Supporting Information

for

Preparation of Anthranils via Chemoselective Oxidative Radical Cyclization of 3-(2-Azidoaryl) Substituted Propargyl Alcohols

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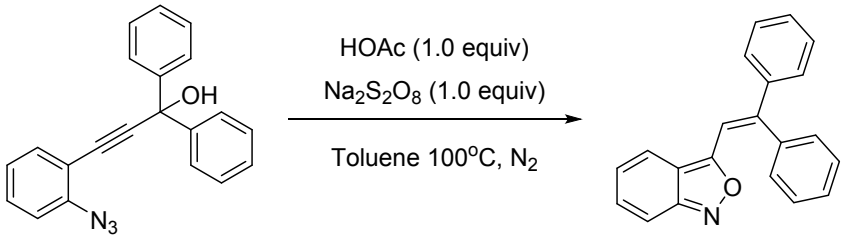
I. General method

All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. Unless otherwise stated, all experiments were conducted in a Shrek bottle under N^2. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz 1H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) or DMSO-d6 (δ = 2.50 for 1H-NMR, δ = 39.60 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (J) were reported in Hertz (Hz).

II. General procedure for the synthesis of 2

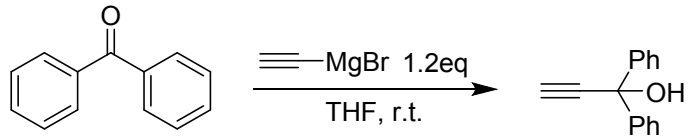


1a **2**

General optimization procedure: To a Schenk tube equipped with a stir bar, 162.5 mg of **1a** (0.5 mmol),119 mg NaS_2O_8 (0.5 mmol) were added. The Schenk tube was capped with a septum, degassed and backfilled with N_2 for at least three times. Then, the solvent (2.0 mL) and 30 uL HOAc (0.5 mmol) were added via syringe. The mixture was stirred at 100 ^{o}C for about 12 h. Then, the combined organic layer was evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

III. The procedure for the synthesis of 1a

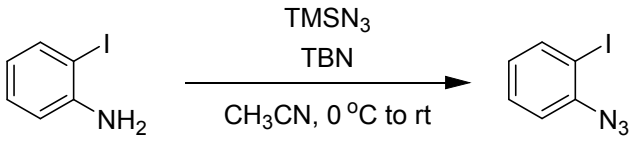
For the synthesis of 1,1-diphenylprop-2-yn-1-ol **B**



A **B**

To a stirred solution of benzophenone **A** (5 mmol) in anhydrous THF (20 mL) under N_2 was added ethynylmagnesium bromide (0.5 mol/L in THF, 1.2 equiv) dropwise slowly at 0 °C. The mixture was allowed to warm and stir for 4 h at room temperature. After completion of the reaction as determined by TLC, the reaction mixture was quenched by aqueous saturated solution of NH_4Cl (20 mL), and extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 50/1) to give 1, 1-diphenylprop-2-yn-1-ol **B** as a white solid.

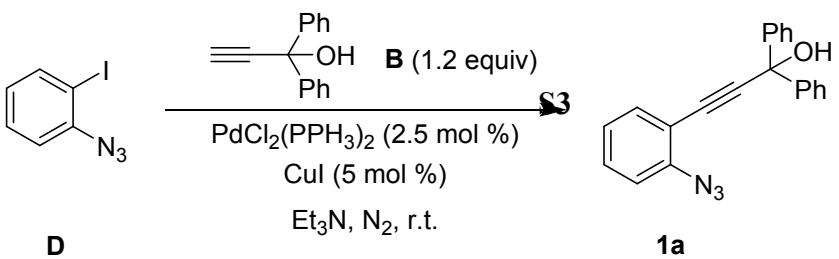
For the synthesis of 1-azido-2-iodobenzene **D**



C **D**

In a round bottomed flask 2.19 g (10 mmol, 1.00 equiv.) **C** was suspended in 15 mL dry acetonitrile under air and cooled to 0 °C with an ice bath. To the stirred suspension, 2.4 mL (4.12 g, 40 mmol, 4.00 equiv.) tert-butylnitrite and 3.95 mL (3.46 g, 30 mmol, 3.00 equiv.) azidotrimethylsilane were slowly added. The reaction mixture was stirred for 2 h and allowed to warm to room temperature. Then, the volatiles were evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (20:1, v/v) as eluent. After purification, 0.720 g (4.50 mmol, 49%) 1-azido-2-iodobenzene **D.**

For the synthesis of 3-(2-azidophenyl)-1,1-diphenylprop-2-yn-1-ol **1a**

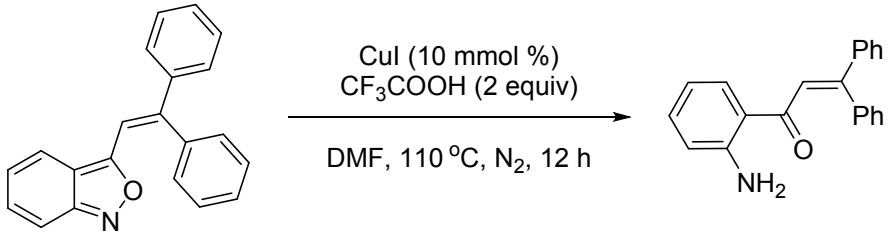


D **1a**

To a solution of 1-azido-2-iodobenzene **D** (1.23 g, 5 mmol) in triethylamine (20 mL) was added $PdCl_2(PPh_3)_2$ (70.2 mg, 0.100 mmol) and CuI (9.5 mg,0.050 mmol) at room temperature, and the mixture was stirred for 15 min at r.t. under N_2 before addition of 1,1-diphenylprop-2-yn-1-ol **B** (1.25 g, 6.0 mmol). The resulting mixture was stirred for 4 h at 80 ^oC under N_2. Then, the mixture was allowed to cool to room temperature, and added saturated NH_4Cl solution, and extracted with ethyl acetate. The combine organic layer was washed with saturated NaCl solution ,dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silicagel, petroleum ether/ethyl acetate= 20:1) to give 1,1-diphenyl-3-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol **1a** (1.38 g,yield: 75 %) as yellow solid.

IV. The procedure for the synthesis of 3a, 4a, 5a

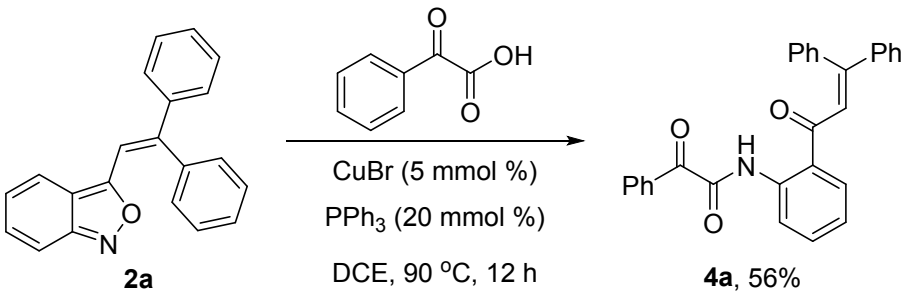
For the synthesis of 1-(2-aminophenyl)-3,3-diphenylprop-2-en-1-one **3a**



2a **3a**, 47%

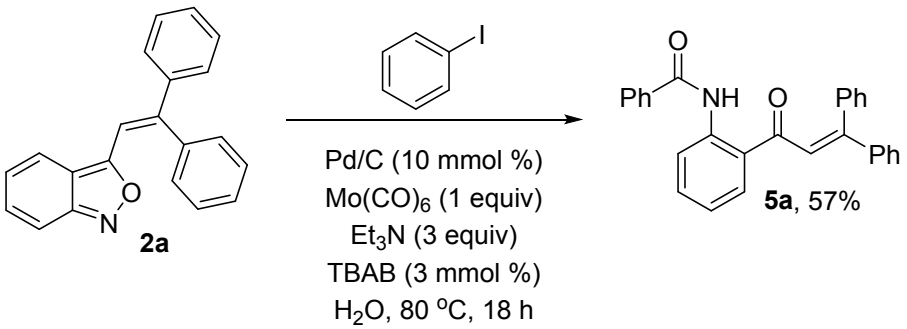
To a Schenk tube equipped with a stir bar, **2a** (0.2 mmol), CuI (0.02 mmol) were added. The Schenk tube was capped with a septum, degassed and backfilled with N_2 for at least three times. Then, the solvent (2.0 ml) and CF_3COOH (0.4 mmol) were added via syringe. The mixture was stirred at 110 ^oC for about 12 h. Then, the combined organic layer was evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent. Purification by column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50:1) afforded product 3a as a yellow solid in 47% yield.

For the synthesis of N-(2-(3,3-diphenylacryloyl)phenyl)-2-oxo-2-phenylacetamide **4a**



In a round bottomed flask **2a** (0.2 mmol), α-keto acid (0.4 mmol), $CuBr_2$ (0.01 equiv) and PPh_3 (0.04 equiv,). After the addition of DCE (3 mL), the reaction was stirred at 110 °C for 12 h. The reaction mixture was filtered through celite and concentrated in vacuo. Purification by column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50:1) afforded product **4a** as a yellow solid in 56% yield.

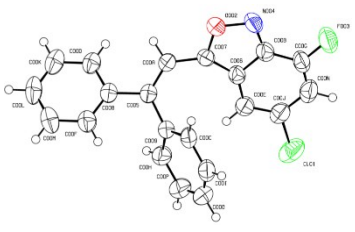
For the synthesis of N-(2-(3,3-diphenylacryloyl)phenyl)benzamide **5a**



In a 25 mL sealed tube, a mixture of **2a** (0.2 mmol, 1 equiv.), aryl iodides 2 (0.5 mmol, 2.5 equiv.), Pd/C (2.1 mg, 10 mol %), $Mo(CO)_6$ (0.1 mmol, 0.5 equiv.), Et_3N (0.6 mmol, 3 equiv.), and TBAB (0.006 mmol, 3 mol %) in distilled water (2 mL) was stirred at 80 °C under air. After 18 h, the mixture was cooled to room temperature. The residue was diluted with H_2O solution (10 mL) and extracted with EtOAc (3×10 mL). The solvent was then evaporated under vacuum. The crude products were purified by using column chromatography on silica gel (pentane/ethyl acetate) to give product **5a** as a yellow solid in 57% yield.

V. Crystal data of 2o

Crystallographic data for compound **2o** (CCDC- 1915267) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0042 A Wavelength=0.71073

Cell: a=14.1901(8) b=13.1981(9) c=9.2973(6)
alpha=90 beta=103.858(14) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1690.54(19)	1690.54(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H13 Cl F N O	C21 H13 Cl F N O
Sum formula	C21 H13 Cl F N O	C21 H13 Cl F N O
Mr	394.77	394.77
Dx,g cm-3	1.374	1.374
Z	4	4
Mu (mm-1)	0.244	0.244
F000	720.0	720.0
F000'	720.91	720.91
h,k,lmax	19,18,12	19,17,12
Nref	4651	3894
Tmin,Tmax		0.244,1.000
Tmin'		

Correction method= Not given Theta(max)= 29.347

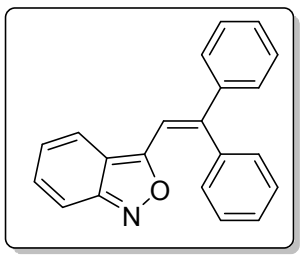
Data completeness= 0.837

R(reflections)= 0.0549(2057) wR2(reflections)= 0.1912(3894)

S = 0.920 Npar= 226

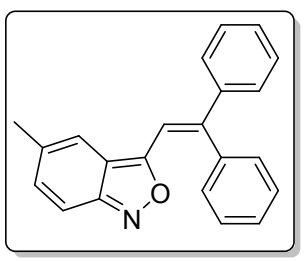
VI. Analytic data of products

3-(2,2-diphenylvinyl)benzo[c]isoxazole (2a)



Compound **2a**:Yellow solid (87% yield, 129 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.0 Hz, 1H), 7.42 – 7.34 (m, 8H), 7.29 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.20 – 7.14 (m, 2H), 6.72 (dd, *J* = 3.2, 1.1 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.0, 157.1, 148.4, 141.8, 139.4, 130.4, 130.3, 129.0, 128.7, 128.7, 128.5, 128.3, 123.6, 120.4, 116.0, 115.0, 112.2.

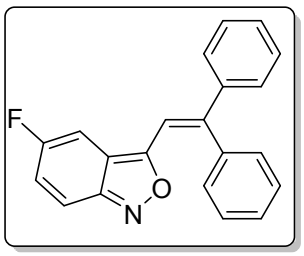
3-(2,2-diphenylvinyl)-5-methylbenzo[c]isoxazole (2b)



Compound **2b**:Yellow solid (33% yield, 51.3 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 9H), 7.33 – 7.28 (m, 2H), 7.20 (s, 1H), 7.06 –

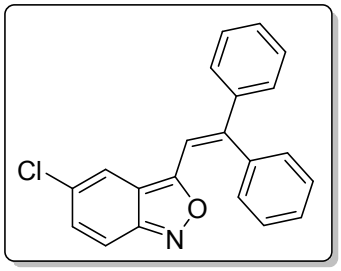
6.99 (m, 1H), 6.29 (d, *J* = 1.0 Hz, 1H), 2.13 (d, *J* = 0.5 Hz, 3H). ^{13}C NMR (12 MHz, $CDCl_3$) δ 163.7, 163.3, 157.1 (d, *J* = 15.7 Hz), 146.0, 142.0, 141.3, 140.9, 140.5, 138.5, 130.5 (t, *J* = 12.3 Hz), 129.9, 129.4, 128.94 (d, *J* = 10.1 Hz), 128.7, 128.4 (d, *J* = 4.1 Hz), 128.1 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 19.1 Hz), 123.9 , 123.6, 120.3 (d, *J* = 9.2 Hz), 116.3 (d, *J* = 6.0 Hz), 115.2 (s), 115.0 (s), 113.4 (s), 110.0 HRMS (ESI, m/z) calcd for $C_{22}H_{17}NO$ [M+H]+: 312.1383; found: 312.1385.

3-(2,2-diphenylvinyl)-5-fluorobenzo[c]isoxazole (2c)



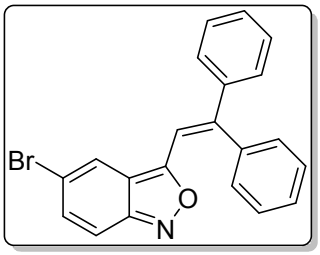
Compound **2c**:Yellow solid (74% yield, 116.6 mg)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 9.5, 4.6 Hz, 1H), 7.44 – 7.35 (m, 8H), 7.30 (dt, *J* = 6.6, 1.6 Hz, 2H), 7.17 (s, 1H), 7.01 (ddd, *J* = 9.6, 8.4, 2.3 Hz, 1H), 6.00 (dd, *J* = 9.3, 2.3 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.4, 148.1, 141.6, 139.3, 130.3, 129.1, 128.9, 128.9, 128.5, 128.3, 123.5, 123.3, 117.6, 117.5, 112.4, 112.4, 102.6, 102.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.3. HRMS (ESI, m/z) calcd for $C_{21}H_{14}FNO$ [M+H]+: 316.1132; found: 316.1128

3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2d)



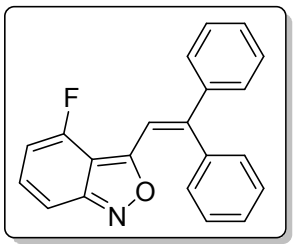
Compound **2d:**Yellow solid (80% yield, 132.5 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.27 (m, 8H), 7.27 – 7.18 (m, 3H), 7.15 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.92 – 6.82 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 155.7, 148.9, 141.39 (s), 139.2, 132.1, 130.3, 129.2, 128.9 (d, *J* = 14.1 Hz), 128.5, 128.3 (s), 119.3, 116.6, 115.7, 112.2. HRMS (ESI, m/z) calcd for $C_{21}H_{14}ClNO$ [M+H]+: 332.0837; found: 316.0835

5-bromo-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2e)



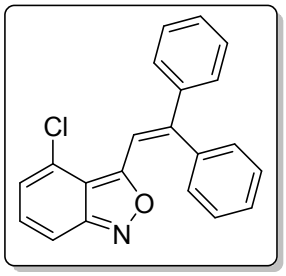
Compound **2e:**Yellow solid (77% yield, 128.0 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.34 (m, 8H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.24 – 7.16 (m, 2H), 6.51 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 155.7, 149.0, 141.4, 139.2, 134.2, 130.3, 129.3, 128.96 (d, *J* = 16.3 Hz), 128.6, 128.3, 123.0,117.0,116.7, 116.3, 112.3 HRMS (ESI, m/z) calcd for $C_{21}H_{14}BrNO$ [M+H]+: 376.0332; found: 376.0332

3-(2,2-diphenylvinyl)-4-fluorobenzo[*c*]isoxazole (2f)



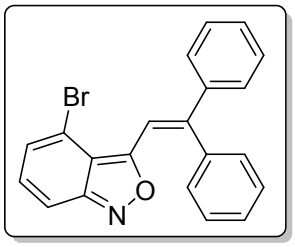
Compound **2f:**Yellow solid (63% yield, 99.2 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 8H), 7.33 – 7.28 (m, 2H), 7.17 (s, 1H), 7.06 – 6.98 (m, 1H), 6.66 – 6.61 (m, 1H), 6.56 – 6.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 164.5, 162.5, 157.4 (d, *J* = 13.0 Hz), 149.4, 141.5, 139.2, 130.3, 129.3, 128.9 (d, *J* = 18.4 Hz), 128.5, 128.4, 123.1 (d, *J* = 11.1 Hz), 116.5, 116.3, 113.5, 112.0, 97.4 , 97.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -106.9. HRMS (ESI, m/z) calcd for $C_{21}H_{14}FNO$ [M+H]+: 316.1132; found: 316.1136

4-chloro-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2g)



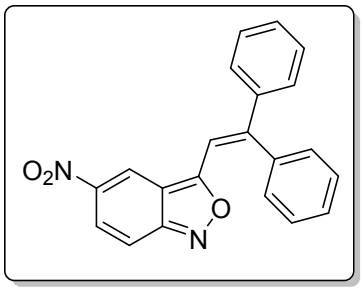
Compound **2g:**Yellow solid (78% yield, 129.1 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 – 7.34 (m, 8H), 7.30 (d, *J* = 6.3 Hz, 2H), 7.18 (s, 1H), 6.70 – 6.60 (m, 1H), 6.55 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 157.3, 149.5, 141.4, 139.2, 136.7, 130.3, 129.3, 128.9 (d, *J* = 18.2 Hz), 128.6, 128.4, 125.3, 122.0, 114.1, 113.6, 112.0. HRMS (ESI, m/z) calcd for $C_{21}H_{14}ClNO$ [M+H]+: 332.0837; found: 332.0834

4-bromo-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2h)



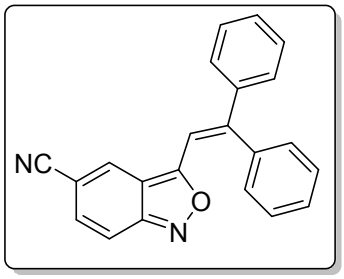
Compound **2h:**Yellow solid (73% yield, 148.2 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 1H), 7.42 – 7.36 (m, 8H), 7.32 – 7.27 (m, 2H), 7.18 (s, 1H), 6.79 – 6.72 (m, 1H), 6.46 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 157.7, 149.5, 141.4, 139.2, 130.3, 129.3, 128.9 (d, *J* = 19.2 Hz), 128.5 (d, *J* = 19.9 Hz), 127.5, 125.3, 121.0, 117.1, 114.2, 112.0. HRMS (ESI, m/z) calcd for $C_{21}H_{14}BrNO$ [M+H]+: 376.0332; found: 376.0332

3-(2,2-diphenylvinyl)-5-nitrobenzo[*c*]isoxazole (2i)



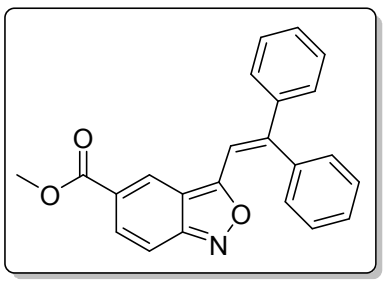
Compound **2i:**Yellow solid (76% yield, 130.0 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.1 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.19 (m, 8H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 6.91 – 6.83 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 156.8, 152.5, 142.1 (d, *J* = 348.9 Hz), 149.8 – 130.2, 129.2, 128.6 (d, *J* = 15.8 Hz), 124.4 (s), 121.3 , 116.3, 113.7, 111.7. HRMS (ESI, m/z) calcd for $C_{21}H_{14}BrN_2O_3$ [M+H]+: 343.1077; found: 376.1075

3-(2,2-diphenylvinyl)benzo[*c*]isoxazole-5-carbonitrile (2j)



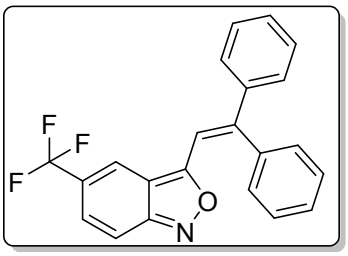
Compound **2j:**Yellow solid (73% yield, 117.5 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 – 7.37 (m, 8H), 7.33 – 7.29 (m, 2H), 7.22 – 7.19 (m, 1H), 6.68 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 156.0, 151.5, 140.8, 138.9, 130.2 (d, *J* = 13.6 Hz), 129.9, 129.6, 129.3, 128.7, 128.5, 118.3, 116.7, 114., 111.9, 107.0. HRMS (ESI, m/z) calcd for $C_{22}H_{14}BrN_2O$ [M+H]+: 323.1179; found: 323.1182

methyl 3-(2,2-diphenylvinyl)benzo[*c*]isoxazole-5-carboxylate (2k)



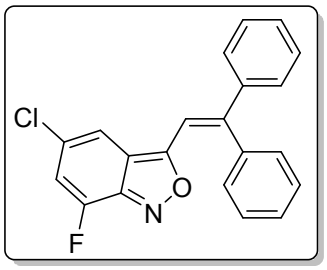
Compound **2k:**Yellow solid (84% yield, 149.2 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 1H), 7.54 (s, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.37 (m, 8H), 7.34 – 7.28 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (12 MHz, $CDCl_3$) δ 167., 166., 157.32 , 150.6, 141.3, 139.0, 130.2, 129.8, 129.5, 129.2, 128.8, 128.5 (d, *J* = 16.3 Hz), 125.9, 125.4, 115.4, 115.0, 111.6, 52.1. HRMS (ESI, m/z) calcd for $C_{23}H_{17}NO_3$ [M+H]+: 356.1281; found: 356.1284

3-(2,2-diphenylvinyl)-5-(trifluoromethyl)benzo[*c*]isoxazole (2l)



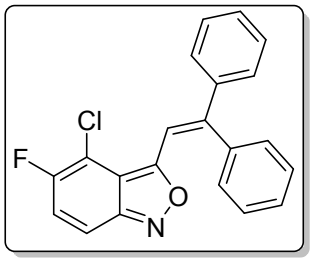
Compound **2l:**Yellow solid (64% yield, 116.8 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.4 Hz, 1H), 7.47 – 7.37 (m, 8H), 7.33 – 7.25 (m, 4H), 6.77 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 157.0, 150.5, 141.2, 139.0, 130.2, 129.51 (d, *J* = 14.1 Hz), 129.0, 128.6, 128.4, 126.9, 126.12 (d, *J* = 2.7 Hz), 125.7, 125.5, 125.2, 124.0, 124.7, 122.5, 120.53 (q, *J* = 5.3 Hz), 116.5, 113.8, 112.2, ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.4. HRMS (ESI, m/z) calcd for $C_{22}H_{14}F_3NO$ [M+H]+: 366.1100; found: 366.1102

5-chloro-3-(2,2-diphenylvinyl)-7-fluorobenzo[*c*]isoxazole (2m)



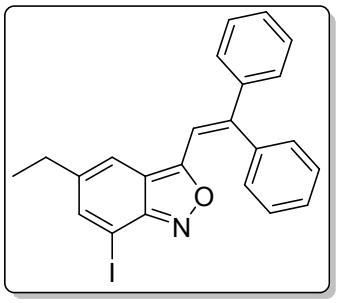
Compound **2m:**Yellow solid (91% yield, 172.4 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 1H), 7.48 – 7.38 (m, 7H), 7.35 – 7.29 (m, 2H), 7.20 (s, 1H), 6.90 – 6.78 (m, 1H), 6.22 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (d, *J* = 3.4 Hz), 151.1, 150.0, 149.1 (d, *J* = 16.6 Hz), 141.1, 139.0, 130.2, 129.5, 129.2, 128.9, 128.6, 128.4, 127.8 (d, *J* = 6.4 Hz), 117.5 (d, *J* = 4.5 Hz), 115.6 (d, *J* = 5.8 Hz), 114.9 (d, *J* = 19.0 Hz), 111.67 (s). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -123.7. HRMS (ESI, m/z) calcd for $C_{21}H_{13}ClFNO$ [M+H]+: 350.0742; found: 350.0745

4-chloro-3-(2,2-diphenylvinyl)-5-fluorobenzo[*c*]isoxazole (2n)

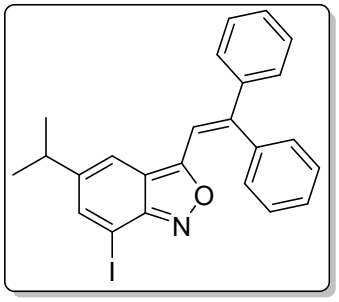


Compound **2n:**Yellow solid (98% yield, 187.2 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.43 – 7.36 (m, 6H), 7.33 (d, *J* = 3.6 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.62 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1 (d, *J* = 3.5 Hz), 157.4, 155.5, 144.9, 139.5, 137.3, 133.4, 132.7, 130.5, 130.2, 129.0 (d, *J* = 2.7 Hz), 128.8, 128.2, 123.9 (d, *J* = 7.6 Hz), 122.7, 122.5, 116.9 (d, *J* = 10.0 Hz), 109.2 , 109.0. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -122.3. HRMS (ESI, m/z) calcd for $C_{21}H_{13}ClFNO$ [M+H]+: 350.0742; found: 350.0743

3-(2,2-diphenylvinyl)-5-ethyl-7-iodobenzo[*c*]isoxazole (2o)



Compound **2o:**Yellow solid (72% yield, 167.4 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.48 – 7.31 (m, 11H), 6.53 (s, 1H), 2.59 (d, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 151.0, 143.5, 139.7, 137.8, 137.6, 132.9, 131.6, 130.6, 130.2, 129.0, 128.8, 128.6, 128.1, 123.8, 123.5, 27.9, 15.8 HRMS (ESI, m/z) calcd for $C_{23}H_{18}INO$ [M+H]+: 452.0506; found: 452.0503

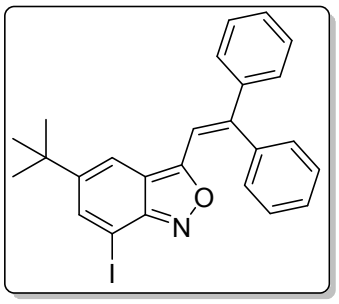


3-(2,2-diphenylvinyl)-7-iodo-5-isopropylbenzo[*c*]isoxazole (2p)

Compound **2p:**Yellow solid (98% yield, 227.9 mg)^{1}H NMR (500

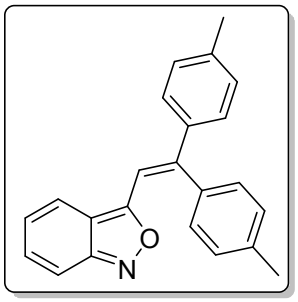
MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.5 Hz, 1H), 7.49 – 7.32 (m, 11H), 6.54 (s, 1H), 2.89 – 2.81 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8 151.1, 142.7, 142.4, 139.8 (s), 137.6, 133.0, 131.7, 130.6, 130.2, 129.0, 128.8, 128.6, 128.1, 123.8, 122.1, 33.4, 24.1. HRMS (ESI, m/z) calcd for $C_{24}H_{20}INO$ [M+H]+: 466.0662; found: 466.0661

5-(tert-butyl)-3-(2,2-diphenylvinyl)-7-iodobenzo[*c*]isoxazole (2q)



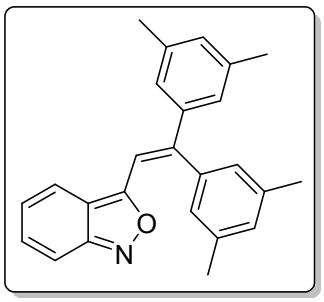
Compound **2q:**Yellow solid (73% yield, 184.4 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.48 – 7.31 (m, 11H), 6.53 (s, 1H), 2.59 (d, *J* = 7.6 Hz, 2H), 1.57 (s, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 150.8, 145.1, 141.4, 139.7, 137.6 133.0, 131.7, 130.6, 130.2, 129.0, 128.8, 128.6, 128.1, 123.5, 121.2, 34.5, 31.4. HRMS (ESI, m/z) calcd for $C_{25}H_{22}INO$ [M+H]+: 466.0662; found: 466.0661

3-(2,2-di-p-tolylvinyl)benzo[*c*]isoxazole (2r)



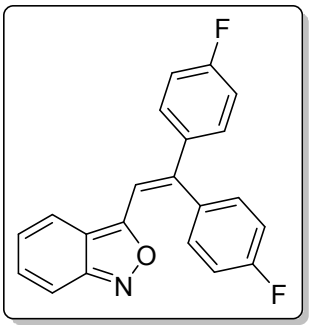
Compound **2r:**Yellow solid(33% yield, 64.9 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.0 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.15 (m, 7H), 7.13 (s, 1H), 6.81 – 6.71 (m, 2H), 2.40 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 157.1, 148.6, 139.2 (d, *J* = 1.4 Hz), 138.6, 136.5, 130.3 (d, *J* = 18.2 Hz), 129.2 (d, *J* = 17.6 Hz), 128.32, 123.2, 120.6, 115.9, 115.0 , 111.1, 21.4 (d, *J* = 14.3 Hz). HRMS (ESI, m/z) calcd for $C_{23}H_{19}NO$ [M+H]+: 326.1539; found: 326.1543

3-(2,2-bis(3,5-dimethylphenyl)vinyl)benzo[*c*]isoxazole (2s)



Compound **2s:**Yellow solid (43% yield, 82.3 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.0 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.13 (s, 1H), 7.05 – 7.00 (m, 4H), 6.90 (s, 2H), 6.75 – 6.65 (m, 2H), 2.33 (s, 6H), 2.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164., 157.1, 149.0, 142.1, 139.32, 138.0 (d, *J* = 15.4 Hz), 130.7, 130.3 (d, *J* = 10.9 Hz), 127.9 , 126.2 , 122.2, 120.8, 115.8, 114.9, 112.0 , 21.3 (d, *J* = 2.7 Hz). HRMS (ESI, m/z) calcd for $C_{25}H_{23}NO$ [M+H]+: 354.1852; found: 354.1855

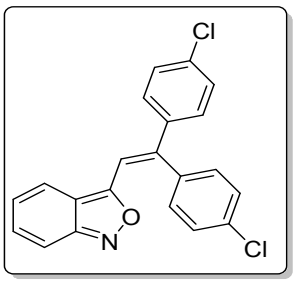
3-(2,2-bis(4-fluorophenyl)vinyl)benzo[*c*]isoxazole (2t)



Compound **2t:**Yellow solid (53% yield, 109.1 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 1H), 7.36 (s, 2H), 7.32 – 7.17 (m, 3H), 7.09 (d, *J* = 18.1 Hz, 5H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.88 – 6.77 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 164.0, 163.4, 162.4, 162.0, 157.0, 146.12, 137.8 (d, *J* = 3.2 Hz), 135.1 (d, *J* = 3.5 Hz), 132.1 (d, *J*

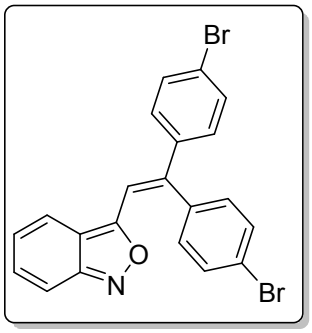
= 8.2 Hz), 130.61, 130.1 (d, *J* = 8.3 Hz), 123.9, 120.0, 116.3, 115.9, 115.7 (d, *J* = 9.0 Hz), 115.5 (s), 115.2 (s), 111.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.8, -112.1. HRMS (ESI, m/z) calcd for $C_{21}H_{13}F_2NO$ [M+H]+: 334.1038; found: 334.1039

3-(2,2-bis(4-chlorophenyl)vinyl)benzo[*c*]isoxazole (2u)



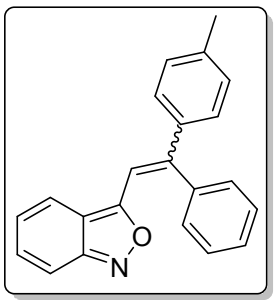
Compound **2u:** Yellow solid (51% yield, 93.1 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.28 (m, 6H), 7.27 – 7.18 (m, 3H), 7.15 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.92 – 6.82 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ 163.0, 157.0, 145.6, 139.8, 137.4, 135.3, 134.9, 131.5, 130.7, 129.5, 129.0, 128.8, 124.2, 119.9, 116.7, 115.3, 112.2. HRMS (ESI, m/z) calcd for $C_{21}H_{13}Cl_2NO$ [M+H]+: 366.0447; found: 366.0445

3-(2,2-bis(4-bromophenyl)vinyl)benzo[*c*]isoxazole (2v)



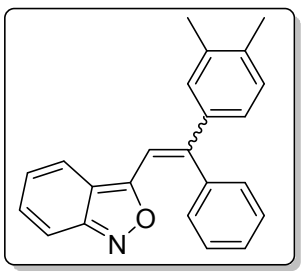
Compound **2v:** Yellow solid (43% yield, 97.4 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.36 (m, 9H), 7.31 (s, 1H), 7.19 (s, 1H), 7.09 (d, *J* = 9.3 Hz, 1H), 6.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 155.7, 148.9, 141.4, 139.2, 132.1 (d, *J* = 19.1 Hz), 131.8 (d, *J* = 1.9 Hz), 130.3, 129.7, 129.3, 129.1 – 128.8, 128.5, 128.3, 119.3, 116.6, 115.7, 112.2 HRMS (ESI, m/z) calcd for $C_{21}H_{13}Br_2NO$ [M+H]+: 453.9437; found: 453.9435

3-(2-phenyl-2-(p-tolyl)vinyl)benzo[*c*]isoxazole (2w)



Compound **2w:** Yellow solid (44% yield, 68.4 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.44 – 7.37 (m, 4H), 7.34 – 7.29 (m, 2H), 7.23 – 7.15 (m, 5H), 6.84 – 6.72 (m, 2H), 2.41 (d, *J* = 3.4 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 157.1 (d, *J* = 2.0 Hz), 148.6, 148.4, 142.0, 139.5, 139,3 138.9, 138.7, 130.4 (dd, *J* = 18.3, 4.9 Hz), 129.3(d, *J* = 16.1 Hz), 129.0, 128.7 (d, *J* = 2.9 Hz), 128.4 (d, *J* = 2.6 Hz), 128.3, 123.4 (d, *J* = 3.7 Hz), 120.5 (d, *J* = 8.9 Hz), 115.0 (d, *J* = 2.4 Hz), 111.8, 111.4, 21.4 (d, *J* = 14.7 Hz). HRMS (ESI, m/z) calcd for $C_{22}H_{17}NO$ [M+H]+: 312.1383; found: 312.1385

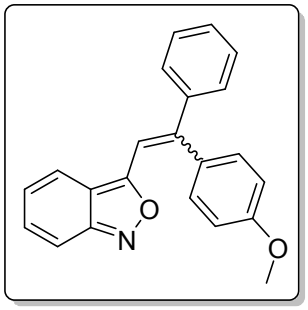
3-(2-(3,4-dimethylphenyl)-2-phenylvinyl)benzo[*c*]isoxazole (2x)



Compound **2x:**Yellow solid (61% yield, 99.1 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.34 – 7.28 (m, 1H), 7.22 – 7.10 (m, 4H), 7.08 – 7.02 (m, 1H), 6.80 – 6.70 (m, 2H), 2.34 – 2.19 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3 (d, *J* = 1.9 Hz), 157.1 (d, *J* = 3.4 Hz), 148.7, 148.6, 142.2, 139.6, 139.4, 138.0, 137.2, 136.8 (d, *J* = 10.8 Hz), 131.3, 130.5 – 130.2 (m), 129.8 (d, *J* = 11.8 Hz), 129.4 , 128.9, 128.6, 128.4, 127.8, 126.0, 123.3 (d, *J* = 10.9 Hz), 120.6 (d, *J* = 17.1 Hz), 116.01 115.8, 115.0, 111.7, 111.4, 19.8 (dd, *J* = 17.3, 12.0 Hz). HRMS (ESI, m/z) calcd for $C_{23}H_{19}NO$ [M+H]+:

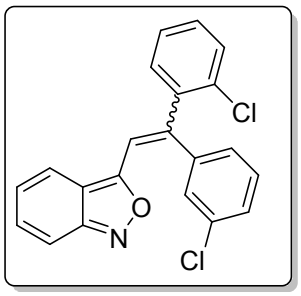
326.1539; found: 326.1543

3-(2-(4-methoxyphenyl)-2-phenylvinyl)benzo[*c*]isoxazole (2y)



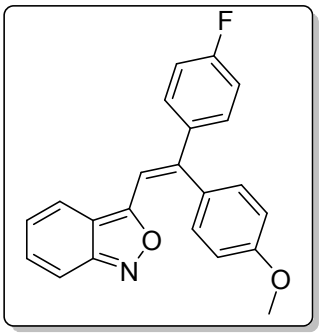
Compound **2y:**Yellow solid (20% yield, 43.6 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 9.1 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.26 – 7.13 (m, 3H), 7.10 (s, 1H), 6.93 – 6.87 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.79 – 6.72 (m, 1H), 3.85 (d, *J* = 2.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 160.0, 157.1, 142.3, 131.8, 131.6, 130.4 (d, *J* = 18.2 Hz), 129.7, 129.0, 128.5 (t, *J* = 14.6 Hz), 123.4, 120.6, 115.0, 114.0 (d, *J* = 22.1 Hz), 111.6, 55.3. HRMS (ESI, m/z) calcd for $C_{22}H_{17}NO_2$ [M+H]+: 328.1332; found: 328.1333

3-(2-(2-chlorophenyl)-2-(3-chlorophenyl)vinyl)benzo[*c*]isoxazole (2z)

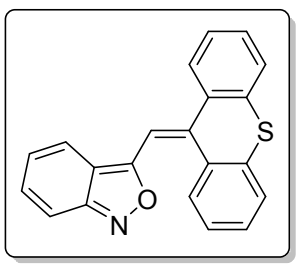


Compound **2z:**Yellow solid (46% yield, 84.2 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.1 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.19 (m, 8H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 6.91 – 6.83 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 157.0, 145.0, 141.0, 137.3, 134.7, 133.3, 131.6, 131.0, 130.7, 130.4, 129.9, 128.6, 126.9, 124.3, 120.0, 116.8, 115.8, 115.3 HRMS (ESI, m/z) calcd for $C_{21}H_{13}Cl_2NO$ [M+H]+: 366.0447; found: 366.0447

5-chloro-7-fluoro-3-(2-(4-fluorophenyl)-2-(4-methoxyphenyl)vinyl)benzo[*c*]isoxazole (2aa)



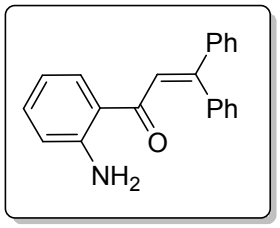
Compound **2aa:**Yellow solid (40% yield, 69.0 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H), 7.11 – 7.03 (m, 3H), 6.95 – 6.82 (m, 3H), 6.81 – 6.75 (m, 1H), 3.85 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1 (d, *J* = 13.4 Hz), 218.3 – 115.2, 132.10 (d, *J* = 8.2 Hz), 131.8, 130.5 (d, *J* = 7.1 Hz), 130.3 (d, *J* = 8.2 Hz), 129.7, 123.5 (d, *J* = 3.6 Hz), 120.5, 120.3 (d, *J* = 41.8 Hz), 120.9 – 115.9, 118.1 (dd, *J* = 555.5, 37.8 Hz), 115.0 (d, *J* = 3.9 Hz), 114.1, 114.0, 55.4 (d, *J* = 11.6 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.4. HRMS (ESI, m/z) calcd for $C_{22}H_{16}FNO_2$ [M+H]+: 346.1238; found: 346.1239



3-((9H-thioxanthen-9-ylidene)methyl)benzo[*c*]isoxazole (2ab)

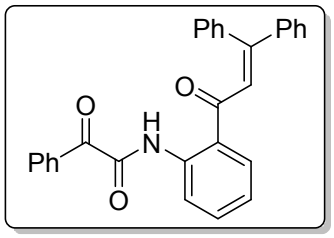
Compound **2aa:** (47% yield, 76.8 mg)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.61 – 7.47 (m, 4H), 7.42 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 7.18 – 7.11 (m, 1H), 7.01 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.82 – 6.76 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 155.7, 149.0, 141.4, 139.2, 134.2, 130.3, 129.3, 129.0(d, *J* = 16.3 Hz), 128.6, 128.3, 123.0, 117.0, 116.7, 116.3, 112.3. HRMS (ESI, m/z) calcd for $C_{21}H_{13}NOS$ [M+H]+: 328.0791; found: 328.0791

1-(2-aminophenyl)-3,3-diphenylprop-2-en-1-one (3a)



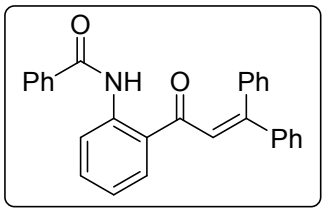
Compound **3a:** (47% yield, 28.2 mg)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.37 (s, 5H), 7.29 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.21 (ddd, *J* = 7.6, 4.2, 2.6 Hz, 3H), 7.06 (s, 1H), 6.65 – 6.55 (m, 2H), 6.15 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.4, 151.7, 150.5, 141.7, 139.3, 134.3, 132.5, 129.7, 128.9, 128.5, 128.4, 128.1, 128.1, 126.4, 119.4, 117.0, 115.7. HRMS (ESI, m/z) calcd for $C_{21}H_{17}NO$ [M+H]+: 300.1383; found: 300.1389

N-(2-(3,3-diphenylacryloyl)phenyl)-2-oxo-2-phenylacetamide (4a)



Compound **4a:** (56% yield, 48.3 mg)^{1}H NMR (500 MHz, Chloroform-*d*) δ 12.37 (s, 1H), 8.72 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.38 – 8.30 (m, 2H), 7.98 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64 (td, *J* = 7.3, 1.4 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.42 – 7.36 (m, 5H), 7.28 (s, 1H), 7.25 (d, *J* = 0.7 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.8, 187.2, 160.8, 154.7, 141.0, 138.9, 138.7, 134.4, 134.2, 133.3, 132.0, 131.2, 129.8, 129.5, 128.7, 128.7, 128.5, 128.2, 125.4, 125.2, 123.6, 121.0. HRMS (ESI, m/z) calcd for $C_{29}H_{21}NO_3$ [M+H]+: 432.1594; found: 432.1601

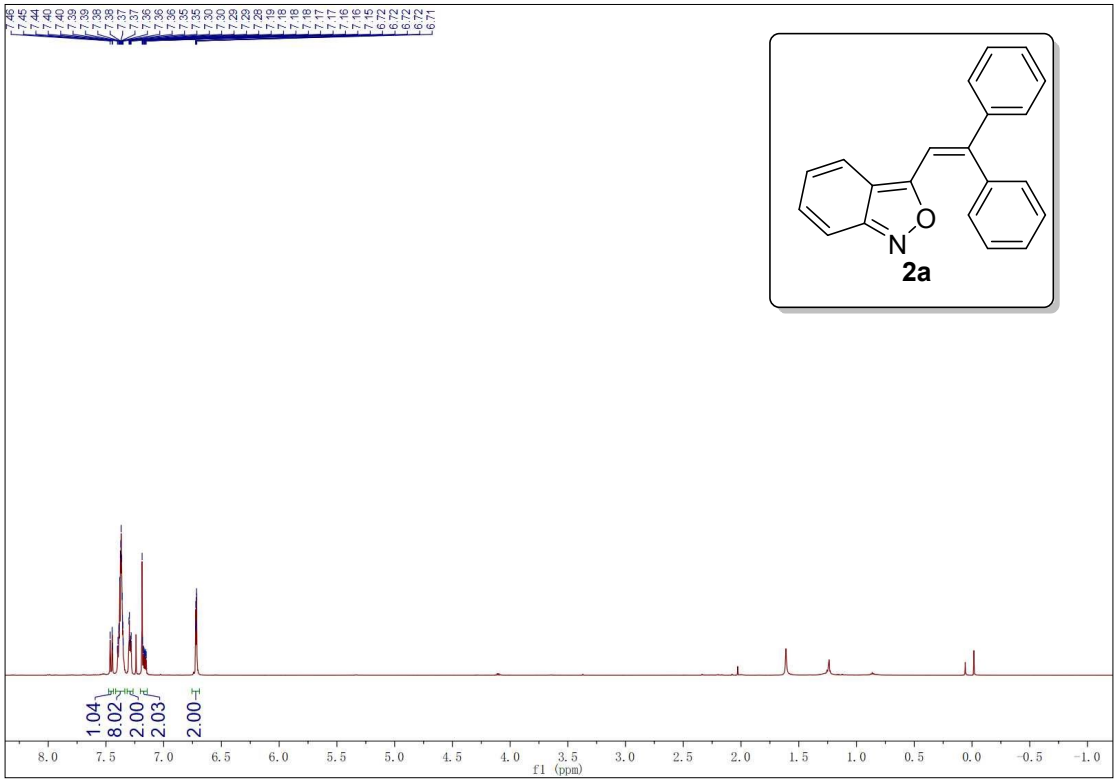
N-(2-(3,3-diphenylacryloyl)phenyl)benzamide (5a)

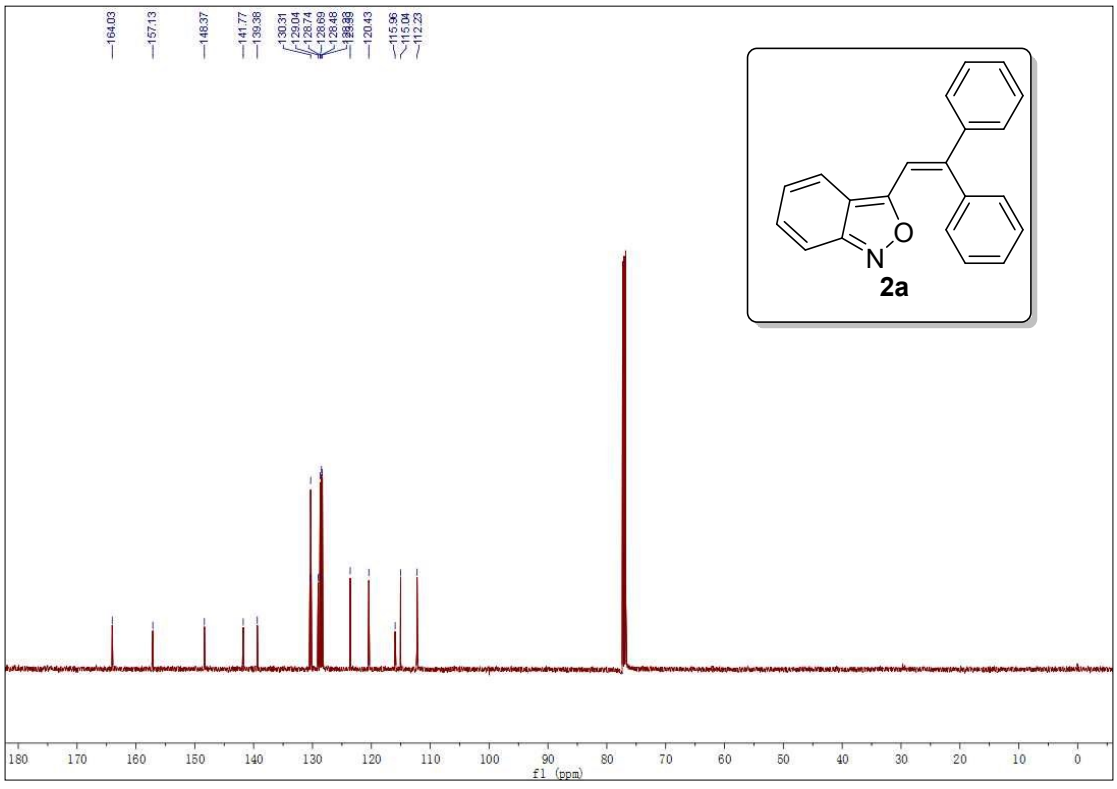


Compound **5a:** (57% yield, 45.9 mg)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.37 (s, 5H), 7.29 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.21 (ddd, *J* = 7.6, 4.2, 2.6 Hz, 3H), 7.06 (s, 1H), 6.65 – 6.55 (m, 2H), 6.15 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.9, 166.1, 154.0, 141.1, 141.0, 138.7, 134.9, 134.7, 132.2, 131.9, 129.8, 129.5, 128.8, 128.7, 128.5, 128.3, 127.6, 125.8, 123.8, 122.5, 120.9. HRMS (ESI, m/z) calcd for $C_{28}H_{21}NO_2$ [M+H]+: 404.1645; found: 404.1640

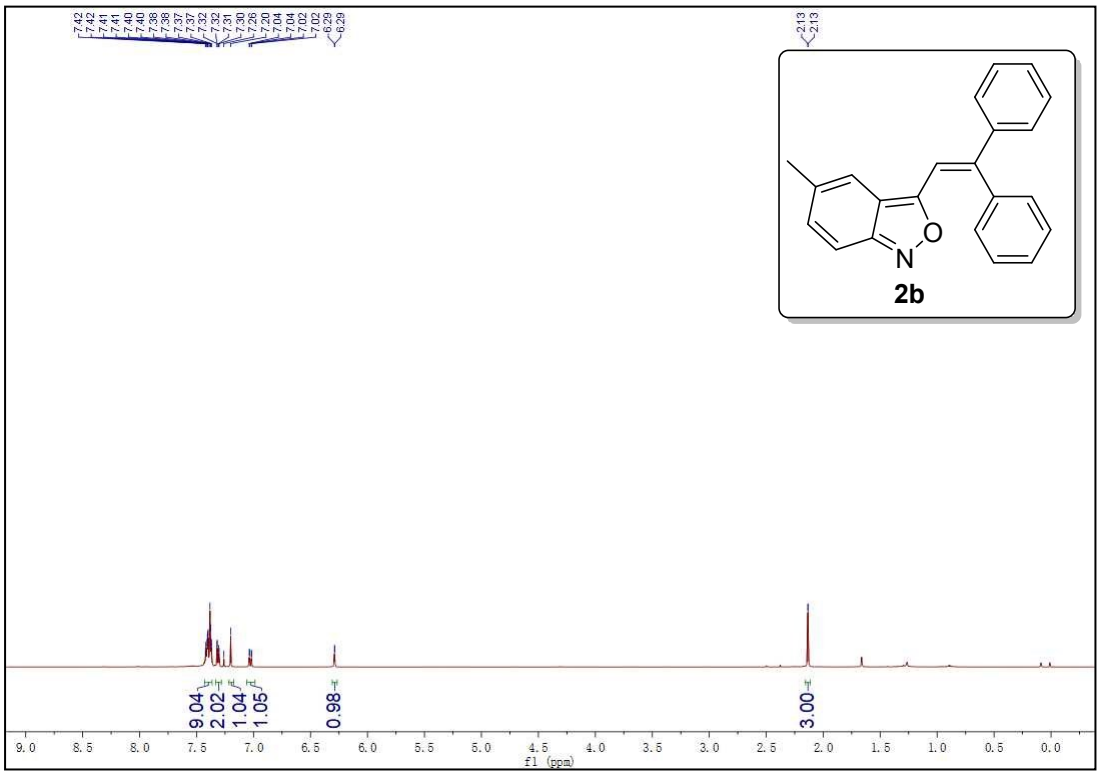
VII. ^{1}H ^{13}C and F^{19} NMR spectra of products

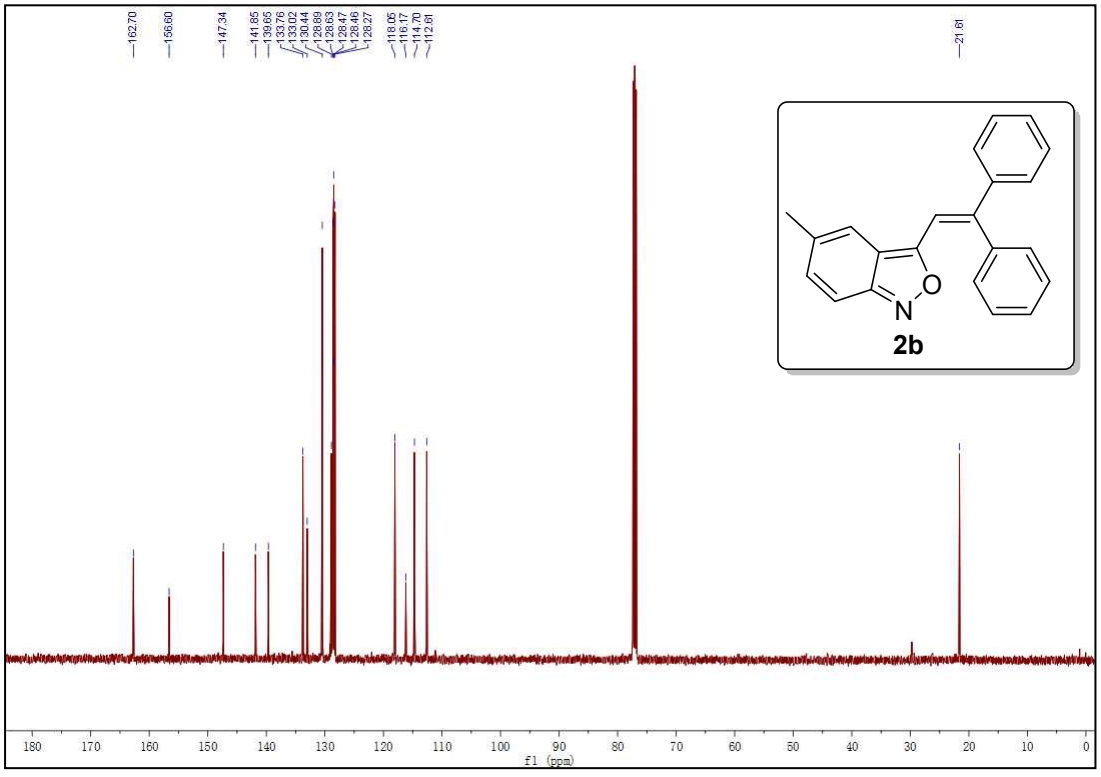
3-(2,2-diphenylvinyl)benzo[c]isoxazole (2a)



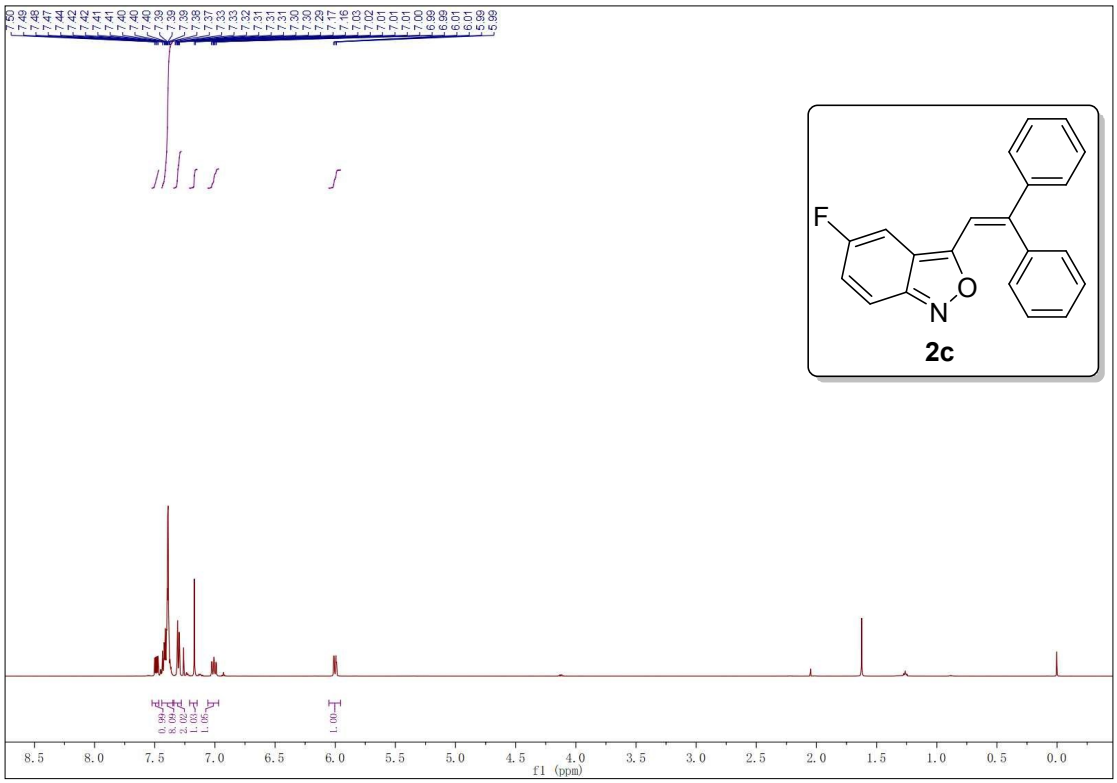


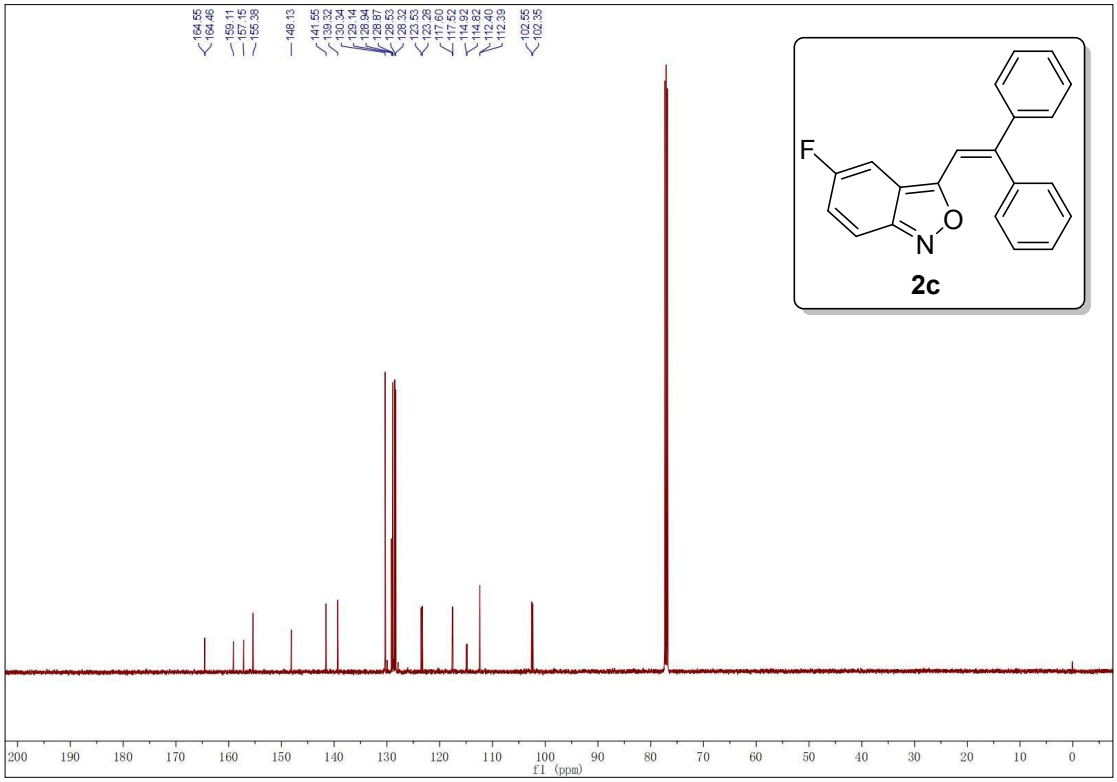
3-(2,2-diphenylvinyl)-5-methylbenzo[*c*]isoxazole (2b)

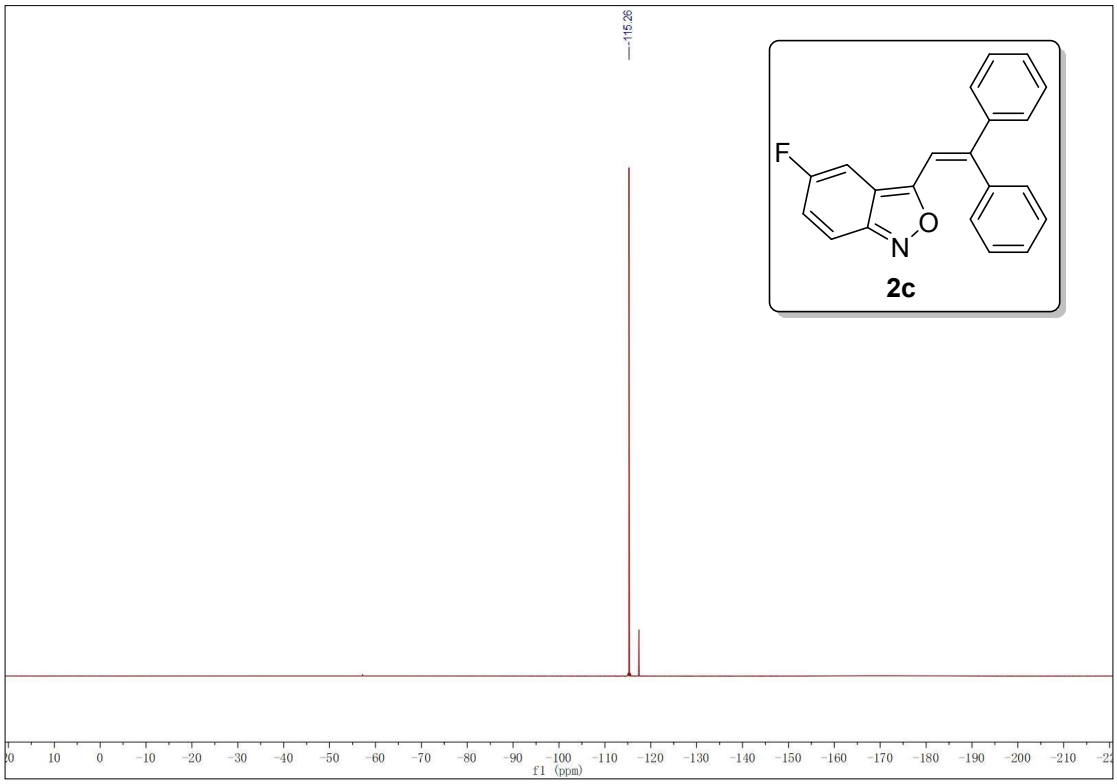

2b
9.04
2.02
1.04
1.05
0.98
3.00
f1 (ppm)


2b
f1 (ppm)

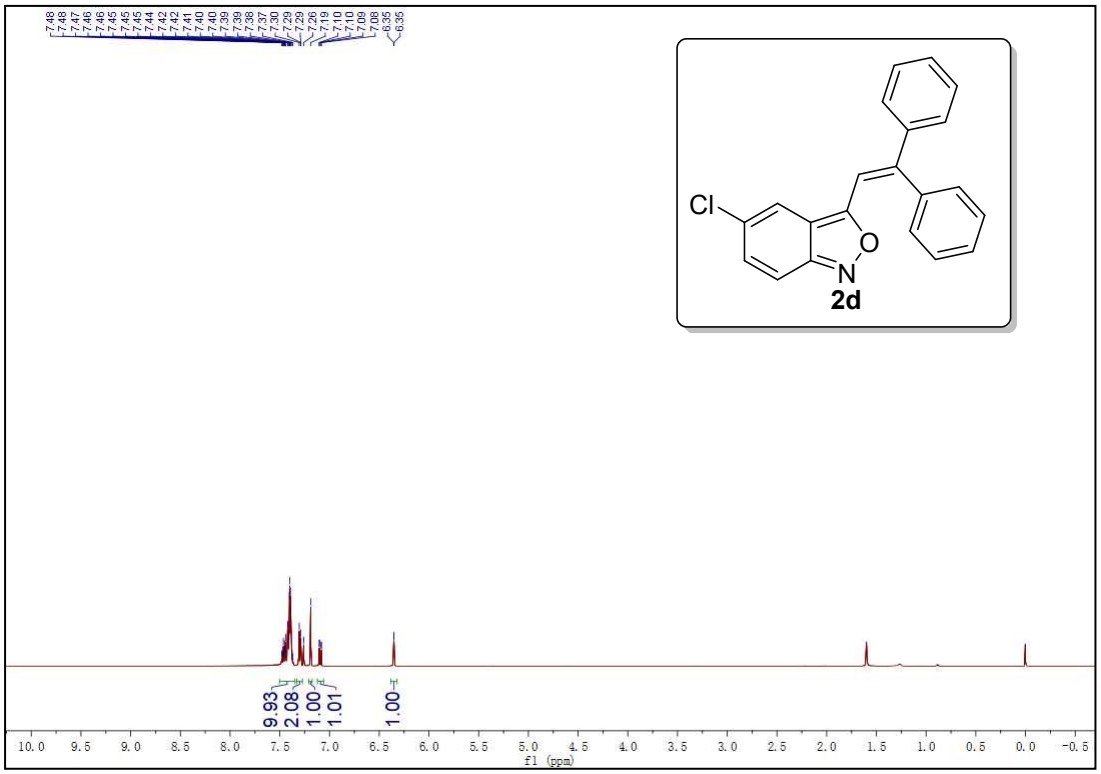
3-(2,2-diphenylvinyl)-5-fluorobenzo[c]isoxazole (2c)

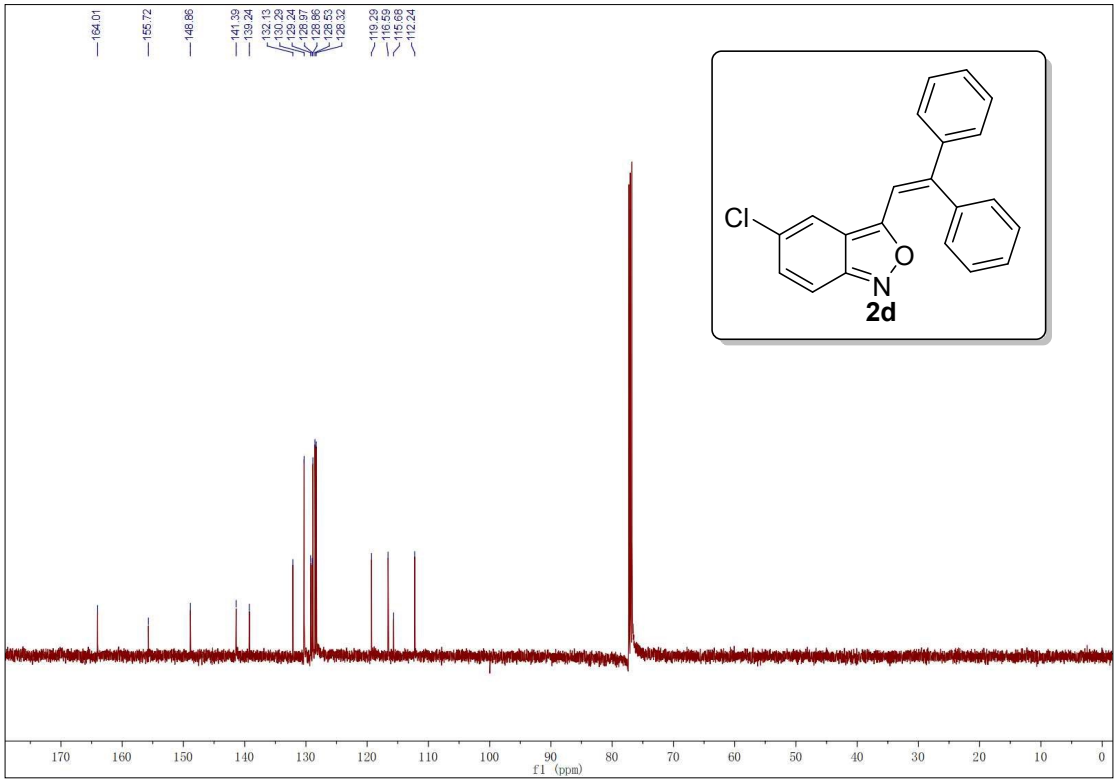




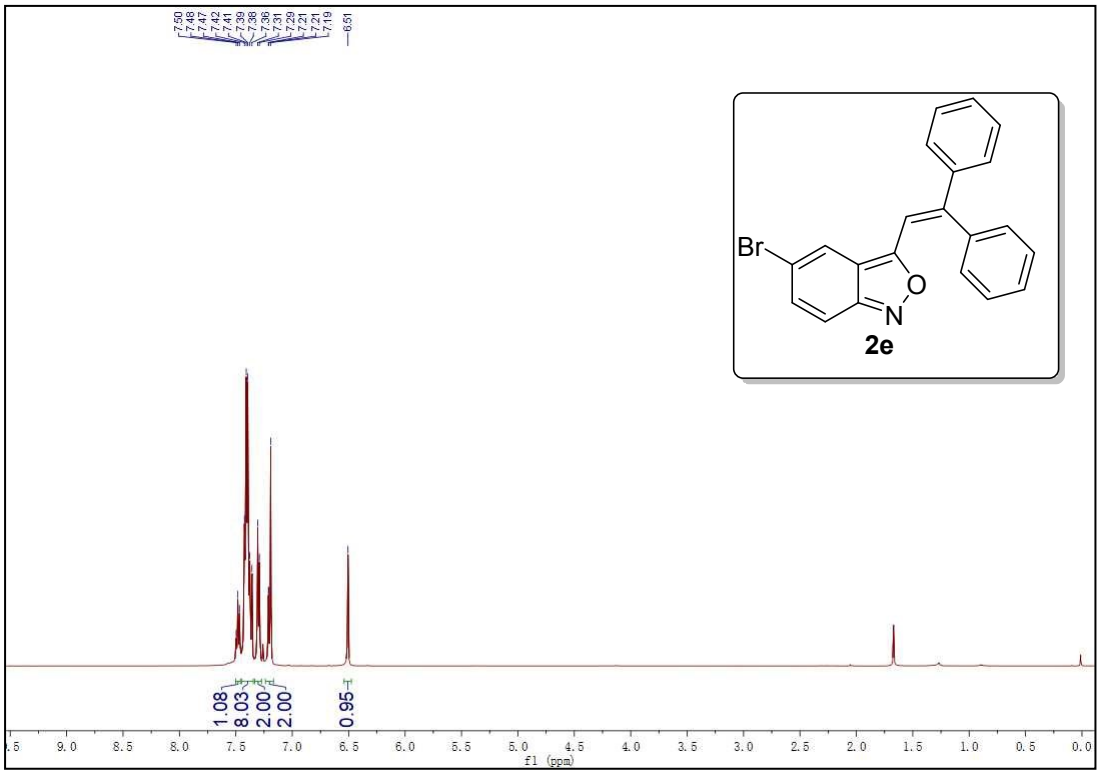

115.26
F
O
N
2c
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

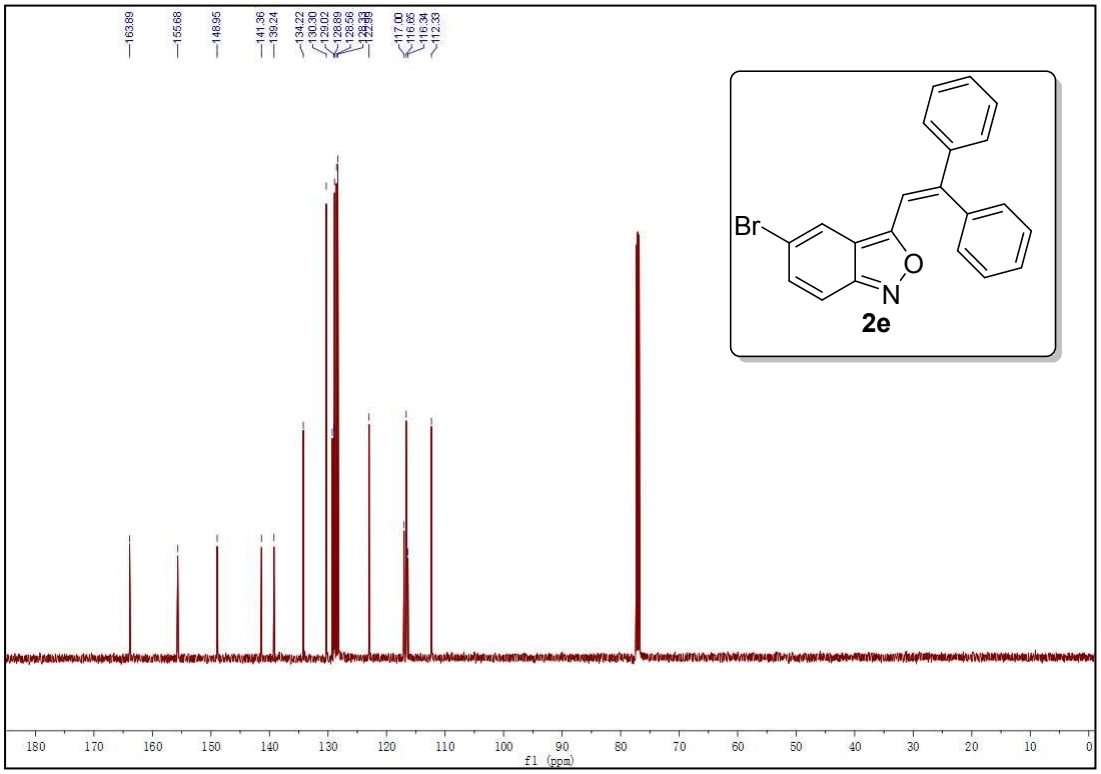
3-(2,2-diphenylvinyl)benzo[*c*]isoxazole(2d)



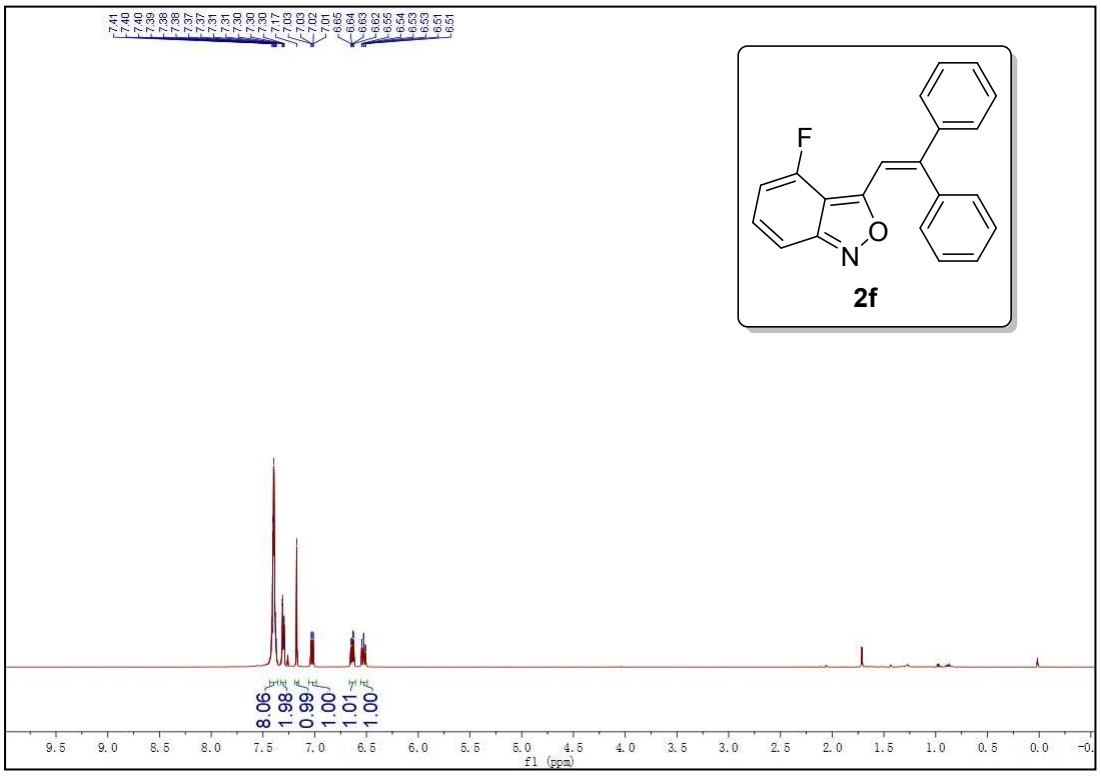


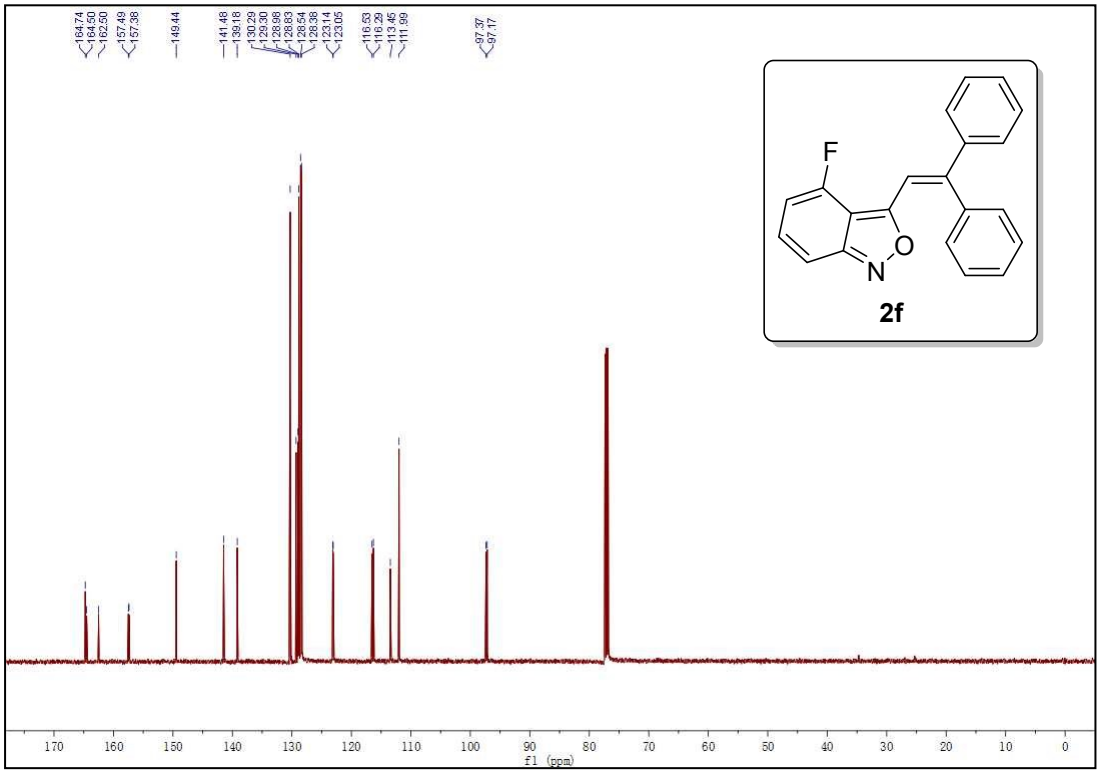
5-bromo-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2e)

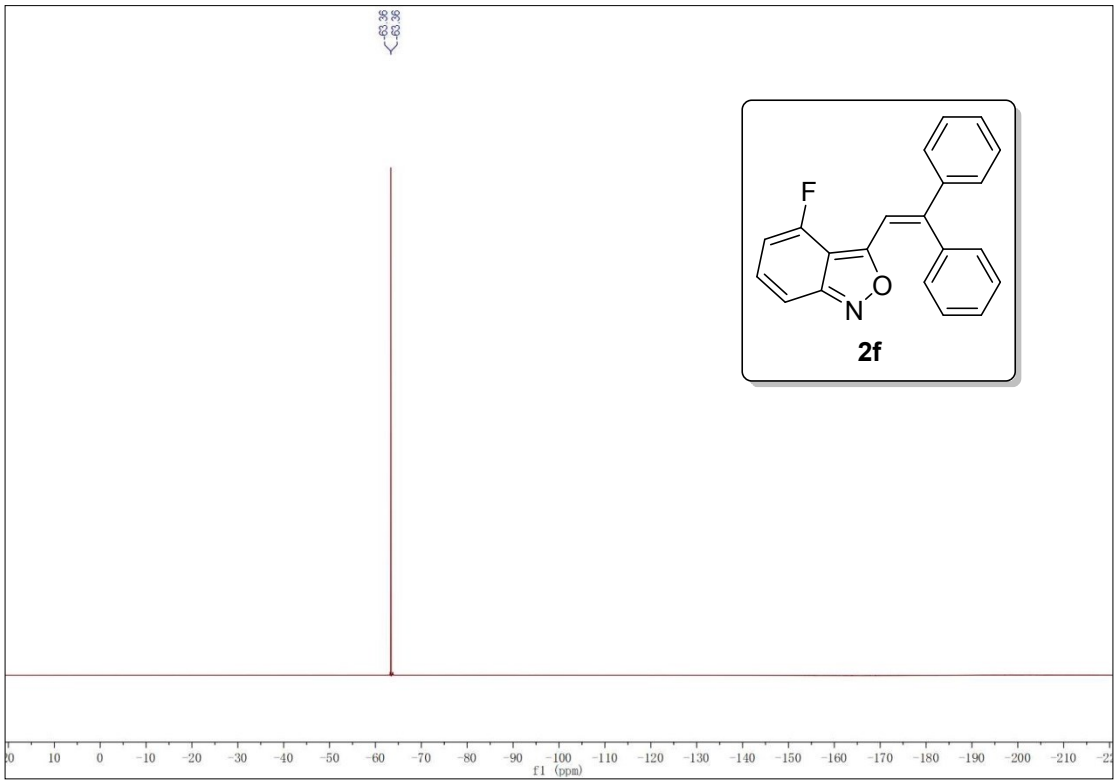




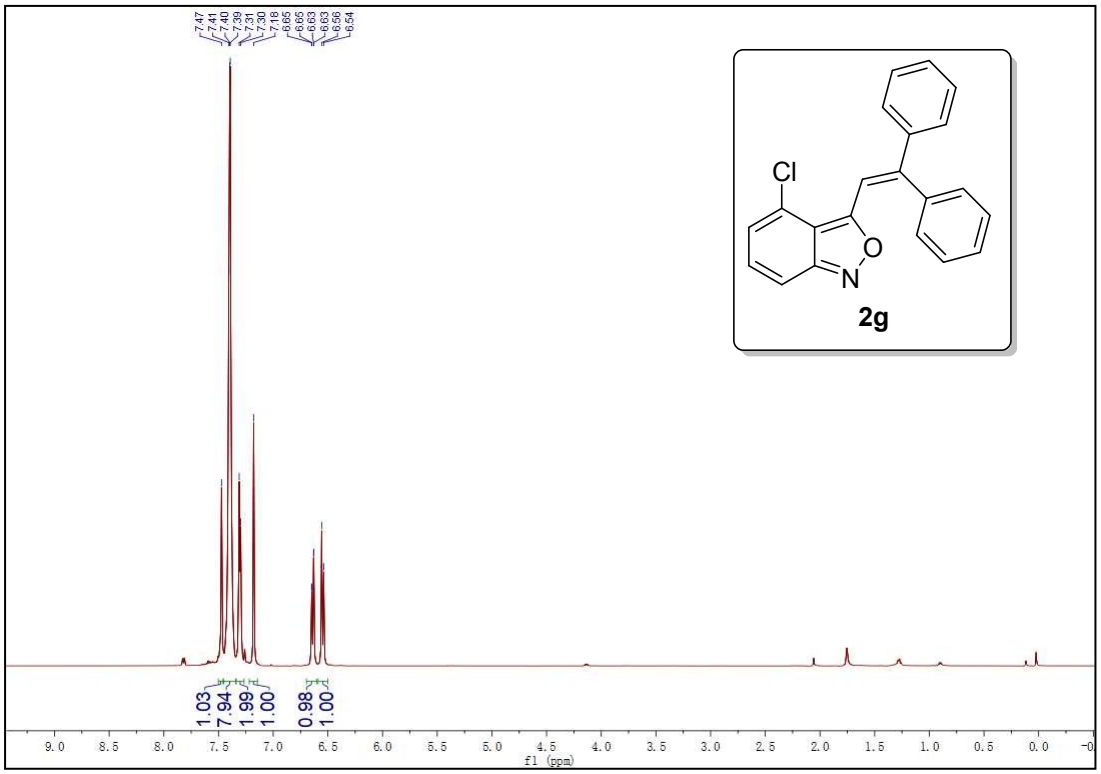
3-(2,2-diphenylvinyl)-4-fluorobenzo[*c*]isoxazole (2f)

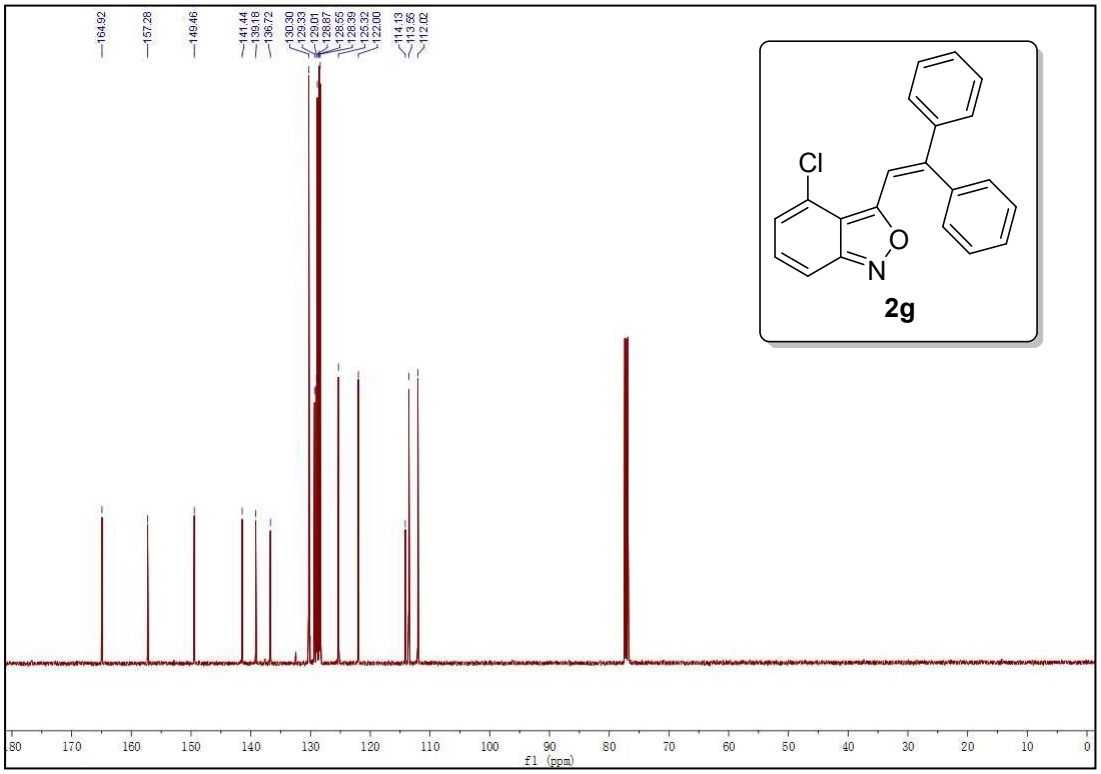

F
O
N
2f
8.06
1.98
0.99
1.00
1.01
1.00
f1 (ppm)


F
O
N
2f
f1 (ppm)

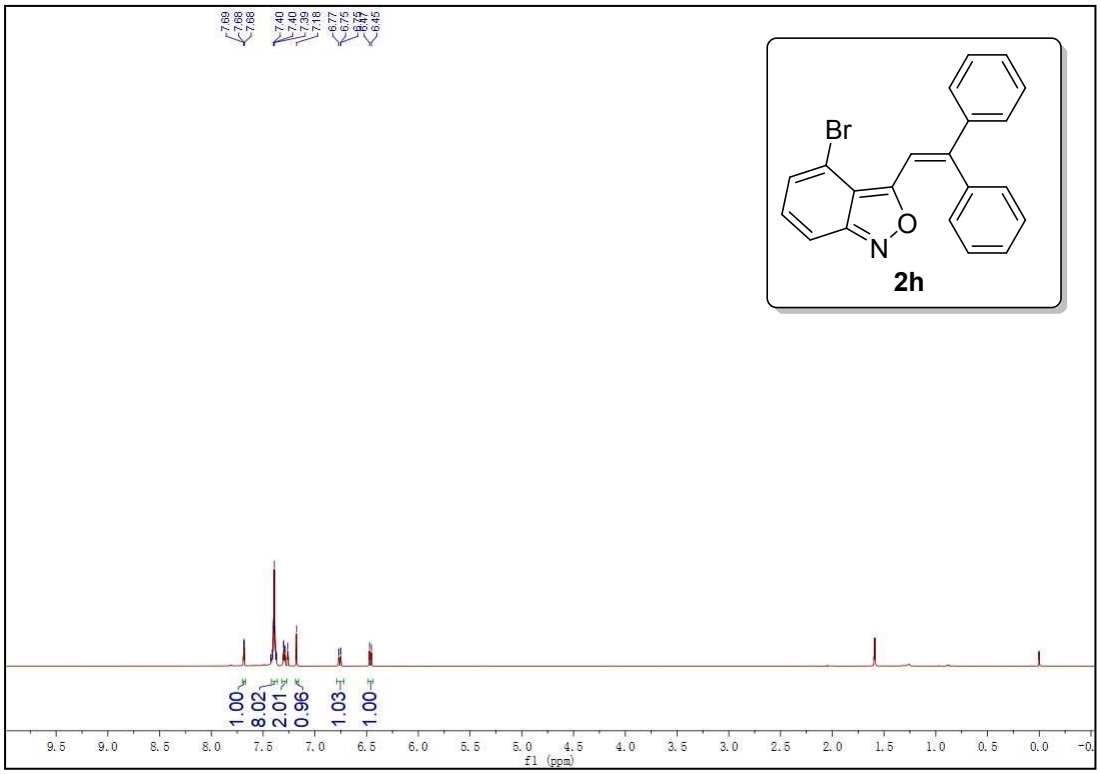

-63.36
-63.36
F
O
N
2f
f1 (ppm)

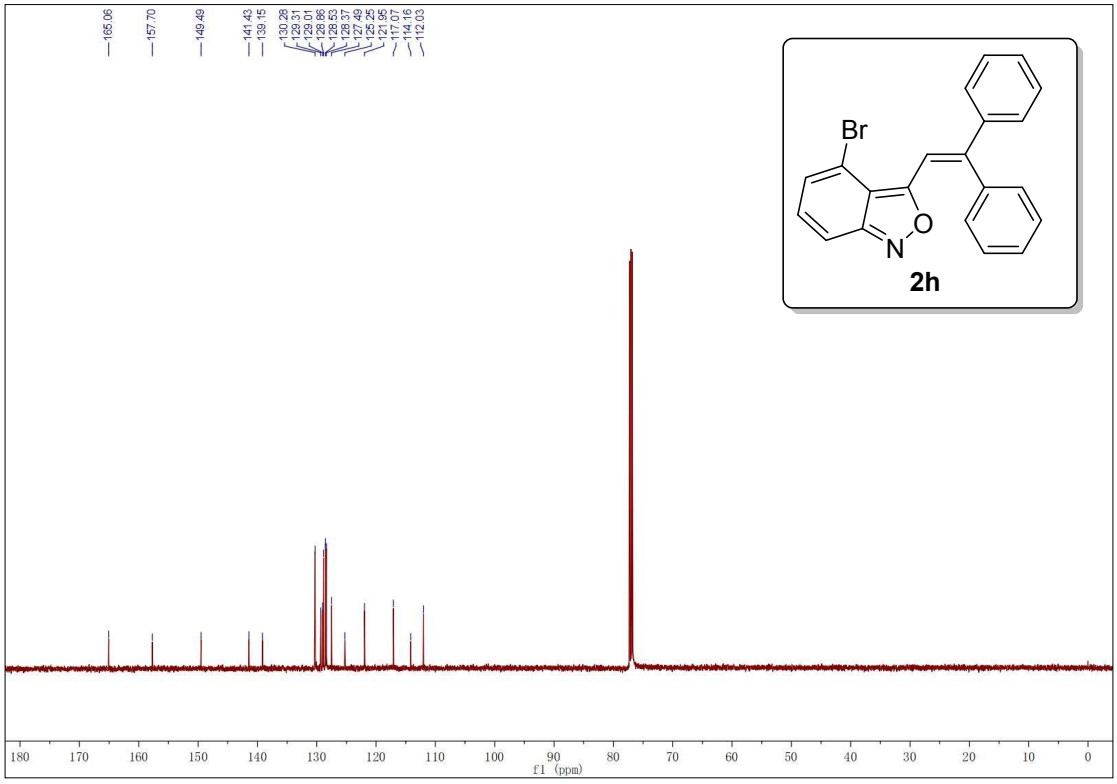
4-chloro-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2g)



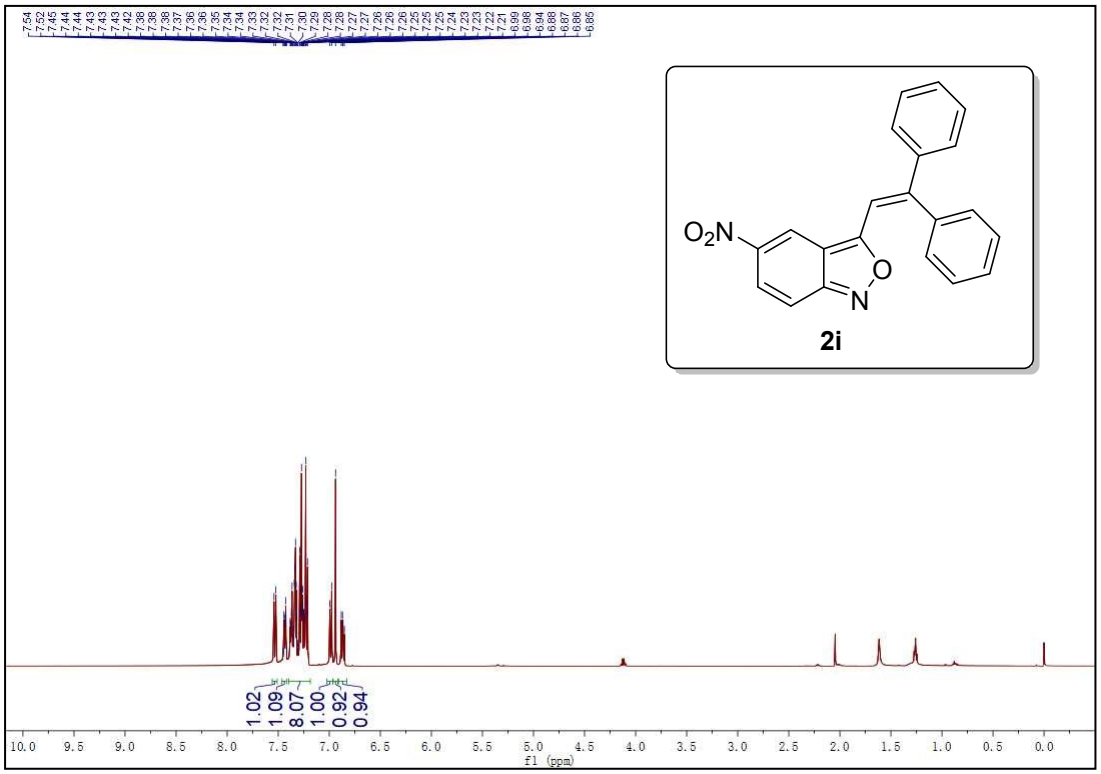


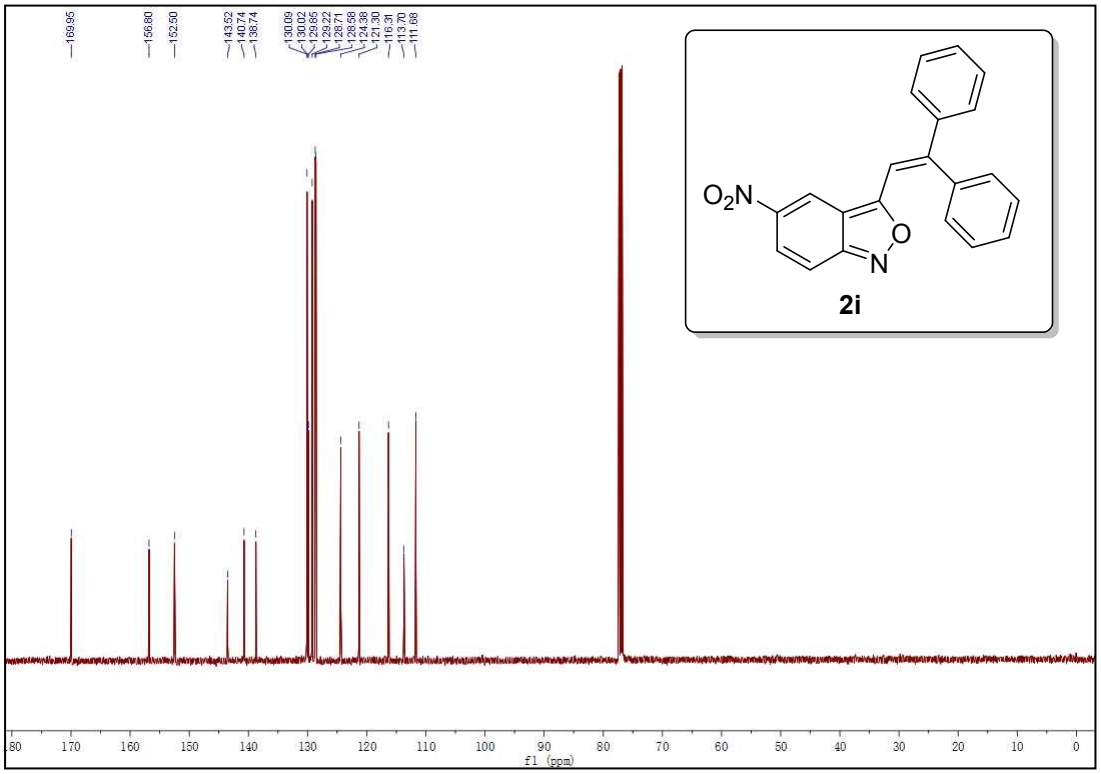
4-bromo-3-(2,2-diphenylvinyl)benzo[*c*]isoxazole (2h)



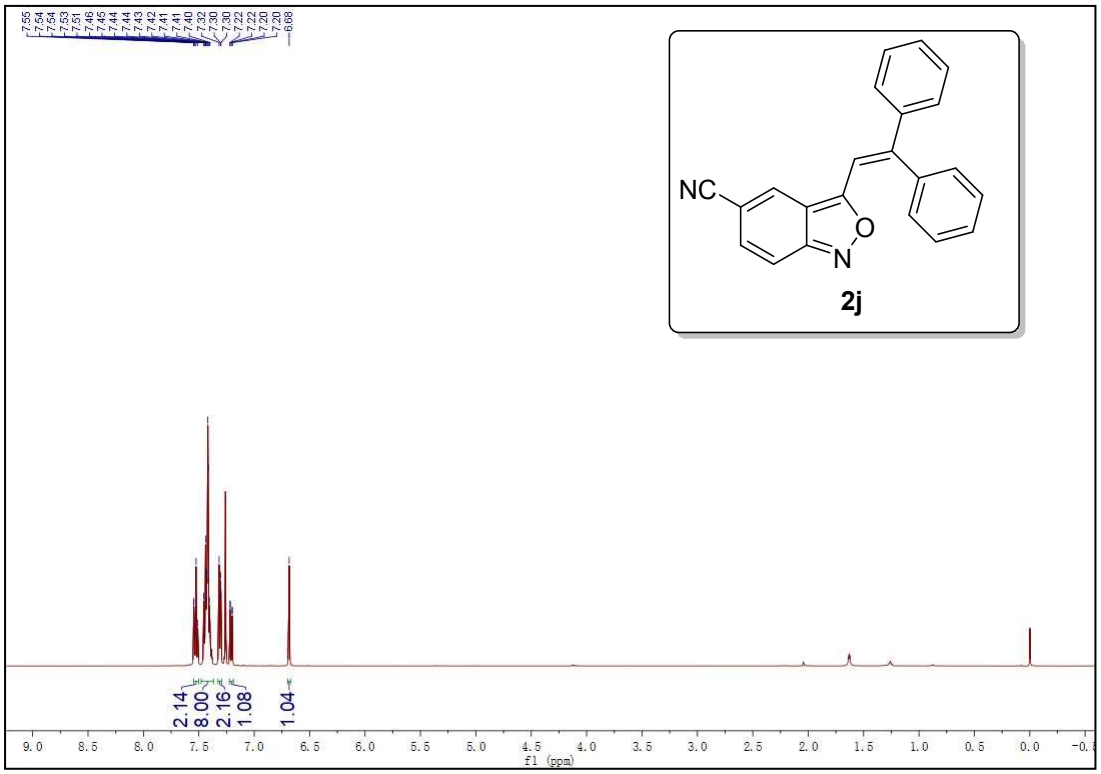


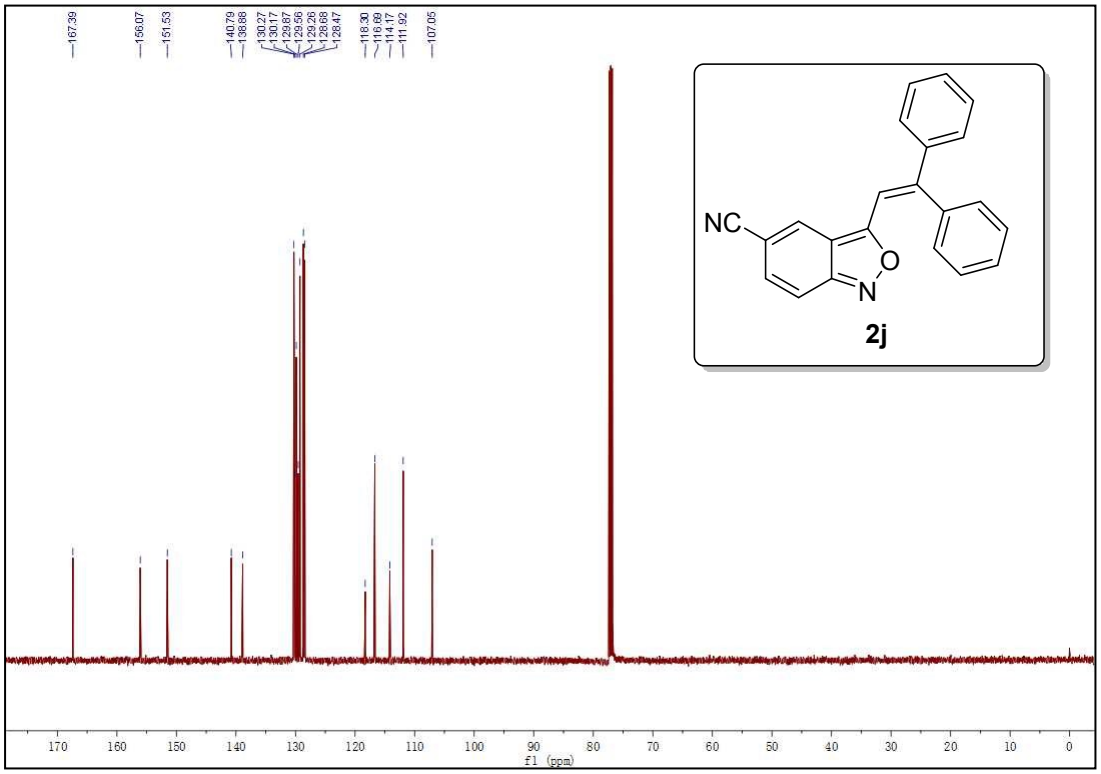
3-(2,2-diphenylvinyl)-5-nitrobenzo[*c*]isoxazole (2i)



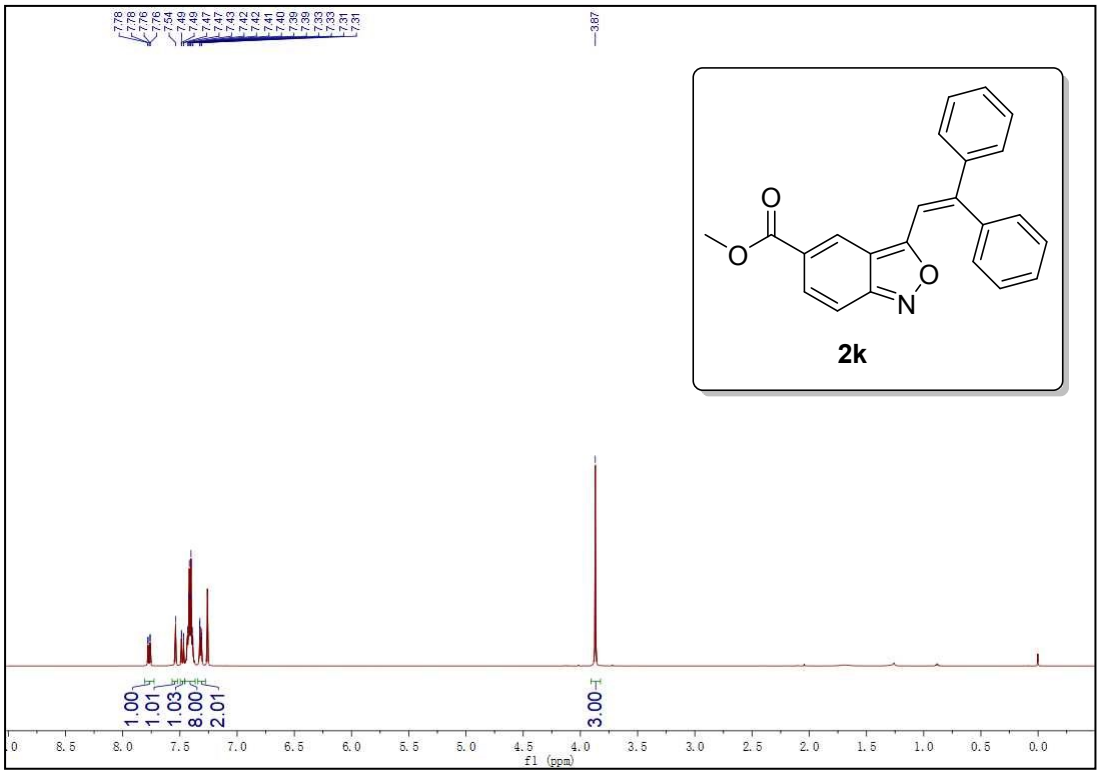


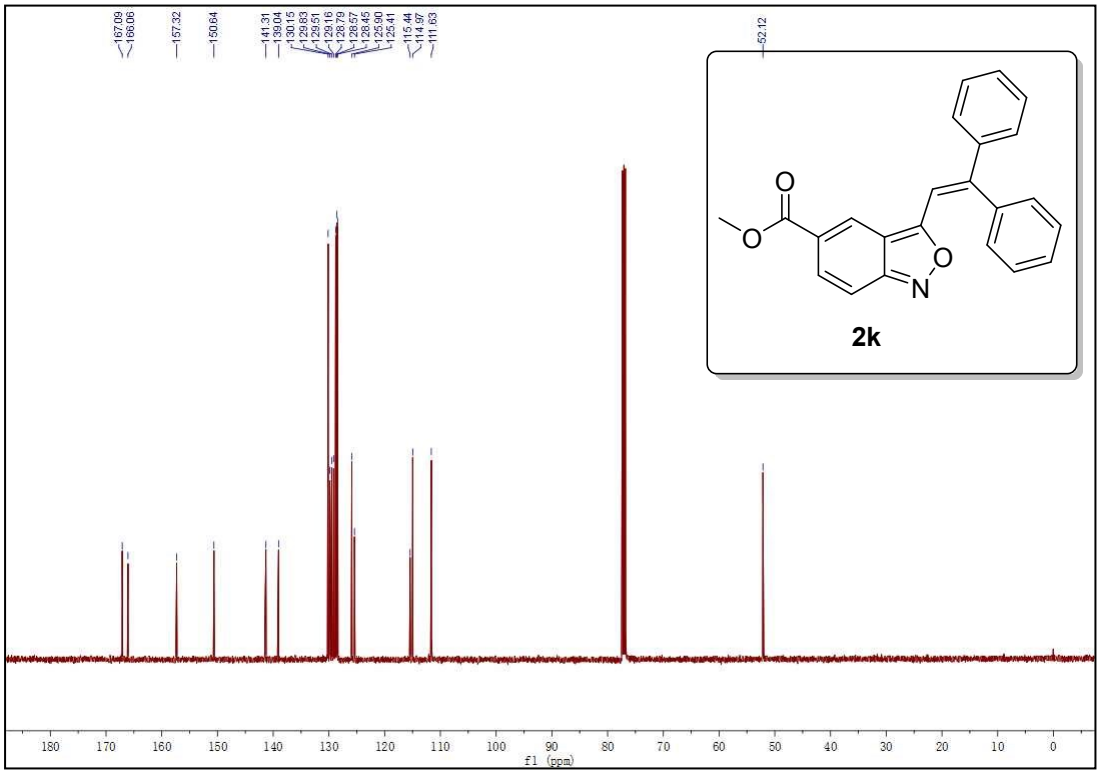
3-(2,2-diphenylvinyl)benzo[*c*]isoxazole-5-carbonitrile (2j)



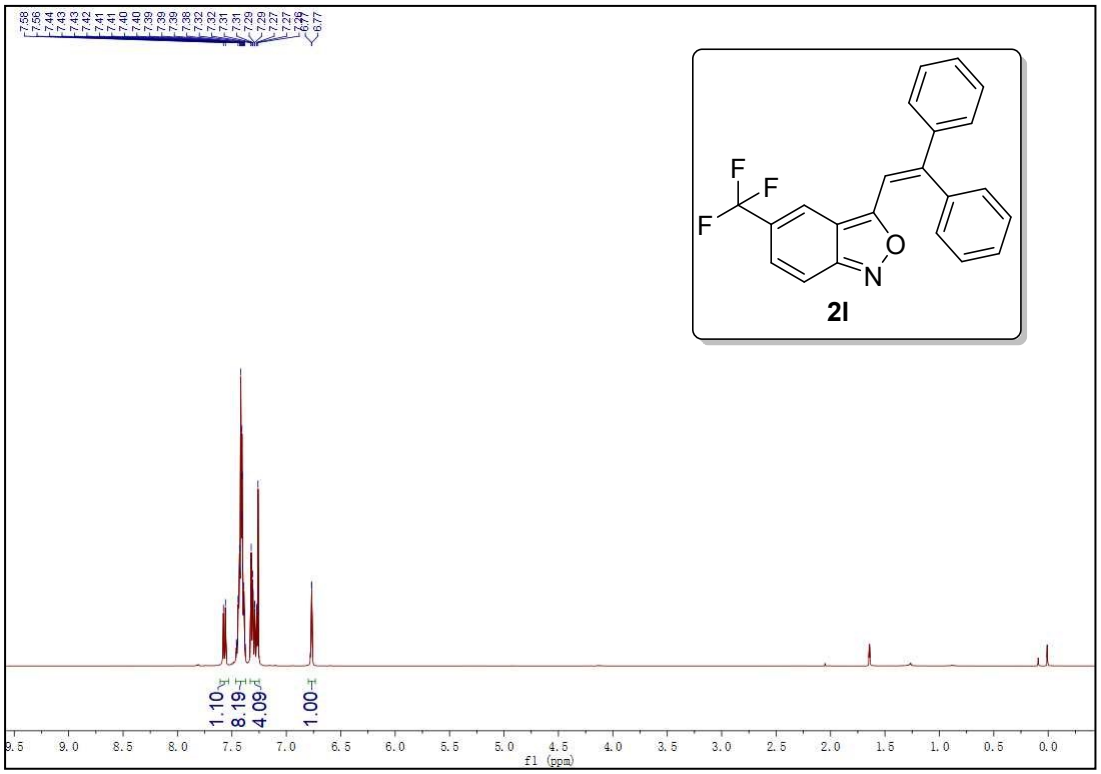


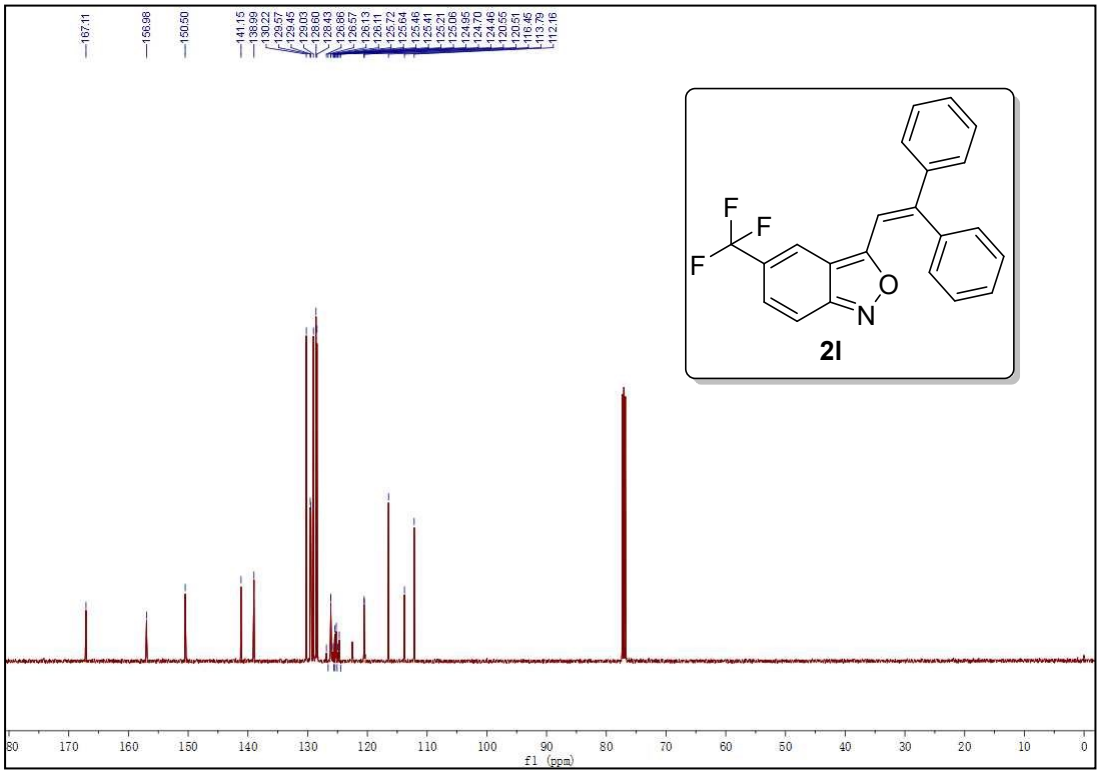
methyl 3-(2,2-diphenylvinyl)benzo[*c*]isoxazole-5-carboxylate (2k)

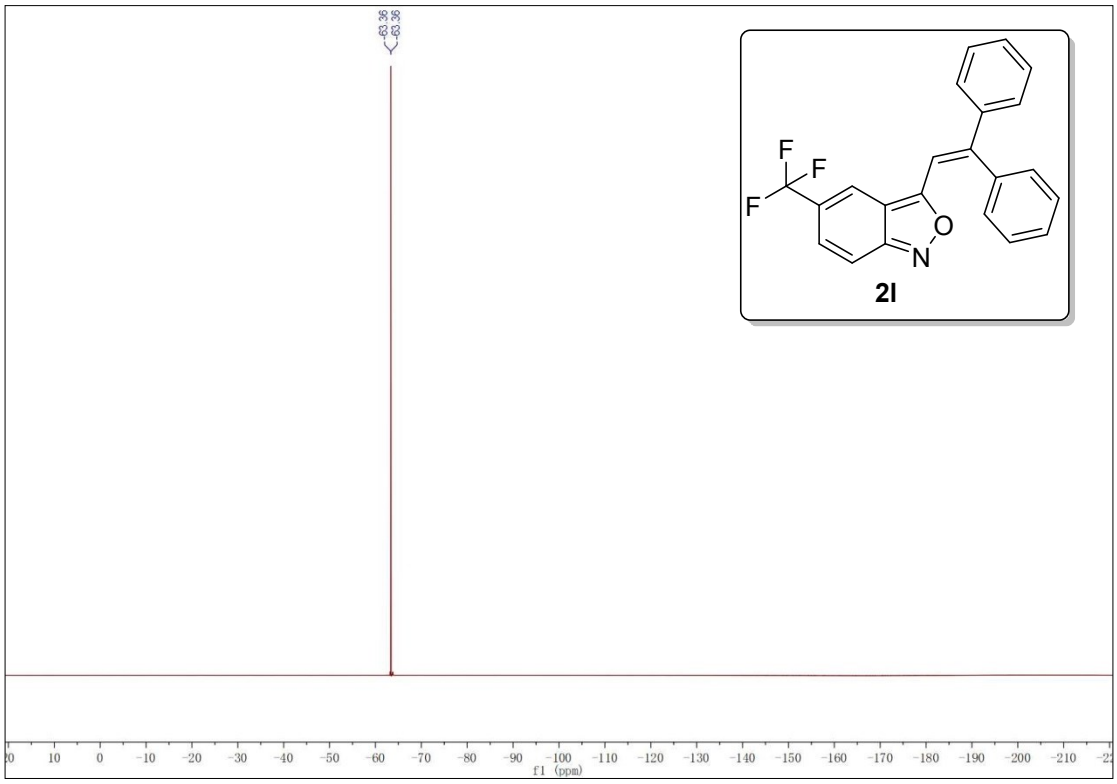




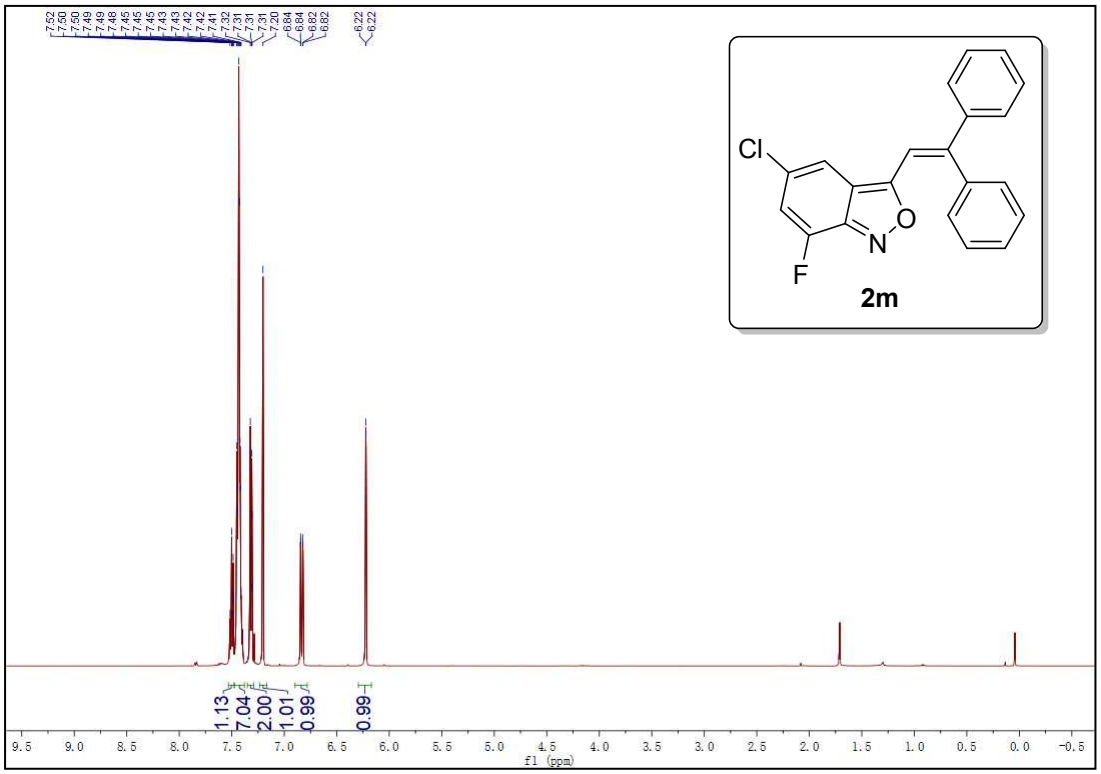
3-(2,2-diphenylvinyl)-5-(trifluoromethyl)benzo[*c*]isoxazole (2l)

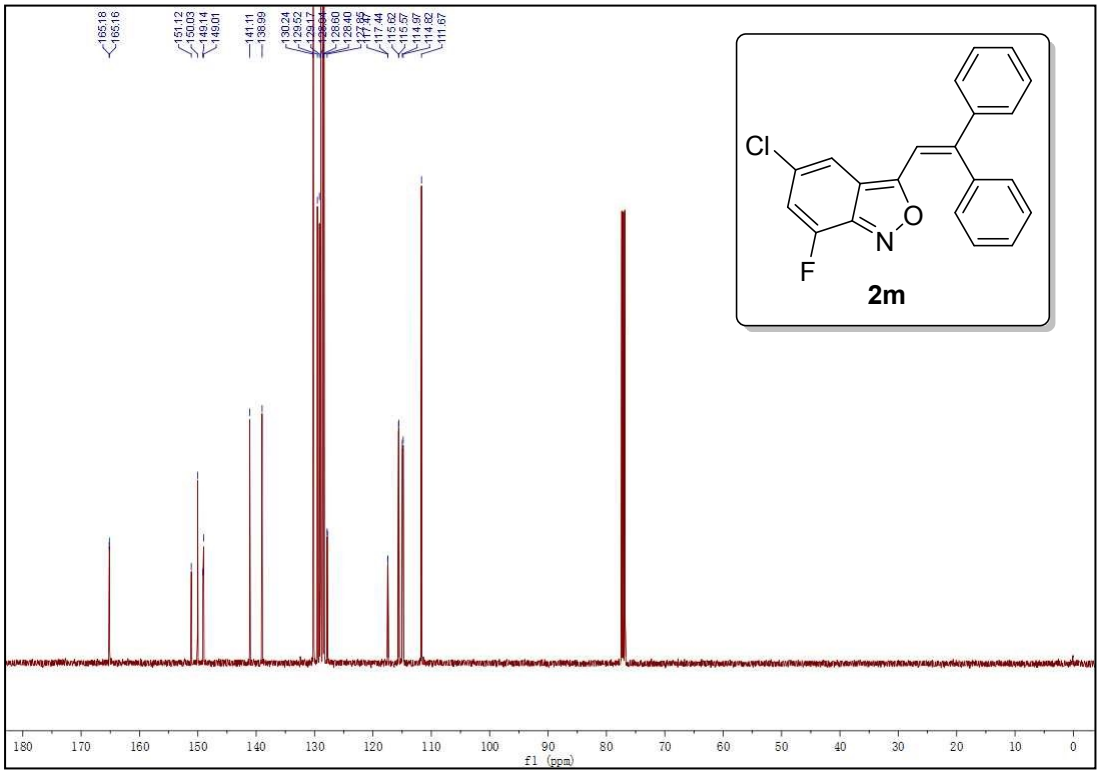


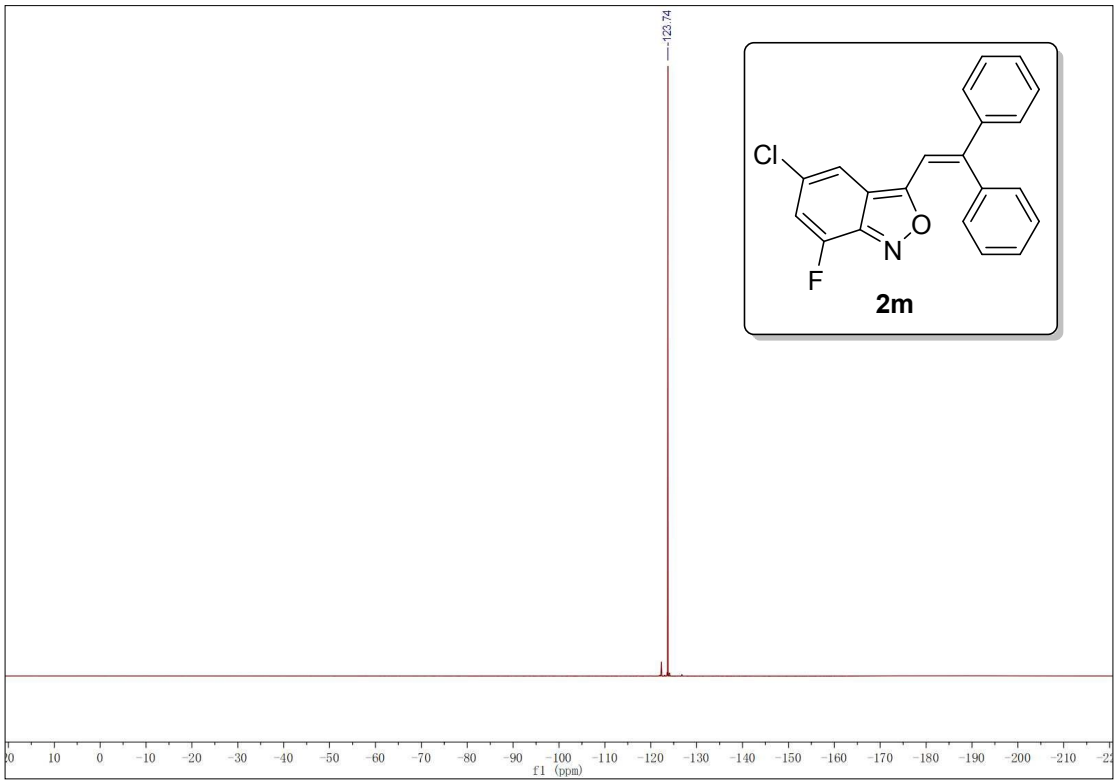



-63.36
-63.36
F
F
F
O
N
2l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

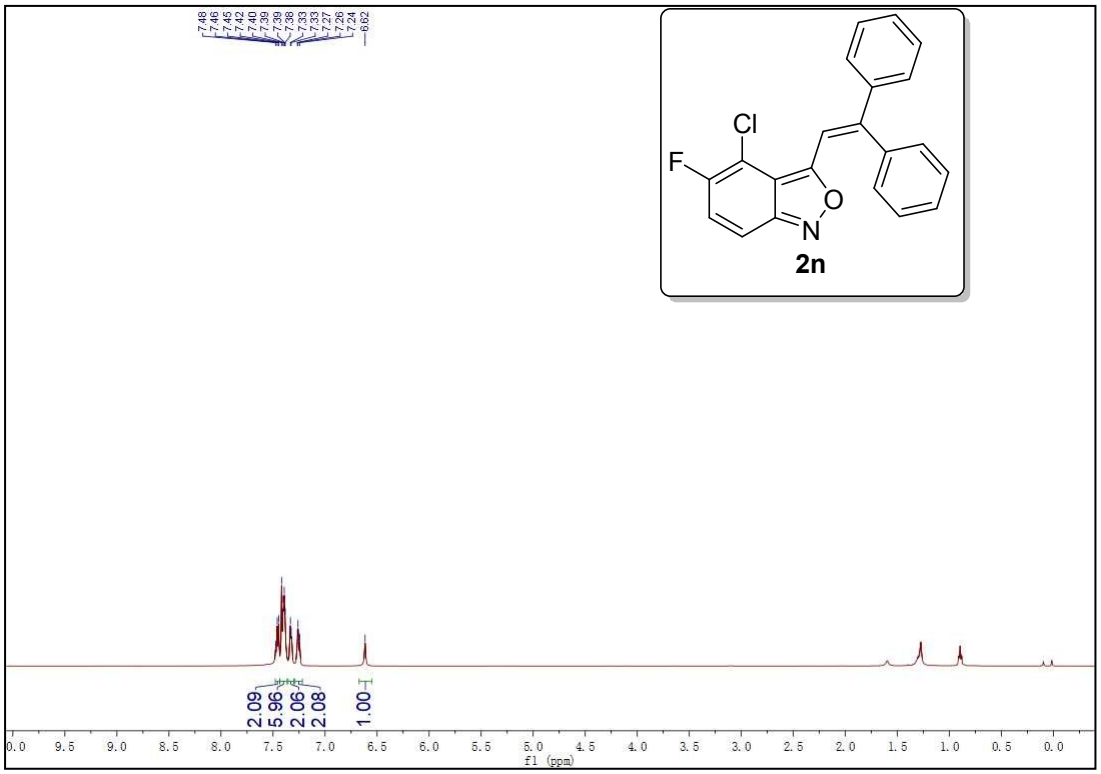
5-chloro-3-(2,2-diphenylvinyl)-7-fluorobenzo[*c*]isoxazole (2m)

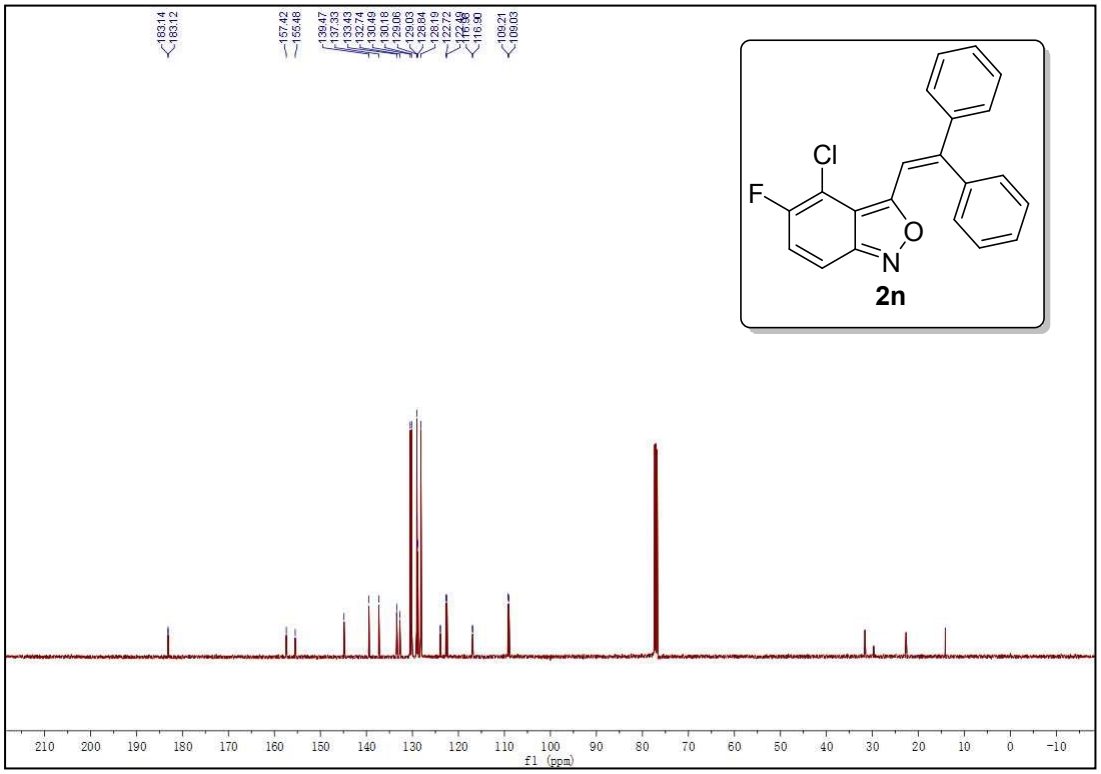


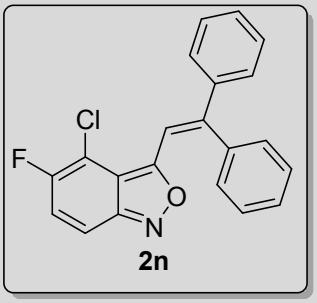



-123.74
Cl
O
N
F
2m
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4-chloro-3-(2,2-diphenylvinyl)-5-fluorobenzo[*c*]isoxazole (2n)

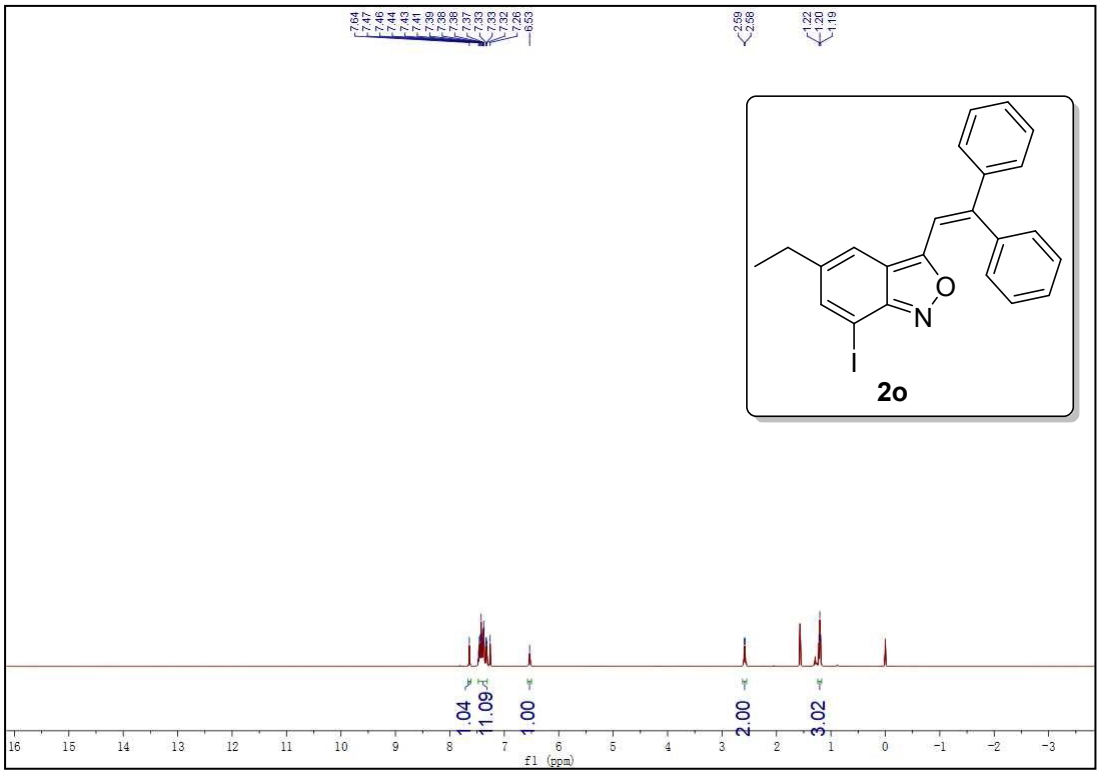


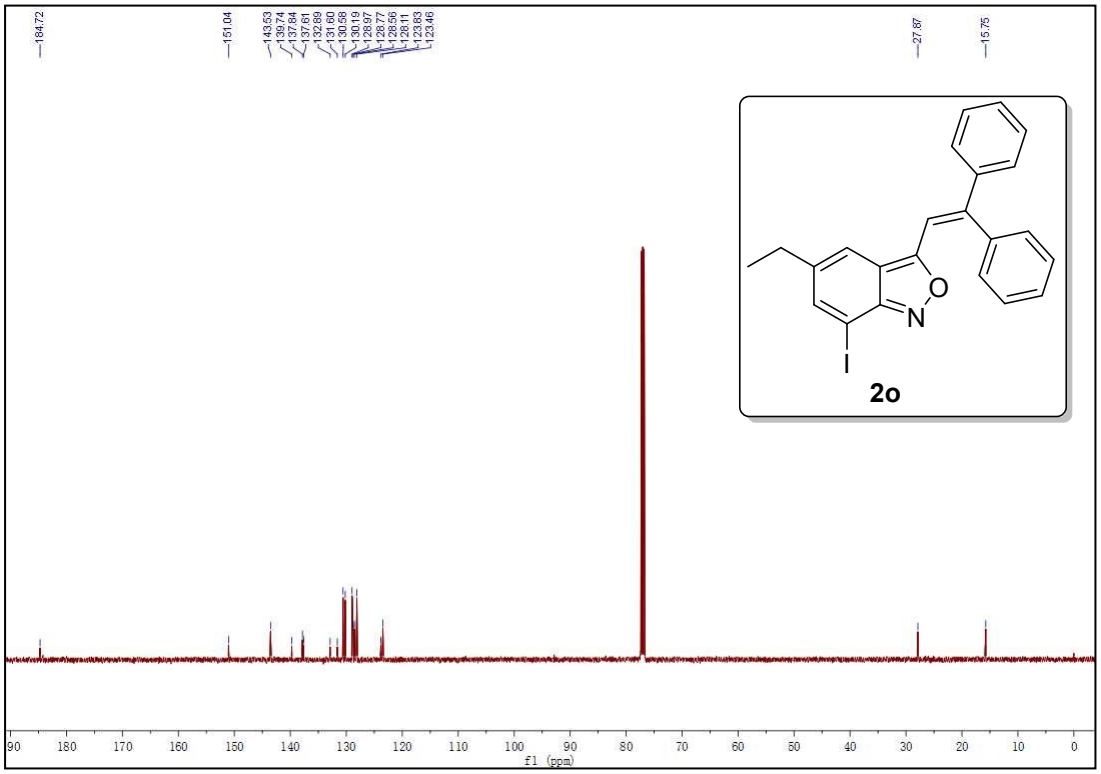




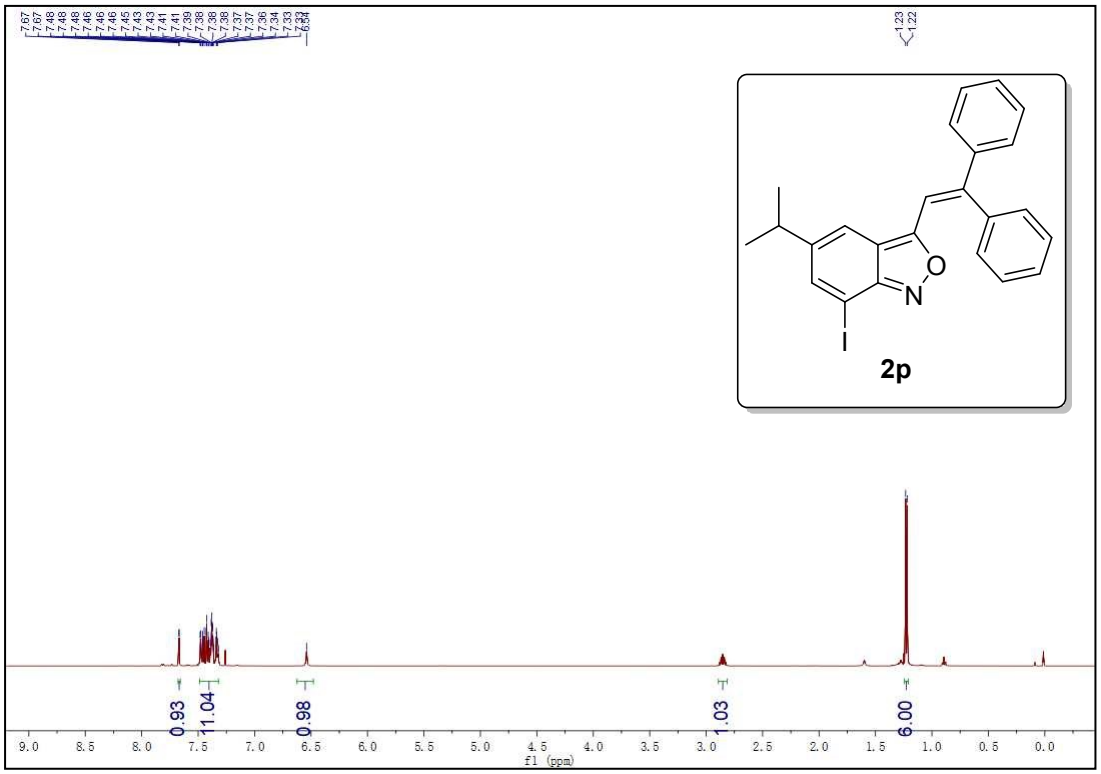
2n

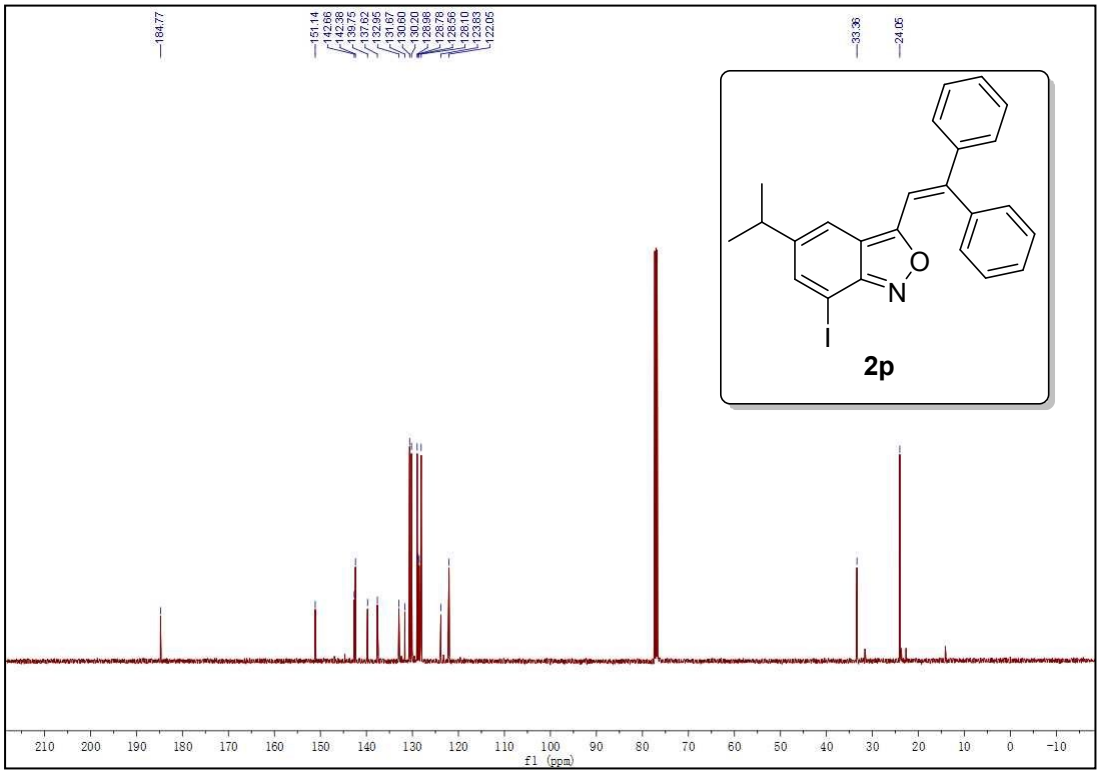
3-(2,2-diphenylvinyl)-5-ethyl-7-iodobenzo[*c*]isoxazole (2o)



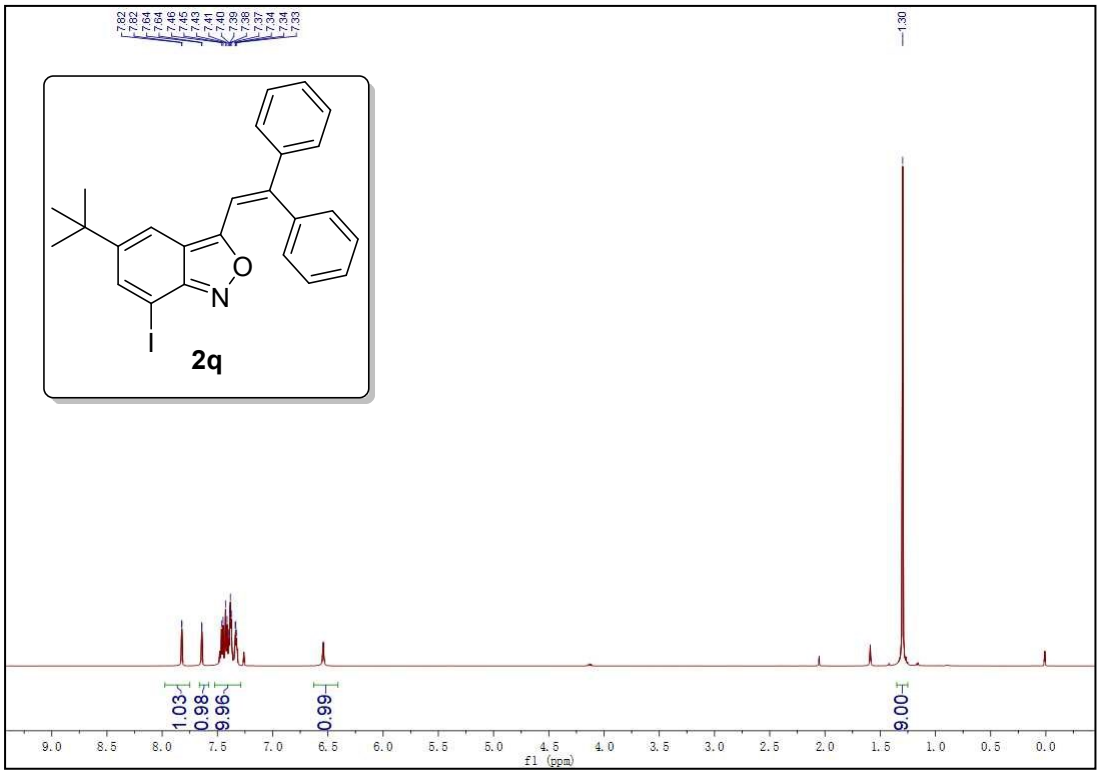


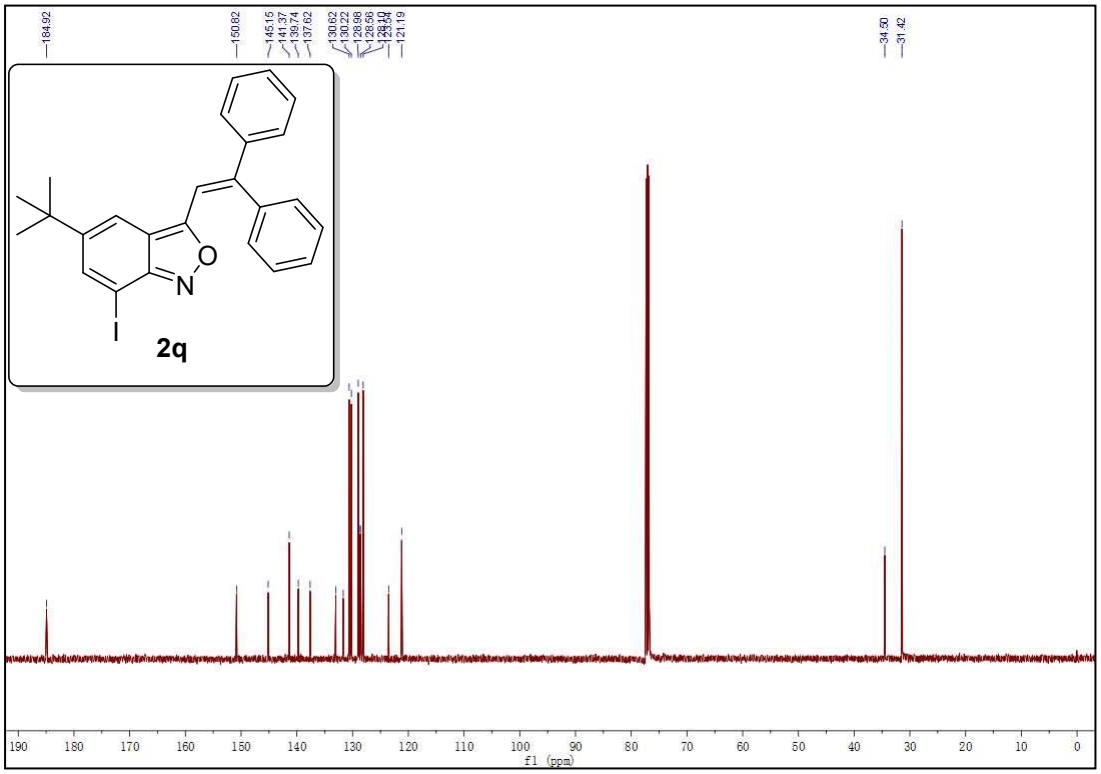
3-(2,2-diphenylvinyl)-7-iodo-5-isopropylbenzo[*c*]isoxazole (2p)



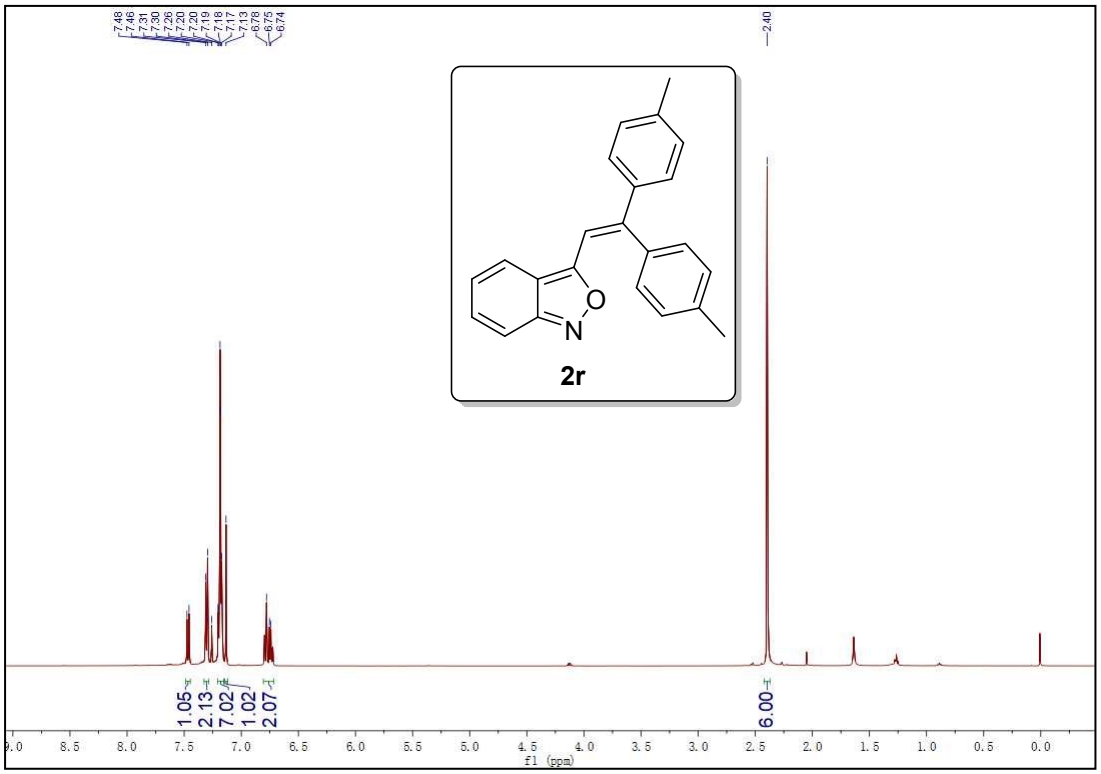


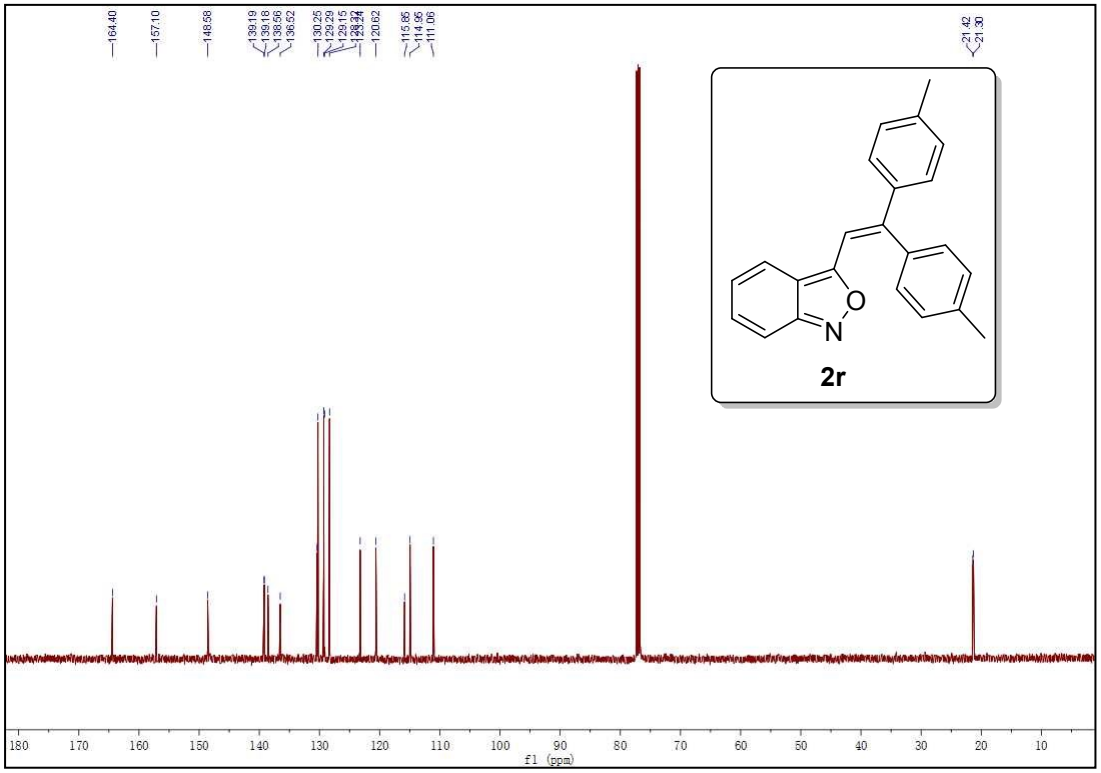
5-(tert-butyl)-3-(2,2-diphenylvinyl)-7-iodobenzo[*c*]isoxazole (2q)



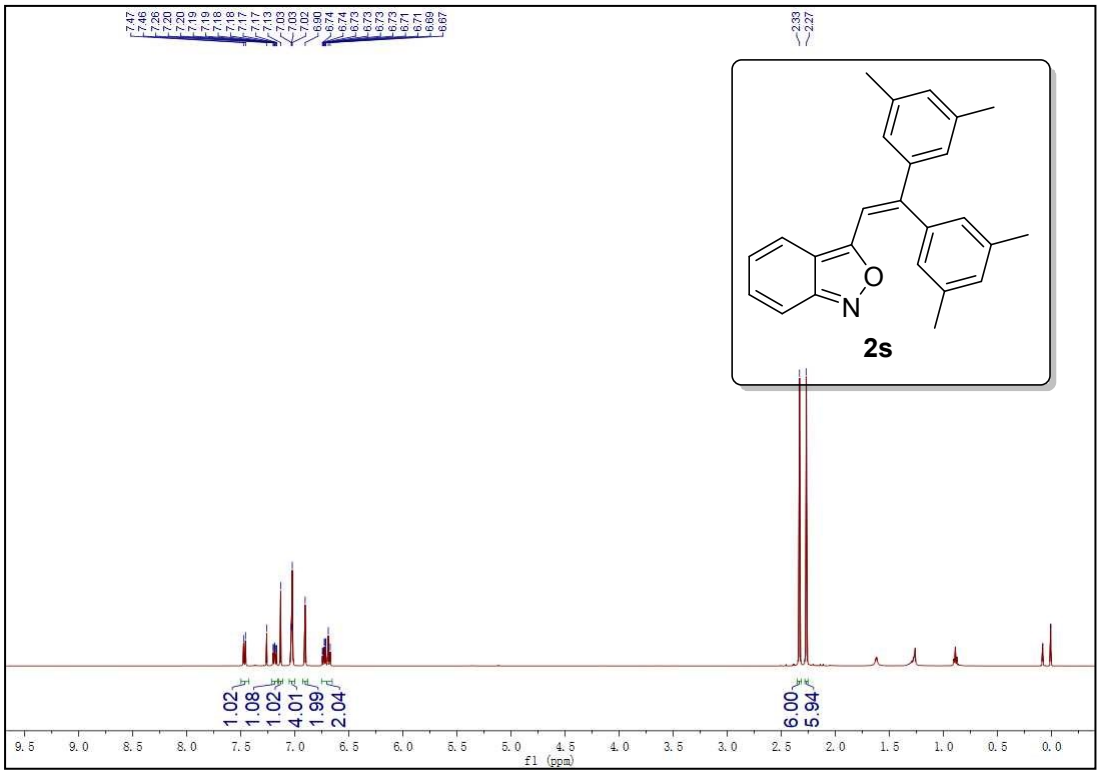


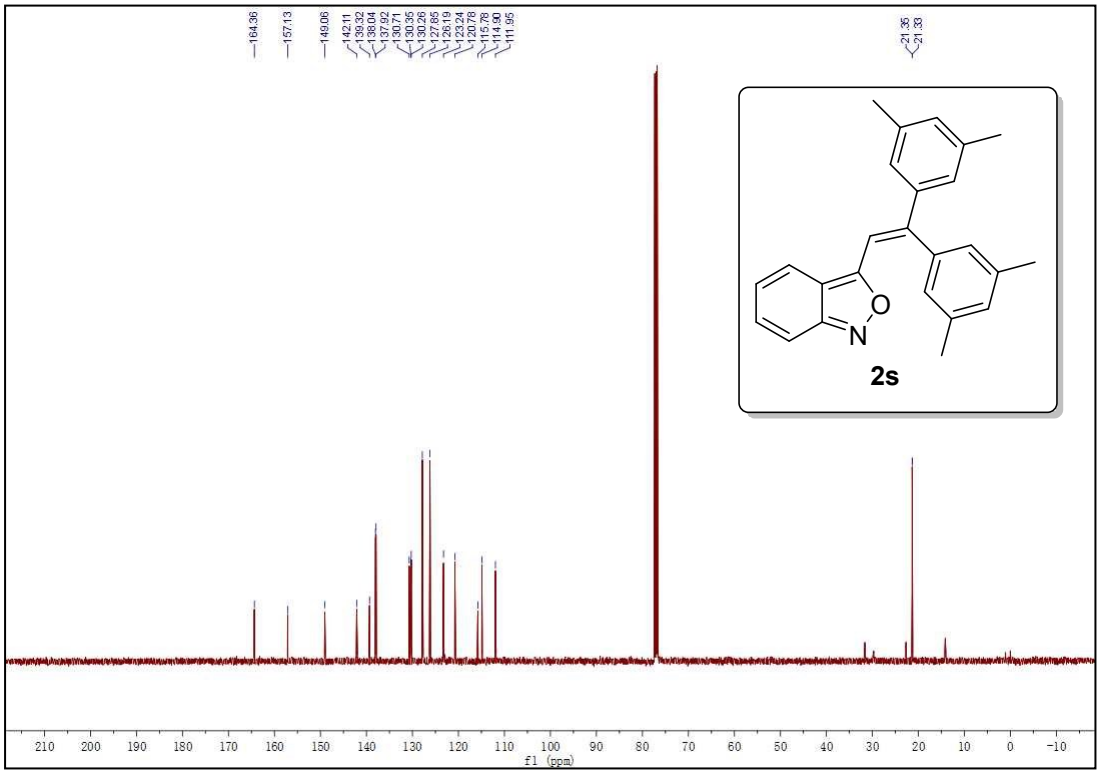
3-(2,2-di-p-tolylvinyl)benzo[*c*]isoxazole (2r)



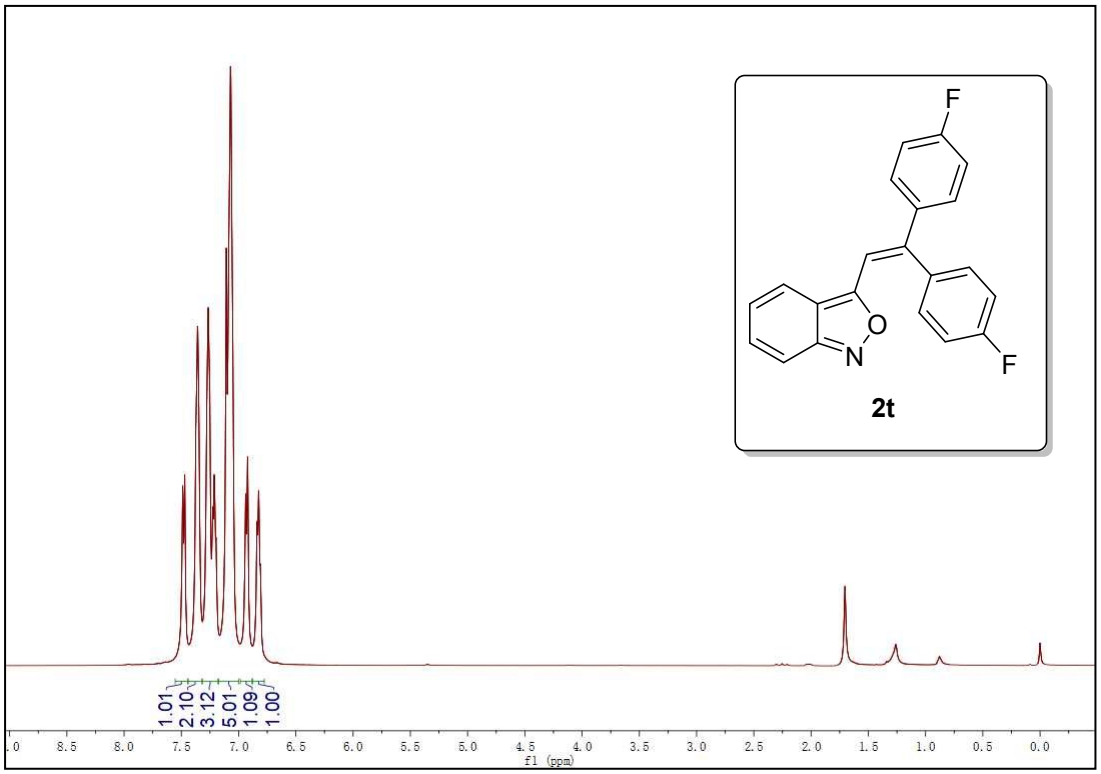


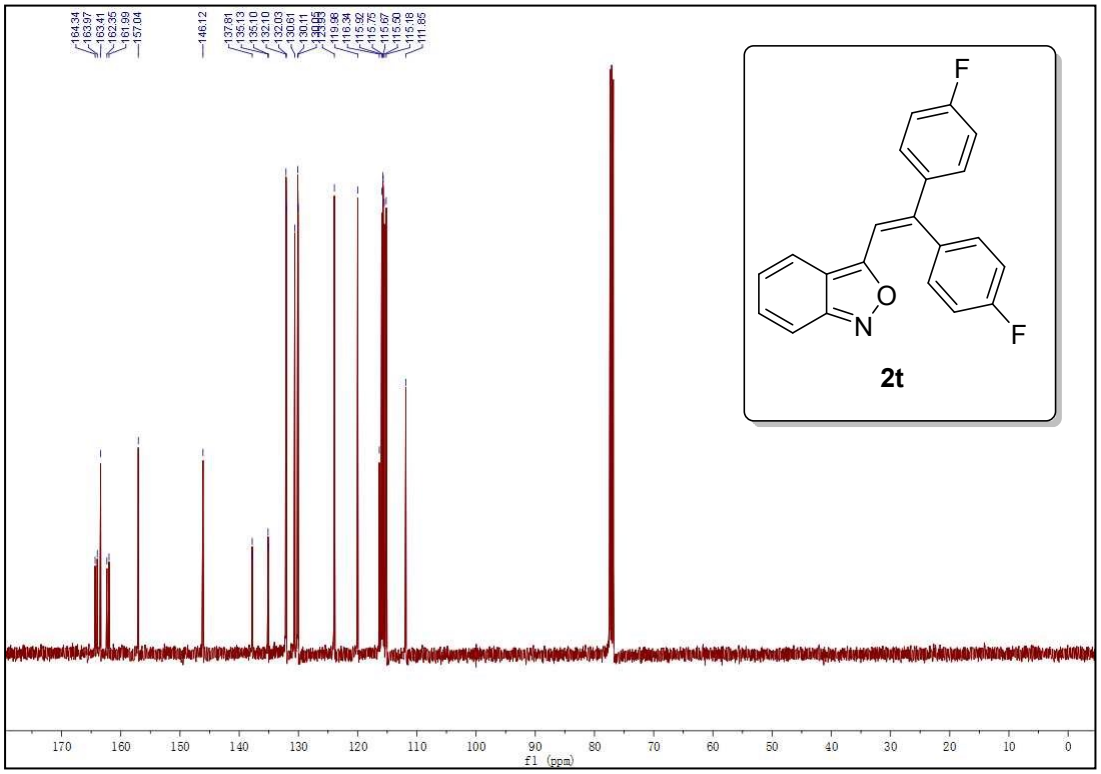
3-(2,2-bis(3,5-dimethylphenyl)vinyl)benzo[*c*]isoxazole (2s)

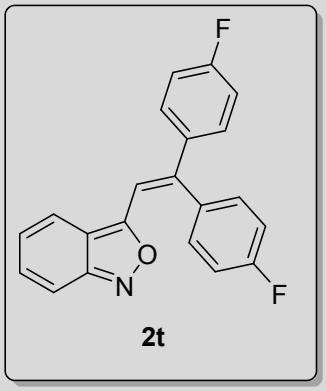




3-(2,2-bis(4-fluorophenyl)vinyl)benzo[*c*]isoxazole (2t)

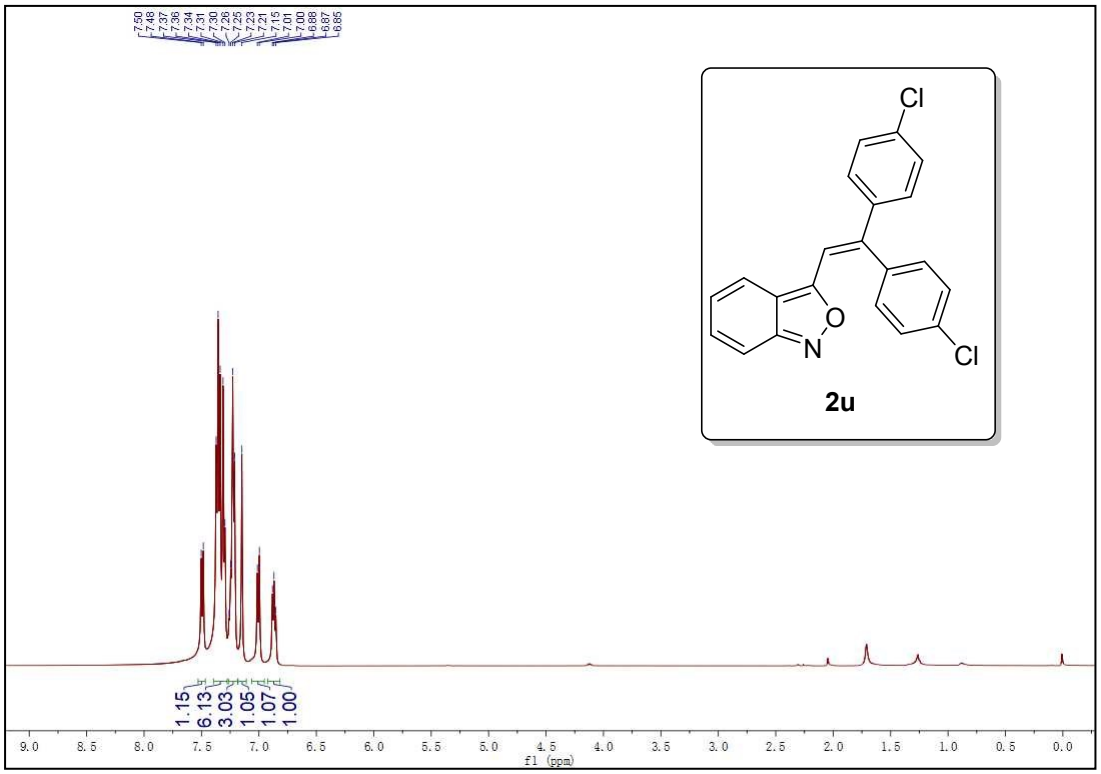


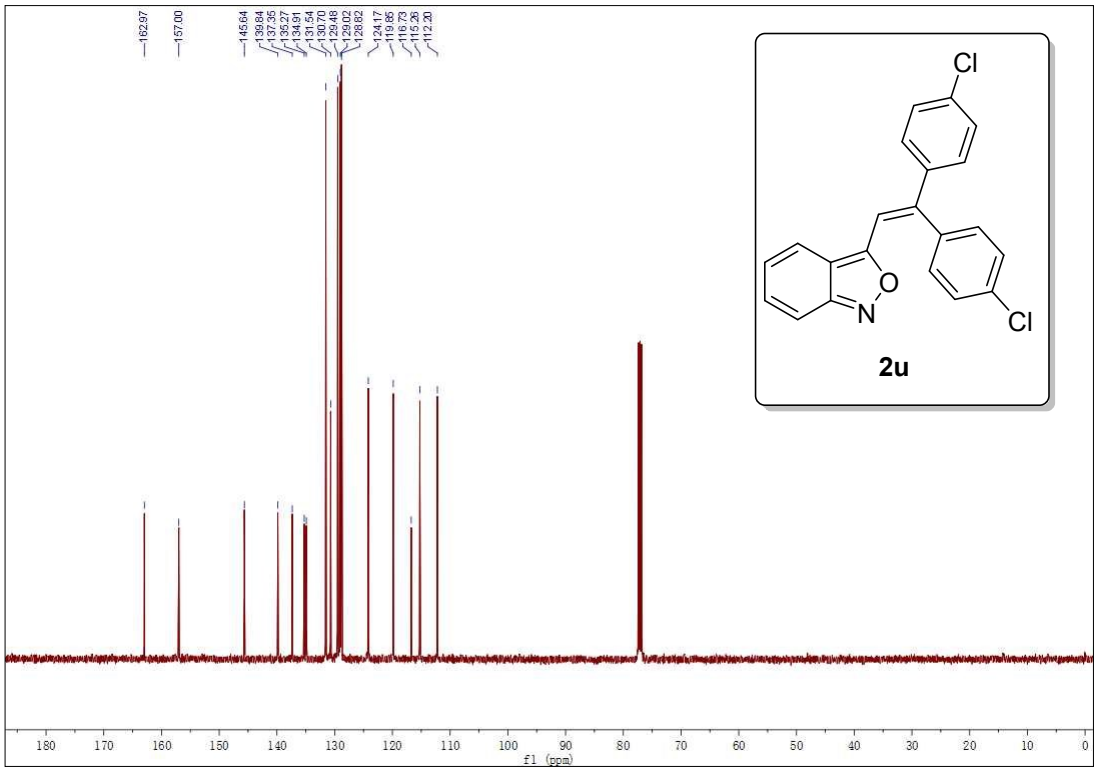




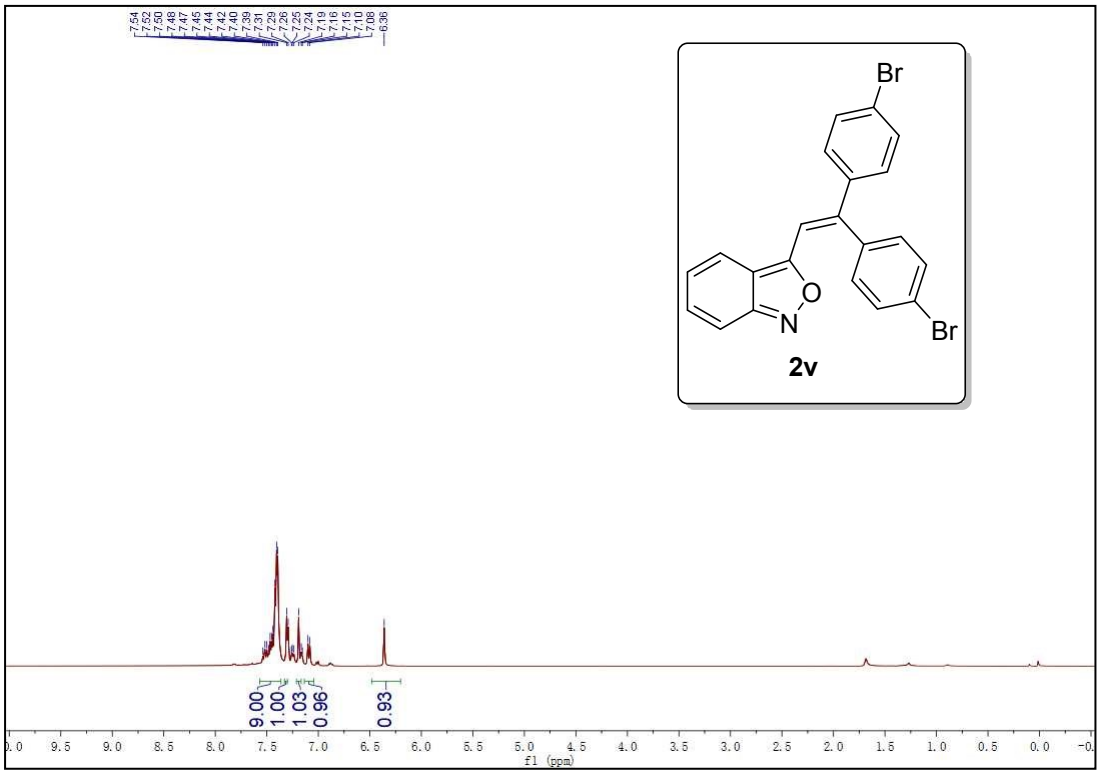
2t

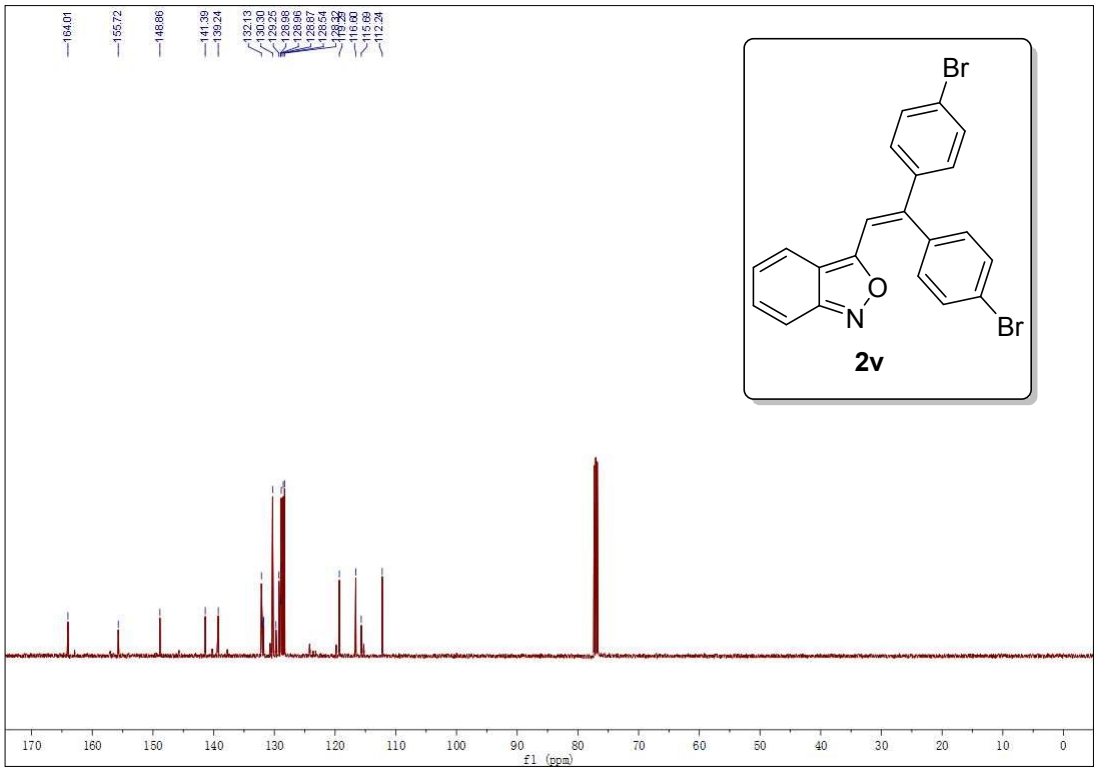
3-(2,2-bis(4-chlorophenyl)vinyl)benzo[*c*]isoxazole (2u)



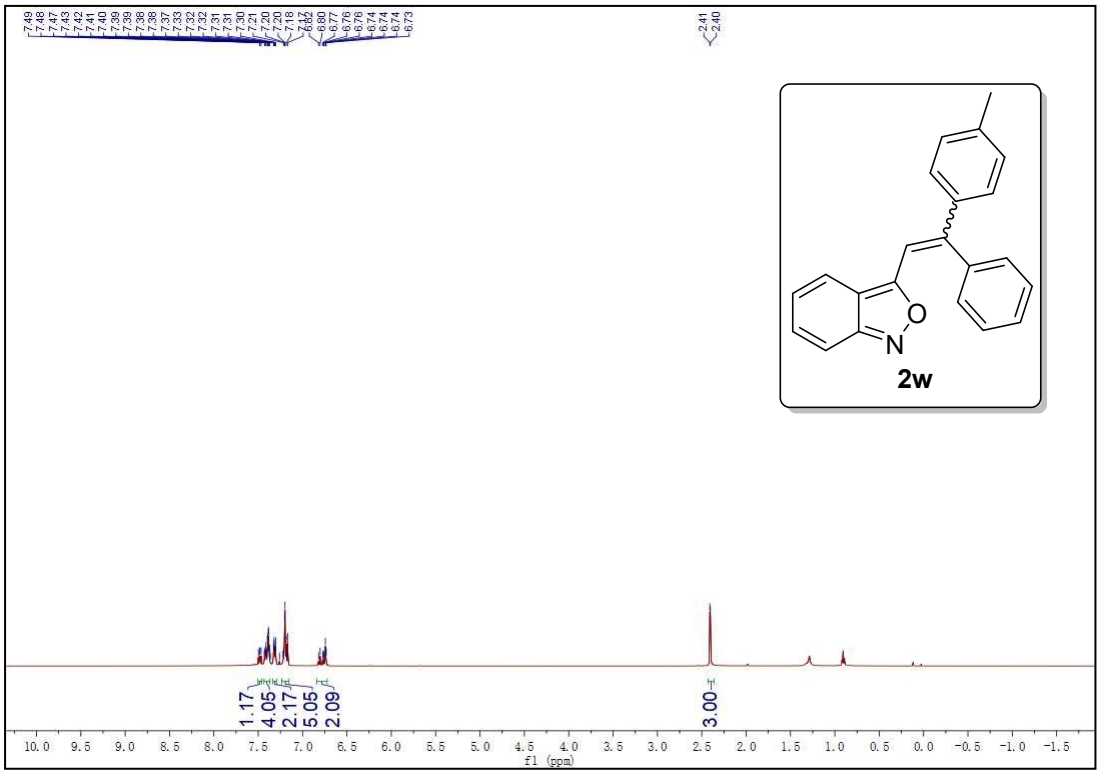


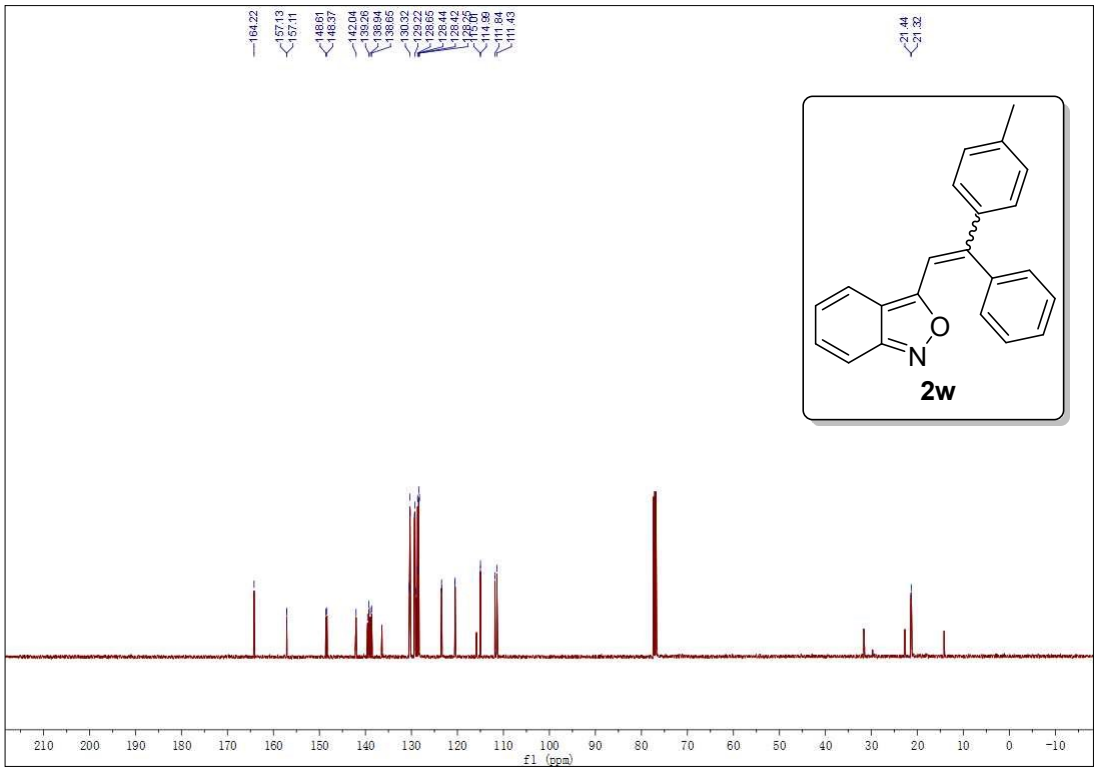
3-(2,2-bis(4-bromophenyl)vinyl)benzo[*c*]isoxazole(2v)



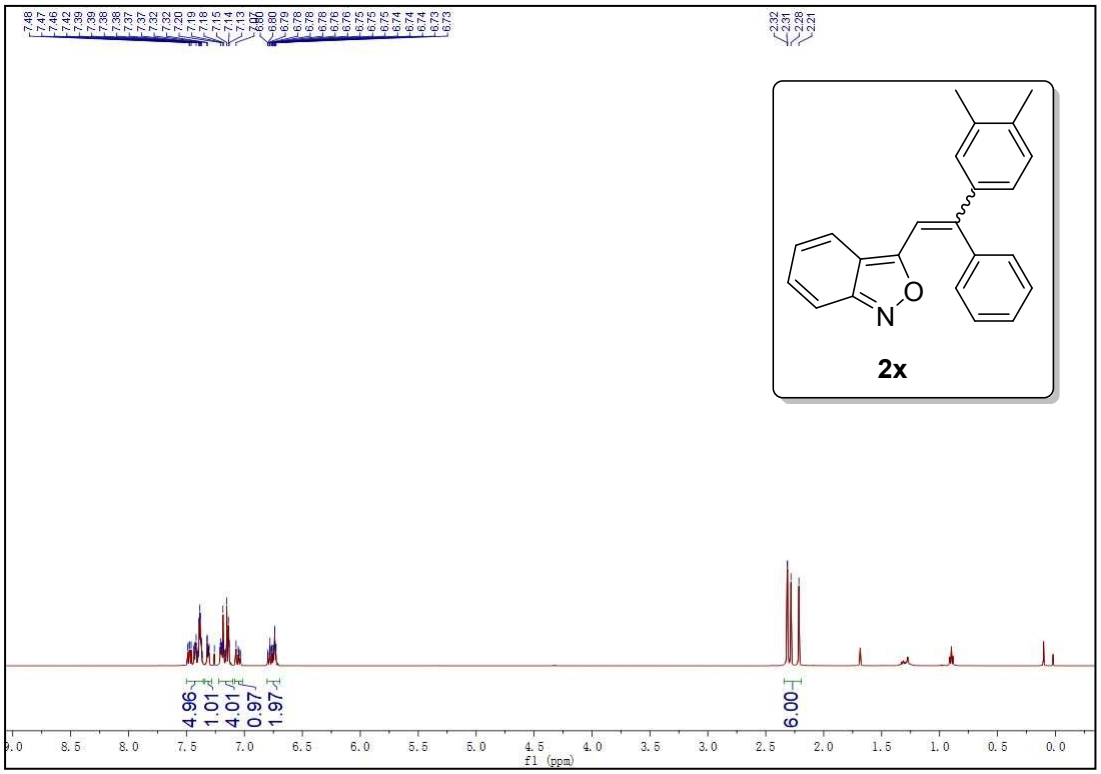


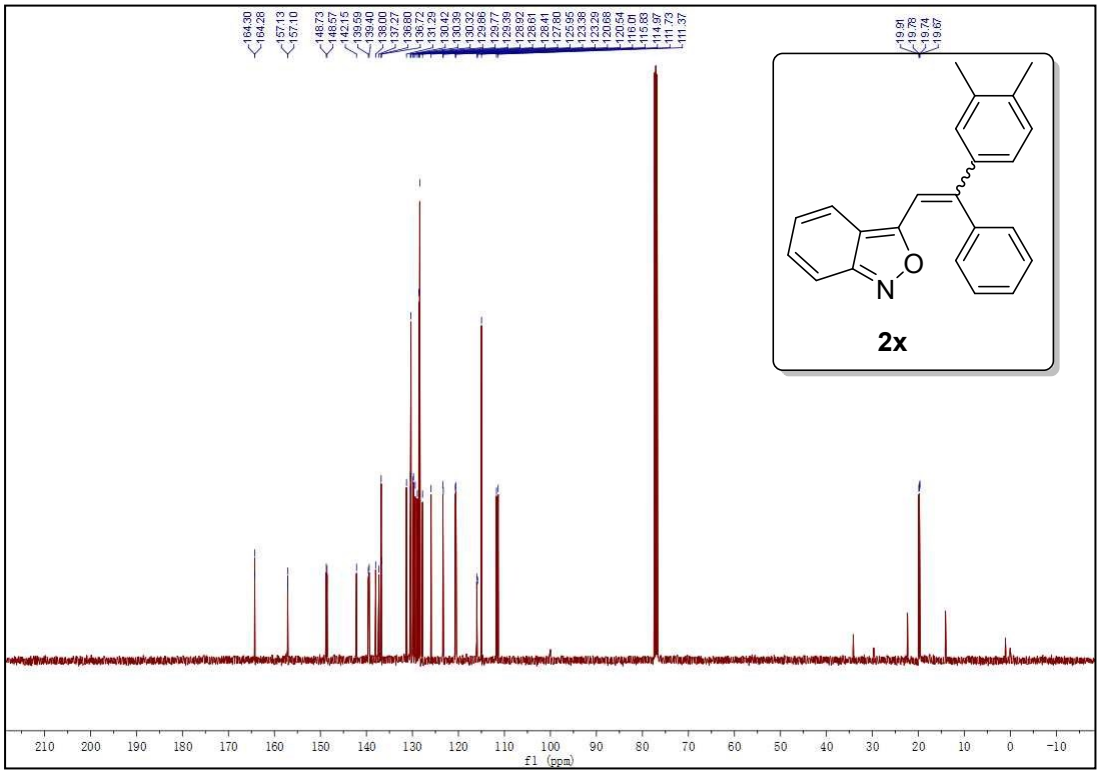
3-(2-phenyl-2-(p-tolyl)vinyl)benzo[*c*]isoxazole (2w)



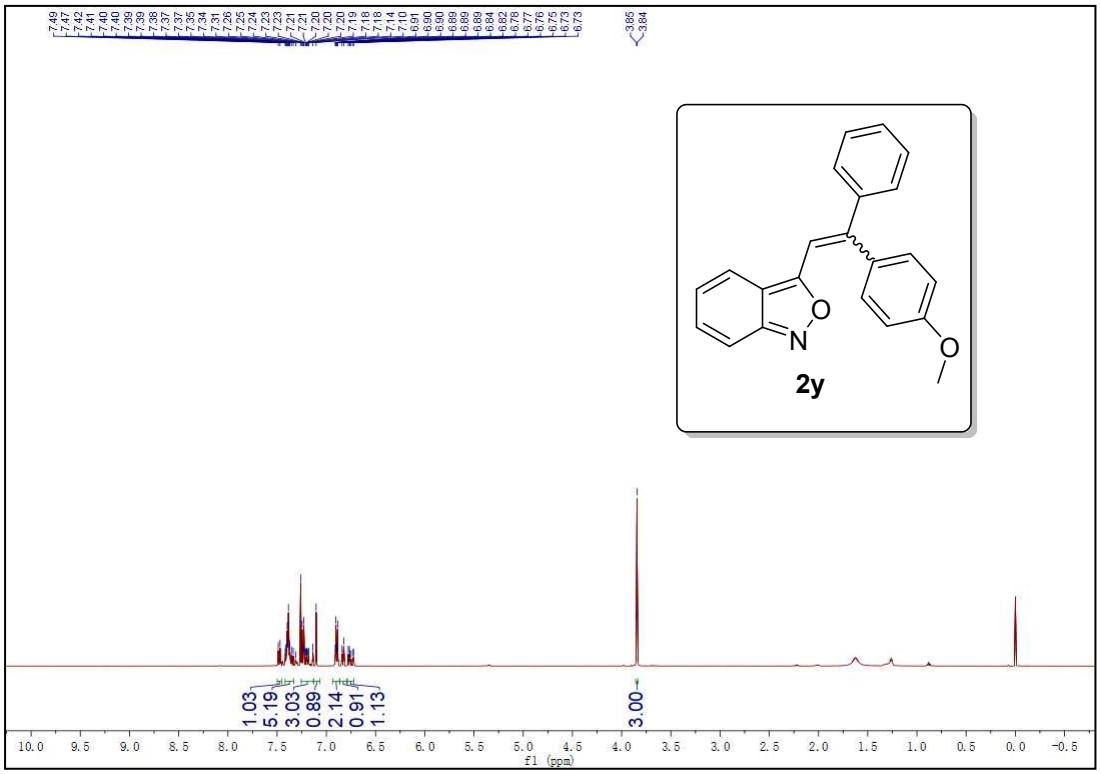


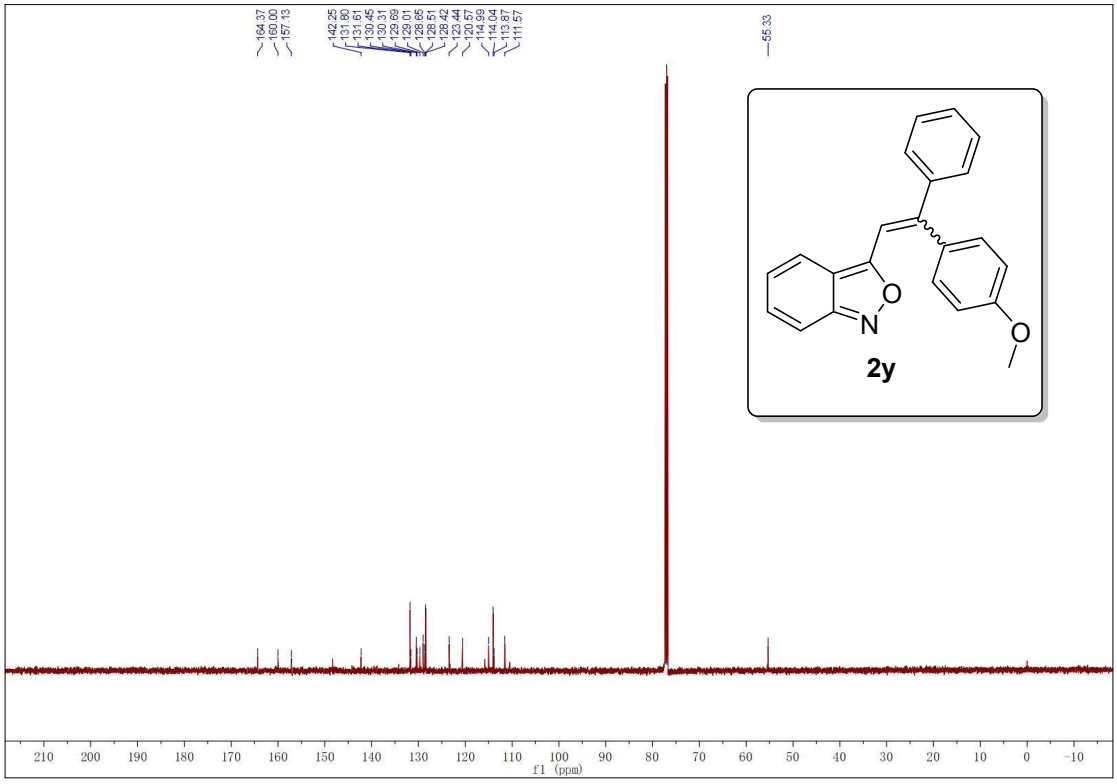
3-(2-(3,4-dimethylphenyl)-2-phenylvinyl)benzo[*c*]isoxazole (2x)



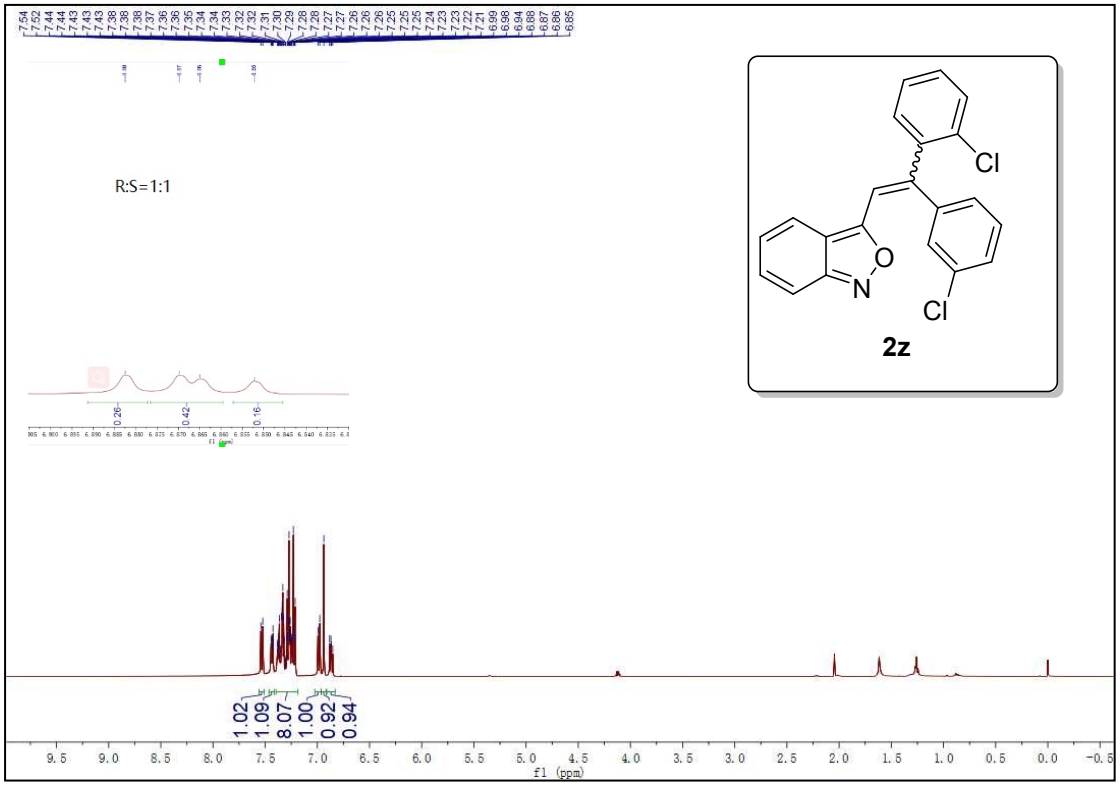


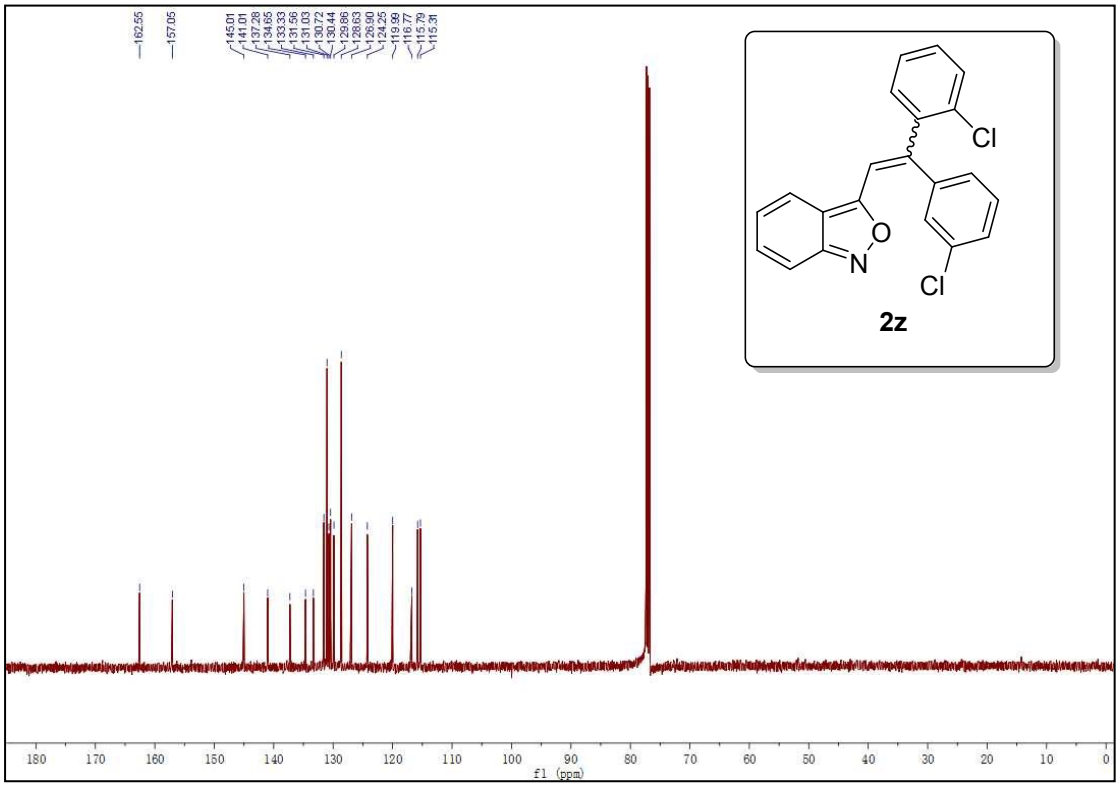
3-(2-(4-methoxyphenyl)-2-phenylvinyl)benzo[*c*]isoxazole (2y)



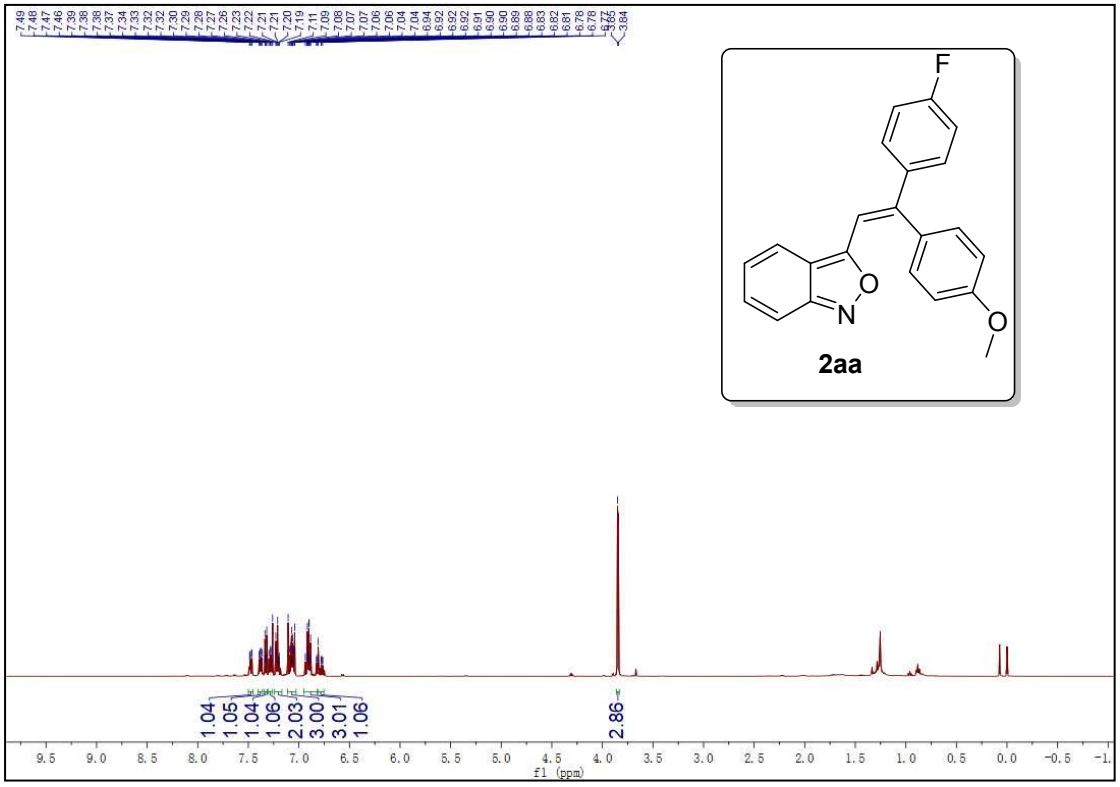


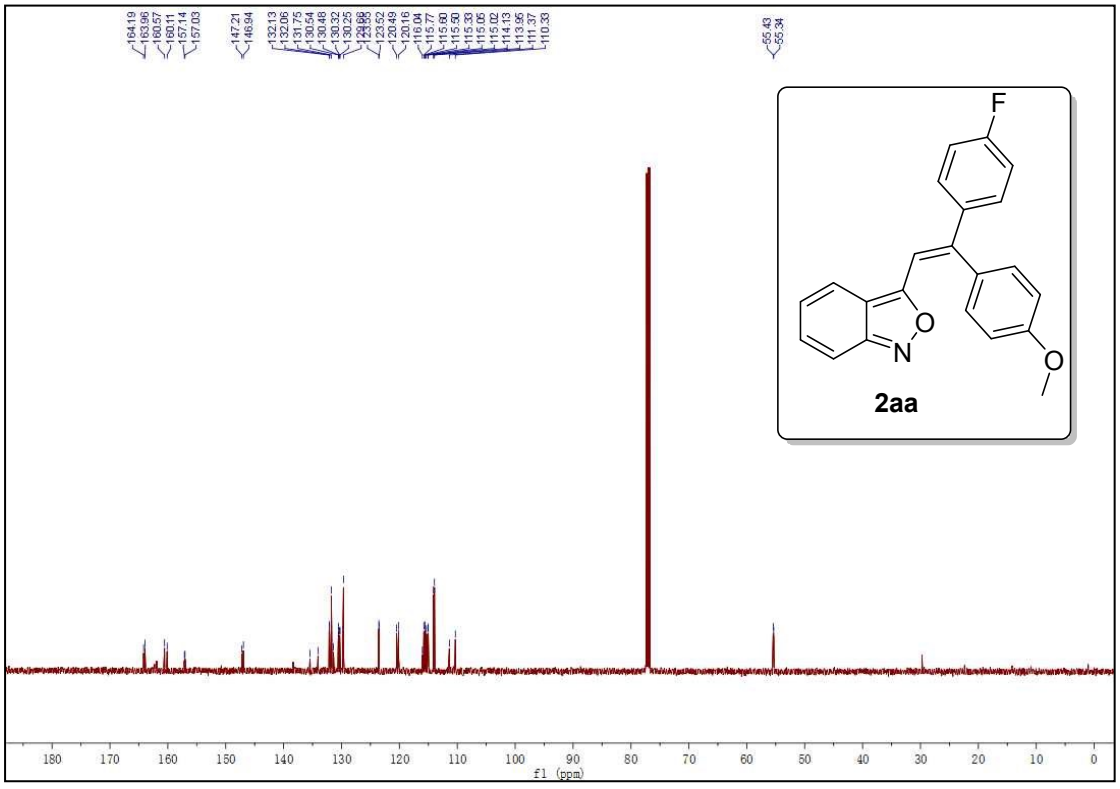
3-(2-(2-chlorophenyl)-2-(3-chlorophenyl)vinyl)benzo[*c*]isoxazole (2z)

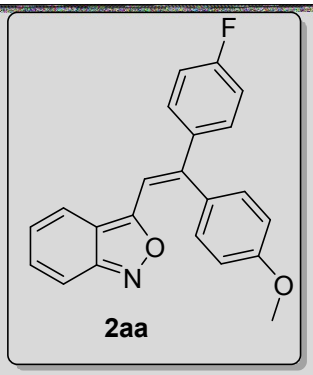




5-chloro-7-fluoro-3-(2-(4-fluorophenyl)-2-(4- methoxyphenyl)vinyl)benzo[*c*]isoxazole (2aa)

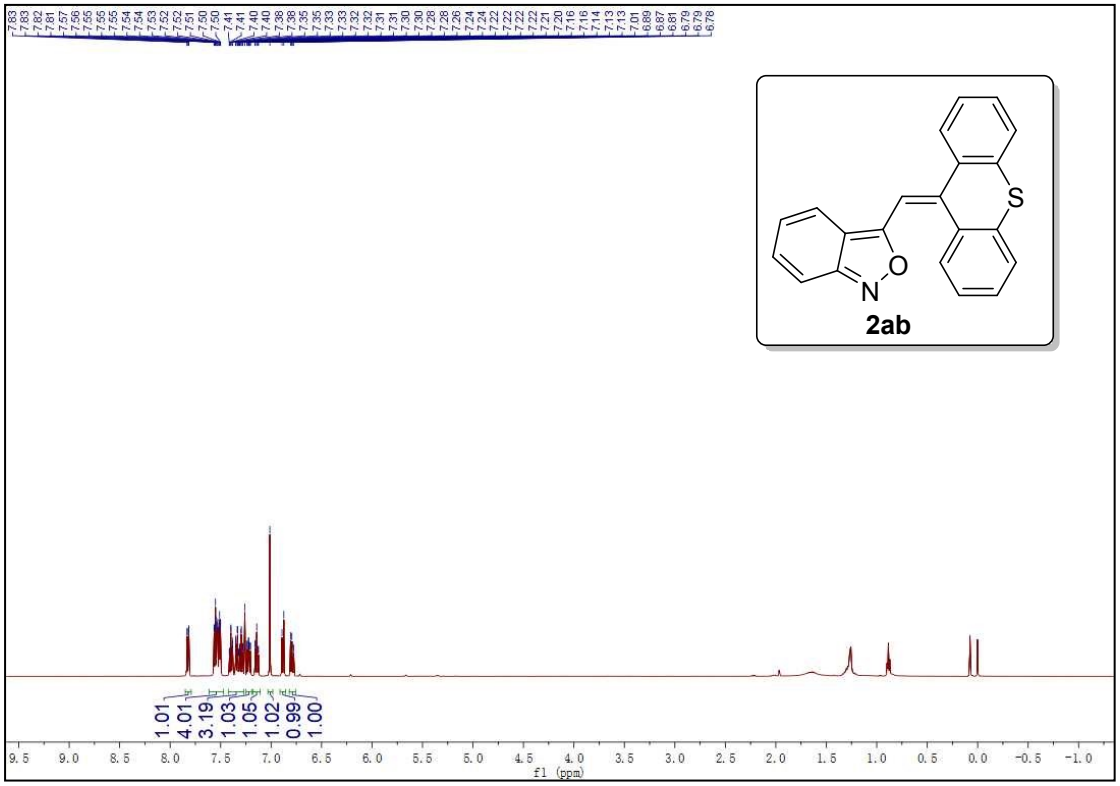


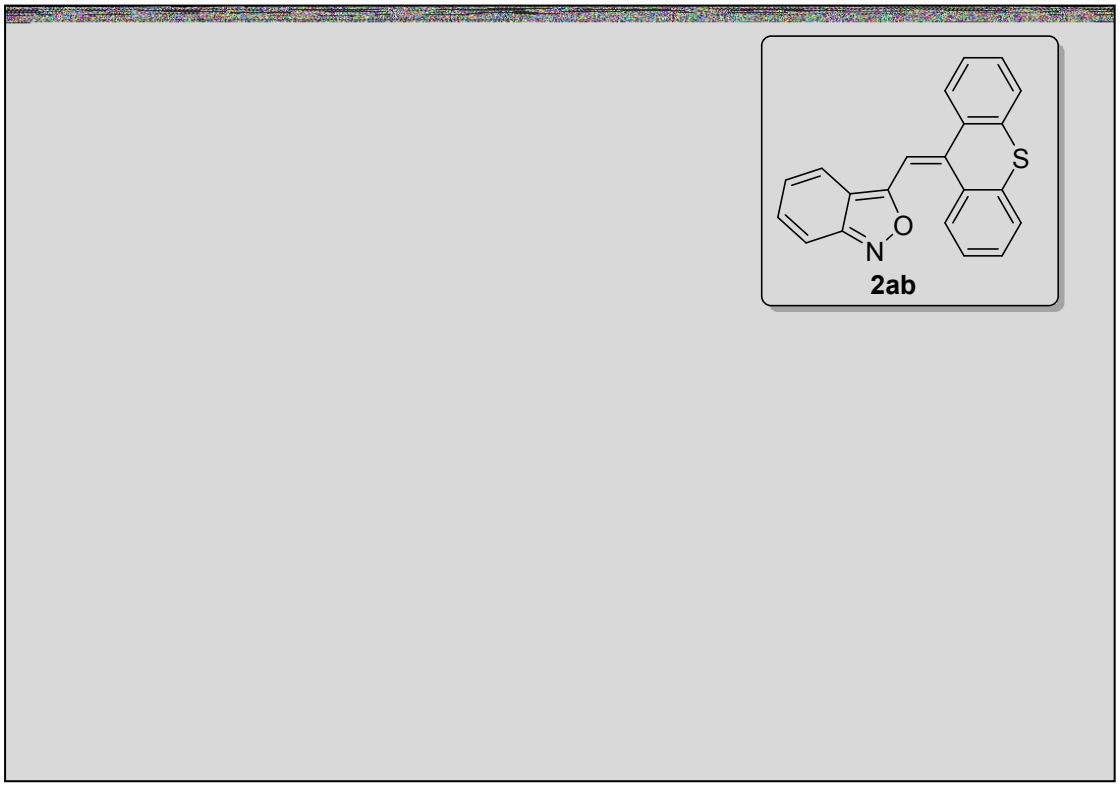




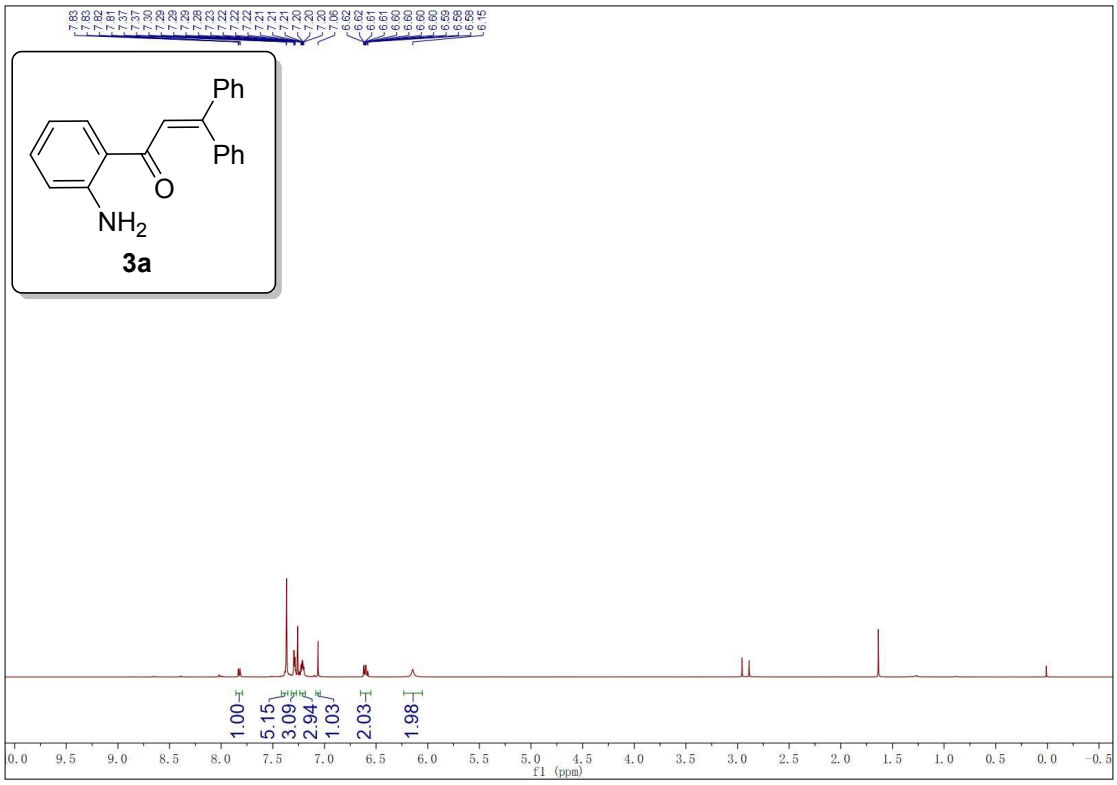
2aa

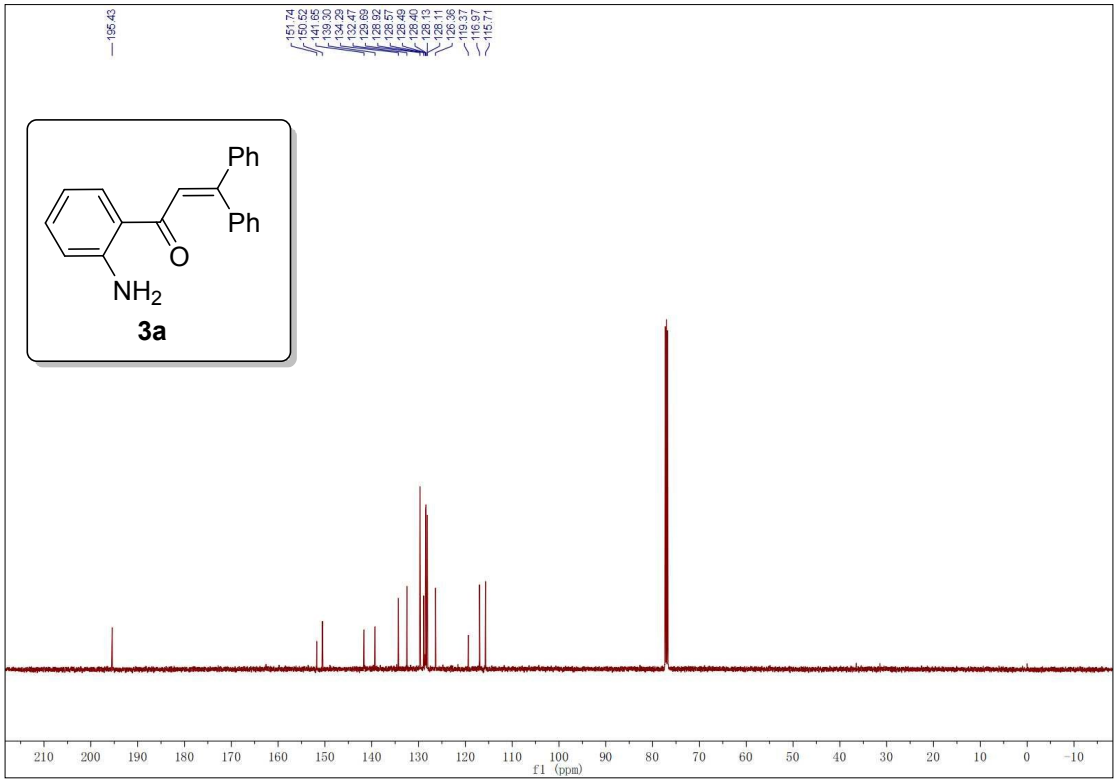
3-((9H-thioxanthen-9-ylidene)methyl)benzo[*c*]isoxazole (2ab)



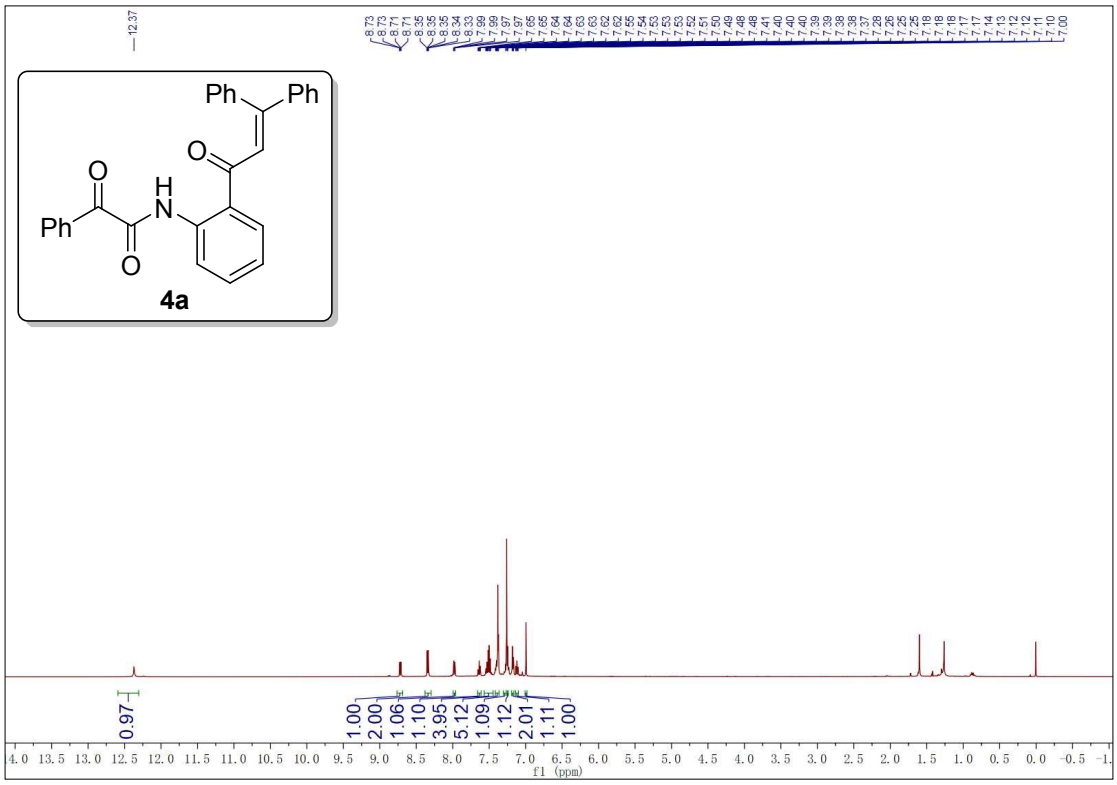


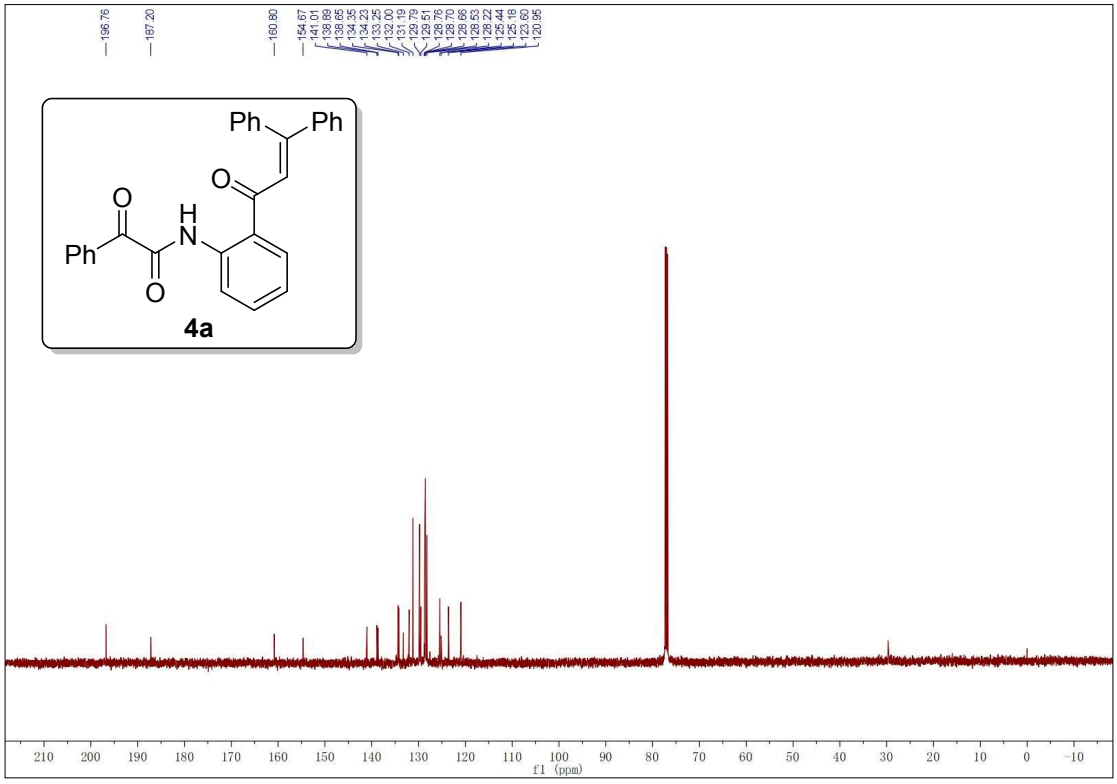
1-(2-aminophenyl)-3,3-diphenylprop-2-en-1-one (3a)





N-(2-(3,3-diphenylacryloyl)phenyl)-2-oxo-2-phenylacetamide (4a)





N-(2-(3,3-diphenylacryloyl)phenyl)benzamide (5a)