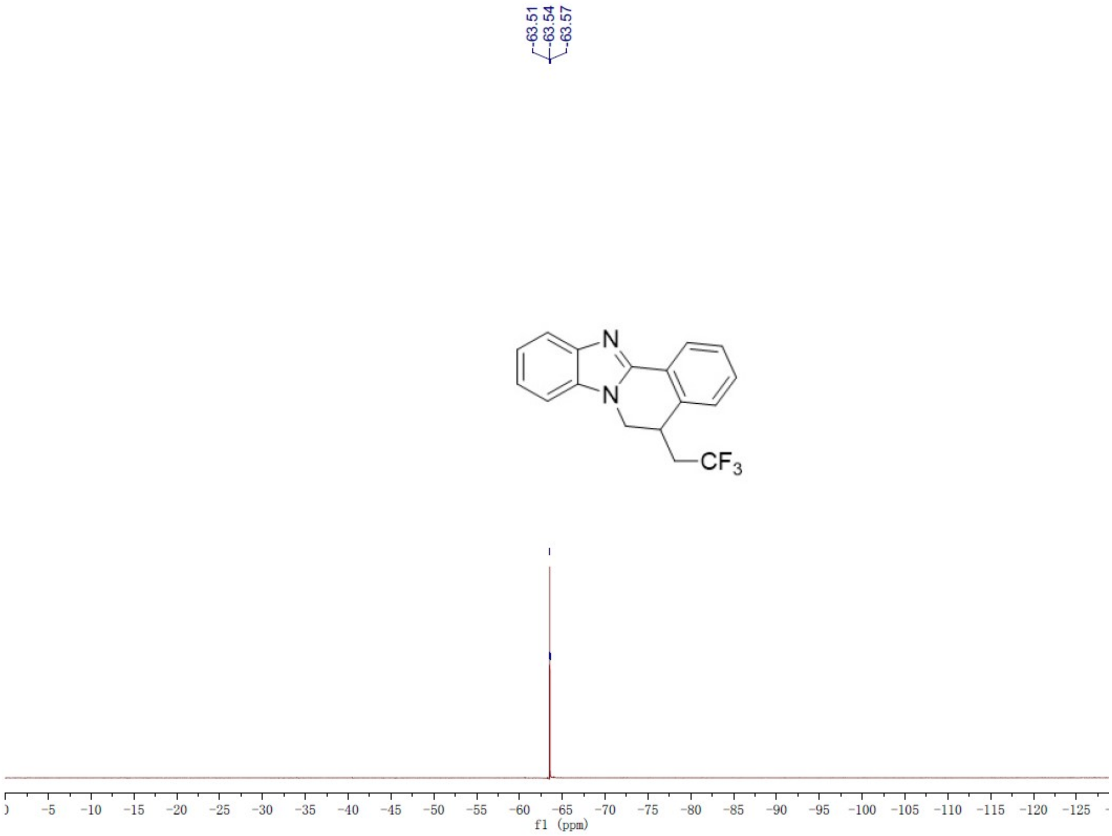


Figure S-118 ^{19}F NMR spectrum of **5**