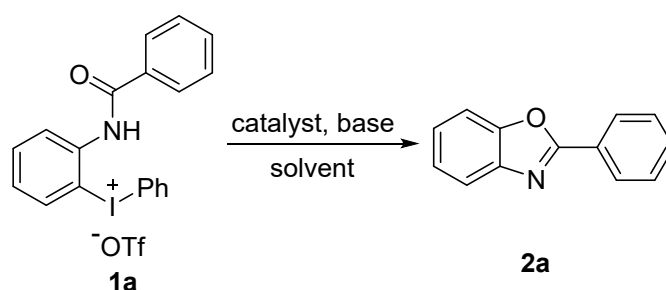


The general information for the synthetic experiments: Synthesis details for key compounds are described here. All solvents were commercially available and were used without a further purification unless stated. The chemicals used were either purchased from commercial sources or prepared according to literature procedures. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance spectrometer 400 at 400 MHz and 100 MHz respectively. Chemical shifts are given in ppm (δ) referenced to CDCl_3 with 7.26 for ^1H and 77.10 for ^{13}C , and to d_6 -DMSO with 2.50 for ^1H and 39.5 for ^{13}C . In the case of multiplet, the signals are reported as intervals. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are expressed in hertz. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher spectrometer, Orbitrap QExactive GC/MS (EI mode) and Orbitrap QExactive LC/MS(ESI mode) or BRUKER VPXII spectrometer (ESI mode). The progress of the reactions was monitored by thin-layer chromatography on a glass plate coated with silica gel with fluorescent indicator (GF254). Column chromatography was performed on silica gel (200-300 mesh).

Table S1. Optimization of the reaction conditions^a



Entry	Catalyst	Base	Solvent	Temp. ($^{\circ}\text{C}$)	Yield ^b (%)
1	$\text{Ni}(\text{acac})_2$	Na_2CO_3	DMF	40	44
2	$\text{Ni}(\text{COD})_2$	Na_2CO_3	DMF	40	28
3	NiCl_2	Na_2CO_3	DMF	40	42
4	NiBr_2	Na_2CO_3	DMF	40	60
5	NiI_2	Na_2CO_3	DMF	40	56
6	$\text{Ni}(\text{OAc})_2$	Na_2CO_3	DMF	40	0
7	$\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$	Na_2CO_3	DMF	40	50
8	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	DMF	40	64
9	CuI	Na_2CO_3	DMF	40	23
10	----	Na_2CO_3	DMF	40	Trace
11	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	MeCN	40	32
12	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	DCE	40	21
13	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	EtOAc	40	18
14	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	EtOH	40	23
15	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	dioxane	40	28
16	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	THF	40	36
17	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	HFIP	40	63
18	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	DMSO	40	75
19	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	DMSO	60	91
20	$\text{Ni}(\text{OTf})_2$	Na_2CO_3	DMSO	80	99 (98 ^c)

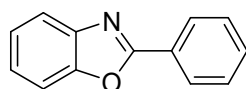
21	Ni(OTf) ₂	NaOAc	DMSO	80	0
22	Ni(OTf) ₂	NaHCO ₃	DMSO	80	83
23	Ni(OTf) ₂	NaOH	DMSO	80	72
24	Ni(OTf) ₂	K ₃ PO ₄	DMSO	80	87
25	Ni(OTf) ₂	Et ₃ N	DMSO	80	52
26	Ni(OTf) ₂	<i>t</i> BuOK	DMSO	80	28

^aReaction conditions: diphenyliodonium **1a** (0.1 mmol), nickel catalysts (0.05 equiv.), base (1.5 equiv.), solvent (0.5 mL), 6 h, argon. ^bNMR yield. ^cIsolated yield. DCE: 1,2-dichloroethane; HFIP: hexafluoroisopropanol.

General procedure for nickel catalyzed synthesis benzoxazole derivatives **2** and **4**:

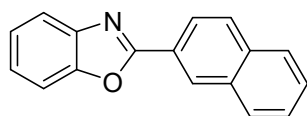
To iodonium **1** (55 mg, 0.1 mmol) in a flask was added Na₂CO₃ (16 mg, 1.5 equiv.), Ni(OTf)₂ (1.8 mg, 5 mol%), DMSO (1.0 mL). The reaction flask was evacuated and backfilled with argon three times, the reaction mixture was stirred at 80 °C heated by an oil bath for 6h. The reaction was monitored by TLC. After the reaction was finished, the residue was dissolved in EtOAc, washed with H₂O and brine, and dried over anhydrous Na₂SO₄, then evaporated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 1/50- 1/10) to provide **2** or **4**.

Characterization data of products



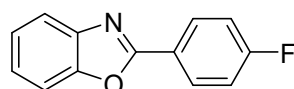
2a

2-Phenylbenzo[d]oxazole (2a): The product was isolated as a white solid (19 mg, 98%). mp 98 – 100 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.22 (m, 2H), 7.79 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.59 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.39 – 7.32 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 150.9, 142.2, 131.7, 129.1, 127.8, 127.3, 125.3, 124.7, 120.2, 110.8 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₁₀NO [M+H]⁺: 196.07569, found: 196.07568.



2b

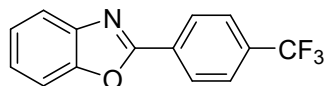
2-(Naphthalen-2-yl)benzo[d]oxazole (2b): The product was isolated as a white solid (22 mg, 90%). mp 107-109 °C ¹H NMR (400 MHz, CDCl₃) δ 8.79 (s, 1H), 8.33 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.99 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.93 – 7.87 (m, 1H), 7.82 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.63 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.58 (ddt, *J* = 10.8, 7.0, 3.5 Hz, 2H), 7.43 – 7.32 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 151.0, 142.3, 134.9, 133.1, 129.1, 129.0, 128.4, 128.1, 128.0, 127.1, 125.4, 124.8, 124.5, 124.1, 120.2, 110.8 ppm. HRMS (ESI, *m/z*) calcd for C₁₇H₁₂NO [M+H]⁺: 246.09134, found: 246.09113.



2c

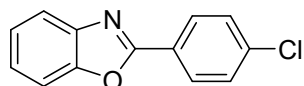
2-(4-Fluorophenyl)benzo[d]oxazole (2c): The product was isolated as a white solid (20 mg, 92%). mp

95-97 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.31 – 8.22 (m, 2H), 7.80 – 7.73 (m, 1H), 7.57 (dt, *J* = 9.6, 3.6 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.26 – 7.17 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 165.0 (d, *J*_{C-F} = 250.0 Hz), 162.3, 150.9, 142.2, 130.0 (d, *J*_{C-F} = 9.0 Hz), 125.3, 124.8, 123.6 (d, *J*_{C-F} = 3.0 Hz), 120.1, 116.3 (d, *J*_{C-F} = 23.0 Hz), 110.7 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉NOF [M+H]⁺: 214.06627, found: 214.06618.



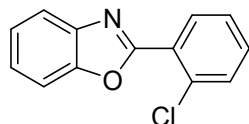
2d

2-(4-(Trifluoromethyl)phenyl)benzo[d]oxazole (2d): The product was isolated as a white solid (24 mg, 91%). mp 141-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 8.2 Hz, 2H), 7.83 – 7.75 (m, 3H), 7.64 – 7.59 (m, 1H), 7.44 – 7.36 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 151.0, 142.0, 133.1 (q, *J*_{C-F} = 27.0 Hz), 130.6, 128.0, 126.1 (q, *J*_{C-F} = 3.0 Hz), 126.0, 125.1, 122.8, 120.6, 111.0 ppm. HRMS (ESI, *m/z*) calcd for C₁₄H₉NOF₃ [M+H]⁺: 264.06290, found: 264.06308.



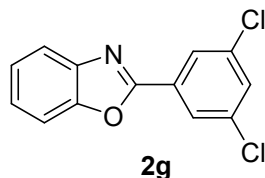
2e

2-(4-Chlorophenyl)benzo[d]oxazole (2e): The product was isolated as a white solid (22 mg, 95%). mp 146-147 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.78 (dd, *J* = 6.1, 2.9 Hz, 1H), 7.58 (dd, *J* = 6.3, 2.8 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.34 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 150.8, 142.1, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.2, 110.8 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉NOCl [M+H]⁺: 230.03672, found: 230.03658.



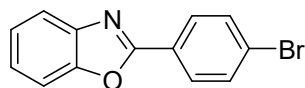
2f

2-(2-Chlorophenyl)benzo[d]oxazole (2f): The product was isolated as a white solid (21 mg, 91%). mp 74 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.81 (m, 1H), 7.63 (dd, *J* = 5.8, 2.5 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.35 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 150.7, 141.8, 133.6, 132.0, 131.9, 131.5, 127.1, 126.4, 125.7, 124.8, 120.6, 110.9 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉NOCl [M+H]⁺: 230.03672, found: 230.03650.



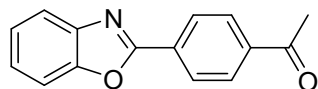
2g

2-(3,5-Dichlorophenyl)benzo[d]oxazole (2g): The product was isolated as a white solid (24 mg, 92%). mp 134-136 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.14 (s, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.51 (s, 1H), 7.46 – 7.35 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 150.9, 141.8, 135.9, 131.3, 130.0, 126.1, 125.9, 125.2, 120.6, 110.9 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₈NOCl₂ [M+H]⁺: 263.99775, found: 263.99750.



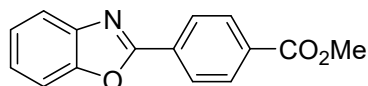
2h

2-(4-Bromophenyl)benzo[d]oxazole (2h): The product was isolated as a white solid (26 mg, 95%). mp 147-149 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 8.6 Hz, 2H), 7.78 (dd, *J* = 6.2, 2.9 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.58 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.40 – 7.34 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 150.9, 142.1, 132.3, 129.1, 126.4, 126.2, 125.5, 124.9, 120.2, 110.8 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉NOBr [M+H]⁺: 273.98620, found: 273.98584.



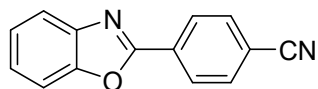
2i

1-(4-(Benzo[d]oxazol-2-yl)phenyl)ethan-1-one (2i): The product was isolated as a white solid (21 mg, 88%). mp 170-173 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 8.3 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.86 – 7.76 (m, 1H), 7.65 – 7.57 (m, 1H), 7.39 (p, *J* = 6.9 Hz, 2H), 2.66 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 197.5, 162.0, 151.0, 142.1, 139.1, 131.2, 129.0, 127.9, 125.9, 125.0, 120.5, 110.9, 26.9 ppm. HRMS (ESI, *m/z*) calcd for C₁₅H₁₂NO₂ [M+H]⁺: 238.08626, found: 238.08611.



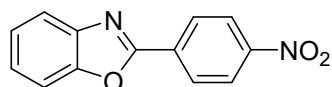
2j

Methyl 4-(benzo[d]oxazol-2-yl)benzoate (2j): The product was isolated as a white solid (21 mg, 84%). mp 195-197 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 8.5 Hz, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.76 (m, 1H), 7.66 – 7.57 (m, 1H), 7.46 – 7.34 (m, 2H), 3.97 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 162.0, 151.0, 142.1, 132.6, 131.1, 130.2, 127.6, 125.8, 125.0, 120.5, 110.9, 52.5 ppm. HRMS (ESI, *m/z*) calcd for C₁₅H₁₂NO₃ [M+H]⁺: 254.08117, found: 254.08089.



2k

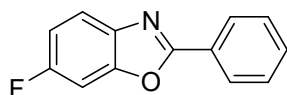
4-(Benzo[d]oxazol-2-yl)benzonitrile (2k): The product was isolated as a white solid (19 mg, 87%). mp 199-201 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.41 – 8.30 (m, 2H), 7.86 – 7.75 (m, 3H), 7.65 – 7.58 (m, 1H), 7.46 – 7.35 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 151.0, 142.0, 132.8, 131.2, 128.1, 126.3, 125.3, 120.7, 118.3, 114.9, 111.0 ppm. HRMS (ESI, *m/z*) calcd for C₁₄H₉N₂O [M+H]⁺: 221.07094, found: 221.07092.



2l

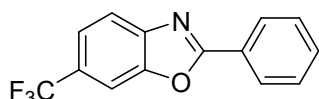
2-(4-Nitrophenyl)benzo[d]oxazole (2l): The product was isolated as a white solid (19 mg, 79%). mp 180-182 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.33 (m, 4H), 7.87 – 7.81 (m, 1H), 7.67 – 7.61 (m, 1H), 7.48 – 7.40 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 151.2, 149.6, 142.0, 132.9, 128.6, 126.5, 125.4, 124.4, 120.8, 111.1 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉N₂O₃ [M+H]⁺: 241.06077,

found: 241.06044.



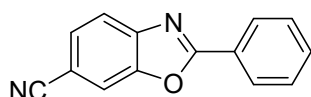
2m

6-Fluoro-2-phenylbenzo[d]oxazole (2m): The product was isolated as a white solid (18 mg, 83%). mp 95-97 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 – 8.17 (m, 2H), 7.70 (dd, *J* = 8.7, 4.9 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.31 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.15 – 7.07 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 160.8 (d, *J*_{C-F} = 243.0 Hz), 159.6, 138.5, 131.8, 129.1, 127.6, 127.0, 120.4 (d, *J*_{C-F} = 10.0 Hz), 112.7 (d, *J*_{C-F} = 25.0 Hz), 99.0, 98.7 ppm. HRMS (ESI, *m/z*) calcd for C₁₃H₉NOF [M+H]⁺: 214.06627, found: 214.06615.



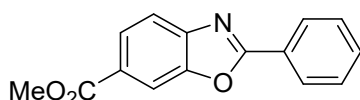
2n

2-Phenyl-6-(trifluoromethyl)benzo[d]oxazole (2n): The product was isolated as a white solid (19 mg, 73%). mp 80-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.24 (m, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.51 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 155.1, 150.3, 145.0, 132.4, 129.2, 128.1, 126.6, 124.3 (q, *J*_{C-F} = 271.0 Hz), 122.4 (q, *J*_{C-F} = 4.0 Hz), 120.5, 108.5 ppm. HRMS (ESI, *m/z*) calcd for C₁₄H₉NOF₃ [M+H]⁺: 264.06308, found: 264.06281.



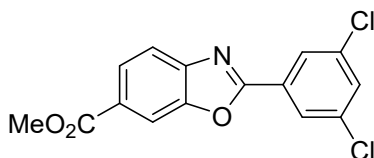
2o

2-Phenylbenzo[d]oxazole-6-carbonitrile (2o): The product was isolated as a white solid (17 mg, 76%). mp 182-185 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 7.6 Hz, 2H), 7.89 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 150.1, 146.1, 132.8, 129.3, 129.0, 128.3, 126.1, 121.1, 118.9, 115.0, 108.2 ppm. HRMS (ESI, *m/z*) calcd for C₁₄H₉N₂O [M+H]⁺: 221.07094, found: 221.07085.



2p

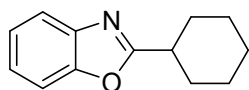
Methyl 2-phenylbenzo[d]oxazole-6-carboxylate (2p): The product was isolated as a white solid (20 mg, 78 %). mp 132-135 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (dd, *J* = 8.0, 1.6 Hz, 3H), 8.09 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.50 (m, 3H), 3.97 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.8, 165.7, 150.6, 146.2, 132.4, 129.2, 128.1, 127.2, 126.7, 126.6, 119.7, 112.4, 52.5 ppm. HRMS (ESI, *m/z*) calcd for C₁₅H₁₂NO₃ [M+H]⁺: 254.08117, found: 254.08086.



2q

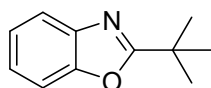
Methyl 2-(3,5-dichlorophenyl)benzo[d]oxazole-6-carboxylate (2q): The product was isolated as a white solid (26 mg, 81%). mp 175-177 °C ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 1.0 Hz, 1H), 8.15

(d, $J = 1.9$ Hz, 2H), 8.12 (dd, $J = 8.4, 1.5$ Hz, 1H), 7.82 – 7.78 (m, 1H), 7.54 (t, $J = 1.9$ Hz, 1H), 3.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 162.9, 150.5, 145.6, 136.0, 132.0, 129.4, 128.0, 126.8, 126.2, 120.1, 112.6, 52.6 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$: 322.00323, found: 322.00281.



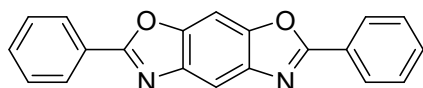
2r

2-Cyclohexylbenzo[d]oxazole (2r): The product was isolated as a white solid (19 mg, 94%). mp 156-158 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.65 (m, 1H), 7.47 (dt, $J = 7.6, 3.4$ Hz, 1H), 7.31 – 7.27 (m, 2H), 2.96 (tt, $J = 11.4, 3.6$ Hz, 1H), 2.22 – 2.14 (m, 2H), 1.93 – 1.82 (m, 2H), 1.71 (ddd, $J = 24.4, 12.2, 3.4$ Hz, 3H), 1.50 – 1.29 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 150.7, 141.3, 124.5, 124.1, 119.7, 110.4, 38.0, 30.6, 25.9, 25.8 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 202.12264, found: 202.12244.



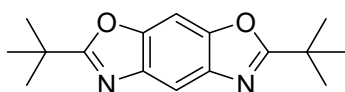
2s

2-(tert-Butyl)benzo[d]oxazole (2s): The product was isolated as a white solid (17 mg, 95%). mp 220-223 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, $J = 5.9, 3.2$ Hz, 1H), 7.49 (dd, $J = 5.9, 3.2$ Hz, 1H), 7.30 (dd, $J = 6.0, 3.2$ Hz, 2H), 1.50 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 141.3, 124.6, 124.1, 119.8, 110.4, 34.3, 28.6 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{11}\text{H}_{13}\text{NO}$ $[\text{M}+\text{H}]^+$: 176.1070, found: 176.1069.



4a

2,6-Diphenylbenzo[1,2-d:5,4-d']bis(oxazole) (4a): The product was isolated as a white solid (23 mg, 73%). mp 180 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (s, 4H), 8.12 (s, 1H), 7.80 (s, 1H), 7.56 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 140.0, 131.8, 129.2, 127.8, 127.1, 110.0, 93.5 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{13}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 313.09715, found: 313.09692.



4b

2,6-di-tert-Butylbenzo[1,2-d:5,4-d']bis(oxazole) (4b): The product was isolated as a white solid (18 mg, 66%). mp 132-133 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.58 (s, 1H), 1.51 (s, 18H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 174.2, 148.5, 138.6, 109.5, 92.9, 34.5, 28.6 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 273.15975, found: 273.15930.

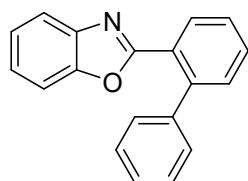
1 mmol scale reaction

To iodonium **1d** (617.3 mg, 1 mmol) in a flask was added Na_2CO_3 (158.98 mg, 1.5 equiv.), $\text{Ni}(\text{OTf})_2$ (17.84 mg, 5 mol%), DMSO (5 mL). The reaction flask was evacuated and backfilled with argon three times, the reaction mixture was stirred at 80 °C heated by an oil bath for 6h. The reaction was monitored

by TLC. After the reaction was finished, the residue was dissolved in EtOAc, washed with H₂O and brine, dried over anhydrous Na₂SO₄, and then evaporated under vacuum. The residue was purified by column chromatography on silica gel to provide **2d** in 65% yield (170.45 mg).

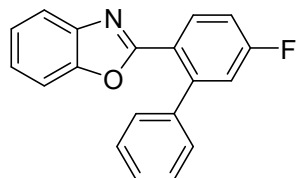
General procedure for nickel/Palladium catalyzed synthesis benzoxazole derivatives 6:

To iodonium **1** (55 mg, 0.1 mmol) in a flask was added Na₂CO₃ (16 mg, 1.5 equiv.), Ni(OTf)₂ (1.8 mg, 5 mol%), DMSO (1.0 mL). The reaction flask was evacuated and backfilled with argon three times, the reaction mixture was stirred at 80 °C heated by an oil bath for 6h. The reaction was monitored by TLC. After the reaction was finished, to the reaction mixture was added PdCl₂ (5 mol%), AgOAc (2.0 equiv.), K₃PO₄ (2.0 equiv.), TFA (1.0 mL), the reaction mixture was stirred at 80 °C heated by an oil bath for 24h. The reaction was monitored by TLC. After the reaction was finished, the residue was dissolved in EtOAc, washed with H₂O and brine, and dried over anhydrous Na₂SO₄, then evaporated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 1/50-1/10) to provide **6**.



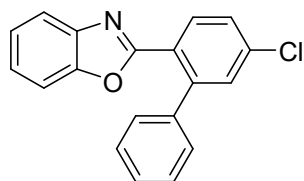
6a

2-([1,1'-Diphenyl]-2-yl)benzo[d]oxazole (6a): The product was isolated as a white solid (21 mg, 77%). mp 87 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.09 (m, 1H), 7.72 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 5.5, 1.4 Hz, 2H), 7.35 – 7.25 (m, 8H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 150.8, 142.6, 141.8, 141.1, 131.3, 131.1, 128.9, 128.2, 127.7, 127.4, 126.4, 125.0, 124.4, 120.2, 110.6 ppm. HRMS (ESI, *m/z*) calcd for C₁₉H₁₄NO [M+H]⁺: 272.10699, found: 272.10657.



6b

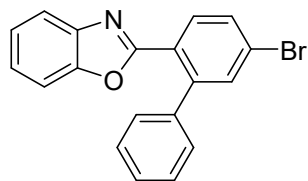
2-(5-Fluoro-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6b): The product was isolated as a white solid (19 mg, 64%). mp 82-85 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.08 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.25 (m, 8H), 7.24 – 7.17 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.1 (d, *J*_{C-F} = 251.0 Hz), 162.8, 150.8, 145.1, 141.7, 140.0, 133.4 (d, *J*_{C-F} = 9.0 Hz), 128.7, 128.4, 127.9, 125.1, 124.5, 122.7 (d, *J*_{C-F} = 3.0 Hz), 120.2, 118.3, 115.0 (d, *J*_{C-F} = 21.0 Hz), 110.6 ppm. HRMS (ESI, *m/z*) calcd for C₁₉H₁₃NOF [M+H]⁺: 290.09757, found: 290.09720.



6c

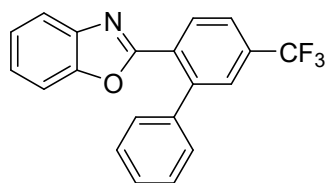
2-(5-Chloro-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6c): The product was isolated as a white solid (22 mg, 71%). mp 79-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.06 (m, 1H), 7.71 (dd, *J* = 7.4, 1.3

Hz, 1H), 7.53 – 7.46 (m, 2H), 7.39 – 7.24 (m, 8H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 150.8, 144.1, 141.6, 139.8, 137.2, 132.4, 131.4, 128.8, 128.4, 127.9, 127.9, 125.3, 124.8, 124.6, 120.2, 110.7 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{13}\text{NOCl}$ $[\text{M}+\text{H}]^+$: 306.06802, found: 306.06775.



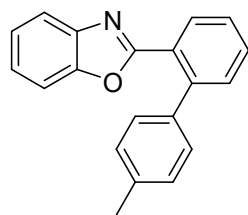
6d

2-(5-Bromo-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6d): The product was isolated as a white solid (20 mg, 57%). mp 104-107 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.38 – 7.24 (m, 8H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 150.8, 144.3, 141.7, 139.8, 134.3, 132.4, 130.8, 128.8, 128.4, 127.9, 125.6, 125.3, 124.6, 120.3, 120.3, 110.7 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{13}\text{NOBr}$ $[\text{M}+\text{H}]^+$: 350.01750, found: 350.01721.



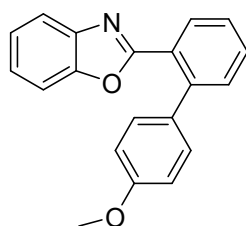
6e

2-(5-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6e): The product was isolated as a white solid (18 mg, 55%). mp 85-87 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 7.9$ Hz, 1H), 7.75 (t, $J = 9.3$ Hz, 3H), 7.42 – 7.27 (m, 8H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 162.5, 150.9, 143.3, 141.6, 139.8, 132.8 (q, $J_{\text{C-F}} = 33.0$ Hz), 131.6, 129.6, 128.8, 128.5, 128.2 (q, $J_{\text{C-F}} = 3.0$ Hz), 128.1, 125.6, 124.8, 124.4 (q, $J_{\text{C-F}} = 3.0$ Hz), 124.4, 120.5, 110.8 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{13}\text{NOF}_3$ $[\text{M}+\text{H}]^+$: 340.09438, found: 340.09399.



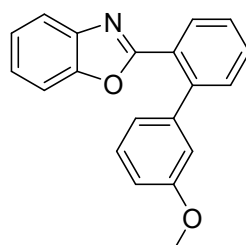
6f

2-(4'-Methyl-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6f): The product was isolated as a white solid (19 mg, 68%). mp 96-97 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.00 (m, 1H), 7.73 – 7.65 (m, 1H), 7.56 – 7.49 (m, 1H), 7.44 (ddd, $J = 5.1, 3.8, 1.9$ Hz, 2H), 7.30 – 7.19 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 150.8, 142.6, 141.7, 138.0, 137.1, 131.3, 131.2, 131.2, 129.0, 128.8, 127.4, 126.3, 125.0, 124.4, 120.2, 110.7, 21.3 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 286.12264, found: 286.12225.



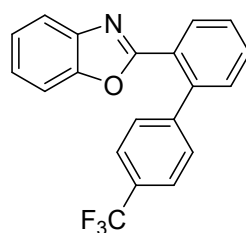
6g

2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6g): The product was isolated as a white solid (22 mg, 73%). mp 102-105 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 13.0, 6.1 Hz, 2H), 7.29 (ddd, *J* = 15.5, 8.0, 3.4 Hz, 3H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 159.1, 150.9, 142.2, 141.8, 133.4, 131.2, 131.2, 131.1, 130.1, 127.3, 126.4, 125.0, 124.4, 120.2, 113.8, 110.7, 55.4 ppm. HRMS (ESI, *m/z*) calcd for C₂₀H₁₆NO₂ [M+H]⁺: 302.11756, found: 302.11716.



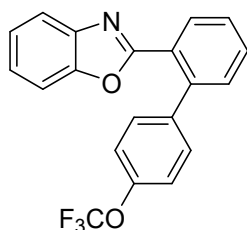
6h

2-(3'-Methoxy-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6h): The product was isolated as a white solid (20 mg, 68%). mp 84-86 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.64 – 7.57 (m, 1H), 7.52 (ddd, *J* = 4.6, 3.8, 2.2 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 6.91 – 6.80 (m, 3H), 3.68 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 159.5, 150.9, 142.4, 141.8, 131.1, 129.2, 127.7, 126.4, 125.1, 124.4, 121.5, 120.2, 114.2, 113.4, 110.7, 55.3 ppm. HRMS (ESI, *m/z*) calcd for C₂₀H₁₆NO₂ [M+H]⁺: 302.11756, found: 302.11713.



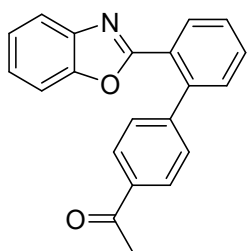
6i

2-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6i): The product was isolated as a white solid (16 mg, 46%). mp 83 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.14 (m, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.50 – 7.44 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.27 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 150.8, 144.9, 141.7, 141.1, 131.3, 131.2, 131.1, 129.4, 128.4, 126.8 (q, *J*_{C-F} = 269.0 Hz), 126.3, 125.4, 125.2 (q, *J*_{C-F} = 3.0 Hz), 124.7, 123.1, 110.7 ppm. HRMS (ESI, *m/z*) calcd for C₂₀H₁₃NOF₃ [M+H]⁺: 340.09438, found: 340.09406.



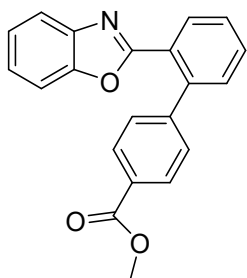
6j

2-(4'-(Trifluoromethoxy)-[1,1'-biphenyl]-2-yl)benzo[d]oxazole (6j): The product was isolated as a white solid (18 mg, 51%). mp 57-60 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.13 (m, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.60 (dt, *J* = 7.5, 3.8 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.44 (m, 1H), 7.35 – 7.26 (m, 5H), 7.19 (d, *J* = 8.2 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 150.8, 148.7, 141.7, 141.1, 140.0, 131.2, 131.2, 131.1, 130.4, 128.2, 126.4, 125.3, 124.6, 120.7, 120.3, 110.6 ppm. HRMS (ESI, *m/z*) calcd for C₂₀H₁₃NO₂F₃ [M+H]⁺: 356.08929, found: 356.08875.



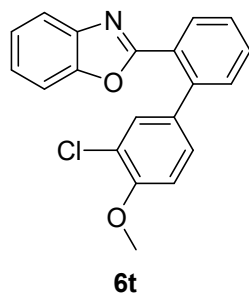
6k

1-(2'-(Benzo[d]oxazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (6k): The product was isolated as a white solid (17 mg, 54%). mp 149 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 6.7 Hz, 2H), 7.34 – 7.25 (m, 3H), 2.62 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 163.3, 150.8, 146.1, 141.7, 141.3, 136.0, 131.2, 131.2, 131.1, 129.3, 128.4, 126.3, 125.3, 124.6, 120.3, 110.7, 26.8 ppm. HRMS (ESI, *m/z*) calcd for C₂₁H₁₆NO₂ [M+H]⁺: 314.11756, found: 314.11697.



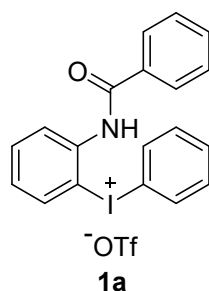
6l

Methyl 2'-(benzo[d]oxazol-2-yl)-[1,1'-biphenyl]-4-carboxylate (6l): The product was isolated as a white solid (17 mg, 51%). mp 165-167 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.56 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.24 (m, 3H), 3.93 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.2, 163.4, 150.8, 145.9, 141.7, 141.4, 131.2, 131.2, 129.6, 129.1, 128.3, 126.3, 125.2, 124.6, 120.3, 110.7, 52.3 ppm. HRMS (ESI, *m/z*) calcd for C₂₁H₁₆NO₃ [M+H]⁺: 330.11247, found: 330.11182.



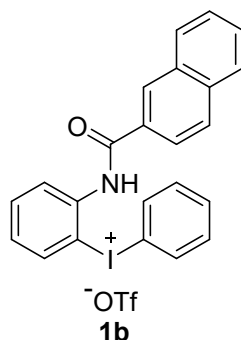
2-(3'-chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)benzo[d]oxazole(6t): The product was isolated as a white solid (18 mg, 53%); mp 89-91 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.76 – 7.69 (m, 1H), 7.60 – 7.54 (m, 1H), 7.53 – 7.47 (m, 1H), 7.45 (dd, $J = 7.6, 1.1$ Hz, 1H), 7.41 (d, $J = 2.2$ Hz, 1H), 7.37 – 7.27 (m, 3H), 7.08 (dd, $J = 8.5, 2.2$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 1H), 3.91 (s, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.7, 154.5, 150.8, 141.8, 140.8, 134.4, 131.3, 131.2, 130.7, 128.5, 127.8, 126.3, 125.2, 124.5, 122.2, 120.3, 111.7, 110.7, 56.3 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 336.07858, found: 336.07797.

Synthesis of diaryliodoniums was done according to reported work.^[1]



(2-benzamidophenyl)(phenyl)iodonium trifluoromethanesulfonate (1a):

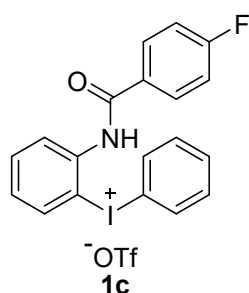
$^1\text{H NMR}$ (400 MHz, DMSO) δ 11.12 (s, 1H), 8.22 (dd, $J = 8.3, 1.0$ Hz, 2H), 8.12 – 8.03 (m, 3H), 7.71 (qd, $J = 7.3, 1.3$ Hz, 3H), 7.67 – 7.59 (m, 3H), 7.58 – 7.53 (m, 2H), 7.40 – 7.34 (m, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, DMSO) δ 167.6, 138.4, 135.7, 133.0, 132.9, 132.8, 132.4, 131.8, 129.3, 128.8, 128.1, 127.8, 116.9, 114.3 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{15}\text{NOI}$ $[\text{M}-\text{OTf}]^+$: 400.01928, found: 400.01892.



(2-(2-naphthamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1b)

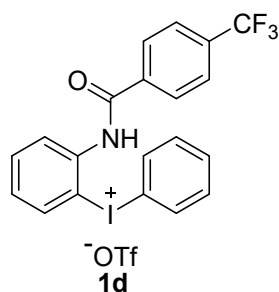
$^1\text{H NMR}$ (500 MHz, DMSO) δ 11.31 (s, 1H), 8.72 (s, 1H), 8.24 (d, $J = 7.9$ Hz, 2H), 8.16 (t, $J = 6.6$ Hz, 2H), 8.10 (dd, $J = 13.8, 6.9$ Hz, 3H), 7.76 – 7.67 (m, 4H), 7.65 (d, $J = 7.2$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 2H), 7.38 (dd, $J = 13.5, 6.2$ Hz, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, DMSO) δ 167.6, 138.4, 135.7, 134.8, 133.0, 132.4, 132.0, 131.8, 130.0, 129.2, 129.2, 129.1, 128.6, 128.5, 127.9, 127.8, 127.3, 124.2, 122.0,

116.9, 114.2 ppm. HRMS (ESI, m/z) calcd for $C_{23}H_{17}NOI$ [M-OTf]⁺: 450.03493, found: 450.03452.



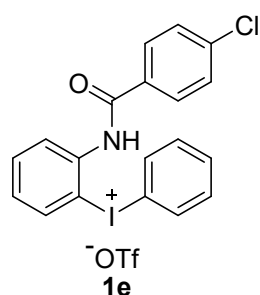
(2-(4-fluorobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1c)

¹H NMR (400 MHz, DMSO) δ 11.11 (s, 1H), 8.20 (d, $J = 7.6$ Hz, 2H), 8.14 (dd, $J = 8.8, 5.5$ Hz, 2H), 8.09 (d, $J = 8.1$ Hz, 1H), 7.70 (td, $J = 7.1, 3.5$ Hz, 2H), 7.62 – 7.52 (m, 3H), 7.48 (t, $J = 8.8$ Hz, 2H), 7.41 – 7.33 (m, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 166.6, 166.5 (d, $J_{C-F} = 250.0$ Hz), 138.4, 135.9, 135.8, 133.2, 132.6, 132.0, 131.1 (d, $J_{C-F} = 10.0$ Hz), 129.5, 128.0, 122.4, 119.2, 116.9, 116.0 (d, $J_{C-F} = 22.0$ Hz), 114.5 ppm. HRMS (ESI, m/z) calcd for $C_{19}H_{14}NOFI$ [M-OTf]⁺: 418.00986, found: 418.00955.



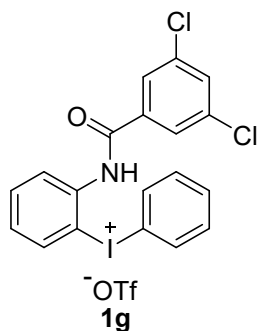
phenyl(2-(4-(trifluoromethyl)benzamido)phenyl)iodonium trifluoromethanesulfonate (1d)

¹H NMR (400 MHz, DMSO) δ 11.21 (s, 1H), 8.27 – 8.15 (m, 5H), 8.03 (d, $J = 8.3$ Hz, 2H), 7.75 – 7.67 (m, 2H), 7.62 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.44 – 7.38 (m, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 166.1, 138.2, 136.9, 136.2, 135.6, 133.1, 132.4, 132.3, 132.1, 131.8, 129.6, 129.0, 128.3, 125.8 (q, $J_{C-F} = 3.0$ Hz), 123.9 (q, $J_{C-F} = 3.0$ Hz), 116.7, 114.8 ppm. HRMS (ESI, m/z) calcd for $C_{20}H_{14}F_3NOI$ [M-OTf]⁺: 468.00667, found: 468.00644.



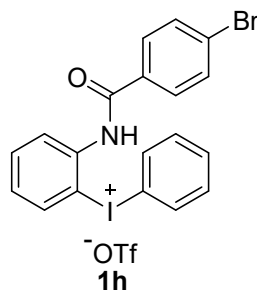
(2-(4-chlorobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1e)

¹H NMR (400 MHz, DMSO) δ 11.12 (s, 1H), 8.20 (d, $J = 7.7$ Hz, 2H), 8.12 (d, $J = 8.2$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 2H), 7.71 (dd, $J = 15.3, 8.0$ Hz, 4H), 7.60 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.41 – 7.35 (m, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 166.4, 138.3, 137.7, 136.0, 135.7, 133.1, 132.4, 131.8, 131.6, 130.1, 129.4, 128.9, 128.0, 116.8, 114.6 ppm. HRMS (ESI, m/z) calcd for $C_{19}H_{14}NOI$ [M-OTf]⁺: 400.01928, found: 400.01892. HRMS (ESI, m/z) calcd for $C_{19}H_{14}NOClI$ [M-OTf]⁺: 433.98031, found: 433.97998.



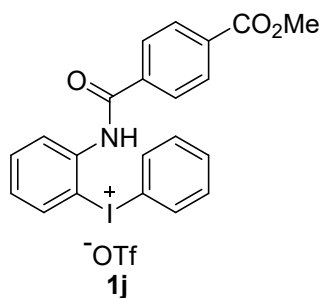
(2-(3,5-dichlorobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1g)

^1H NMR (400 MHz, DMSO) δ 11.16 (s, 1H), 8.23 – 8.14 (m, 3H), 8.06 – 7.94 (m, 3H), 7.75 – 7.66 (m, 2H), 7.61 – 7.57 (m, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.44 – 7.38 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 164.7, 138.0, 136.5, 136.4, 135.6, 134.7, 133.3, 132.4, 132.0, 131.9, 129.8, 128.4, 127.0, 116.8, 114.8 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{13}\text{NOCl}_2$ [M-OTf] $^+$: 467.94134, found: 467.94128.



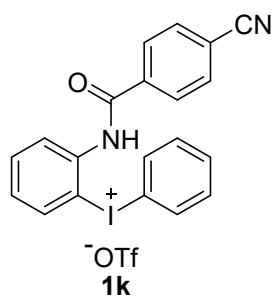
(2-(4-bromobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1h)

^1H NMR (400 MHz, DMSO) δ 11.12 (s, 1H), 8.20 (d, J = 7.8 Hz, 2H), 8.12 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.42 – 7.34 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 166.6, 138.3, 136.0, 135.7, 133.1, 132.4, 132.0, 131.9, 131.9, 130.2, 129.4, 128.0, 126.7, 116.8, 114.6 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{14}\text{NOBr}$ [M-OTf] $^+$: 477.92980, found: 477.92963.



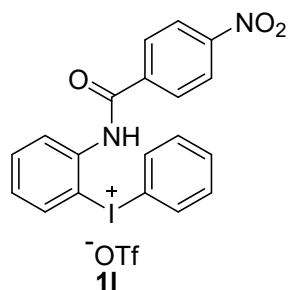
(2-(4-(methoxycarbonyl)benzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1j)

^1H NMR (400 MHz, DMSO) δ 11.23 (s, 1H), 8.24 – 8.11 (m, 7H), 7.71 (ddd, J = 12.1, 5.0, 2.4 Hz, 2H), 7.61 (dd, J = 8.0, 1.4 Hz, 1H), 7.54 (dd, J = 10.8, 4.8 Hz, 2H), 7.43 – 7.37 (m, 1H), 3.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 166.5, 165.7, 138.2, 137.0, 136.1, 135.6, 133.1, 133.0, 132.4, 131.8, 129.5, 128.5, 128.2, 116.8, 114.7, 52.6 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_3$ [M-OTf] $^+$: 458.02476, found: 458.02426.



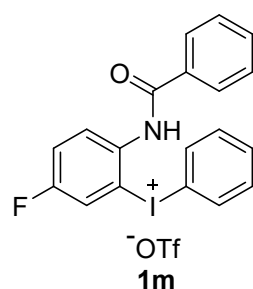
(2-(4-cyanobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1k)

^1H NMR (400 MHz, DMSO) δ 11.22 (s, 1H), 8.15 (dd, J = 19.8, 8.4 Hz, 7H), 7.71 (dd, J = 16.5, 8.3 Hz, 2H), 7.61 (d, J = 6.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.41 (dd, J = 11.2, 4.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 166.2, 138.2, 137.2, 136.5, 135.7, 133.4, 133.0, 132.6, 132.0, 130.9, 129.9, 129.1, 128.5, 128.2, 118.4, 116.9, 115.0 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{OI}$ $[\text{M}-\text{OTf}]^+$: 425.01453, found: 425.01389.



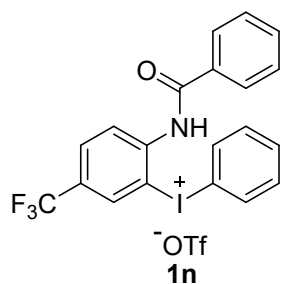
(2-(4-nitrobenzamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1l)

^1H NMR (400 MHz, DMSO) δ 11.27 (s, 1H), 8.48 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 8.22 – 8.14 (m, 3H), 7.76 – 7.66 (m, 2H), 7.63 (dd, J = 7.9, 1.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.45 – 7.38 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 165.6, 149.8, 138.7, 138.1, 136.4, 135.5, 133.2, 132.3, 131.8, 129.7, 129.6, 128.4, 123.9, 116.7, 115.0 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{I}$ $[\text{M}-\text{OTf}]^+$: 445.00436, found: 445.00409.



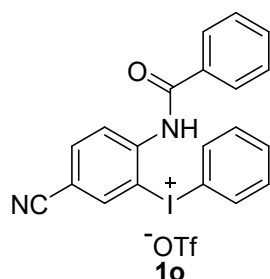
(2-benzamido-5-fluorophenyl)(phenyl)iodonium trifluoromethanesulfonate (1m)

^1H NMR (400 MHz, DMSO) δ 11.01 (s, 1H), 8.23 (dd, J = 8.3, 1.0 Hz, 2H), 8.12 (dd, J = 7.7, 2.6 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.72 (ddd, J = 5.6, 4.9, 2.6 Hz, 2H), 7.65 (dt, J = 8.2, 6.3 Hz, 4H), 7.60 – 7.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 167.4, 159.8 (d, $J_{\text{C-F}}$ = 248.0 Hz), 135.6, 135.3, 132.8, 132.5, 131.9, 129.4 (d, $J_{\text{C-F}}$ = 8.0 Hz), 128.8, 128.1, 122.8, 122.5, 120.2 (d, $J_{\text{C-F}}$ = 22.0 Hz), 117.1, 114.9, 114.9 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{14}\text{NOFI}$ $[\text{M}-\text{OTf}]^+$: 418.00986, found: 418.00937.



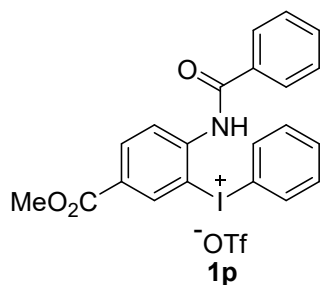
(2-benzamido-5-(trifluoromethyl)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1n)

^1H NMR (400 MHz, DMSO) δ 11.30 (s, 1H), 8.51 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 2H), 8.08 (t, $J = 9.1$ Hz, 3H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.73 (q, $J = 7.4$ Hz, 2H), 7.65 (t, $J = 7.6$ Hz, 2H), 7.57 (t, $J = 7.8$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 167.5, 142.4, 135.7, 133.1, 132.6, 132.5, 131.9, 129.9 (q, $J_{\text{C-F}} = 3.0$ Hz), 128.9, 128.5, 128.2, 128.1, 122.9 (q, $J_{\text{C-F}} = 272.0$ Hz), 117.4, 114.1 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{14}\text{NOF}_3\text{I}$ $[\text{M-OTf}]^+$: 468.00667, found: 468.00632.



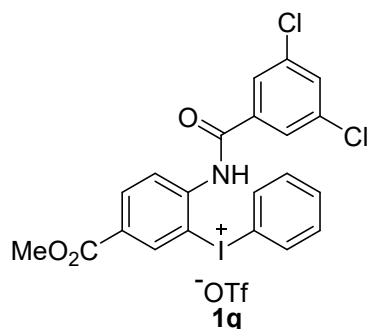
(2-benzamido-5-cyanophenyl)(phenyl)iodonium trifluoromethanesulfonate (1o)

^1H NMR (400 MHz, DMSO) δ 11.31 (s, 1H), 8.68 (d, $J = 1.7$ Hz, 1H), 8.25 (d, $J = 7.5$ Hz, 2H), 8.17 (dd, $J = 8.4, 1.8$ Hz, 1H), 8.09 – 8.02 (m, 2H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.76 – 7.70 (m, 2H), 7.65 (t, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 167.4, 142.9, 140.0, 136.6, 135.7, 133.2, 132.7, 132.5, 132.0, 128.9, 128.3, 127.9, 117.4, 116.9, 113.7, 110.7 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{OI}$ $[\text{M-OTf}]^+$: 425.01453, found: 425.01404.



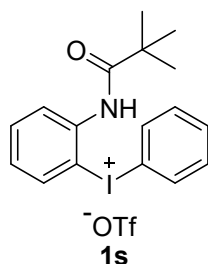
(2-benzamido-5-(methoxycarbonyl)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1p)

^1H NMR (400 MHz, DMSO) δ 11.30 (s, 1H), 8.60 (d, $J = 1.8$ Hz, 1H), 8.25 (d, $J = 7.4$ Hz, 2H), 8.21 (dd, $J = 8.4, 1.8$ Hz, 1H), 8.10 – 8.04 (m, 2H), 7.73 (dd, $J = 13.1, 7.8$ Hz, 3H), 7.65 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.8$ Hz, 2H), 3.85 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 167.6, 164.1, 142.6, 136.7, 135.7, 133.2, 133.1, 132.6, 132.5, 131.9, 129.3, 128.9, 128.2, 127.4, 117.2, 113.5, 52.8 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_3\text{I}$ $[\text{M-OTf}]^+$: 458.02476, found: 458.02411.



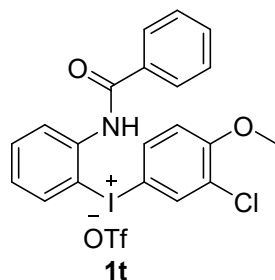
(2-(3,5-dichlorobenzamido)-5-(methoxycarbonyl)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1q)

^1H NMR (400 MHz, DMSO) δ 10.43 (s, 1H), 8.42 (d, J = 1.9 Hz, 1H), 8.01 (dd, J = 6.7, 1.9 Hz, 3H), 7.93 (t, J = 1.9 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 3.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 164.6, 162.7, 143.7, 139.6, 137.1, 134.5, 131.5, 129.6, 129.1, 128.0, 126.6, 97.8, 52.5 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{21}\text{H}_{15}\text{NO}_3\text{Cl}_2\text{I}$ $[\text{M}-\text{OTf}]^+$: 525.94682, found: 525.94659.



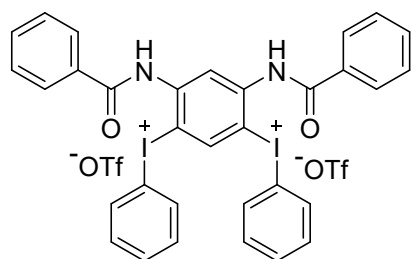
phenyl(2-pivalamidophenyl)iodonium trifluoromethanesulfonate (1s)

^1H NMR (400 MHz, DMSO) δ 10.17 (s, 1H), 8.18 (d, J = 7.7 Hz, 2H), 8.00 (d, J = 8.1 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.34 – 7.27 (m, 1H), 1.32 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 179.4, 138.5, 135.7, 135.4, 133.0, 132.5, 131.9, 129.1, 127.6, 116.7, 114.7, 27.0 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{17}\text{H}_{19}\text{NOI}$ $[\text{M}-\text{OTf}]^+$: 380.05058, found: 380.05011.



(2-benzamidophenyl)(3-chloro-4-methoxyphenyl)iodonium trifluoromethanesulfonate (1t)

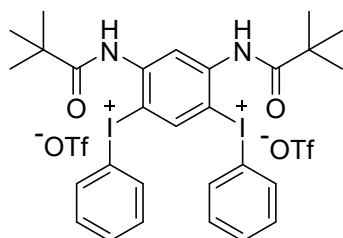
^1H NMR (400 MHz, DMSO) δ 11.13 (s, 1H), 8.39 (d, J = 2.2 Hz, 1H), 8.19 (dd, J = 8.9, 2.1 Hz, 1H), 8.07 (t, J = 7.6 Hz, 3H), 7.75 – 7.58 (m, 5H), 7.38 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H), 3.93 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 167.6, 157.8, 138.1, 136.7, 136.6, 135.5, 132.9, 132.7, 129.3, 128.8, 128.1, 127.7, 123.2, 115.6, 114.9, 105.4, 56.8. HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2\text{ClI}$ $[\text{M}-\text{OTf}]^+$: 463.99088, found: 463.99030.



3a

(4,6-bis(benzamido)-1,3-phenylene)bis(phenyliodonium) trifluoromethanesulfonate (3a)

^1H NMR (400 MHz, DMSO) δ 11.21 (s, 2H), 8.97 (s, 1H), 8.11 (d, $J = 7.5$ Hz, 4H), 8.06 – 8.00 (m, 4H), 7.89 (s, 1H), 7.72 (q, $J = 7.3$ Hz, 4H), 7.64 (t, $J = 7.5$ Hz, 4H), 7.52 (t, $J = 7.8$ Hz, 4H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 167.3, 143.4, 142.6, 135.4, 133.1, 132.7, 132.0, 128.9, 128.2, 125.4, 122.0, 119.4, 117.3, 112.1 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{32}\text{H}_{23}\text{N}_2\text{O}_2\text{I}_2$ $[\text{M}-2\text{OTf}-\text{H}]^+$: 720.98434, found: 720.98279; HRMS (ESI, m/z) calcd for $\text{C}_{33}\text{H}_{24}\text{N}_2\text{O}_5\text{F}_3\text{SI}_2$ $[\text{M}-\text{OTf}]^+$: 870.94419, found: 870.94250.



3b

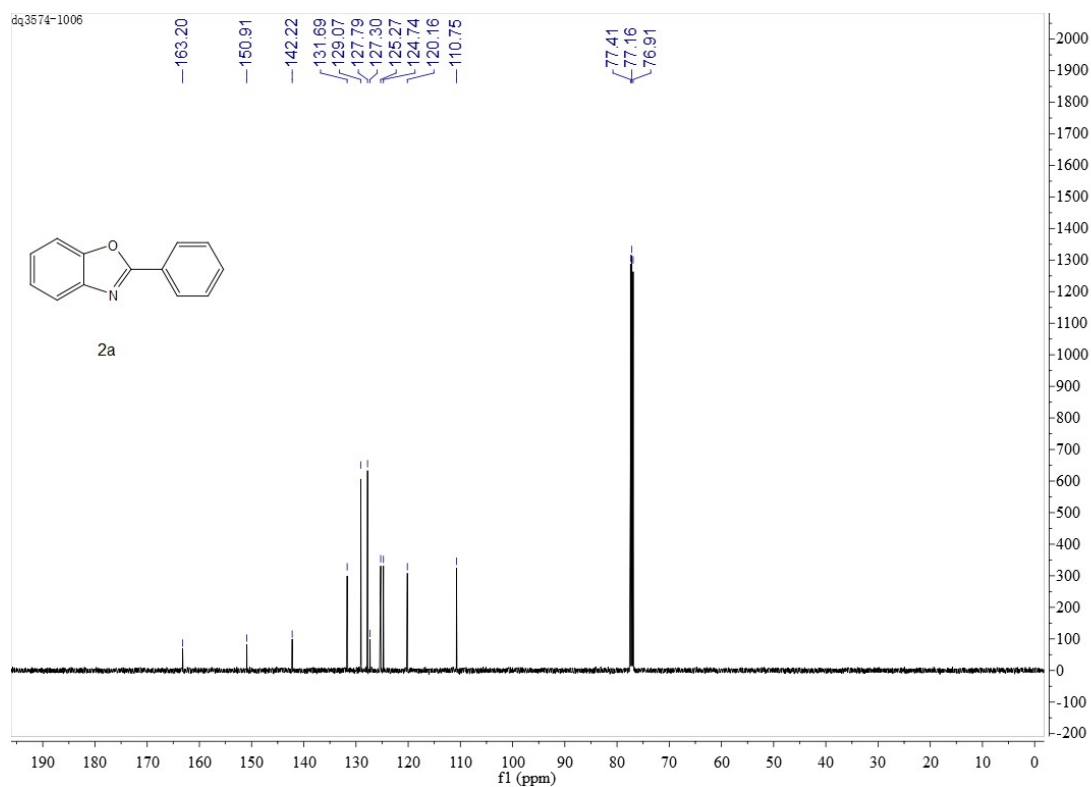
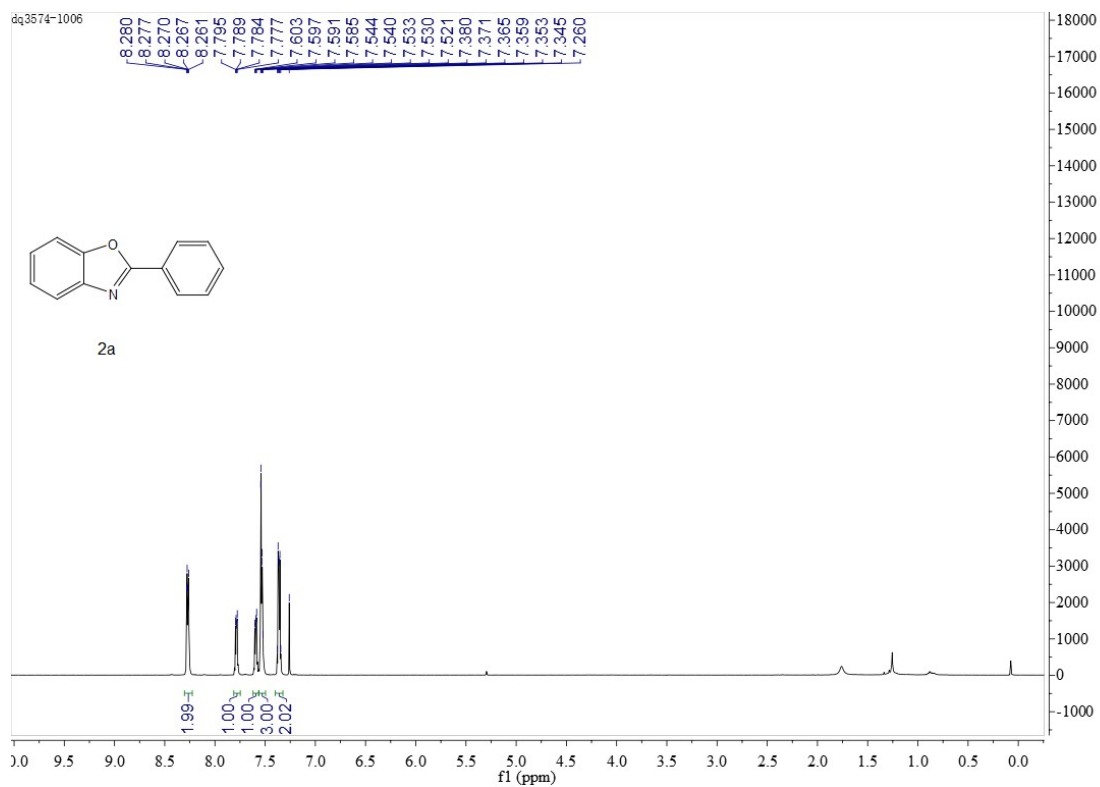
(4,6-dipivalamido-1,3-phenylene)bis(phenyliodonium) trifluoromethanesulfonate (3b)

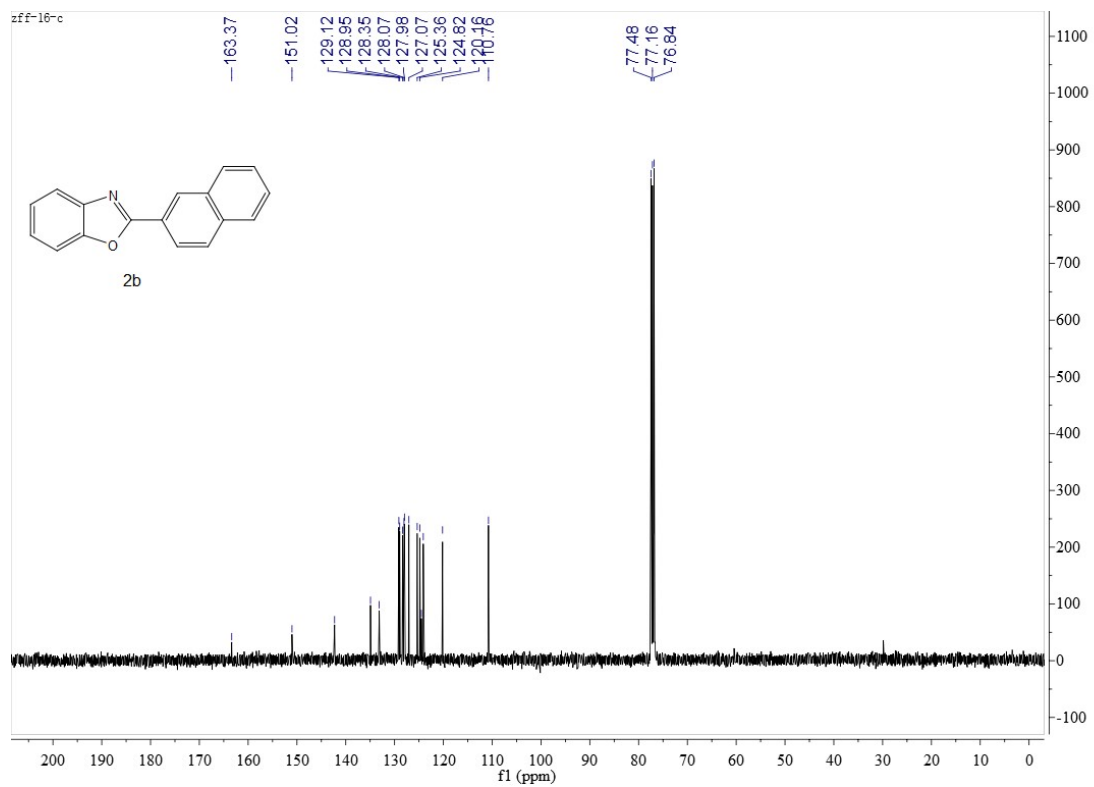
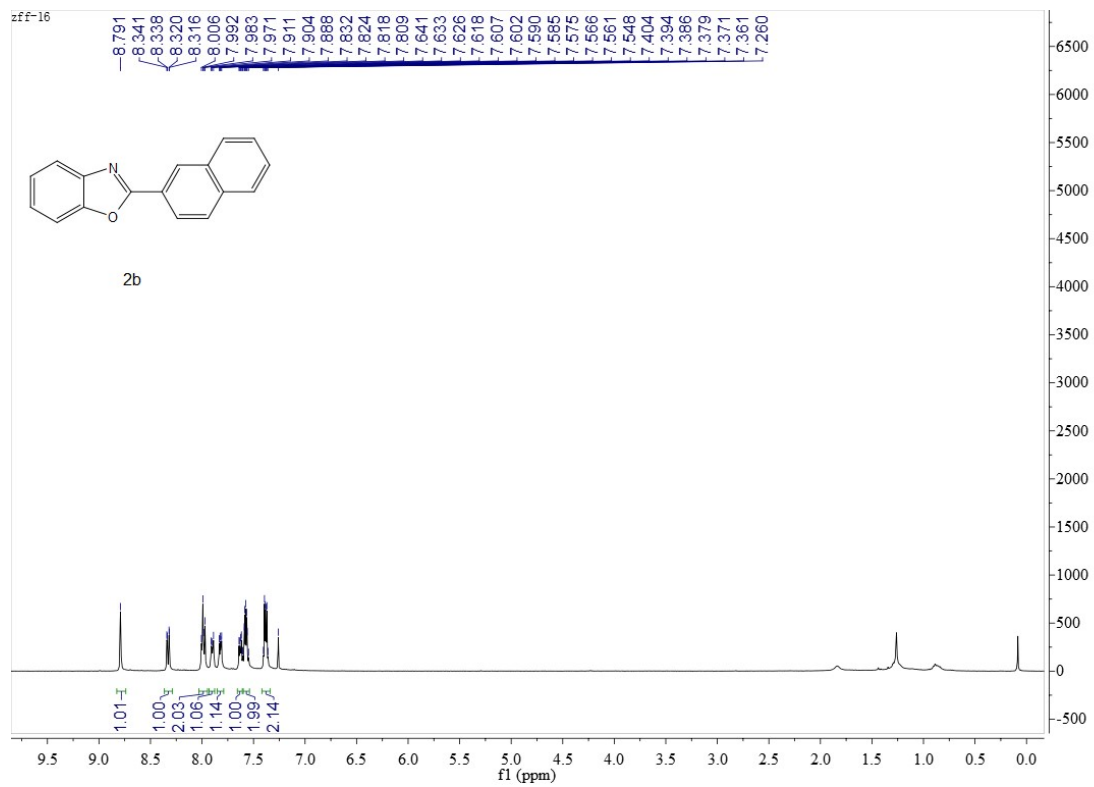
^1H NMR (400 MHz, DMSO) δ 10.16 (d, $J = 23.8$ Hz, 2H), 8.83 (s, 1H), 8.04 (d, $J = 7.9$ Hz, 4H), 7.70 (t, $J = 7.3$ Hz, 2H), 7.57 (s, 1H), 7.50 (t, $J = 7.5$ Hz, 4H), 1.30 (s, 18H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 179.1, 143.1, 135.7, 133.0, 132.4, 125.7, 117.6, 112.9, 100.0, 39.7, 27.3 ppm. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_2\text{I}_2$ $[\text{M}-2\text{OTf}-\text{H}]^+$: 681.04694, found: 681.04633; HRMS (ESI, m/z) calcd for $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_5\text{F}_3\text{SI}_2$ $[\text{M}-\text{OTf}]^+$: 831.00679, found: 831.00586.

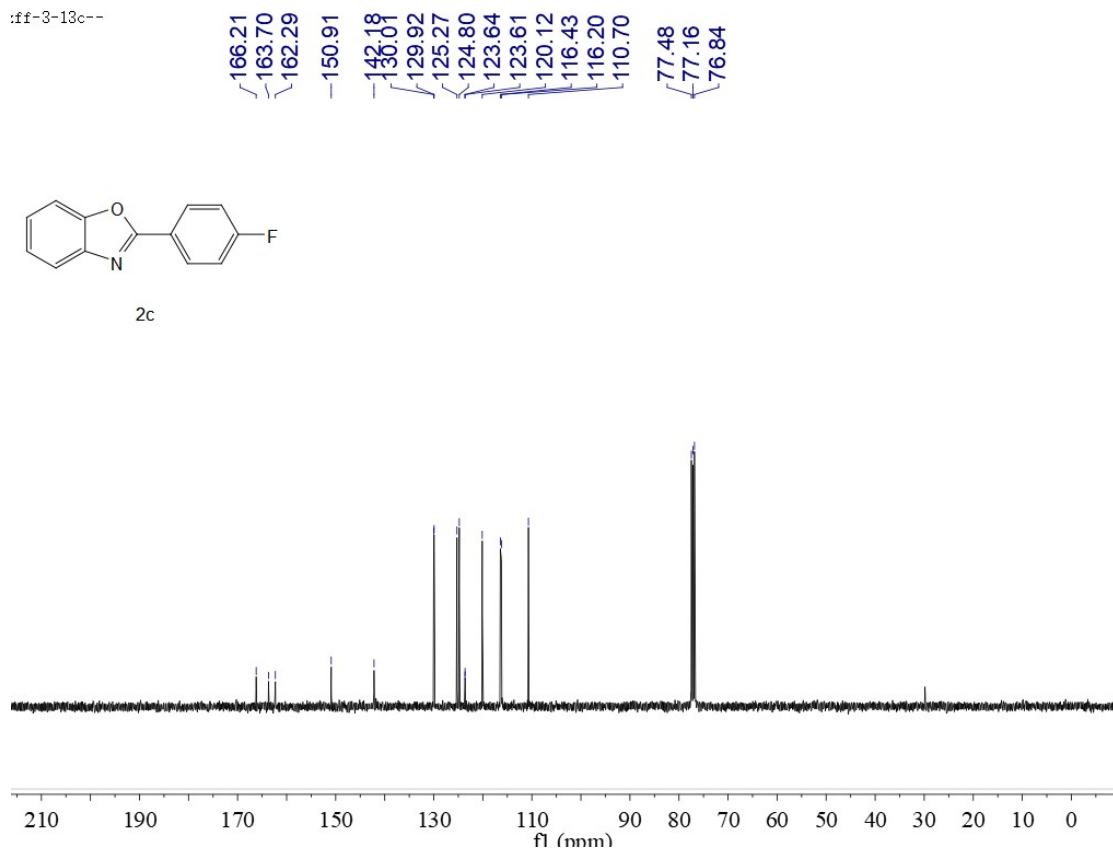
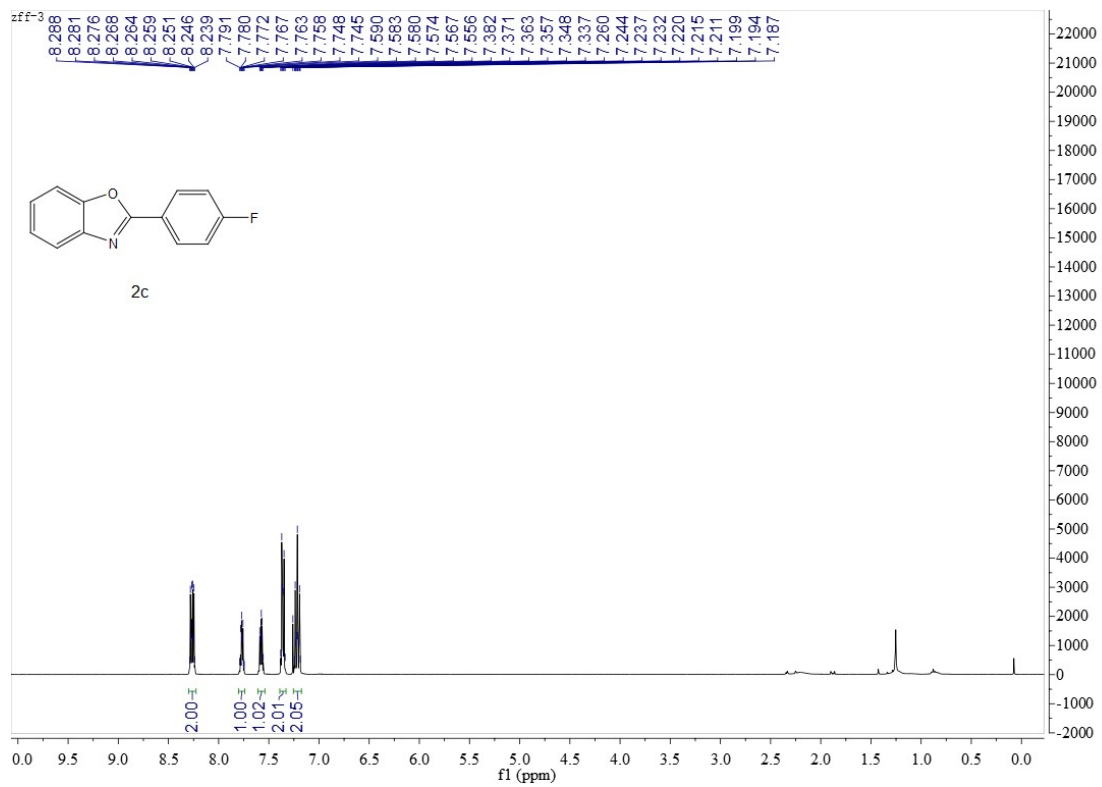
Reference

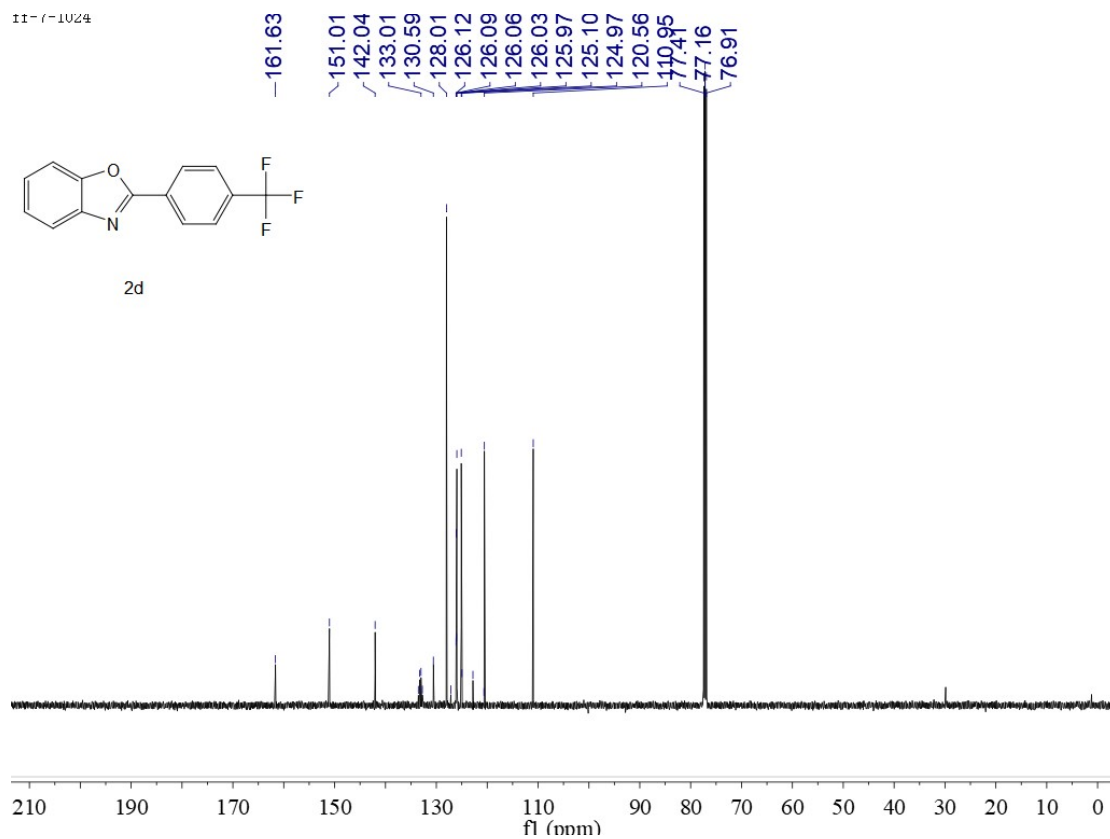
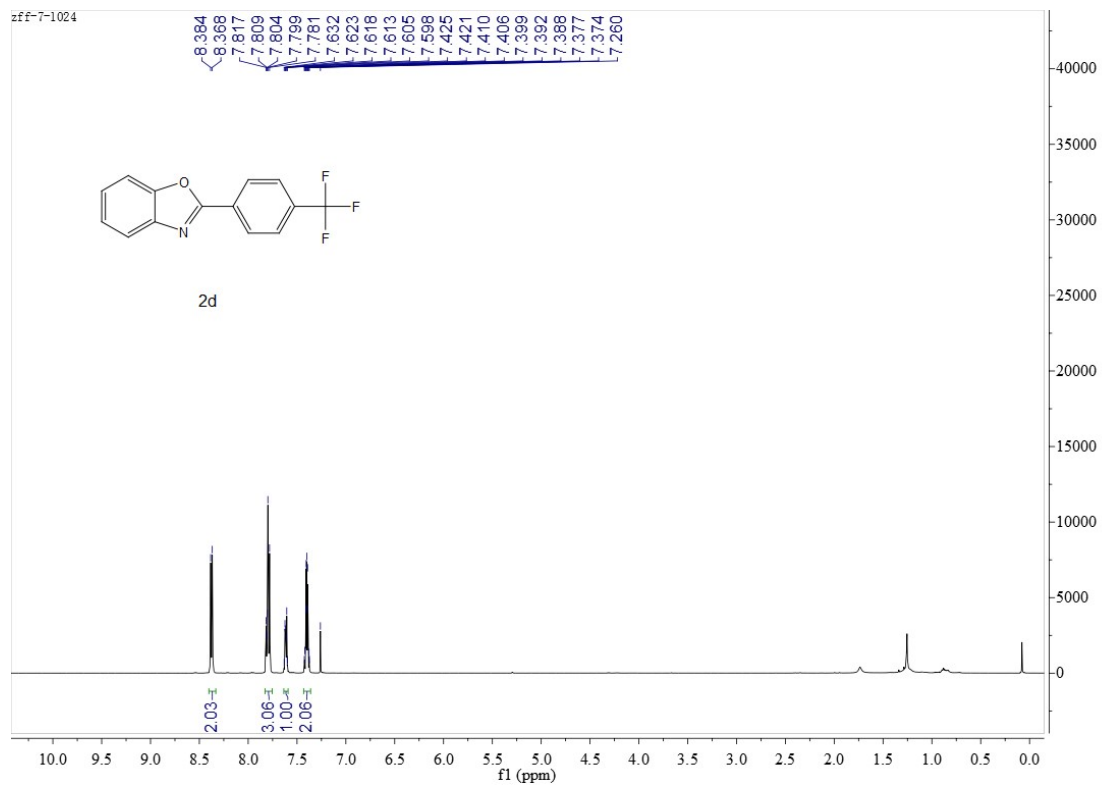
- [1] a) C. Dey, E. Lindstedt, B. Olofsson, *Org. Lett.* **2015**, *17*, 4554-4557; b) M. Bielawski, B. Olofsson, *Chem. Commun.*, **2007**, 2521-2523; c) M. Reitti, P. Villo, B. Olofsson, *Angew. Chem. Int. Ed.* **2016**, *55*, 8928-8932; *Angew. Chem.* **2016**, *128*, 9074-9078.

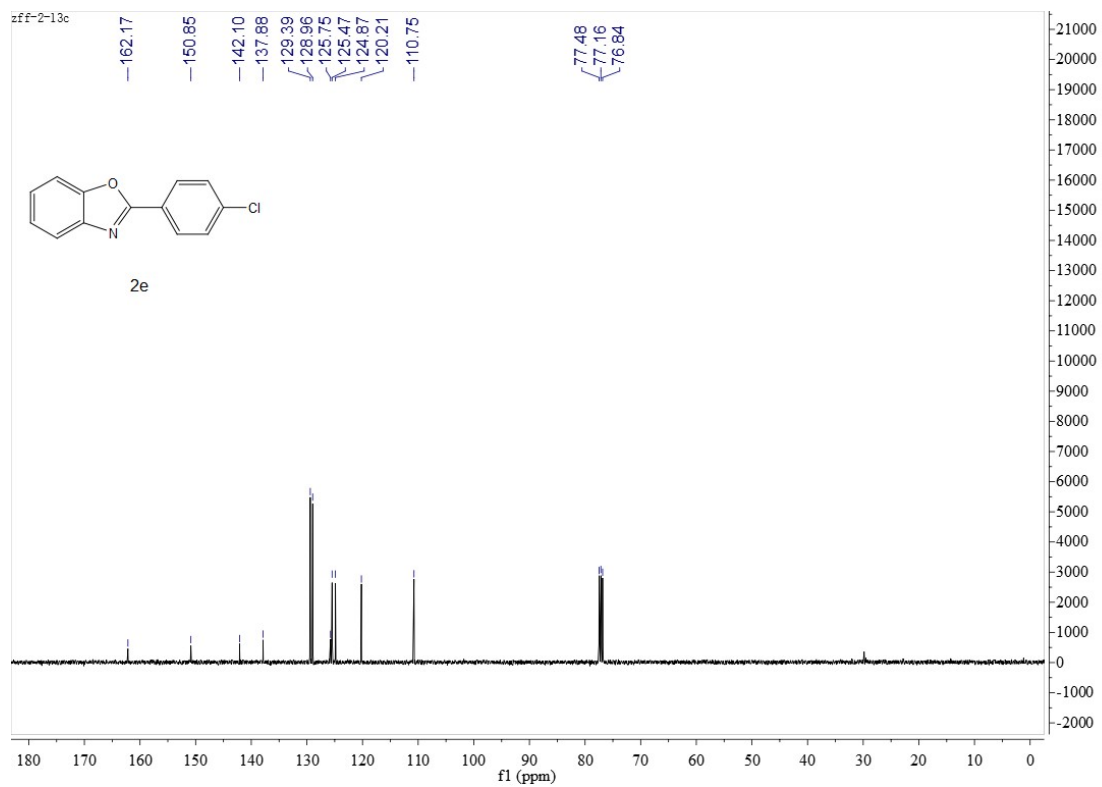
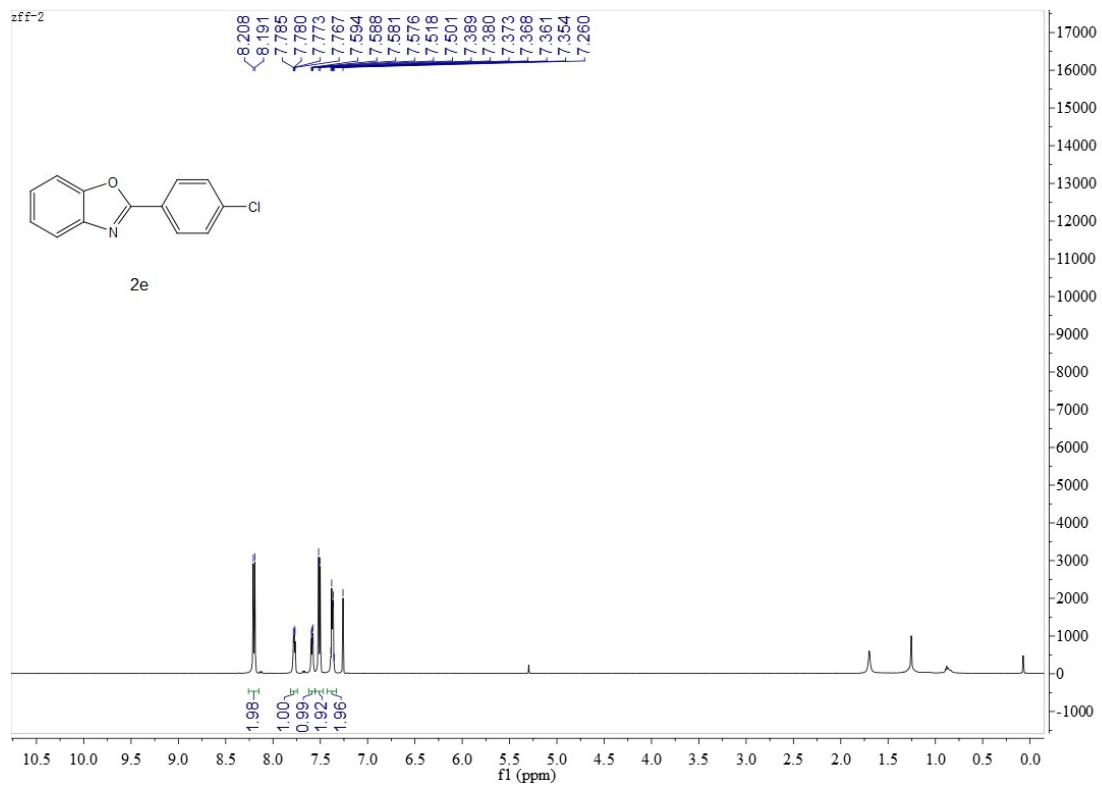
¹H and ¹³C NMR spectra of all products

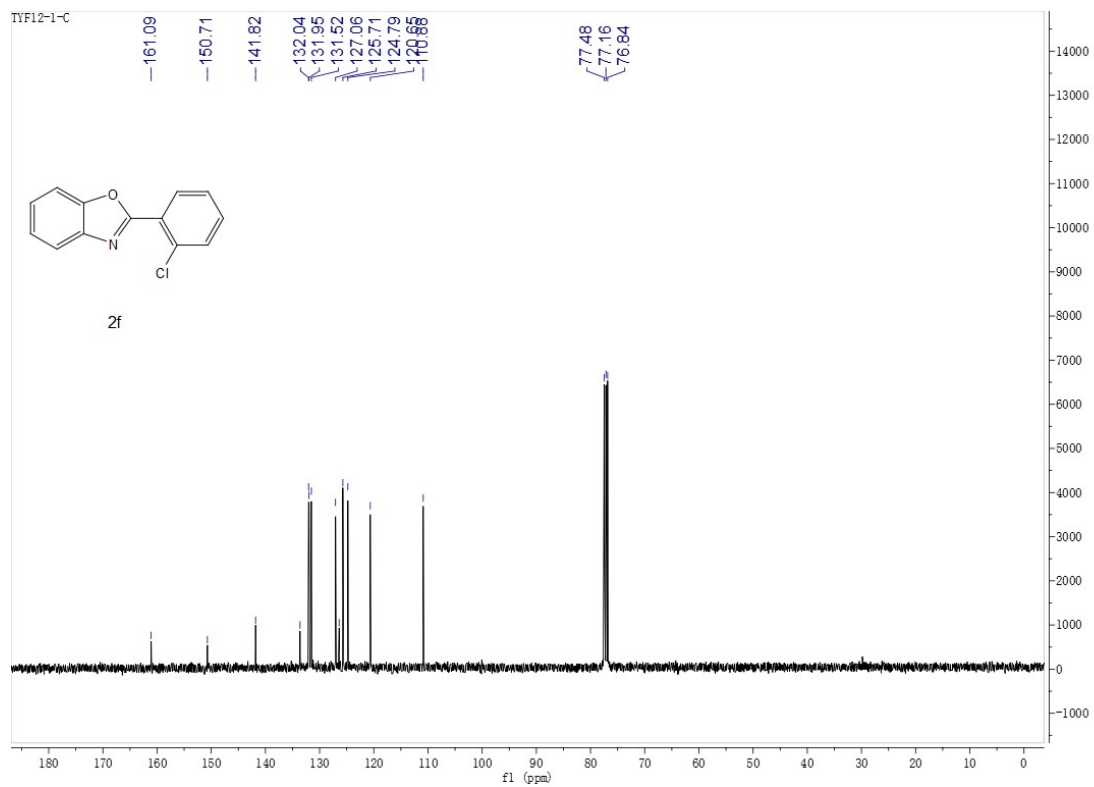
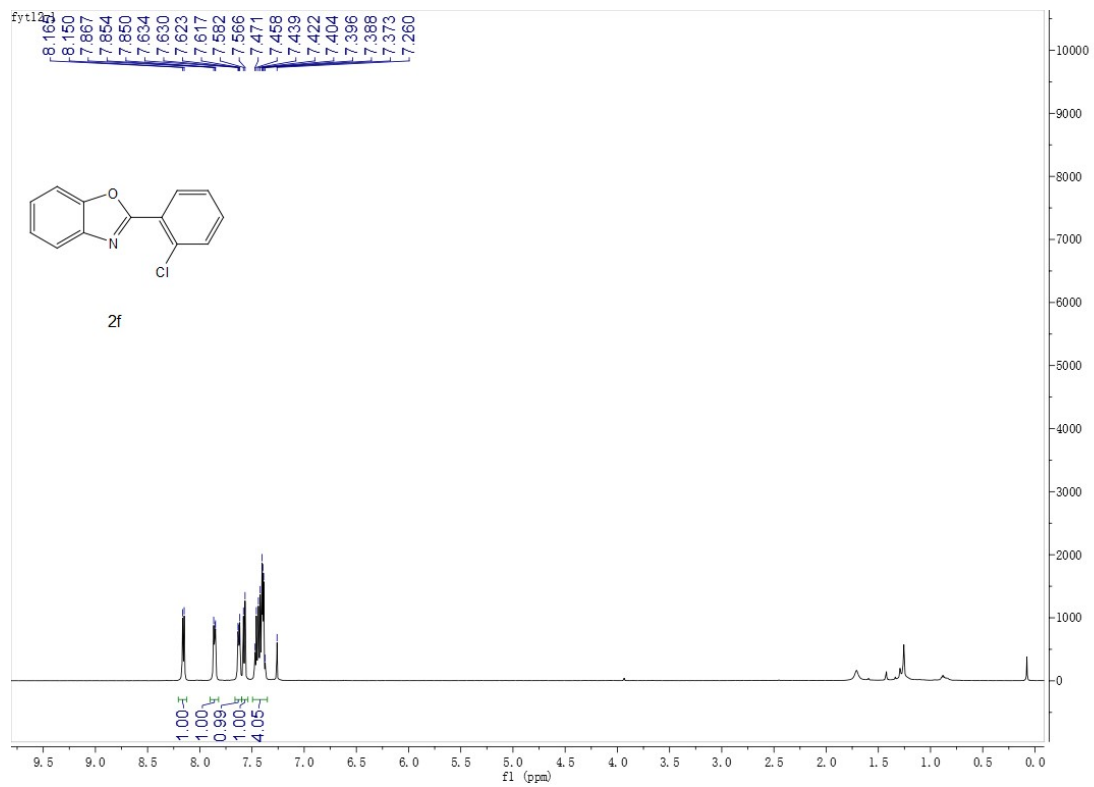


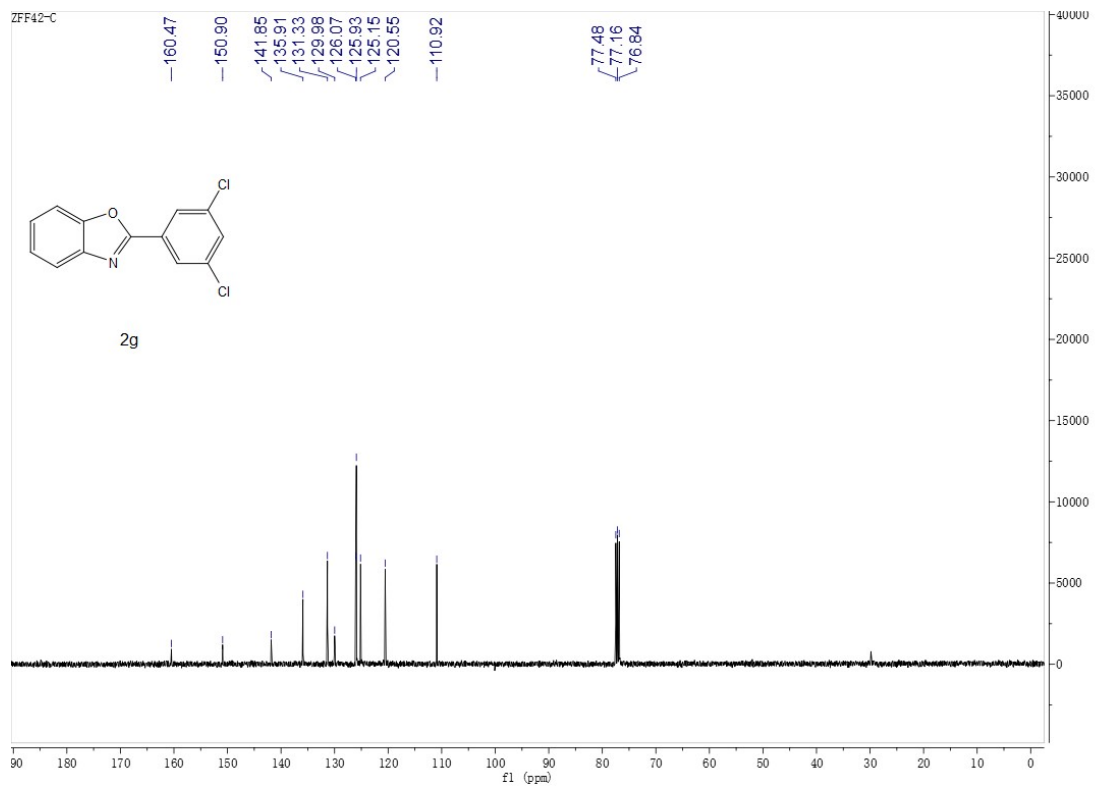
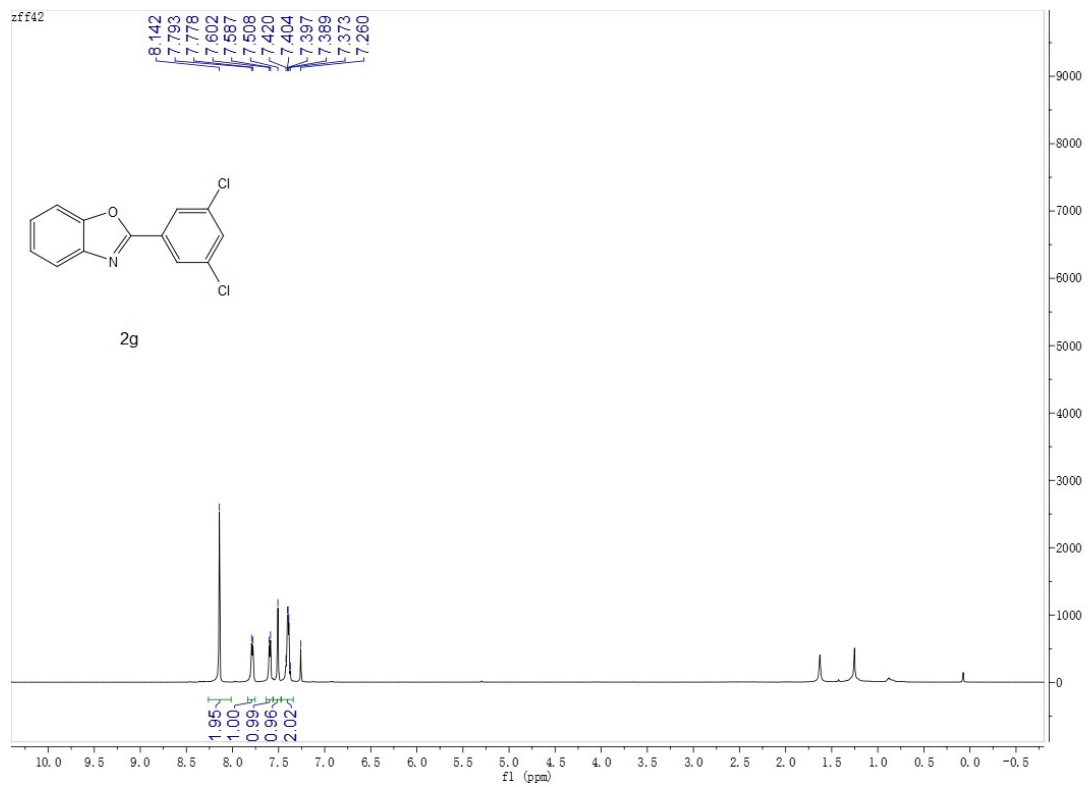


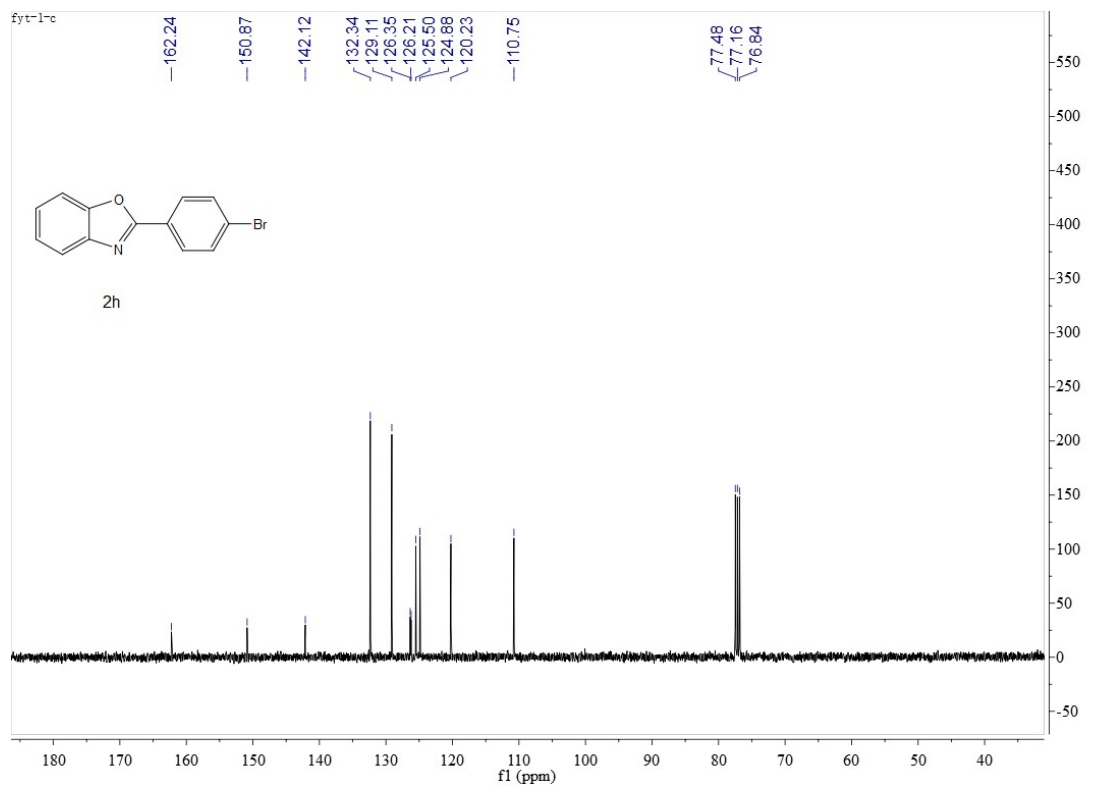
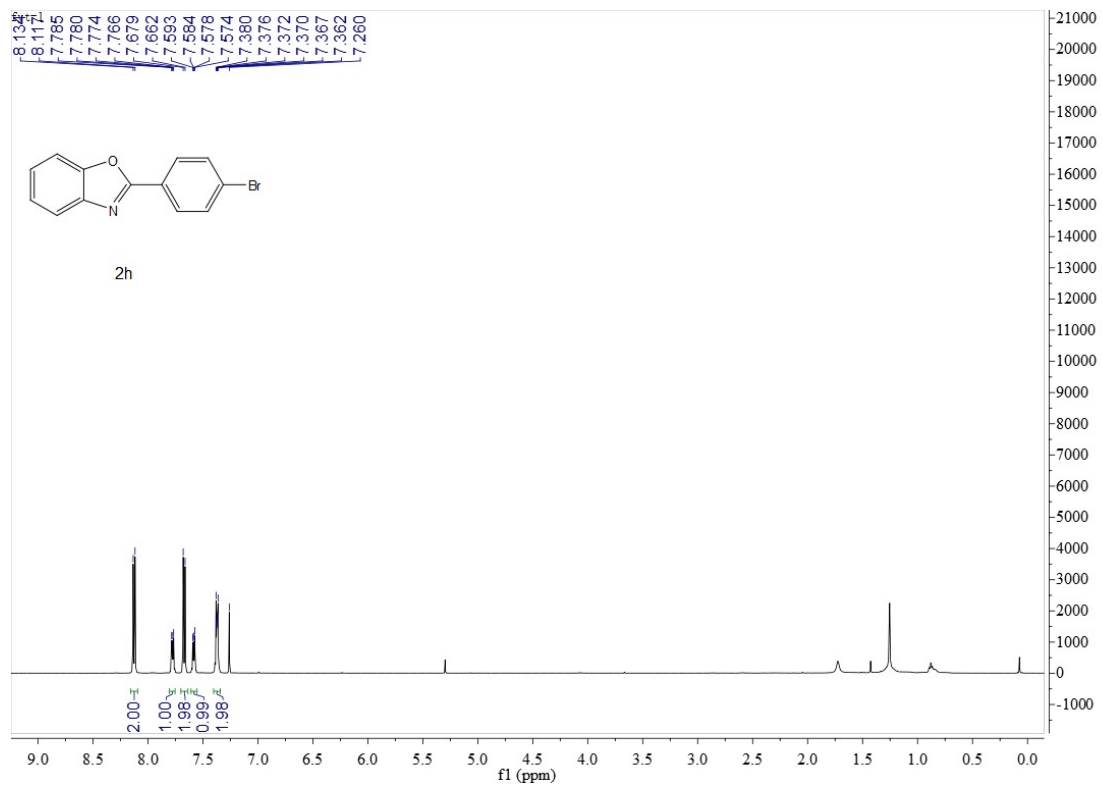


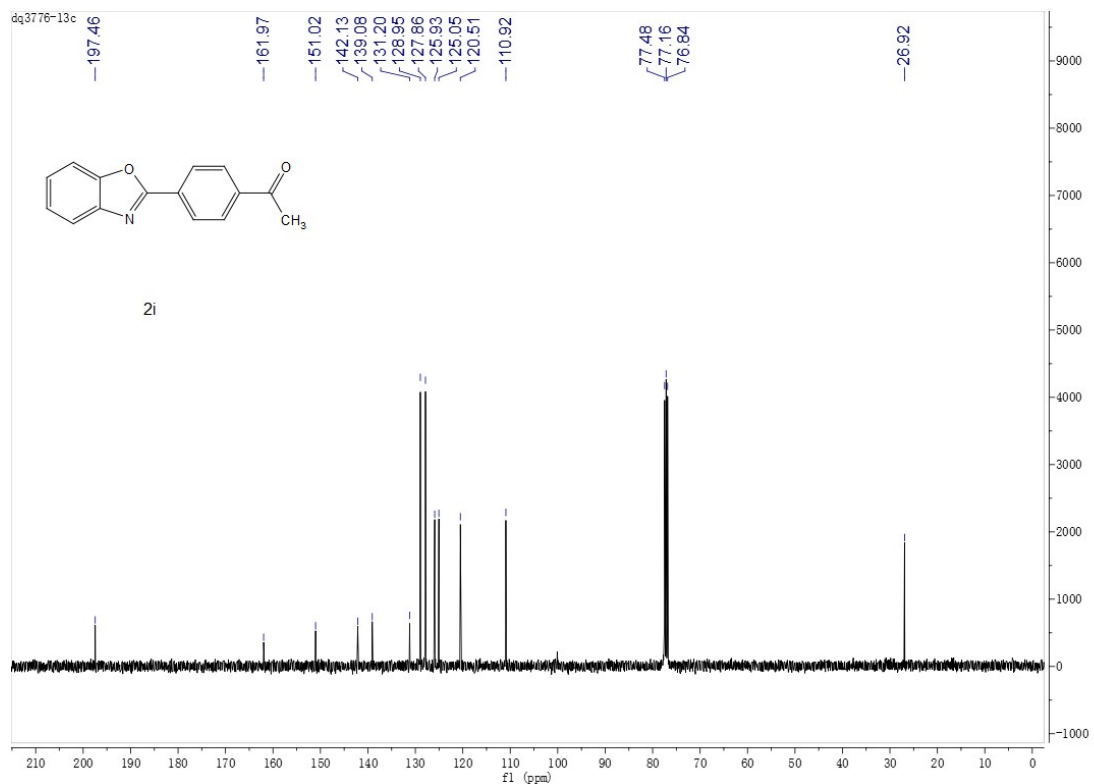
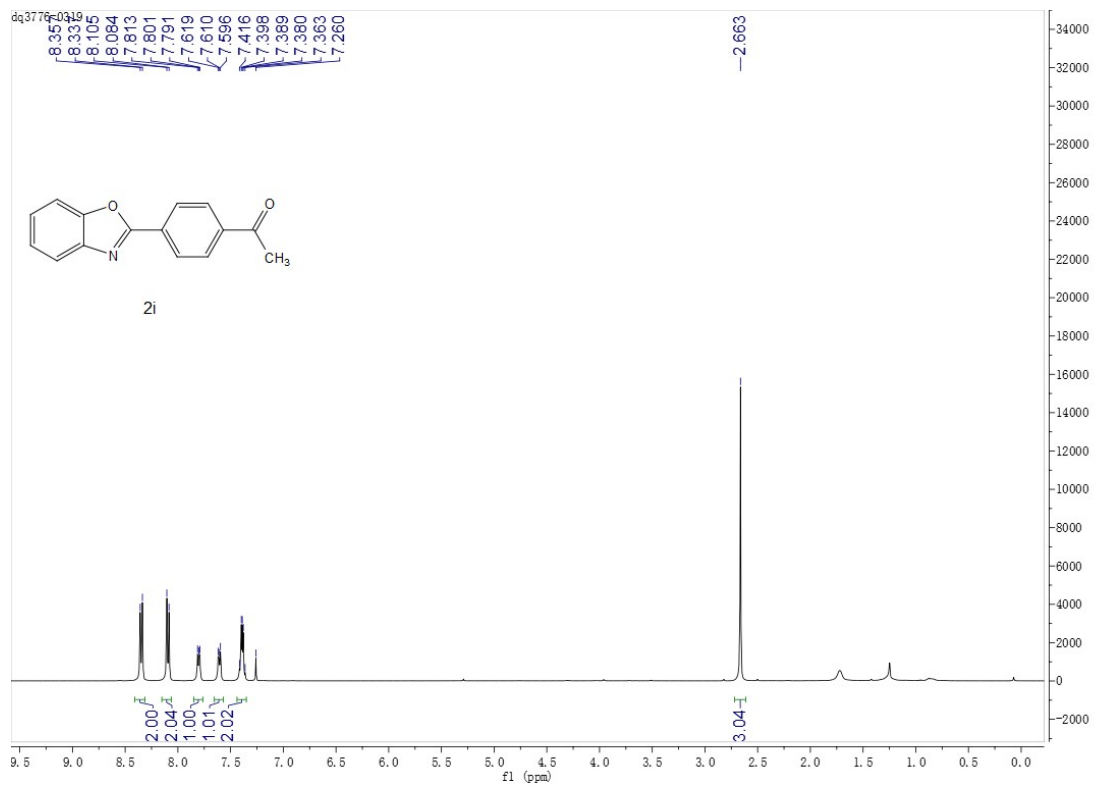


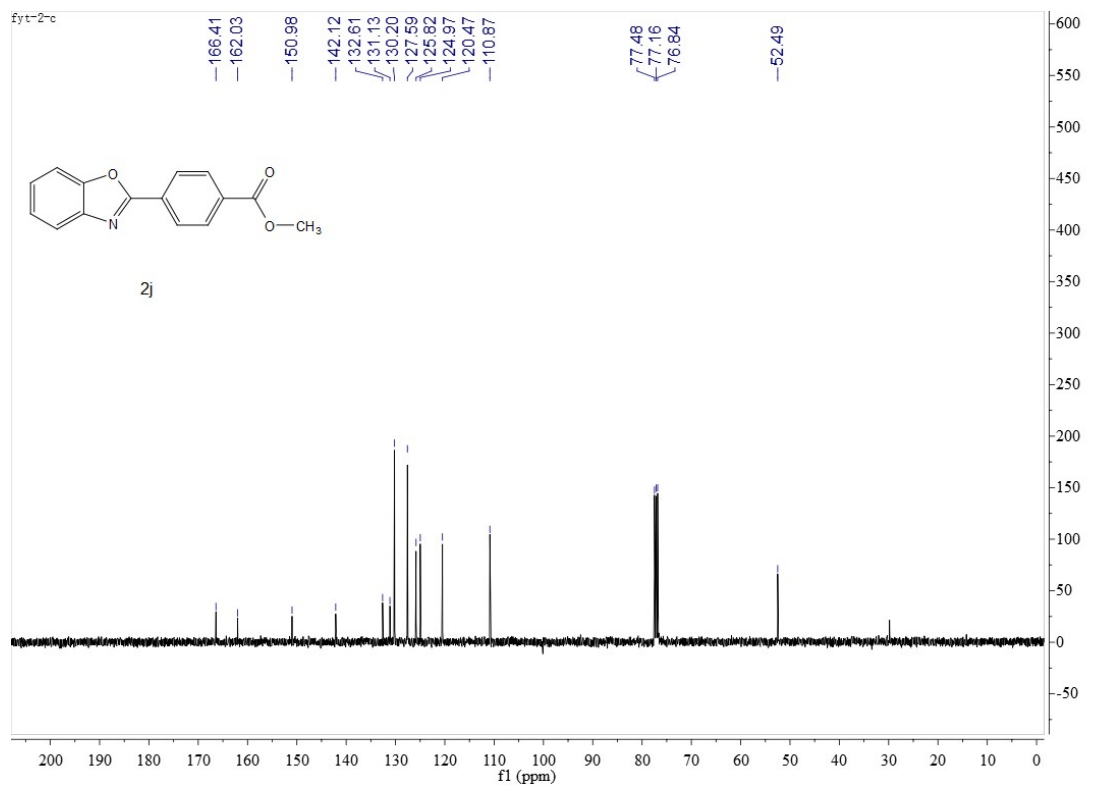
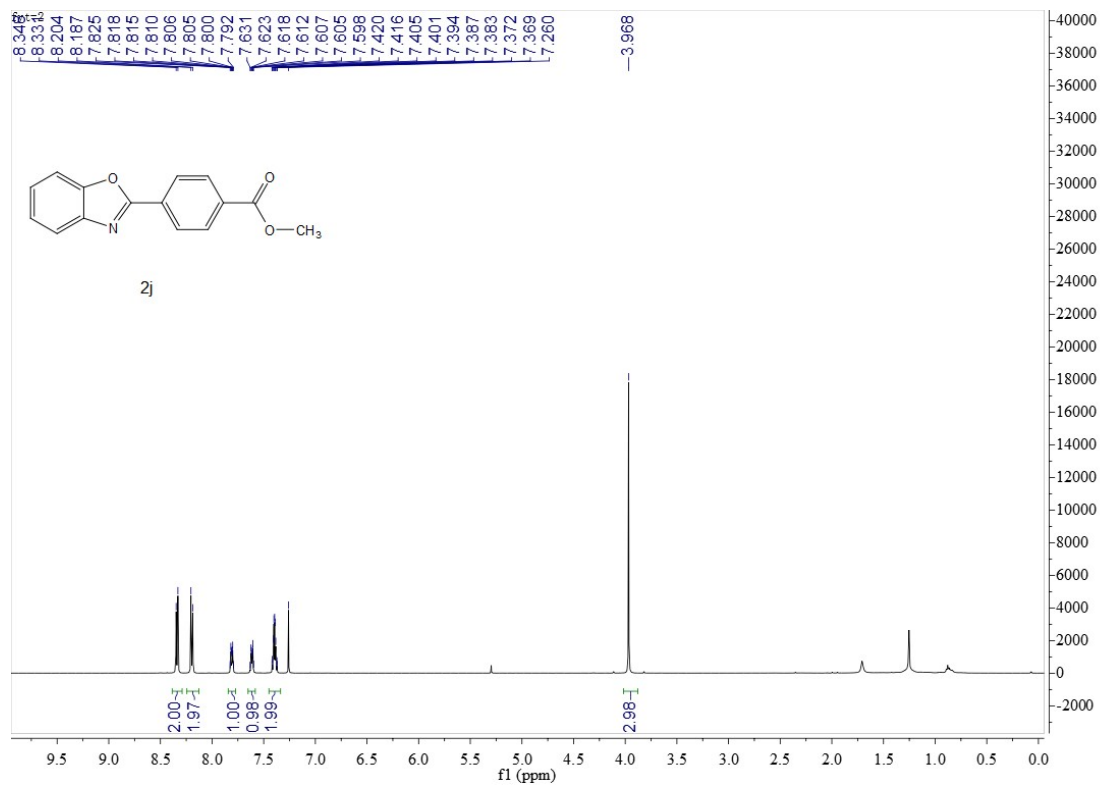


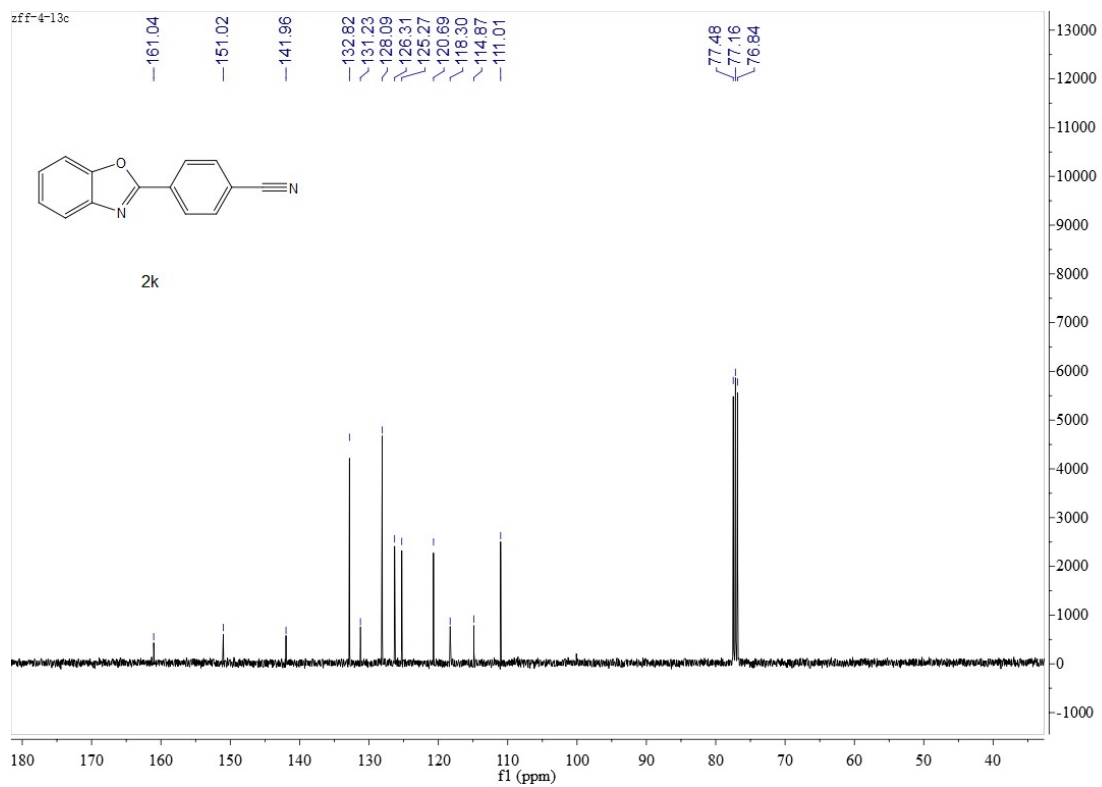
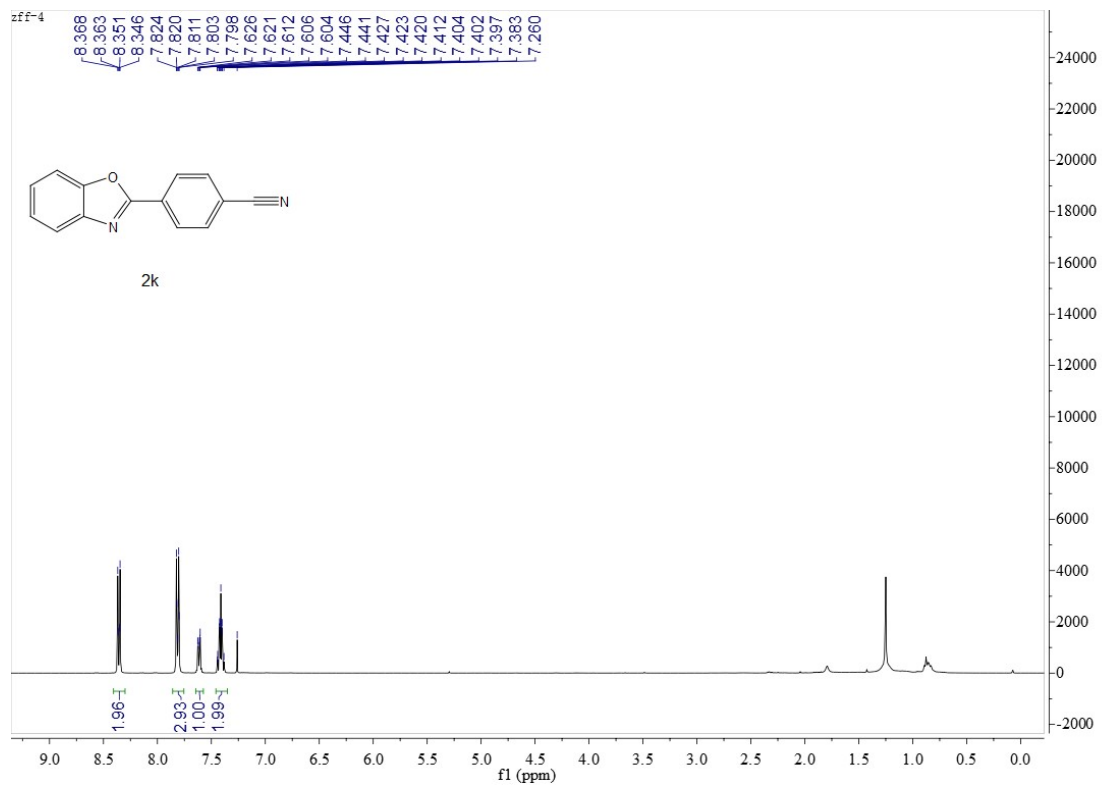


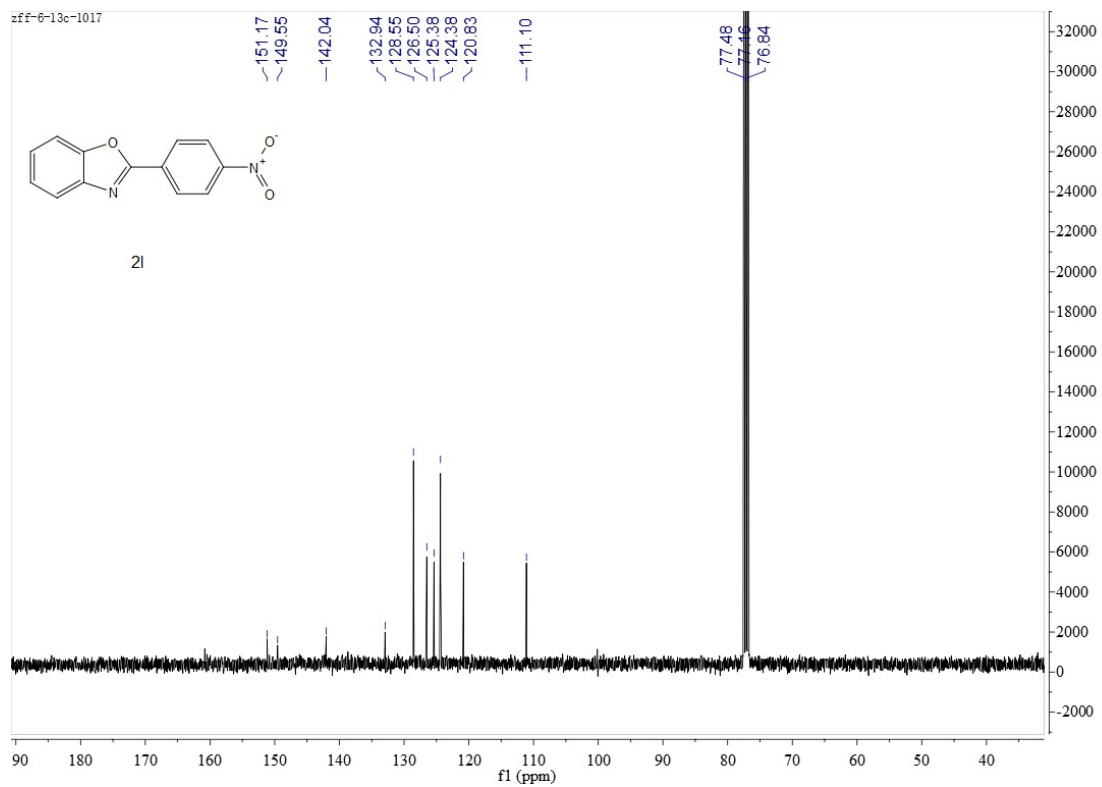
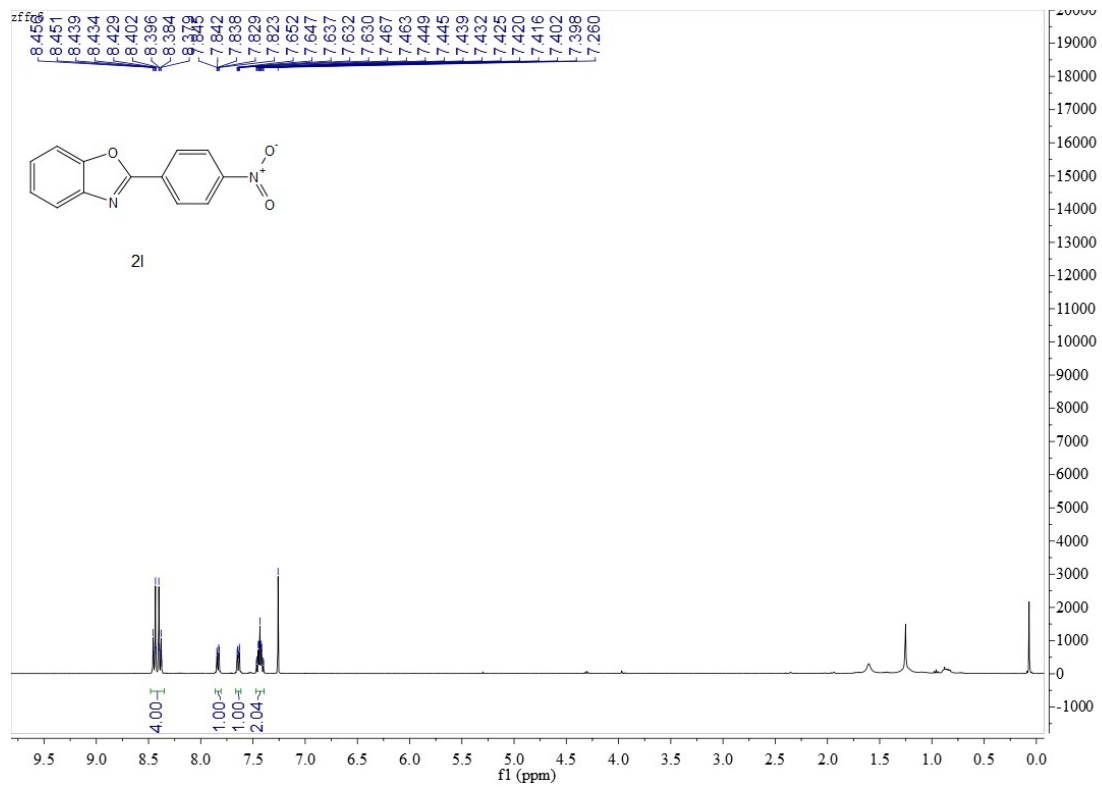


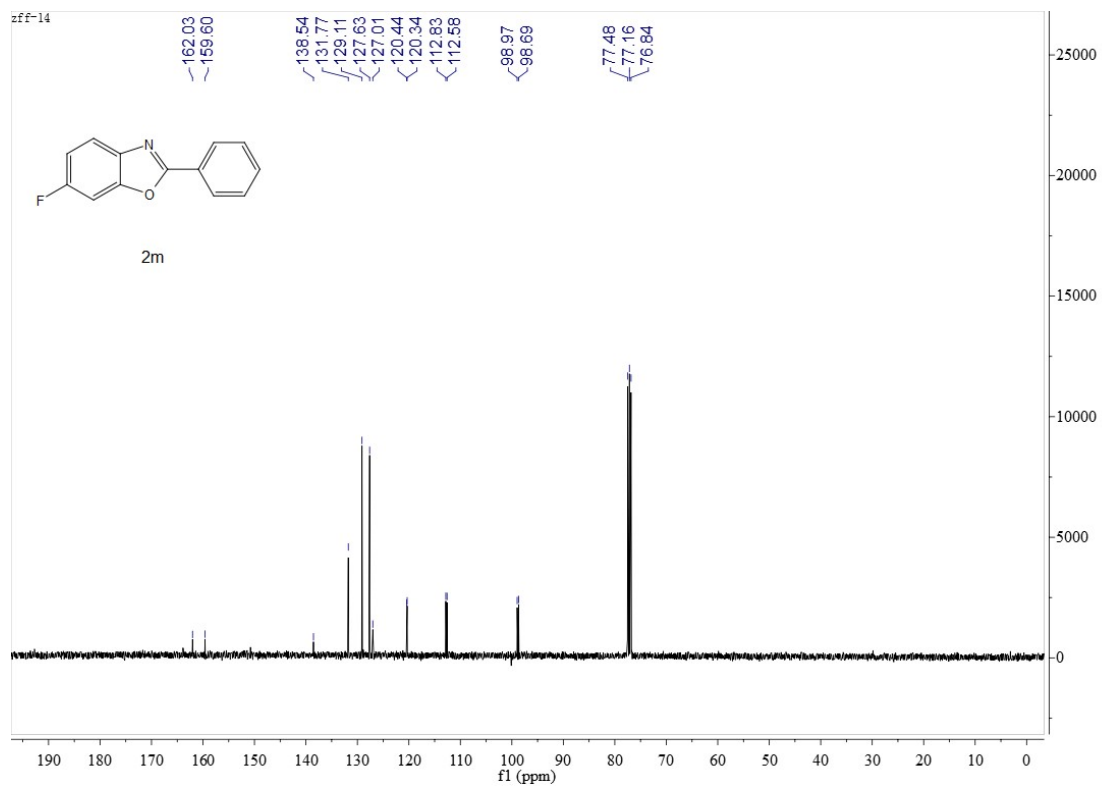
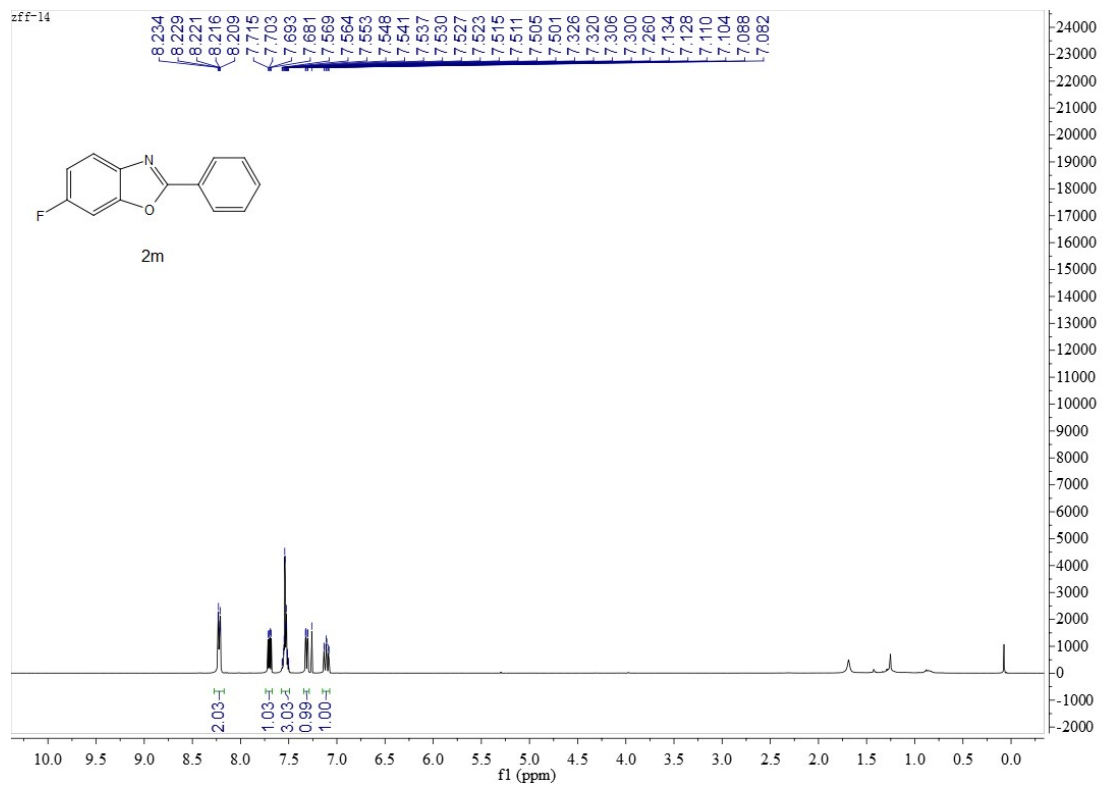


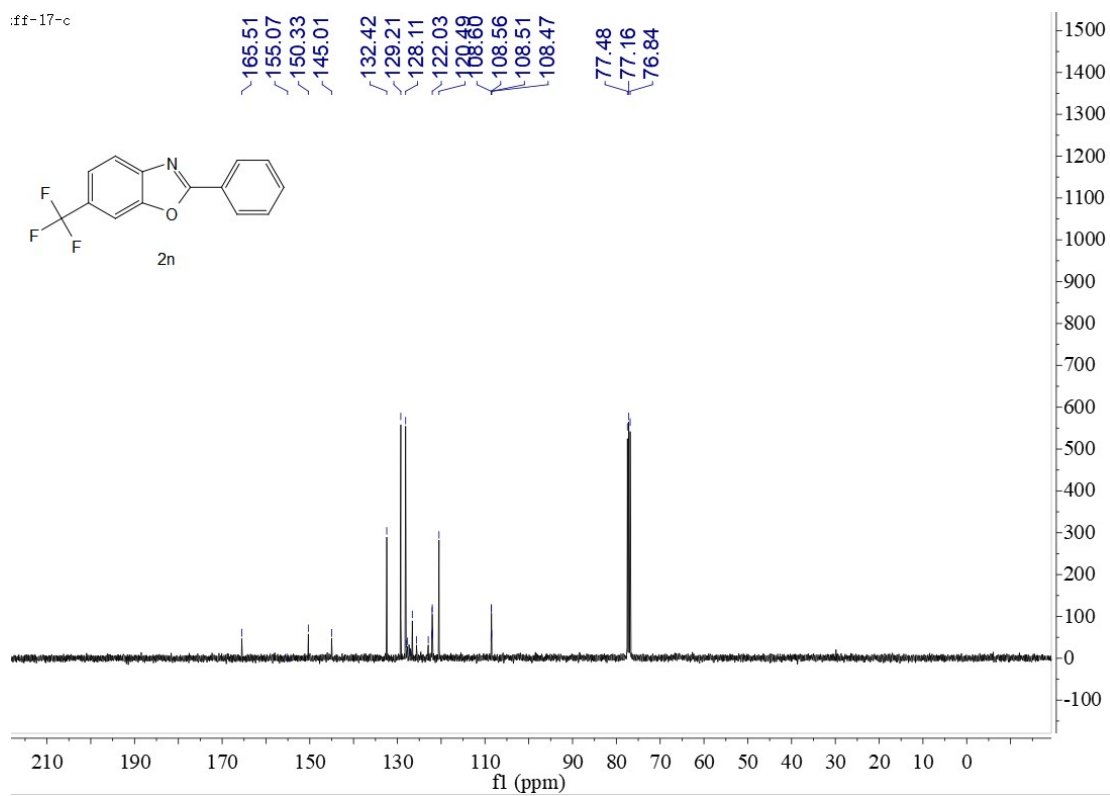
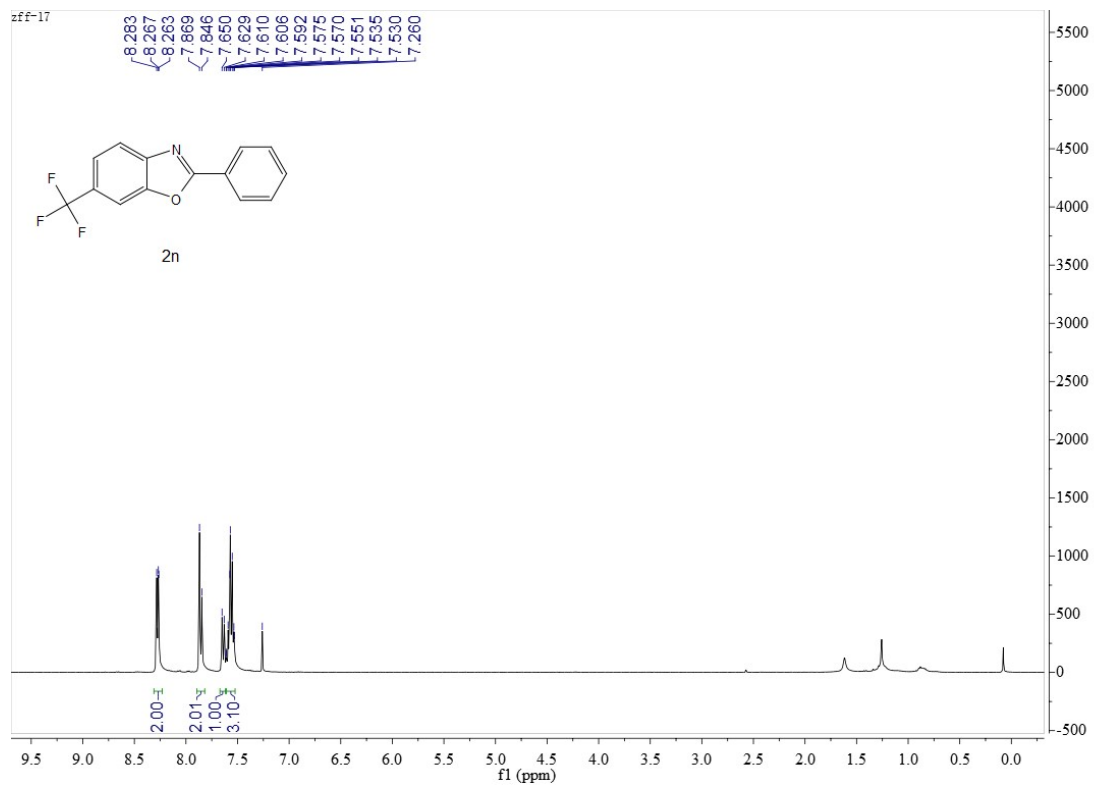


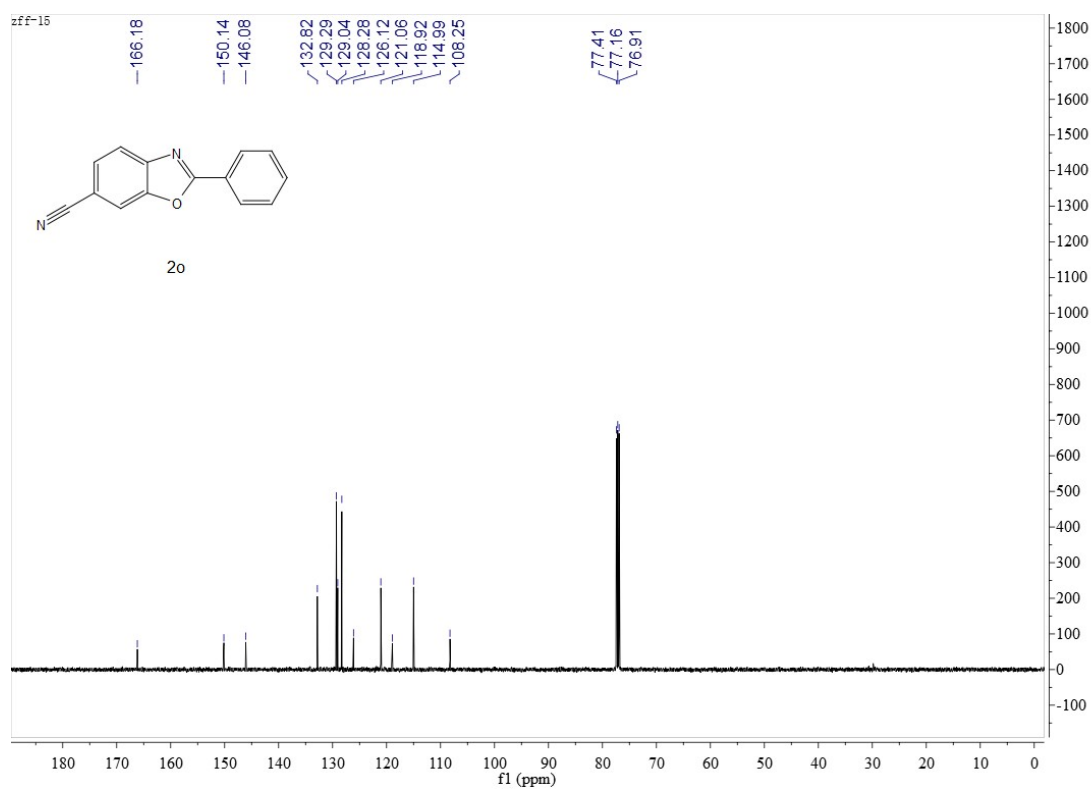
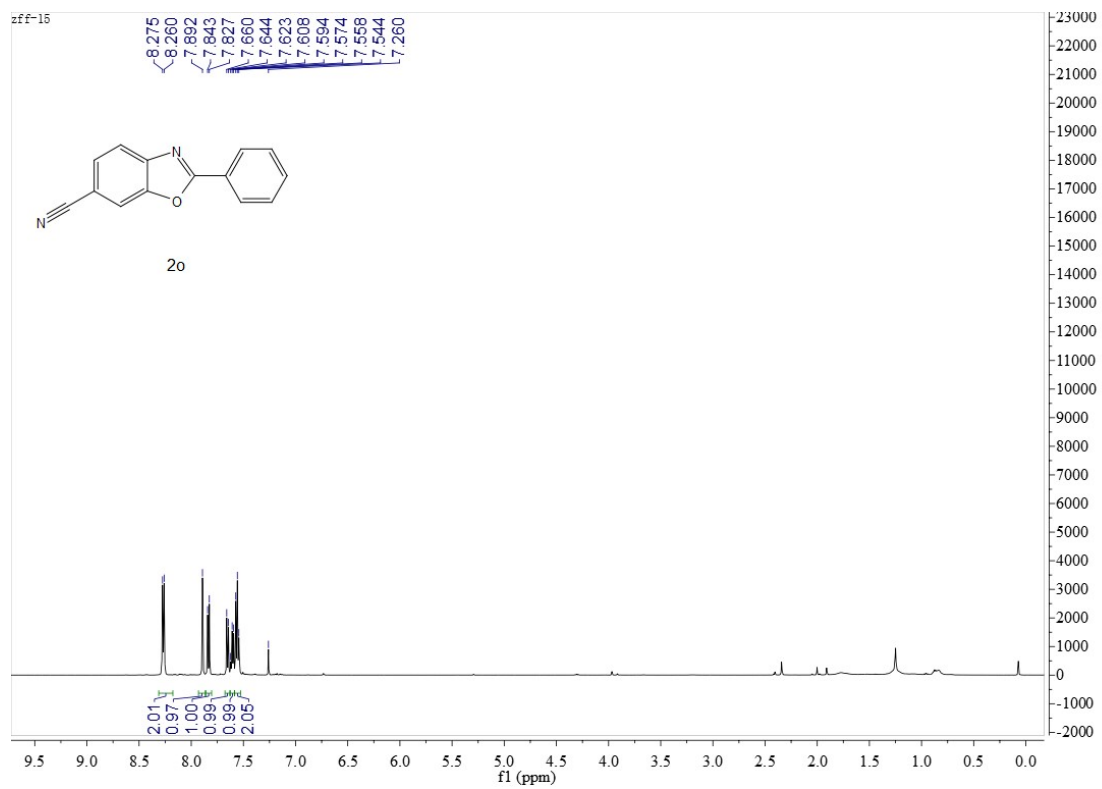


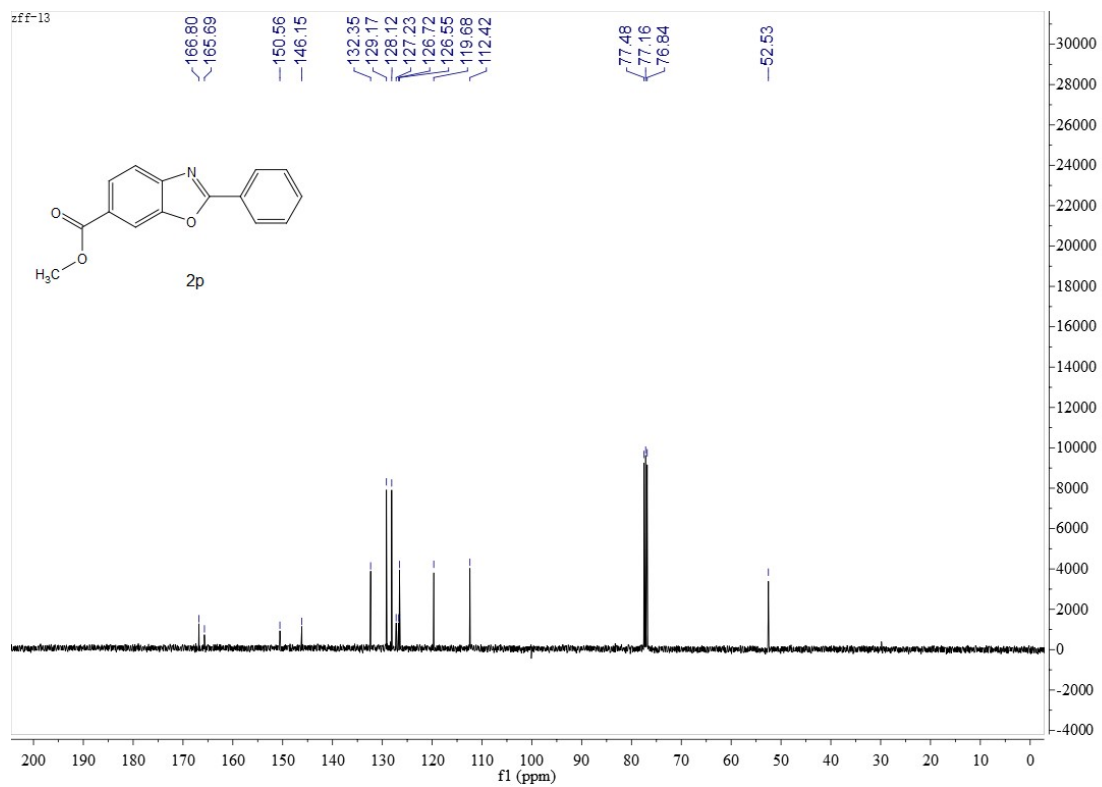
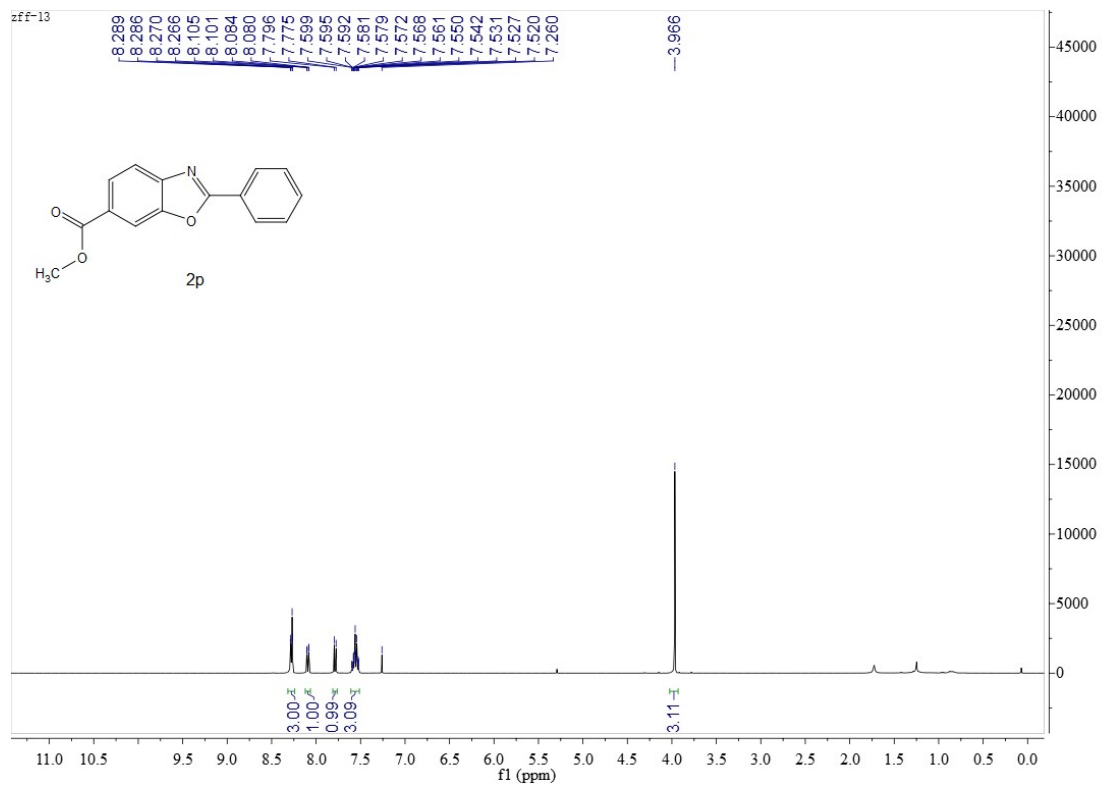


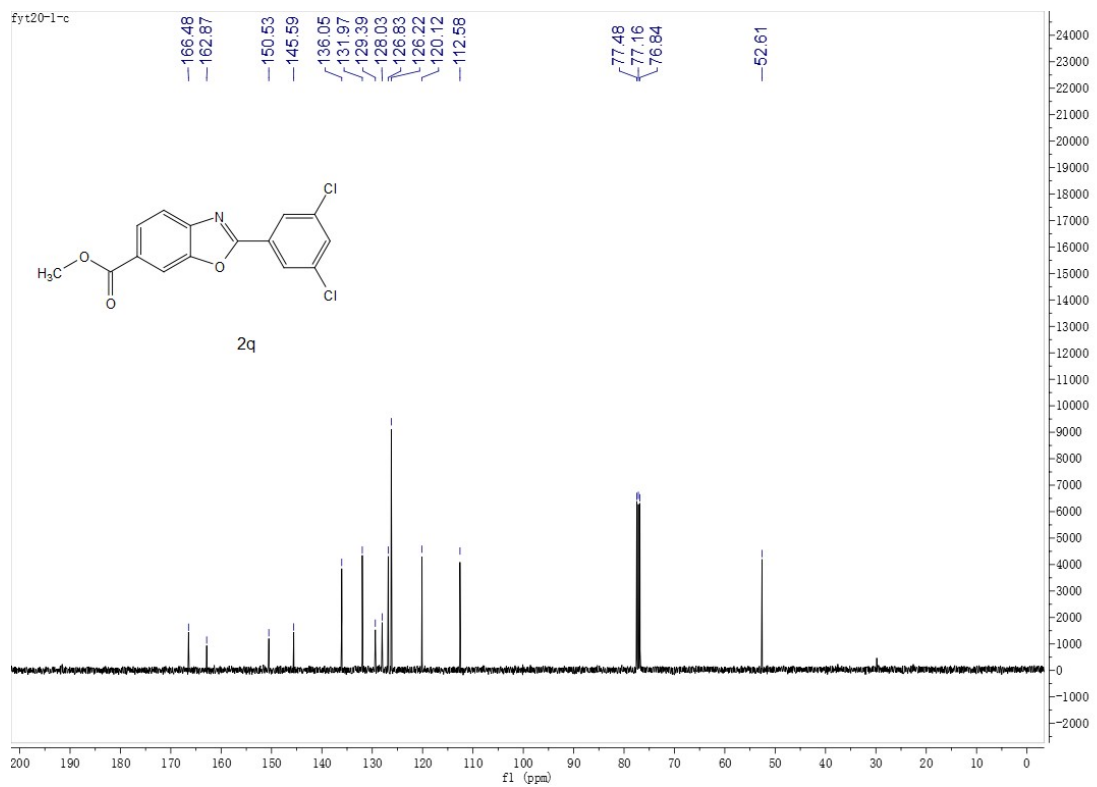
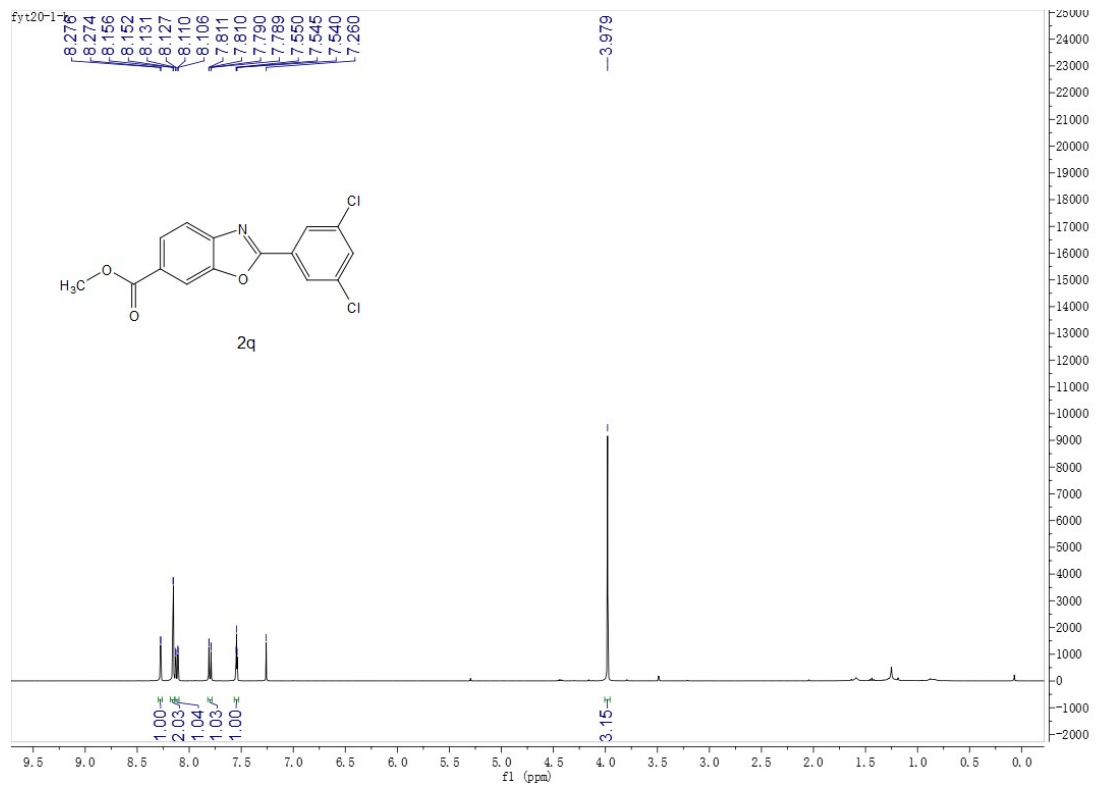


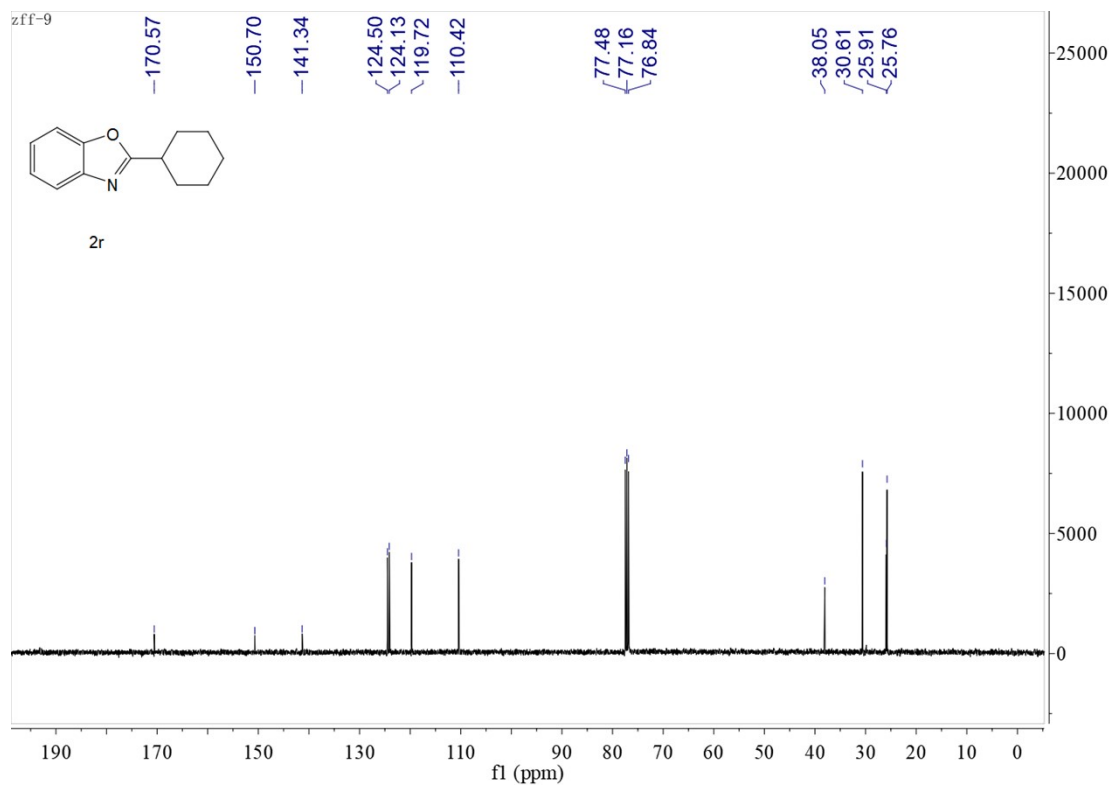
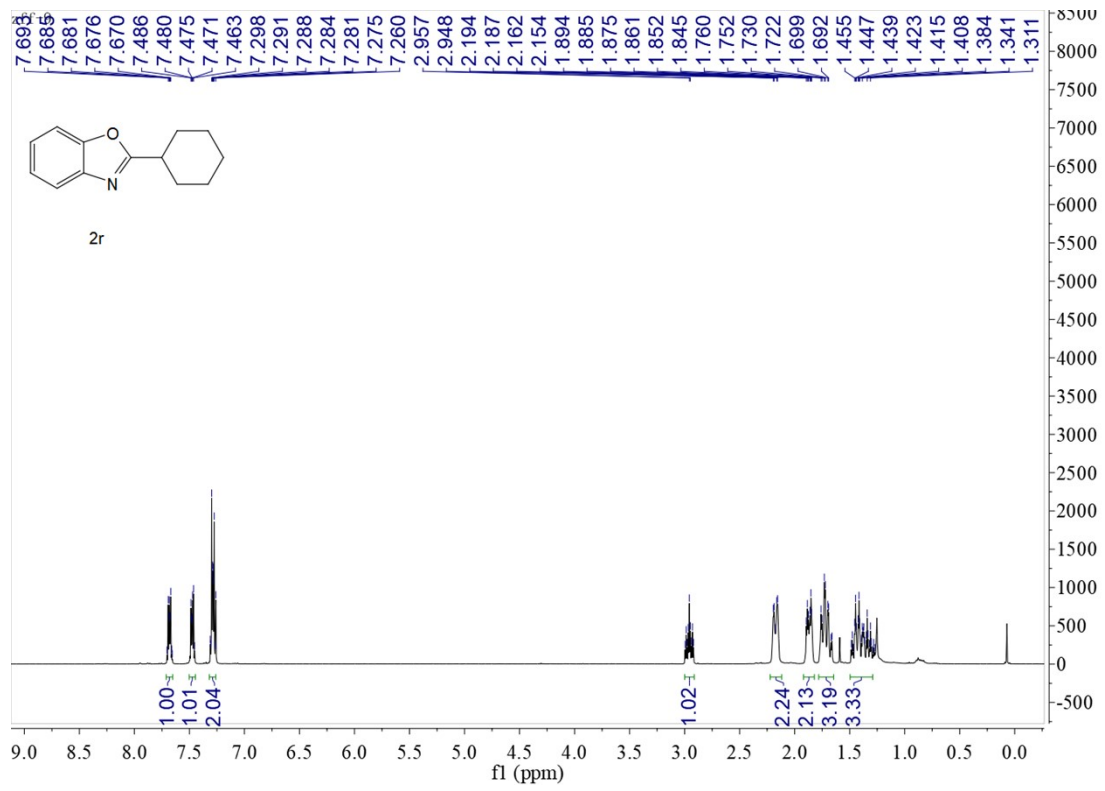


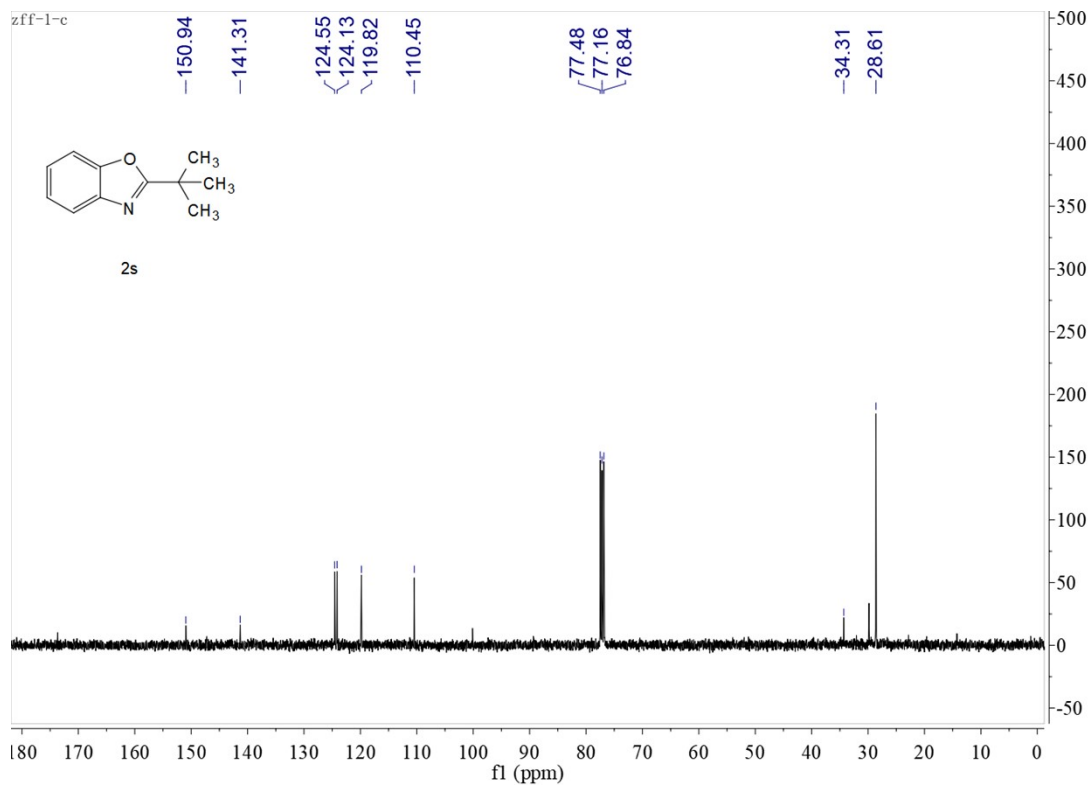
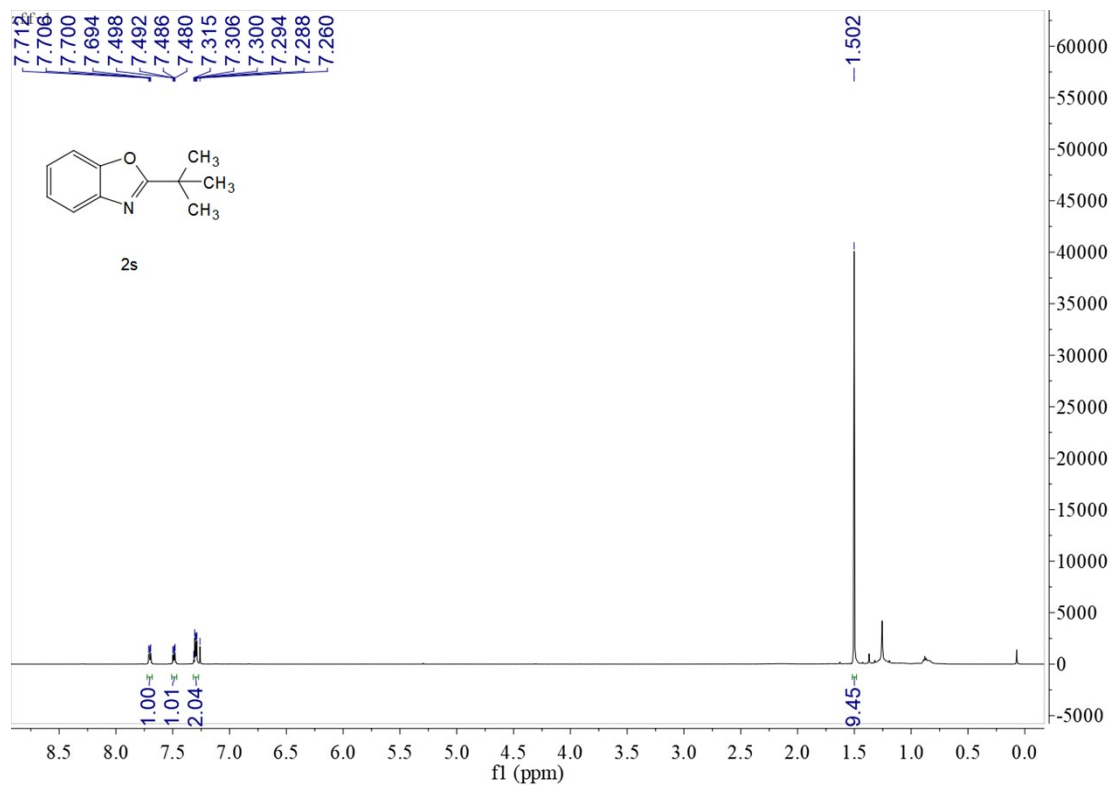


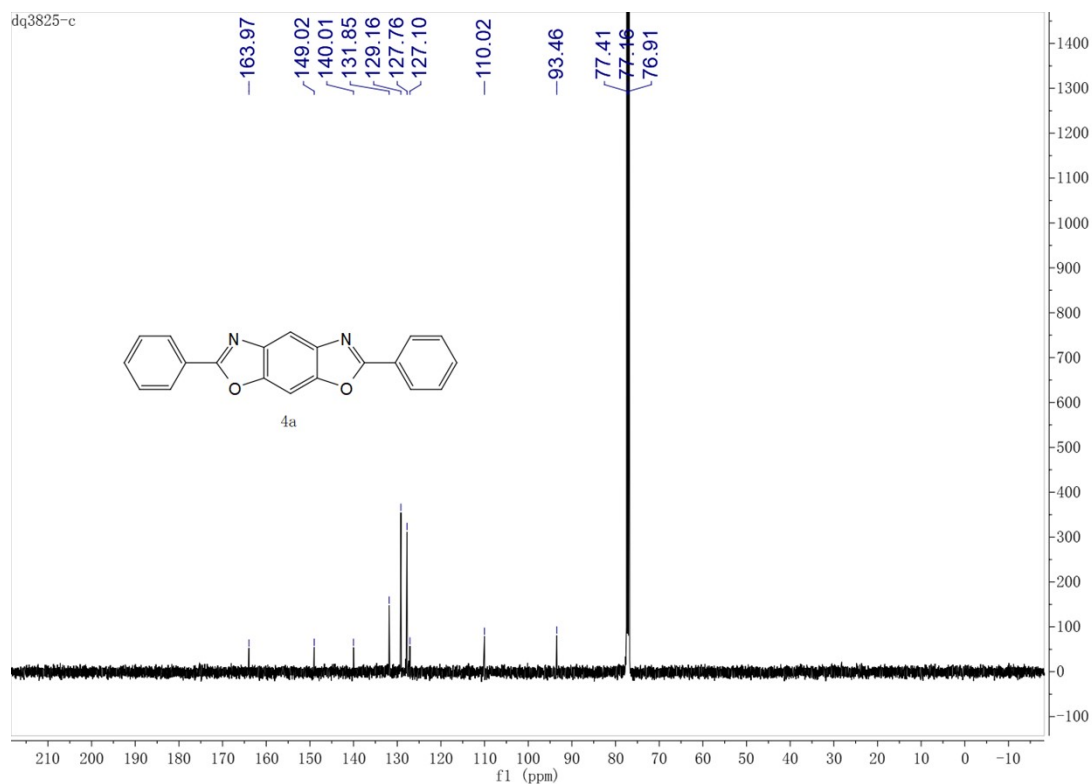
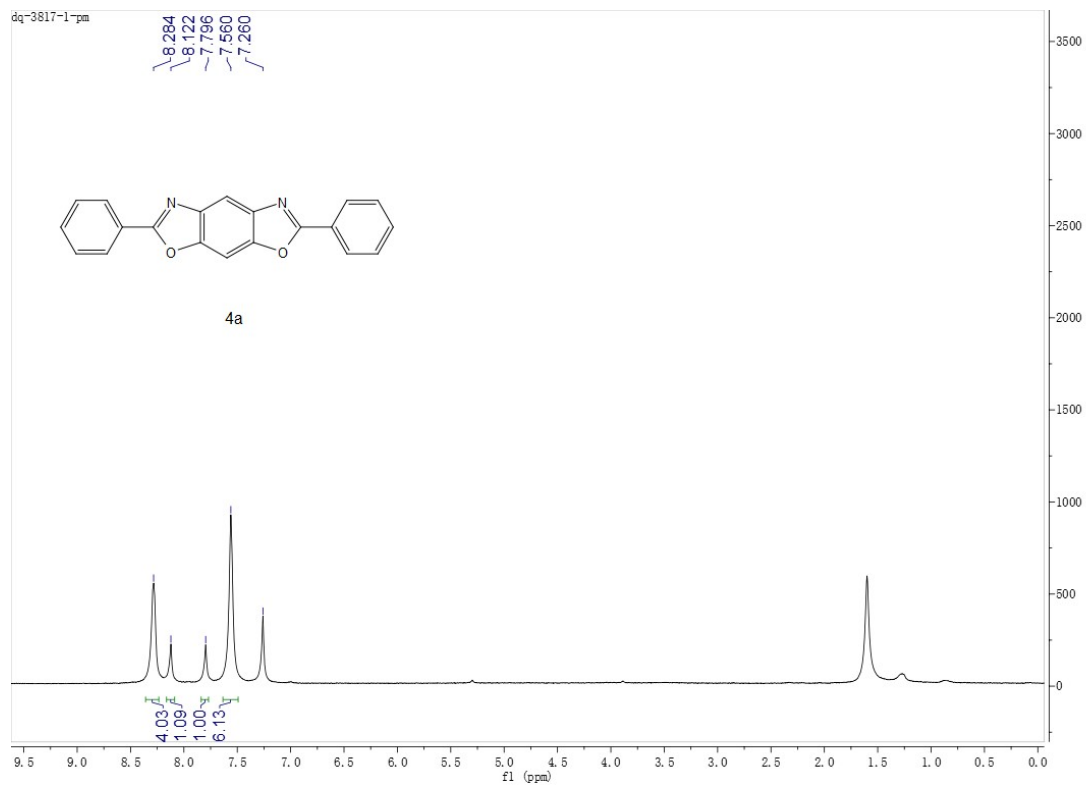




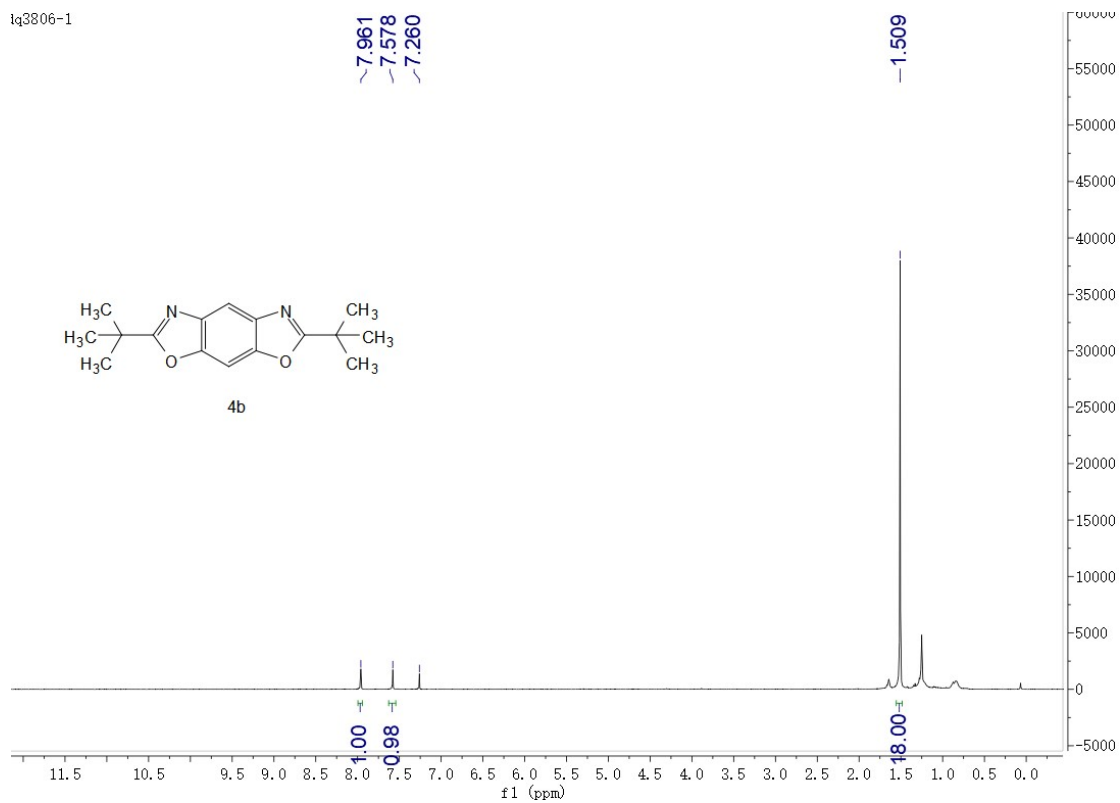




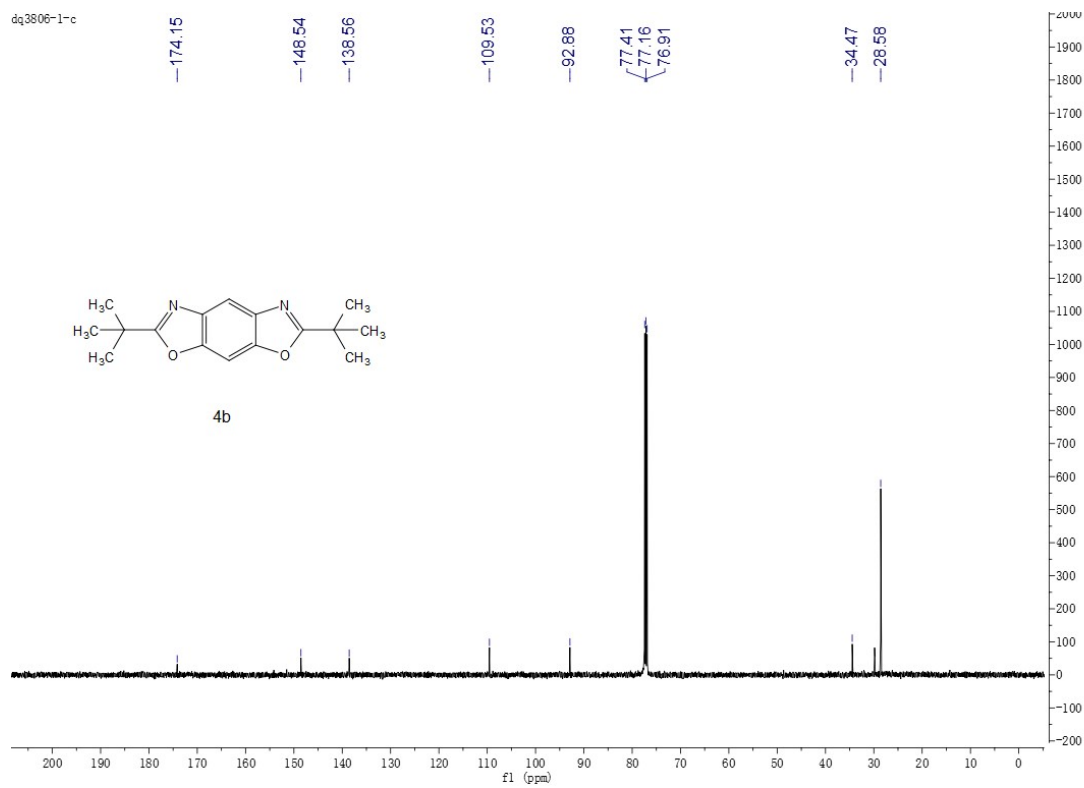


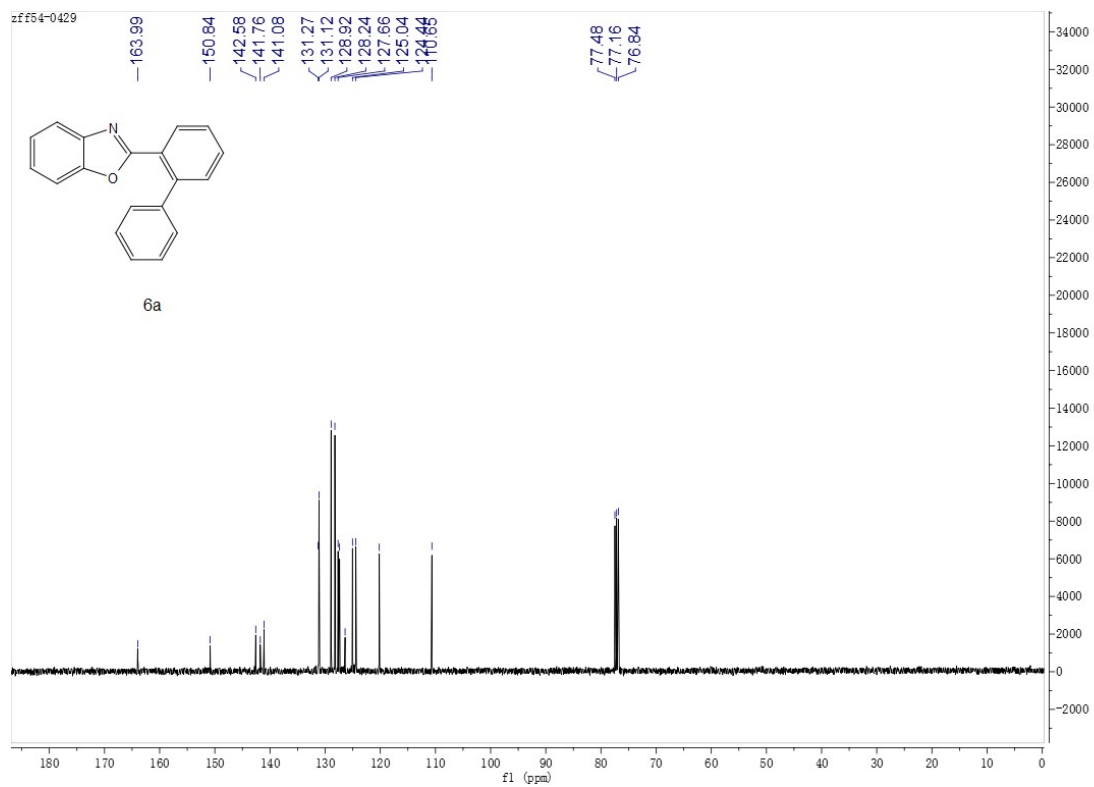
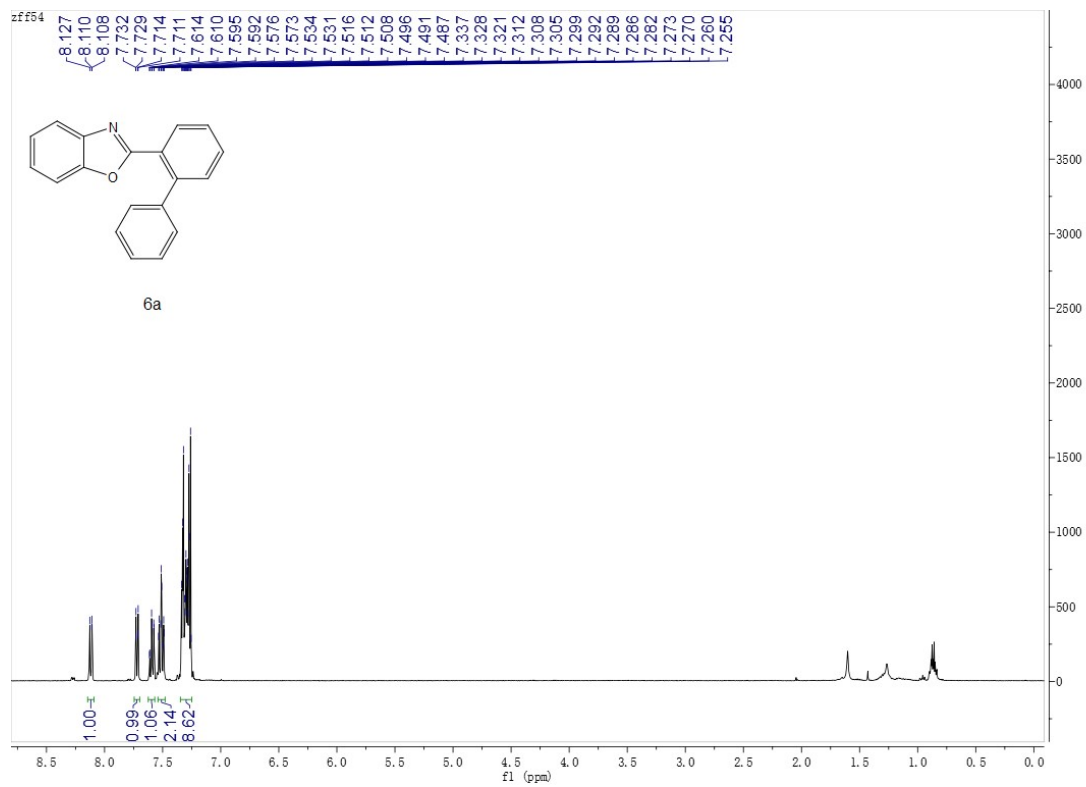


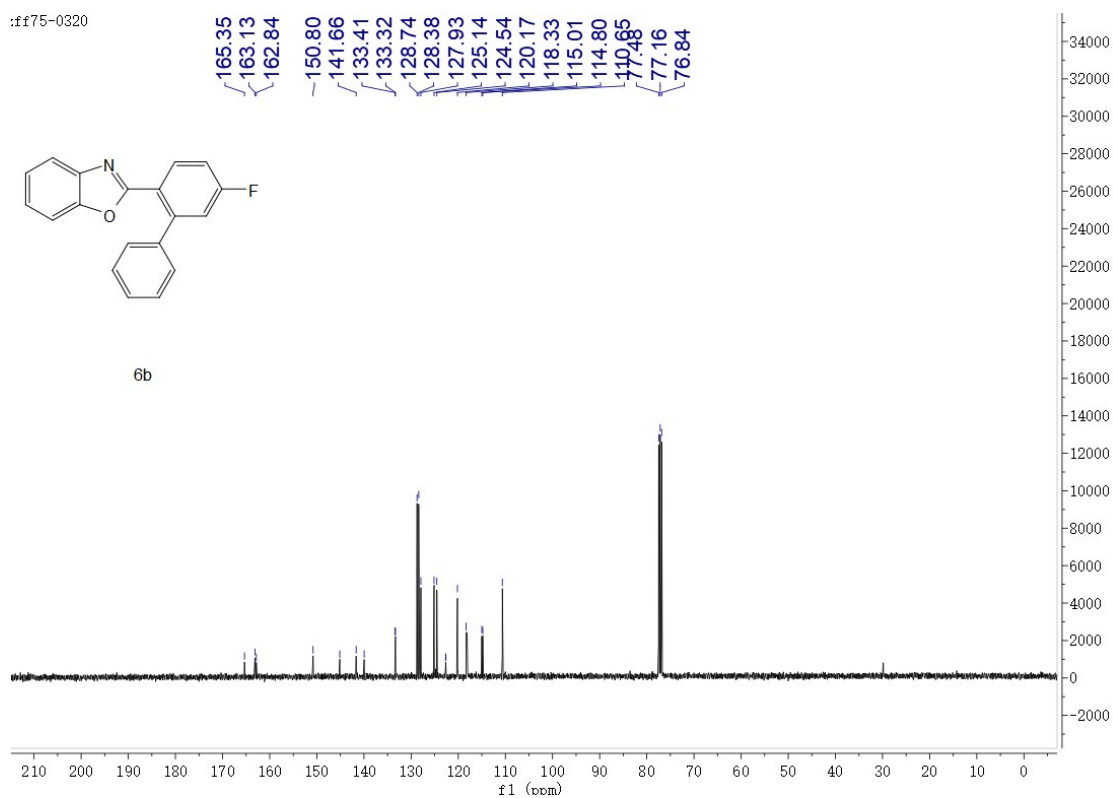
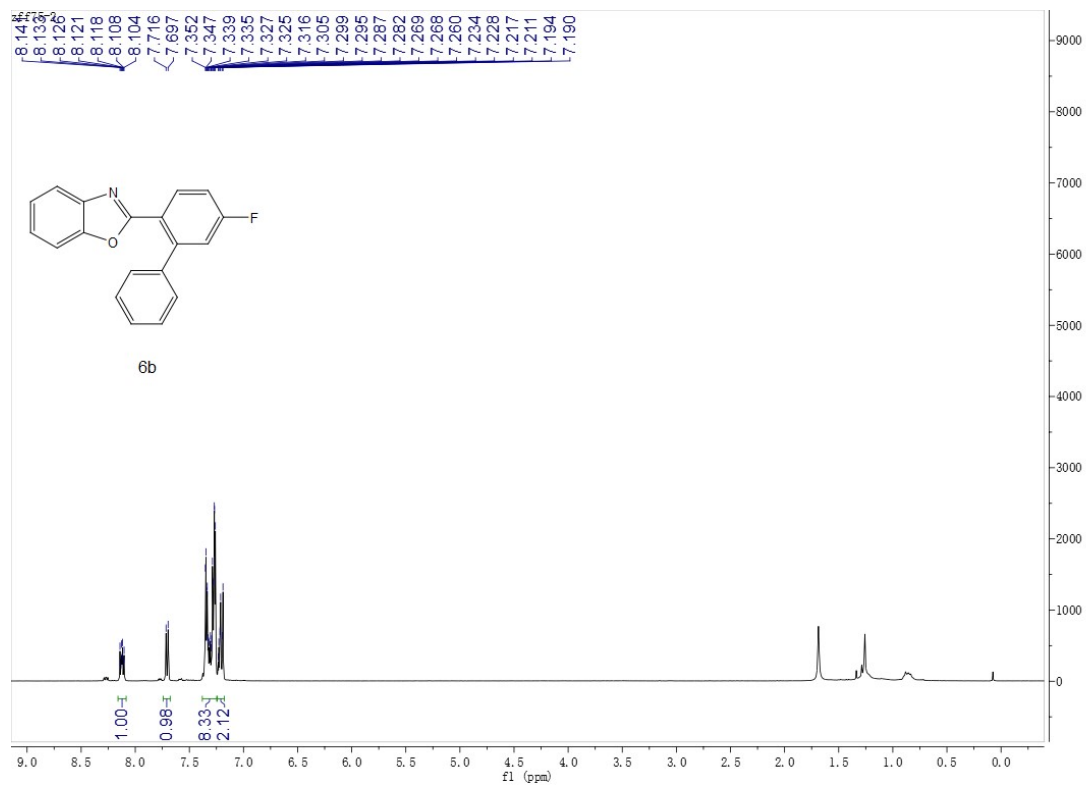
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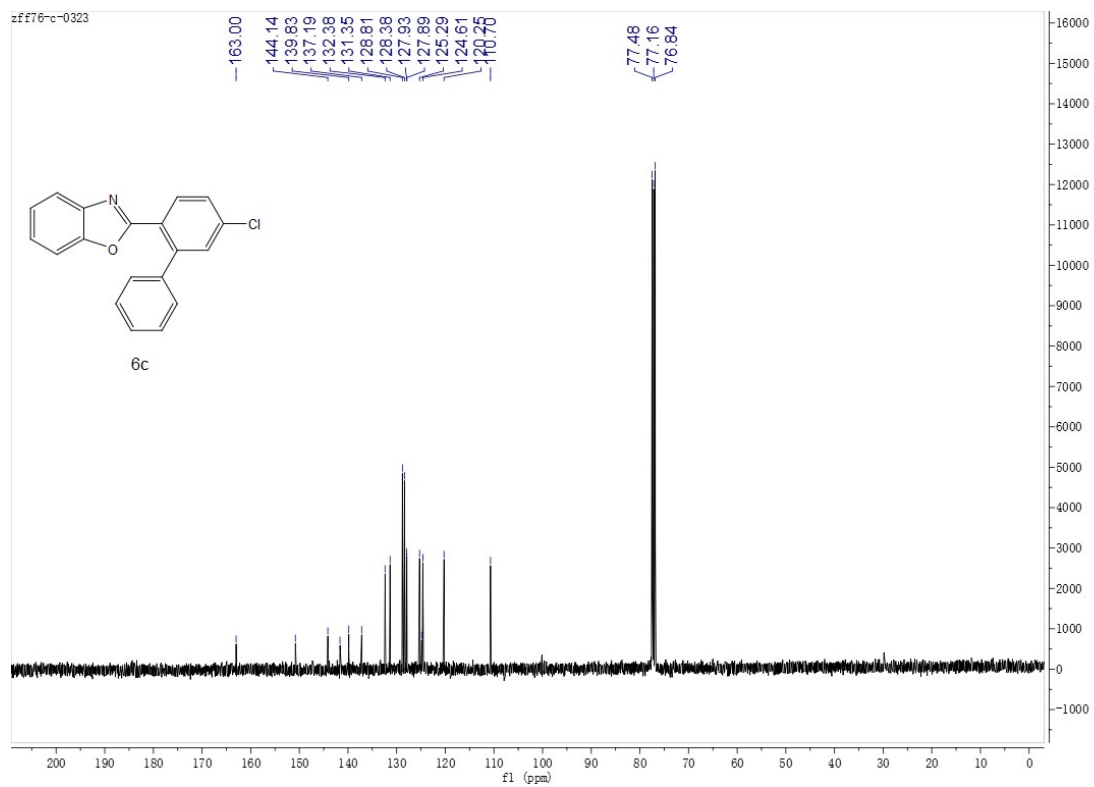
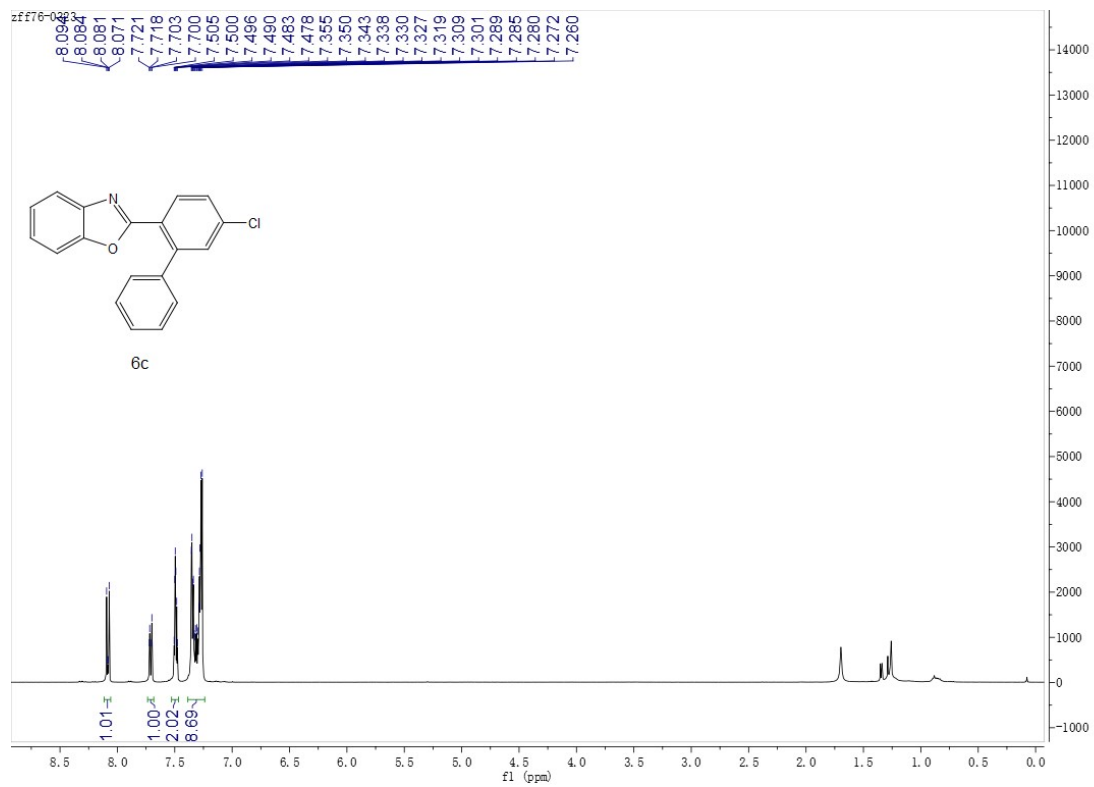


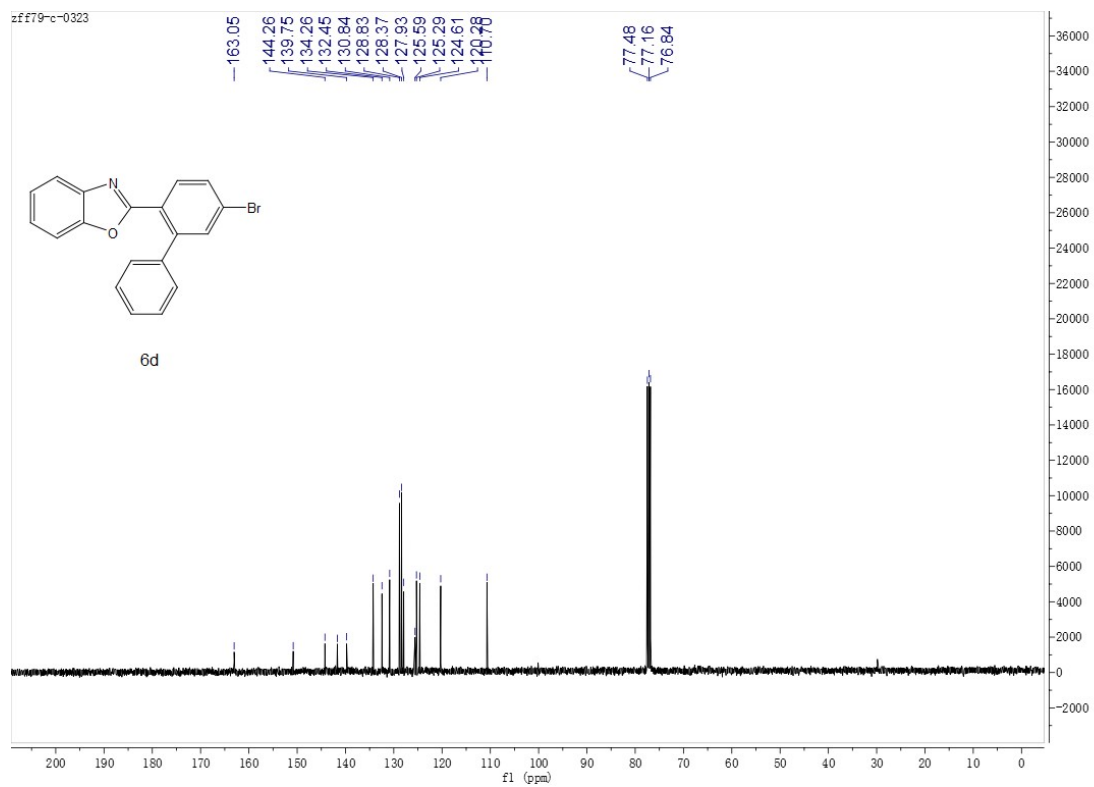
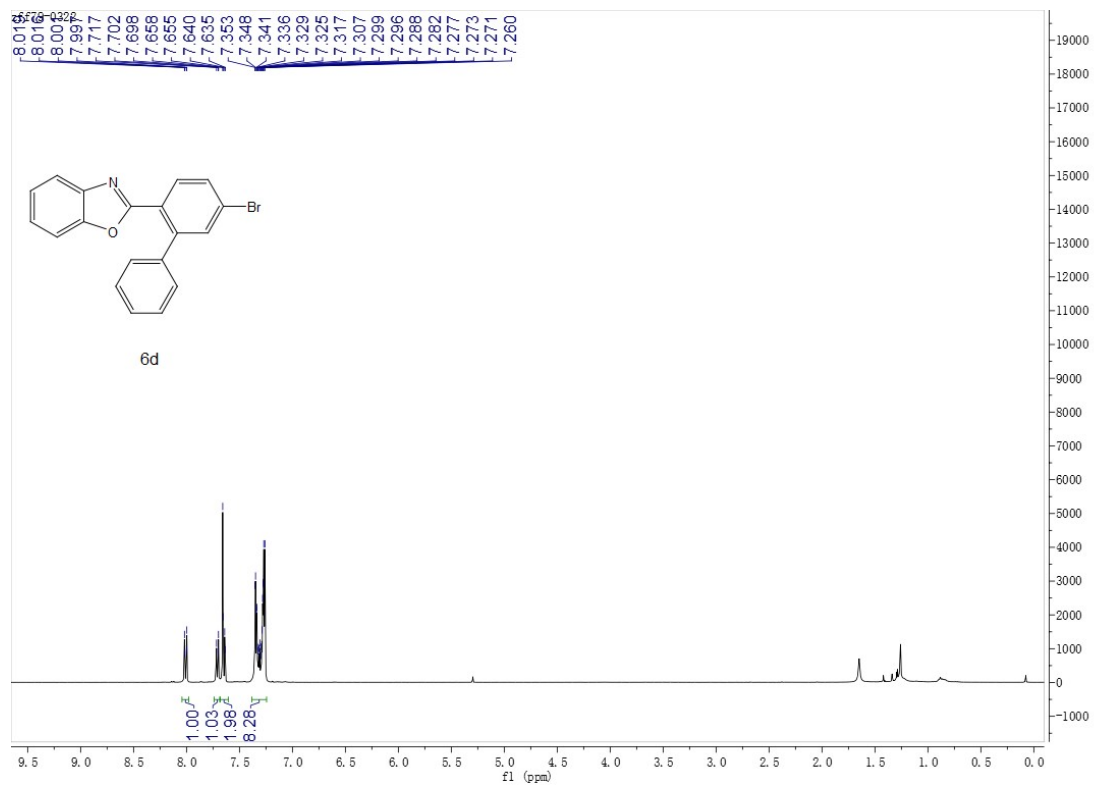
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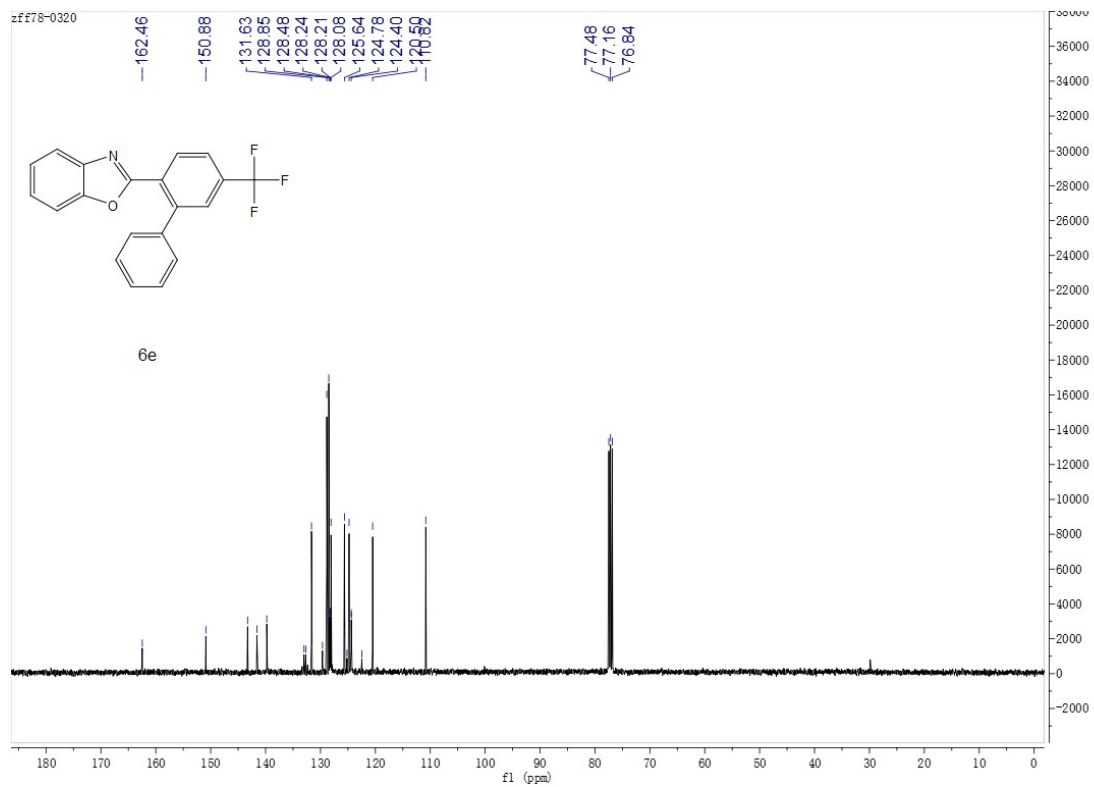
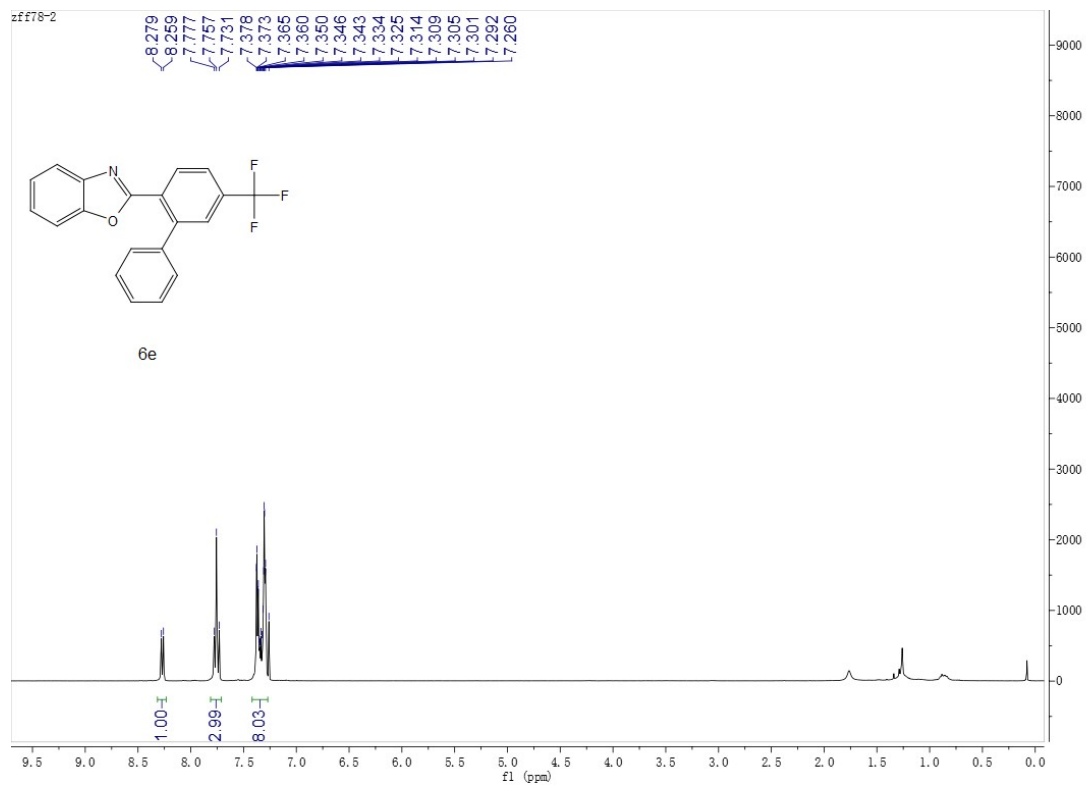


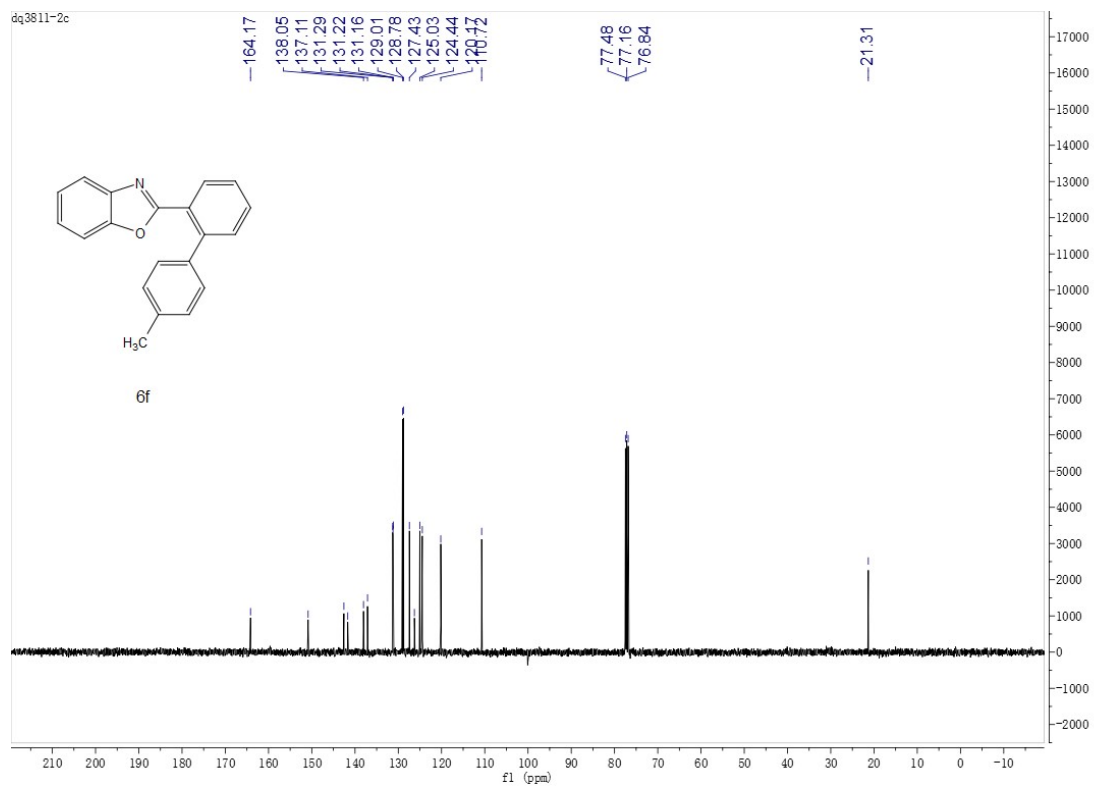
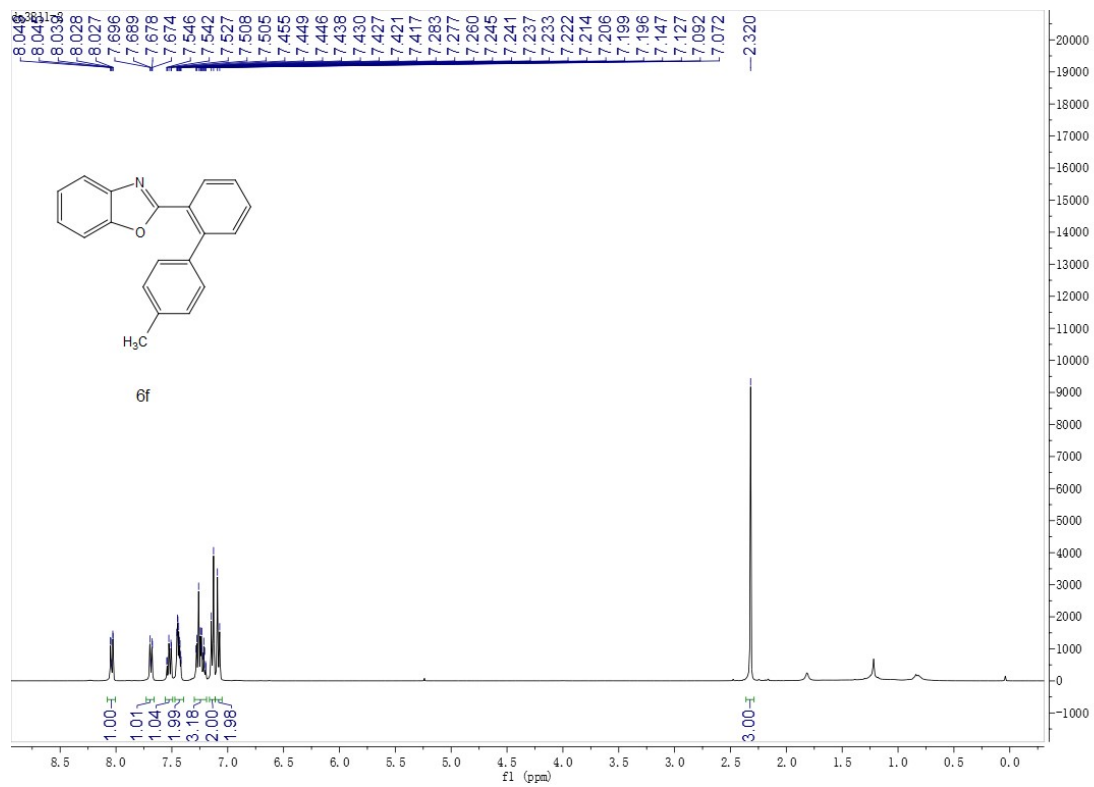


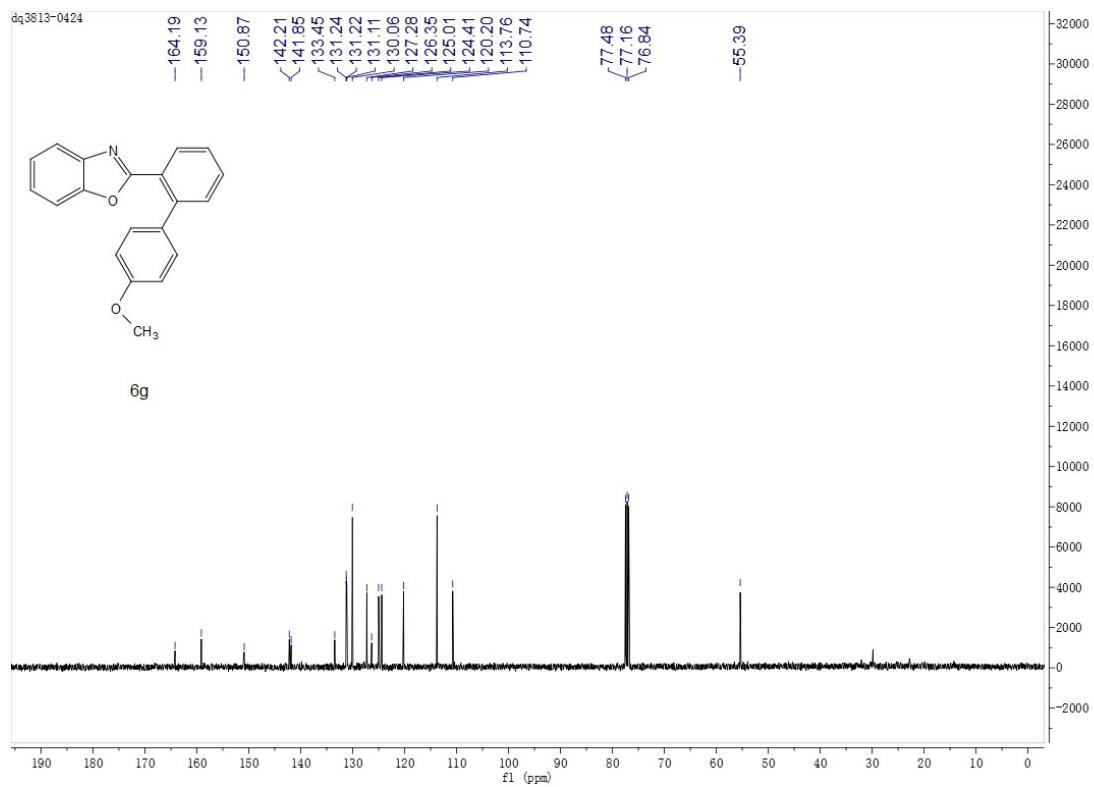
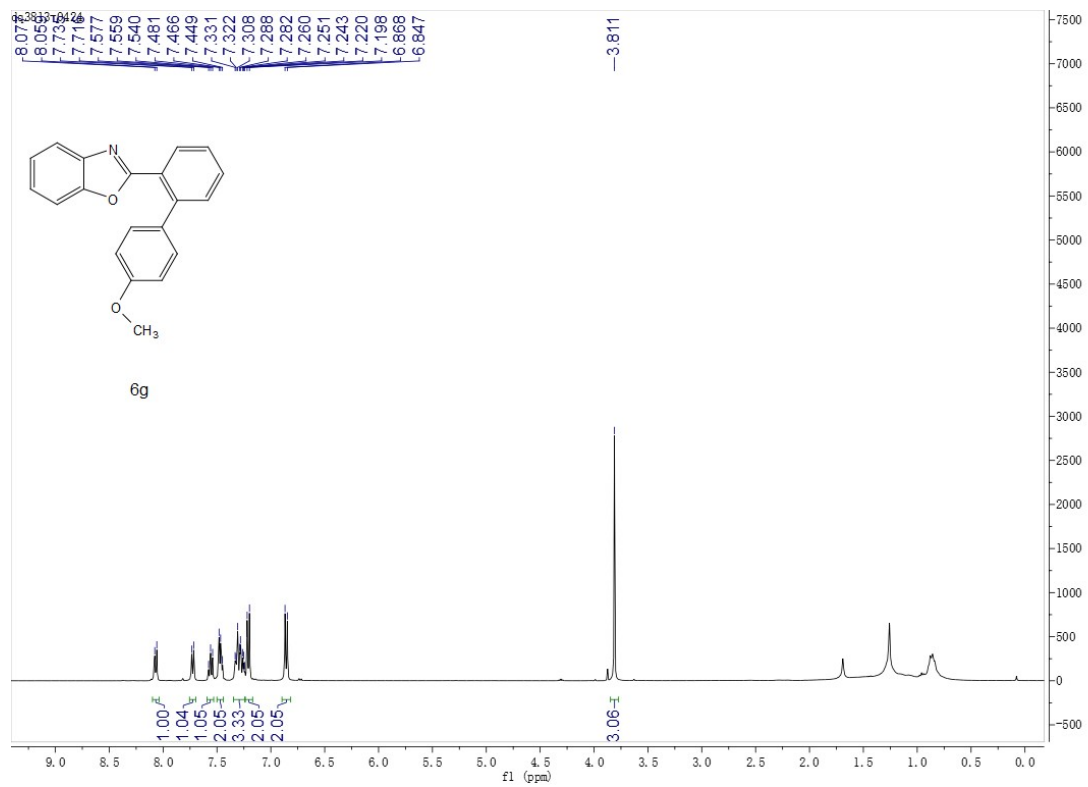


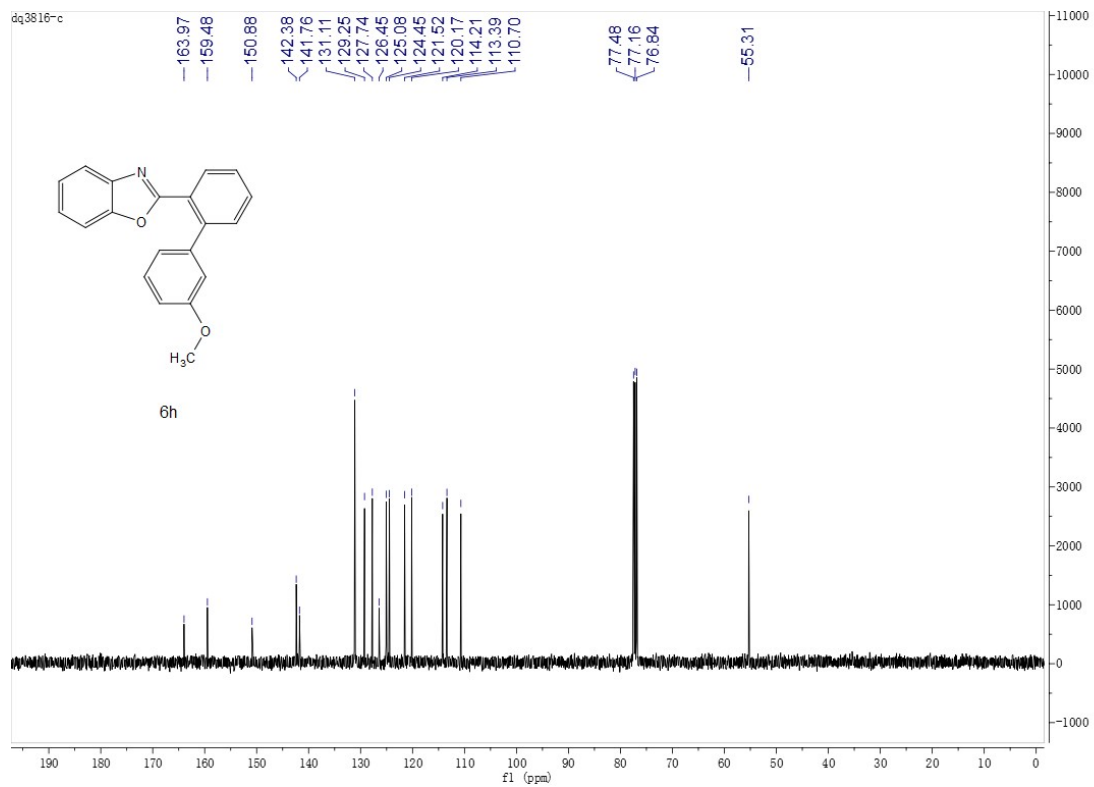
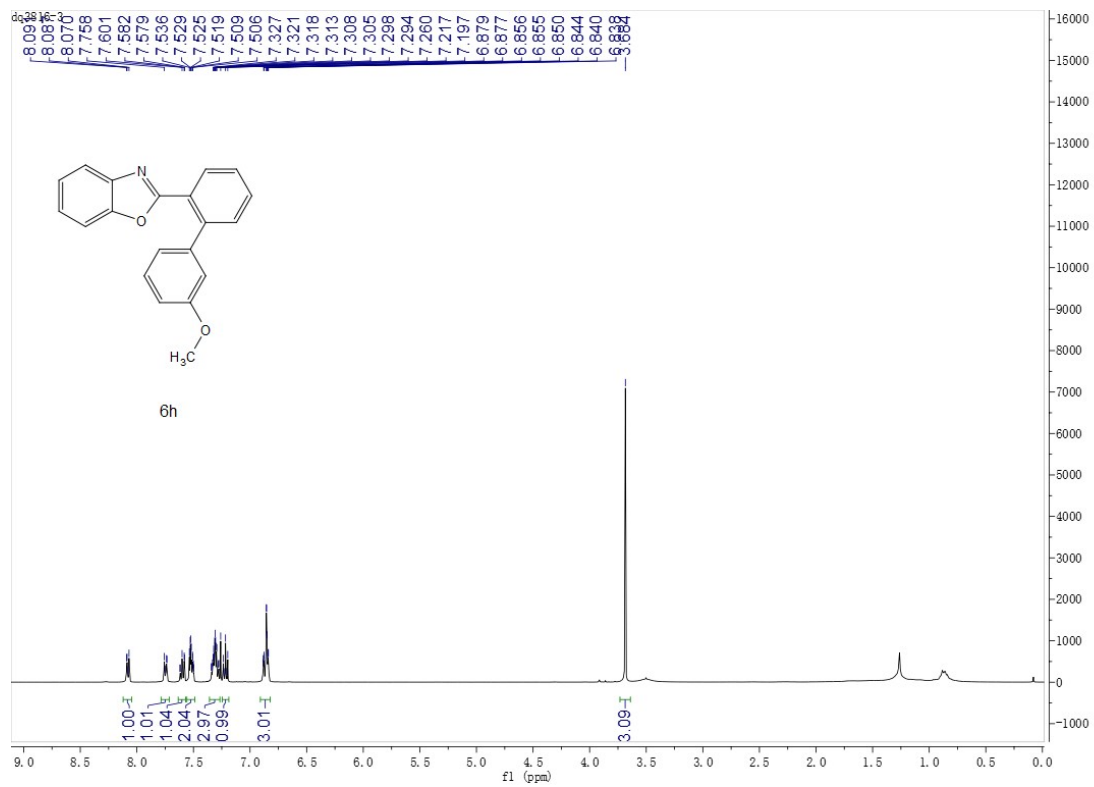


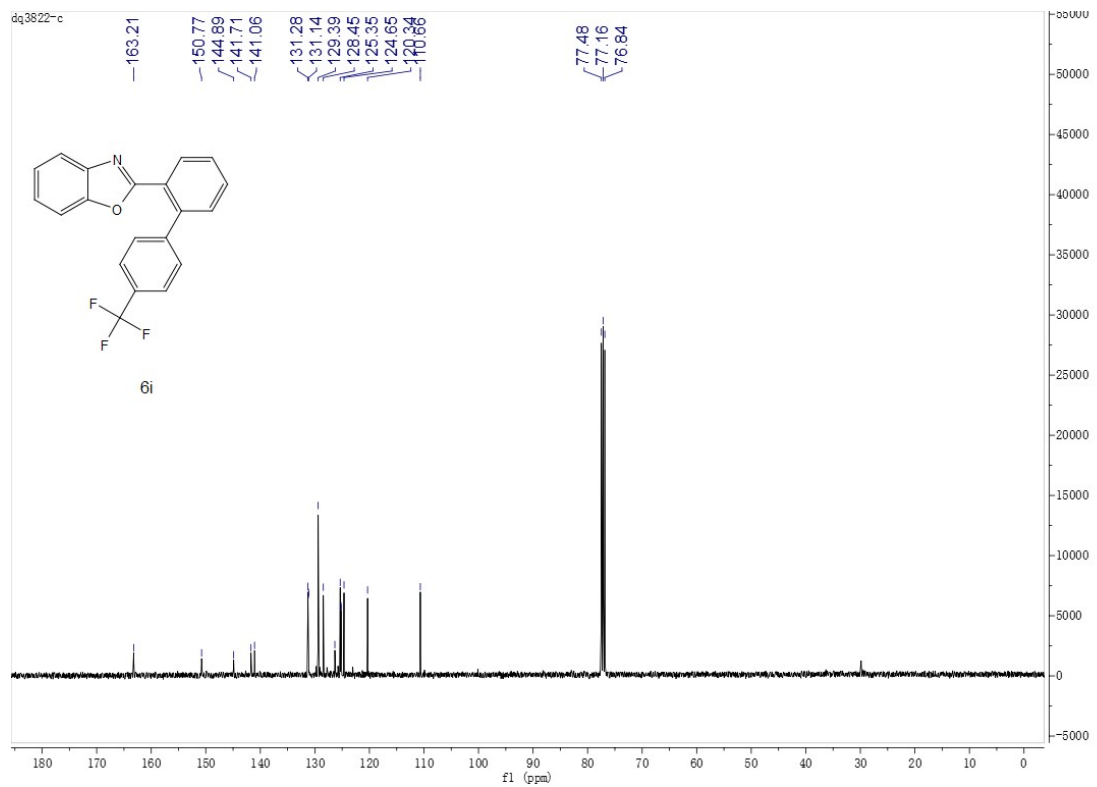
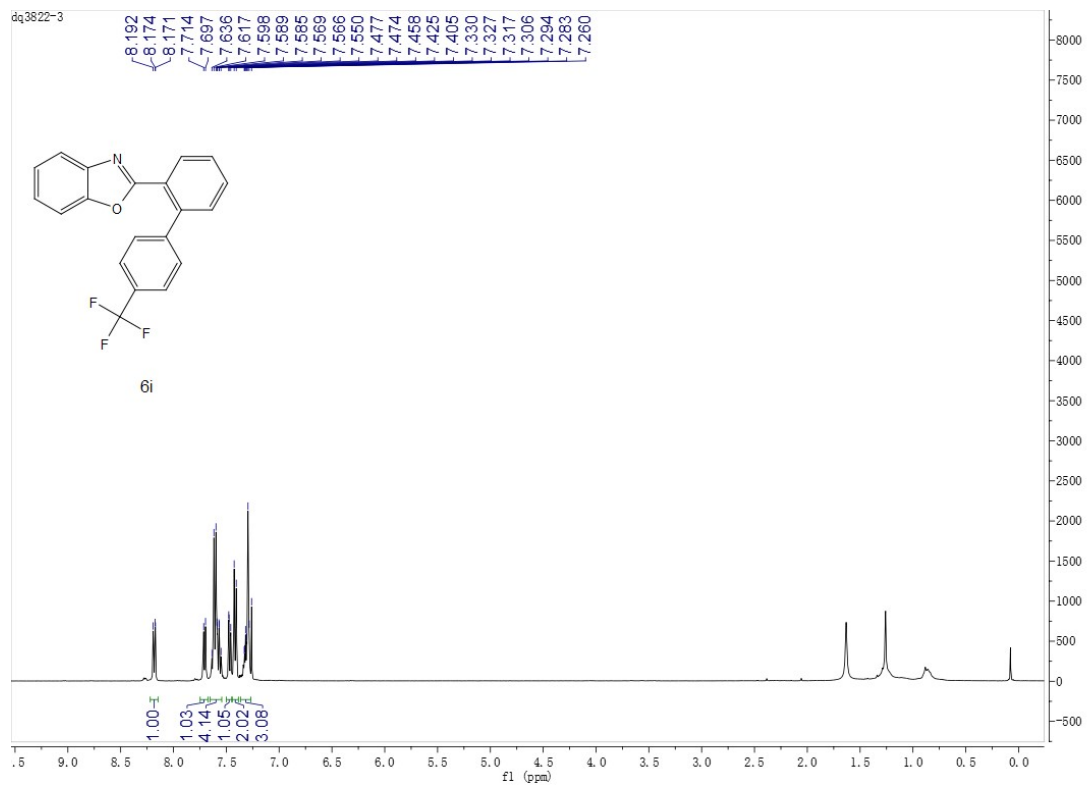


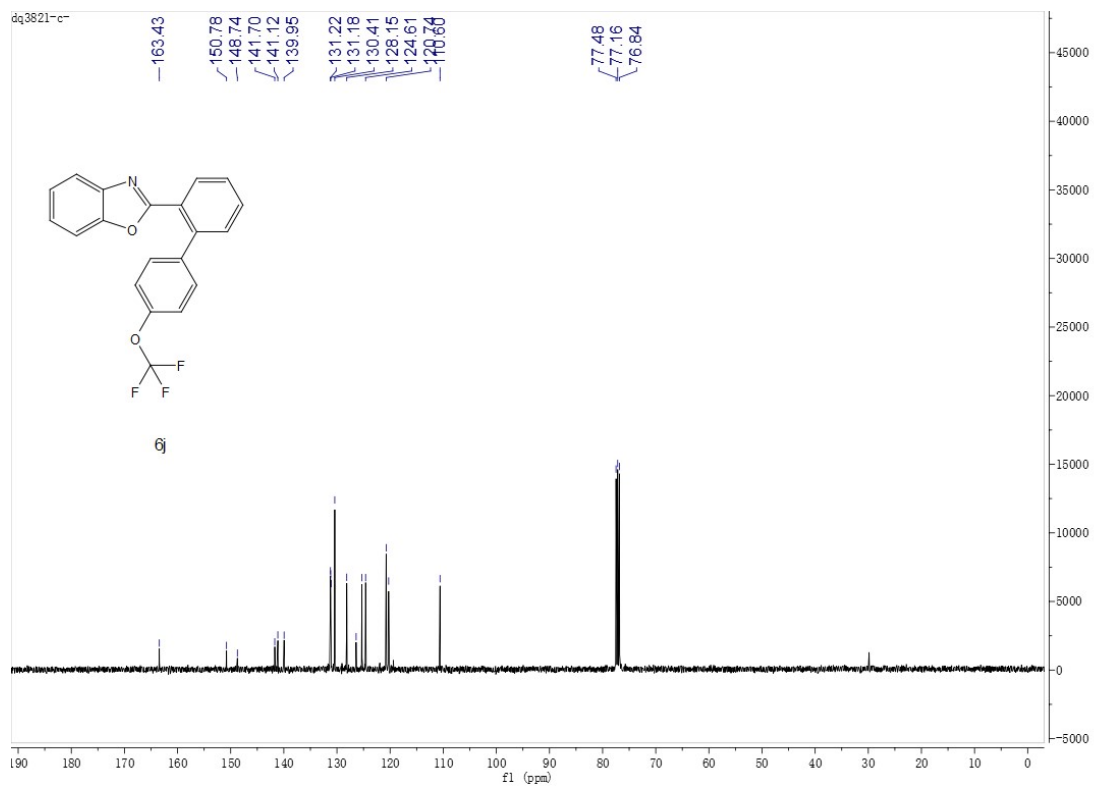
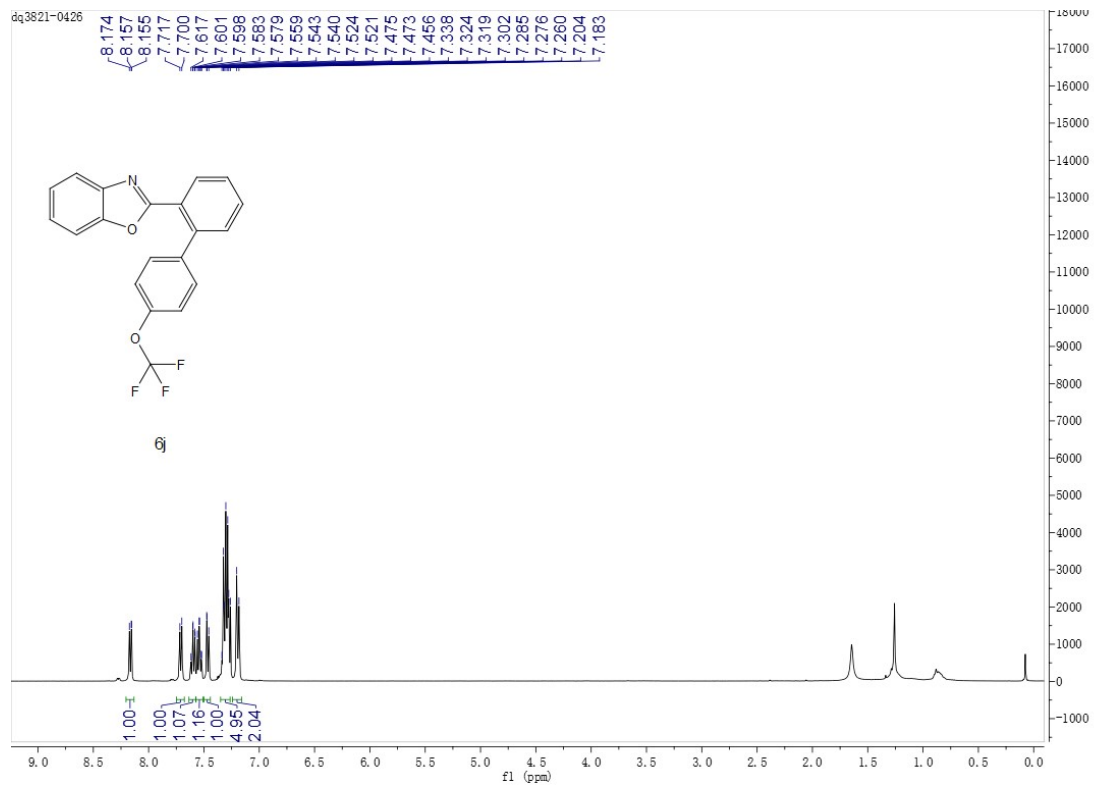


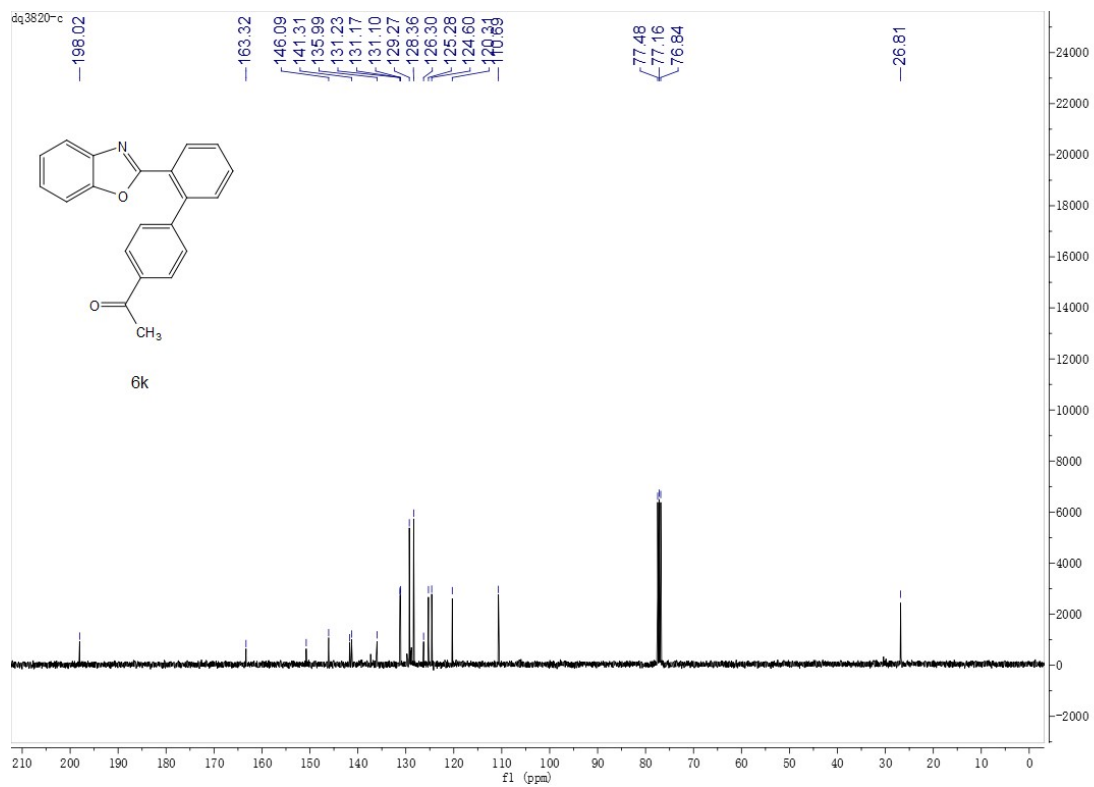
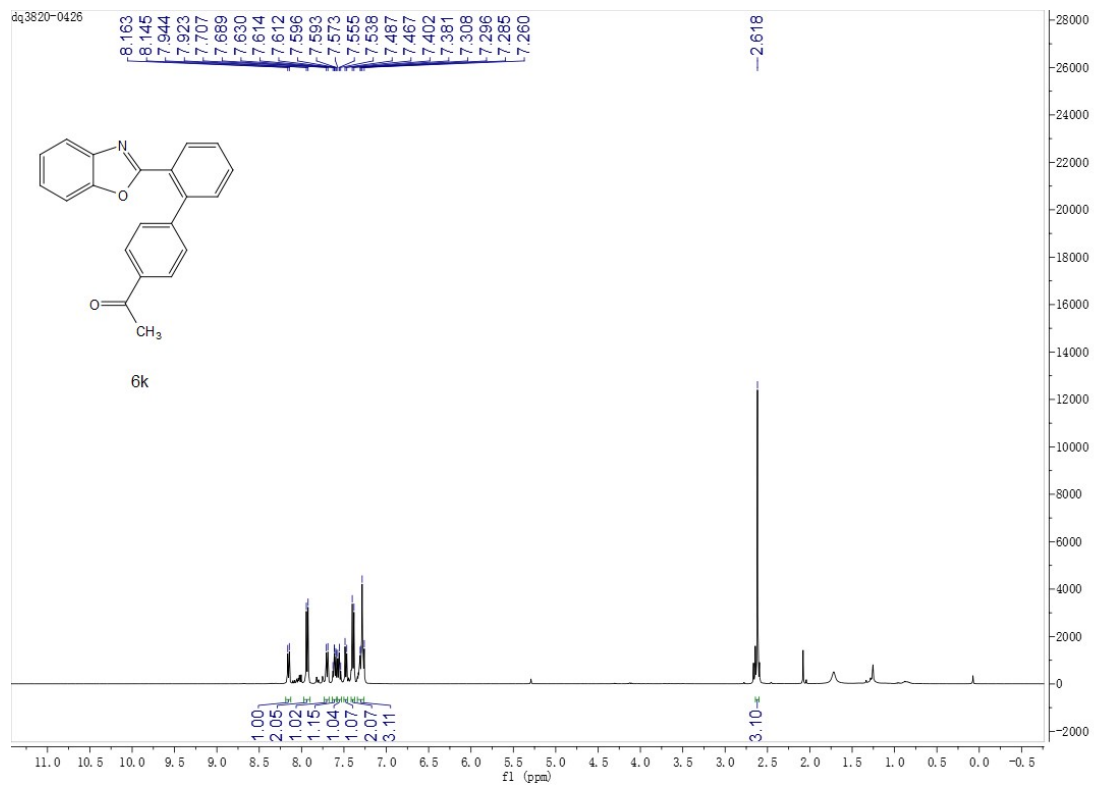


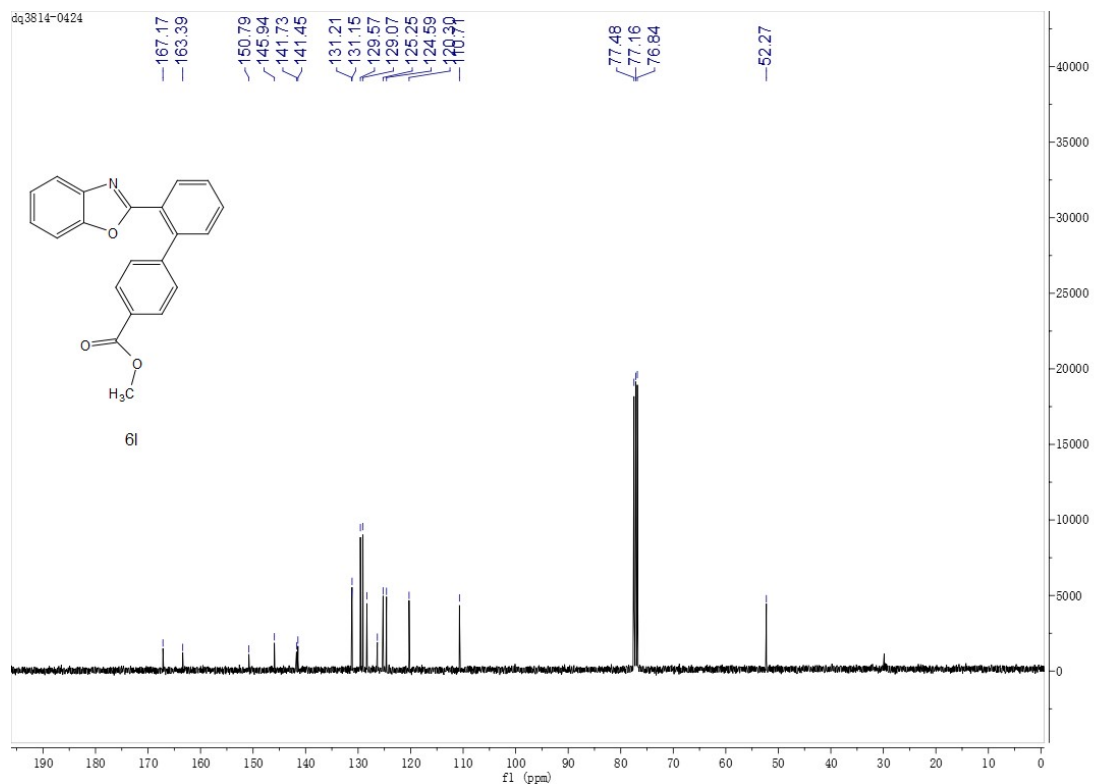
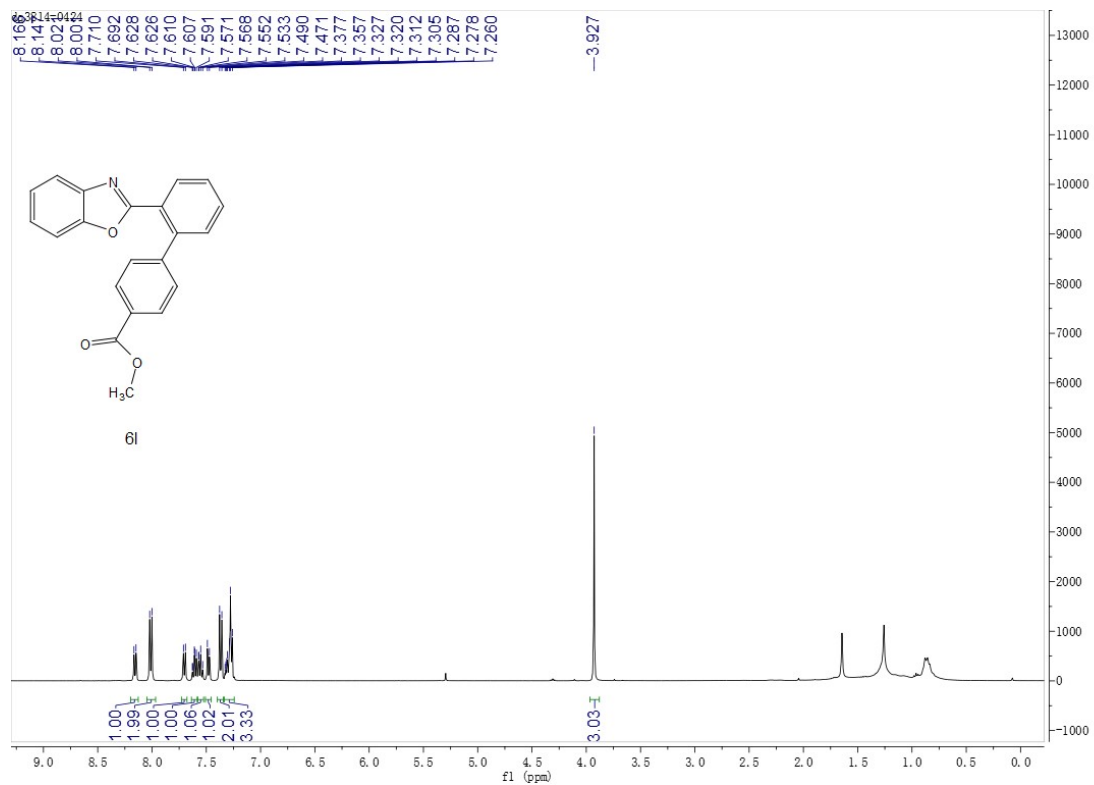


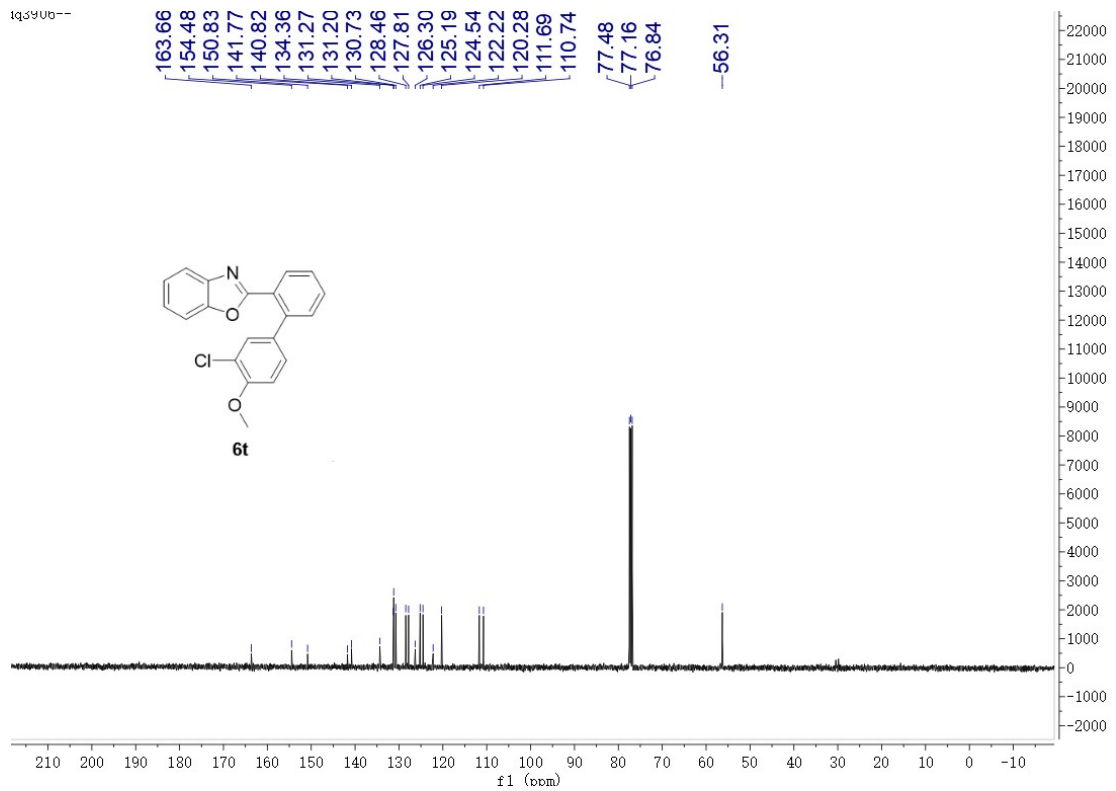
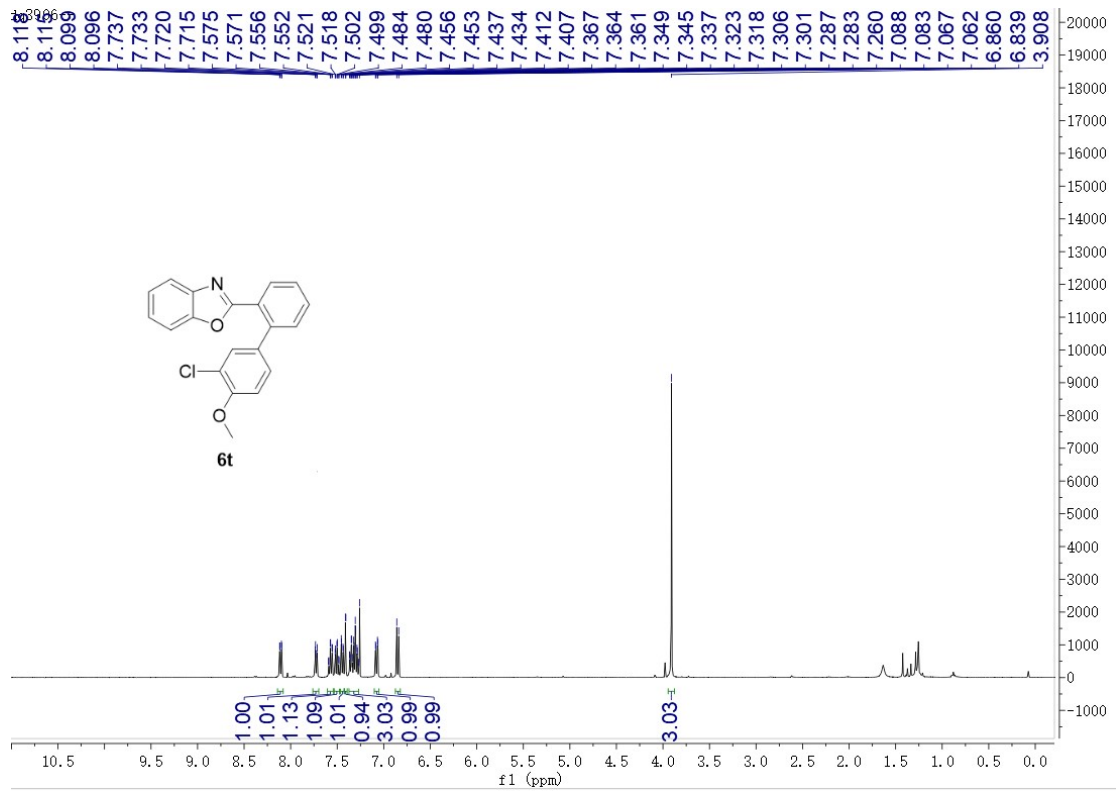


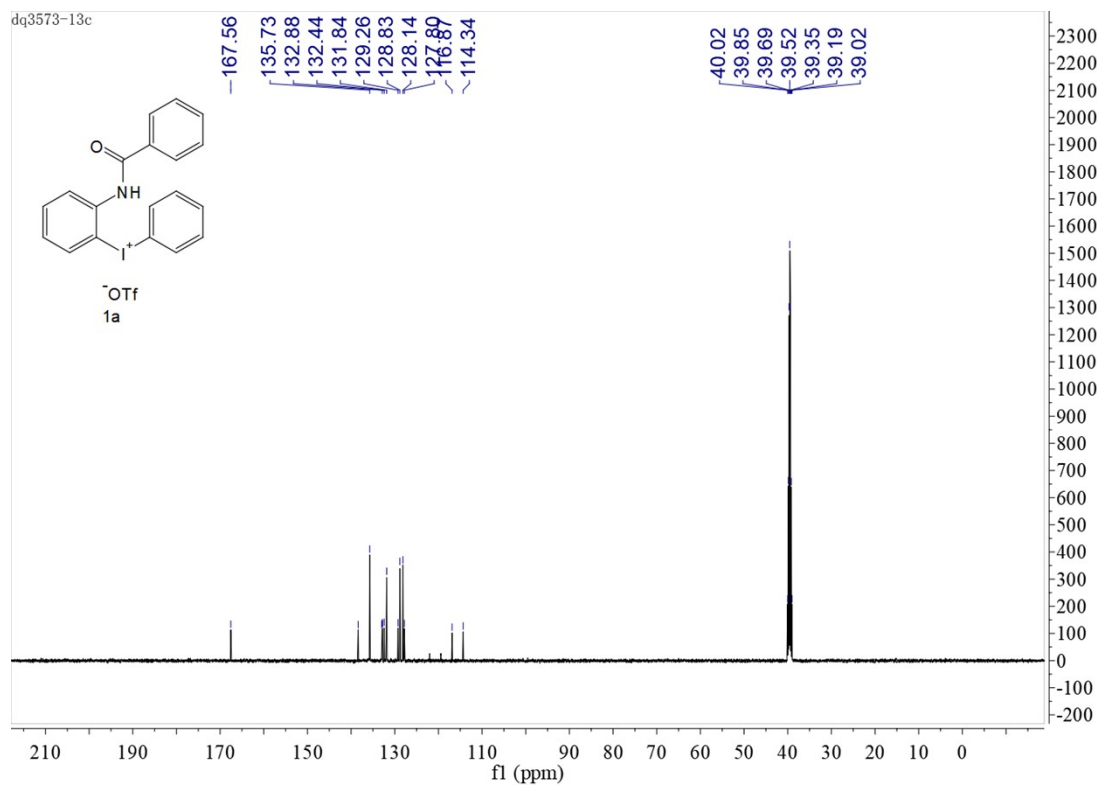
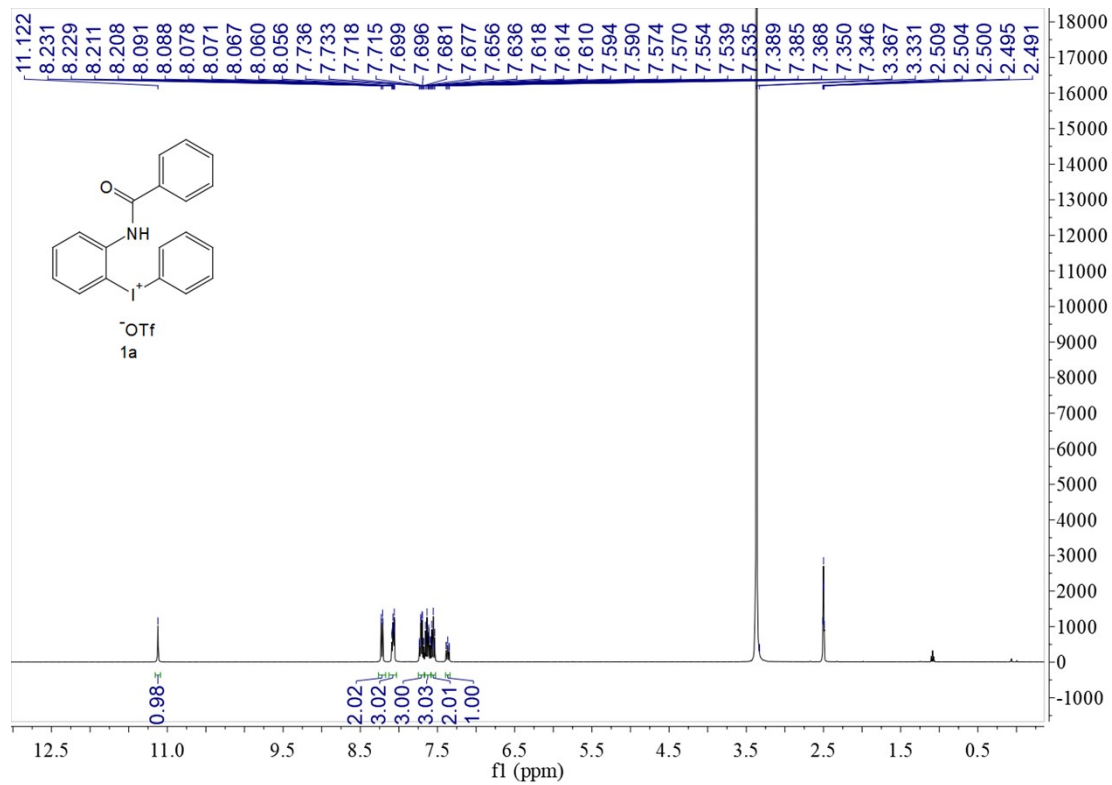


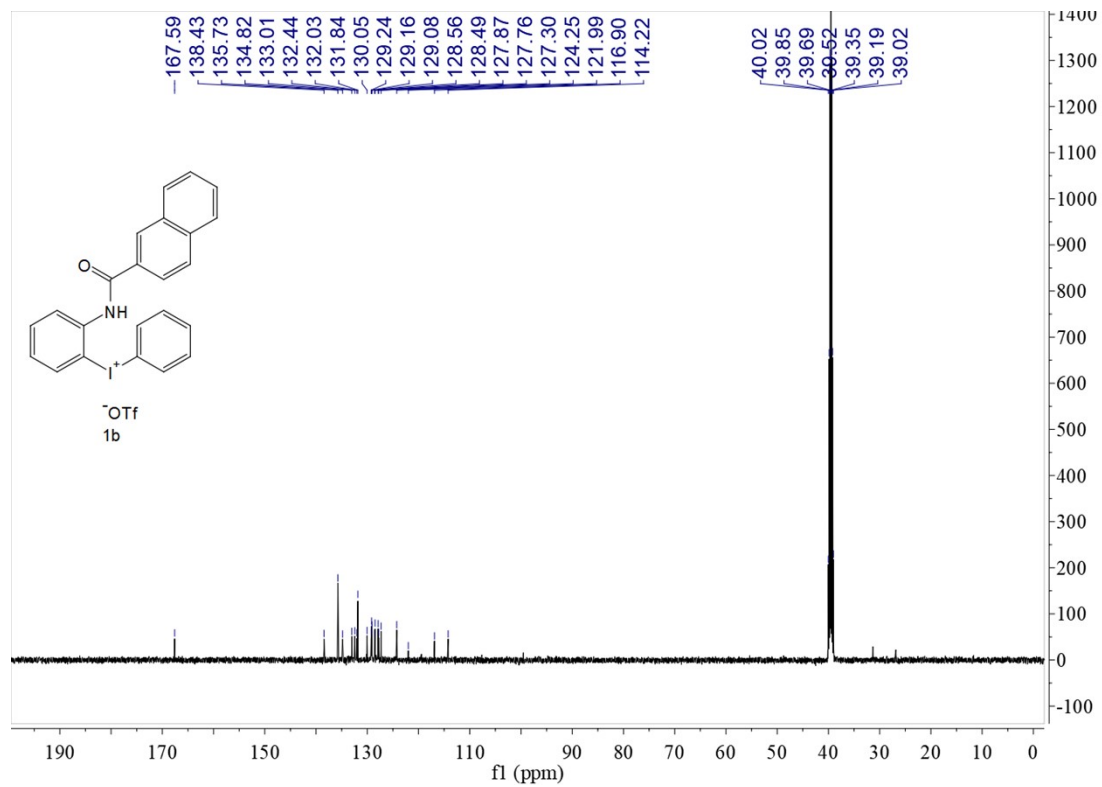
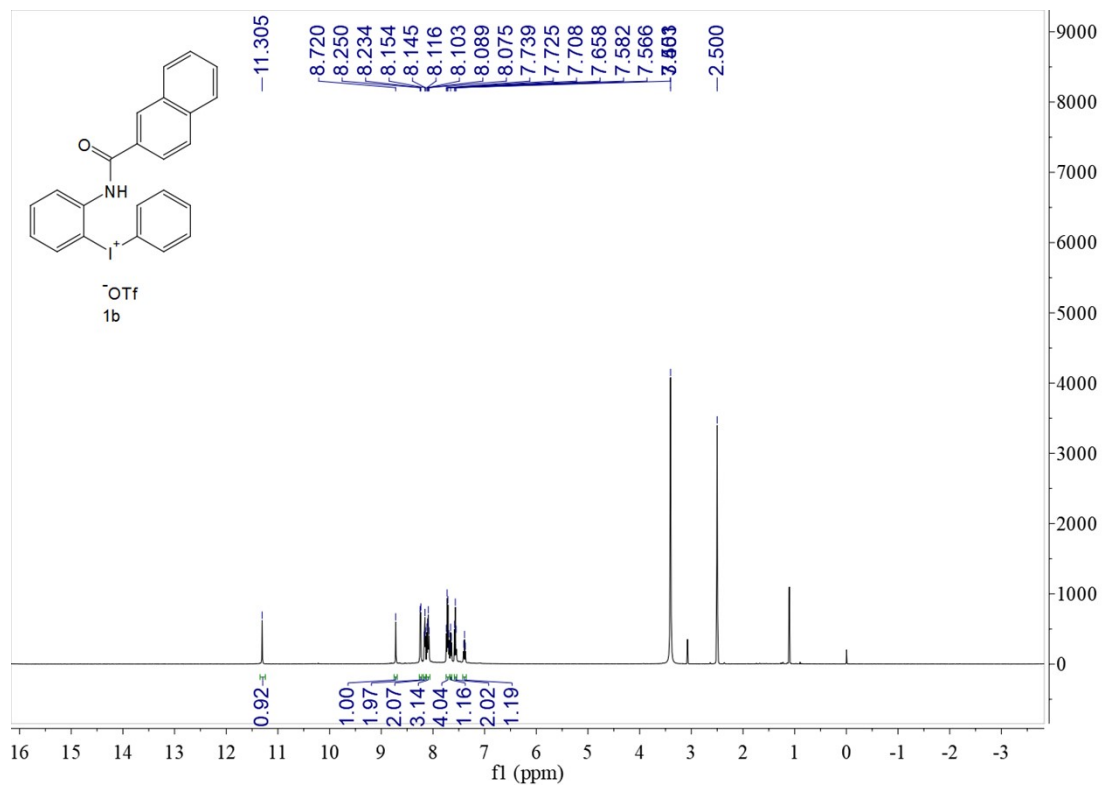


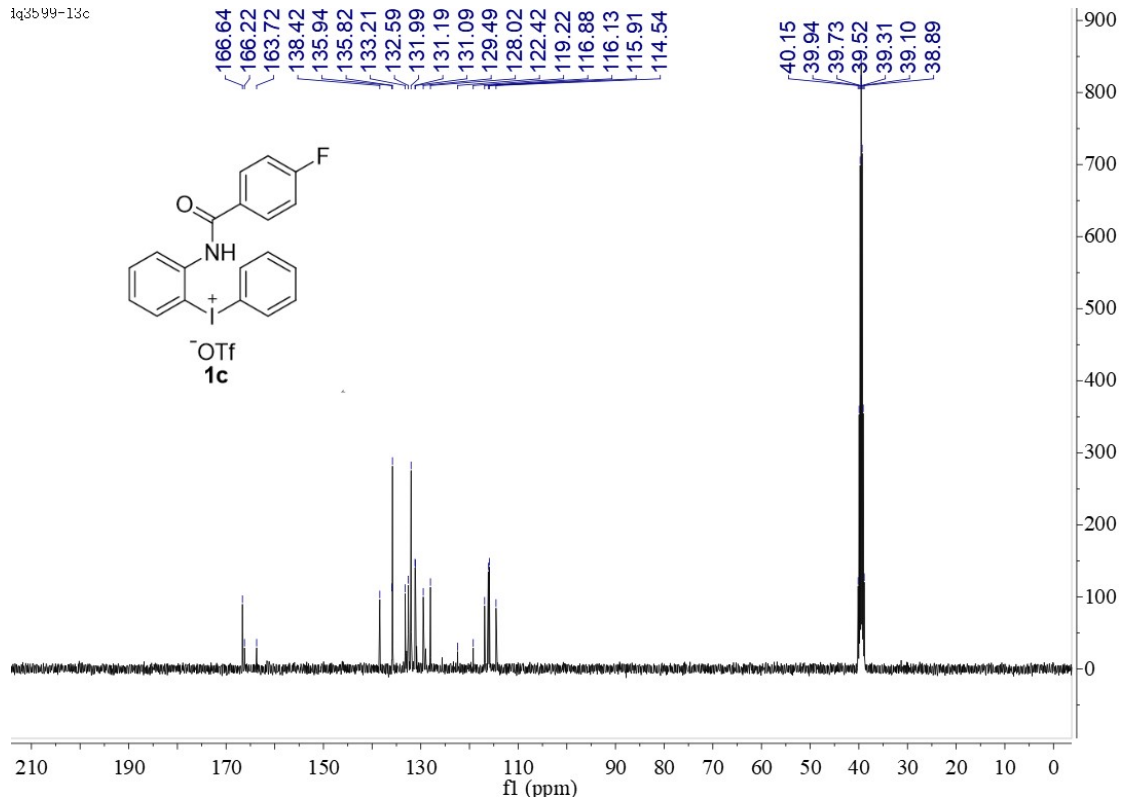
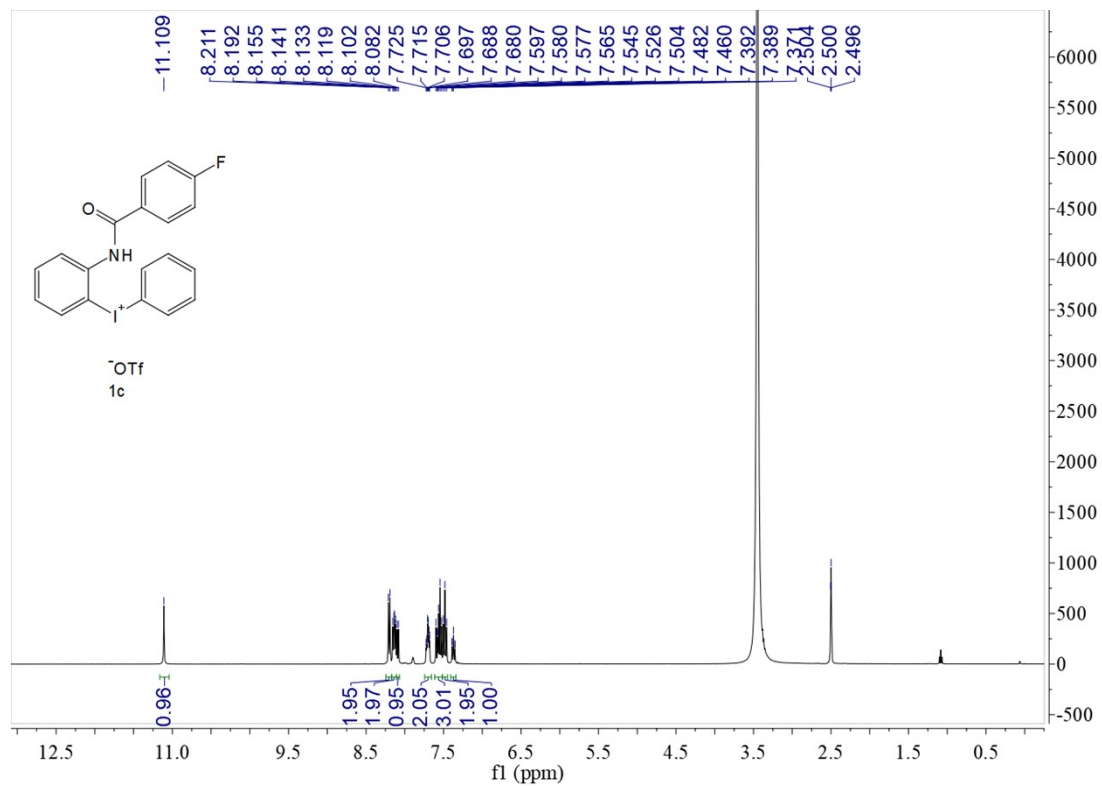


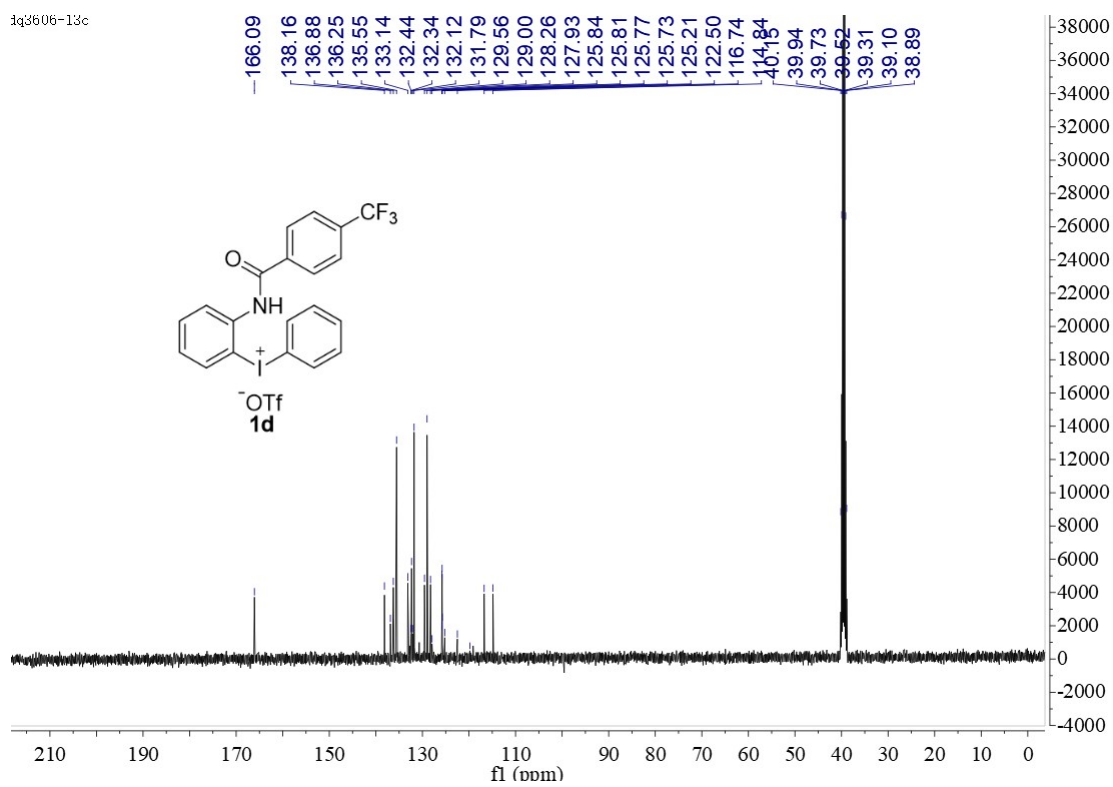
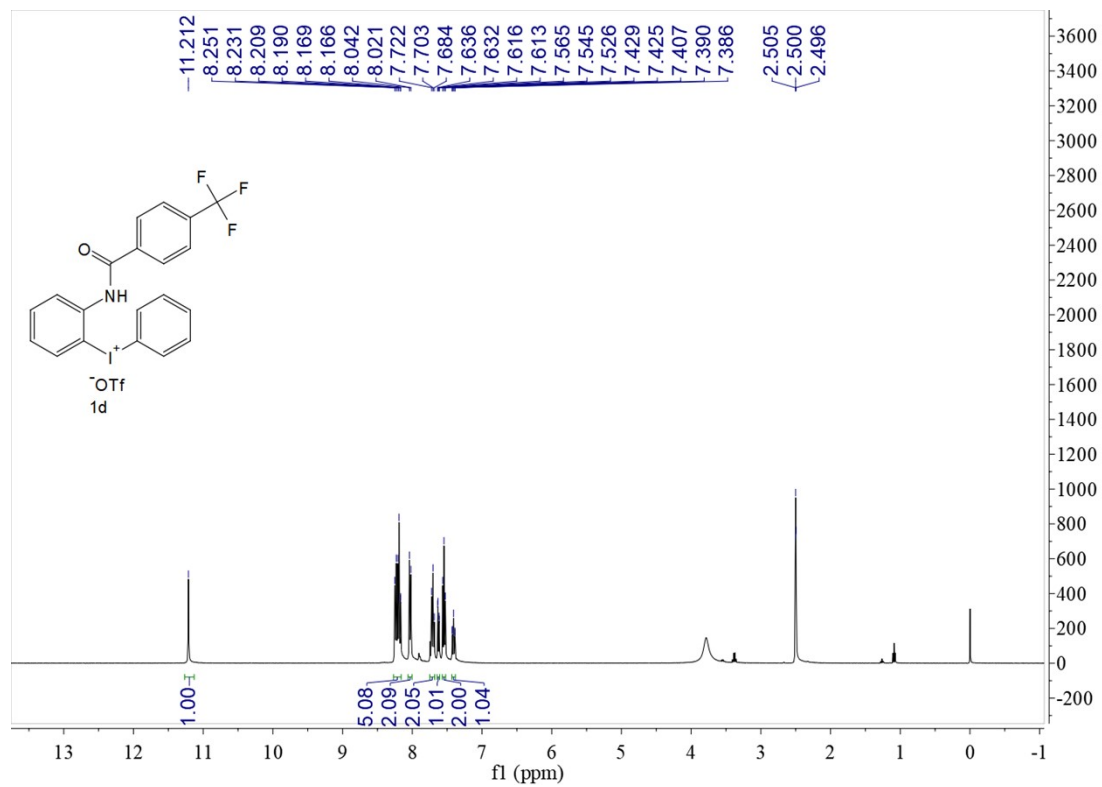


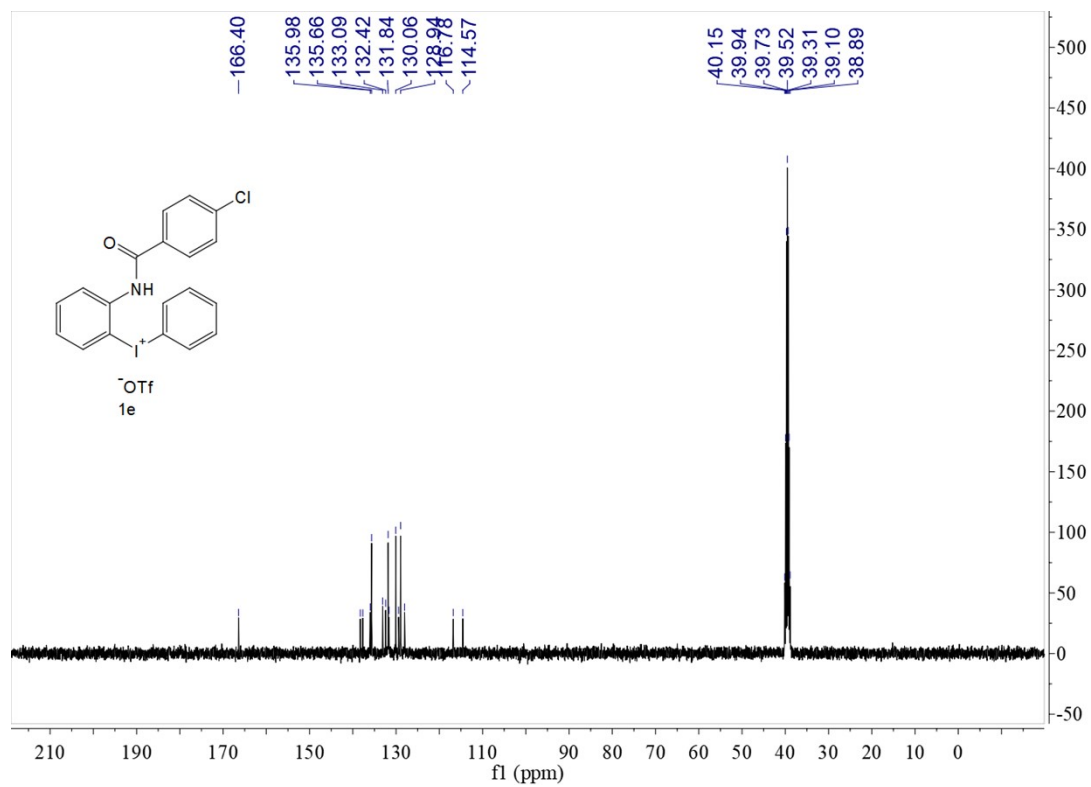
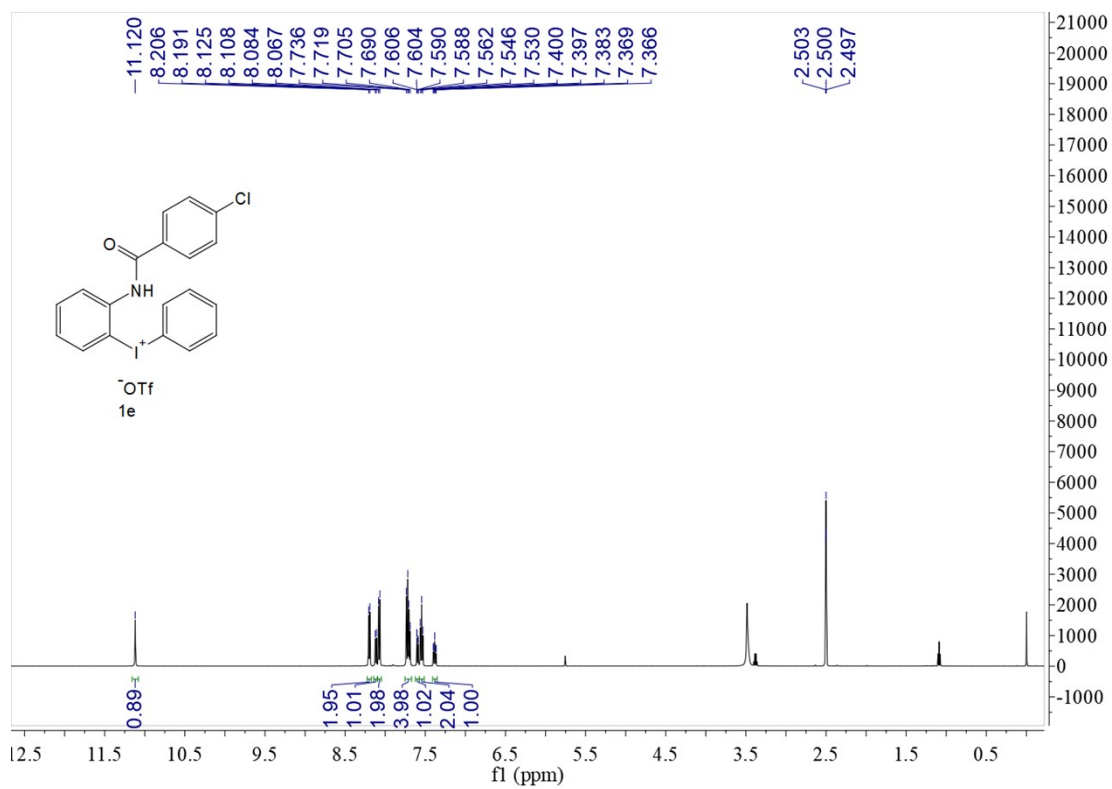


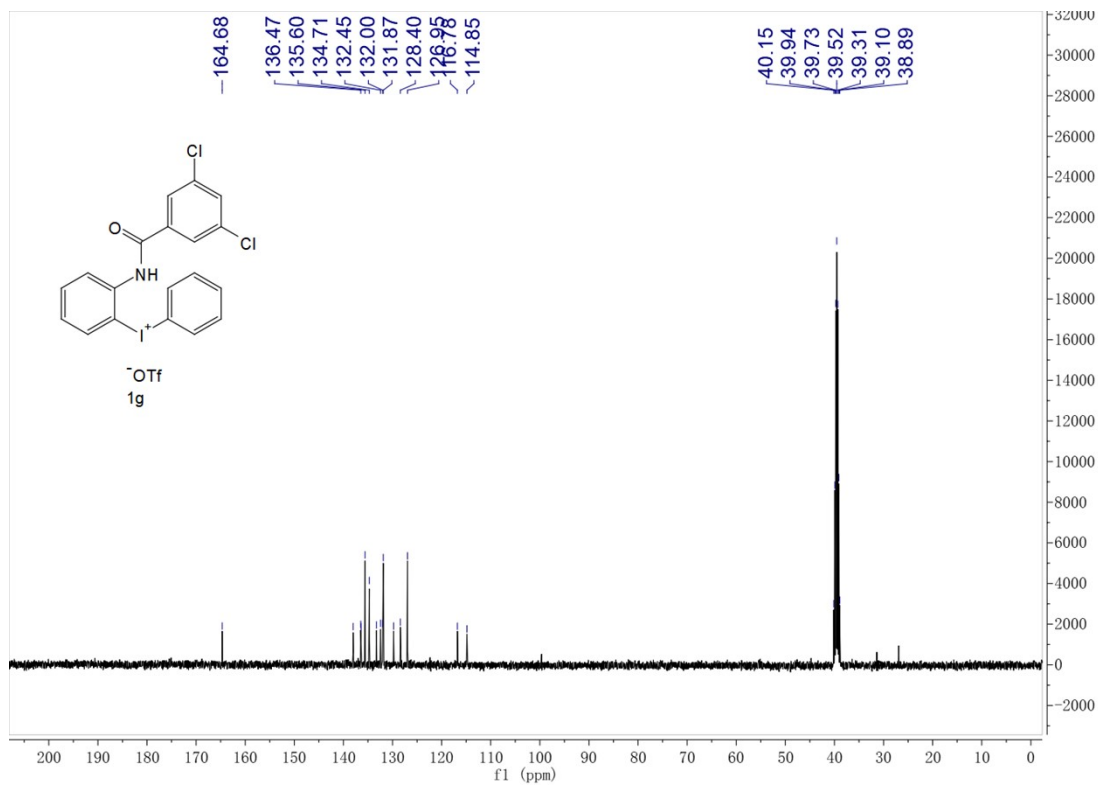
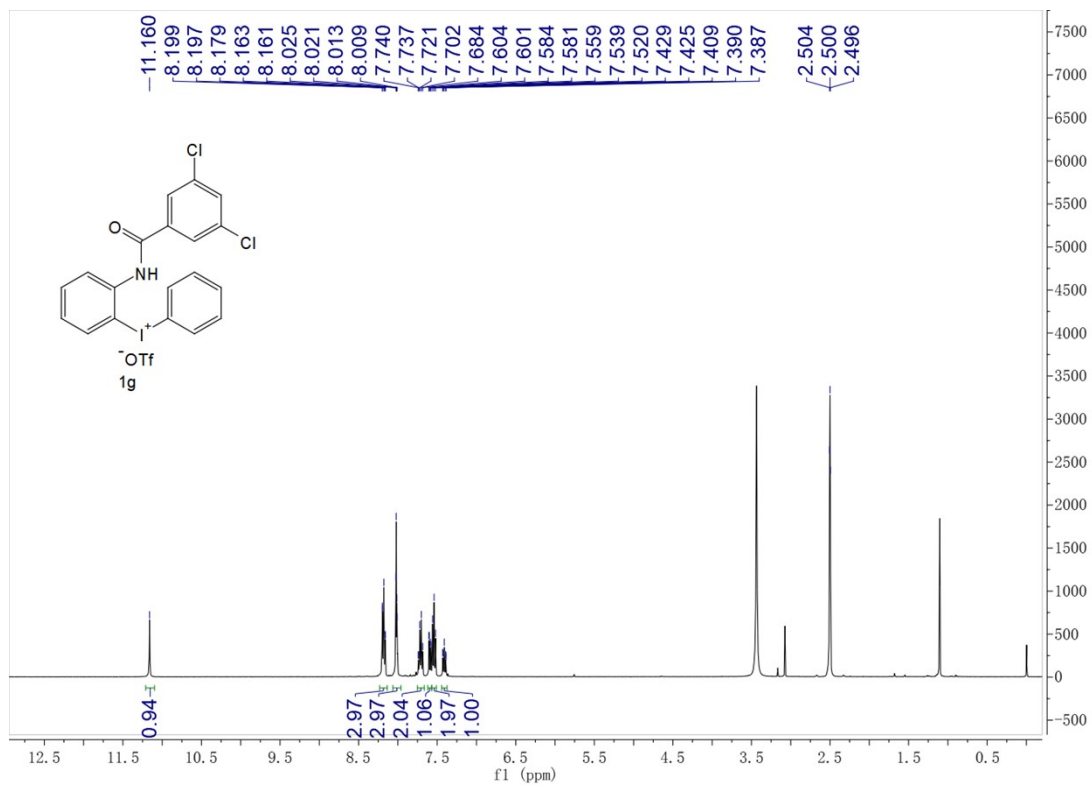


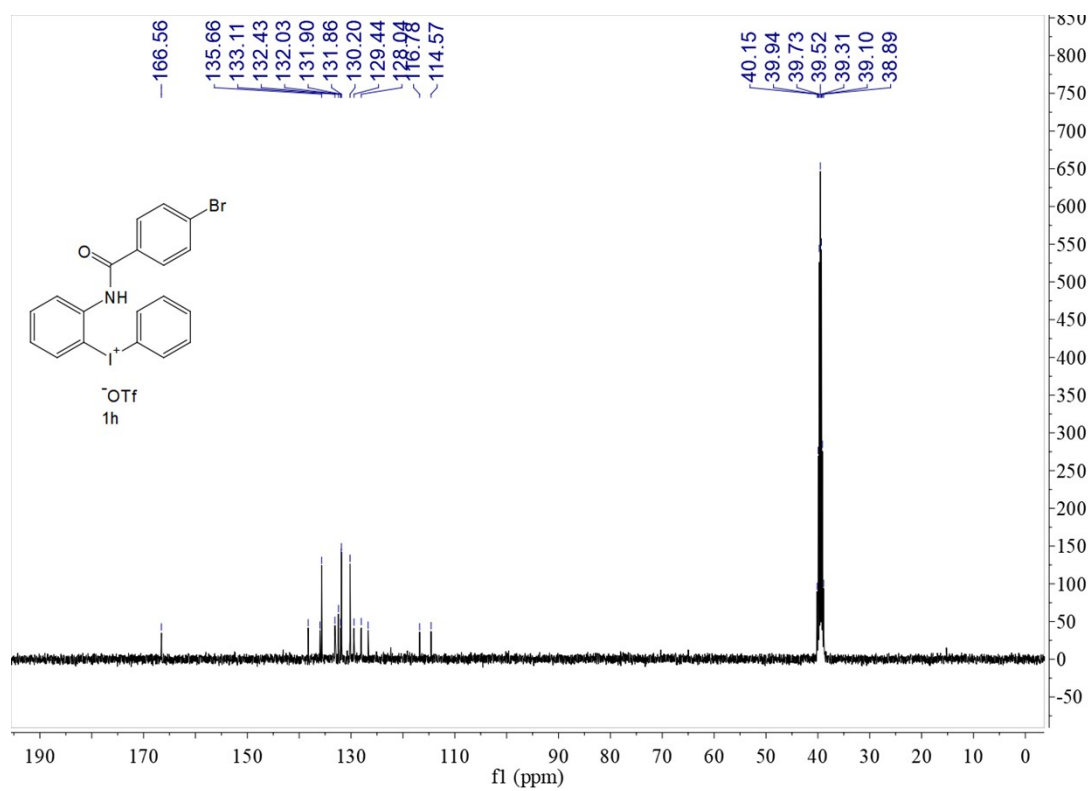
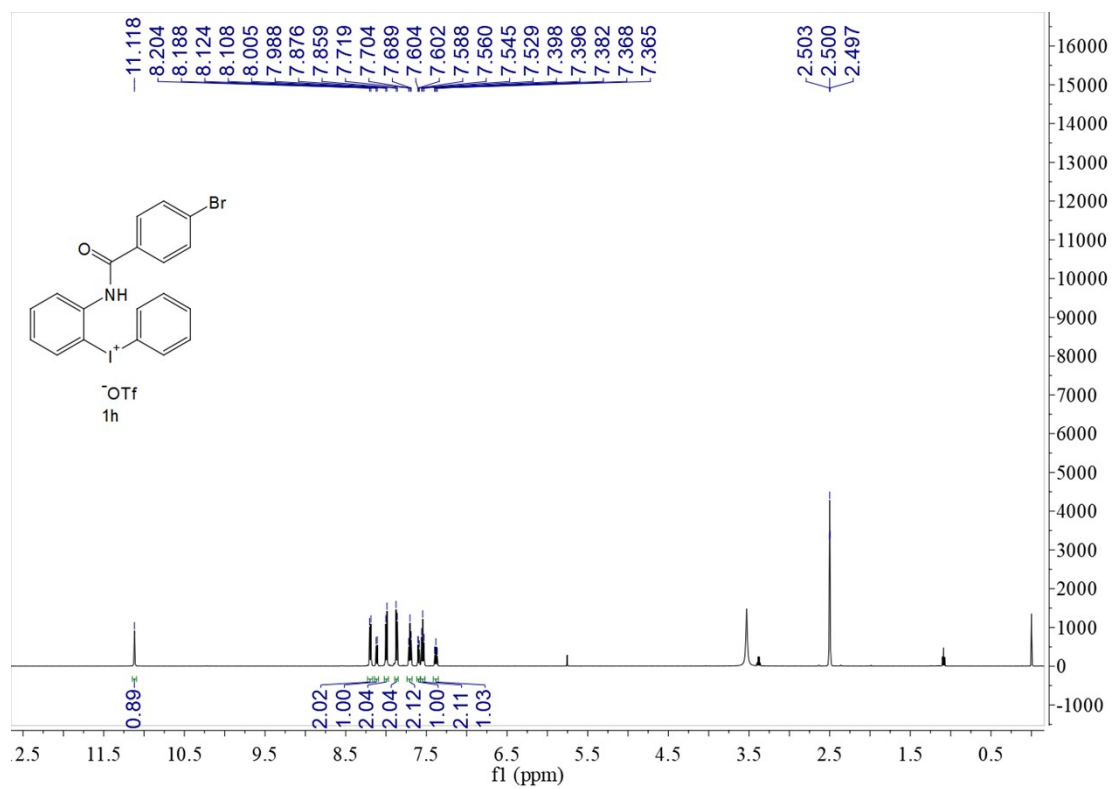


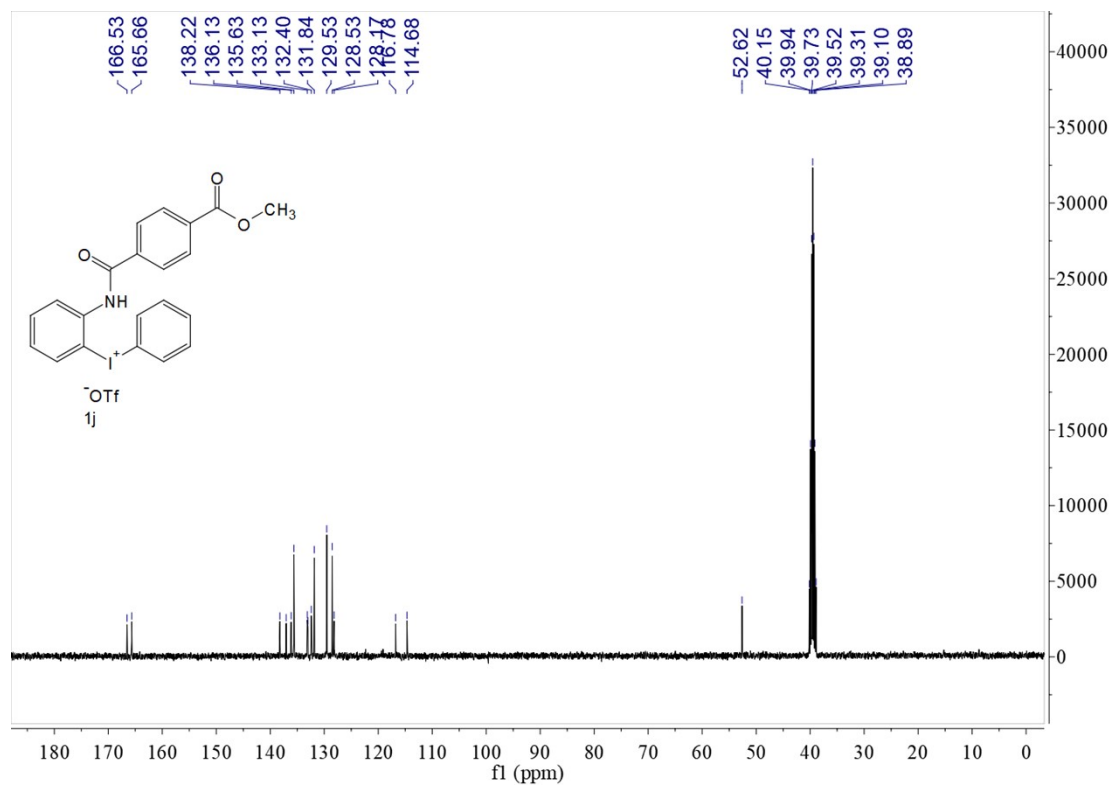
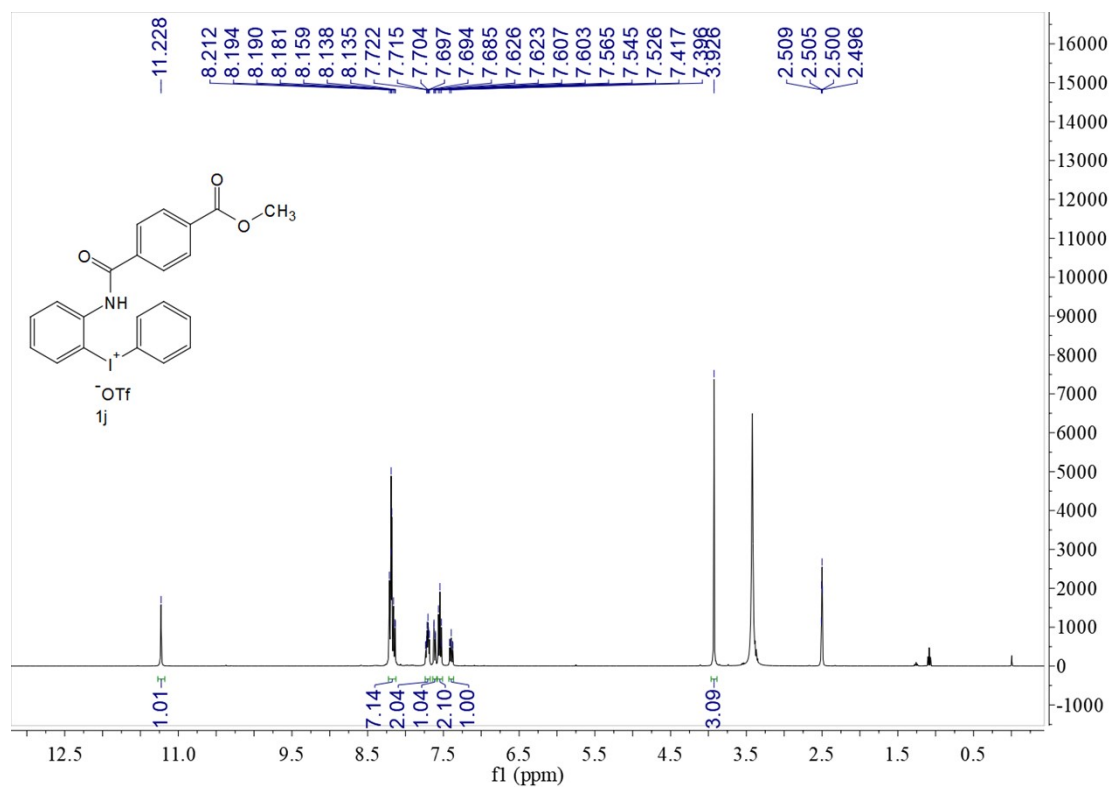


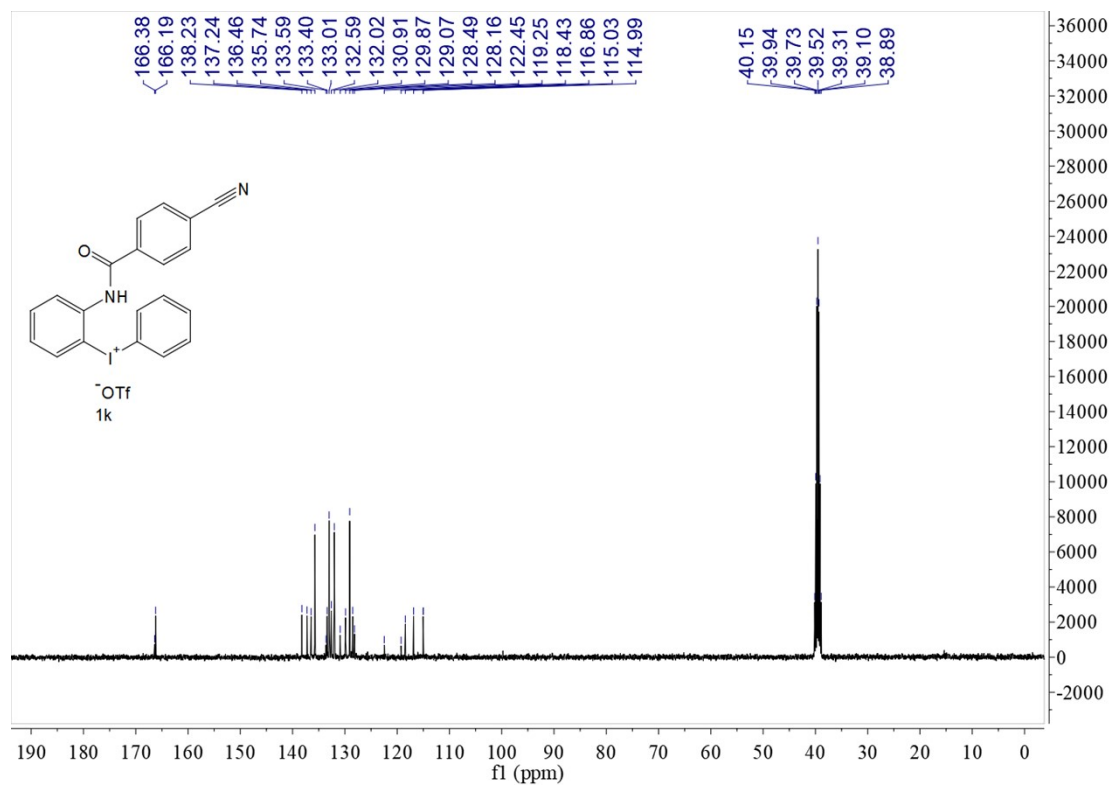
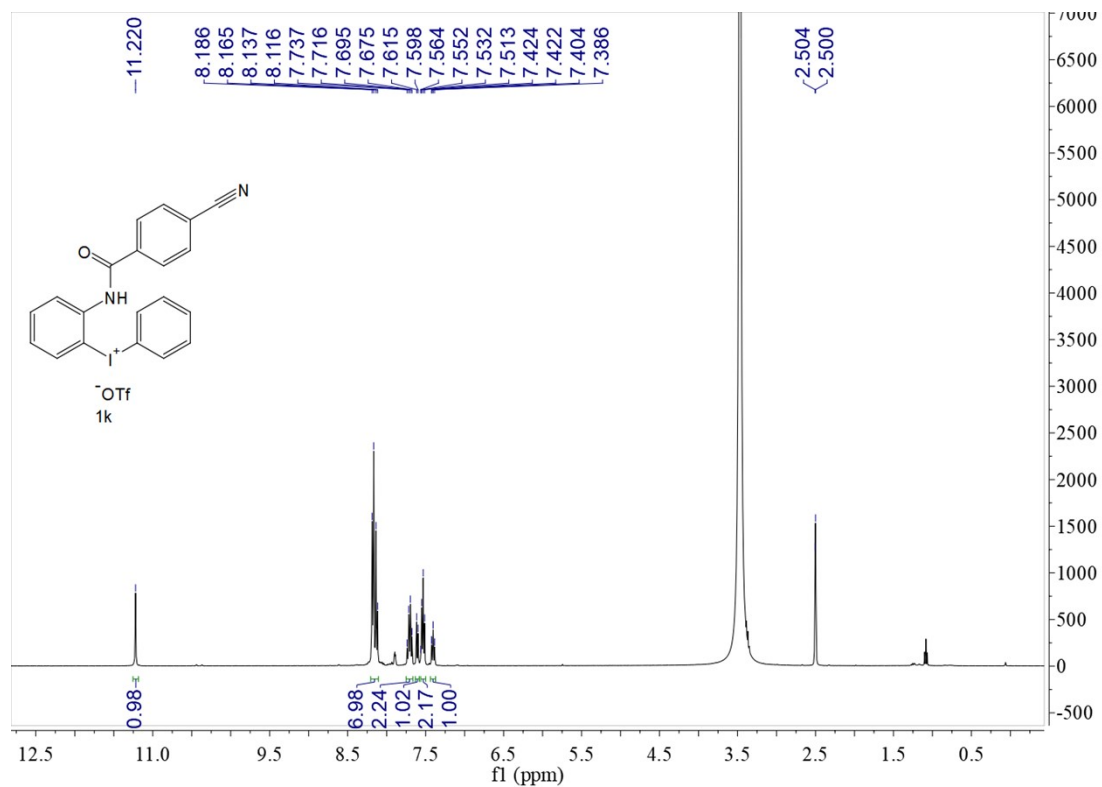


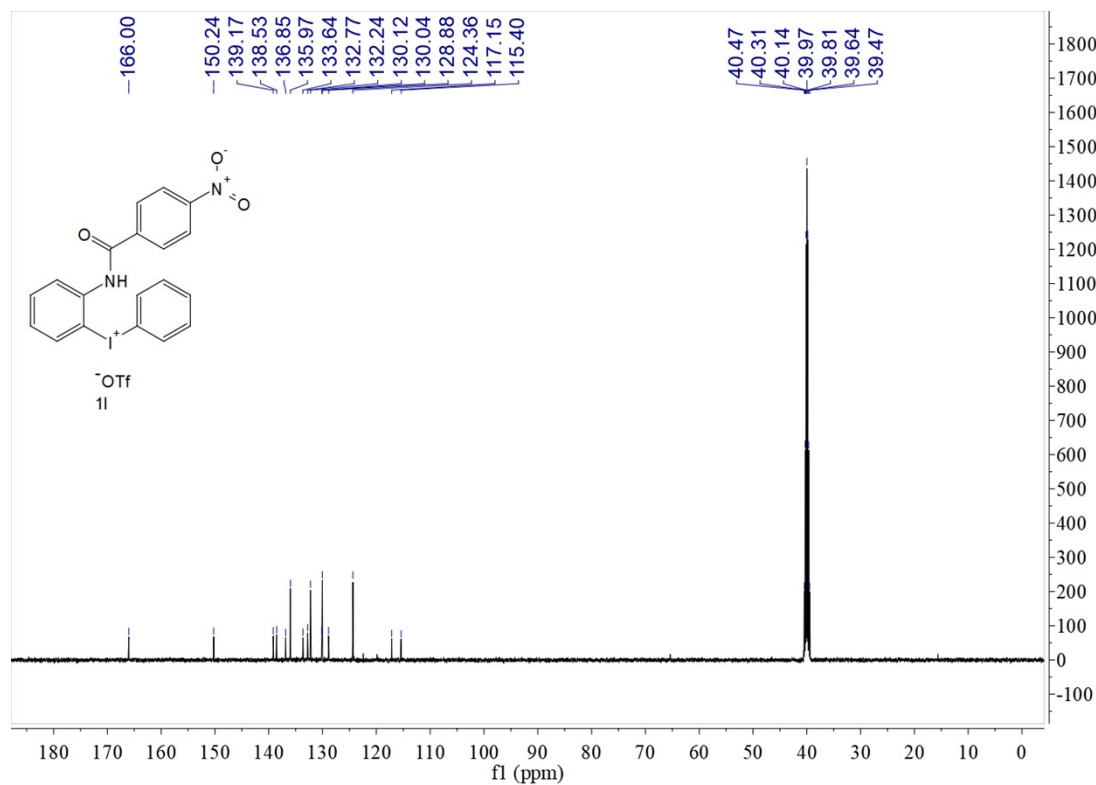
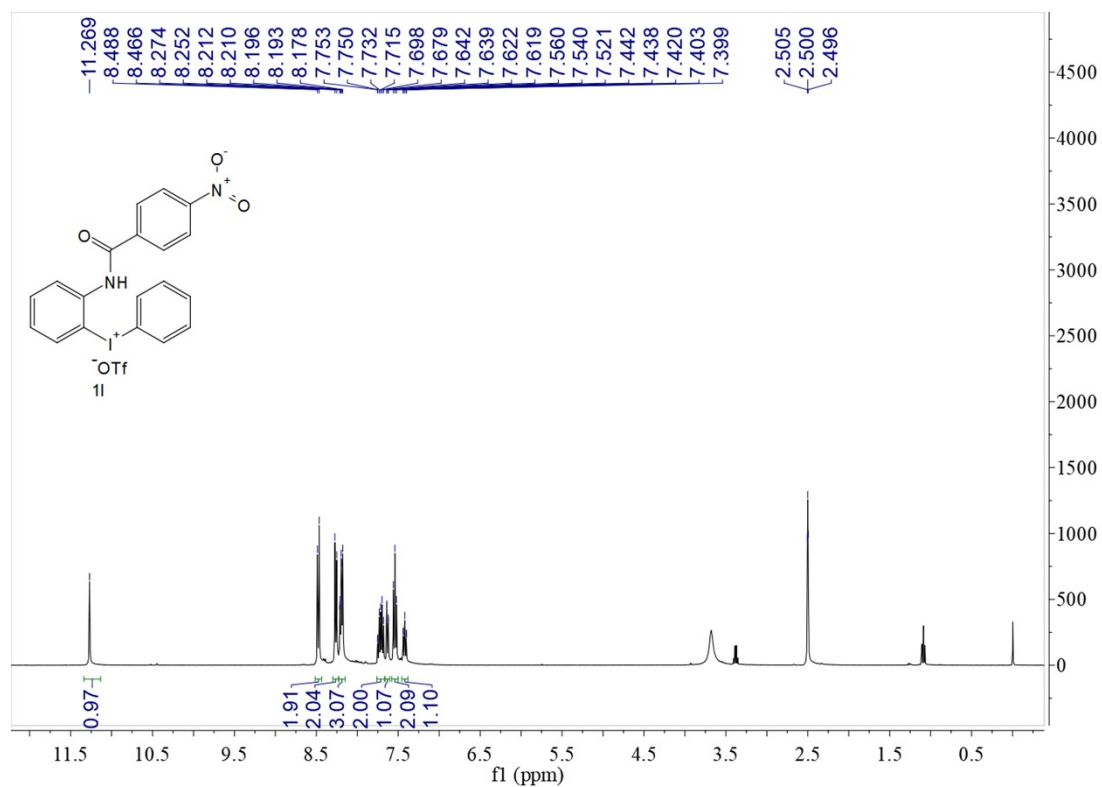


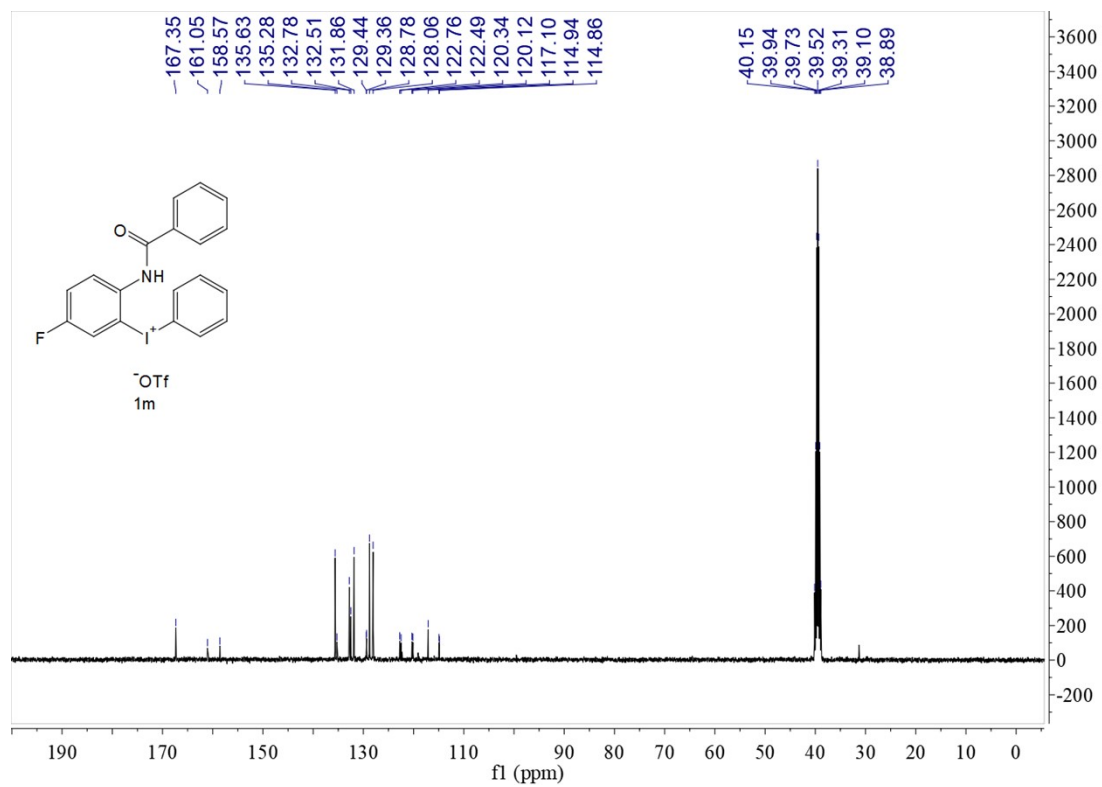
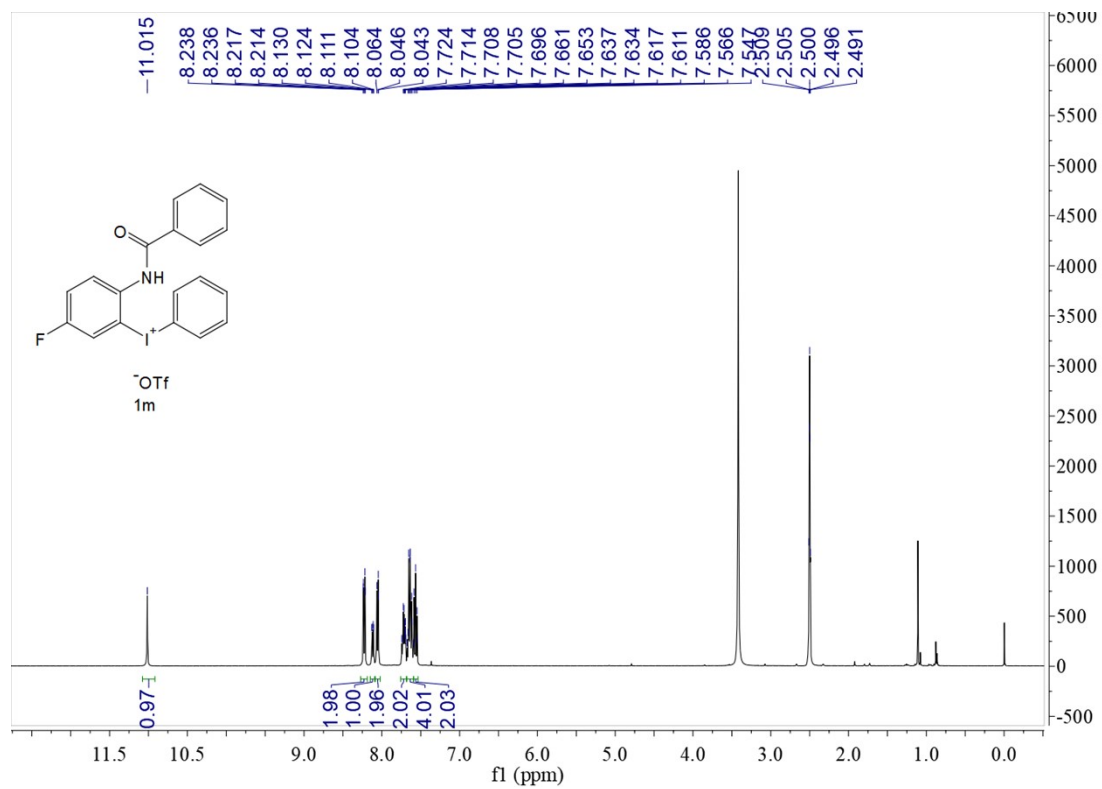


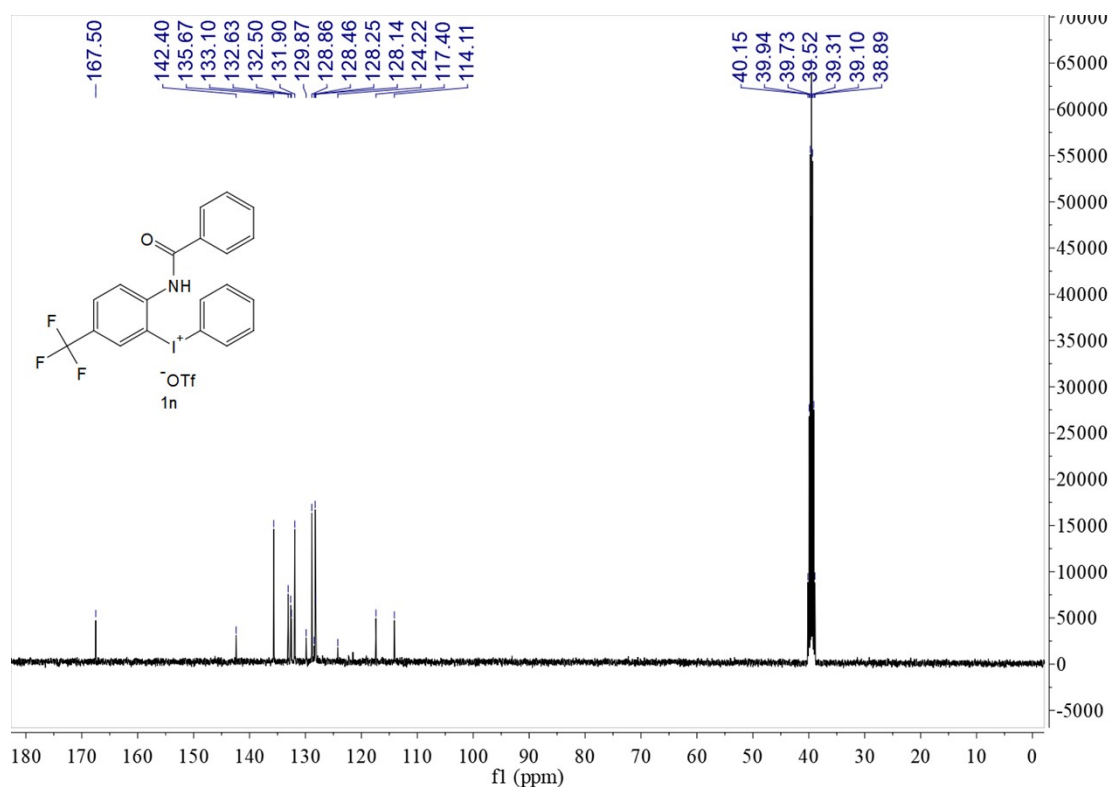
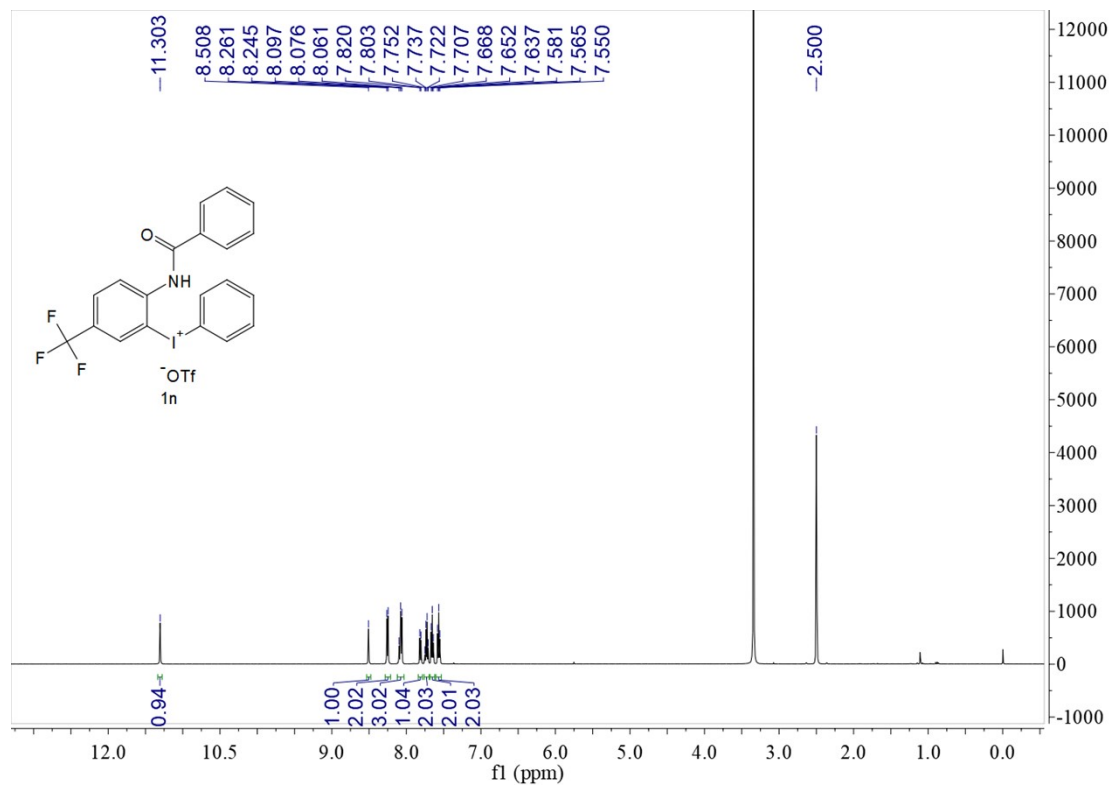


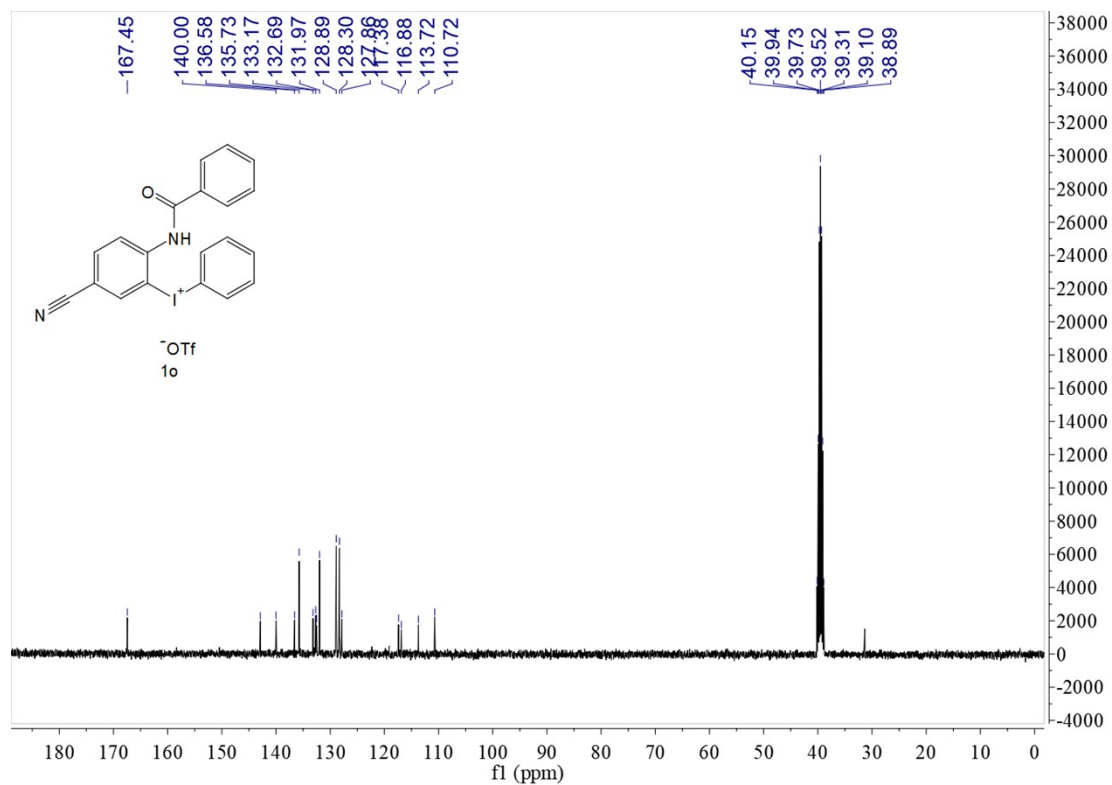
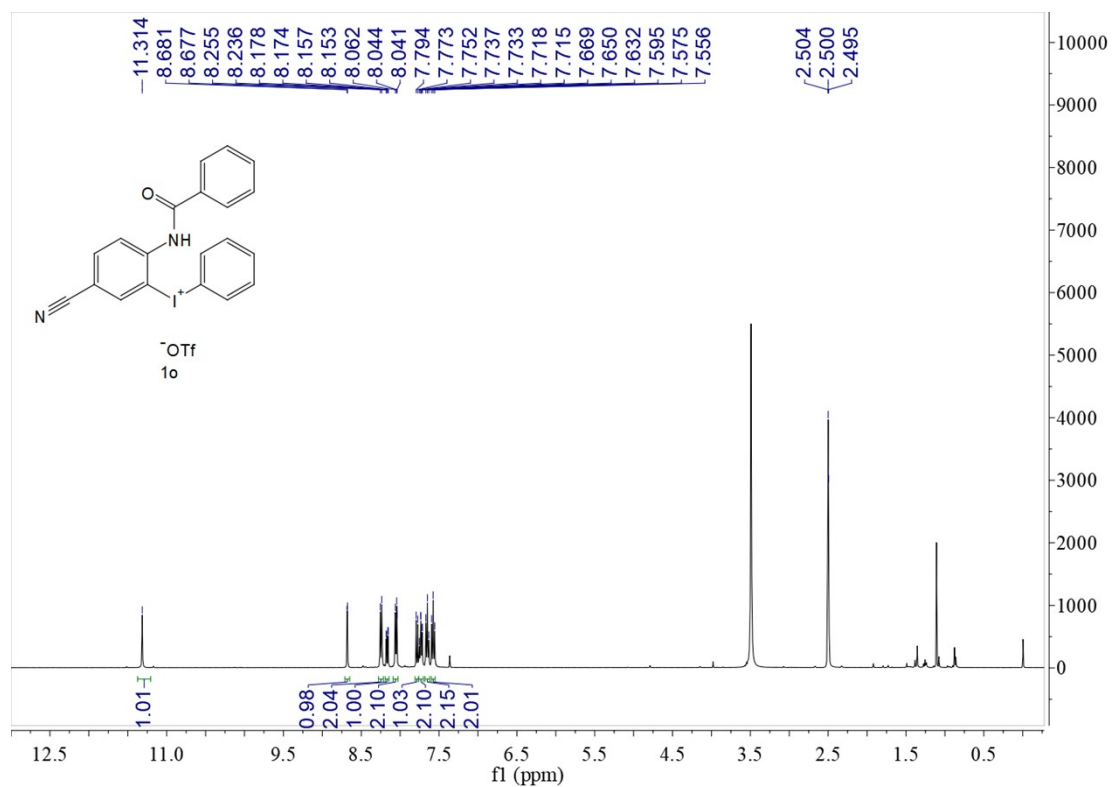


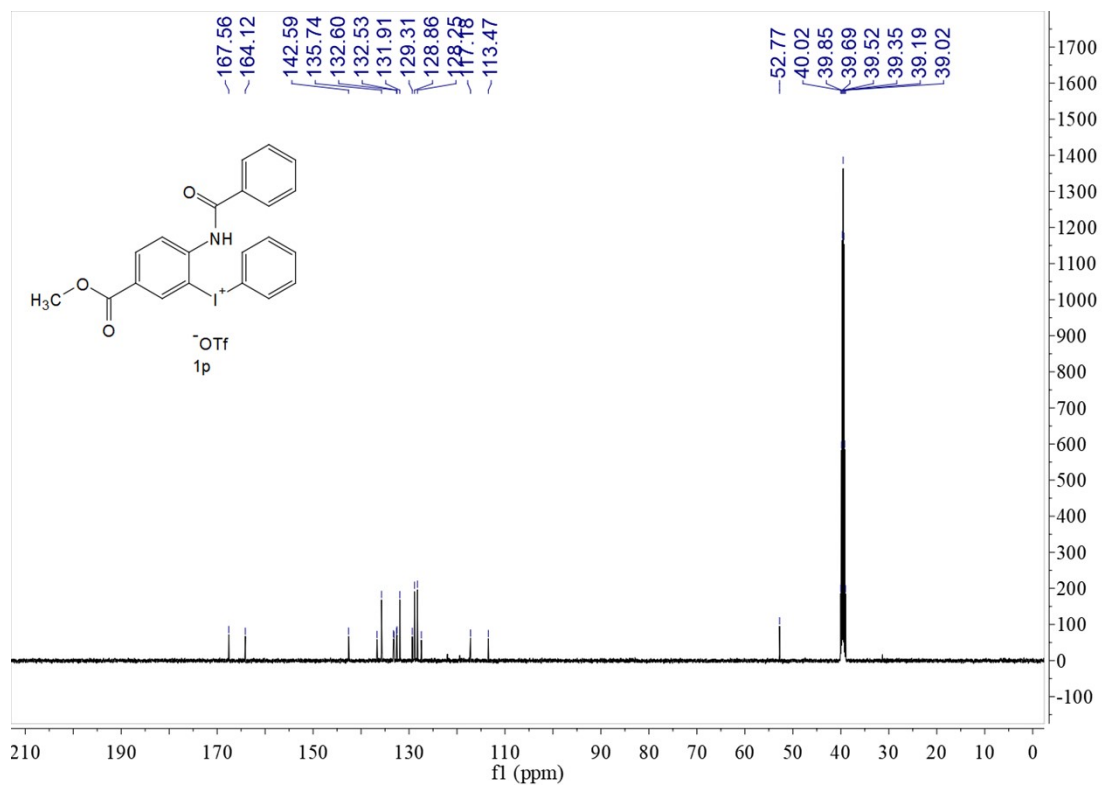
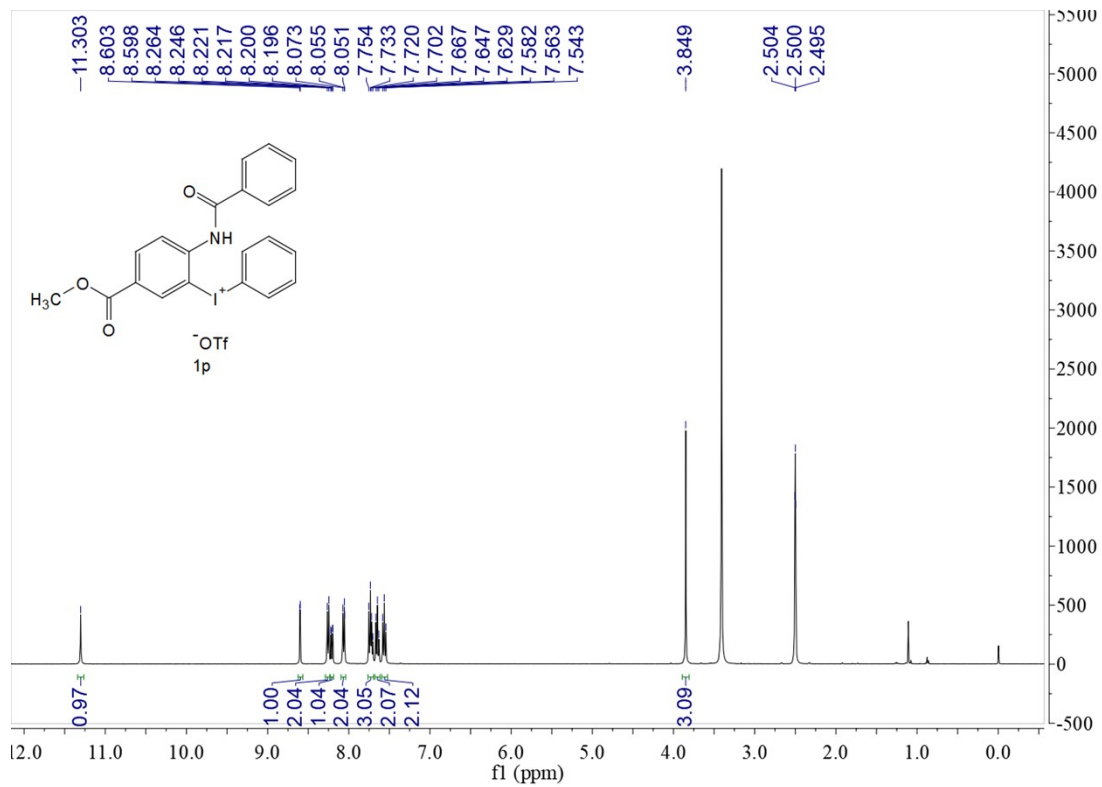


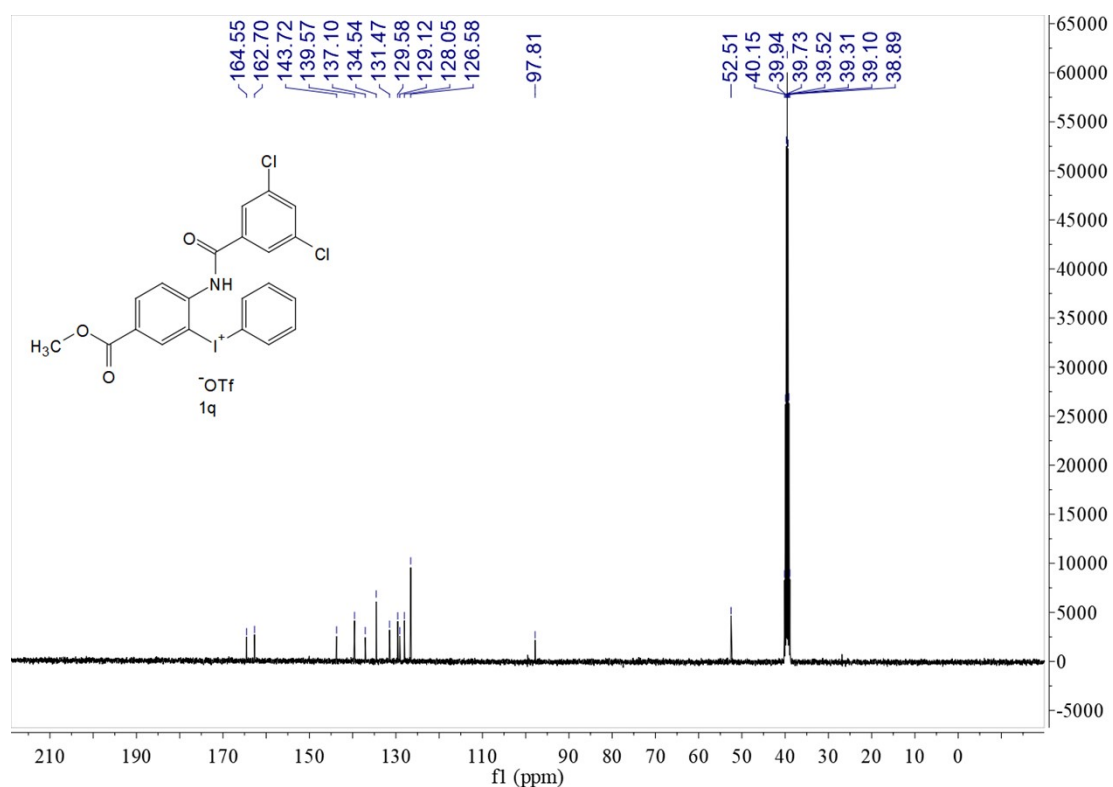
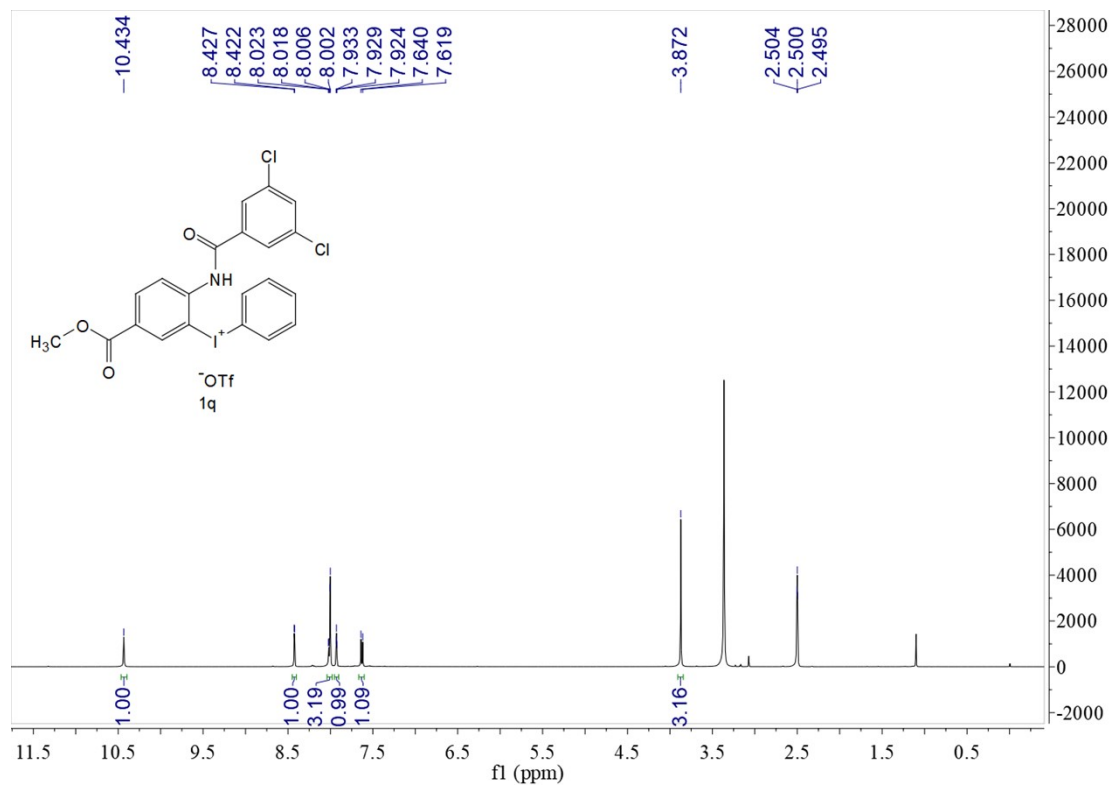


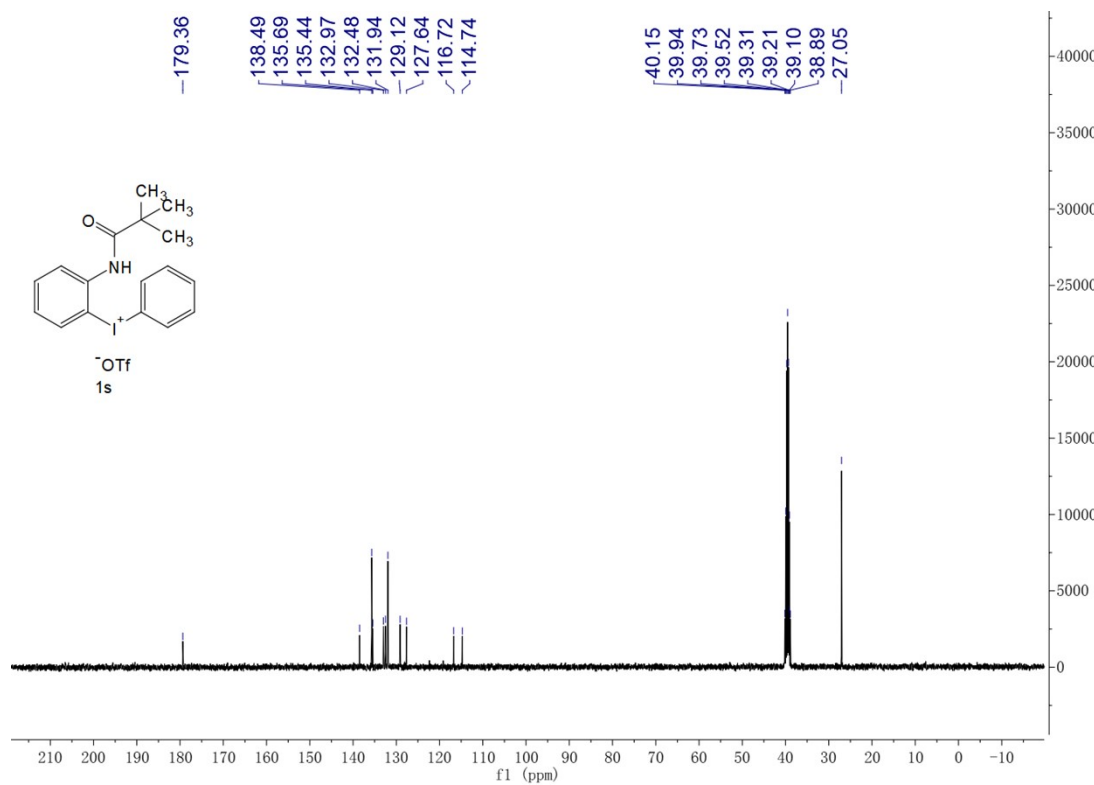
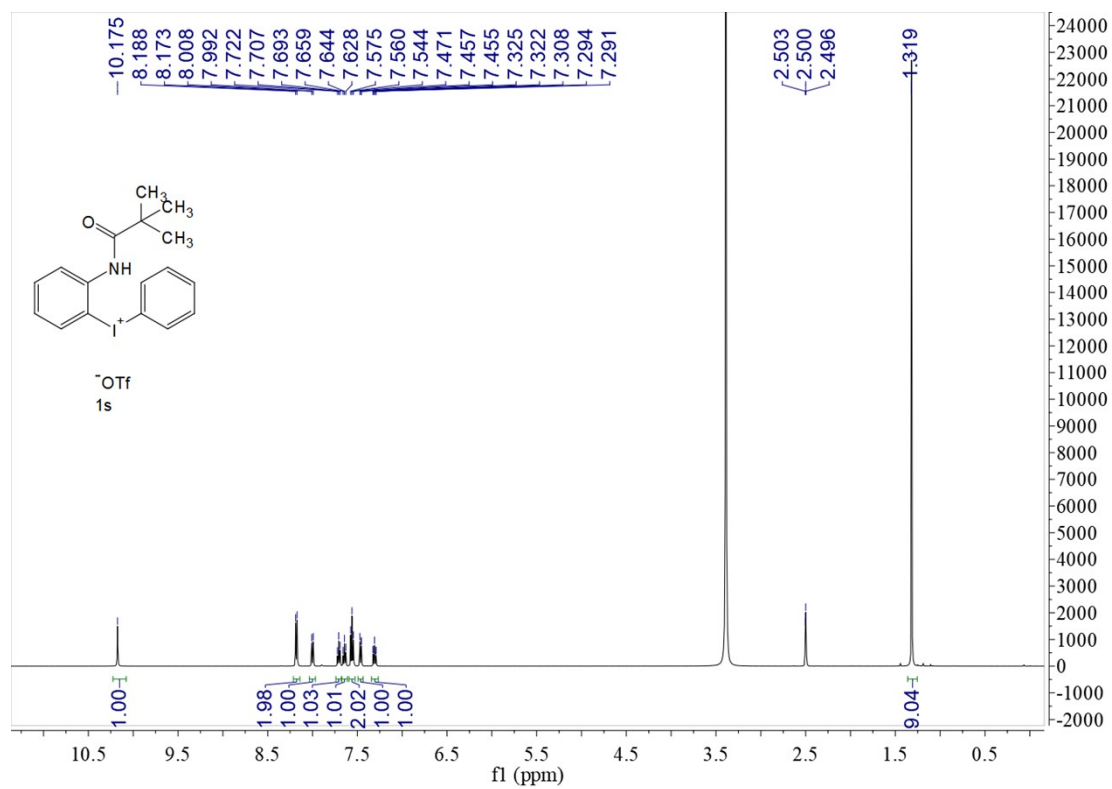




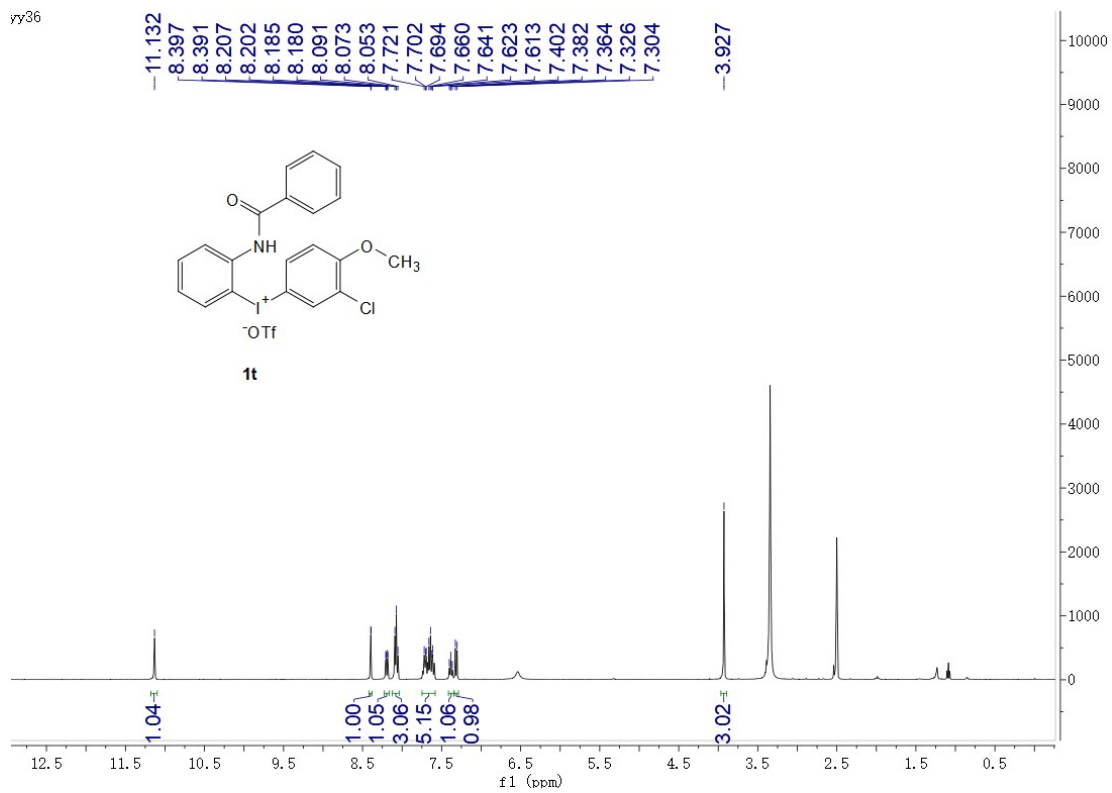








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