Supporting Information

Practical Synthesis of 3-Aryl Anthranils via an Electrophilic Aromatic Substitution Strategy

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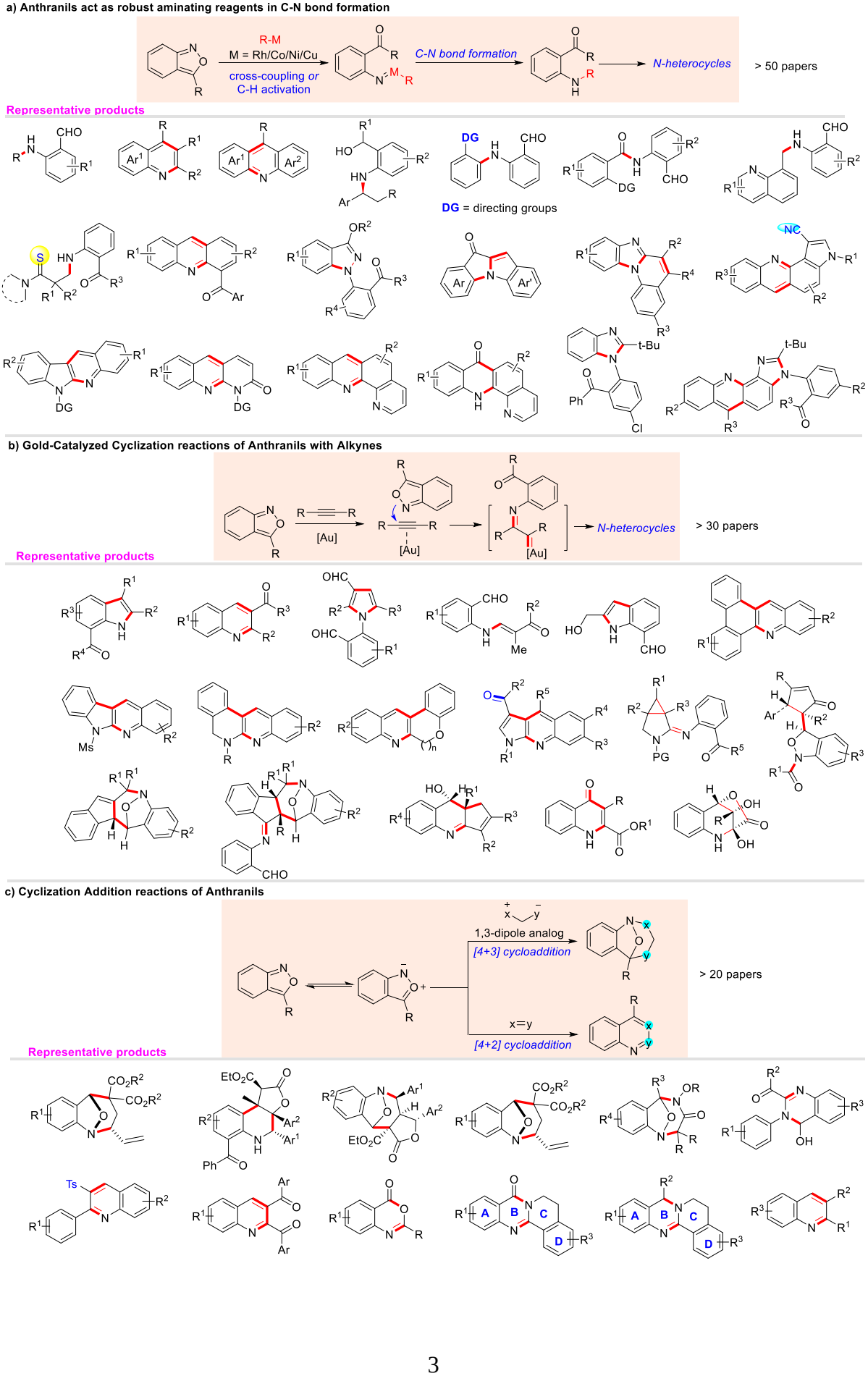
Figure S1. Anthranils as versatile building blocks in organic synthesis.[1]



1. General Methods

General analytical information:

All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum under argon atmosphere. All optimization reactions were monitored by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. NMR spectra were recorded at ambient temperature using $CDCl_3$ as solvent, with proton, carbon, and fluorine resonances at 400, 100 and 375 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Column chromatography was performed with 200-300 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}). Mass spectral data were acquired on a Varian GC-MS Saturn 2100 T. The ionization was achieved by EI AGC. HRMS analyses were carried out on a Waters GCT Premier CAB163 with a TOF mass analyzer. The MS ionization was achieved by EI^+. Melting points were measured on a Mettler FP 61 and are uncorrected. Parallel heating mantle were used in our experiments.

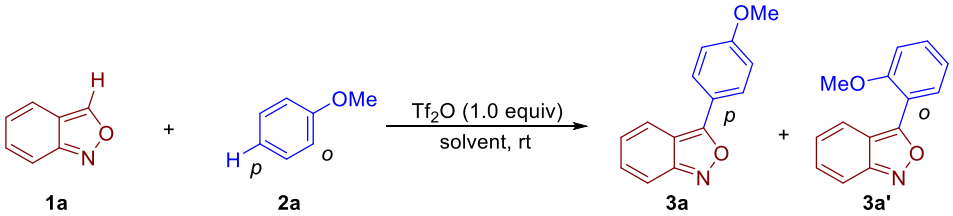
General reagent information:

All solvents were purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system. Commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Acros, Innochem, Adamas-beta, Aladdin, Bide Pharmatech, and were used as received.

3-Position unsubstituted anthranils were synthesized according to the literature procedure,[2] and were reported in our previous works.[3]

2. Conditions Optimization

Table S1. The screening of reaction solvent.[a]

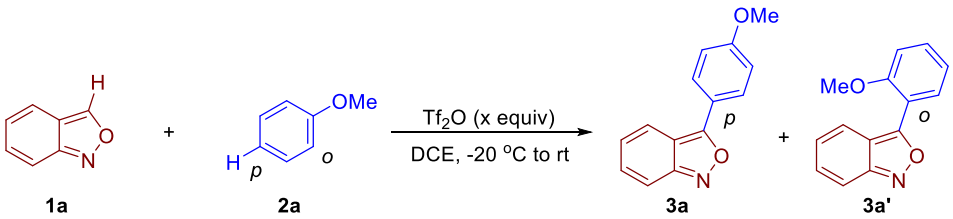


entry	solvent	*p*:*o*[b]	yield of **3a** (%)[c]
1	DCM	13:1	45
2	DCE	13:1	68
3	$CHCl_3$	12:1	32
4	CCl_4	13:1	53
5	MeCN	-	0
6	1,4-dioxane	-	0
7	DMF	-	0

[a] Reaction conditions: To a solution of **1a** (0.2 mmol) in the specified solvent (1.0 mL), Tf_2O (0.2 mmol) was added at room temperature. Subsequently, **2a** (0.2 mmol) was added and the resulting mixture continued to

stir under air atmosphere for 5 h. [b] Ratio was determined by GC-MS analysis. [c] Yields was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

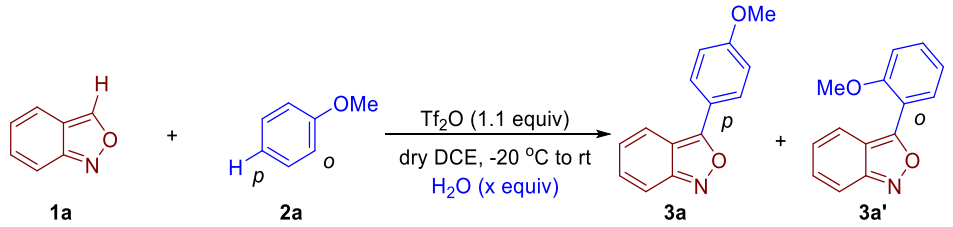
Table S2. Screening the amount of Tf_2O.[a]



entry	Tf_2O (x equiv)	*p:o*[b]	yield of **3a** (%)[c]
1	0.5	13:1	42
2	1.0	13:1	79
3	1.1	14:1	86
4	1.2	14:1	80
5	1.5	13:1	78
6	2.0	12:1	75

[a] Reaction conditions: To a solution of **1a** (0.2 mmol) in DCE (1.0 mL), Tf_2O (x equiv) was added at -20 °C. Subsequently, **2a** (0.24 mmol) was added. The resulting mixture slowly increased to room temperature, and continued to stir under air atmosphere for 5 h. [b] Ratio was determined by GC-MS analysis. [c] Yields was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

Table S3. The influence of H_2O on the reaction.[a]



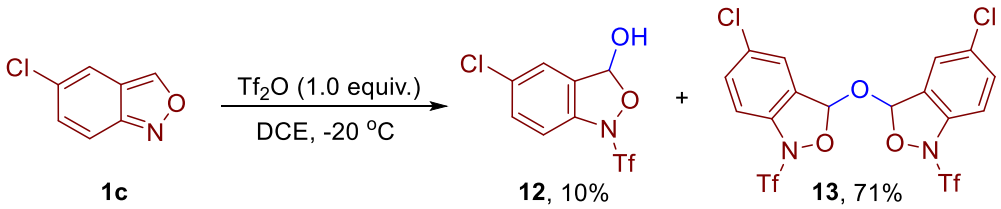
entry	x	*p:o*[b]	yield of **3a** (%)[b]
1	0	14:1	86
2	1	14:1	83
3	2	13:1	80

[a] Reaction conditions: To a solution of **1a** (0.2 mmol) in DCE (1.0 mL), x equivalent of H_2O was added. Subsequently, Tf_2O (0.22 mmol) and **2a** (0.24 mmol) was successively added at -20 °C. The resulting mixture slowly increased to room temperature, and continued to stir under air atmosphere for 5 h. [b] Ratio was determined by GC-MS analysis. [c] Yields was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

As indicated in Table S3, the reaction still proceeded smoothly when a small amount of H_2O was added and no significant decrease on the yield of **3a** was observed.

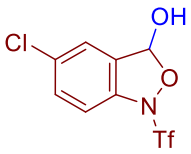
3. Mechanistic study

3.1 The reaction of anthranil 1c and Tf_2O.



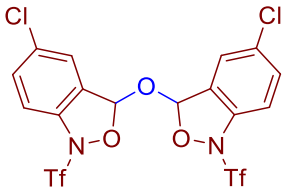
To a solution of 5-chlorobenzo[c]isoxazole **1c** (0.2 mmol) in 1.0 mL DCE, Tf_2O (0.2 mmol) was added dropwisely via syringe at -20 °C. After stirring at -20 °C for 5 min, the reaction mixture was quenched with saturated sodium bicarbonate aqueous solution (2 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). Compound **12** (6.1 mg) was obtained in 10% yield and **13** (41.8 mg) was isolated in 71% yield.

5-Chloro-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazol-3-ol (12)



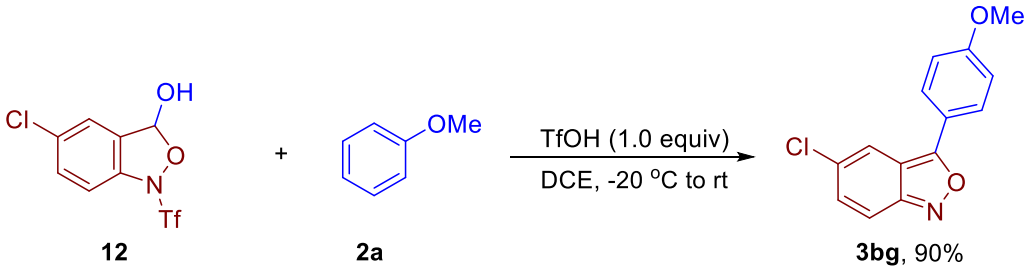
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.52 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 6.80 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.94, 134.12, 132.00, 128.18, 125.15, 119.50 (q, *J* = 327.6 Hz), 116.82, 102.84. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.13. **HRMS (ESI)** m/z calcd. for $C_8H_4ClF_3NO_4S$ $[M-H]^-$ 301.95071, found 301.95092.

3,3'-Oxybis(5-chloro-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole) (13)



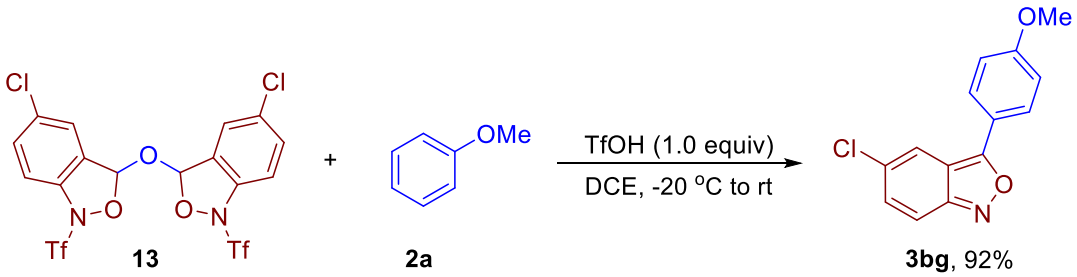
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.7 Hz, 2H), 7.47 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.82 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.73, 133.97, 131.46, 129.76, 124.54, 119.2 (q, *J* = 324.6 Hz), 117.36, 101.16. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.85. **HRMS (ESI)** m/z calcd. for $C_{16}H_9F_6N_2O_7S_2$ $[M-H]^-$ 518.97608, found 518.97435.

3.2 The reaction of intermediate 10 and anisole.



To a solution of **12** (0.05 mmol) in 0.5 mL DCE, anisole **2a** (0.1 mmol) was added. The solution was cooled to -20 °C and TfOH (0.05 mmol) was added dropwisely via microsyringe. The resulting mixture was slowly warmed to room temperature and the reaction was continued for 5 hours. After the completion of the reaction, the reaction mixture was quenched with saturated sodium bicarbonate aqueous solution (2 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The crude product was analyzed with ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The expected product **3bg** was detected in 90% yield.

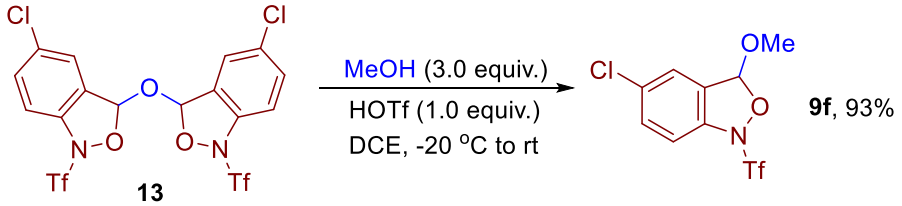
3.3 The reaction of intermediate 13 and anisole.



To a solution of **13** (0.1 mmol) in 1.0 mL DCE, anisole **2a** (0.12 mmol) was added. The solution was cooled to -20 °C and TfOH (0.1 mmol) was added dropwisely via microsyringe. The resulting mixture was slowly warmed to room temperature and the reaction was continued for 5 hours. After working up, the crude product was analyzed with ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The expected product **3bg** was detected in 92% yield.

These experiments indicated that compound **12** and **13** are possible intermediates in the formation of 3-aryl anthranils.

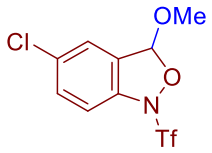
3.4 Nucleophilic substitution of 13 with MeOH



To a solution of **13** (0.1 mmol) in 1.0 mL DCE, MeOH (0.3 mmol) was added. The solution was cooled to -20 °C and TfOH (0.1 mmol) was added dropwisely via syringe. The resulting mixture was slowly warmed to room temperature and the reaction was continued for 30 min. The reaction was quenched with saturated

sodium bicarbonate aqueous solution (2 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). Compound **9f** (58.9 mg) was obtained in 93% yield.

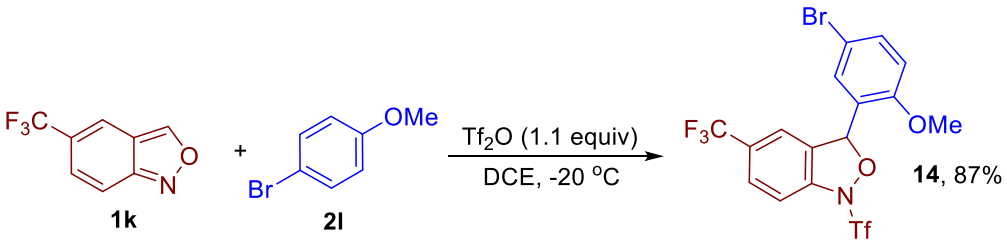
5-Chloro-3-methoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (9f)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 11.1, 2.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 6.30 (s, 1H), 3.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.0, 133.3, 131.2, 129.8, 124.2, 119.8 (q, *J* = 328.4 Hz), 116.6, 107.3, 56.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.64. **HRMS (ESI)** m/z calcd. for $C_9H_6ClF_3NO_4S$ $[M-H]^-$ 315.96636, found 315.96671.

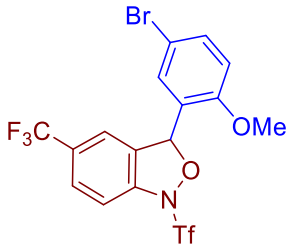
This experiment indicated that compound **13** could undergo a nucleophilic substitution with MeOH in the present of TfOH. The reaction of **13** and **2a** may also go through a similar nucleophilic substitution process.

3.5 Synthesis of intermediate 14.



To a solution of 5-(trifluoromethyl)benzo[c]isoxazole **1k** (0.2 mmol) in 1.0 mL DCE, Tf_2O (0.22 mmol) was added dropwisely via syringe at -20 °C. Then 1-bromo-4-methoxybenzene **2l** (0.24 mmol) was added. After stirring at 0 °C for 30 min, the resulting mixture was quenched with saturated sodium bicarbonate aqueous solution (2 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). Intermediate **14** was obtained in 87% yield (86.5 mg) and was full characterization.

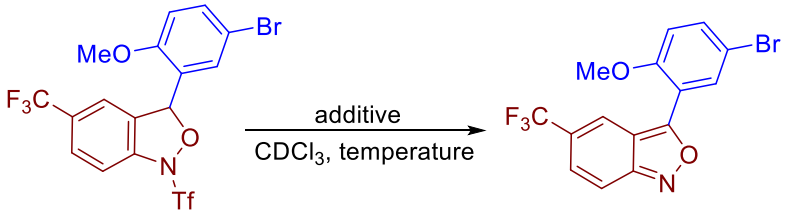
3-(5-Bromo-2-methoxyphenyl)-5-(trifluoromethyl)-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (14)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (m, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.28 (s, 1H), 7.12 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 137.5, 137.3, 133.7, 132.2 (q, *J* = 33.4 Hz), 131.0, 126.2, 125.6 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 272.8 Hz), 123.8, 119.6 (q, *J* = 325.4 Hz), 113.9 (q, *J* =3.7 Hz), 113.3, 112.9, 82.3, 56.0. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.4, -71.0. **HRMS (ESI)** m/z calcd. for $C_{16}H_9BrF_6NO_4S$ $[M-H]^-$ 503.93453, found 503.93467.

3.6 Rearomatization of intermediate 14 for the synthesis of 3bs.

Table S4. Conditions optimization and control experiments for the rearomatization of intermediate **14**.[a]



14 **3bs**

entry	additive	oxidant	T/^{o}C	yield of **3bs** (%)[b]
1	-	air	rt-60	0
2	-	DDQ (2 equiv.)	rt-60	0
3	-	$K_2S_2O_8$ (2 equiv.)	rt-60	0
4	-	Ag_2O (2 equiv.)	rt-60	0
5	TfOH (5 equiv.)	air	rt	91
6	TfOH (5 equiv.)	DDQ (2 equiv.)	rt	100
7	TfOH (5 equiv.)	$K_2S_2O_8$ (2 equiv.)	rt	100
8	MsOH (5 equiv.)	air	60	86
9	TFA (5 equiv.)	air	60	71
10	HOAc (10 equiv.)	air	80	21
11[c]	TfOH (5 equiv.)	-	rt	23
12[c]	TfOH (10 equiv.)	-	rt	53
13[c]	TfOH (15 equiv.)	-	rt	100
14[d]	K_2CO_3	air	60	100
15[c], [d]	K_2CO_3	-	60	100
16[e]	TfOH (2 equiv.)	air	rt	100

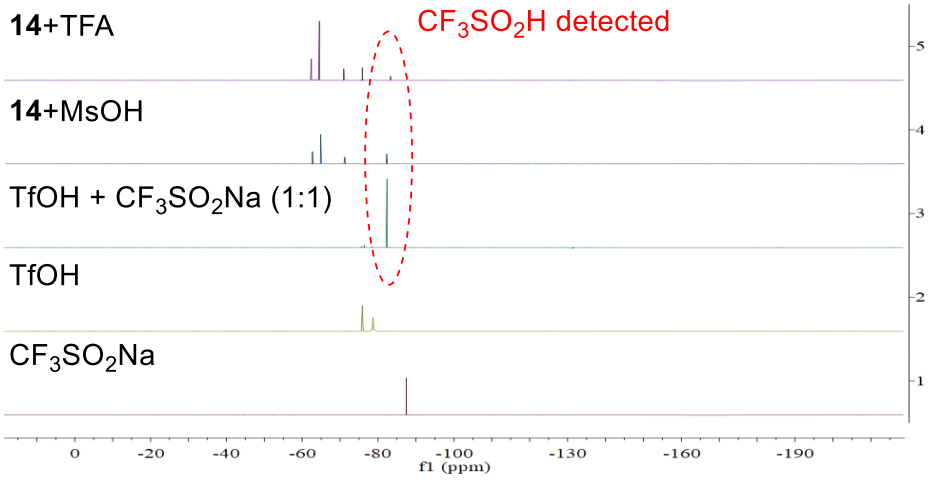
[a] Intermediate **14** (10.1 mg, 0.02 mmol) was dissolved in 0.6 mL $CDCl_3$, and then additive and/or oxidant was added. The reaction mixture was stirred overnight at specified temperature. [b] Yields were detected by ^{1}F MNR using (trifluoromethyl)benzene as the internal standard. [c] Under an argon atomsphere. [d] DMSO was used as the solvent. [e] The reaction was conducted on 0.1 mmol scale.

First, the aromatization of **14** was conducted with different oxidants such as air, DDQ, $K_2S_2O_8$ and Ag_2O. However, the desired product **3bs** was not detected and **14** was recovered (entries 1-4). The addition of TfOH to simulate the real reaction environment significantly promoted this conversion (entries 5-7). Other acid such asmethanesulfonic acid (MsOH), trifluoroacetate (TFA), and even acetic acid (HOAc) could aslo promote this conversion (entries 8 and 10). Furthermore control experiments revealed that this conversion could proceed smoothly without any additional oxidants, and increasing the amount of TfOH could improve the conversion (entries 11 and 13). In addition, the conditions used in Cory and Tan's work were tested.[4] The conversion could proceed smoothly in the presence of K_2CO_3/DMSO either under air or agron (entries 14 and 15). It should be mentioned that 2.0 equivlent of TfOH is enough to promot this conversion efficently when the reaction was conducted on 0.1 mmol scale (entry 16).

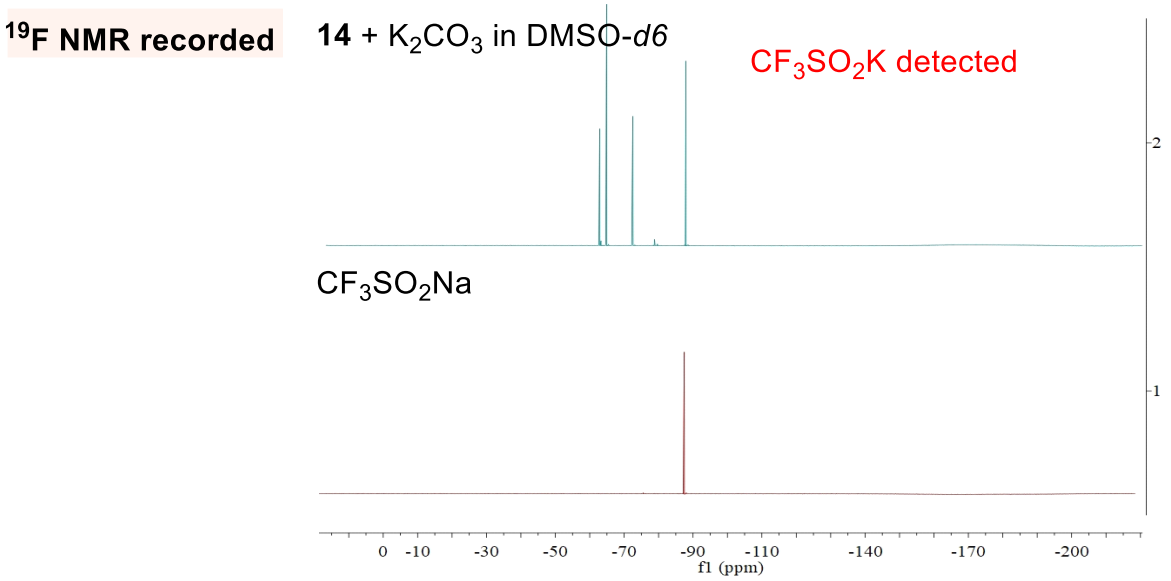
This result suggests that aromatization of **14** could occur under either acidic or basic conditions, and oxidant is not necessary for this conversion.

Detection of CF_3SO_2H

^{19}F NMR recorded



CF_3SO_2H was in situ-formed as a standard via the reaction of TfOH and CF_3SO_2Na in $CDCl_3$. The new peak at -82.4 ppm was assigned to be CF_3SO_2H. From the ^{19}F NMR spectrum recorded, the same peak at -82.4 ppm was detected when MsOH or TFA was used as an additive in the aromatization of **14**. These results indicated that the aromatization of **14** is likely to be an elimination process of CF_3SO_2H.

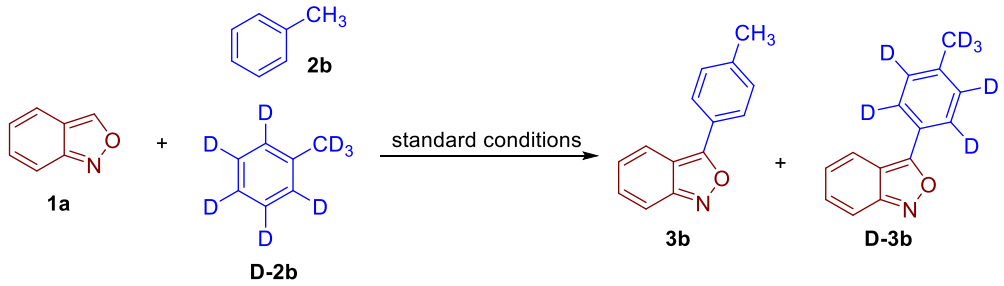


The ^{19}F NMR of CF_3SO_2Na was recorded in D_2O, and the peak at -87.4 ppm was assigned to CF_3SO_2Na. Under the conditions of K_2CO_3 in DMSO-*d6*, **3bs** was detected in 67% yield after 2 h. Meanwhile, the same peak at -87.4 ppm was obseved. This result was consistent with the elimination of CF_3SO_2H in the aromatization of **14**.

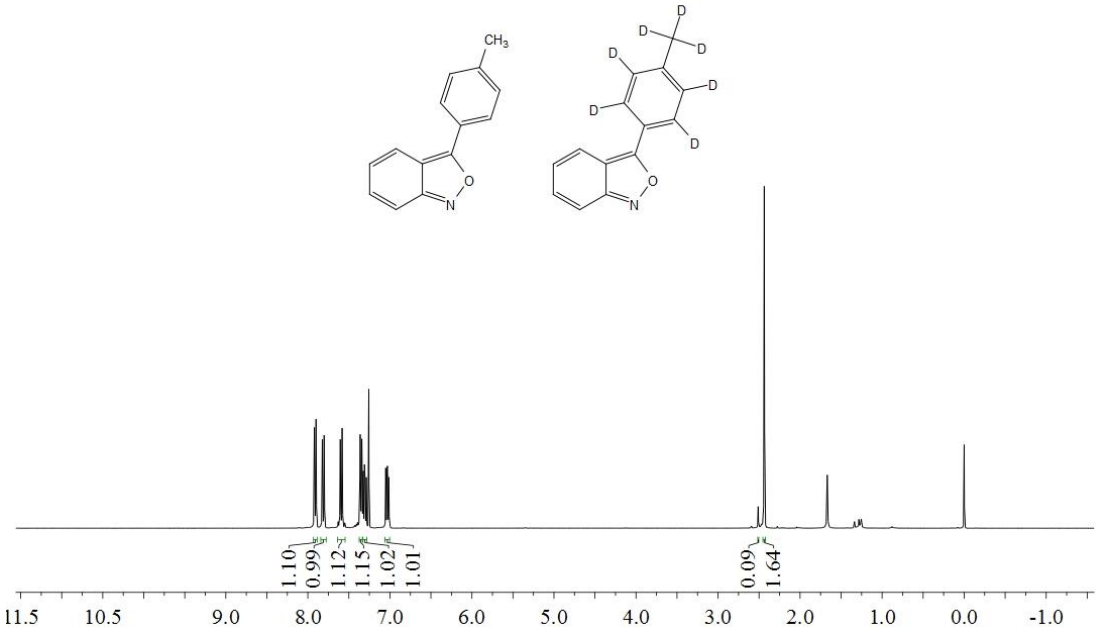
In addition, compared with the reaction under argon atmosphere (entry 11), the reaction with oxidant such as air, DDQ, and $K_2S_2O_8$ gave higher conversions (entries 5-7). This may because the eliminated CF_3SO_2H was smoothly oxidized to TfOH in the presence of oxidants, thus could further promot the conversion.

3.7 Kinetic isotope effects (KIE) experiments.

3.7.1 Competitive kinetic isotope effect measurement

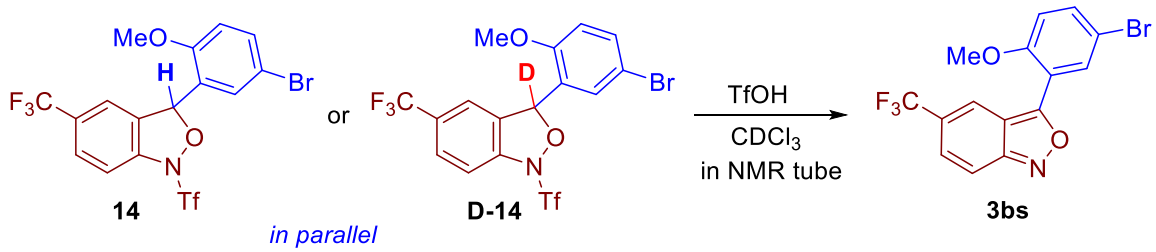


An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with anthranils **1a** (0.3 mmol) and DCE (1.0 mL). The resulting solution was cooled to -20 ^oC and Tf_2O (0.33 mmol) was added dropwisely via syringe. Then toluene (0.3 mmol) and toluene-*d8* (0.3 mmol) was added. The reaction was slowly raised to room temperature, and continued to stir for 30 min. Saturated sodium bicarbonate aqueous solution (2 mL) was added to quench the reaction. After evaporating the solvent under reduced pressure (rotary evaporator), the residue was purified by by column chromatography. A mixture of **3b** and **D-3b** were obtianed in 45% yield and the KIE value 1.1 was determined by the ^1H NMR spectrum of the obtained product.



This result suggests that C-H bond cleavage of nucleophilic arenes is not likely involved in the rate-determining step in this reaction.

3.7.2 Parallel kinetic isotope effect of 14 and deuterated D-14



To a NMR tube, a solution of (10.1 mg, 0.02 mmol) **14** in $CDCl_3$ (0.3 mL) and trifluorotoluene (4.9 ul, 0.04 mmol) as an internal standard was successively added. Then, a solution of TfOH (0.1 mmol) in $CDCl_3$ (0.3 mL) was added in one pot. The reaction mixture was analyzed by ^{19}F NMR in 5 min, 10 min, 15 min and 25 min. The yields of **3bs** was determined by the integration of the characteristic peak against the internal standard (trifluorotoluene) and was collected in Table S3. **The actual recording time is when the ^{19}F NMR is completed.** The parallel experiments with **D-14** were conducted in the same procedure described above and the ^{19}F NMR yields were collected.

Table S5. ^{19}F NMR yields of 3bm detected in the parallel KIE experiments

Time(min)	6.3	13.3	20	29.3
D-14	5%	10%	14%	16%
Time(min)	6.8	14.4	21.7	29
14	8%	18%	24%	30%

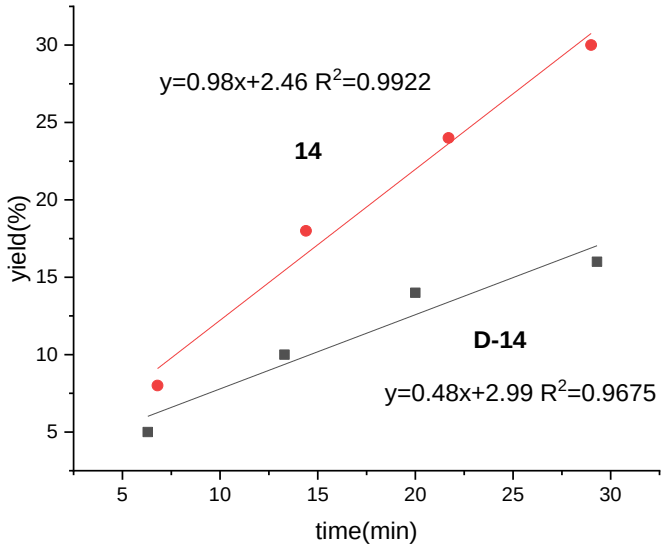
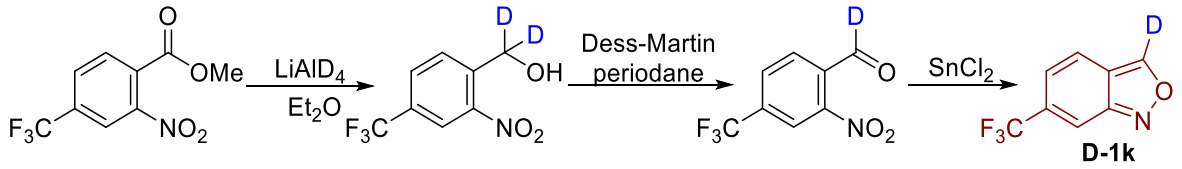


Figure S2. Reaction profile of **14** and **D-14**.

The observed K_H/K_D is 2.04, suggesting that elimination of CF_3SO_2H is likely the rate-determining step in this reaction.

The synthesis of deuterated D-14

6-(Trifluoromethyl)benzo[c]isoxazole-3-d (**D-1k**) was synthesized following the reported procedure.[5]

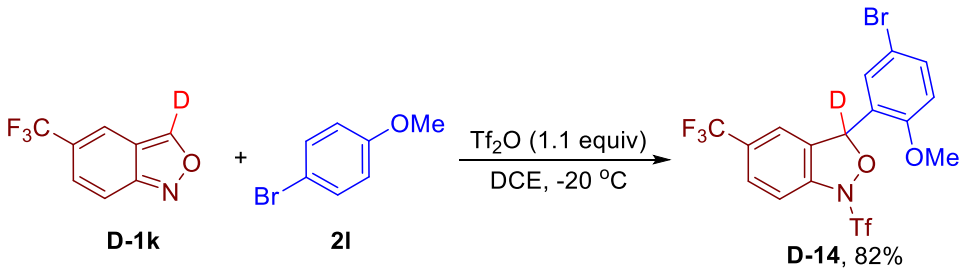


(2-Nitro-4-(trifluoromethyl)phenyl)methan-d2-ol: In a flame-dried schlenk flask, methyl 2-nitro-4-(trifluoromethyl)benzoate (4.0 mmol) was placed under argon, and dissolved in ether (20 mL). The solution was cooled to 0 ºC and $LiAlD_4$ (6.0 mmol) was added portionwise and stirred overnight at room temperature. Then, cold water was added dropwise and the aqueous phase was extracted with ether (3x20mL). The combined organic layers were washed with a saturated aqueous solution of brine and dried over $MgSO_4$. Solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) to give 0.67 g (2-nitro-4-(trifluoromethyl)phenyl)methan-d2-ol in 75% yield.

2-Nitro-4-(trifluoromethyl)benzaldehyde-d: The obtained benzyl alcohol (2.0 mmol) was dissolved in dry dichloromethane (15 mL), and Dess-Martin periodane (3.0 mmol) was added. The reaction was stirred for 2 hours at room temperature. The reaction was washed with an aqueous solution of $Na_2S_2O_3$ (10%) and a saturated aqueous solution of $NaHCO_3$ (1:1), dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) to give the expected product in 60% yield (264 mg).

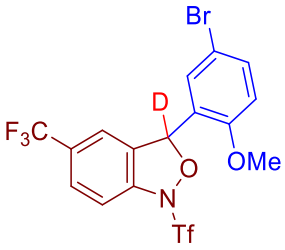
6-(Trifluoromethyl)benzo[c]isoxazole-3-d (D-1k): The above obtained aldehyde (264 mg) was dissolved in Ethyl acetate/Methanol 1:1 (10 mL) and was added $SnCl_2{\cdot}2H_2O$ (3.6 mmol). The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by saturated $NaHCO_3$, and filtered and

washed with DCM. Organic layer was then washed with water and brine, dried over $MgSO_4$ and concentrated. Crude product was then purified by flash chromatography on silica gel using (EA/Hexane = 1:50) to give 198 mg 6-(trifluoromethyl)benzo[c]isoxazole-3-d in 88% yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.0 Hz, 1H), 7.71 (d, *J* = 9.1 Hz, 1H), 7.14 (dd, *J* = 9.1, 1.0 Hz, 1H). **^{19}F NMR** (375 MHz, $CDCl_3$) δ -64.64.

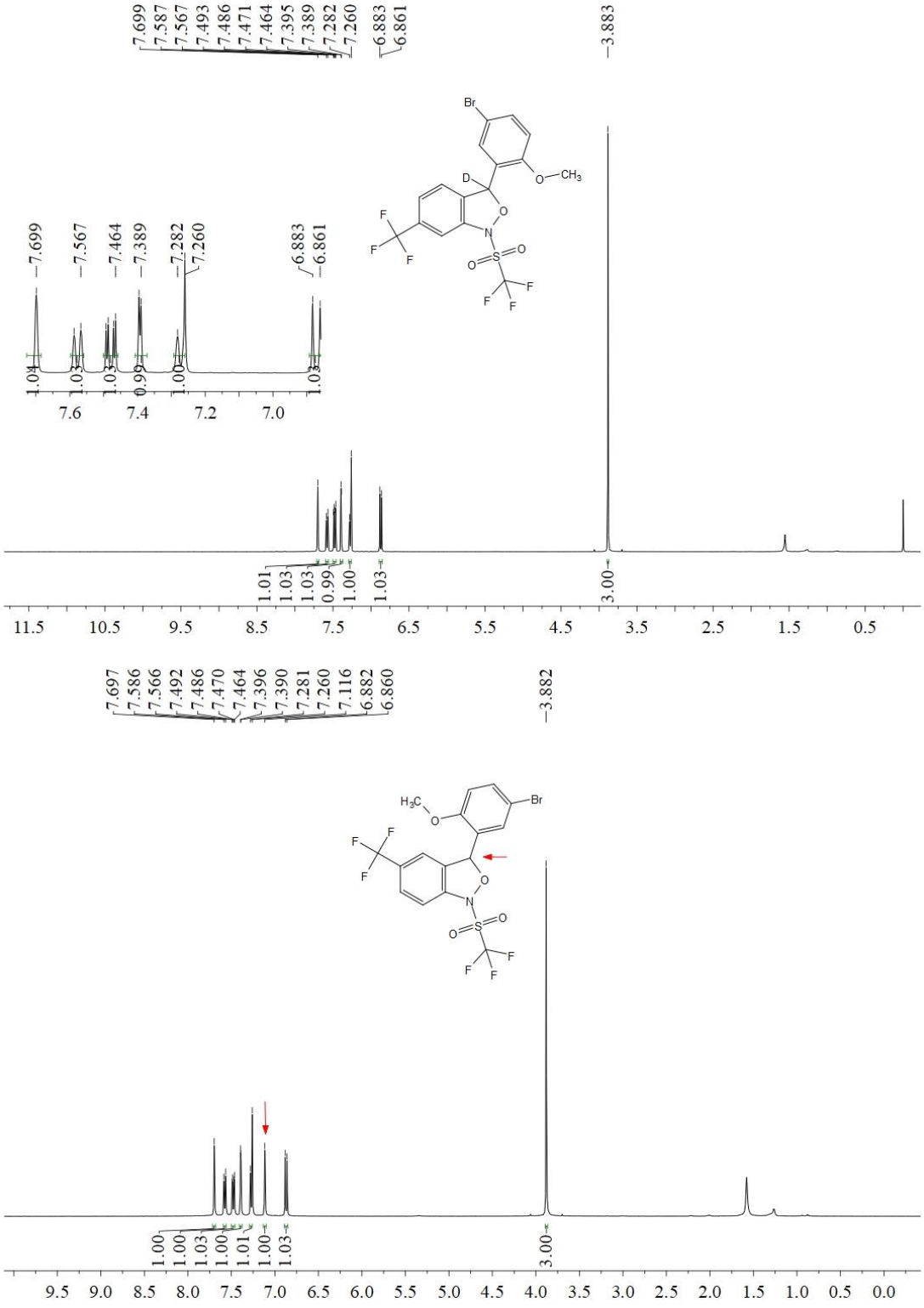


To a solution of 5-(trifluoromethyl)benzo[c]isoxazole-3-*d* **D-1k** (0.2 mmol) in 1.0 mL DCE, Tf_2O (0.22 mmol) was added dropwisely via syringe at -20 °C. Then 1-bromo-4-methoxybenzene **2l** (0.24 mmol) was added. After stirring at 0 °C for 30 min, the resulting mixture was quenched with saturated sodium bicarbonate aqueous solution (2 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). **D-14** (83.0 mg) was obtained in 82% yield.

3-(5-Bromo-2-methoxyphenyl)-5-(trifluoromethyl)-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole-3-d (D-14)

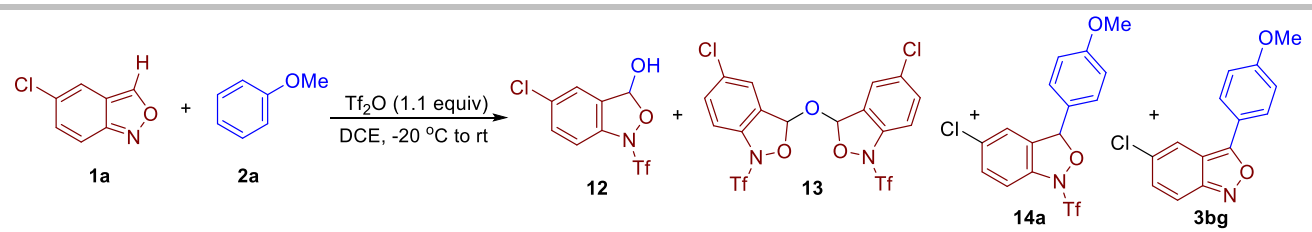


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.28 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H) ppm.



3.8 The direct addition of anisole 2a to oxonium intermediate

As described above, anthranils would rapidly react with Tf_2O to produce intermediates **12** and **13**, which then reacted with anisole **2a** to give the desired products. However, when anisole **2a** was added before the addition of Tf_2O, only a small amount of intermediates **12** and **13** was detected, instead intermediate **14a** was smoothly formed in good yields. This result indicated that nucleophilic arenes could directly add to the active oxonium intermediate. The detailed experiments are as follows:

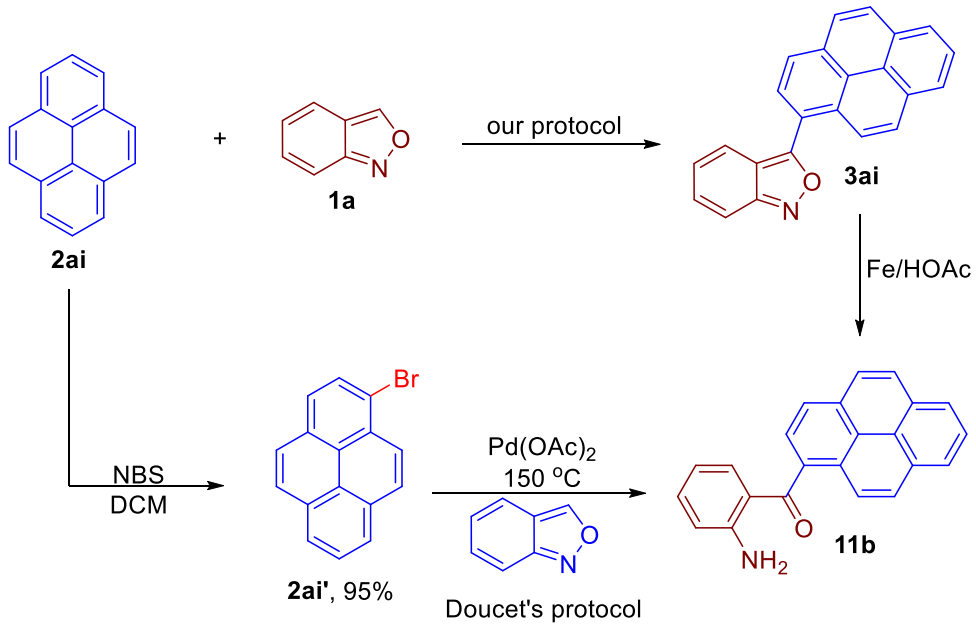


To a solution of anthranil **1a** (0.2 mmol) and anisole **2a** (0.24 mmol) in 1.0 mL DCE, CH_2Br_2 (0.1 mmol) was added as the internal standard. Then Tf_2O (0.22 mmol) was added dropwisely via syringe at -20 °C. The reaction was stirred at -20 °C, and a set of samples were taken at 1 min (once Tf_2O was added), 2 min, 5 min and 10 min. The samples were transferred to a NMR tube with $CDCl_3$ as the solvent. The yields of each compounds were determined by the integration of the characteristic peak against the internal standard and were recorded in the table below.

Time (min) / Yields (%)	1	2	5	15
12	trace	trace	0	0
13	6	12	7	5
14a	53	65	77	58
3bg	0	0	5	16

Intermediate **14a** was formed in relatively high yields and only a small amount of **13** was detected when anisole was added before the addition of Tf_2O. This is probably because anisole is a favorable nucleophile in the competition with H_2O in the reaction with oxonium intermediate. These results indicated that anisole could directly add to the oxonium intermediate.

4. Comparing the regioselectivity of this reaction with electrophilic bromination of PAHs.



Bromopyrene (**2ai'**) was synthesized according to the reported method: To a solution of pyrene (507.3 mg, 2.508 mmol, 1 equiv) in DCM (8.5 mL), NBS (467.1 mg, 2.624 mmol, 1.05 equiv) was added and the

resulting solution stirred for 6 h at room temperature. The reaction mixture was diluted with DCM (20 mL) and washed with brine (2x15 mL). The aq. layer was washed with DCM (10 mL) and the combined organic layers were dried over $MgSO_4$ and evaporated. Purification by column chromatography (silica; hexane) gave 1-bromopyrene **2ai'** (673.0 mg, 95%).

(2-Aminophenyl)(pyren-1-yl)methanone (**11b**) was synthesized according to the method reported by Doucet et al.:[6] The obtained 1-bromopyrene **2ai'** (1 mmol), anthranil **1a** (0.179 g, 1.5 mmol), KOAc (0.196 g, 2 mmol), and $Pd(OAc)_2$ (4.4 mg, 0.02 mmol) were dissolved in DMA (4 mL) under an Ar atmosphere. The reaction mixture was stirred at 150 ^oC for 20 h. Then the solvent was evaporated and the product was purified by silica gel column chromatography, giving **11b** in 51% yields.

The same product (**11b**) was obtained through our method and following reduction by Fe/HOAc. This result indicated that the regioselectivity of polycyclic aromatic hydrocarbons (PAHs) in this cross-dehydrogenative-coupling is similar to the selectivity in electrophilic bromination. The reaction occurs selectively at the most nucleophilic carbon atom of the benzene ring with the lowest aromaticity.[7]

5. General procedure A for the synthesis of C3 functionalized anthranils 3, 5, 7 and 9

An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with anthranil **1** (0.3 mmol) and DCE (1.0 mL). The resulting mixture was cooled to -20 ^oC and Tf_2O (0.33 mmol) was added dropwisely via syringe. Subsequently, nucleophilic arene **2** was added in one pot. The resulting mixture was stirred at -20 ^oC for 5 min. Then, the reaction was slowly raised to room temperature, and continued to stir for 5 hours. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with DCM (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator).The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

6. Gram scale synthesis of 4-(benzo[c]isoxazol-3-yl)-*N*,*N*-diphenylaniline (3i)

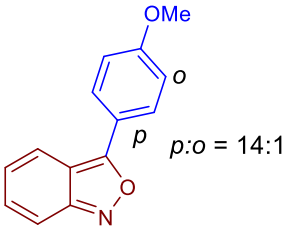
An oven-dried 50 mL flask equipped with a Teflon-coated stirring bar was charged with anthranil **1** (5 mmol) and DCE (15 mL). The resulting mixture was cooled to -20 ^oC and Tf_2O (5.5 mmol) was added dropwisely via syringe. Subsequently, the obtained mixture was added dropwisely to a solution of triphenylamine (6 mmol) in 15 mL DCE at -20 ^oC. After finishing, the reaction continued to stir for at -20 ^oC for another 5 min (extending the reaction time leads to lower yield). Then, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with DCM (20 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator).The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient), and 1.05 g 4-(benzo[c]isoxazol-3-yl)-*N*,*N*-diphenylaniline (**3i**) was obtained in 58% yield.

7. General procedure B for the synthesis of 2-aminodiaryl ketones (11)

The first step was following the standard reaction conditions. An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with anthranil **1** (0.3 mmol) and DCE (1.0 mL). The resulting mixture was cooled to -20 ^{o}C and Tf_2O (0.33 mmol) was added dropwisely via syringe. Subsequently, nucleophilic arene **2** was added in one pot. The resulting mixture was stirred at -20 ^{o}C for 5 min. Then, the reaction was slowly raised to room temperature, and continued to stir for 5 hours. After completion of the reaction, DCE was removed using rotary evaporator and 1.5 mL HOAc/H_2O (2:1) was added as solvent. Fe powder (0.6 mmol) was added and the resulting mixture was vigorous stirring at 90 ^{o}C for 4 hours. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

8. Synthesis and Characterization of the Corresponding Products

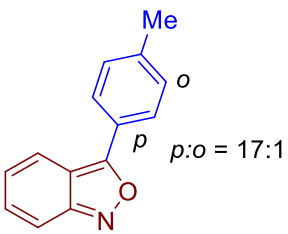
3-(4-Methoxyphenyl)benzo[c]isoxazole (3a)[8]



The title compound **3a** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and anisole **2a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (54.7 mg, 81%), m.p 86-88 °C; (lit. [8] 97-99 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 9.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.04 (dd, *J* = 6.7, 4.8 Hz, 2H), 6.99 (dd, *J* = 8.7, 6.4 Hz, 1H), 3.86 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 161.1, 157.7, 130.5, 128.1, 123.9, 121.1, 120.7, 115.2, 114.7, 113.5, 55.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.08626, found 226.08619.

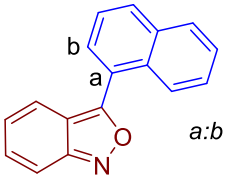
3-(*p*-Tolyl)benzo[c]isoxazole (3b)[6]



The title compound **3b** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and toluene **2b** (0.90 mmol) and purified by column chromatography (SiO_2, PE/EA = 15:1) as a light yellow solid (47.7 mg, 76%), m.p 84-86 °C; (lit. [6] 90-92 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (m, 1H), 7.05 – 7.00 (m, 1H), 2.43 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 157.8, 140.6, 130.5, 129.9, 126.5, 125.6, 124.2, 120.7, 115.3, 114.0, 21.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}NO$ $[M+H]^+$ 210.09134, found 210.09113.

3-(Naphthalen-1-yl)benzo[c]isoxazole (3c)[6]

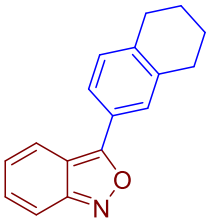


a:b = 10:1

The title compound **3c** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and naphthalene **2c** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 15:1) as a white solid (47.0 mg, 64%), m.p 78-79 °C; (lit. [6] 84-86 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.98 – 7.95 (m, 1H), 7.85 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.60 – 7.56 (m, 3H), 7.39 – 7.34 (m, 1H), 7.03 (dd, *J* = 8.8, 6.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 157.5, 133.9, 131.1, 130.8, 130.6, 128.6, 128.5, 127.4, 126.7, 125.4, 125.4, 125.2, 124.3, 120.8, 116.6, 115.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}NO$ $[M+H]^+$ 246.09134, found 246.09105.

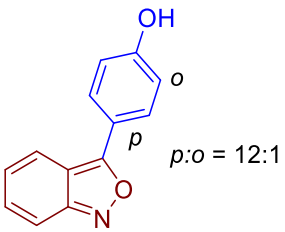
3-(5,6,7,8-Tetrahydronaphthalen-2-yl)benzo[c]isoxazole (3d)



The title compound **3d** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,2,3,4-tetrahydronaphthalene **2d** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 15:1) as a yellow solid (50.2 mg, 67%), m.p 67-69 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.30 (dd, *J* = 8.9, 6.5 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.86 (d, *J* = 16.1 Hz, 4H), 1.85 (t, *J* = 3.1 Hz, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 157.8, 140.1, 138.2, 130.5, 130.0, 127.2, 125.6, 124.1, 123.7, 120.9, 115.3, 114.0, 29.4, 22.9, 22.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.12264, found 250.12263.

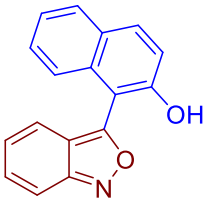
4-(Benzo[c]isoxazol-3-yl)phenol (3e)



The title compound **3e** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and phenol **2e** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 4:1) as a yellow solid (49.4 mg, 78%), m.p 180-182 °C.

^{1}H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.40 (dd, *J* = 9.1, 6.4 Hz, 1H), 7.09 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.03 – 6.97 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 160.3, 157.7, 131.7, 128.8, 124.6, 121.8, 119.2, 117.0, 115.0, 113.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{13}H_{10}NO_2$ $[M+H]^+$ 212.07060, found 212.07040.

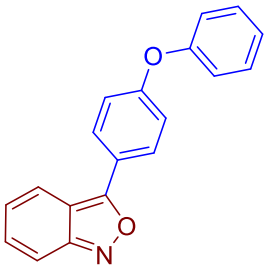
1-(Benzo[c]isoxazol-3-yl)naphthalen-2-ol (3f)



The title compound **3f** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and naphthalen-2-ol **2f** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 4:1) as a yellow solid (64.2 mg, 82%), m.p 188-190 °C.

^{1}H NMR (400 MHz, DMSO) δ 10.57 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.46 – 7.33 (m, 6H), 7.04 (dd, *J* = 8.7, 6.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 163.8, 157.2, 155.3, 133.4, 133.4, 131.8, 128.9, 128.2, 124.2, 124.0, 123.6, 122.1, 118.8, 117.8, 115.2, 106.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}NO_2$ $[M+H]^+$ 262.08626, found 262.08588.

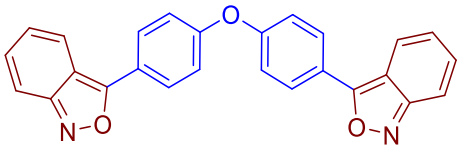
3-(4-Phenoxyphenyl)benzo[c]isoxazole (3g)



The title compound **3g** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and oxydibenzene **2g** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (64.5 mg, 75%), m.p 49-50 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 7.13 – 7.08 (m, 2H), 7.05 –7.02 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 159.5, 157.8, 155.9, 130.6, 130.0, 128.3, 124.3, 123.1, 120.6, 119.8, 118.7, 115.4, 113.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.10191, found 288.10161.

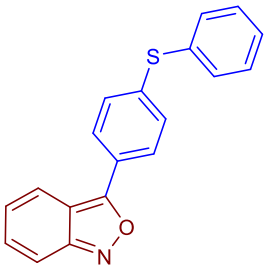
3,3'-(Oxybis(4,1-phenylene))bis(benzo[c]isoxazole) (3g')



The title compound **3g'** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.75 mmol) and oxydibenzene **2g** (0.3 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a light yellow solid (58.2 mg, 48%), m.p 221-223 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 4H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 9.1 Hz, 2H), 7.34 (m, 2H), 7.28 – 7.25 (m, 4H), 7.07 m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 158.1, 157.9, 130.7, 128.5, 124.6, 124.2, 120.4, 119.8, 115.5, 114.1 ppm. **HRMS** (ESI) m/z calcd. for Chemical Formula: $C_{26}H_{17}N_2O_3$ $[M+H]^+$ 405.12337, found 405.12320.

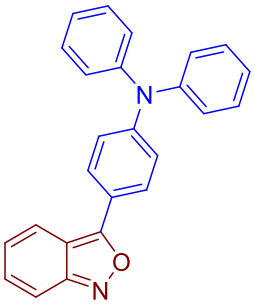
3-(4-(Phenylthio)phenyl)benzo[c]isoxazole (3h)



The title compound **3h** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and diphenylsulfane **2h** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (61.8 mg, 68%), m.p 69-71 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.42 - 7.37 (m, 5H), 7.34 – 7.30 (m, 1H), 7.04 (dd, *J* = 8.5, 6.7 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 157.8, 140.7, 133.2, 133.0, 130.6, 129.6, 129.2, 128.4, 127.0, 126.0, 124.6, 120.5, 115.5, 114.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{19}H_{14}NOS$ $[M+H]^+$ 304.07906, found 304.07858.

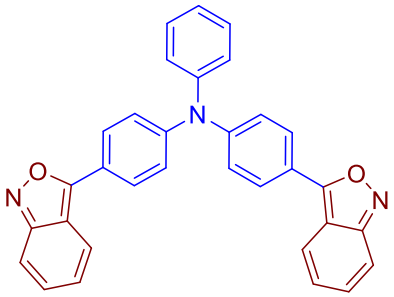
4-(Benzo[c]isoxazol-3-yl)-*N*,*N*-diphenylaniline (3i)



The title compound **3i** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and triphenylamine **2i** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (80.3 mg, 74%), m.p 131-133 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.31 (m, 5H), 7.22 – 7.09 (m, 8H), 7.00 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 157.8, 149.6, 146.7, 130.5, 129.5, 127.5, 125.5, 124.2, 123.8, 121.7, 121.1, 120.8, 115.2, 113.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{25}H_{19}N_2O$ $[M+H]^+$ 363.14919, found 363.14796.

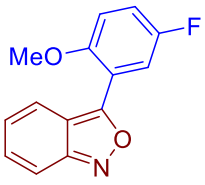
4-(Benzo[c]isoxazol-3-yl)-*N*-(4-(benzo[c]isoxazol-3-yl)phenyl)-*N*-phenylaniline (3i')



The title compound **3i'** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and triphenylamine **2i** (0.75 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow solid (43.2 mg, 30%), m.p 214-216 °C.

1H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 8.7 Hz, 4H), 7.82 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 9.1 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.31 (d, J = 8.7 Hz, 4H), 7.25 (m, 3H), 7.06 (dd, J = 8.7, 6.5 Hz, 2H) ppm. **13C NMR** (100 MHz, CDCl3) δ 164.1, 157.8, 148.6, 146.1, 130.6, 129.9, 127.7, 126.2, 125.2, 124.2, 123.6, 122.8, 120.7, 115.4, 113.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{32}H_{22}N_3O_2$ $[M+H]^+$ 480.17065, found 480.17031.

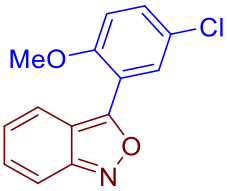
3-(5-Fluoro-2-methoxyphenyl)benzo[c]isoxazole (3j)



The title compound **3j** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-fluoro-4-methoxybenzene **2j** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a viscous yellow oil (44.5 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.30 (ddd, *J* = 9.1, 6.3, 0.8 Hz, 1H), 7.17 (ddd, *J* = 9.1, 7.6, 3.1 Hz, 1H), 7.03 – 6.97 (m, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 2.1 Hz), 157.9, 156.9 (d, *J* = 240.1 Hz), 152.5 (d, *J* = 2.1 Hz), 130.6, 123.7, 122.3, 118.6 (d, *J* = 8.3 Hz), 117.9 (d, *J* = 23.1 Hz), 116.7 (d, *J* = 25.1 Hz), 116.1, 115.2, 112.8 (d, *J* = 8.2 Hz), 56.11 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -122.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}FNO_2$ $[M+H]^+$ 244.07683, found 244.07661.

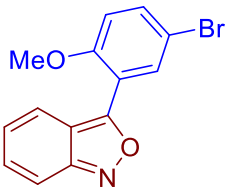
3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazole (3k)



The title compound **3k** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (57.5 mg, 74%), m.p 77-79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.6 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.41 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.30 (dd, *J* = 9.0, 6.4 Hz, 1H), 6.99 (dd, *J* = 8.9, 5.1 Hz, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 157.8, 154.8, 131.3, 130.6, 129.8, 126.2, 123.8, 122.1, 118.9, 116.1, 115.1, 112.9, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}ClNO_2$ $[M+H]^+$ 260.04728, found 260.04709.

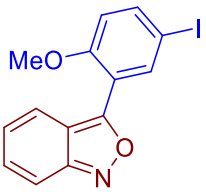
3-(5-Bromo-2-methoxyphenyl)benzo[c]isoxazole (3l)



The title compound **3l** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (71.4 mg, 78%), m.p 90-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.5 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.30 (ddd, *J* = 9.1, 6.3, 0.8 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 3.92 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 157.8, 155.4, 134.2, 132.7, 130.6, 123.8, 122.1, 119.4, 116.2, 115.2, 113.4, 113.3, 55.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}BrNO_2$ $[M+H]^+$ 303.99677, found 303.99651.

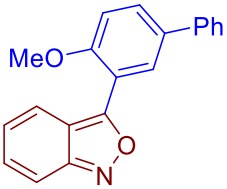
3-(5-Iodo-2-methylphenyl)benzo[c]isoxazole (3m)



The title compound **3m** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-iodo-4-methoxybenzene **2m** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (61.0 mg, 58%), m.p 85-87 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.72 (m, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.29 (m, 1H), 6.98 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 157.7, 156.1, 140.2, 138.5, 130.6, 128.4, 123.7, 122.1, 119.8, 115.1, 113.8, 82.8, 55.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}INO_2$ $[M+H]^+$ 351.98290, found 351.98237.

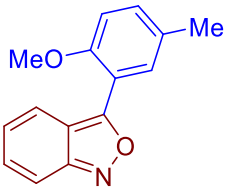
3-(4-Methoxy-[1,1'-biphenyl]-3-yl)benzo[c]isoxazole (3n)



The title compound **3n** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 4-methoxy-1,1'-biphenyl **2n** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a viscous oil (68.6 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.3 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.70 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.00 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.96 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 157.8, 155.7, 139.7, 134.2, 130.5, 130.2, 128.9, 128.8, 127.2, 126.7, 123.3, 122.4, 117.9, 116.0, 115.0, 112.0, 55.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.11756, found 302.11725.

3-(2-Methoxy-5-methylphenyl)benzo[c]isoxazole (3o)

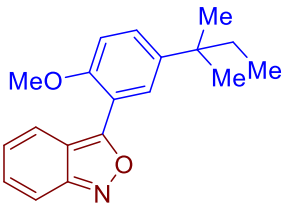


The title compound **3o** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-methoxy-4-methylbenzene **2o** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (58.8 mg, 82%), m.p 70-71 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.95 (dd, *J* = 8.6, 5.1 Hz, 2H), 3.88 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ

163.5, 157.7, 154.3, 132.3, 130.7, 130.4, 130.4, 123.1, 122.6, 117.3, 115.8, 114.9, 111.6, 55.6, 20.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{14}NO_2$ $[M+H]^+$ 240.10191, found 240.10176.

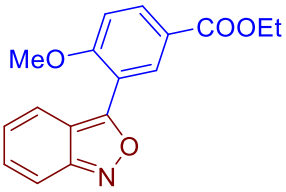
3-(2-Methoxy-5-(*tert*-pentyl)phenyl)benzo[c]isoxazole (3p)



The title compound **3p** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-methoxy-4-(*tert*-pentyl)benzene (0.36 mmol) **2p** and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (73.4 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.44 (m, 1H), 7.29 (m, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.96 (m, 1H), 3.91 (s, 3H), 1.68 (q, *J* = 7.4 Hz, 2H), 1.32 (s, 6H), 0.73 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 157.8, 154.1, 142.1, 130.4, 129.4, 128.1, 123.0, 122.6, 116.9, 115.8, 114.9, 111.2, 55.5, 37.5, 36.8, 28.5, 9.1 ppm. **HRMS** (ESI) m/z calcd. for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.16451, found 296.16406.

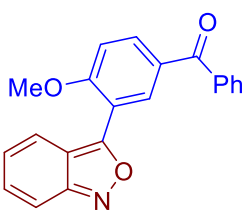
Ethyl 3-(benzo[c]isoxazol-3-yl)-4-methoxybenzoate (3q)



The title compound **3q** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and ethyl 4-methoxybenzoate **2q** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (46.1 mg, 52%), m.p 80-82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.2 Hz, 1H), 8.18 (m, 1H), 7.72 – 7.67 (m, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.31 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.00 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 162.2, 159.6, 157.8, 133.5, 132.1, 130.6, 123.7, 123.6, 122.1, 117.6, 116.2, 115.2, 111.2, 61.1, 55.9, 14.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{16}NO_4$ $[M+H]^+$ 298.10738, found 298.10714.

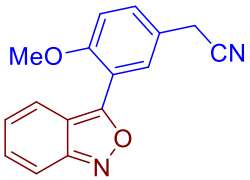
(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)(phenyl)methanone (3r)



The title compound **3r** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and (4-methoxyphenyl)(phenyl)methanone **2r** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow oil (27.6 mg, 28%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.2 Hz, 1H), 8.05 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.60 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.31 (m, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.01 (m, 1H), 4.04 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8, 162.1, 159.5, 157.8, 137.8, 134.1, 133.0, 132.4, 130.6, 129.8, 128.4, 123.8, 122.0, 117.4, 116.2, 115.2, 111.4, 56.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{16}NO_3$ $[M+H]^+$ 330.11247, found 330.11203.

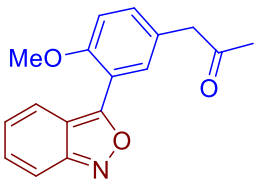
2-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)acetonitrile (3s)



The title compound **3s** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 2-(4-methoxyphenyl)acetonitrile **2s** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow solid (76.2 mg, 86%), m.p 114-116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.42 (m, 1H), 7.29 (m, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.98 (m, 1H), 3.92 (s, 3H), 3.77 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 157.6, 155.7, 131.0, 130.5, 129.6, 123.5, 122.4, 122.2, 118.0, 117.7, 115.9, 114.9, 112.2, 55.6, 22.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{16}H_{13}N_2O_2$ $[M+H]^+$ 265.09715, found 265.09679.

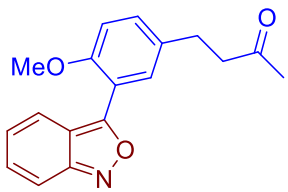
1-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)propan-2-one (3t)



The title compound **3t** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-(4-methoxyphenyl)propan-2-one **2t** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow oil (38.1 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.30 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.97 m, 1H), 3.93 (s, 3H), 3.75 (s, 2H), 2.22 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.0, 162.9, 157.8, 155.4, 132.7, 131.3, 130.5, 126.8, 123.4, 122.5, 117.8, 116.0, 115.0, 112.0, 55.6, 49.6, 29.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.11247, found 282.11214.

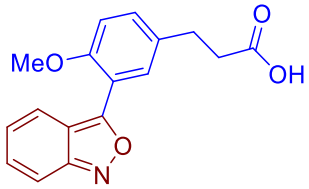
4-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)butan-2-one (3u)



The title compound **3u** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 4-(4-methoxyphenyl)butan-2-one **2u** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow oil (70.0 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.29 (m, 2H), 7.00 – 6.93 (m, 2H), 3.89 (s, 3H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.15 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.6, 163.2, 157.6, 154.6, 133.5, 131.7, 130.4, 129.9, 123.1, 122.4, 117.3, 115.7, 114.8, 111.6, 55.4, 44.9, 30.0, 28.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}NO_3$ $[M+H]^+$ 296.12812, found 296.12775.

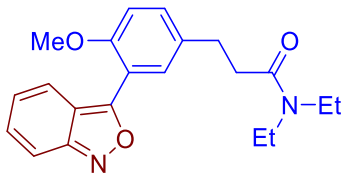
3-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)propanoic acid (3v)



The title compound **3v** was prepared following the **general procedure** from benzo[c]isoxazole **1a** (0.30 mmol) and 3-(4-methoxyphenyl)propanoic acid **2v** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow solid (71.4 mg, 80%), m.p 102-104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.30 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.93 (m, 1H), 3.90 (s, 3H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 163.2, 157.6, 154.9, 132.9, 131.7, 130.6, 130.2, 123.3, 122.5, 117.5, 115.9, 114.9, 111.8, 55.6, 35.6, 29.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{16}NO_4$ $[M+H]^+$ 298.10738, found 298.10705.

3-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)-*N*,*N*-diethylpropanamide (3w)

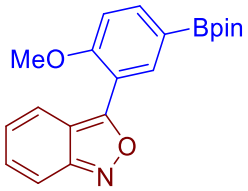


The title compound **3w** was prepared following the **general procedure** from benzo[c]isoxazole **1a** (0.30 mmol) and *N*,*N*-diethyl-3-(4-methoxyphenyl)propanamide **2w** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow oil (86.6 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 9.1 Hz, 1H), 7.35 (m, 1H), 7.28 (m, 1H), 7.01 – 6.93 (m, 2H), 3.90 (s, 3H), 3.37 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H),

3.05 – 2.98 (m, 2H), 2.65 – 2.59 (m, 2H), 1.10 (q, *J* = 7.3 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 163.3, 157.7, 154.7, 134.2, 132.0, 130.5, 130.0, 123.2, 122.5, 117.4, 115.8, 114.9, 111.7, 55.6, 41.9, 40.2, 34.8, 30.5, 14.3, 13.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{25}N_2O_3$ $[M+H]^+$ 353.18597, found 353.18523.

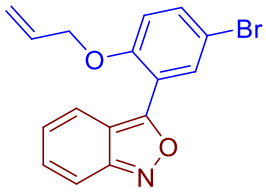
3-(2-Methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[c]isoxazole (3x)



The title compound **3x** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2x** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (76.8 mg, 73%), m.p 86-88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.5 Hz, 1H), 7.93 (m, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.96 (m, 1H), 3.95 (s, 3H), 1.35 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 158.7, 157.6, 138.6, 137.4, 130.4, 123.2, 122.4, 117.2, 115.9, 115.0, 110.8, 83.9, 55.5, 24.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{23}BNO_4$ $[M+H]^+$ 352.17147, found 352.17104.

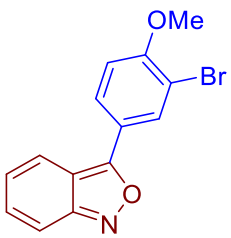
3-(2-(Allyloxy)-5-bromophenyl)benzo[c]isoxazole (3y)



The title compound **3y** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 5-bromobenzo[d][1,3]dioxole **2y** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (59.2 mg, 60%), m.p 87-88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.53 (m, 1H), 7.33 – 7.27 (m, 1H), 7.01 – 6.92 (m, 2H), 5.99 (m, 1H), 5.40 – 5.32 (m, 1H), 5.27 (m, 1H), 4.65 (d, *J* = 5.2 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 157.7, 154.3, 134.1, 132.8, 131.9, 130.6, 123.6, 122.4, 119.7, 118.5, 116.1, 115.1, 114.7, 113.4, 69.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{16}H_{13}BrNO_2$ $[M+H]^+$ 330.01242, found 330.01203.

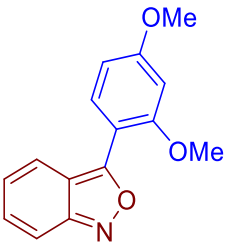
3-(3-Bromo-4-methoxyphenyl)benzo[c]isoxazole (3z)



The title compound **3z** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-bromo-2-methoxybenzene **2z** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a a yellow solid (72.5 mg, 80%), m.p 152-154 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.1 Hz, 1H), 7.91 (m, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.30 (m, 1H), 7.06 – 7.01 (m, 2H), 3.97 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 157.8, 157.3, 131.3, 130.6, 127.0, 124.5, 122.3, 120.3, 115.4, 113.8, 112.6, 112.2, 56.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}BrNO_2$ $[M+H]^+$ 303.99677, found 303.99651.

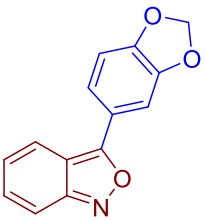
3-(2,4-Dimethoxyphenyl)benzo[c]isoxazole (3aa)



The title compound **3aa** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,3-dimethoxybenzene **2aa** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (48.0 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 9.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.93 (m, 1H), 6.66 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 162.9, 157.8, 157.7, 131.5, 130.4, 122.7, 122.7, 115.2, 114.8, 110.8, 105.5, 99.0, 55.6, 55.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{14}NO_3$ $[M+H]^+$ 256.09682, found 256.09670.

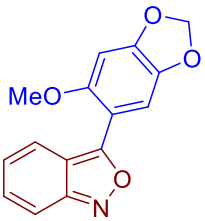
3-(Benzo[d][1,3]dioxol-5-yl)benzo[c]isoxazole (3ab)



The title compound **3ab** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and benzo[d][1,3]dioxole **2ab** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (54.1 mg, 67%), m.p 112-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.46 (d, *J* = 1.5 Hz, 1H), 7.29 (m, 1H), 7.02 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.06 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 157.8, 149.4, 148.5, 130.6, 124.2, 122.5, 121.4, 120.6, 115.3, 113.7, 109.1, 106.7, 101.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}NO_3$ $[M+H]^+$ 240.06552, found 240.06548.

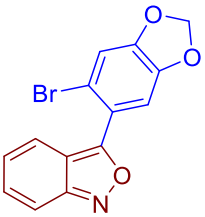
3-(6-Methoxybenzo[d][1,3]dioxol-5-yl)benzo[c]isoxazole (3ac)



The title compound **3ac** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 5-methoxybenzo[d][1,3]dioxole **2ac** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (50.2 mg, 70%), m.p 101-102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 9.1 Hz, 1H), 7.27 (q, *J* = 5.1 Hz, 2H), 6.93 (m, 1H), 6.66 (s, 1H), 6.02 (s, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 157.8, 152.8, 150.6, 141.9, 130.4, 122.8, 122.6, 115.2, 114.9, 109.9, 108.9, 102.0, 95.0, 56.40 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{12}NO_4$ $[M+H]^+$ 270.07608, found 270.07592.

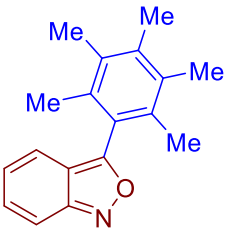
3-(6-Bromobenzo[d][1,3]dioxol-4-yl)benzo[c]isoxazole (3ad)



The title compound **3ad** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 5-bromobenzo[d][1,3]dioxole **2ad** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (61.8 mg, 65%), m.p 88-89 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.1 Hz, 1H), 7.55 (m, 1H), 7.32 (m, 1H), 7.21 (s, 1H), 7.06 – 6.99 (m, 2H), 6.10 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 157.3, 150.2, 147.6, 130.7, 124.2, 122.3, 121.1, 115.9, 115.4, 114.0, 113.9, 111.0, 102.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_9BrNO_3$ $[M+H]^+$ 317.97603, found 317.97582.

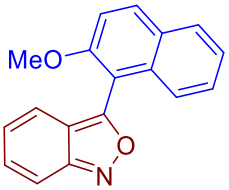
3-(2,3,4,5,6-Pentamethylphenyl)benzo[c]isoxazole (3ae)



The title compound **3ae** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,2,3,4,5-pentamethylbenzene **2ae** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (43.7 mg, 55%), m.p165-167 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.1 Hz, 1H), 7.31 (dd, *J* = 9.1, 6.3 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 1H), 6.94 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 6H), 1.94 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 156.9, 137.8, 133.9, 133.1, 130.7, 124.7, 123.6, 120.5, 117.2, 115.2, 18.0, 17.0, 16.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{18}H_{20}NO$ $[M+H]^+$ 266.15394, found 266.15374.

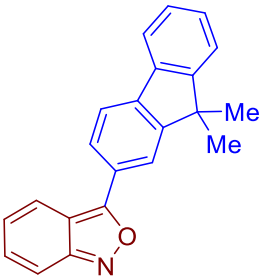
3-(2-Methoxynaphthalen-1-yl)benzo[c]isoxazole (3af)



The title compound **3af** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 2-methoxynaphthalene **2af** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (70.1 mg, 85%), m.p 149-150 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 9.4 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.32 (m, 5H), 6.96 (dd, *J* = 8.7, 6.4 Hz, 1H), 3.90 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 157.3, 156.0, 133.1, 133.0, 130.6, 128.7, 128.2, 127.8, 124.3, 124.2, 123.5, 121.4, 118.0, 115.2, 112.9, 110.2, 56.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{18}H_{14}NO_2$ $[M+H]^+$ 276.10191, found 276.10166.

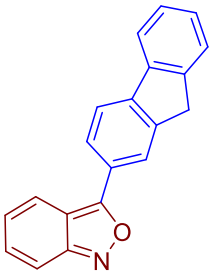
3-(9,9-Dimethyl-9H-fluoren-3-yl)benzo[c]isoxazole (3ag)



The title compound **3ag** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 9,9-dimethyl-9H-fluorene **2ag** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (82.3 mg, 88%), m.p 148-149 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.88 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.49 (dt, *J* = 7.4, 3.7 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.34 (dd, *J* = 9.0, 6.4 Hz, 1H), 7.08 (dd, *J* = 8.8, 6.4 Hz, 1H), 1.58 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 157.9, 154.5, 154.1, 141.4, 138.0, 130.6, 128.2, 127.2, 127.0, 125.7, 124.4, 122.7, 120.9, 120.8, 120.6, 120.6, 115.4, 114.2, 47.08, 27.01 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{18}NO$ $[M+H]^+$ 312.13829, found 312.13800.

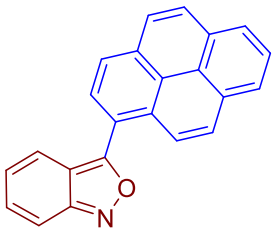
3-(9*H*-fluoren-3-yl)benzo[c]isoxazole (3ah)



The title compound **3ah** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 9H-fluorene **2ah** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (71.5 mg, 84%), m.p 144-146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 0.6 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.89 (t, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.60 (dd, *J* = 12.5, 8.2 Hz, 2H), 7.45 – 7.29 (m, 3H), 7.06 (ddd, *J* = 8.8, 6.4, 0.5 Hz, 1H), 3.98 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 157.9, 144.0, 143.8, 143.7, 140.6, 130.5, 127.6, 127.0, 126.5, 125.5, 125.1, 124.3, 123.0, 120.8, 120.5, 120.4, 115.4, 114.2, 36.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{14}NO$ $[M+H]^+$ 284.10699, found 284.10678.

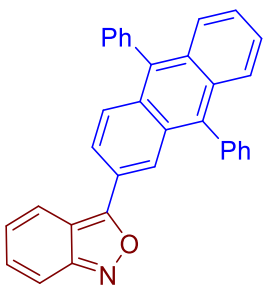
3-(Pyren-2-yl)benzo[c]isoxazole (3ai)



The title compound **3ai** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and pyrene **2ai** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a viscous yellow oil (53.6 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 9.3 Hz, 1H), 8.31 (t, *J* = 9.3 Hz, 2H), 8.27 – 8.23 (m, 2H), 8.17 (dd, *J* = 9.1, 3.7 Hz, 2H), 8.12 – 8.04 (m, 2H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.40 (dd, *J* = 9.1, 6.3 Hz, 1H), 7.07 (dd, *J* = 8.8, 6.3 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 157.7, 132.7, 131.2, 130.9, 130.7, 129.1, 129.0, 127.3, 127.1, 126.5 126.1, 125.9, 125.0, 124.8, 124.5, 124.4, 124.4, 121.9, 121.0, 116.8, 115.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{23}H_{14}NO$ $[M+H]^+$ 320.10699, found 320.10648.

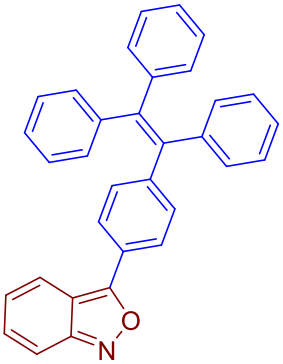
3-(9,10-Diphenylanthracen-2-yl)benzo[c]isoxazole (3aj)



The title compound **3aj** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 9,10-diphenylanthracene **2aj** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (60.3 mg, 45%), m.p 185-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.98 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.80 (dd, *J* = 6.8, 3.3 Hz, 1H), 7.75 (dd, *J* = 6.8, 3.2 Hz, 1H), 7.64 (ddd, *J* = 10.3, 9.7, 4.9 Hz, 6H), 7.59 – 7.55 (m, 3H), 7.54 – 7.49 (m, 3H), 7.43 – 7.39 (m, 2H), 7.29 (dd, *J* = 8.9, 6.2 Hz, 1H), 6.98 (dd, *J* = 8.8, 6.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.45, 157.81, 138.63, 138.38, 138.34, 137.46, 131.26, 131.20, 130.96, 130.50, 129.52, 129.44, 128.63, 128.55, 128.39, 127.96, 127.76, 127.12, 126.04, 125.93, 125.70, 124.67, 124.56, 122.03, 120.54, 115.48, 114.69 ppm. **HRMS** (ESI) m/z calcd. for $C_{33}H_{22}NO$ $[M+H]^+$ 448.16959, found 448.16916.

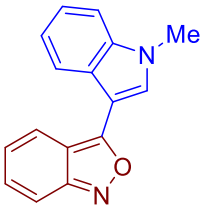
3-(4-(1,2,2-Triphenylvinyl)phenyl)benzo[c]isoxazole (3ak)



The title compound **3ak** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,1,2,2-tetraphenylethene **2ak** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (78.1 mg, 58%), m.p 180-182 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.30 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.11 (m, 15H), 7.02 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 157.8, 146.0, 143.3, 143.2, 143.1, 142.3, 139.8, 132.2, 131.3, 131.3, 131.2, 130.5, 127.9, 127.8, 127.7, 126.9, 126.7, 126.7, 126.2, 125.8, 124.4, 120.7, 115.4, 114.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{33}H_{24}NO$ $[M+H]^+$ 450.18524, found 450.18414.

3-(1-Methyl-1H-indol-3-yl)benzo[c]isoxazole (3al)

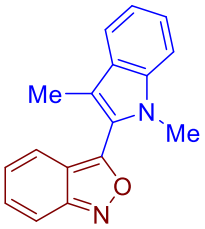


The title compound **3al** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-methyl-1H-indole **2al** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (44.6 mg, 60%), m.p 145-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.65 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.34 – 7.24 (m, 4H), 6.96 – 6.89 (m, 1H), 3.83 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3,

157.2, 136.9, 130.6, 128.3, 125.2, 123.4, 122.4, 121.7, 121.6, 120.8, 114.7, 112.9, 109.7, 105.0, 33.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{16}H_{13}N_2O$ $[M+H]^+$ 249.10224, found 249.10155.

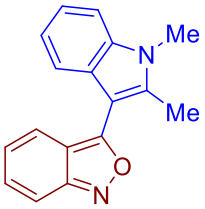
3-(1,3-Dimethyl-1H-indol-2-yl)benzo[c]isoxazole (3am)



The title compound **3am** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,3-dimethyl-1H-indole **2am** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (45.6 mg, 58%), m.p 129-131 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.22 m, 1H), 7.08 (m, 1H), 3.81 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 157.4, 138.8, 130.9, 128.0, 124.5, 124.1, 123.9, 120.8, 119.9, 119.8, 117.2, 115.4, 114.9, 109.7, 31.6, 10.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.11789, found 263.11746.

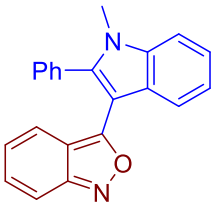
3-(1,2-Dimethyl-1H-indol-3-yl)benzo[c]isoxazole (3an)



The title compound **3an** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,2-dimethyl-1H-indole **2an** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (60.5 mg, 77%), m.p 99-101 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 15.4, 8.9 Hz, 2H), 7.33 – 7.18 (m, 4H), 6.94 – 6.90 (m, 1H), 3.71 (s, 3H), 2.61 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 157.5, 138.0, 136.9, 130.6, 125.6, 122.3, 122.1, 121.6, 121.0, 119.3, 114.8, 114.6, 109.3, 101.8, 29.8, 11.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.11789, found 263.11712.

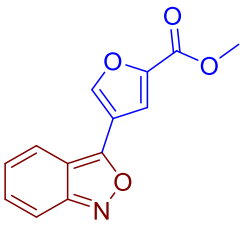
3-(1-Methyl-2-phenyl-1H-indol-3-yl)benzo[c]isoxazole (3ao)



The title compound **3ao** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-methyl-2-phenyl-1H-indole **2ao** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as an orange solid (77.8 mg, 80%), m.p 128-130 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.44 (m, 7H), 7.42 – 7.37 (m, 1H), 7.36 – 7.30 (m, 1H), 7.14 (m, 1H), 6.59 – 6.50 (m, 2H), 3.75 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 157.5, 140.6, 137.4, 130.9, 130.8, 130.2, 129.2, 128.9, 126.2, 123.3, 122.1, 121.8, 121.3, 120.9, 114.5, 113.8, 110.0, 103.5, 31.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.13354, found 325.12642.

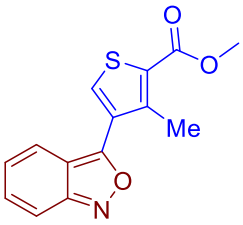
Methyl 5-(benzo[c]isoxazol-3-yl)furan-2-carboxylate (3ap)



The title compound **3ap** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methyl furan-2-carboxylate **2ap** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (48.1 mg, 66%), m.p 142-144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 7.3 Hz, 1H), 7.58 (m, 1H), 7.34 (m, 2H), 7.17 – 7.08 (m, 2H), 3.96 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 157.3, 154.8, 147.0, 145.5, 131.4, 125.6, 120.8, 119.4, 115.3, 115.0, 112.2, 52.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{13}H_{10}NO_4$ $[M+H]^+$ 244.06043, found 244.06006.

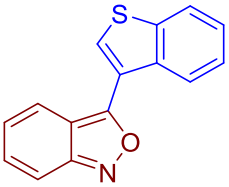
Methyl 4-(benzo[c]isoxazol-3-yl)-3-methylthiophene-2-carboxylate (3aq)



The title compound **3aq** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methyl 3-methylthiophene-2-carboxylate **2aq** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (50.2 mg, 61%), m.p 124-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.49 (s, 1H), 7.30 (m, 1H), 7.09 – 7.04 (m, 1H), 3.89 (s, 3H), 2.58 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 158.5, 157.5, 146.7, 132.1, 131.0, 130.6, 128.5, 125.3, 119.9, 115.5, 114.8, 52.02, 15.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}NO_3S$ $[M+H]^+$ 274.05324, found 274.05219.

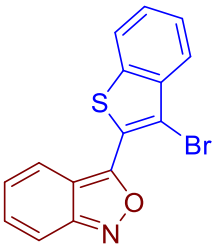
3-(Benzo[b]thiophen-2-yl)benzo[c]isoxazole (3ar)



The title compound **3ar** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and benzo[b]thiophene **2ar** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as an orange solid (48.9 mg, 65%), m.p 135-137 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 3.5 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.79 – 7.74 (m, 1H), 7.66 (m, 1H), 7.54 (m, 1H), 7.51 – 7.45 (m, 1H), 7.39 – 7.32 (m, 1H), 7.10 – 7.04 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 157.3, 140.0, 136.1, 130.8, 127.7, 125.5, 125.5, 124.5, 124.4, 124.2, 122.7, 120.4, 115.4, 115.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{10}NOS$ $[M+H]^+$ 252.04776, found 252.04749.

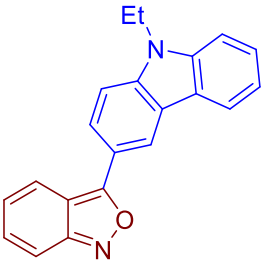
3-(3-Bromobenzo[b]thiophen-2-yl)benzo[c]isoxazole (3as)



The title compound **3as** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 3-bromobenzo[b]thiophene **2as** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (78.0 mg, 79%), m.p 128-130 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.87 (m, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.39 – 7.30 (m, 1H), 7.10 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 157.4, 138.5, 138.4, 130.9, 127.0, 125.8, 125.1, 124.4, 122.3, 120.9, 116.6, 115.5, 109.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ 329.95827, found 329.95806.

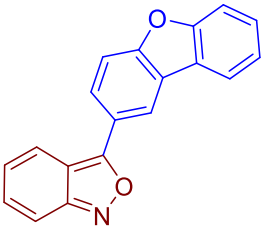
3-(9-Ethyl-9H-carbazol-3-yl)benzo[c]isoxazole (3at)



The title compound **3at** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 9-ethyl-9H-carbazole **2at** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (47.7 mg, 51%), m.p 108-110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 1.4 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.12 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.55 - 7.52 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 14.7, 6.6 Hz, 2H), 7.06 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 158.0, 140.8, 140.5, 130.6, 126.5, 124.3, 123.7, 123.5, 122.8, 121.2, 120.7, 119.7, 119.4, 119.2, 115.2, 113.5, 109.1, 108.9, 37.8, 13.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.13354, found 313.13315.

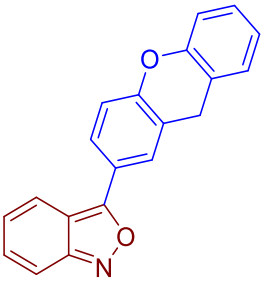
3-(Dibenzo[b,d]furan-2-yl)benzo[c]isoxazole (3au)



The title compound **3au** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and dibenzo[b,d]furan **2au** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (51.3 mg, 60%), m.p 158-160 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.06 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 11.9, 8.7 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 9.0, 6.4 Hz, 1H), 7.09 – 7.05 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 157.9, 156.9, 156.7, 130.6, 128.0, 125.7, 125.2, 124.4, 123.5, 123.4, 123.2, 120.9, 120.6, 119.1, 115.4, 114.0, 112.5, 111.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{19}H_{12}NO_2$ $[M+H]^+$ 286.08626, found 286.08578.

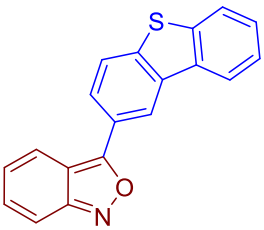
3-(9H-Xanthen-2-yl)benzo[c]isoxazole (3av)



The title compound **3av** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 9H-xanthene **2av** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (52.0 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 17.4, 8.3 Hz, 3H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.32 (dd, *J* = 9.0, 6.4 Hz, 1H), 7.22 (t, *J* = 6.8 Hz, 3H), 7.10 – 7.03 (m, 3H), 4.17 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 157.8, 153.5, 151.4, 130.6, 128.9, 127.9, 127.5, 126.2, 124.3, 123.6, 123.4, 121.6, 120.6, 119.8, 117.5, 116.6, 115.4, 113.8, 27.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{14}NO_2$ $[M+H]^+$ 300.10191, found 300.10159.

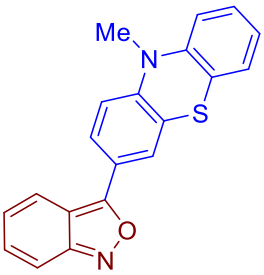
3-(Dibenzo[b,d]thiophen-2-yl)benzo[c]isoxazole (3aw)



The title compound **3aw** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and dibenzo[b,d]thiophene **2aw** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (57.8 mg, 64%), m.p 113-115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 1.3 Hz, 1H), 8.24 – 8.21 (m, 1H), 8.03 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.87 (ddd, *J* = 5.6, 4.7, 2.9 Hz, 2H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.35 – 7.31 (m, 1H), 7.08 (dd, *J* = 8.8, 6.3 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 157.9, 141.4, 139.8, 136.2, 134.9, 130.6, 127.4, 124.8, 124.7, 124.6, 124.4, 123.5, 122.9, 121.8, 120.6, 119.5, 115.5, 114.3, ppm. **HRMS** (ESI) m/z calcd. for $C_{19}H_{12}NOS$ $[M+H]^+$ 302.06341, found 302.06297.

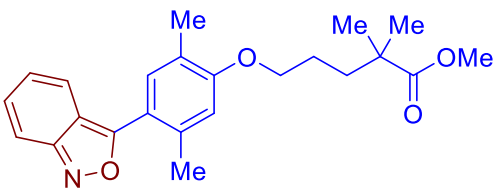
3-(10-Methyl-10H-phenothiazin-3-yl)benzo[c]isoxazole (3ax)



The title compound **3ax** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 10-methyl-10H-phenothiazine **2ax** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (61.4 mg, 62%), m.p 155-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.73 (m, 3H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.29 (ddd, *J* = 9.1, 6.4, 0.5 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.04 – 6.95 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.41 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 157.8, 147.3, 144.7, 130.6, 127.7, 127.2, 126.0, 124.7, 124.4, 124.1, 123.1, 122.7, 122.4, 120.6, 115.3, 114.4, 114.3, 113.7, 35.5 ppm. **HRMS** (ESI) m/z calcd. for C20H15N2OS $[M+H]^+$ 331.08996, found 331.08961.

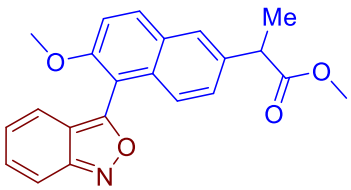
Methyl 5-(4-(benzo[c]isoxazol-3-yl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3ay)



The title compound **3ay** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **2ay** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (99.5 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.37 (s, 1H), 7.31 – 7.26 (m, 1H), 7.00 – 6.92 (m, 1H), 6.76 (s, 1H), 4.00 (t, *J* = 5.7 Hz, 2H), 3.67 (s, 3H), 2.46 (s, 3H), 2.25 (s, 3H), 1.81 – 1.70 (m, 4H), 1.23 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 166.9, 158.5, 157.2, 136.6, 131.5, 130.4, 124.5, 123.5, 121.0, 119.1, 115.3, 114.8, 113.5, 68.0, 67.7, 51.6, 42.0, 36.9, 25.1, 25.0, 20.7, 15.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{23}H_{28}NO_4$ $[M+H]^+$ 382.20128, found 382.20013.

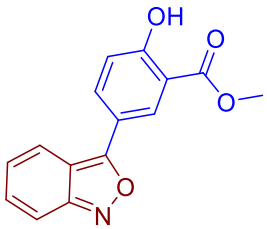
Methyl 2-(1-(benzo[c]isoxazol-3-yl)-6-methoxynaphthalen-2-yl)propanoate (3az)



The title compound **3az** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methyl 2-(6-methoxynaphthalen-2-yl)propanoate **2az** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (93.1 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.1 Hz, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 6.94 (m, 1H), 3.92 – 3.85 (m, 4H), 3.66 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 162.8, 157.2, 155.9, 136.3, 132.8, 132.2, 130.6, 128.7, 127.7, 126.2, 124.8, 123.5, 121.3, 117.9, 115.1, 113.2, 110.0, 56.4, 52.0, 45.0, 18.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{20}NO_4$ $[M+H]^+$ 362.13868, found 362.13828.

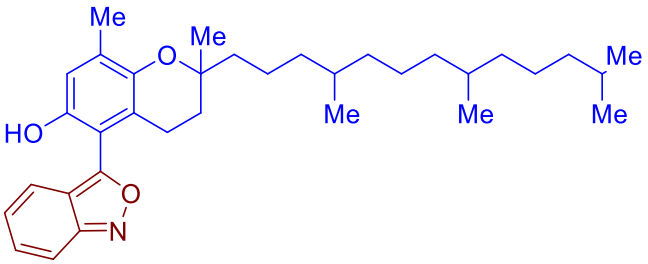
Methyl 5-(benzo[c]isoxazol-3-yl)-2-hydroxybenzoate (3ba)



The title compound **3ba** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methyl 2-acetoxybenzoate **2ba** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow solid (54.1 mg, 67%), m.p 153-154 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.50 (d, *J* = 2.3 Hz, 1H), 8.09 (m, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.31 (m, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.05 (m, 1H), 4.03 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 163.3, 162.9, 157.8, 133.4, 130.6, 128.4, 124.4, 120.3, 120.0, 118.8, 115.4, 113.7, 113.1, 52.8 ppm. **HRMS** (ESI) m/z calcd. for for $C_{15}H_{12}NO_4$ $[M+H]^+$ 270.07608, found 270.07574.

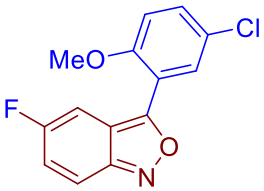
5-(Benzo[c]isoxazol-3-yl)-2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol (3bb)



The title compound **3bb** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol **2bb** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (90.3 mg, 58%), m.p 60-62 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.95 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.76 (s, 1H), 6.26 (s, 1H), 2.59 – 2.50 (m, 2H), 2.20 (s, 3H), 1.73 – 1.63 (m, 2H), 1.62 – 1.55 (m, 2H), 1.55 – 1.47 (m, 2H), 1.45 – 1.33 (m, 5H), 1.30 – 1.26 (m, 6H), 1.16 – 1.04 (m, 6H), 0.87 – 0.84 (m, 12H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 157.0, 146.9, 146.2, 131.4, 131.0, 123.7, 121.3, 120.7, 117.0, 114.8, 111.0, 75.4, 40.0, 39.3, 37.4, 37.2, 32.8, 32.7, 30.9, 27.9, 24.8, 24.4, 23.9, 22.7, 22.6, 21.3, 20.9, 19.7, 19.6, 16.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{34}H_{50}NO_3$ $[M+H]^+$ 520.37852, found 520.37836.

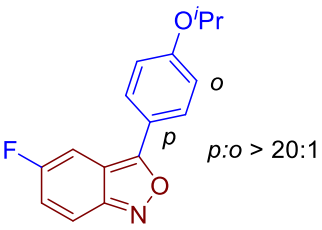
3-(5-Chloro-2-methoxyphenyl)-5-fluorobenzo[c]isoxazole (3bc)



The title compound **3bc** was prepared following the **general procedure A** from 5-fluorobenzo[c]isoxazole **1b** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (70.6 mg, 85%), m.p 120-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.6 Hz, 1H), 7.58 (dd, *J* = 9.6, 4.7 Hz, 1H), 7.39 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.13 (ddd, *J* = 9.6, 8.6, 2.3 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 10.9 Hz), 158.3 (d, *J* = 245.8 Hz), 155.9, 154.5, 131.3, 129.5, 126.3, 123.7 (d, *J* = 31.6 Hz), 118.6, 117.6 (d, *J* = 9.7 Hz), 115.4 (d, *J* = 11.9 Hz), 112.9, 104.0 (d, *J* = 26.2 Hz), 55.8 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -115.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}ClFNO_2$ $[M+H]^+$ 278.03786, found 278.03802.

5-Fluoro-3-(4-isopropoxyphenyl)benzo[c]isoxazole (3bd)

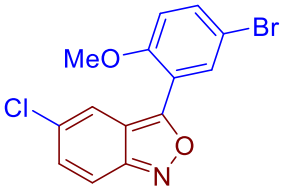


p:o > 20:1

The title compound **3bd** was prepared following the **general procedure A** from 5-fluorobenzo[c]isoxazole **1b** (0.30 mmol) and isopropoxybenzene **2bc** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (61.8 mg, 76%), m.p 98-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.59 (m, 1H), 7.35 (m, 1H), 7.15 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.66 (m, 1H), 1.39 (d, *J* = 6.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0 (d, *J* = 10.9 Hz), 159.0 (d, *J* = 246.1 Hz), 159.6, 155.9, 127.9, 123.6 (d, *J* = 31.2 Hz), 120.5, 117.8 (d, *J* = 9.5 Hz), 116.3, 112.4 (d, *J* = 11.0 Hz), 102.4 (d, *J* = 25.4 Hz), 70.1, 21.9 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -116.35. **HRMS** (ESI) m/z calcd. for $C_{16}H_{15}FNO_2$ $[M+H]^+$ 272.10813, found 272.10723.

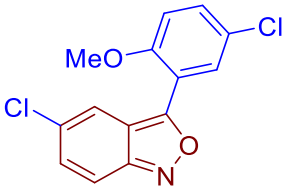
3-(5-Bromo-2-methoxyphenyl)-5-chlorobenzo[c]isoxazole (3be)



The title compound **3be** was prepared following the **general procedure A** from 1-chloro-4-methoxybenzene **1c** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (75.8 mg, 75%), m.p 115-117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.5 Hz, 1H), 7.72 (s, 1H), 7.58 – 7.53 (m, 2H), 7.22 (dd, *J* = 9.4, 1.8 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.2, 156.3, 155.2, 154.0, 134.5, 132.7, 132.5, 132.4, 129.2, 120.7, 118.9, 117.8, 116.8, 116.7, 116.3, 113.4, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}BrClNO_2$ $[M+H]^+$ 337.95780, found 337.95731.

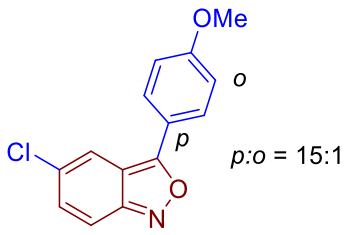
5-Chloro-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (3bf)



The title compound **3bf** was prepared following the **general procedure A** from 5-chlorobenzo[c]isoxazole **1c** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (63.3 mg, 72%), m.p 109-111 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.6 Hz, 1H), 7.73 (s, 1H), 7.55 (dd, *J* = 9.4, 0.8 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.22 (dd, *J* = 9.4, 1.8 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 156.3, 154.7, 132.4, 131.6, 129.7, 129.3, 126.4, 120.7, 118.5, 116.8, 116.3, 112.9, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}Cl_2NO_2$ $[M+H]^+$ 294.00831, found 294.00806.

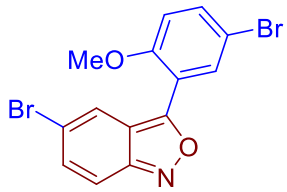
5-Chloro-3-(4-methoxyphenyl)benzo[c]isoxazole (3bg)[8]



The title compound **3bg** was prepared following the **general procedure A** from 5-chlorobenzo[c]isoxazole **1c** (0.30 mmol) and anisole **2a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (60.6 mg, 78%), m.p 139-141 °C; (lit. [8] 143-145 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.74 (d, *J* = 0.7 Hz, 1H), 7.51 (d, *J* = 9.4 Hz, 1H), 7.20 (m, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 161.3, 156.2, 132.2, 129.4, 128.0, 120.6, 119.1, 116.8, 114.8, 113.6, 55.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}ClNO_2$ $[M+H]^+$ 260.04728, found 260.04654.

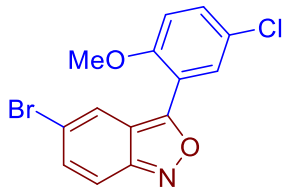
5-Bromo-3-(5-bromo-2-methoxyphenyl)benzo[c]isoxazole (3bh)



The title compound **3bh** was prepared following the **general procedure A** from 5-bromobenzo[c]isoxazole **1d** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (90.8 mg, 79%), m.p 126-127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.59 – 7.54 (m, 1H), 7.48 (d, *J* = 9.4 Hz, 1H), 7.33 (d, *J* = 9.4 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 156.2, 155.2, 134.5, 134.4, 132.6, 124.3, 118.9, 117.3, 117.1, 116.8, 113.4, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}Br_2NO_2$ $[M+H]^+$ 381.90728, found 381.90704.

5-Bromo-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (3bi)

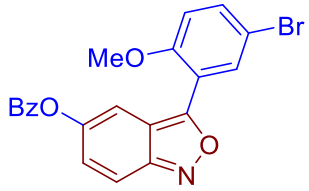


The title compound **3bi** was prepared following the **general procedure A** from 5-bromobenzo[c]isoxazole **1d** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (82.9 mg, 82%), m.p 134-136 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.78 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 9.4 Hz, 1H), 7.41 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.32 (dd, *J* = 9.4, 1.7 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100

MHz, $CDCl_3$) δ 161.2, 156.2, 154.6, 134.4, 131.6, 129.7, 126.3, 124.3, 118.4, 117.2, 117.0, 116.8, 112.9, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}BrClNO_2$ $[M+H]^+$ 337.95780, found 337.95662.

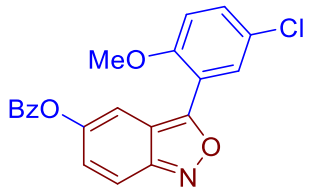
3-(5-Bromo-2-methoxyphenyl)benzo[c]isoxazol-5-yl benzoate (3bj)



The title compound **3bj** was prepared following the **general procedure A** from benzo[c]isoxazol-5-yl benzoate **1e** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (82.5 mg, 65%), m.p 155-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 2.4 Hz, 1H), 7.68 - 7.62 (m, 3H), 7.56 - 7.51 (m, 3H), 7.19 (dd, *J* = 9.5, 2.0 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 162.0, 156.4, 155.2, 146.4, 134.3, 133.8, 132.5, 130.2, 129.2, 128.6, 127.9, 119.2, 116.7, 115.7, 113.4, 113.3, 112.5, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}BrNO_4$ $[M+H]^+$ 424.01790, found 424.01761.

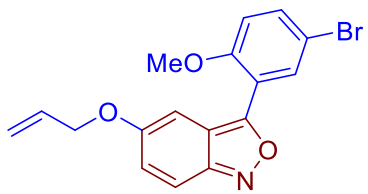
3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazol-5-yl benzoate (3bk)



The title compound **3bk** was prepared following the **general procedure A** from benzo[c]isoxazol-5-yl benzoate **1e** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (79.6 mg, 70%), m.p 136-138 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.3 Hz, 2H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.68 - 7.63 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.19 (dd, *J* = 9.5, 2.1 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 162.1, 156.4, 154.7, 146.4, 133.8, 131.4, 130.2, 129.7, 129.2, 128.6, 127.9, 126.2, 118.7, 116.7, 115.7, 112.9, 112.5, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}ClNO_4$ $[M+H]^+$ 380.06841, found 380.06824.

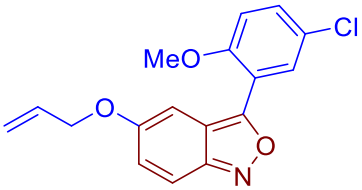
5-(Allyloxy)-3-(5-bromo-2-methoxyphenyl)benzo[c]isoxazole (3bl)



The title compound **3bl** was prepared following the **general procedure A** from 5-(allyloxy)benzo[c]isoxazole **1f** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (53.8 mg, 50%), m.p 85-87 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.10 – 7.06 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.12 – 6.04 (m, 1H), 5.45 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.34 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.54 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 155.9, 155.1, 154.5, 133.7, 132.7, 132.5, 127.9, 119.8, 118.0, 116.7, 116.3, 113.4, 113.4, 97.0, 68.8, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{15}BrNO_3$ $[M+H]^+$ 360.02298, found 360.02213.

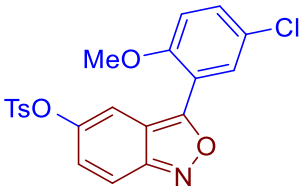
5-(Allyloxy)-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (3bm)



The title compound **3bm** was prepared following the **general procedure A** from 5-(allyloxy)benzo[c]isoxazole **1f** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (43.5 mg, 46%), m.p 106-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.6 Hz, 1H), 7.52 (d, *J* = 9.6 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.07 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.09 (ddd, *J* = 22.5, 10.5, 5.3 Hz, 1H), 5.45 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.34 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.54 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 155.9, 154.6, 154.5, 132.7, 130.7, 129.6, 127.9, 126.3, 119.4, 118.0, 116.7, 116.3, 113.0, 97.1, 68.8, 56.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{15}ClNO_3$ $[M+H]^+$ 316.07350, found 316.07300.

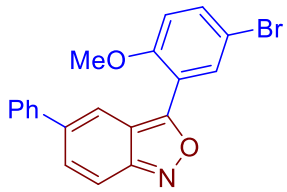
3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazol-5-yl 4-methylbenzenesulfonate (3bn)



The title compound **3bn** was prepared following the **general procedure A** from benzo[c]isoxazol-5-yl 4-methylbenzenesulfonate **1g** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (101.0 mg, 78%), m.p 99-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.6 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 1.4 Hz, 1H), 7.42 (dd, *J* = 14.2, 5.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.77 (dd, *J* = 9.6, 2.1 Hz, 1H), 3.92 (s, 3H), 2.43 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 156.2, 154.6, 145.7, 144.8, 132.2, 131.7, 129.9, 129.5, 128.4, 127.2, 126.2, 118.2, 116.9, 115.3, 115.1, 112.9, 55.7, 21.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}ClNO_5S$ $[M+H]^+$ 430.05105, found 430.04988.

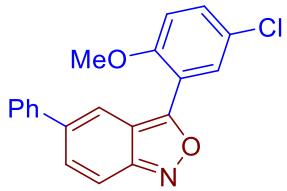
3-(5-Bromo-2-methoxyphenyl)-5-phenylbenzo[c]isoxazole (3bo)



The title compound **3bo** was prepared following the **general procedure A** from 5-phenylbenzo[c]isoxazole **1h** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (86.4 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.4 Hz, 1H), 7.87 (s, 1H), 7.68 (d, *J* = 9.3 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.57 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 157.3, 155.3, 140.5, 136.7, 134.2, 132.7, 131.8, 128.9, 127.6, 127.0, 119.4, 119.3, 116.7, 115.6, 113.4, 113.3, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}BrNO_2$ $[M+H]^+$ 380.02807, found 380.02756.

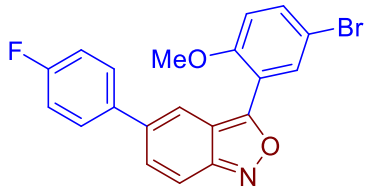
3-(5-Chloro-2-methoxyphenyl)-5-phenylbenzo[c]isoxazole (3bp)



The title compound **3bp** was prepared following the **general procedure A** from 5-phenylbenzo[c]isoxazole **1h** (0.30 mmol) and 1-chloro-4-methoxybenzene **2k** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (80.4 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.83 (d, *J* = 2.6 Hz, 1H), 7.68 (d, *J* = 9.3 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 2H), 7.49 – 7.36 (m, 5H), 7.02 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 157.3, 154.9, 140.5, 136.7, 131.8, 131.3, 129.8, 128.9, 127.6, 127.0, 126.3, 119.3, 119.0, 116.7, 115.6, 113.0, 56.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}ClNO_2$ $[M+H]^+$ 336.07858, found 336.07807.

3-(5-Bromo-2-methoxyphenyl)-5-(4-fluorophenyl)benzo[c]isoxazole (3bq)

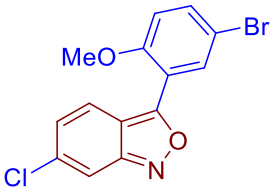


The title compound **3bq** was prepared following the **general procedure A** from 5-(4-fluorophenyl)benzo[c]isoxazole **1i** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (87.9 mg, 83%), m.p 119-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.79 (s, 1H), 7.64 (d, *J* = 9.3 Hz, 1H), 7.53 (m, 4H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J*

= 247.3 Hz, 2H), 161.8, 157.2, 155.2, 136.6 (d, *J* = 3.3 Hz, 1H), 135.6, 134.2, 132.6, 131.6, 128.5 (d, *J* = 8.1 Hz, 5H), 119.3, 119.1, 116.6, 115.9, 115.7 (d, *J* = 3.6 Hz, 4H), 113.4, 113.3, 55.9 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -114.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}BrNO_2$ $[M+H]^+$ 398.01865, found 398.01821.

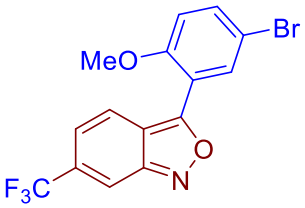
3-(5-Bromo-2-methoxyphenyl)-6-chlorobenzo[c]isoxazole (3br)



The title compound **3br** was prepared following the **general procedure A** from 6-chlorobenzo[c]isoxazole **1j** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (80.9 mg, 80%), m.p 128-129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 1H), 7.68 (d, *J* = 9.3 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 6.97 – 6.90 (m, 2H), 3.93 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 157.8, 155.2, 136.9, 134.6, 132.6, 125.6, 123.7, 118.8, 114.6, 113.5, 113.4, 113.3, 55.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}BrClNO_2$ $[M+H]^+$ 337.95780, found 337.95723.

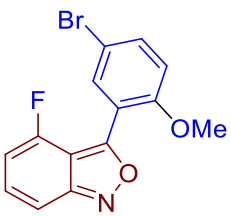
3-(5-Bromo-2-methoxyphenyl)-5-(trifluoromethyl)benzo[c]isoxazole (3bs)



The title compound **3bs** was prepared following the **general procedure A** from 5-(trifluoromethyl)benzo[c]isoxazole **1k** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (91.2 mg, 82%), m.p 117-119 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.59 (m, 1H), 7.12 (d, *J* = 9.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 156.5, 155.3, 134.9, 132.7, 132.7 (q, *J* = 32.3 Hz), 123.4 (q, *J* = 272.8 Hz), 124.4, 119.3 (q, *J* = 5.3 Hz), 118.7, 116.4, 114.2 (q, *J* = 5.2 Hz), 113.5, 113.4, 55.9 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -64.5 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{10}BrF_3NO_2$ $[M+H]^+$ 371.98415, found 371.98367.

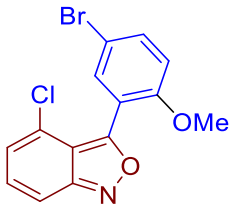
3-(5-Bromo-2-methoxyphenyl)-4-fluorobenzo[c]isoxazole (3bt)



The title compound **3bt** was prepared following the **general procedure A** from 4-fluorobenzo[c]isoxazole **1l** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (81.7 mg, 85%), m.p 109-111 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 1H), 7.60 (m, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.22 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.61 (m, 1H), 3.86 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 6.4 Hz), 159.1 (d, *J* = 3.6 Hz), 156.5, 154.9 (d, *J* = 260.6 Hz), 134.9, 133.5 (d, *J* = 1.8 Hz), 131.0 (d, *J* = 7.1 Hz), 118.4, 113.2, 112.5, 111.4 (d, *J* = 5.6 Hz), 109.5 (d, *J* = 21.3 Hz), 106.3 (d, *J* = 18.9 Hz), 55.9 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -114.5. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}BrFNO_2$ $[M+H]^+$ 321.98735, found 321.98708.

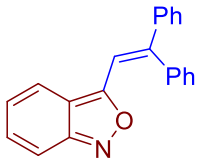
3-(5-Bromo-2-methoxyphenyl)-4-chlorobenzo[c]isoxazole (3bu)



The title compound **3bu** was prepared following the **general procedure A** from 4-chlorobenzo[c]isoxazole **1m** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (82.4 mg, 82%), m.p 138-140 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.21 (m, 1H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.91 (d, *J* = 9.3 Hz, 1H), 3.79 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 157.9, 157.1, 135.0, 134.4, 130.8, 126.3, 123.9, 118.6, 115.7, 114.2, 112.8, 112.1, 55.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}BrClNO_2$ $[M+H]^+$ 337.95780, found 337.95745.

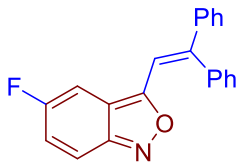
3-(2,2-Diphenylvinyl)benzo[c]isoxazole (5a)[9]



The title compound **5a** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1,1-diphenylethene **4a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (62.4 mg, 70%), m.p 93-95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 9.1 Hz, 1H), 7.43 – 7.37 (m, 8H), 7.32 (m, 2H), 7.21 (s, 1H), 7.20 – 7.17 (m, 1H), 6.77 – 6.73 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 157.1, 148.3, 141.7, 139.3, 130.4, 130.3, 129.0, 128.7, 128.6, 128.4, 128.3, 123.5, 120.4, 115.9, 115.0, 112.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{16}NO$ $[M+H]^+$ 298.12264, found 298.12208.

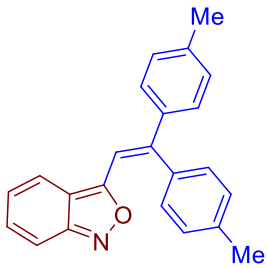
3-(2,2-Diphenylvinyl)-5-fluorobenzo[c]isoxazole (5b)[9]



The title compound **5b** was prepared following the **general procedure A** from 5-fluorobenzo[c]isoxazole **1b** (0.30 mmol) and 1,1-diphenylethene **4a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (71.0 mg, 75%), m.p 130-132 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 1H), 7.44 – 7.38 (m, 8H), 7.30 (m, 2H), 7.17 (s, 1H), 7.04 – 6.97 (m, 1H), 6.02 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 10.9 Hz), 158.1 (d, *J* = 246.5 Hz), 155.3, 148.1, 141.5, 139.3, 130.3, 129.1, 128.9, 128.8, 128.5, 128.3, 123.3 (d, *J* = 31.3 Hz), 117.5 (d, *J* = 9.4 Hz), 114.8 (d, *J* = 11.5 Hz), 112.3 (d, *J* = 1.3 Hz), 102.4 (d, *J* = 26.3 Hz) ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -115.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}FNO$ $[M+H]^+$ 316.11322, found 316.11269.

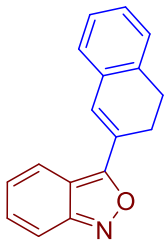
3-(2,2-Di-*p*-tolylvinyl)benzo[c]isoxazole (5c)[9]



The title compound **5c** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 4,4'-(ethene-1,1-diyl)bis(methylbenzene) **4b** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (61.4 mg, 63%), m.p 142-144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.16 (m, 7H), 7.14 (s, 1H), 6.80 (m, 1H), 6.74 (m,1H), 2.40 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 157.0, 148.5, 139.1, 139.1, 138.5, 136.5, 130.4, 130.2, 129.2, 129.1, 128.3, 123.2, 120.6, 115.8, 114.9, 111.0, 21.4, 21.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{23}H_{20}NO$ $[M+H]^+$ 326.15394, found 326.15363.

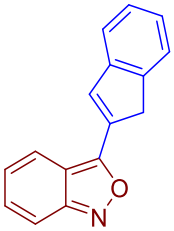
3-(3,4-Dihydronaphthalen-2-yl)benzo[c]isoxazole (5d)



The title compound **5d** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and cyclohexene **4c** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (60.0 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.40 (s, 1H), 7.28 (dd, *J* = 9.0, 6.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.17 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.00 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.00 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 157.6, 135.4, 133.0, 130.4, 129.3, 128.7, 127.8, 127.6, 126.9, 126.7, 124.0, 120.9, 115.4, 114.6, 27.2, 23.6. **HRMS** (ESI) m/z calcd. for $C_{17}H_{14}NO$ $[M+H]^+$ 248.10699, found 248.10623.

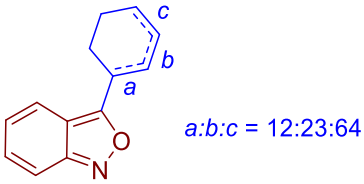
3-(1H-Inden-2-yl)benzo[c]isoxazole (5e)



The title compound **5e** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and cyclohexene **4d** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (36.4 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.68 (s, 1H), 7.58 (dd, *J* = 18.1, 8.6 Hz, 3H), 7.39 – 7.29 (m, 3H), 7.07 (dd, *J* = 8.6, 6.5 Hz, 1H), 4.08 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 157.5, 143.7, 143.1, 132.7, 132.6, 130.7, 127.2, 126.6, 124.3, 124.0, 122.5, 120.5, 115.4, 115.1, 38.6. **HRMS** (ESI) m/z calcd. for $C_{16}H_{12}NO$ $[M+H]^+$ 234.09134, found 234.09058.

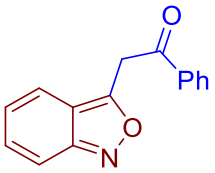
Mixture of 3-(cyclohex-1-en-1-yl)benzo[c]isoxazole, 3-(cyclohex-2-en-1-yl)benzo[c]isoxazole and 3-(cyclohex-3-en-1-yl)benzo[c]isoxazole (5f)



The title compound **5f** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and cyclohexene **4e** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (47.5 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 0.12H), 7.49 – 7.40 (m, 1.84H), 7.19 – 7.13 (m, 1H), 6.88 – 6.77 (m, 1H), 6.76 – 6.72 (m, 0.12H), 5.97 (ddd, *J* = 9.9, 6.1, 3.7 Hz, 0.23H), 5.81 – 5.68 (m, 1.53H), 4.03 (ddd, *J* = 10.4, 5.7, 2.8 Hz, 0.23H), 3.46 (dddd, *J* = 11.1, 10.2, 5.6, 3.1 Hz, 0.64H), 2.63 – 2.57 (m, 0.24H), 2.54 – 2.35 (m, 1.43H), 2.26 (qd, *J* = 6.5, 2.8 Hz, 0.28H), 2.19 – 1.97 (m, 3.45H), 1.93 – 1.84 (m, 0.32H), 1.79 – 1.69 (m, 0.81H), 1.68 – 1.58 (m, 0.54H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 171.3, 157.4, 157.2, 157.1, 132.3, 130.6, 130.5, 130.2, 127.5, 127.0, 125.2, 124.7, 123.4, 122.7, 122.6, 121.2, 120.6, 120.1, 115.1, 115.0, 114.9, 114.8, 114.2, 35.2, 33.7, 29.6, 28.56, 27.1, 25.8, 25.3, 24.8, 24.6, 22.0, 21.6, 20.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}NO$ $[M+H]^+$ 200.10699, found 200.10680.

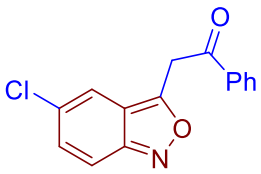
2-(Benzo[c]isoxazol-3-yl)-1-phenylethan-1-one (7a)



The title compound **7a** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-phenylvinyl trifluoromethanesulfonate **6a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a red solid (39.1 mg, 55%), m.p 54-56 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.30 – 7.26 (m, 1H), 6.96 (m, 1H), 4.83 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 161.3, 157.3, 135.6, 134.0, 130.9, 128.9, 128.7, 123.9, 119.8, 116.9, 115.1, 37.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{12}NO_2$ $[M+H]^+$ 238.08626, found 238.08598.

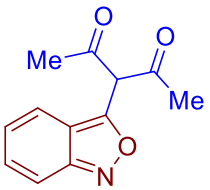
2-(5-Chlorobenzo[c]isoxazol-3-yl)-1-phenylethan-1-one (7b)



The title compound **7b** was prepared following the **general procedure A** from 5-chlorobenzo[c]isoxazole **1c** (0.30 mmol) and 1-phenylvinyl trifluoromethanesulfonate **6a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a red solid (48.8 mg, 60%), m.p 91-93 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.48 (m, 4H), 7.20 (m, 1H), 4.81 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9, 161.2, 155.8, 135.4, 134.2, 132.8, 129.6, 129.0, 128.6, 118.2, 117.2, 116.9, 37.1 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{11}ClNO_2$ $[M+H]^+$ 272.04728, found 272.04690.

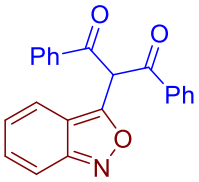
3-(Benzo[c]isoxazol-3-yl)pentane-2,4-dione (7c)



The title compound **7c** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and pentane-2,4-dione **8a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (50.8 mg, 78%), m.p 84-86 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 17.17 (s, 1H), 7.59 (d, *J* = 9.3 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.03 (dd, *J* = 8.6, 6.5 Hz, 1H), 1.96 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 162.8, 157.3, 130.8, 124.7, 119.5, 117.5, 115.7, 101.9, 24.0. **HRMS** (ESI) m/z calcd. for $C_{12}H_{12}NO_3$ $[M+H]^+$ 218.08117, found 218.08049.

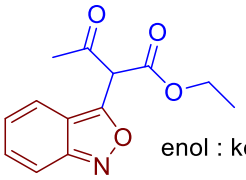
2-(Benzo[c]isoxazol-3-yl)-1,3-diphenylpropane-1,3-dione (7d)



The title compound **7d** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and pentane-2,4-dione **8b** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow oil (75.7 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 0.3H), 7.62 – 7.55 (m, 0.3H), 7.54 – 7.46 (m, 0.6H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.31 (dd, *J* = 10.1, 4.3 Hz, 2H), 7.24 – 7.09 (m, 9H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 6.3 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.6, 189.6, 163.1, 157.1, 135.6, 134.9, 134.3, 131.7, 131.1, 130.5, 129.2, 128.8, 128.2, 127.7, 124.7, 124.2, 121.0, 119.1, 118.2, 115.0, 115.0, 100.1, 56.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{16}NO_3$ $[M+H]^+$ 342.11247, found 342.11215.

Ethyl 2-(benzo[c]isoxazol-3-yl)-3-oxobutanoate (7e)

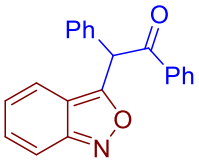


enol : ketone = 3 : 2

The title compound **7e** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and ethyl 3-oxobutanoate **8c** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (46.0 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.77 (s, 0.6H), 7.57 (t, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 0.4H), 7.37 (d, *J* = 8.8 Hz, 0.6H), 7.33 – 7.28 (m, 1H), 7.03 – 6.96 (m, 1H), 4.28 – 4.19 (m, 2.7H), 2.01 (s, 1.6H), 1.29 (d, *J* = 7.1 Hz, 1.3H), 1.20 (t, *J* = 7.1 Hz, 1.8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.0, 170.8, 167.0, 161.5, 160.6, 157.2, 157.1, 130.8, 130.5, 123.8, 123.6, 120.5, 119.6, 117.2, 116.4, 115.2, 115.1, 92.2, 61.8, 61.4, 32.9, 20.4, 14.0, 13.9. **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}NO_4$ $[M+H]^+$ 248.09173, found 248.09093.

2-(Benzo[c]isoxazol-3-yl)-1,2-diphenylethan-1-one (7f)

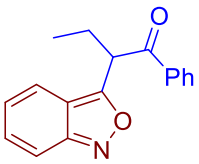


The title compound **7f** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and ethyl 3-oxobutanoate **8d** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (77.2 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 – 7.42 (m, 3H), 7.41 – 7.35(m, 3H), 7.34 – 7.29 (m, 1H), 7.19 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 6.4 Hz,

1H), 6.61 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 164.2, 157.4, 135.4, 134.2, 133.7, 130.6, 129.2, 129.1, 128.9, 128.8, 128.3, 123.9, 120.2, 116.4, 115.1, 53.1 ppm. **HRMS** (ESI) m/z calcd. for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.11756, found 314.11713.

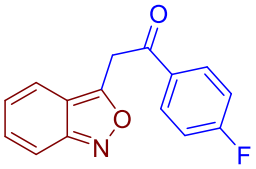
2-(Benzo[c]isoxazol-3-yl)-1-phenylbutan-1-one (7g)



The title compound **7g** was prepared following the **general procedur**e A from benzo[c]isoxazole **1a** (0.30 mmol) and 1-phenylbutan-1-one **8e** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a light yellow oil (46.2 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.21 (m, 1H), 6.90 (m, 1H), 5.22 (m, 1H), 2.38 (m, 1H), 2.27 – 2.17 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0, 164.9, 157.4, 135.8, 133.6, 130.8, 128.8, 128.5, 123.8, 120.0, 115.3, 115.0, 48.6, 24.6, 12.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.11756, found 266.11733.

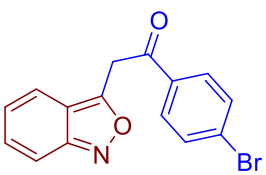
2-(Benzo[c]isoxazol-3-yl)-1-(4-fluorophenyl)ethan-1-one (7h)



The title compound **7h** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-(4-fluorophenyl)ethan-1-one **8g** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a light yellow solid (32.1 mg, 42%), m.p 83-85 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 7.56 (d, *J* = 9.1 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.23 – 7.15 (m, 2H), 6.99 (m, 1H), 4.83 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.6, 166.2 (d, *J* = 256.8 Hz), 160.9, 157.3, 132.0 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.6 Hz), 131.0, 124.0, 119.7, 116.9, 116.2 (d, *J* = 22.1 Hz, 1H), 115.2, 37.2 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -103.09. **HRMS** (ESI) m/z calcd. for $C_{15}H_{11}FNO_2$ $[M+H]^+$ 256.07683, found 256.07667.

2-(Benzo[c]isoxazol-3-yl)-1-(4-bromophenyl)ethan-1-one (7i)



The title compound **7i** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-(4-bromophenyl)ethan-1-one **8h** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a light yellow solid (47.5 mg, 50%), m.p 102-104 °C.

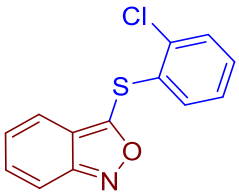
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.95 (m, 1H), 4.78 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2, 160.7, 157.2, 134.2, 132.2, 130.9, 130.1, 129.4, 124.0, 119.6, 116.8, 115.1, 37.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{11}BrNO_2$ $[M+H]^+$ 315.99677, found 315.99652.

3-(Decylthio)benzo[c]isoxazole (9a)

The title compound **9a** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and decane-1-thiol **10a** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow oil (38.8 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.1 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.93 (m, 1H), 3.22 (t, *J* = 7.4 Hz, 2H), 1.74 (m, 2H), 1.42 (m, 2H), 1.27 (d, *J* = 13.2 Hz, 12H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 157.6, 131.2, 123.1, 119.9, 118.0, 114.9, 33.7, 31.8, 30.1, 29.5, 29.4, 29.2, 29.0, 28.4, 22.6, 14.1 ppm. **HRMS** (ESI) m/z calcd. for Chemical Formula: $C_{17}H_{26}NOS$ $[M+H]^+$ 292.17296, found 292.17273.

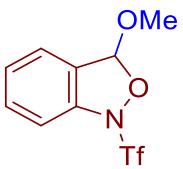
3-((2-Chlorophenyl)thio)benzo[c]isoxazole (9b)



The title compound **9b** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 2-chlorobenzenethiol **10b** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow oil (62.8 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.32 (m, 1H), 7.22 (m, 1H), 7.18 – 7.09 (m, 2H), 7.02 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 157.3, 134.2, 131.5, 131.2, 131.0, 130.2, 129.2, 127.6, 125.1, 121.1, 119.5, 115.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{13}H_9ClNOS$ $[M+H]^+$ 262.00879, found 262.00877.

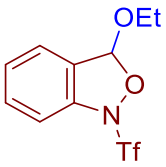
3-Methoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (9c)



The title compound **9c** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and methanol **10c** (0.60 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow solid (63.7 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 3H), 7.37 (ddd, *J* = 7.9, 5.9, 2.3 Hz, 1H), 6.36 (s, 1H), 3.61 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.31, 130.92, 128.10, 127.62, 123.88, 119.9 (q, *J* = 328.7 Hz), 115.4, 107.8, 56.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.6 ppm. **HRMS** (ESI) m/z calcd. for $C_9H_7F_3NO_4S$ $[M-H]^-$ 282.00534, found 282.00555.

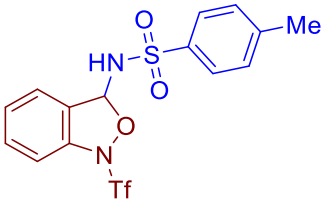
3-Ethoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (9d)



The title compound **9d** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and ethanol **10d** (0.60 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow oil (72.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.39 – 7.35 (m, 1H), 6.44 (s, 1H), 4.00 (m, 1H), 3.80 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.3, 130.8, 128.3, 127.6, 123.9, 119.8 (q, *J* = 328.8 Hz), 115.4, 106.8, 65.7, 14.8 ppm. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -69.6 ppm. **HRMS** (ESI) m/z calcd. for Chemical Formula: $C_{10}H_9F_3NO_4S$ $[M-H]^-$ 296.02099, found 296.02107.

4-Methyl-N-(1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazol-3-yl)benzenesulfonamide (9e)



The title compound **9e** was prepared following the **general procedure A** from benzo[c]isoxazole **1a** (0.30 mmol) and 4-methylbenzenesulfonamide **10e** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light white solid (114.2 mg, 90%), m.p 123-125 °C.

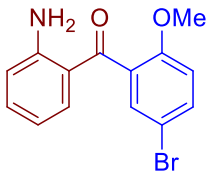
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 8.3 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 11.3 Hz, 1H), 5.74 (d, *J* = 11.3 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.2, 136.1, 131.0, 129.7, 128.8, 128.2, 127.3, 124.2, 119.0 (q, *J* = 325.9 Hz), 117.3, 90.1, 21.5.

^{19}F NMR (375 MHz, $CDCl_3$) δ -71.8 ppm.

HRMS (ESI) m/z calcd. for Chemical Formula: $C_{15}H_{12}F_3N_2O_5S_2$ $[M-H]^-$ 421.01452, found 421.01536.

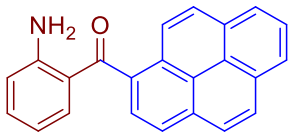
(2-Aminophenyl)(5-bromo-2-methoxyphenyl)methanone (11a)



The title compound **11a** was prepared following the **general procedure B** from benzo[c]isoxazole **1a** (0.30 mmol) and 1-bromo-4-methoxybenzene **2l** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (65.9 mg, 72%), m.p 124-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.60 (m, 1H), 6.45 (m, 1H), 6.32 (s, 2H), 3.65 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 155.4, 151.1, 134.9, 134.7, 133.2, 132.0, 130.9, 117.9, 116.8, 115.6, 113.0, 112.6, 55.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{13}BrNO_2$ $[M+H]^+$ 306.01242, found 306.01147.

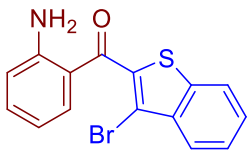
(2-Aminophenyl)(pyren-1-yl)methanone (11b)



The title compound **11b** was prepared following the **general procedure B** from benzo[c]isoxazole **1a** (0.30 mmol) and pyrene **2ac** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (40.5 mg, 42%), m.p 183-185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 15.0, 7.3 Hz, 3H), 8.14 (q, *J* = 8.7 Hz, 3H), 8.08 – 7.99 (m, 3H), 7.33 – 7.27 (m, 1H), 7.20 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.58 (s, 2H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.44 (t, *J* = 7.6 Hz, 1H) ppm.**^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 151.3, 135.5, 135.4, 134.9, 132.1, 131.2, 130.8, 128.6, 128.4, 128.4, 127.2, 126.3, 125.7, 125.6, 125.4, 124.7, 124.6, 124.5, 124.0, 119.2, 117.0, 115.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{23}H_{16}NO$ $[M+H]^+$ 322.12264, found 322.12172.

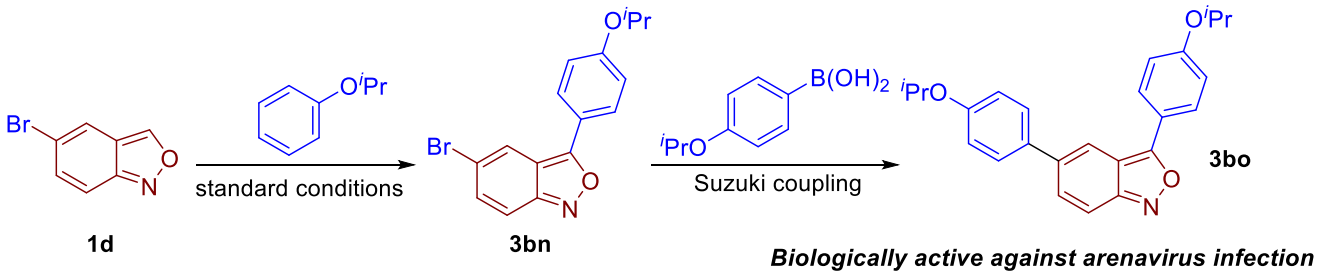
(2-Aminophenyl)(3-bromobenzo[b]thiophen-2-yl)methanone (11c)



The title compound **11c** was prepared following the **general procedure B** from benzo[c]isoxazole **1a** (0.30 mmol) and 3-bromobenzo[b]thiophene **2am** (0.36 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (74.5 mg, 75%), m.p 127-129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 1H), 7.86 (m, 1H), 7.58 – 7.55 (m, 1H), 7.50 (m, 2H), 7.33 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.64 – 6.59 (m, 1H), 6.31 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 151.2, 138.3, 137.7, 136.3, 135.5, 134.9, 126.8, 125.6, 124.2, 122.5, 117.7, 116.9, 115.9, 108.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{15}H_{11}BrNOS$ $[M+H]^+$ 331.97392, found 331.97327.

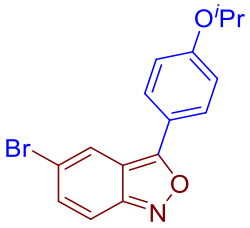
The synthesis of bioactive compound against arenavirus infection.



Biologically active against arenavirus infection

Step1: 5-Bromo-3-(4-isopropoxyphenyl)benzo[c]isoxazole (**3bn**) was obtained following the **general procedure A** from 5-bromobenzo[c]isoxazole **1d** (1.0 mmol) and isopropoxybenzene (1.2 mmol) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (274.7 mg, 83%), m.p 104-105 °C.

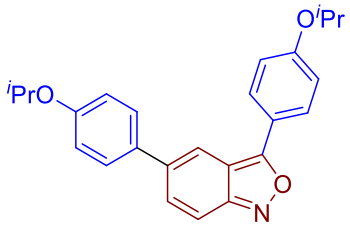
5-Bromo-3-(4-isopropoxyphenyl)benzo[c]isoxazole (3bv)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 9.4 Hz, 1H), 7.33 (d, *J* = 9.4 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 4.65 (m, 1H), 1.39 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 159.9, 156.2, 134.4, 128.2, 122.8, 120.2, 117.2, 116.9, 116.3, 114.4, 70.1, 21.9. **HRMS** (ESI) m/z calcd. for $C_{16}H_{15}BrNO_2$ $[M+H]^+$ 332.02807, found 332.02703.

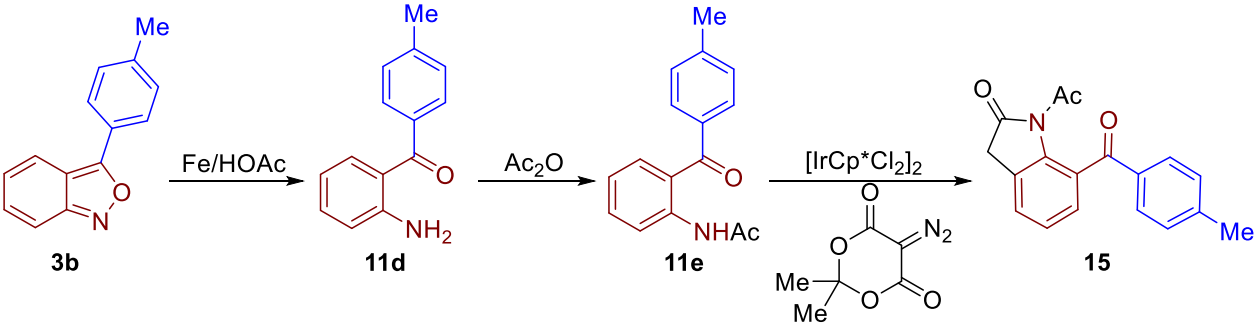
Step 2: 3,5-Bis(4-isopropoxyphenyl)benzo[c]isoxazole (**3bw**) was synthesized via Suzuki coupling from **3bv**. An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with compound **3** (166 mg, 0.5 mmol), (4-isopropoxyphenyl)boronic acid (108 mg, 0.6 mmol), K_3PO_4 (318.4 mg, 1.5 mmol) and $(PPh_3)_2PdCl_2$ (17.5 mg, 0.025 mmol). After back forth 3 times with N_2, toluene (4.0 mL) and H_2O (0.1 mL) were added via syringe. The resulting mixture was heated to 100 °C for 14 h. The reaction was cooled to room temperature and diluted with H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried with $MgSO_4$, and evaporated under reduced pressure (rotary evaporator) and then purified by silica gel column chromatography. 3,5-Bis(4-isopropoxyphenyl)benzo[c]isoxazole **3bo** was obtained in 75% yield (145.1 mg) as a light yellow oil.

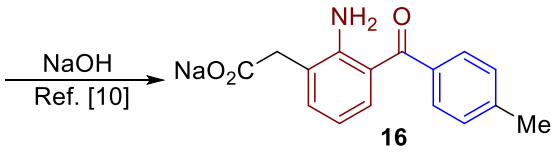
3,5-Bis(4-isopropoxyphenyl)benzo[c]isoxazole (3bw)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.85 (s, 1H), 7.65 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.66 (m, 1H), 4.63 – 4.57 (m, 1H), 1.39 (t, *J* = 6.3 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 159.6, 157.7, 157.3, 136.7, 132.6, 131.8, 128.1, 128.1, 120.9, 116.8, 116.3, 116.2, 115.5, 114.2, 70.1, 70.0, 22.0, 21.9. **HRMS** (ESI) m/z calcd. for $C_{25}H_{26}NO_3$ $[M+H]^+$ 388.19072, found 388.18982.

The synthesis of compound 16.[10]

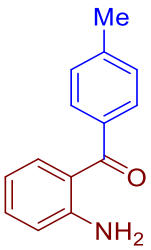




Amfenac derivatives

Step1: (2-Aminophenyl)(*p*-tolyl)methanone **11d** was synthesized from the reductive ring opening of **3b**. To a solution of **3b** (3 mmol) obtained through our method in 9 mL HOAc/H_2O (2:1), Fe powder (6 mmol) was added. The resulting mixture was vigorous stirring at 90 °C for 10 hours. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). (2-Aminophenyl)(*p*-tolyl)methanone **11d** was obtained in 90% yield (570 mg).

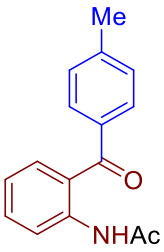
(2-Aminophenyl)(p-tolyl)methanone (11d)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.35 (m, 1H), 7.15 (m, 3H), 6.61 (m, 1H), 6.49 (m, 1H), 5.92 (s, 2H), 2.31 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.7, 150.6, 141.6, 137.1, 134.3, 133.9, 129.3, 128.6, 118.4, 116.9, 115.3, 21.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NO$ $[M+H]^+$ 212.10699, found 212.10613.

Step 2: To a solution of (2-Aminophenyl)(*p*-tolyl)methanone **11d** (1 mmol) and Et_3N (1.5 mmol) in 5 mL dry DCM, Ac_2O (1.5 mmol) was added dropwisely at 0 ^{o}C. After stirring at 0 ^{o}C for 30 min, the reaction mixture slowly increased to room temperature, and continued to stir for 12 h. After the reaction was completed, saturated brine 10 mL was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). 2-Chloro-N-(2-(4-methylbenzoyl)phenyl)acetamide **11e** was obtained in 93% yield (235 mg).

2-Chloro-N-(2-(4-methylbenzoyl)phenyl)acetamide (11e)

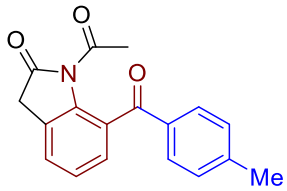


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.60 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.54 (ddd, *J* = 7.3, 4.1, 1.5 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.07 (td, *J* = 7.8, 1.1 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 168.9, 143.3, 140.0, 135.7, 133.8, 133.1, 130.0, 128.9, 123.5, 121.9, 121.4, 25.1, 21.5. **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$ 254.11756, found 254.11652.

Step 3: An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with **11e** (0.5 mmol), diazotized Meldrum's acid (0.6 mmol), $[IrCp^*Cl_2]_2$ (2.0 mol %), $AgNTf_2$ (8.0 mol %), NaOAc (0.5 mmol) and 1,2-dichloroethane (1.0 mL) under air. The reaction mixture was stirred at 70 °C for 10 h. After the completion of reaction, the reaction mixture was filtered through a pad of celite followed by washing of the pad with CH_2Cl_2 (10 mL x 2). The combined solvents were removed under reduced pressure and the

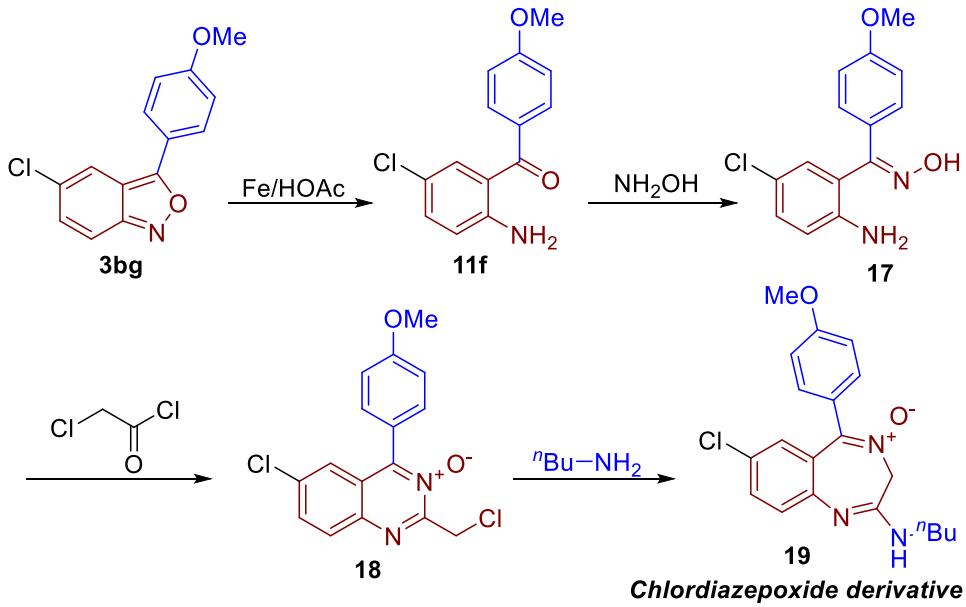
residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). 1-Acetyl-7-(4-methylbenzoyl)indolin-2-one **15** was obtained in 52% yield (76.2 mg).

1-Acetyl-7-(4-methylbenzoyl)indolin-2-one (15)



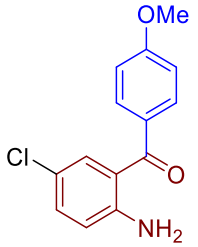
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.29 (t, *J* = 6.7 Hz, 3H), 7.26 – 7.21 (m, 1H), 3.81 (s, 2H), 2.51 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 174.6, 170.6, 143.8, 137.6, 134.1, 130.2, 129.1, 128.1, 128.0, 125.8, 125.2, 124.4, 37.1, 25.8, 21.7. **HRMS** (ESI) m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.11247, found 294.11148.

<u>The synthesis of chlordiazepoxide derivatives.</u>



Step1: To a solution of **3bg** (3 mmol) obtained through our method in 9 mL $HOAc/H_2O$ (2:1), Fe powder (6 mmol) was added. The resulting mixture was vigorous stirring at 90 °C for 10 hours. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). (2-Amino-5-chlorophenyl)(4-methoxyphenyl)methanone **11f** was obtained in 92% yield (720 mg) as a yellow solid, m.p 95-97 °C.

(2-Amino-5-chlorophenyl)(4-methoxyphenyl)methanone (11f)

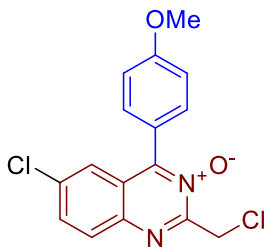


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.21 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 1H), 5.83 (s, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 162.6, 148.7, 133.4, 132.7, 131.7, 131.5, 119.9, 119.6, 118.3, 113.5, 55.4 ppm. **HRMS** (ESI) m/z calcd. for $C_{14}H_{13}ClNO_2$ $[M+H]^+$ 262.06293, found 262.06221.

Step 2: To a 500 mL round bottom flask charged with a stir bar, sodium acetate (164 mg, 2.0 mmol,) and hydroxylamine hydrochloride (104 mg, 1.5 mmol), was added a solution of the obtained ketone (1 mmol) in 10 mL ethanol/water (4:1). The reaction mixture was then heated to reflux until all the ketone starting material was consumed as indicated by TLC. After reflux, the reaction was allowed to cool to room temperature. The crude mixture was obtained after removal of excess ethanol. To the crude mixture was added 10 mL of water. The resulting aqueous solution was extracted with EtOAc (3×10 mL). The combined organic layers were then washed with water (2×10 mL) and brine (1×10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The oxime product **17** (256.7 mg, 93% yield) was obtained after flash column chromatography as a white solid, m.p 174-176 °C.

Step 3: To a warm solution (50 °C) of the obtained oxime (0.8 mmol) in 2 mL acetic acid were added chloroacetyl chloride (2.2 equiv). The mixture was heated for 10 minutes at 50 °C and then stirred at room temperature for 15 hours. After completion of the reaction, the mixture was dissolved in 10 mL DCM and washed with ice cold sodium carbonate solution. The organic solution was dried, concentrated in vacuo to afford the crude product. The desired 6-chloro-2-(chloromethyl)-4-(4-methoxyphenyl)quinazoline 3-oxide product (227 mg, 85% yield) was obtained after flash column chromatography as a yellow solid, m.p 142-144 °C.

6-Chloro-2-(chloromethyl)-4-(4-methoxyphenyl)quinazoline 3-oxide (18)

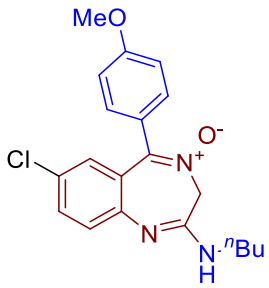


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.60 (s, 0H), 7.58 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 5.08 (s, 2H), 3.91 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 154.9,

149.7, 138.7, 135.7, 131.9, 131.7, 130.3, 125.0, 123.9, 119.4, 114.2, 55.4, 41.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{16}H_{13}Cl_2N_2O_2$ $[M+H]^+$ 335.03486, found 335.03387.

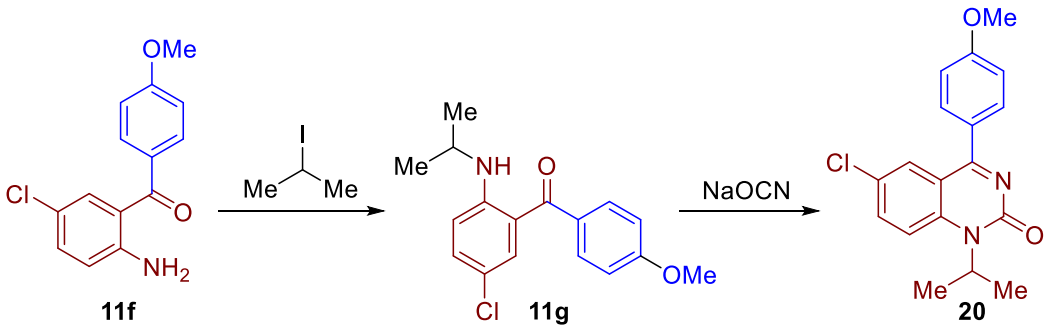
Step 4: The above obtained 6-chloro-2-(chloromethyl)-4-(4-methoxyphenyl)quinazoline 3-oxide (0.5 mmol) was added to a N-butylamine solution in MeOH at 0 °C. Then the mixture was slowly increased to room temperature. After 15 hours, the reaction was concentrated in vacuo to dryness. The residue was dissolved in DCM, washed with water and dried with sodium sulfate. The desired product (165 mg, 89% yield) was obtianed after flash column chromatography as a white solid, m.p 151-153 °C.

2-(Butylamino)-7-chloro-5-(4-methoxyphenyl)-3H-benzo[e][1,4]diazepine 4-oxide (19)



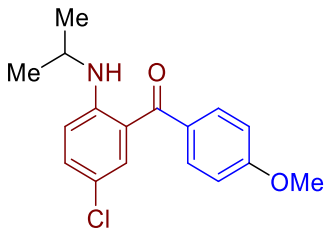
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.28 (m, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.03 (d, *J* = 12.2 Hz, 1H), 4.08 (d, *J* = 12.1 Hz, 1H), 3.85 (s, 3H), 3.39 (m, 1H), 3.14 (m, 1H), 1.35 (m, 2H), 1.29 – 1.24 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 152.3, 148.7, 144.6, 133.0, 130.2, 130.1, 128.3, 125.9, 125.8, 124.9, 113.3, 63.5, 55.3, 41.8, 30.4, 20.1, 13.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{20}H_{23}ClN_3O_2$ $[M+H]^+$ 372.14733, found 372.14642.

<u>The synthesis of proquazone derivatives.</u>



Step 1: A mixture of **11f** (1 mmol) and potassium carbonate (1.2 mmol) in 5 mL of 2-iodopropane was stirred for two days at 110 ^oC. The mixture was distributed between ethyl acetate and water, the layers were separated, and the organics concentrated in vacuo. The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). (5-Chloro-2-(isopropylamino)phenyl)(4-methoxyphenyl)methanone **11g** was obtained in 83% yield (251.5 mg) as a yellow oil.

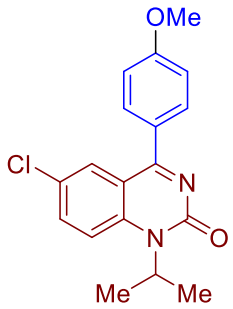
(5-Chloro-2-(isopropylamino)phenyl)(4-methoxyphenyl)methanone (11g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.5 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.28 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 9.1 Hz, 1H), 3.88 (s, 3H), 3.76 – 3.68 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 162.3, 149.1, 134.2, 133.8, 132.1, 131.6, 118.3, 117.7, 113.5, 113.4, 55.4, 43.5, 22.6 ppm. **HRMS** (ESI) m/z calcd. for $C_{17}H_{19}ClNO_2$ $[M+H]^+$ 304.10988, found 304.10889.

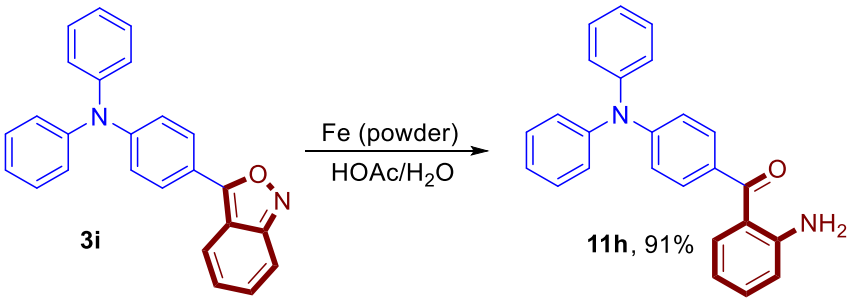
Step 2: A solution of **11g** (0.80 mmol) in 5 mL of glacial acetic acid was treated at room temperature with sodium cyanate (1.2 mmol). The resulting mixture was stirred overnight and quenched with saturated sodium bicarbonate aqueous solution. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). 6-Chloro-1-isopropyl-4-(4-methoxyphenyl)quinazolin-2(1H)-one **20** was obtained in 78% yield (204.7 mg) as a yellow solid, m.p 109-110 °C.

6-Chloro-1-isopropyl-4-(4-methoxyphenyl)quinazolin-2(1H)-one (20)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.4 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.63 (m, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.07 – 7.01 (m, 2H), 5.12 (m, 1H), 3.89 (s, 3H), 1.68 (d, *J* = 7.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 162.0, 155.0, 142.2, 134.2, 131.7, 129.1, 128.1, 126.9, 117.6, 115.9, 114.0, 55.4, 49.2, 19.3 ppm. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}ClN_2O_2$ $[M+H]^+$ 329.10513, found 329.10403.

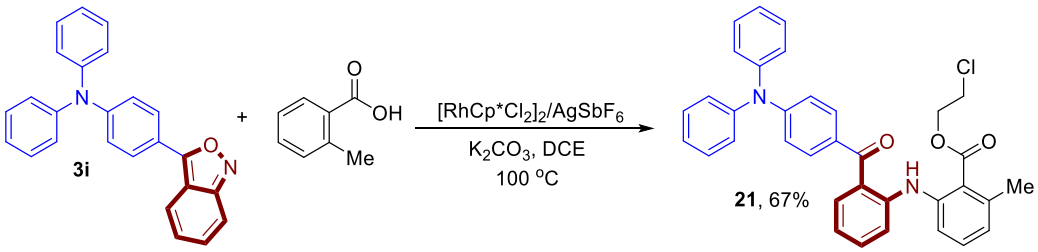
(2-Aminophenyl)(4-(diphenylamino)phenyl)methanone (11h)



To a solution of **3i** (0.1 mmol) in 1.5 mL HOAc/H_2O (2:1), Fe powder (0.2 mmol) was added. The resulting mixture was vigorous stirring for 4 hours. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient) to give (2-aminophenyl)(4-(diphenylamino)phenyl)methanone **11h** (33.1 mg) as a bright yellow solid in 91% yield, m.p 124-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.52 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 4H), 7.25 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 4H), 7.11 (t, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 5.81 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.4, 151.0, 150.2, 146.8, 133.8, 133.5, 132.1, 131.2, 129.5, 125.7, 124.2, 120.1, 119.1, 116.9, 115.5 ppm. **MS** (EI) m/z $C_{25}H_{20}N_2O$: 364.2 $[M]^+$, 347.2, 245.2, 167.2, 120.2, 92.1, 77.1.

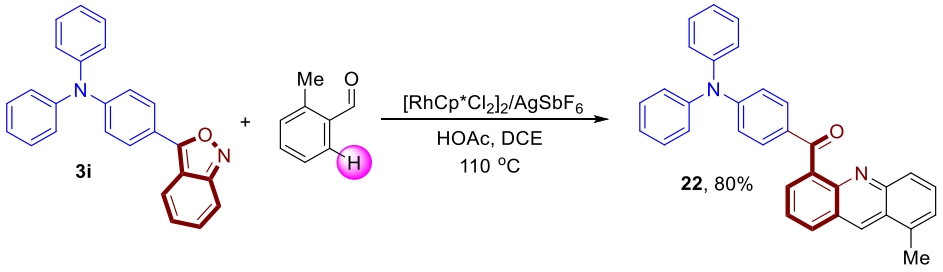
2-Chloroethyl 2-((2-(4-(diphenylamino)benzoyl)phenyl)amino)-6-methylbenzoate (21)



An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (10 mol%), 2-methylbenzoic acid (0.15 mmol), K_2CO_3 (0.15 mmol) and was closed with a septum cap. Then DCE (2.0 mL) and **3i** (0.1 mmol) were added via syringe. The resulting mixture was stirred at 100 °C for 12 h. After completion of the reaction, the resulting mixture was diluted with saturated NaCl aqueous solution (5 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate gradient) to give **21** (37.5 mg) as a yellow solid in 67% yield, m.p 167-169 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.58 (m, 1H), 7.40 – 7.29 (m, 7H), 7.24 – 7.20 (m, 1H), 7.20 – 7.10 (m, 6H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.85 – 6.79 (m, 1H), 4.68 (t, *J* = 5.9 Hz, 2H), 3.90 (t, *J* = 5.9 Hz, 2H), 2.46 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 167.8, 151.5, 146.6, 145.3, 141.0, 138.7, 133.3, 132.7, 131.8, 131.0, 130.7, 129.6, 125.8, 124.5, 123.8, 123.7, 119.7, 118.1, 117.8, 117.0, 64.8, 41.3, 21.2 ppm. **HRMS** (ESI) m/z calcd. for $C_{35}H_{30}ClN_2O_3$ $[M+H]^+$ 561.19395, found 561.19379.

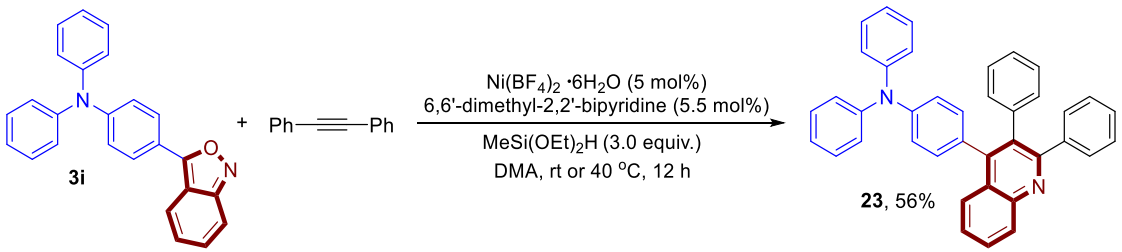
(4-(Diphenylamino)phenyl)(8-methylacridin-4-yl)methanone (22)



An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (10 mol%), 2-methylbenzaldehyde (0.15 mmol), HOAc (0.1 mmol) and was closed with a septum cap. Then DCE (2.0 mL) and **3i** (0.1 mmol) were added via syringe. The resulting mixture was stirred at 110 °C for 24 h. After completion of the reaction, the resulting mixture was diluted with saturated NaCl aqueous solution (5 mL). Following phase separation, the aqueous layer was extracted 3 times with DCM (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate gradient) to give **22** (37.1 mg) as a solid in 80% yield, m.p 152-154 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.12 (m, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.79 (m, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.58 (m, 2H), 7.33 (d, *J* = 6.7 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 4H), 7.15 (d, *J* = 7.6 Hz, 4H), 7.10 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 2.81 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 152.1, 149.5, 146.5, 146.4, 139.6, 134.5, 132.4, 131.9, 130.7, 130.0, 129.9, 129.5, 128.6, 128.6, 126.4, 126.0, 124.6, 124.6, 119.2, 18.9 ppm. **HRMS** (ESI) m/z calcd. for $C_{33}H_{25}N_2O$ $[M+H]^+$ 465.19614, found 465.19589.

4-(2,3-Diphenylquinolin-4-yl)-N,N-diphenylaniline (23)

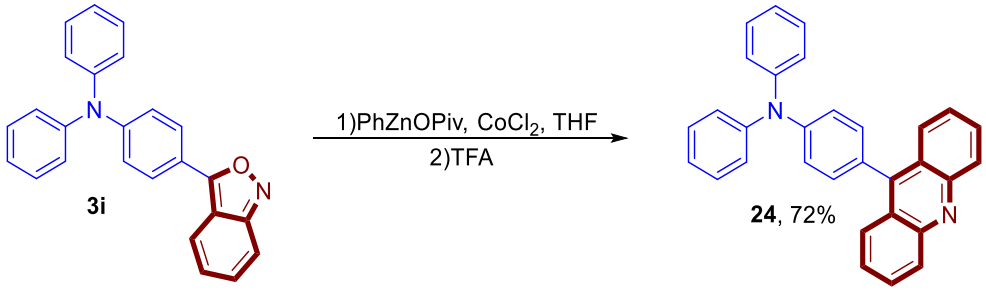


An oven-dried 20 mL vial was charged with $Ni(BF_4)_2.6H_2O$ (5 mol%) and 6,6'-dimethyl-2,2'-bipyridin (5.5 mol%), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMA (1.0 mL), $Me(OEt)_2SiH$ (0.2 mmol, 2.0 equiv) and alkyne (0.1 mmol, 1 equiv) were successively added via

syringe, and the mixture was stirred at room temperature for 5 min. Then, **3i** (0.11 mmol, 1.1 equiv) was added and the mixture was stirred under an argon atmosphere at room temperature or 40 °C for 12 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient) to give **23** (29.3 mg) as a light yellow solid in 56% yield, m.p 173-175 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 (m, 1H), 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.31 – 7.24 (m, 7H), 7.15 – 7.07 (m, 7H), 7.05 (m, 6H), 6.98 – 6.92 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 147.6, 147.5, 147.3, 146.8, 141.1, 138.6, 133.2, 131.4, 131.3, 130.9, 129.9, 129.7, 129.3, 129.2, 127.6, 127.5, 127.2, 126.6, 126.6, 126.5, 126.1, 124.2, 123.1, 122.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{39}H_{29}N_2$ $[M+H]^+$ 525.23253, found 525.23230.

4-(Acridin-9-yl)-N,N-diphenylaniline (24)



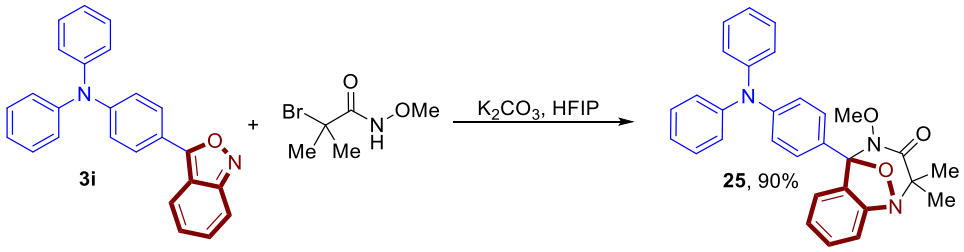
An oven-dried 20 mL vial was charged with $CoCl_2$ (10 mol%) and PhZnOPiv (0.12 mmol) and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, THF (1.0 mL) and **3i** (0.1 mmol) were successively added, and the mixture was stirred at room temperature for 5 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator).

The residue was dissolved in 1 mL TFA and the resulting solution was stirred at 80 °C for 2 h. After completion of the reaction, saturated sodium bicarbonate aqueous solution was added to quench the reaction. Following phase separation, the aqueous layer was extracted 3 times with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient) to give **24** (30.4 mg) as a light yellow solid in 72% yield, m.p 179-180 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.79 – 7.72 (m, 2H), 7.47 – 7.42 (m, 2H), 7.32 (m, 4H), 7.25 (m, 8H), 7.08 (t, *J* = 7.2 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8,

148.0, 147.5, 147.3, 131.4, 129.9, 129.6, 129.5, 128.9, 127.0, 125.5, 125.3, 125.0, 123.5, 122.3 ppm. **MS** (EI) m/z $C_{31}H_{22}N_2$: 422.3 $[M]^+$, 343.2, 254.2, 210.9, 167.1, 77.1.

5-(4-(Diphenylamino)phenyl)-4-methoxy-2,2-dimethyl-4,5-dihydro-1,5-epoxybenzo[e][1,4]diazepin-3(2H)-one (25)

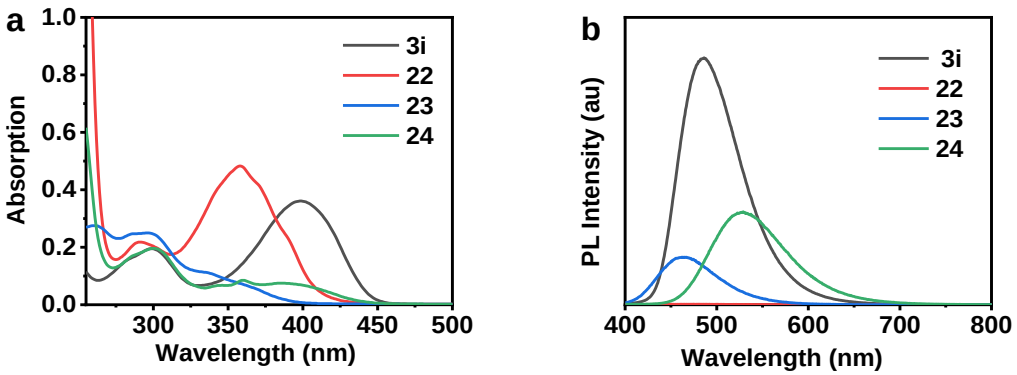


To a solution of 2-bromo-N-methoxy-2-methylpropanamide (0.2 mmol) in 1 mL HFIP, K_2CO_3 (0.2 mmol) and **3i** (0.1 mmol) were successively added. The reaction was stirred at room temperature and finished in 30 min. After completion of the reaction, the resulting mixture was diluted with water (2 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient) to give **25** (43.0 mg) as a reddish brown oil in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.26 (m, 6H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.14 (m, 6H), 7.08 (t, *J* = 7.3 Hz, 2H), 3.73 (s, 3H), 1.90 (s, 3H), 1.33 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 149.6, 149.4, 147.1, 138.4, 129.4, 129.2, 128.2, 126.3, 125.2, 124.5, 123.7, 123.0, 121.7, 118.9, 101.7, 71.2, 63.8, 27.6, 21.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{30}H_{28}N_3O_3$ $[M+H]^+$ 478.21252, found 478.21231.

9. Photophysical properties investigation

9.1 Photophysical Properties of 3i, 22, 23 and 24 in THF.



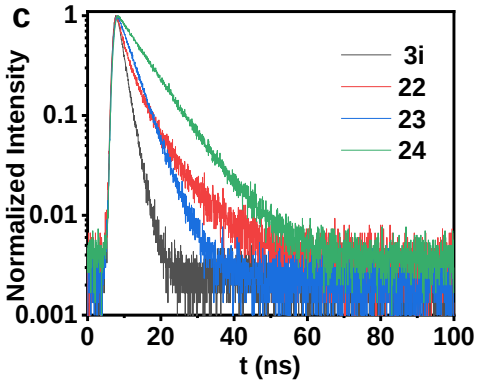


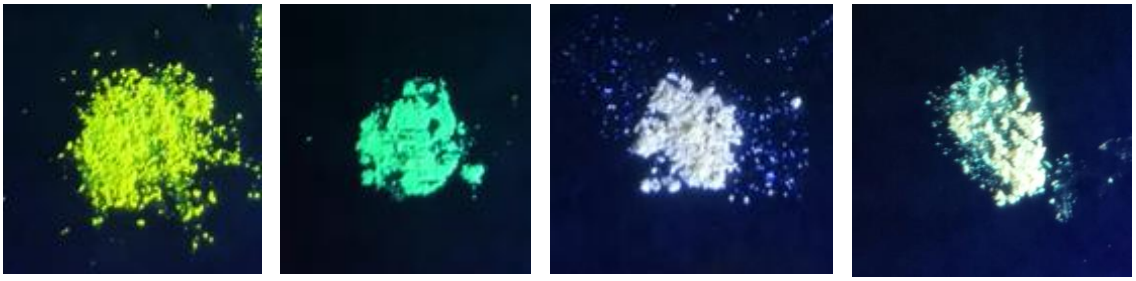
Figure 2. (a) The absorption spectra of **3i**, **22**, **23** and **24** in THF solutions (10^{-5} M). (b) The emission spectra of **3i**, **22**, **23** and **24** in THF solutions (10^{-5} M). (c) Time-correlated single photon counting in solution (10^{-5} M in THF).

Table 2. Photophysical Properties of **3i**, **22**, **23** and **24** in THF solutions (10^{-5} M).

Comp.	λ_{max} abs. (nm)	λ_{em} em. (nm)	Φ (%)[a]	τ (ns)
3i	400	486	43	1.85
22	358	475	0.77	7.47
23	298	464.5	81.7	3.93
24	360	528	88.4	7.74

[a] Fluorescence quantum yields with anthracene in ethanol (Φ= 27%) as standard.

9.2 Photophysical Properties of 3i, 22, 23 and 24 in solid.



3i **22** **23** **24**

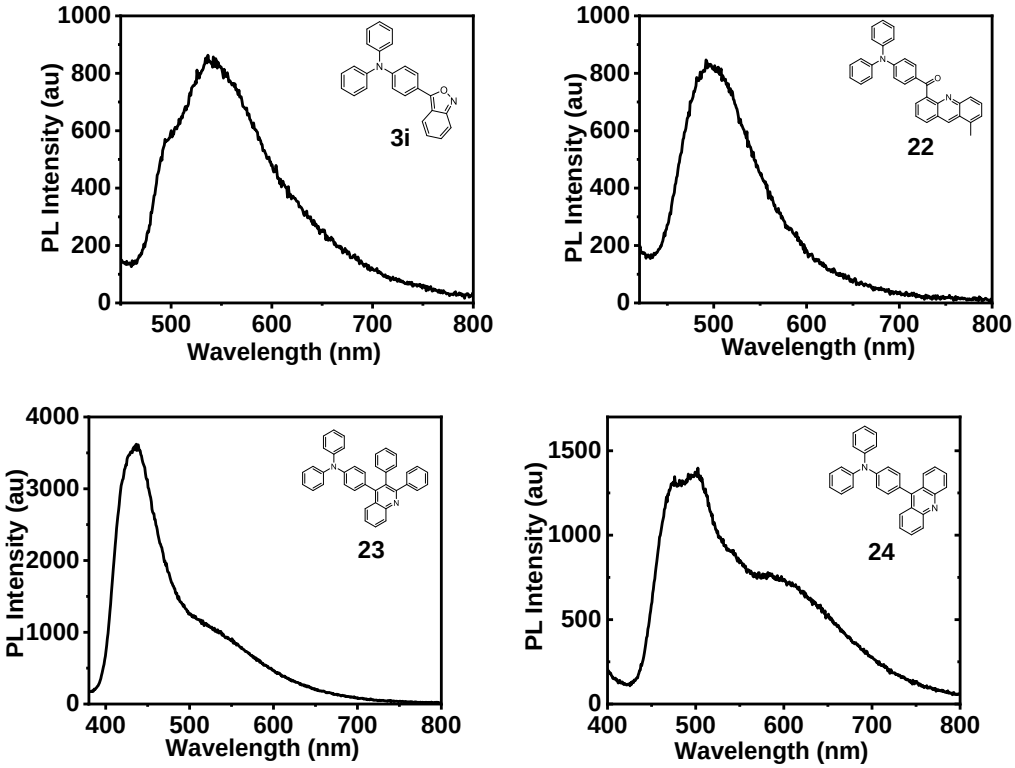


Figure 4. The emission spectra of **3i**, **22**, **23**, and **24** solids.

9.3 Investigation the AIE effect of 3i, 22, 23 and 24.

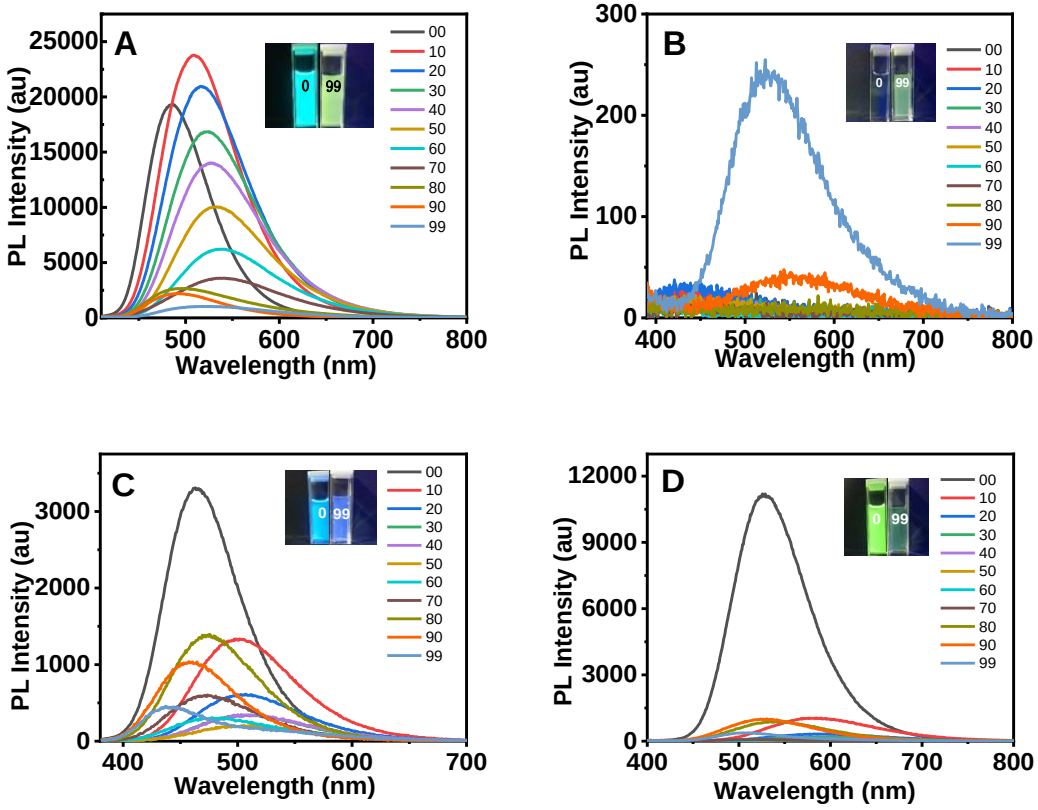


Figure 3. The emission spectra of **3i**, **22**, **23**, and **24** in H_2O/THF mixture with different water content (10^{-5} M).

10. Crystal structure of 3ax.

The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2094464 (for **3ax**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Datablock: I

Bond precision: C-C = 0.0032 A Wavelength=0.71073

Cell: a=15.6620(4) b=10.0274(2) c=10.2923(3)
alpha=90 beta=104.545(1) gamma=90
Temperature: 230 K

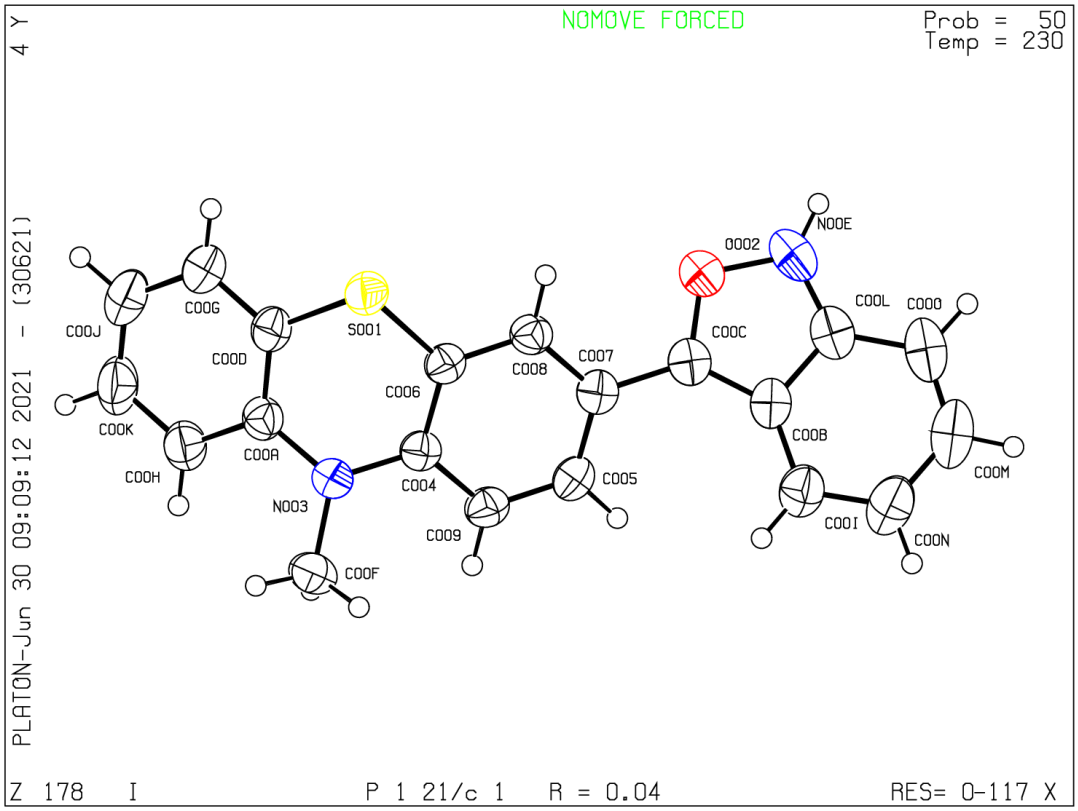
	Calculated	Reported
Volume	1564.59(7)	1564.59(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H15 N2 O S	C20 H15 N2 O S
Sum formula	C20 H15 N2 O S	C20 H15 N2 O S
Mr	331.40	331.40
Dx,g cm-3	1.407	1.407
Z	4	4
Mu (mm-1)	0.216	0.216
F000	692.0	692.0
F000'	692.74	
h,k,lmax	19,12,12	19,12,12
Nref	3193	3165
Tmin,Tmax	0.947,0.962	0.641,0.745
Tmin'	0.947	

Correction method= # Reported T Limits: Tmin=0.641 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 26.368

R(reflections)= 0.0441(2483) wR2(reflections)= 0.1304(3165)

S = 1.061 Npar= 218



11. References

[1] Y. Gao, J. Nie, Y. Huo, X.-Q. Hu, *Org. Chem. Front.* **2020**, *7*, 1177–1196.

[2] J. Chauhan, S. Fletcher, *Tetrahedron Lett.* **2012**, *53*, 4951–4954.

[3] a) Y. Gao, S. Yang, Y. Huo, Q. Chen, X. Li, X.-Q. Hu, *ACS Catal.* **2021**, *11*, 7772–777; b) Y. Gao, J. Nie, Y. Li, X. Li, Q. Chen, Y. Huo, X.-Q. Hu, *Org. Lett.* **2020**, *22*, 2600–2605.

[4] a) P.-Y. Jiang, K.-F. Fan, S. Li, S.-H. Xiang, B. Tan, *Nat Commun* **2021**, 12, 2384; b) E. J. Corey, Y. Tian, *Org. Lett.* **2005**, 7, 5535–5537.

[5] L. Fra, A. Millán, J. A. Souto, K. Muñiz, *Angew. Chem. Int. Ed.* **2014**, *53*, 7349–7353.

[6] M. Aidene, F. Belkessam, J.-F. Soulé, H. Doucet, *ChemCatChem* **2016**, *8*, 1583–1590.

[7] a) M. Murai, T. Ogita, K. Takai, *Chem. Commun.* **2019**, *55*, 2332–2335; b) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[8] M. Więcław, M. Bobin, A. Kwast, R. Bujok, Z. Wróbel and K. Wojciechowski, *Mol Divers*, **2015**, *19*, 807–816.

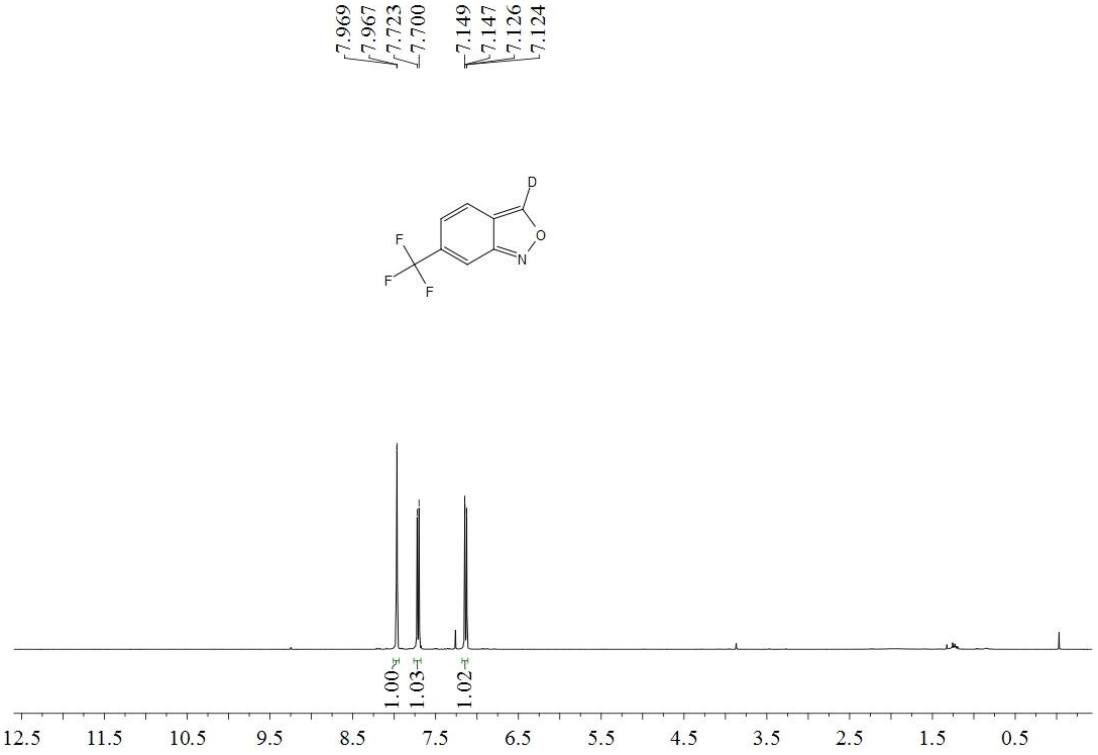
[9] C. Gao, J. Xu, S. Zhu, K. Jian, Q. Xuan and Q. Song, *Chem. Commun.*, **2021**, *57*, 2037–2040.

[10] D. A. Walsh, H. W. Moran, D. A. Shamblee, I. M. Uwaydah, W. J. Welstead, L. F. Sancilio, W. N. Dannenburg, *J. Med. Chem.* **1984**, *27*, 1379–1388.

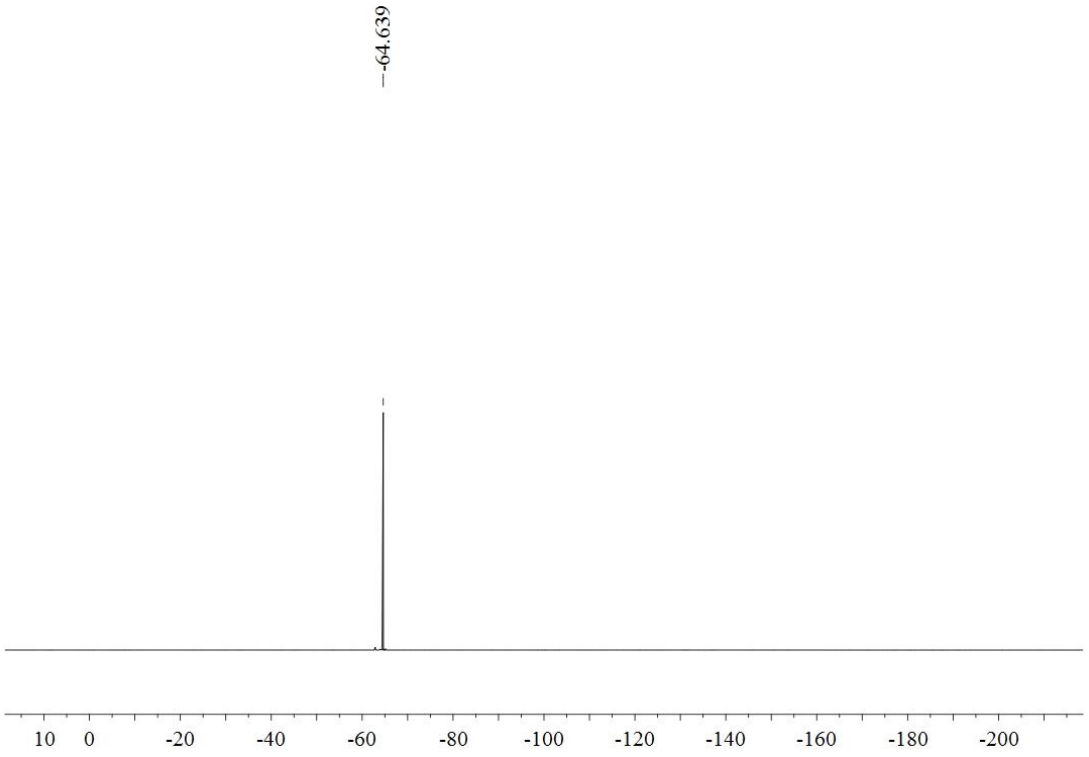
12. NMR Spectra

6-(Trifluoromethyl)benzo[c]isoxazole-3-d (**D-1k**)

^{1}H NMR (400 MHz, $CDCl_3$)

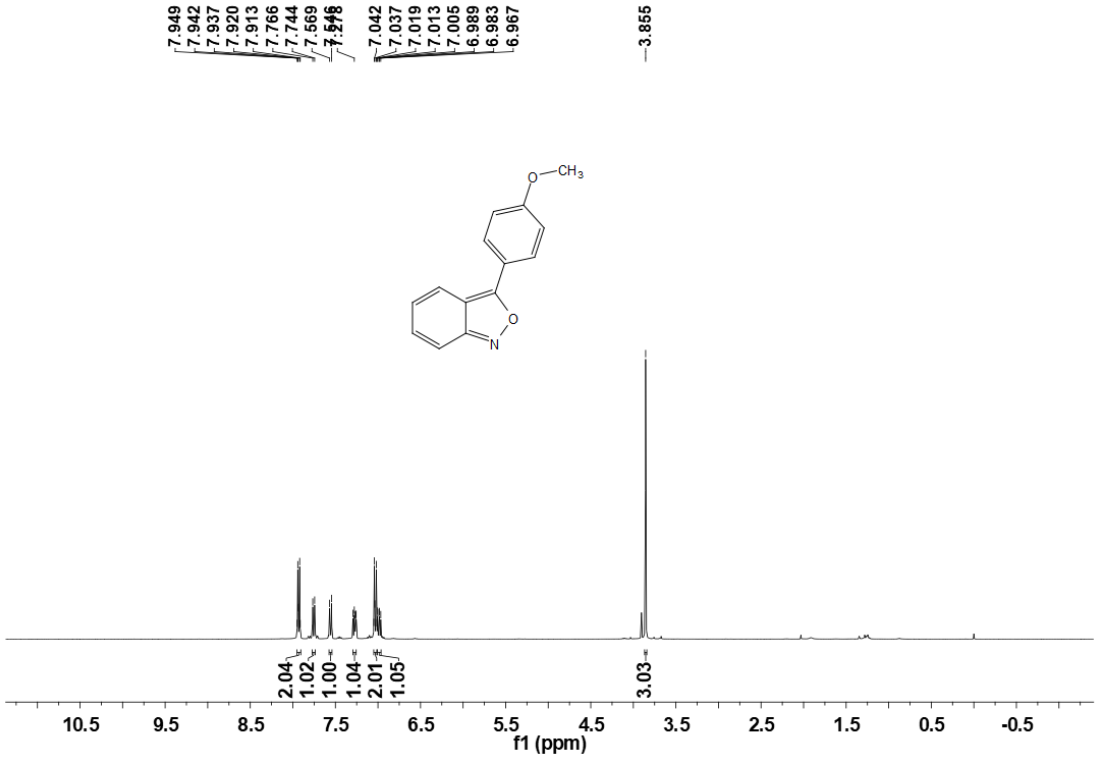


^{19}F NMR (376 MHz, $CDCl_3$)

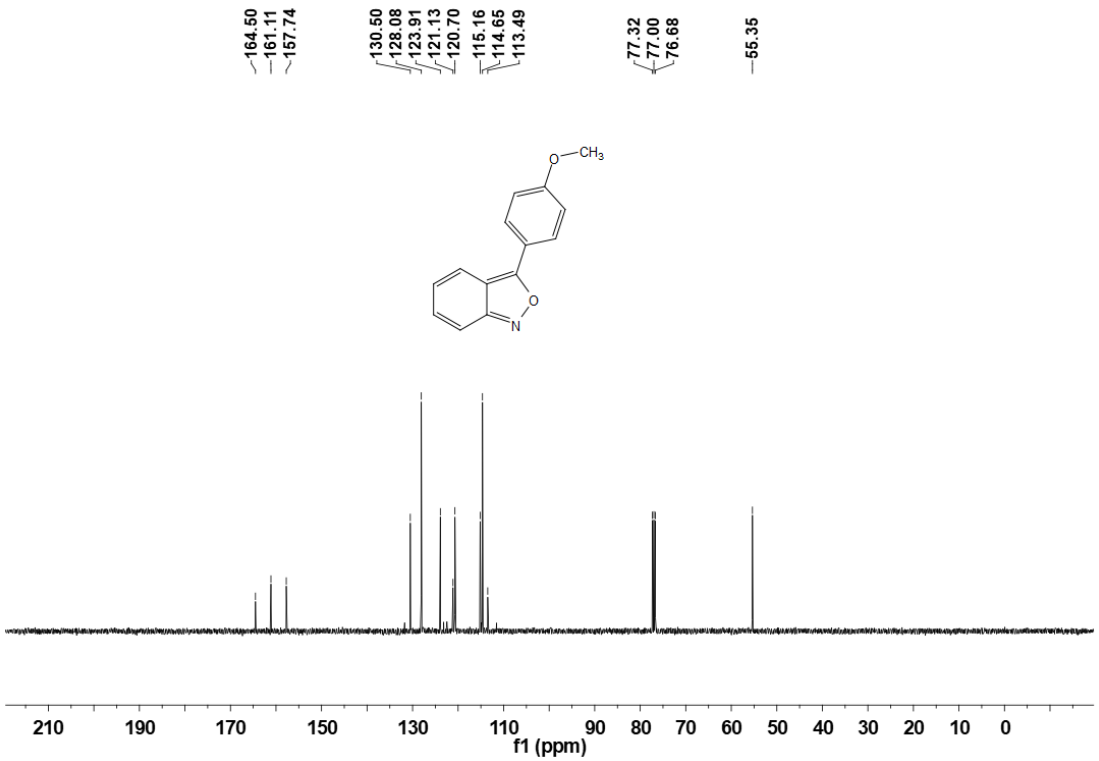


3-(4-Methoxyphenyl)benzo[c]isoxazole (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$)

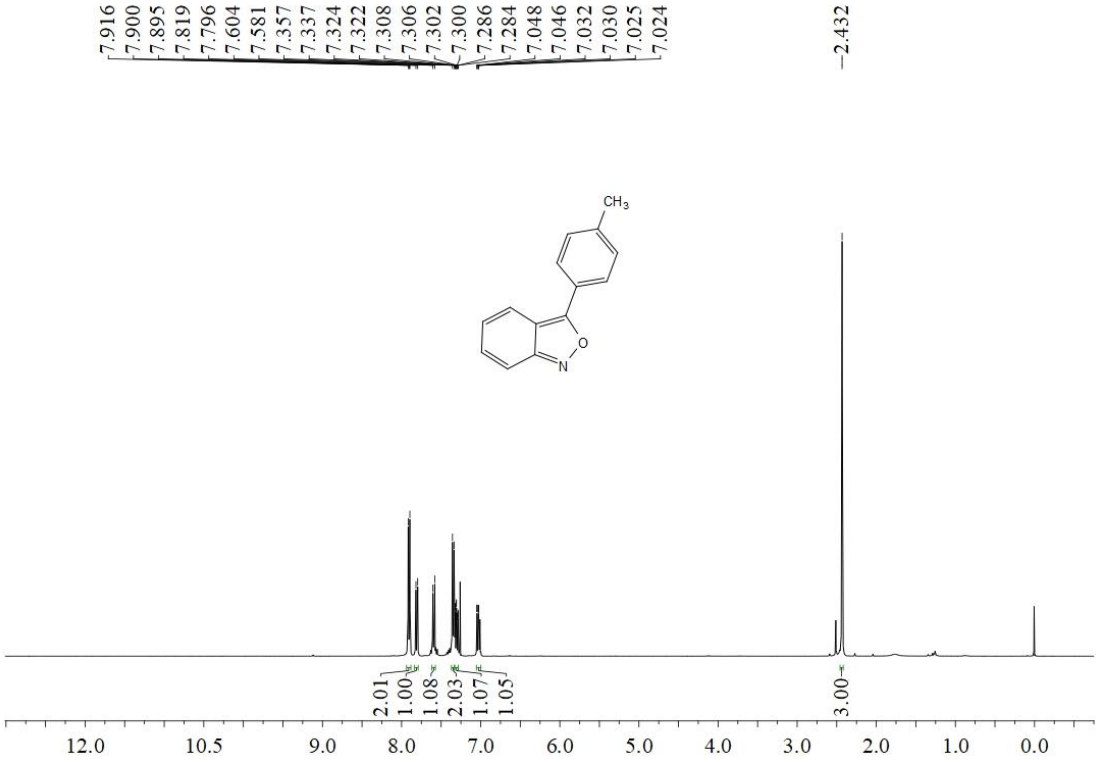


^{13}C NMR (100 MHz, $CDCl_3$)

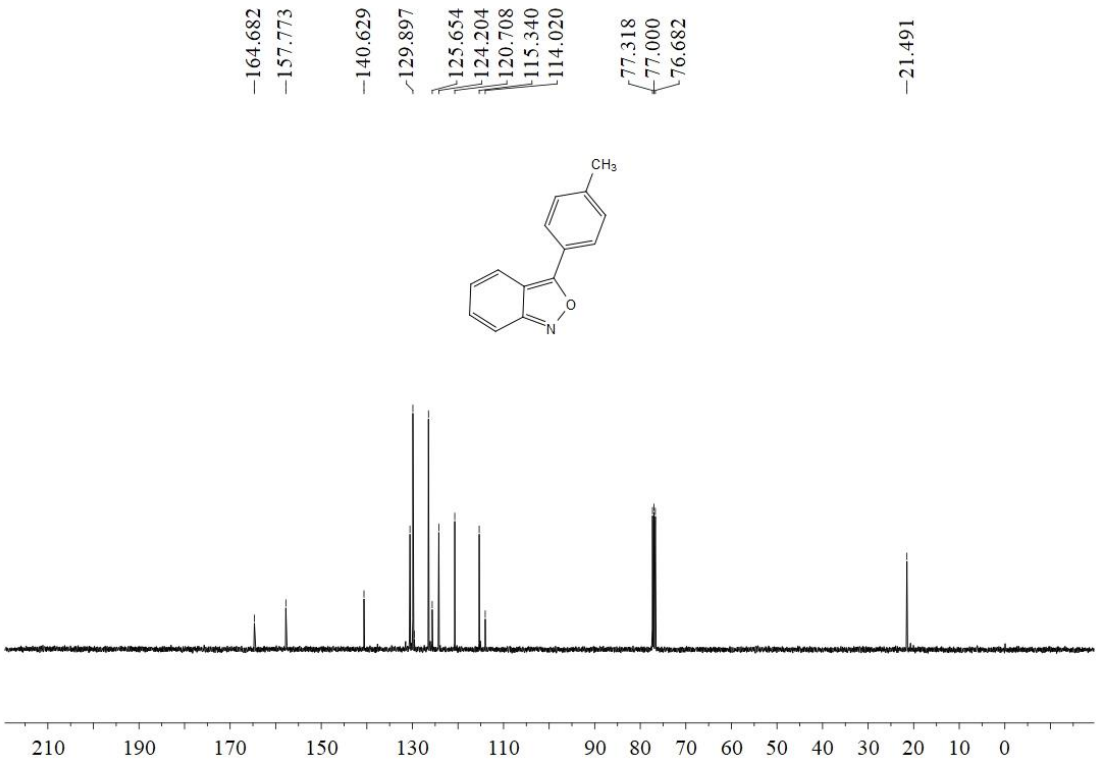


3-(*p*-Tolyl)benzo[c]isoxazole (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$)

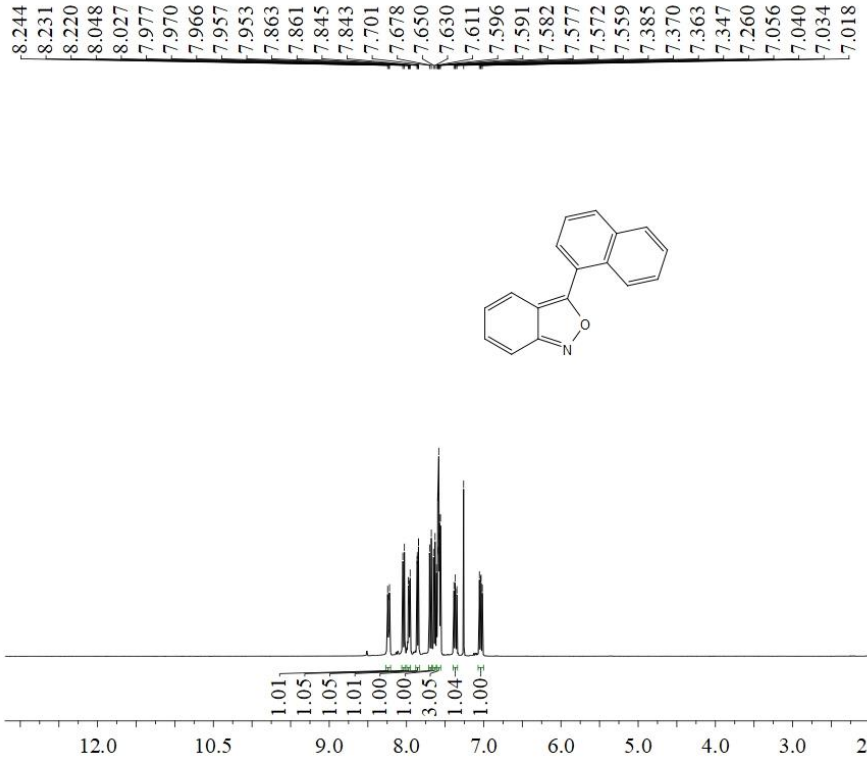


^{13}C NMR (100 MHz, $CDCl_3$)

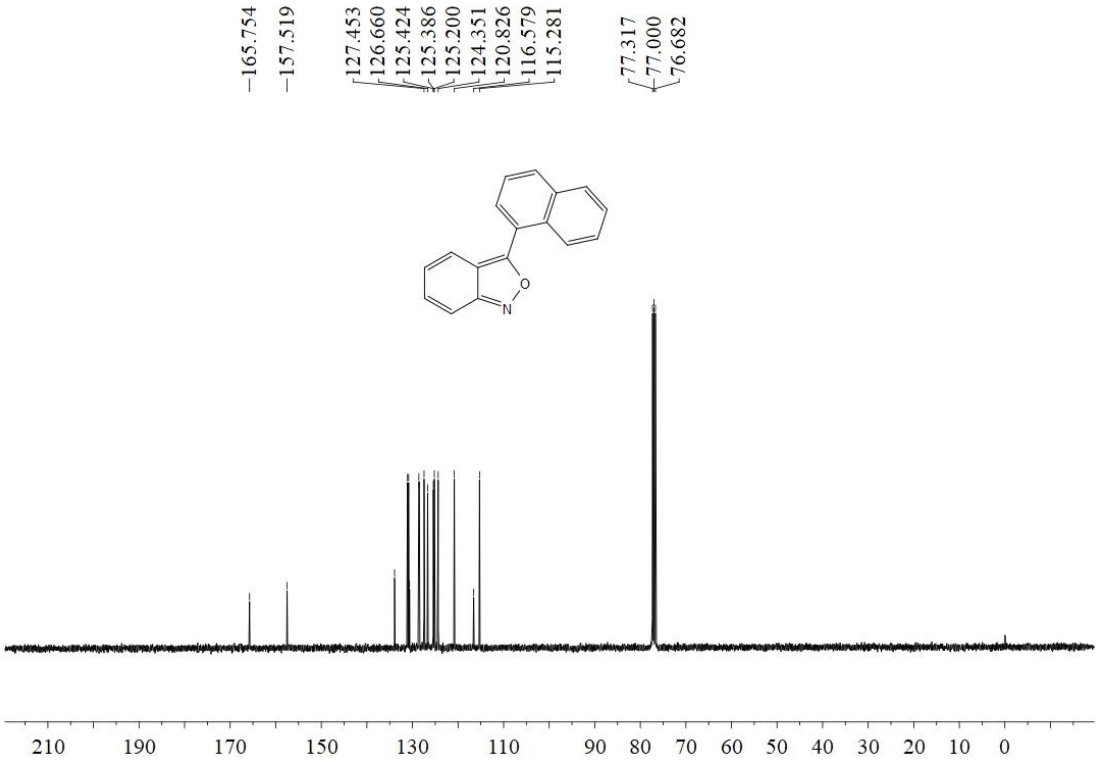


3-(Naphthalen-1-yl)benzo[c]isoxazole (**3c**)

^{1}H NMR (400 MHz, $CDCl_3$)

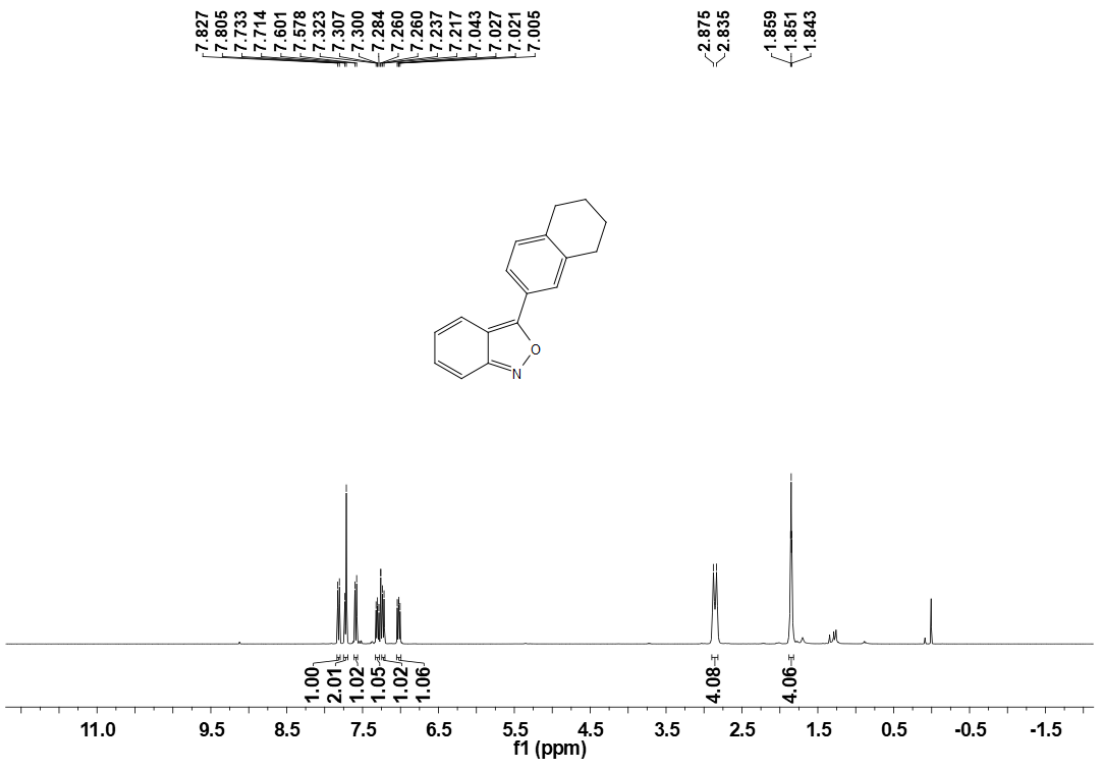


^{13}C NMR (100 MHz, $CDCl_3$)

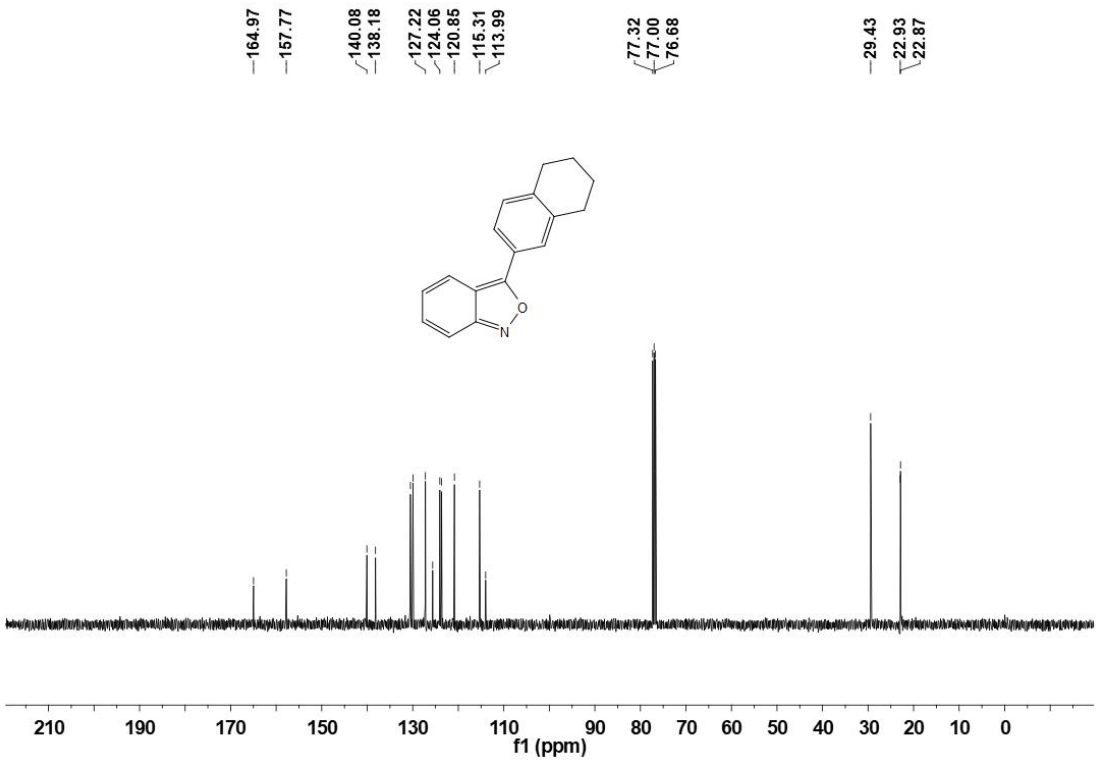


3-(5,6,7,8-Tetrahydronaphthalen-2-yl)benzo[c]isoxazole (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$)

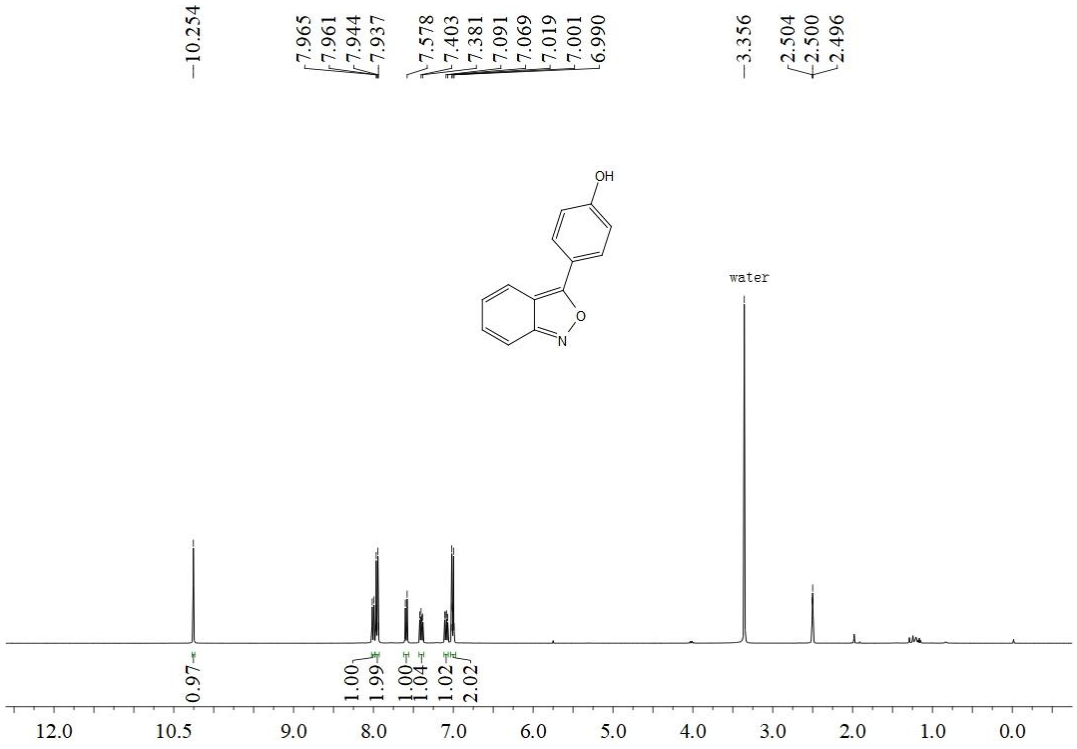


^{13}C NMR (100 MHz, $CDCl_3$)

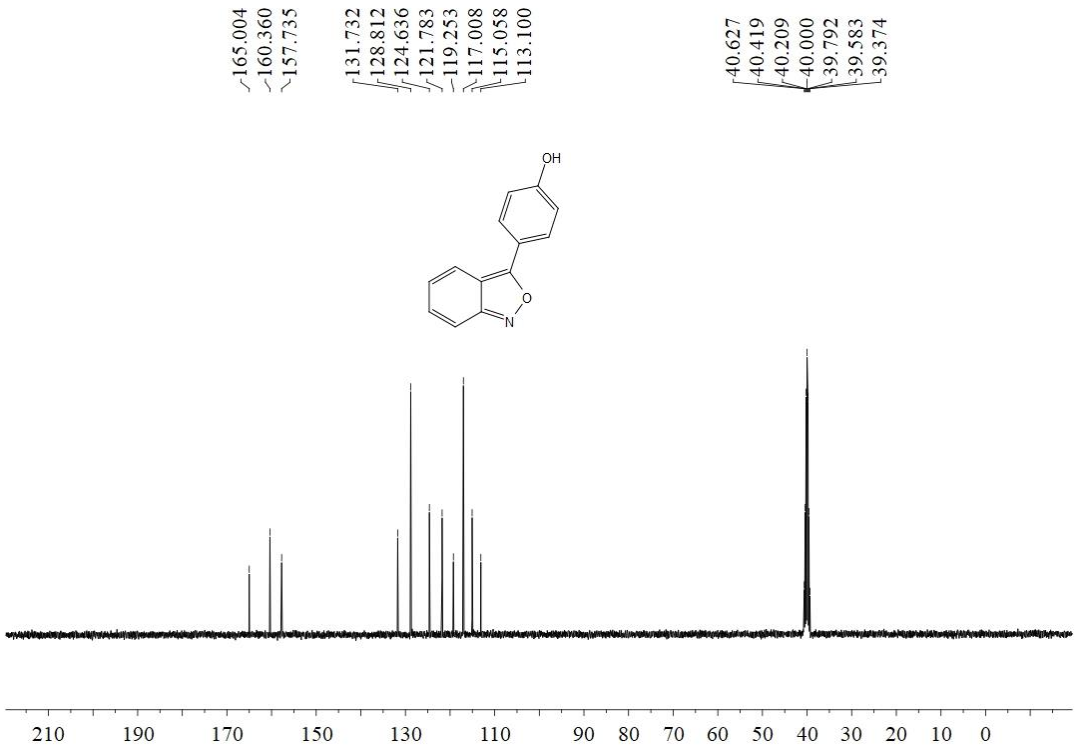


4-(Benzo[c]isoxazol-3-yl)phenol (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$)

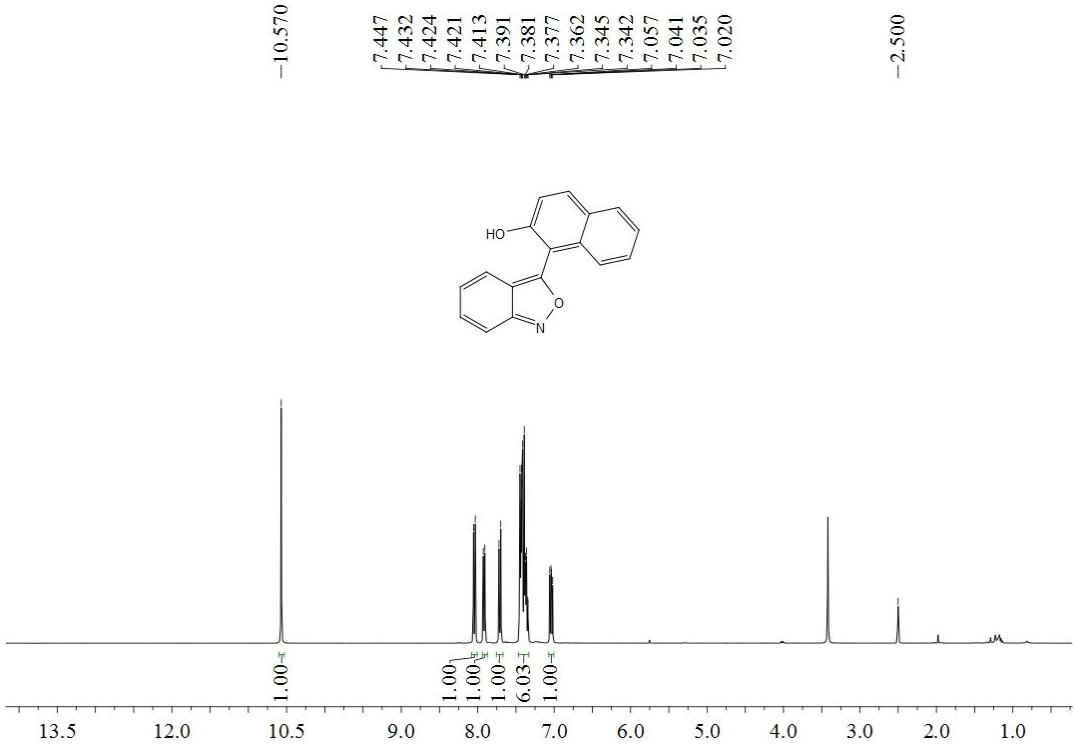


^{13}C NMR (100 MHz, $CDCl_3$)

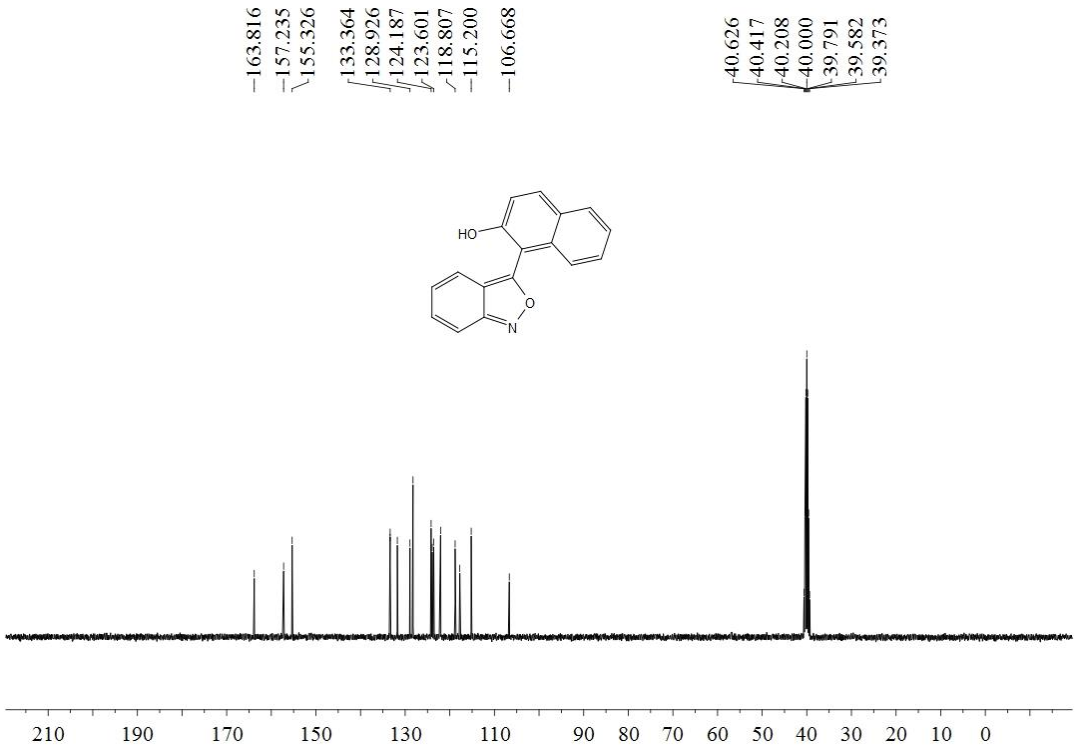


1-(Benzo[c]isoxazol-3-yl)naphthalen-2-ol (**3f**)

^{1}H NMR (400 MHz, DMSO)

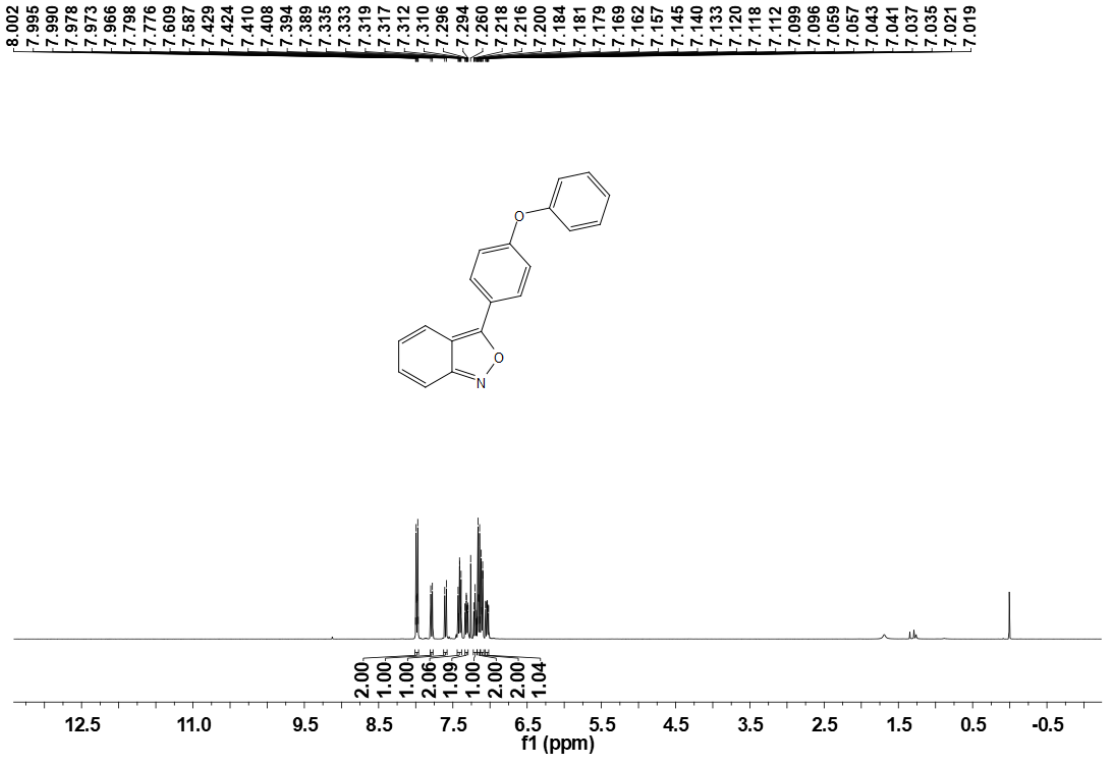


^{13}C NMR (100 MHz, DMSO)

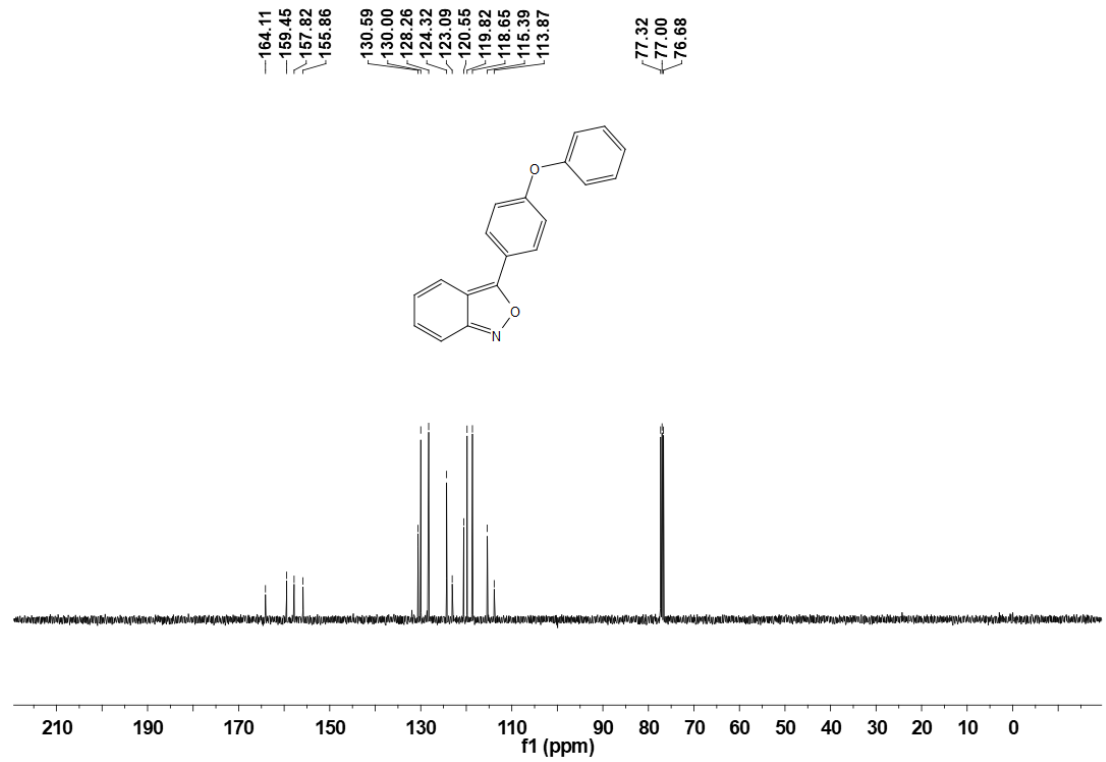


3-(4-Phenoxyphenyl)benzo[c]isoxazole (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$)

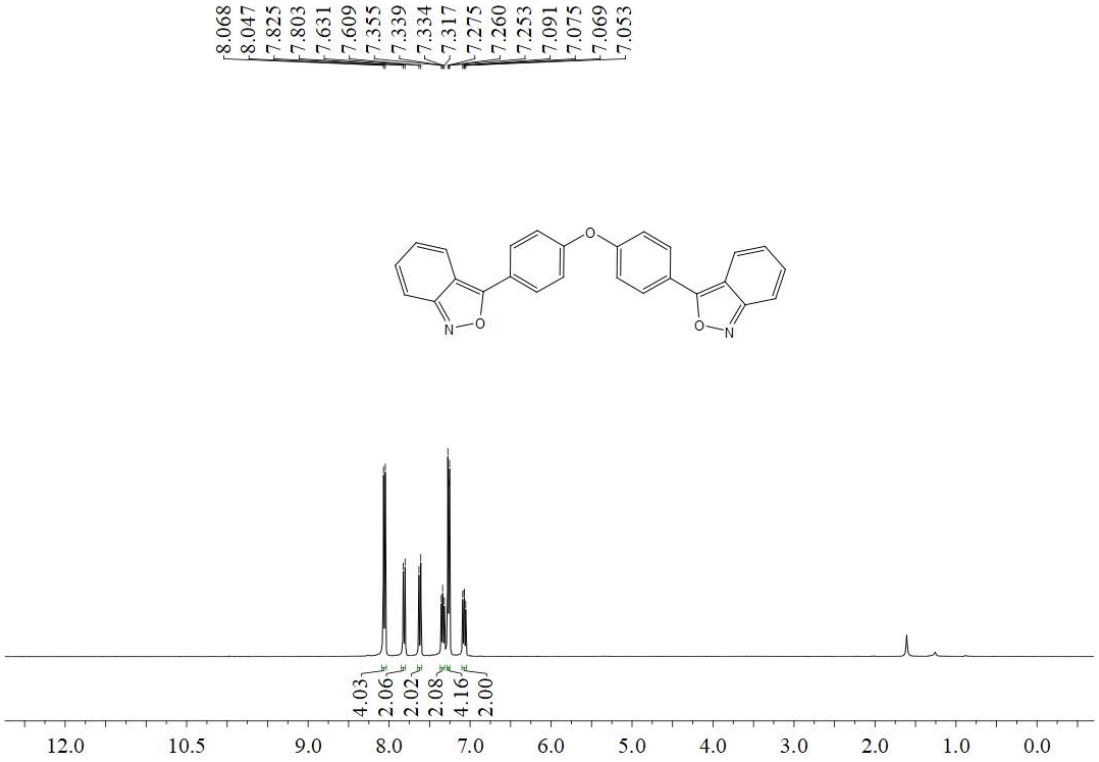


^{13}C NMR (100 MHz, $CDCl_3$)

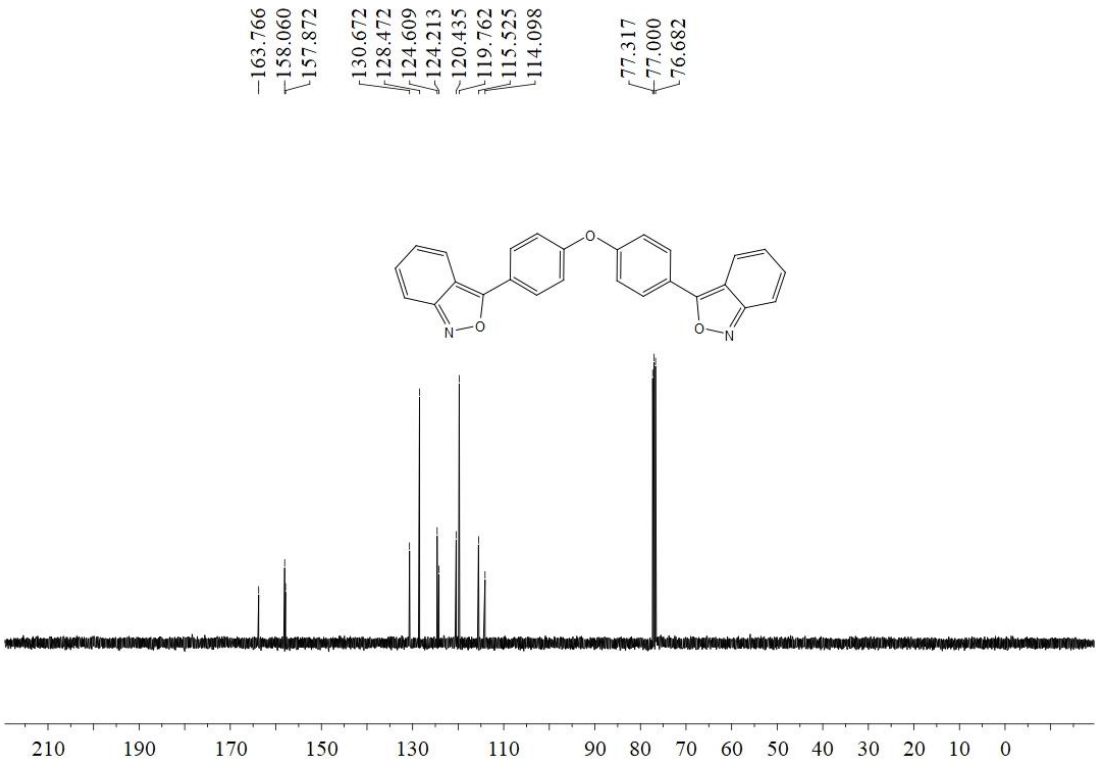


3,3'-(Oxybis(4,1-phenylene))bis(benzo[c]isoxazole) (**3g'**)

^{1}H NMR (400 MHz, $CDCl_3$)

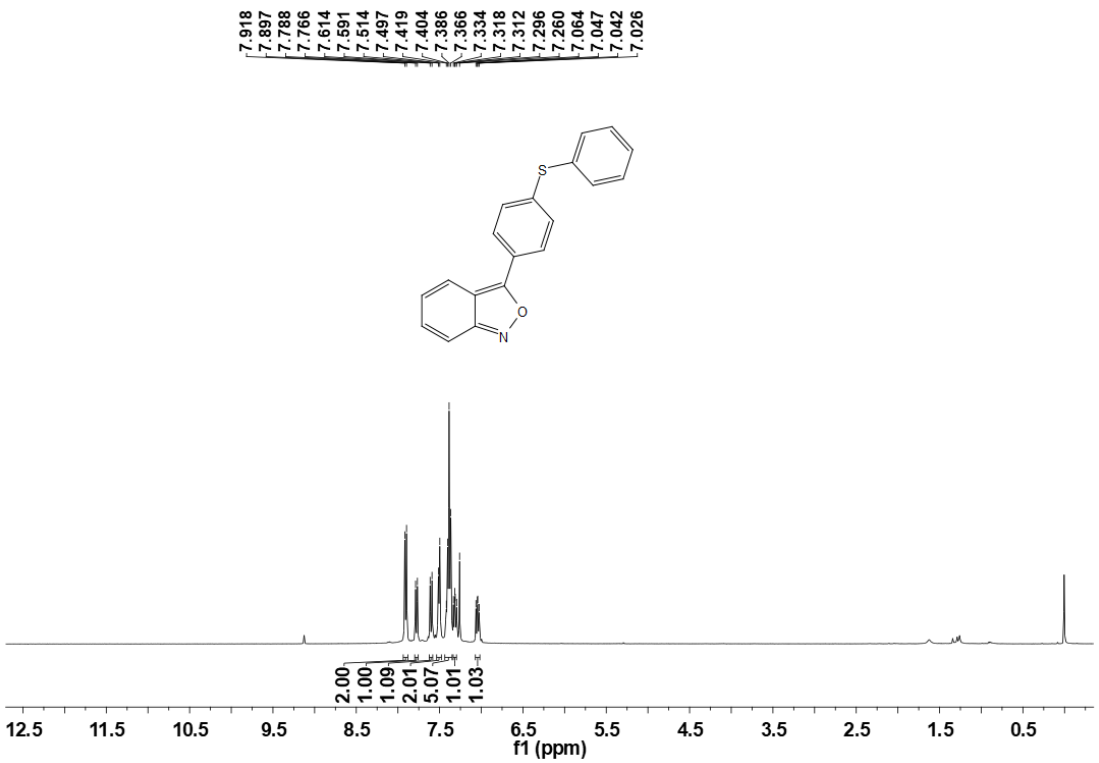


^{13}C NMR (100 MHz, $CDCl_3$)

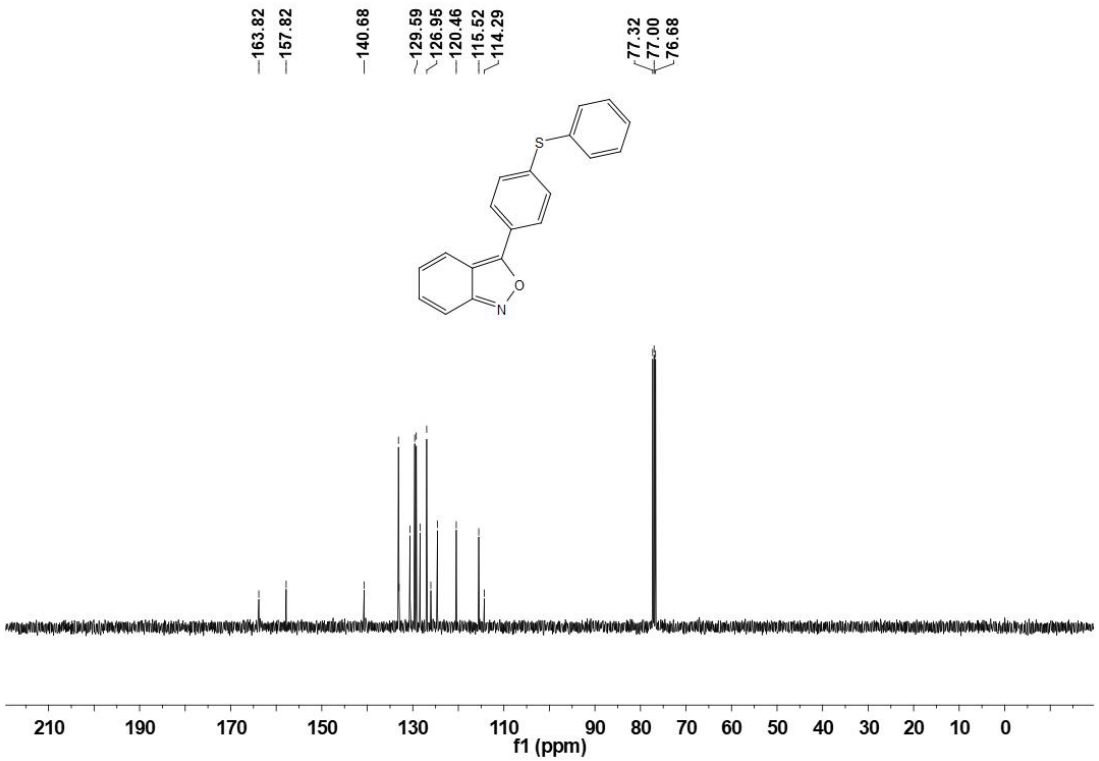


3-(4-(Phenylthio)phenyl)benzo[c]isoxazole (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$)

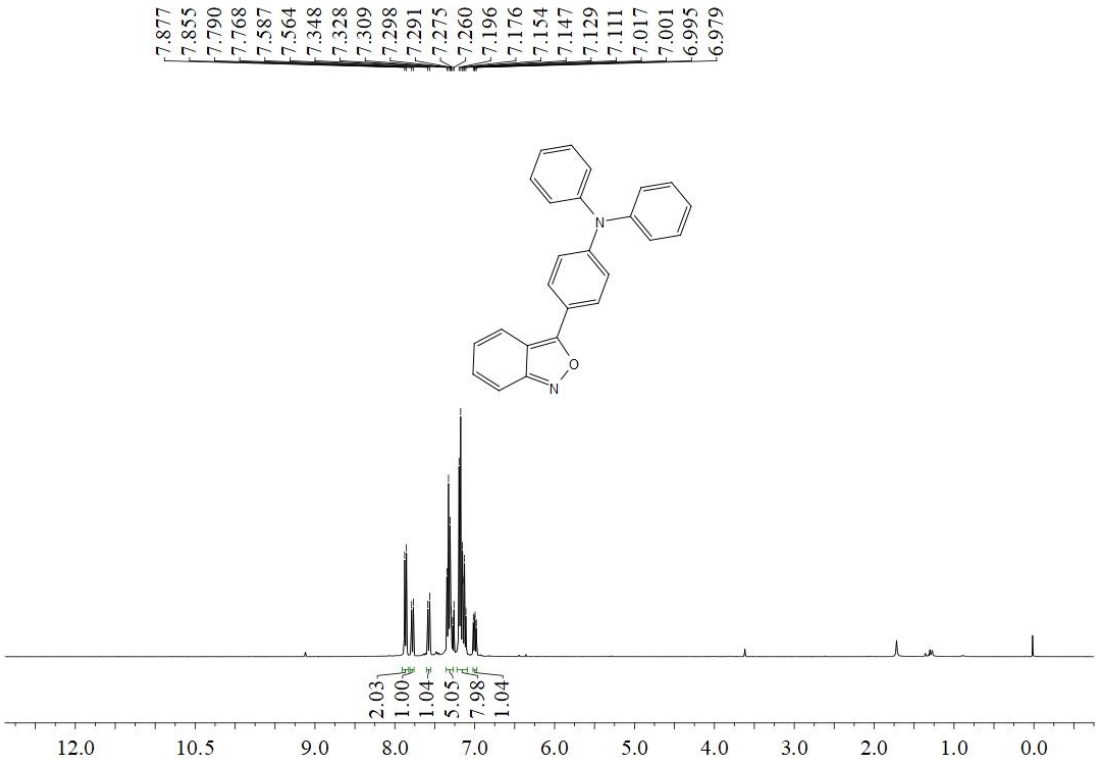


^{13}C NMR (100 MHz, $CDCl_3$)

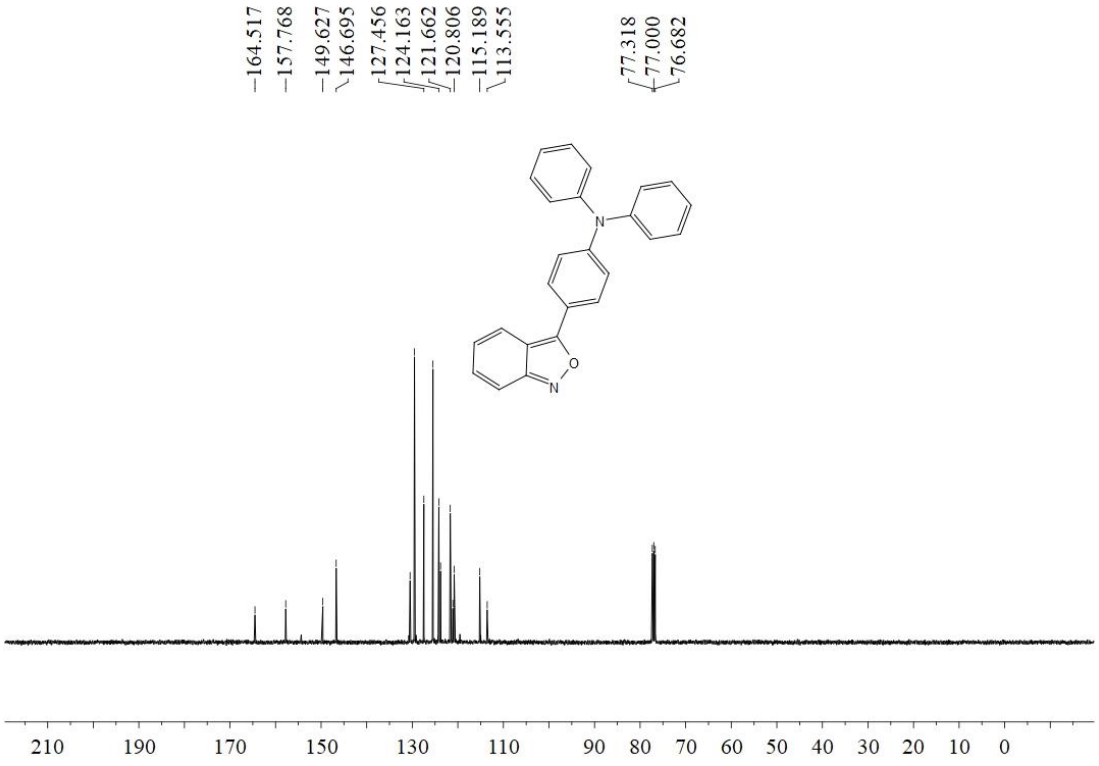


4-(Benzo[c]isoxazol-3-yl)-*N*,*N*-diphenylaniline (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$)

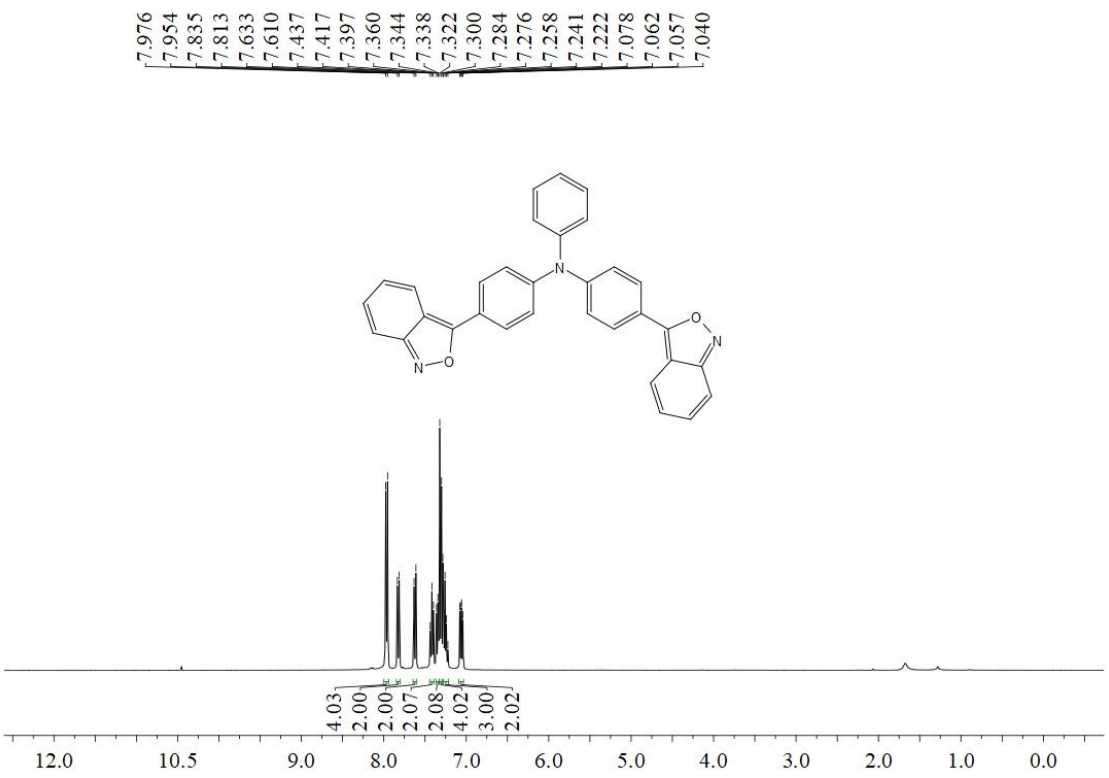


^{13}C NMR (100 MHz, $CDCl_3$)

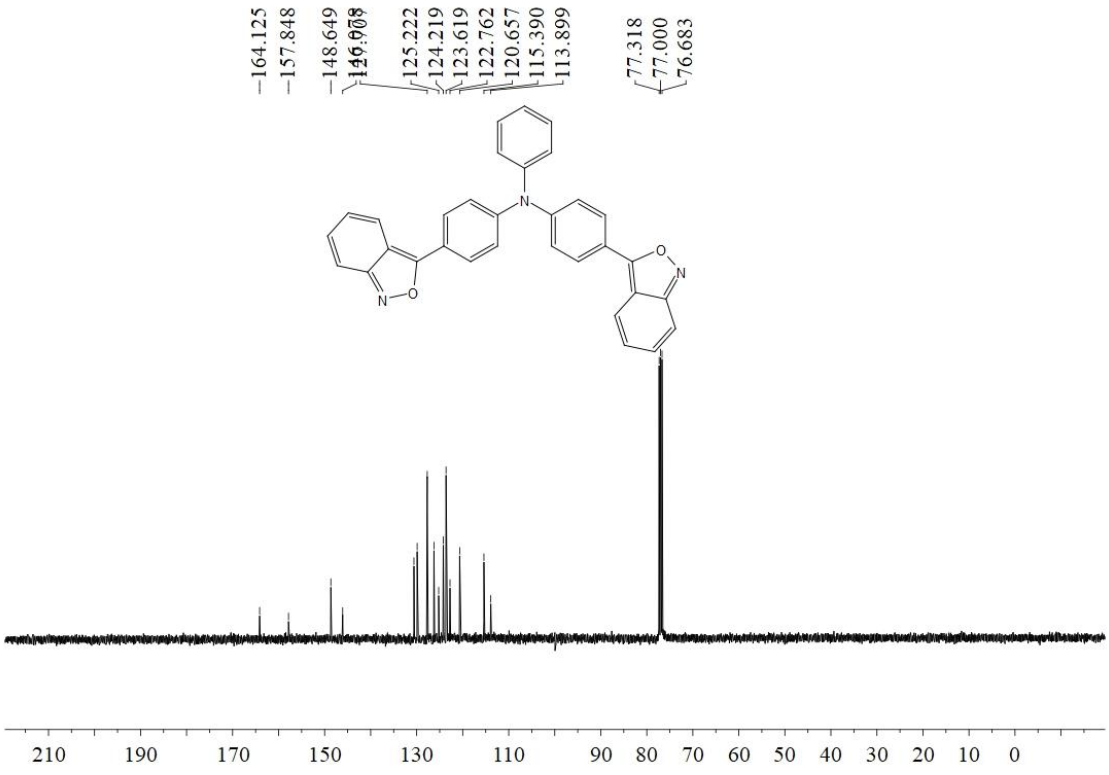


4-(Benzo[c]isoxazol-3-yl)-*N*-(4-(benzo[c]isoxazol-3-yl)phenyl)-*N*-phenylaniline (**3i'**)

^{1}H NMR (400 MHz, $CDCl_3$)

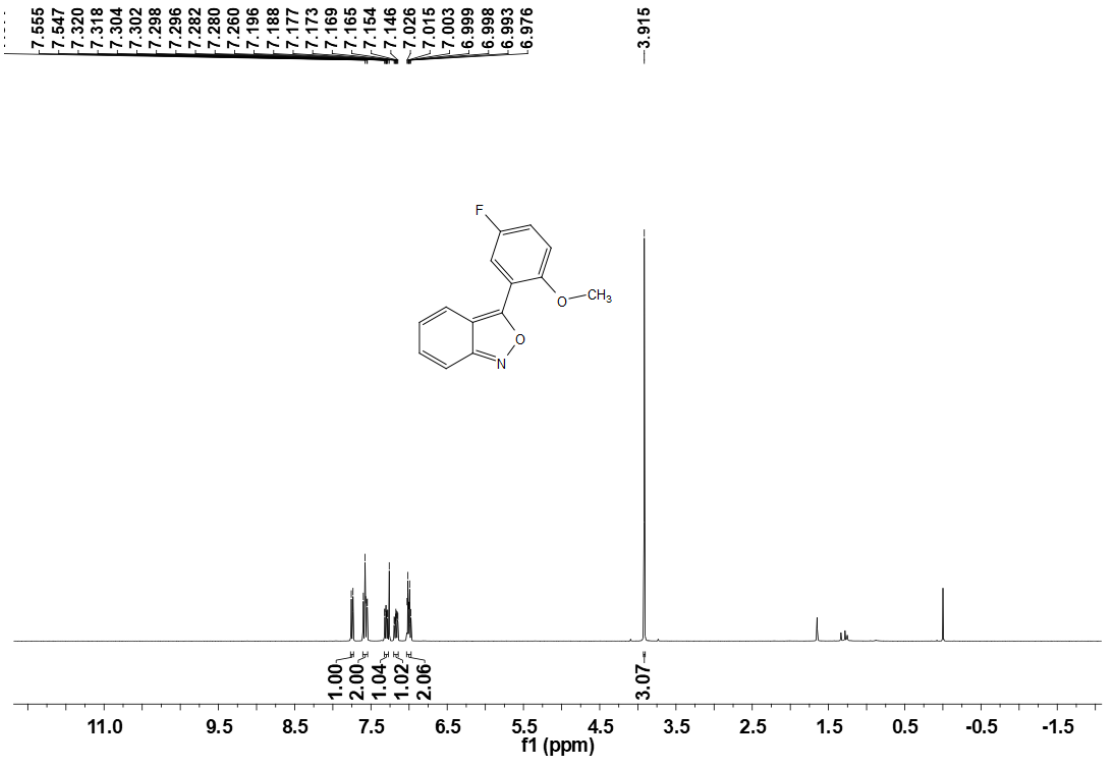


^{13}C NMR (100 MHz, $CDCl_3$)

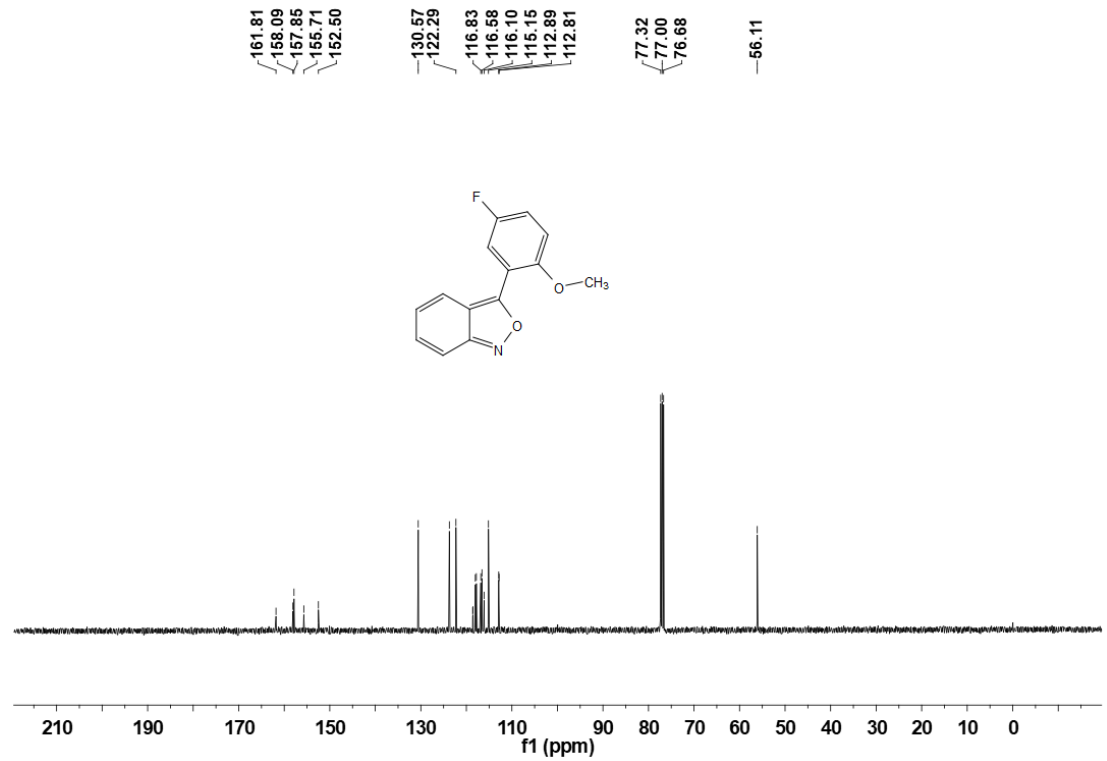


3-(5-Fluoro-2-methoxyphenyl)benzo[c]isoxazole (**3j**)

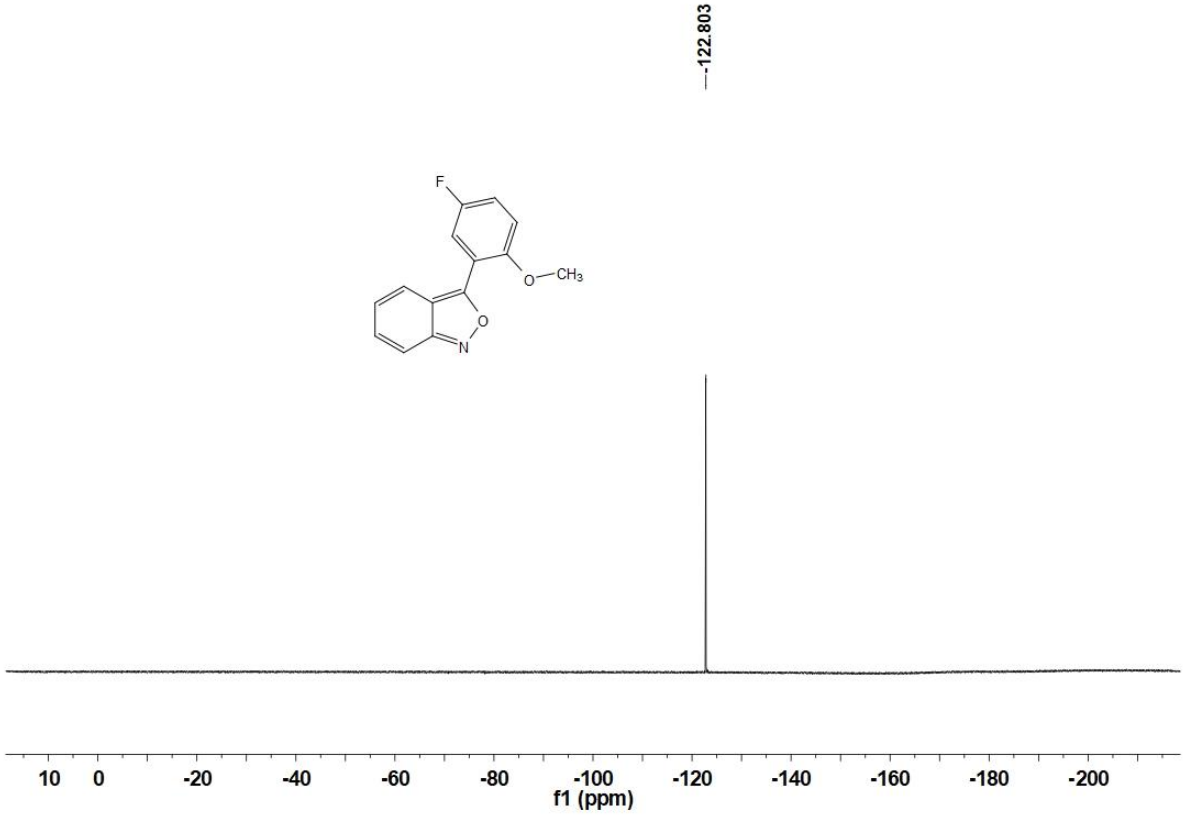
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

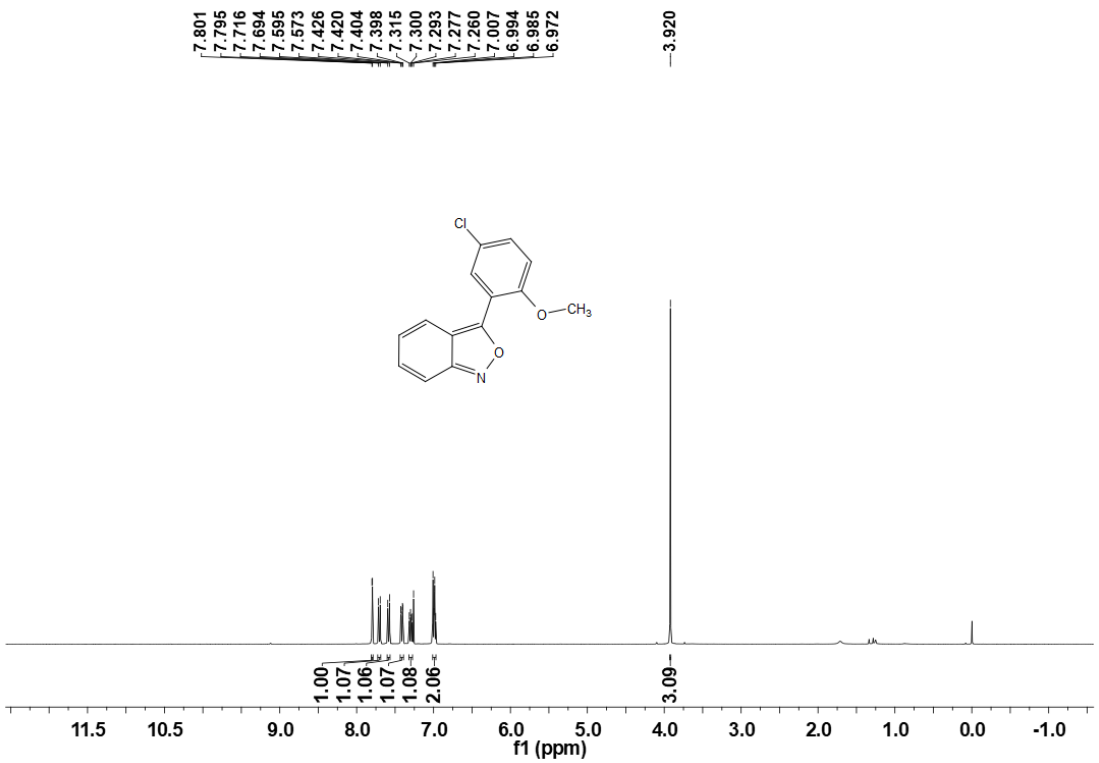


^{19}F NMR (300 MHz, $CDCl_3$)

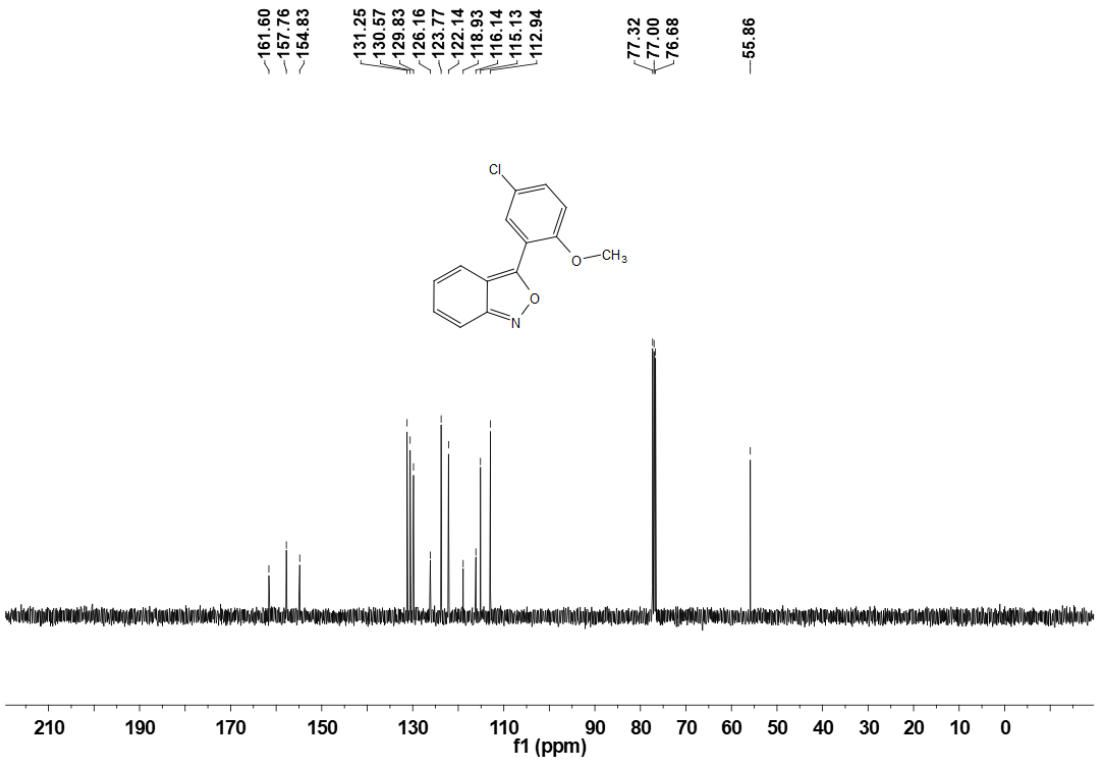

-122.803
F
O
CH3
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazole (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$)

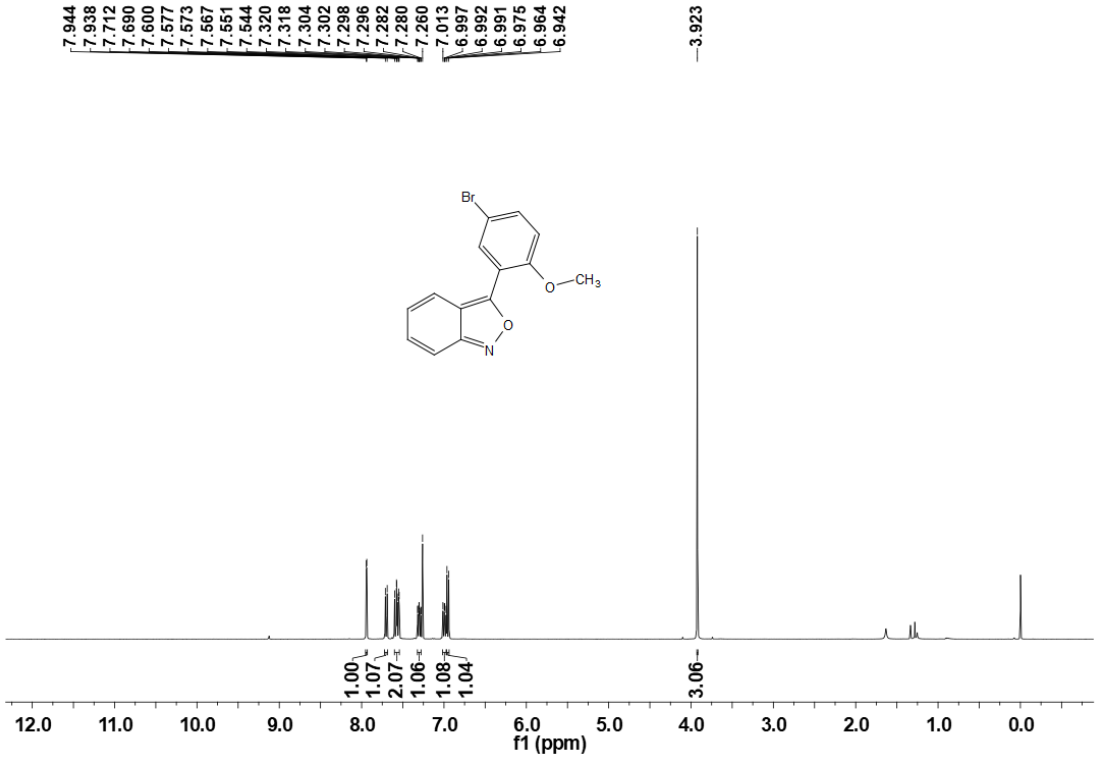


^{13}C NMR (100 MHz, $CDCl_3$)

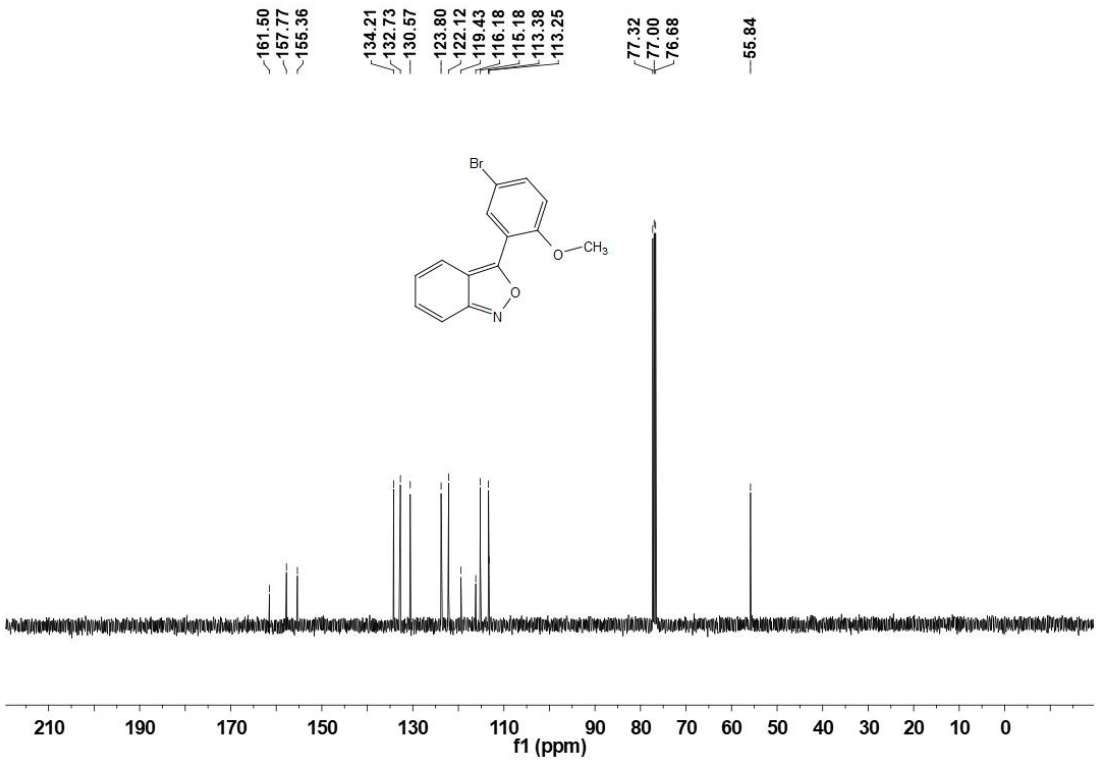


3-(5-Bromo-2-methoxyphenyl)benzo[c]isoxazole (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$)

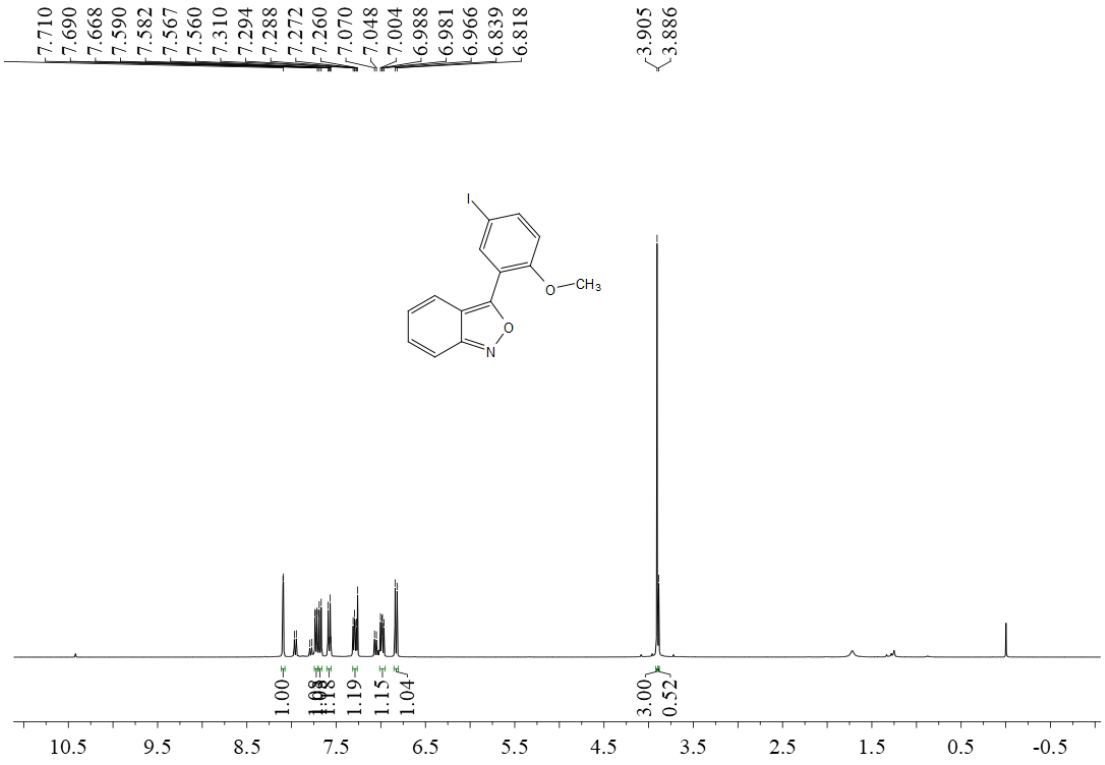


^{13}C NMR (100 MHz, $CDCl_3$)

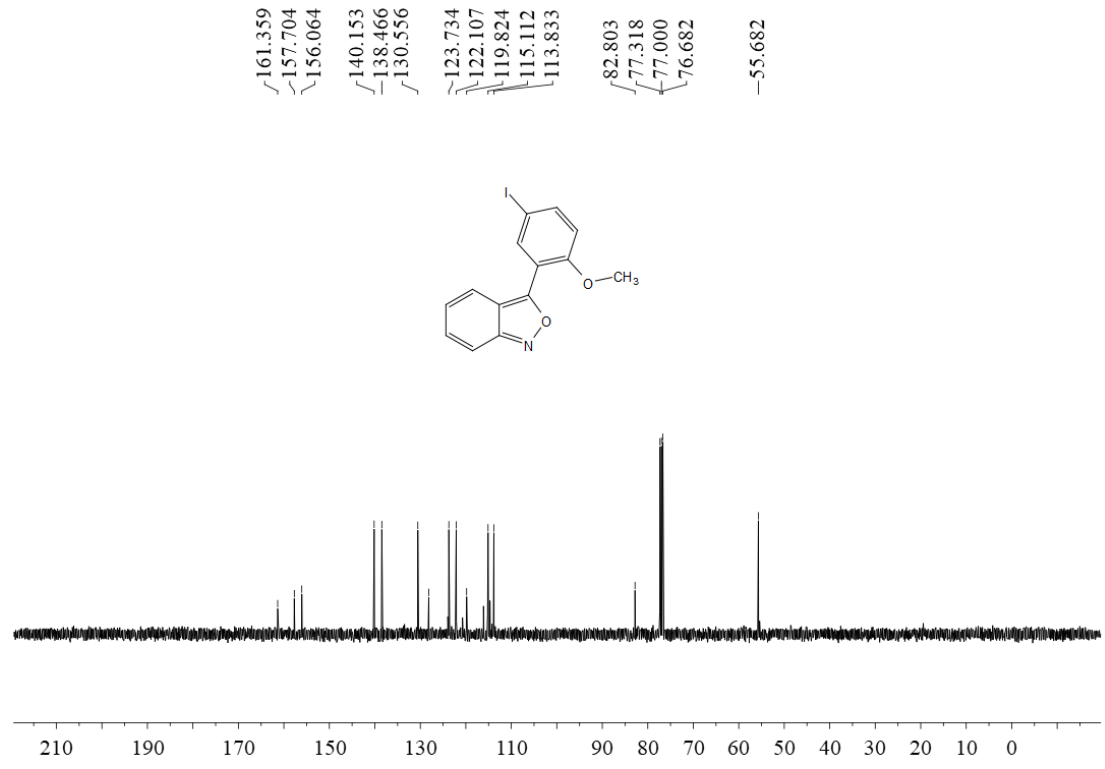


3-(5-Iodo-2-methylphenyl)benzo[c]isoxazole (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$)

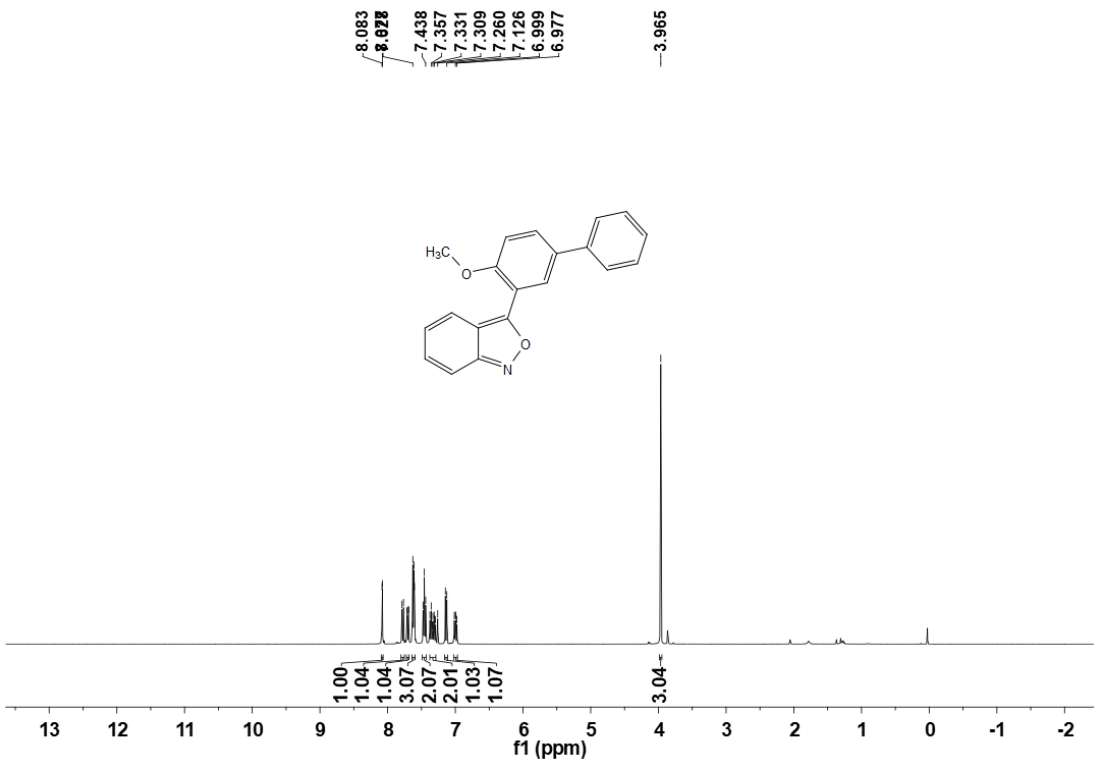


^{13}C NMR (100 MHz, $CDCl_3$)

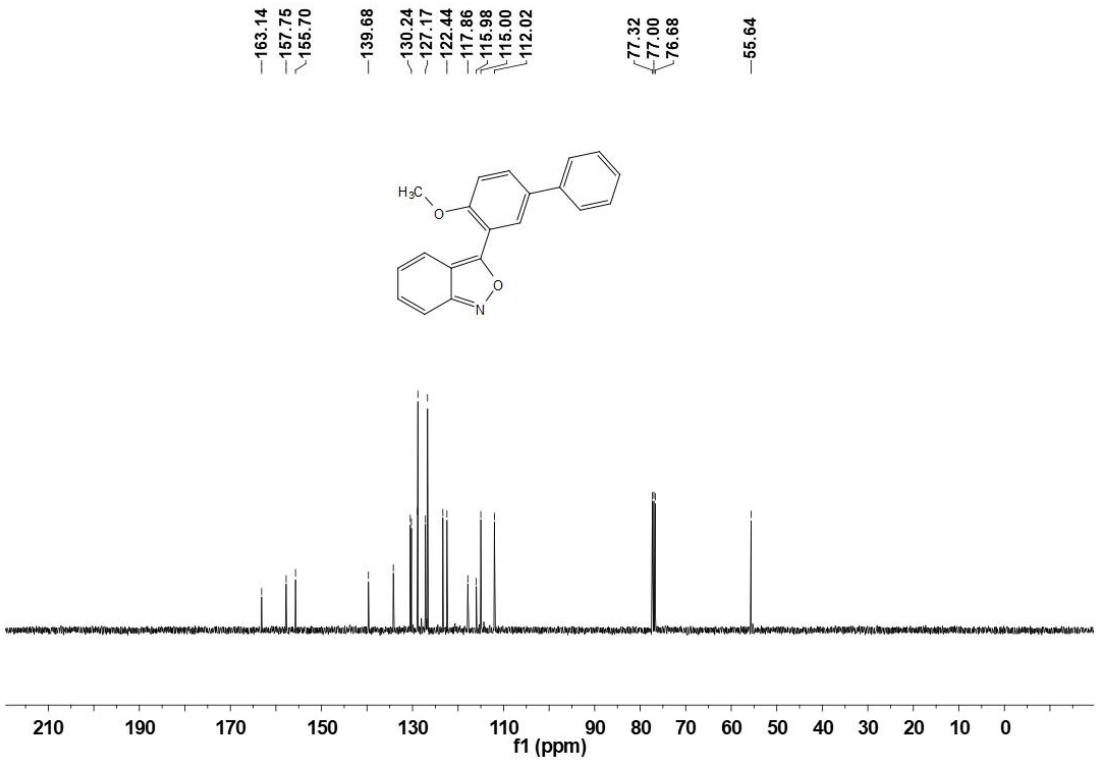


3-(4-Methoxy-[1,1'-biphenyl]-3-yl)benzo[c]isoxazole (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$)

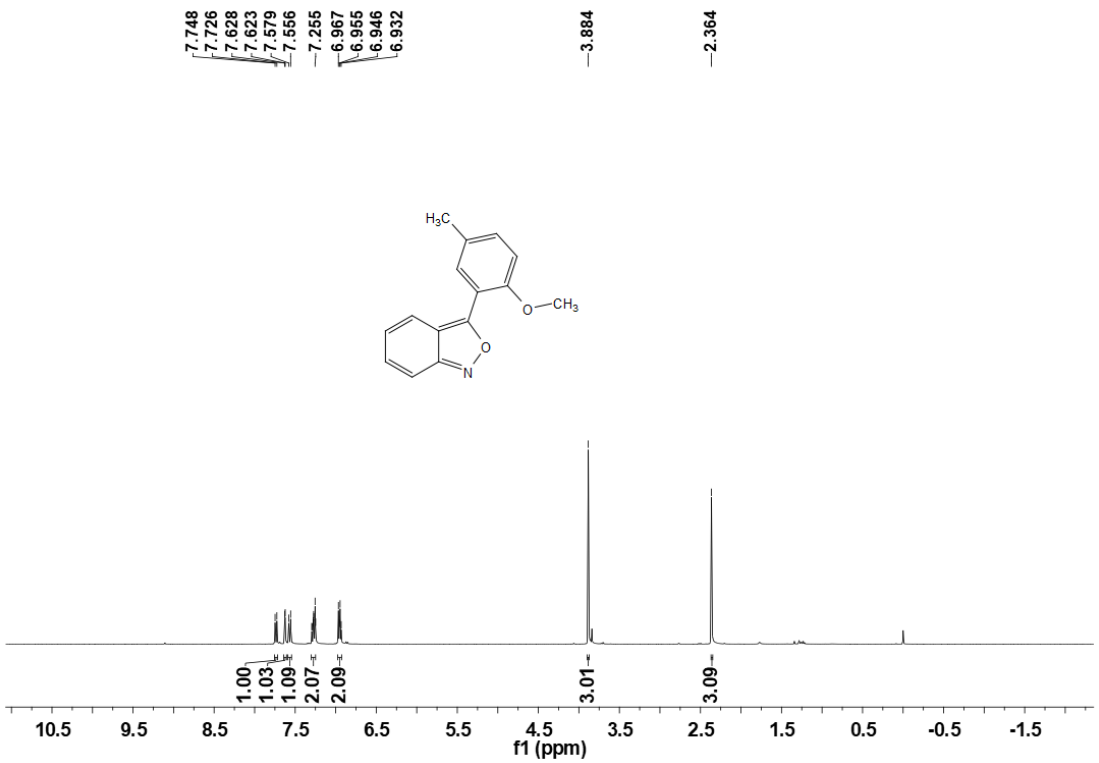


^{13}C NMR (100 MHz, $CDCl_3$)

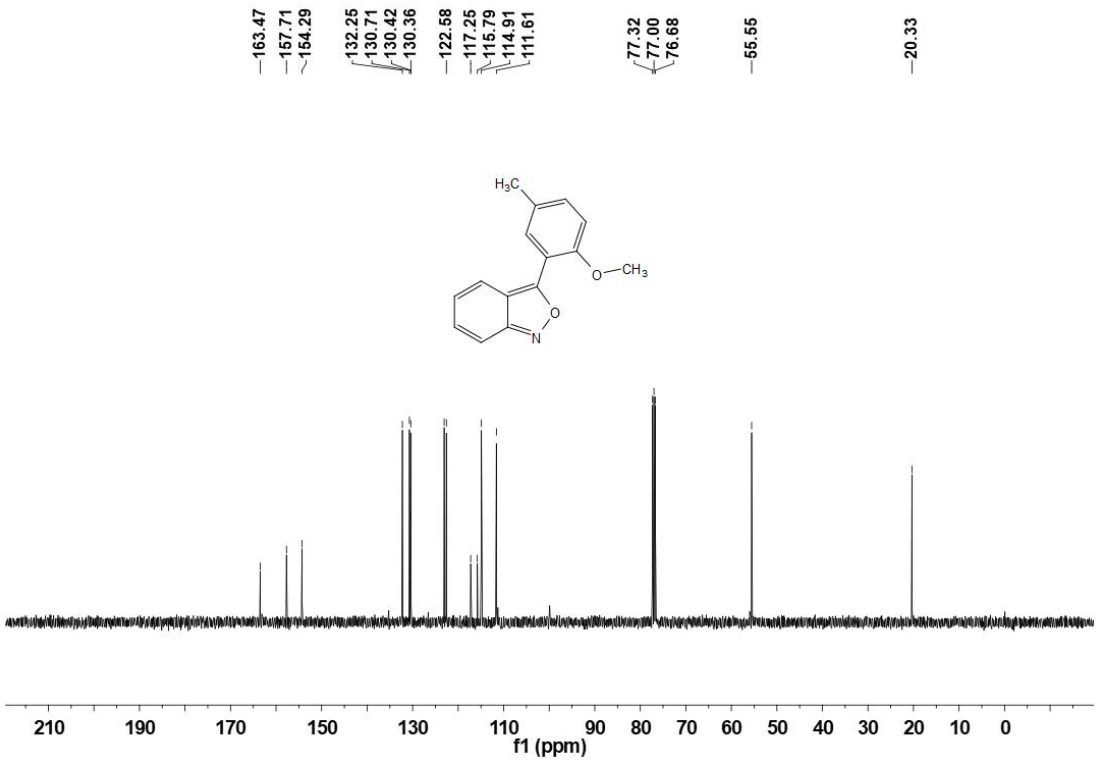


3-(2-Methoxy-5-methylphenyl)benzo[c]isoxazole (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$)

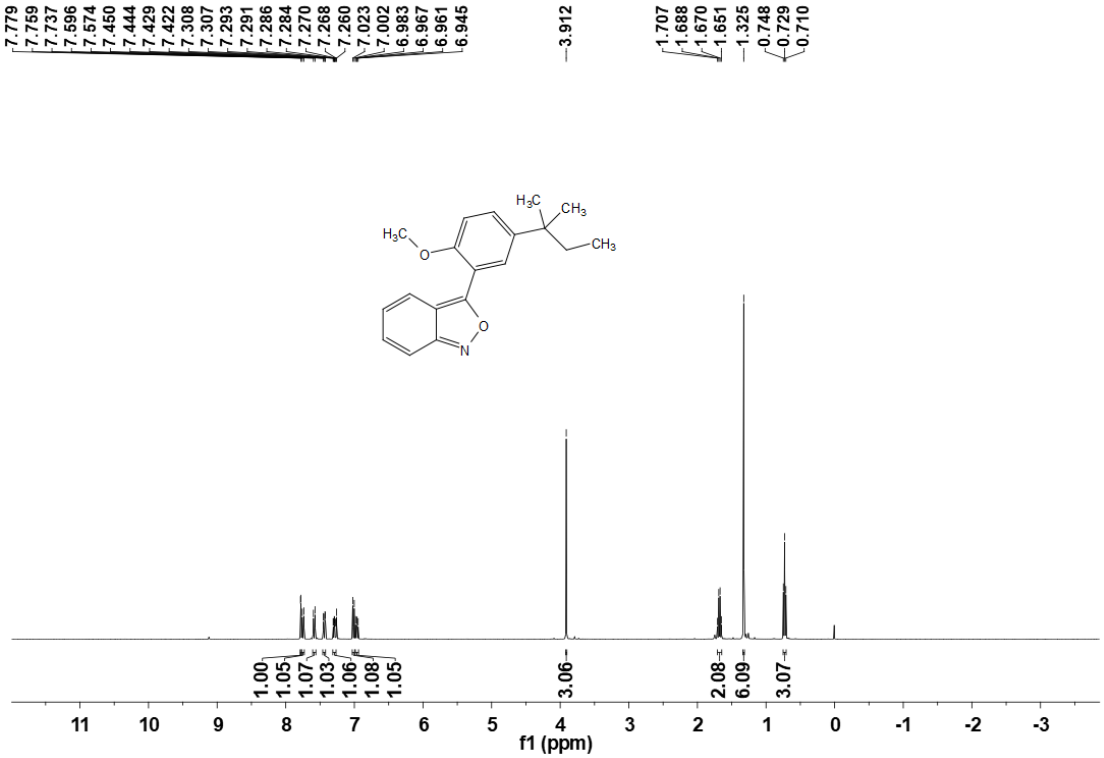


^{13}C NMR (100 MHz, $CDCl_3$)

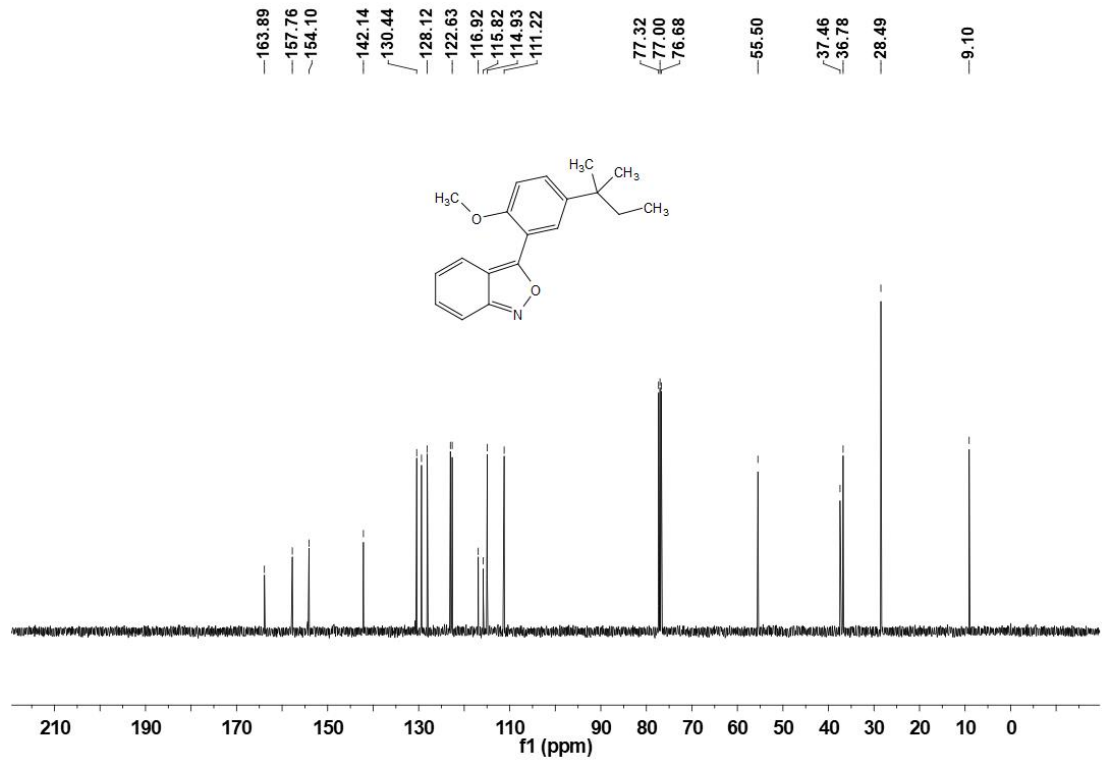


3-(2-Methoxy-5-(*tert*-pentyl)phenyl)benzo[c]isoxazole (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$)

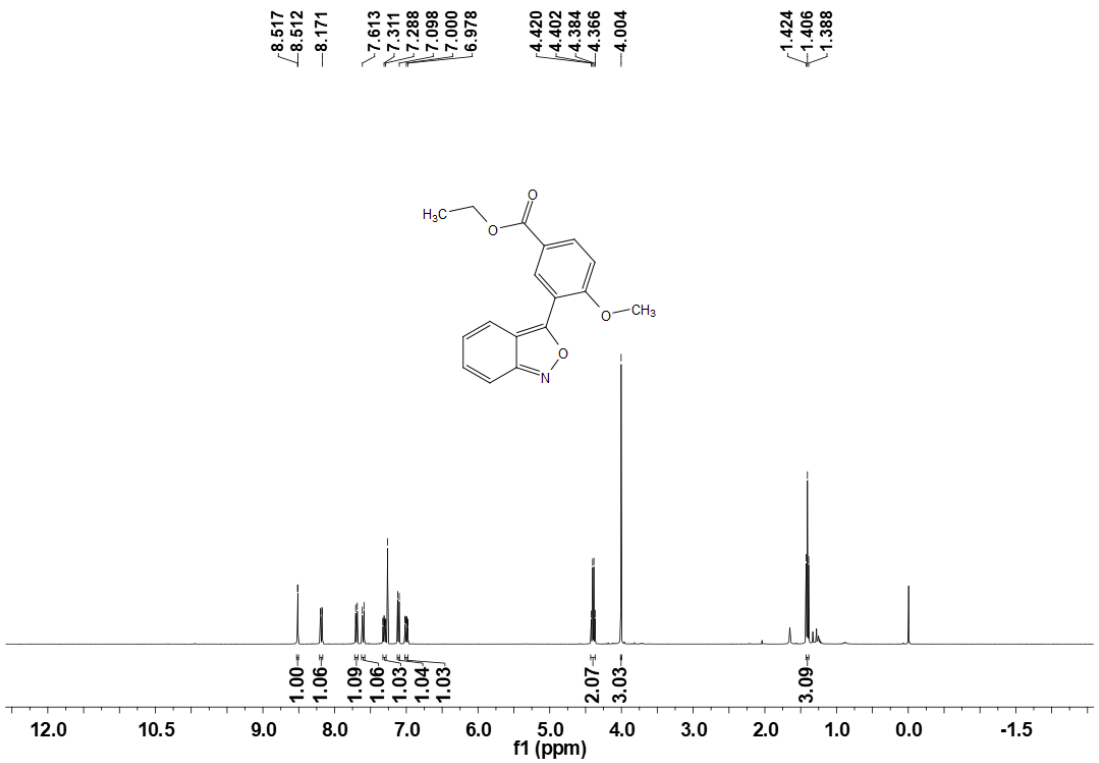


^{13}C NMR (100 MHz, $CDCl_3$)

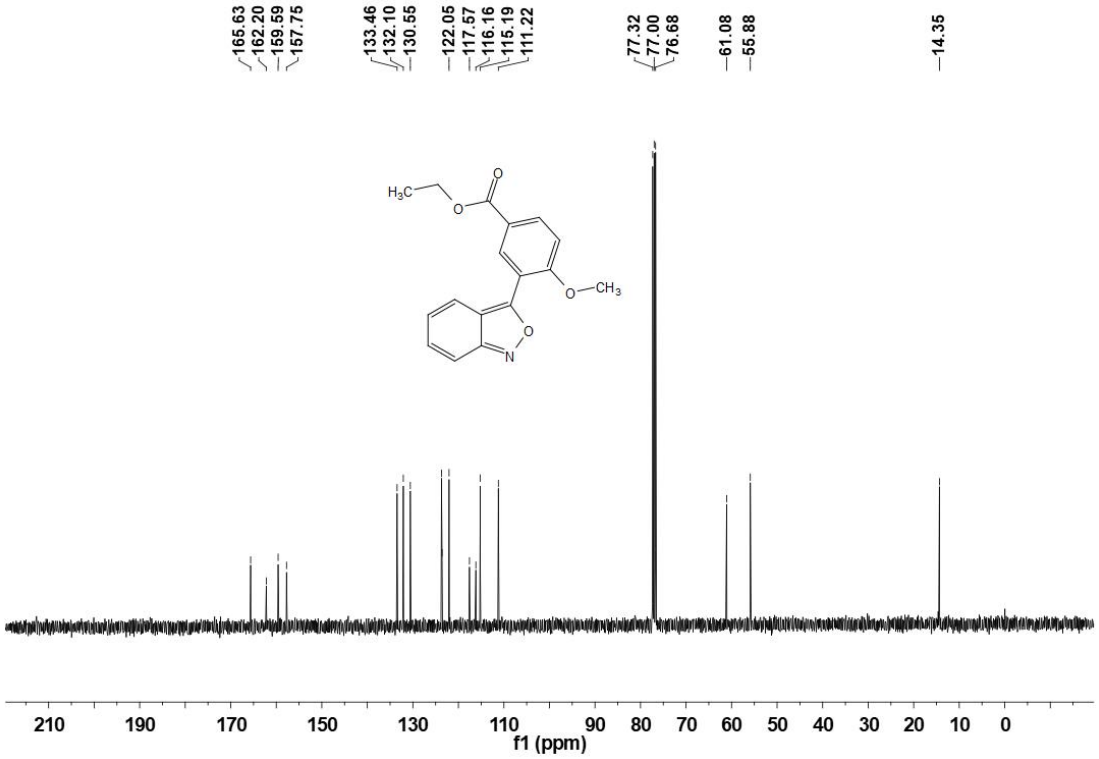


Ethyl 3-(benzo[c]isoxazol-3-yl)-4-methoxybenzoate (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$)

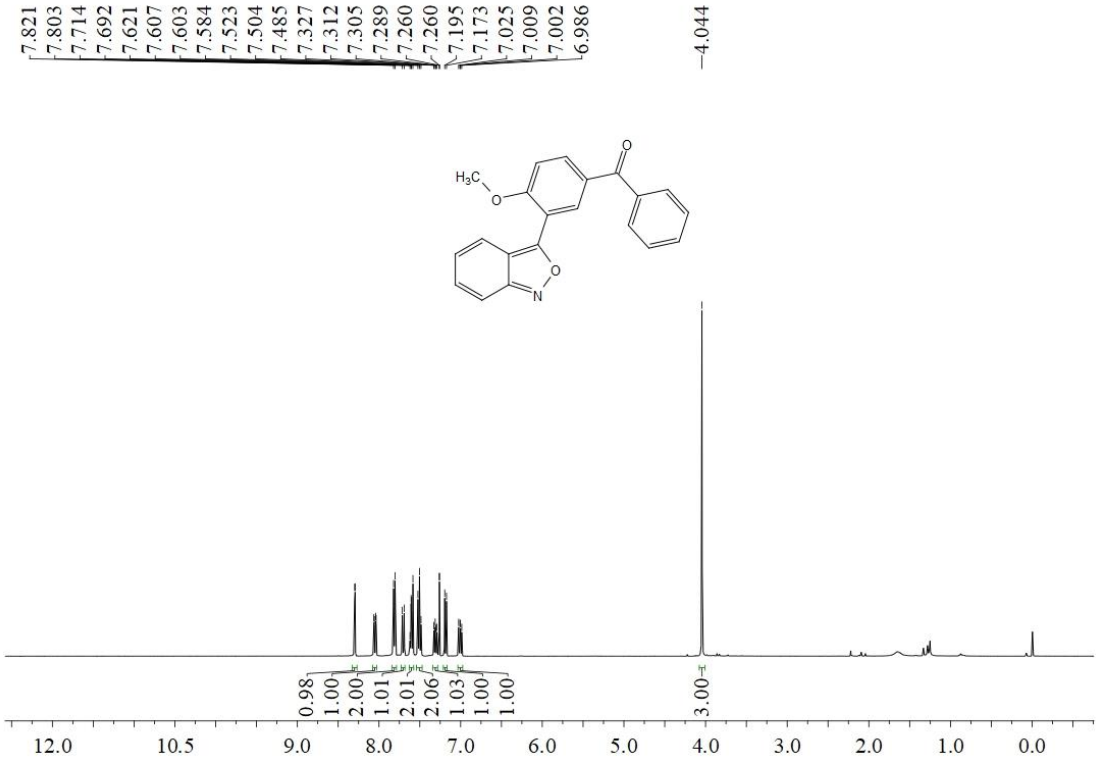


^{13}C NMR (100 MHz, $CDCl_3$)

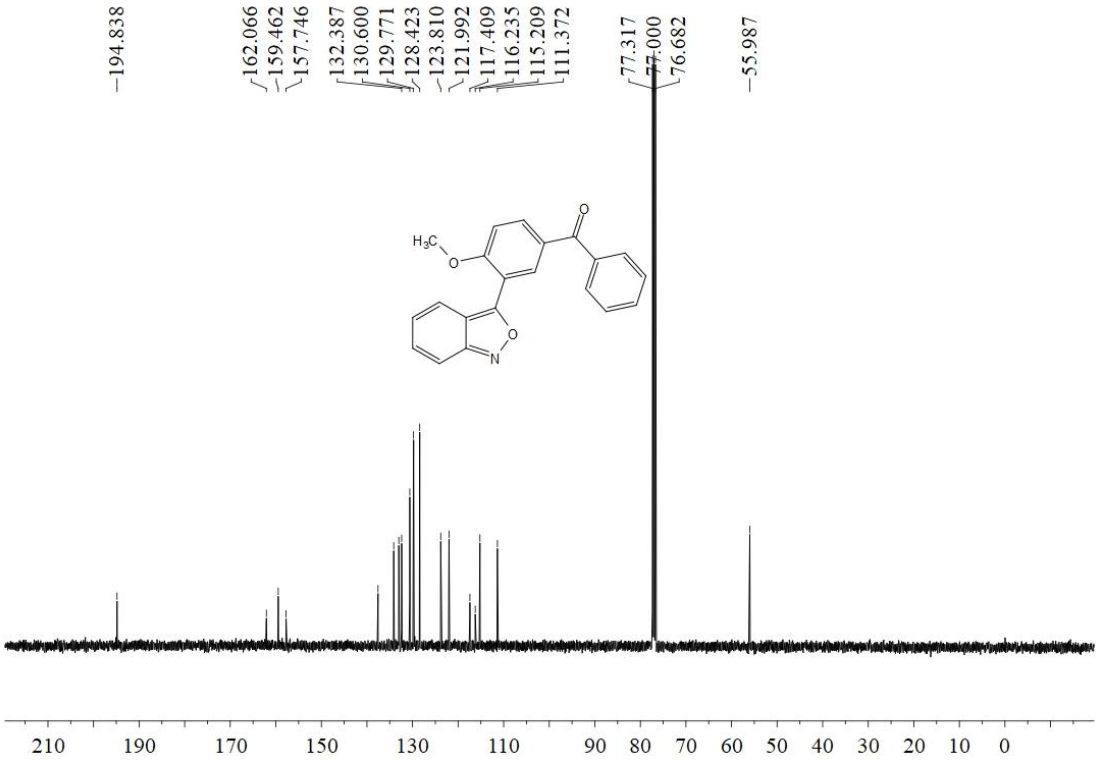


(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)(phenyl)methanone (**3r**)

^{1}H NMR (400 MHz, $CDCl_3$)

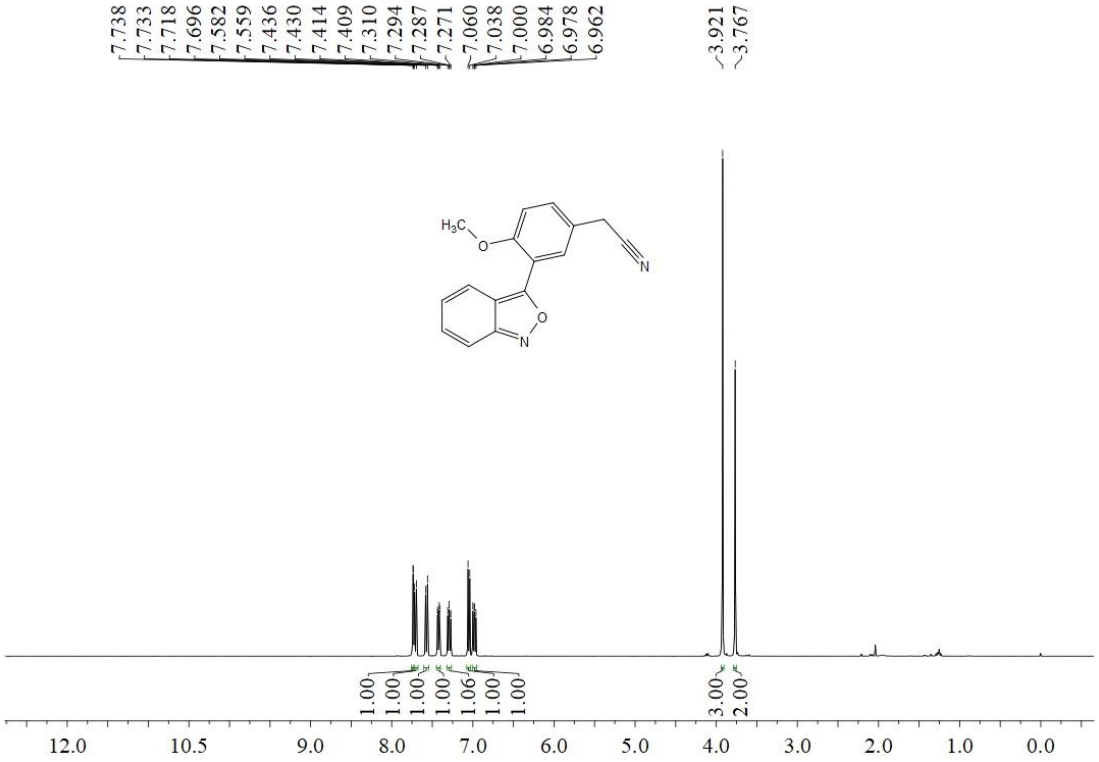


^{13}C NMR (100 MHz, $CDCl_3$)

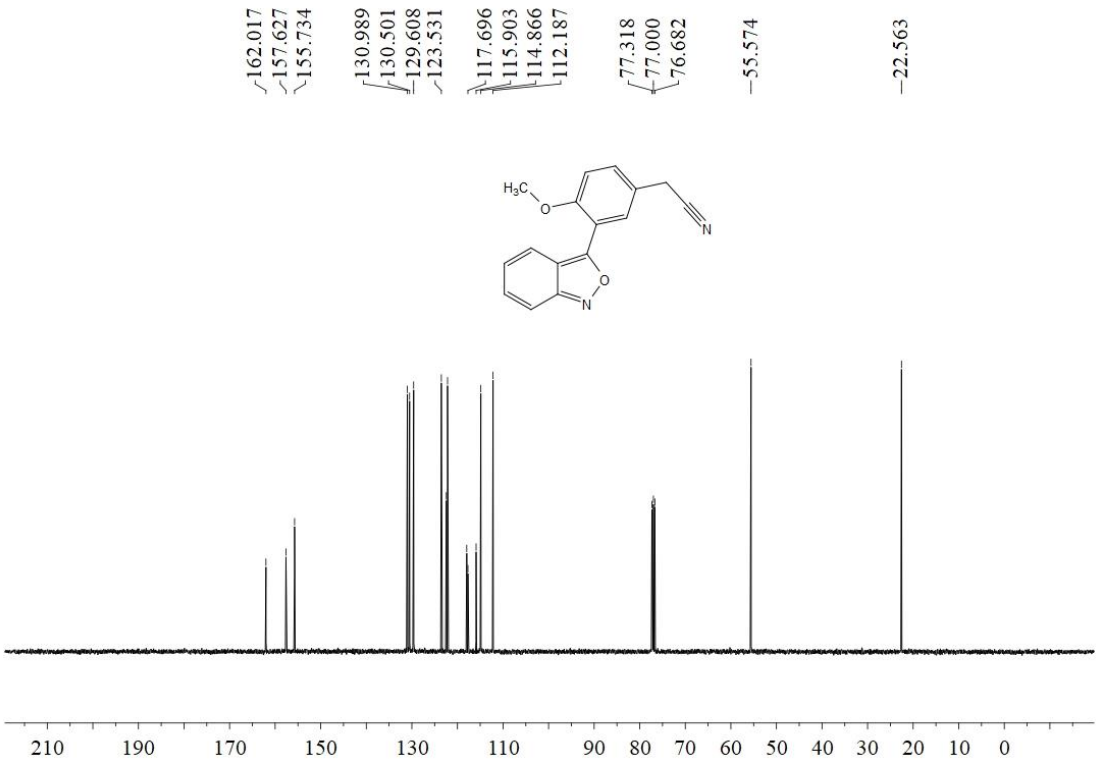


2-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)acetonitrile (**3s**)

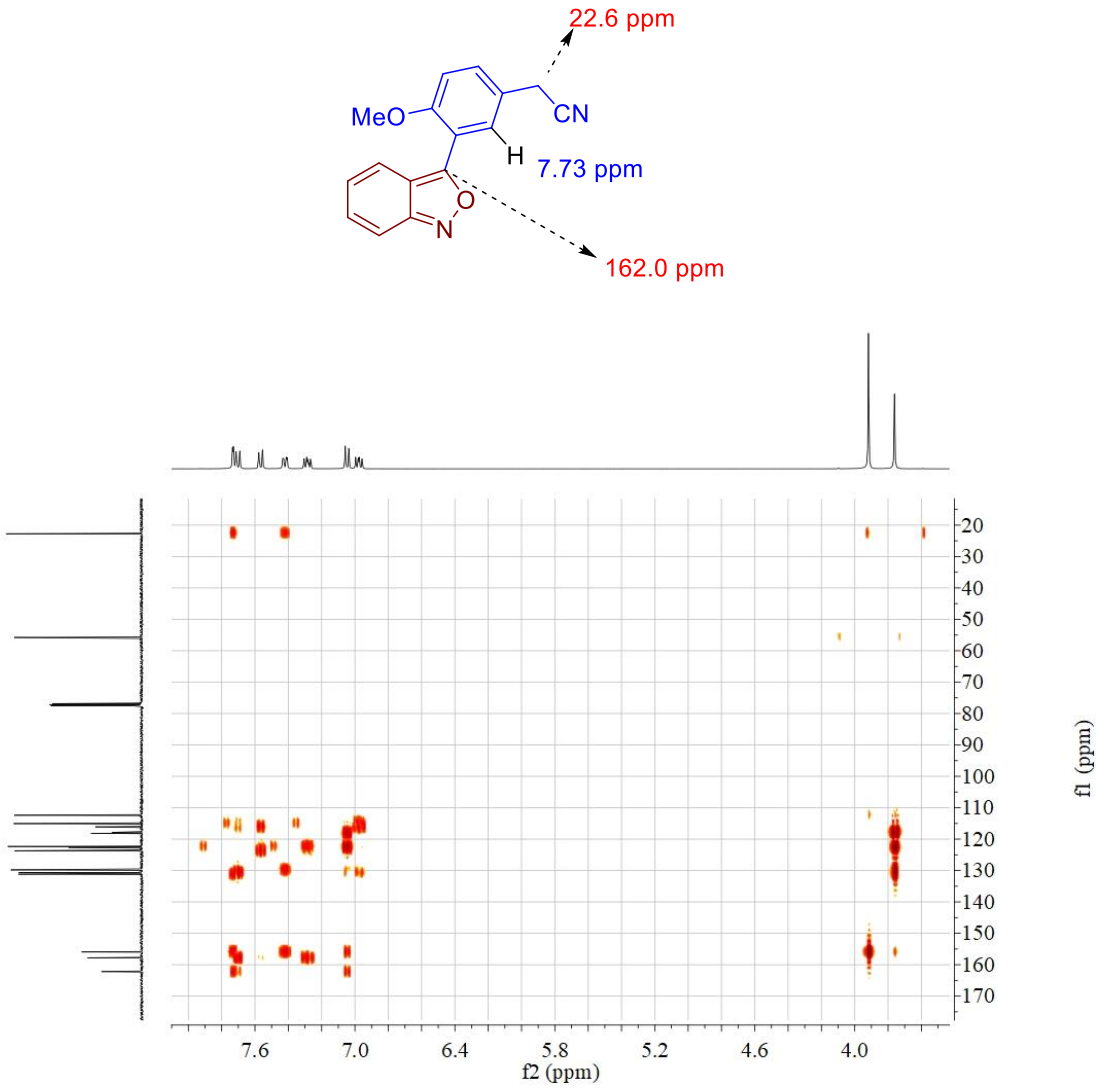
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

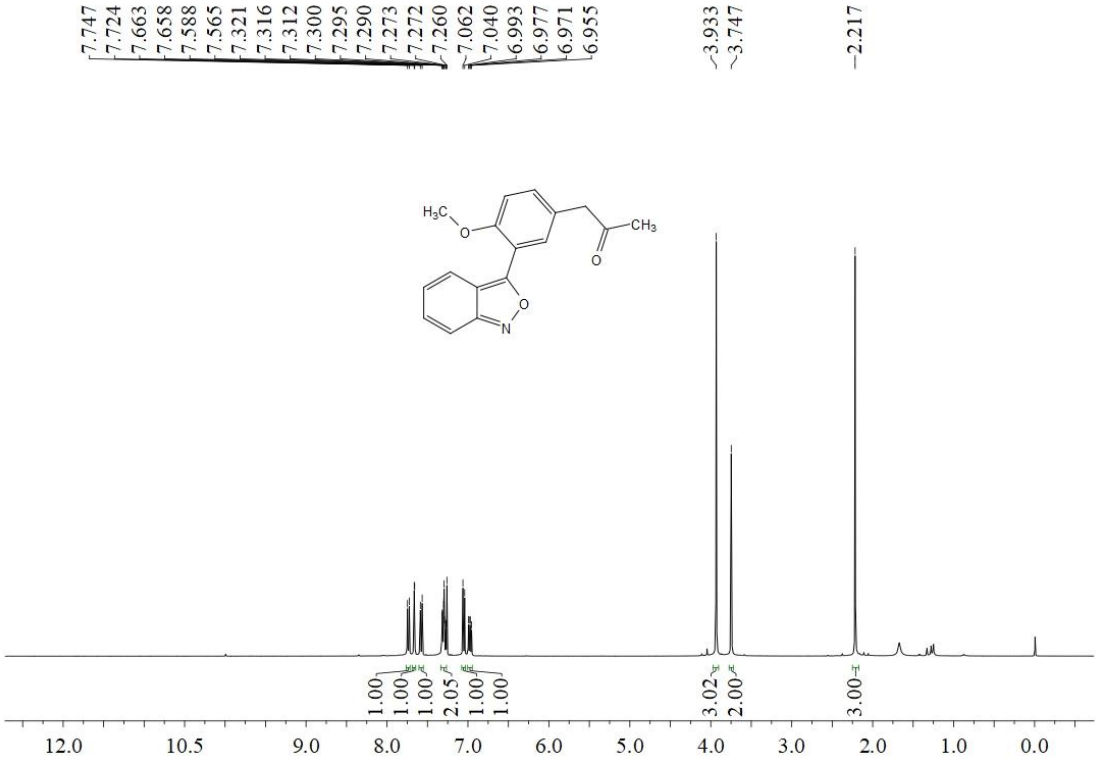


HMBC spectrum of **3s**

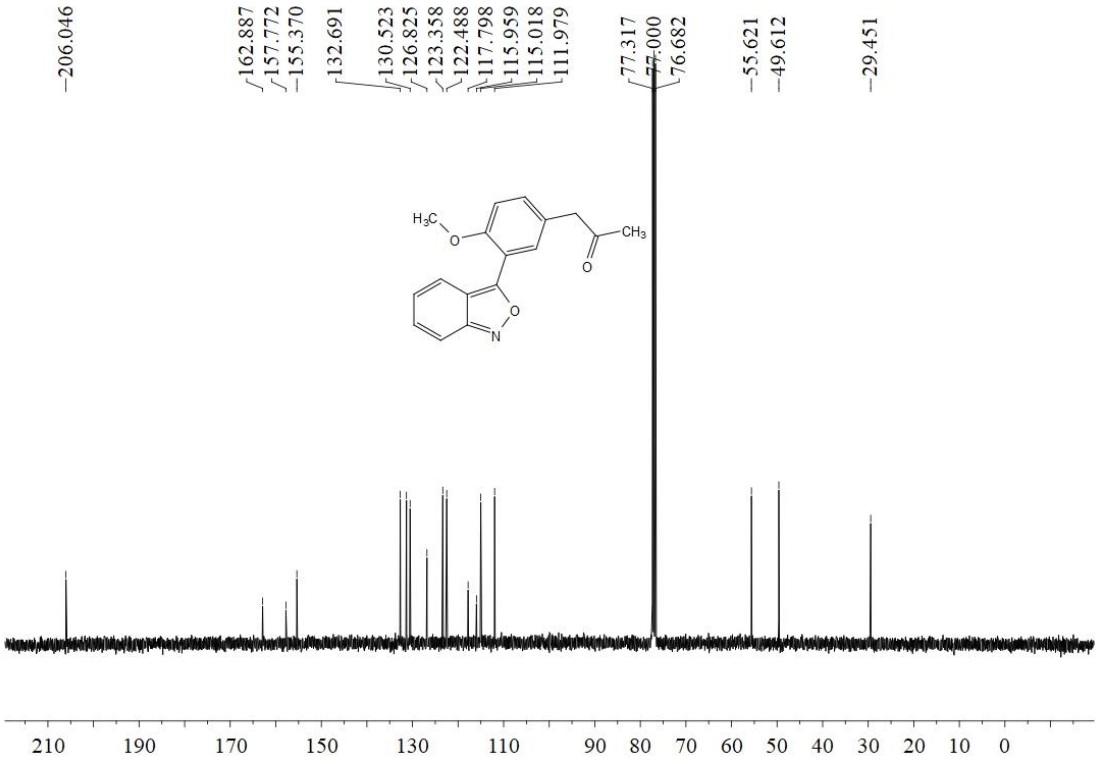


1-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)propan-2-one (**3t**)

^{1}H NMR (400 MHz, $CDCl_3$)

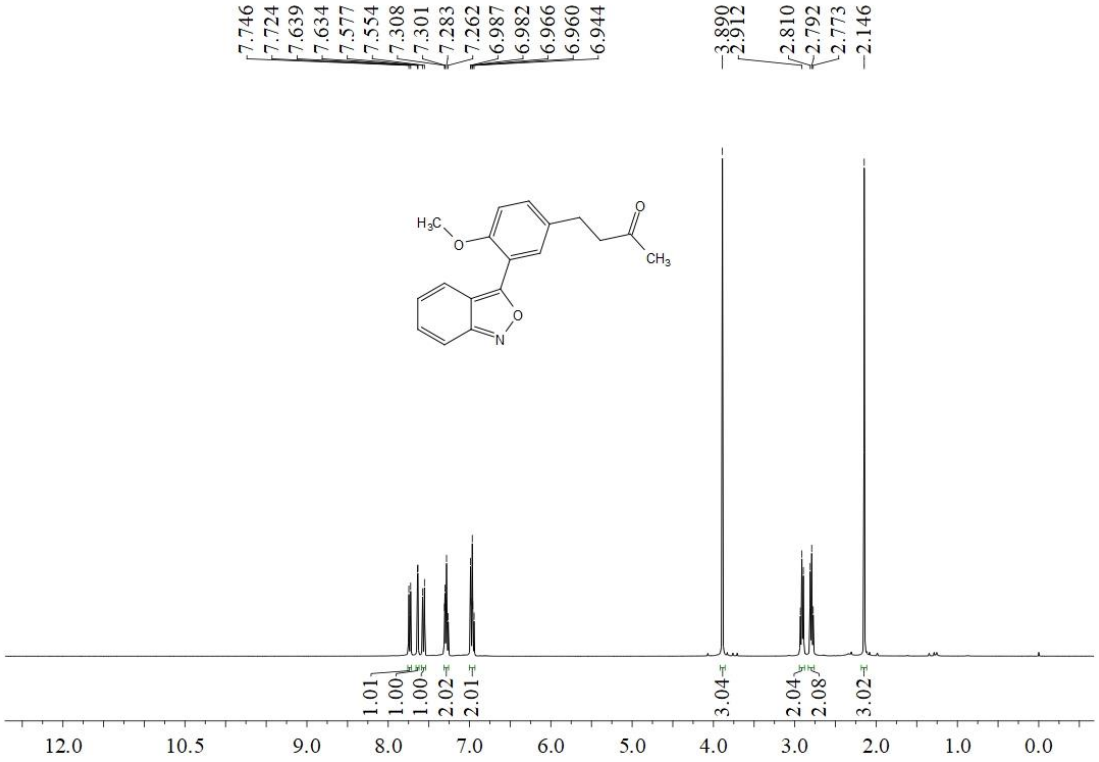


^{13}C NMR (100 MHz, $CDCl_3$)

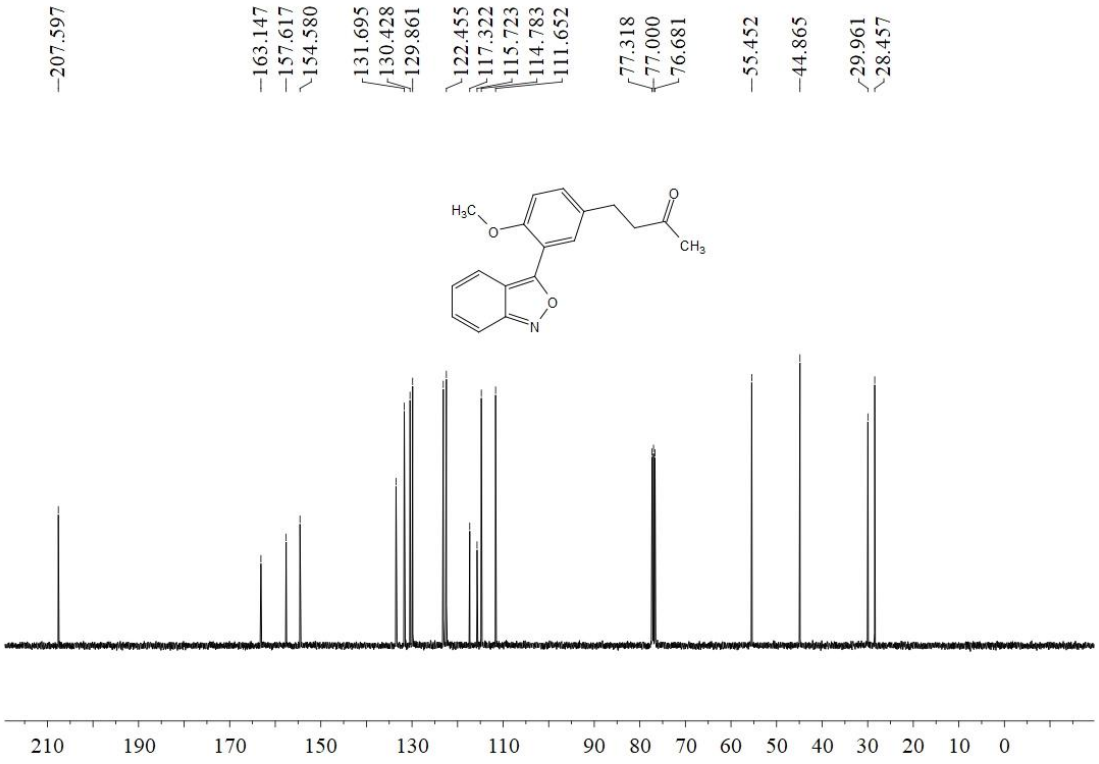


4-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)butan-2-one (**3u**)

^{1}H NMR (400 MHz, $CDCl_3$)

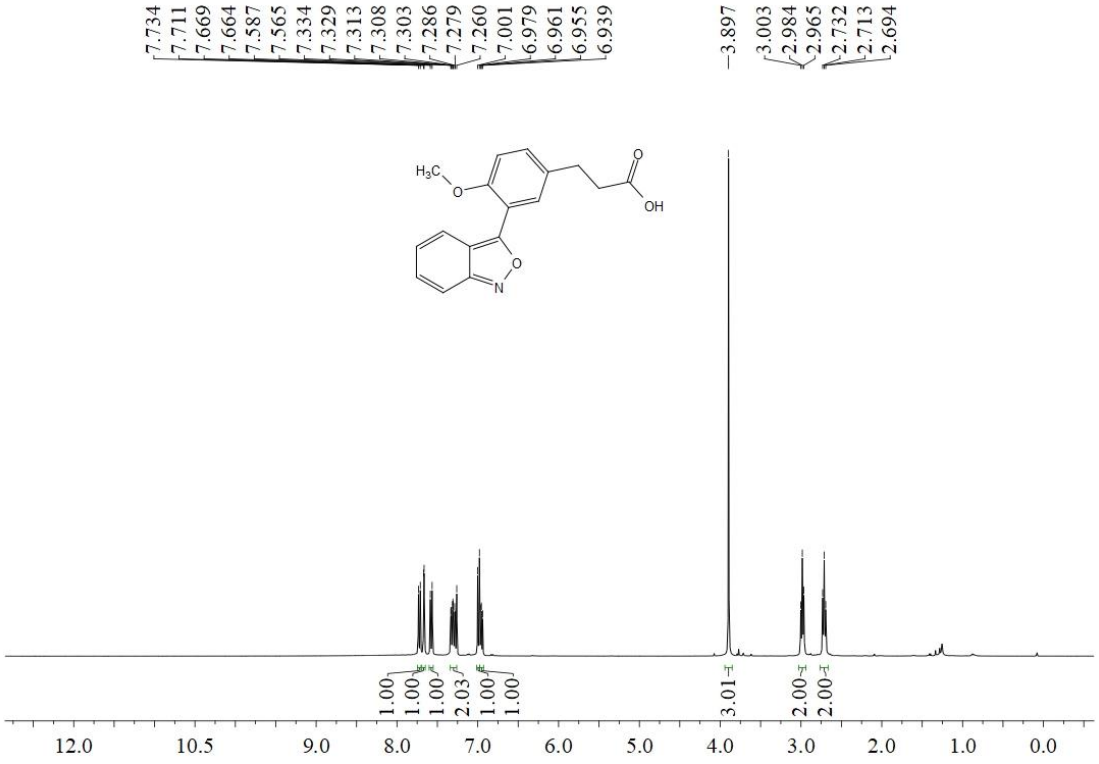


^{13}C NMR (100 MHz, $CDCl_3$)

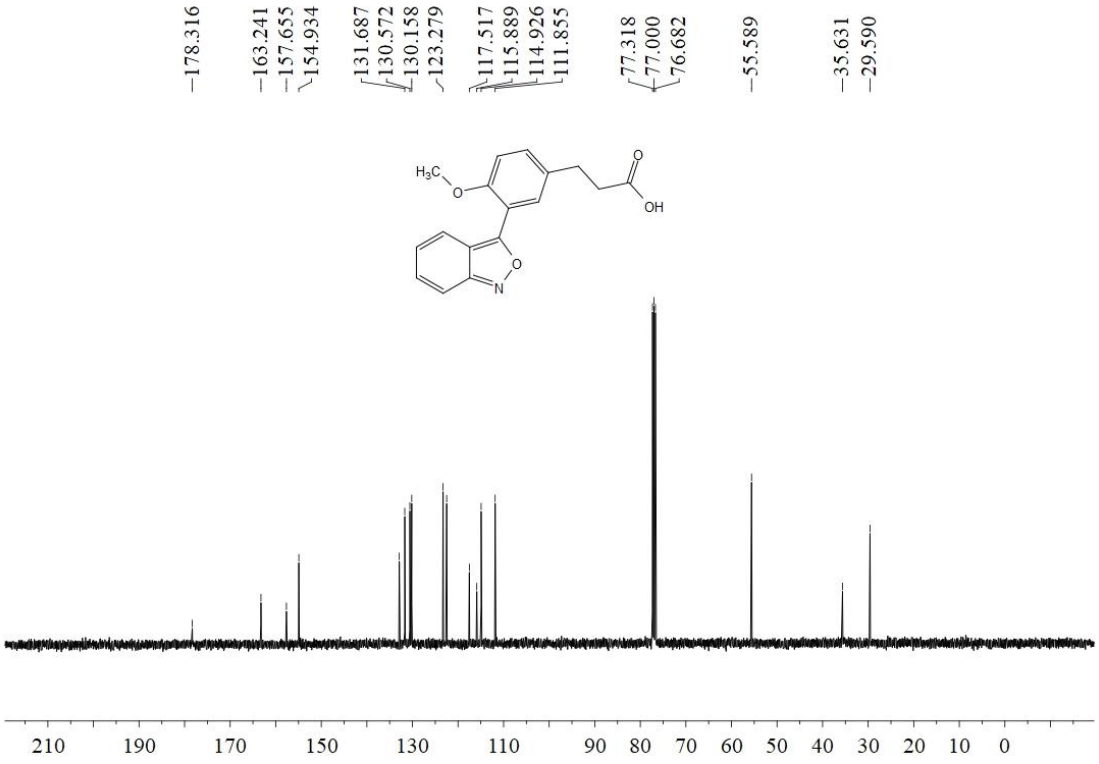


3-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)propanoic acid (**3v**)

^{1}H NMR (400 MHz, $CDCl_3$)

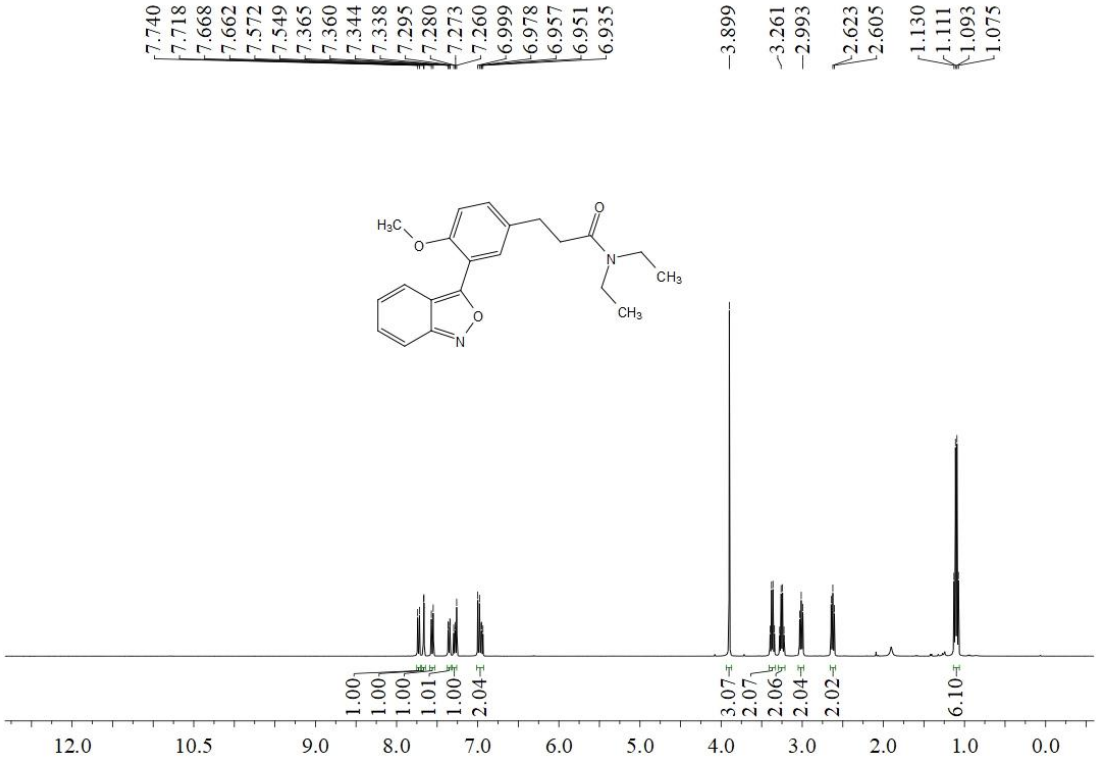


^{13}C NMR (100 MHz, $CDCl_3$)

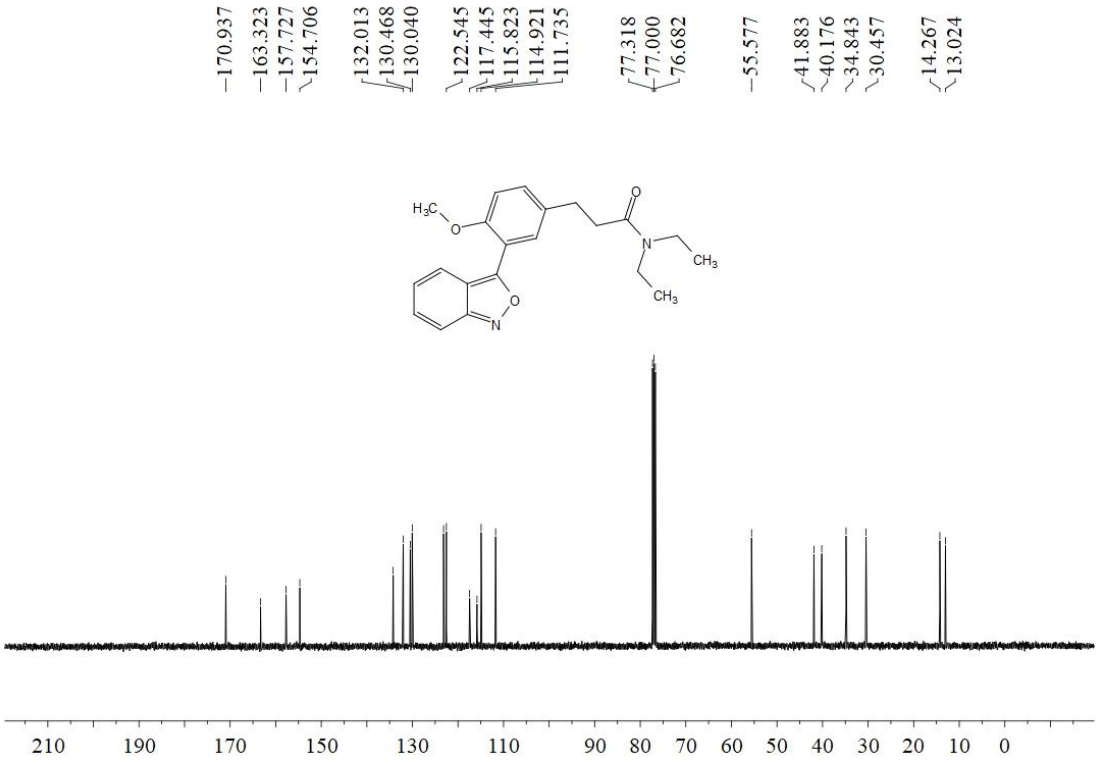


3-(3-(Benzo[c]isoxazol-3-yl)-4-methoxyphenyl)-*N*,*N*-diethylpropanamide (**3w**)

^{1}H NMR (400 MHz, $CDCl_3$)

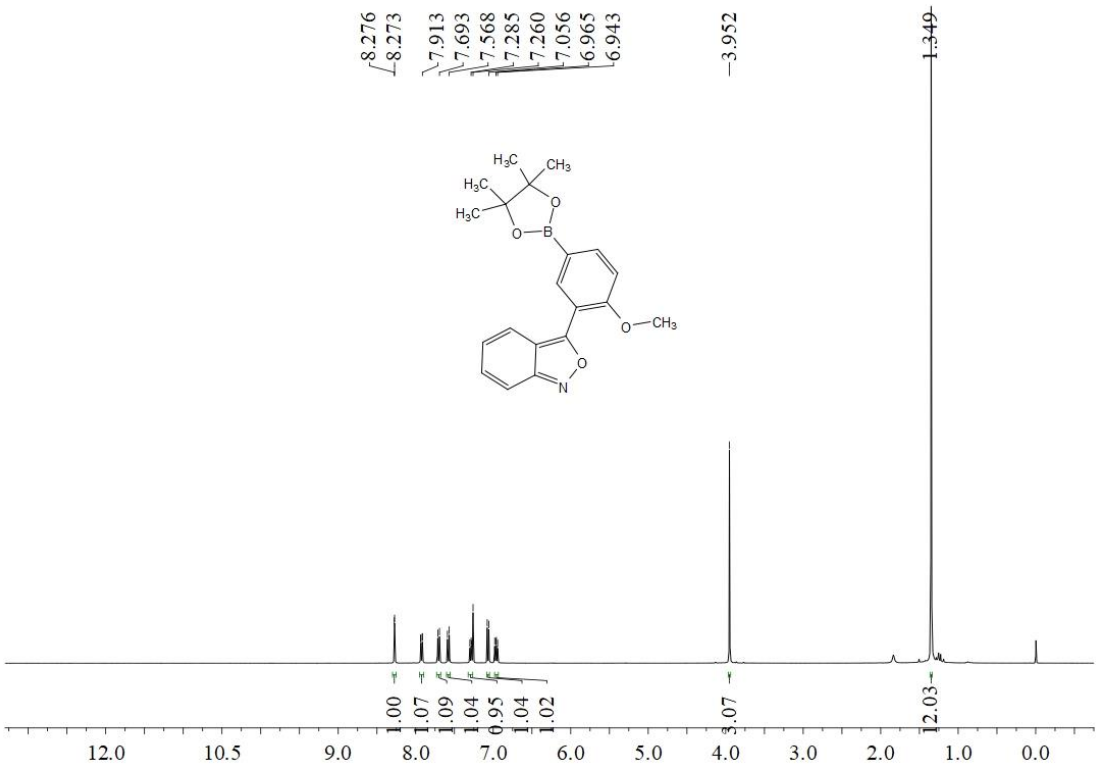


^{13}C NMR (100 MHz, $CDCl_3$)

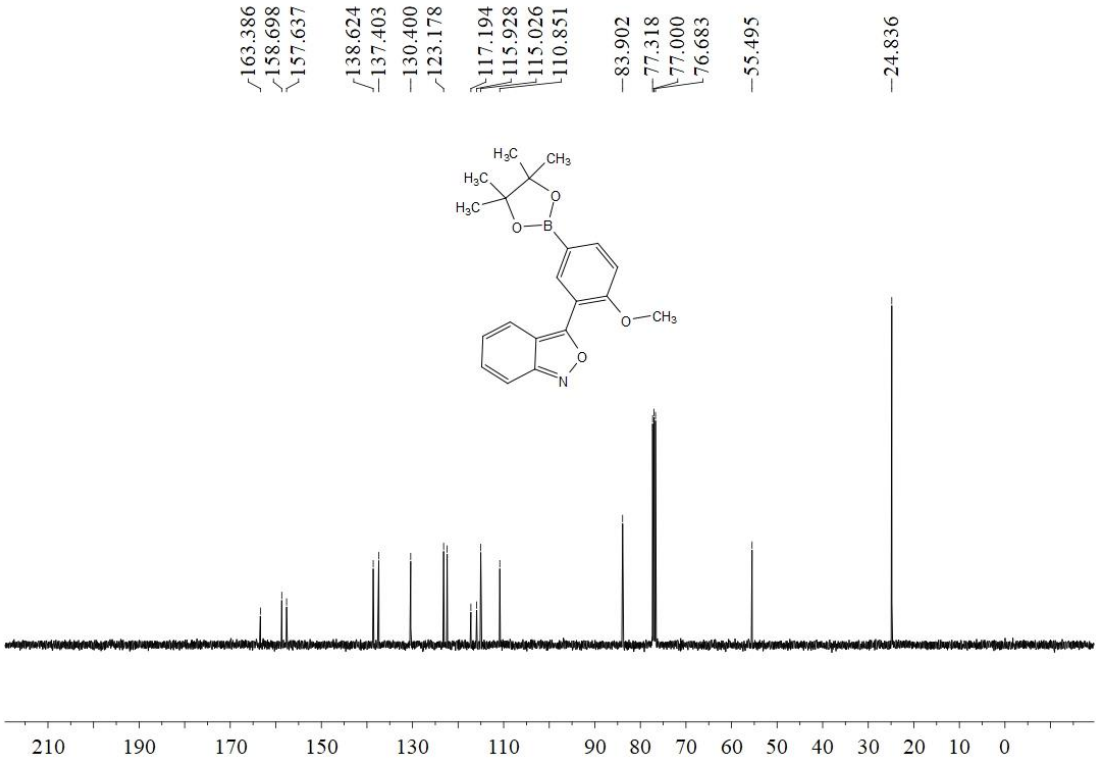


3-(2-Methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[c]isoxazole (**3x**)

^{1}H NMR (400 MHz, $CDCl_3$)

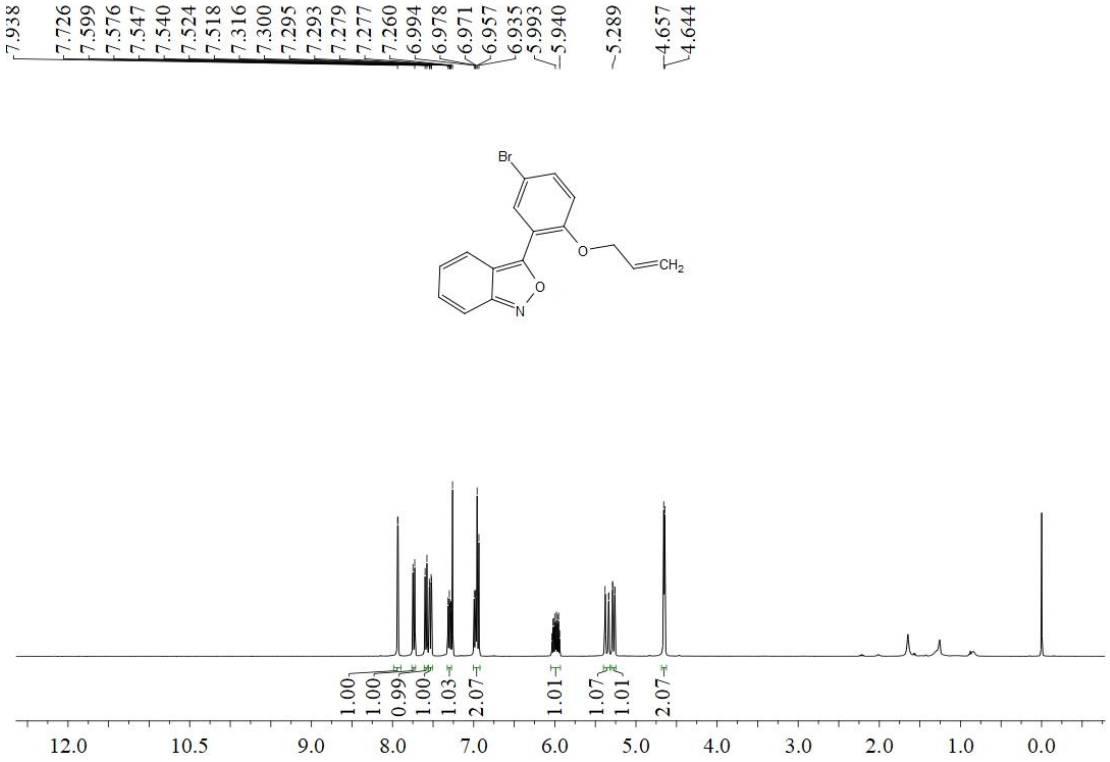


^{13}C NMR (100 MHz, $CDCl_3$)

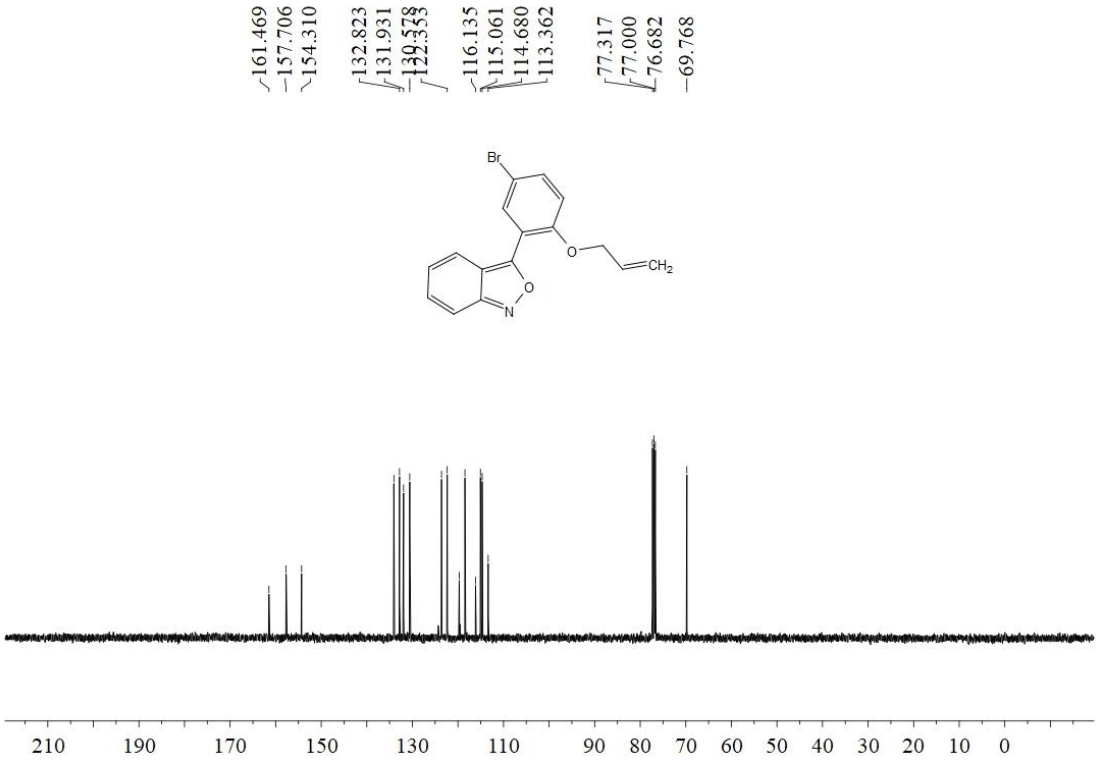


3-(2-(Allyloxy)-5-bromophenyl)benzo[c]isoxazole (**3y**)

^{1}H NMR (400 MHz, $CDCl_3$)

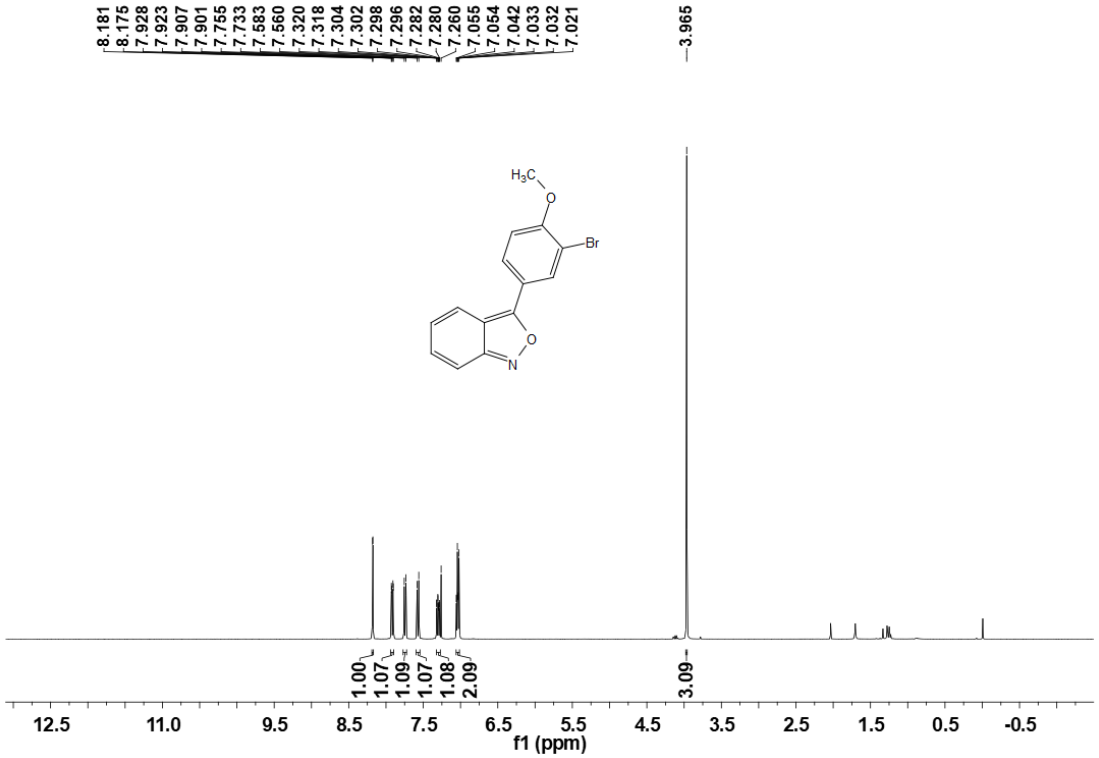


^{13}C NMR (100 MHz, $CDCl_3$)

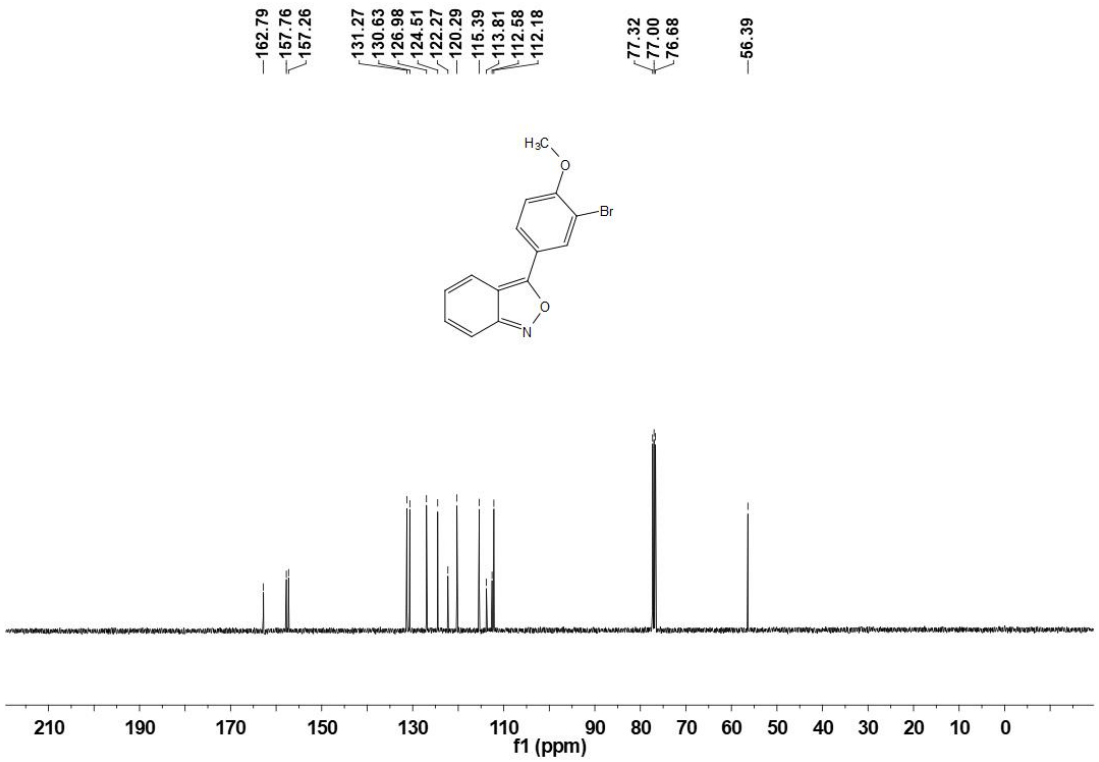


3-(3-Bromo-4-methoxyphenyl)benzo[c]isoxazole (**3z**)

^{1}H NMR (400 MHz, $CDCl_3$)

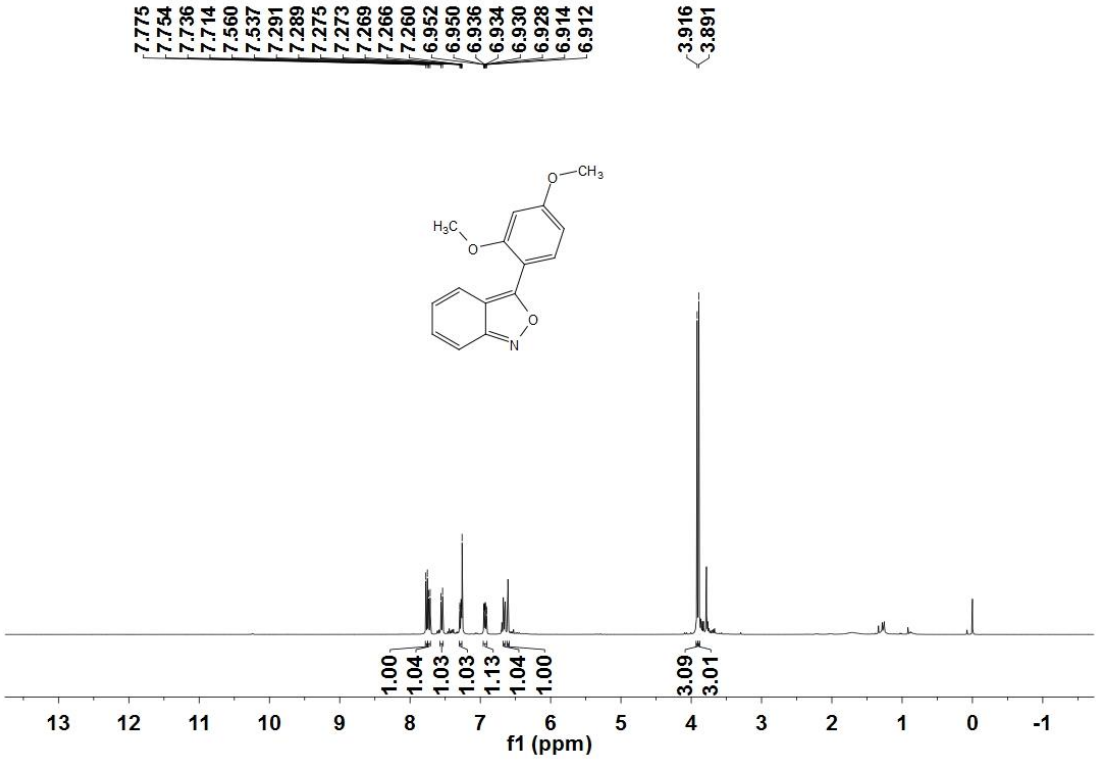


^{13}C NMR (100 MHz, $CDCl_3$)

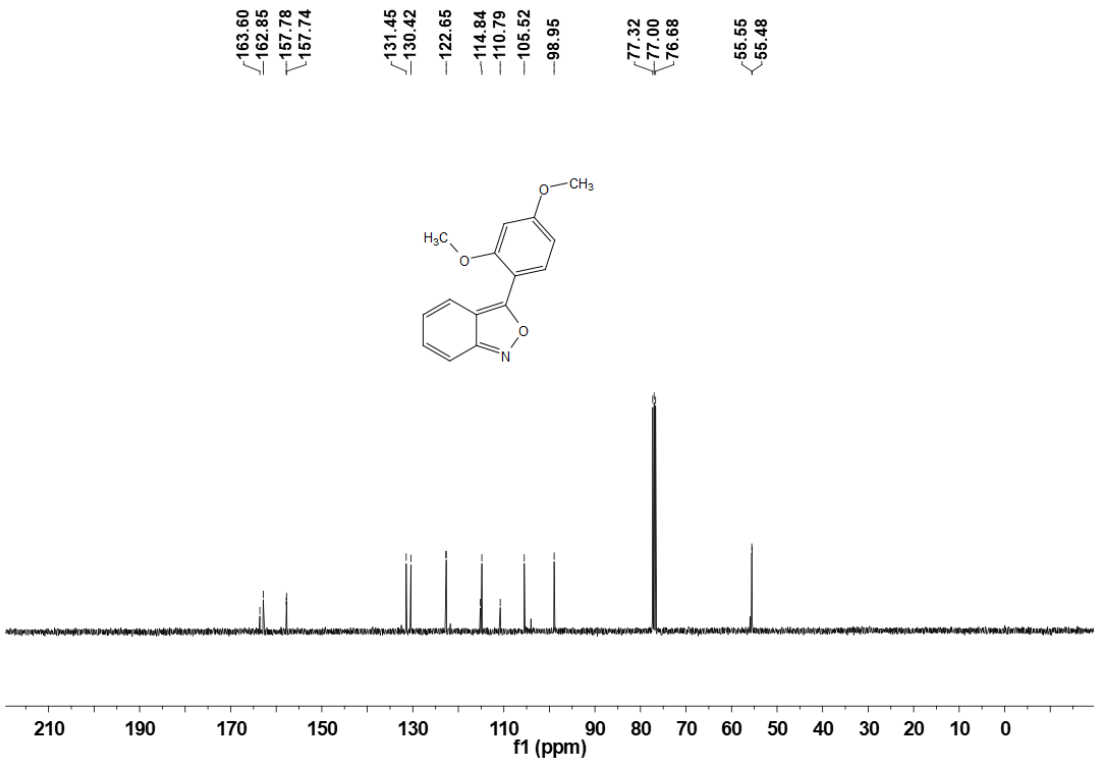


3-(2,4-Dimethoxyphenyl)benzo[c]isoxazole (**3aa**)

^{1}H NMR (400 MHz, $CDCl_3$)

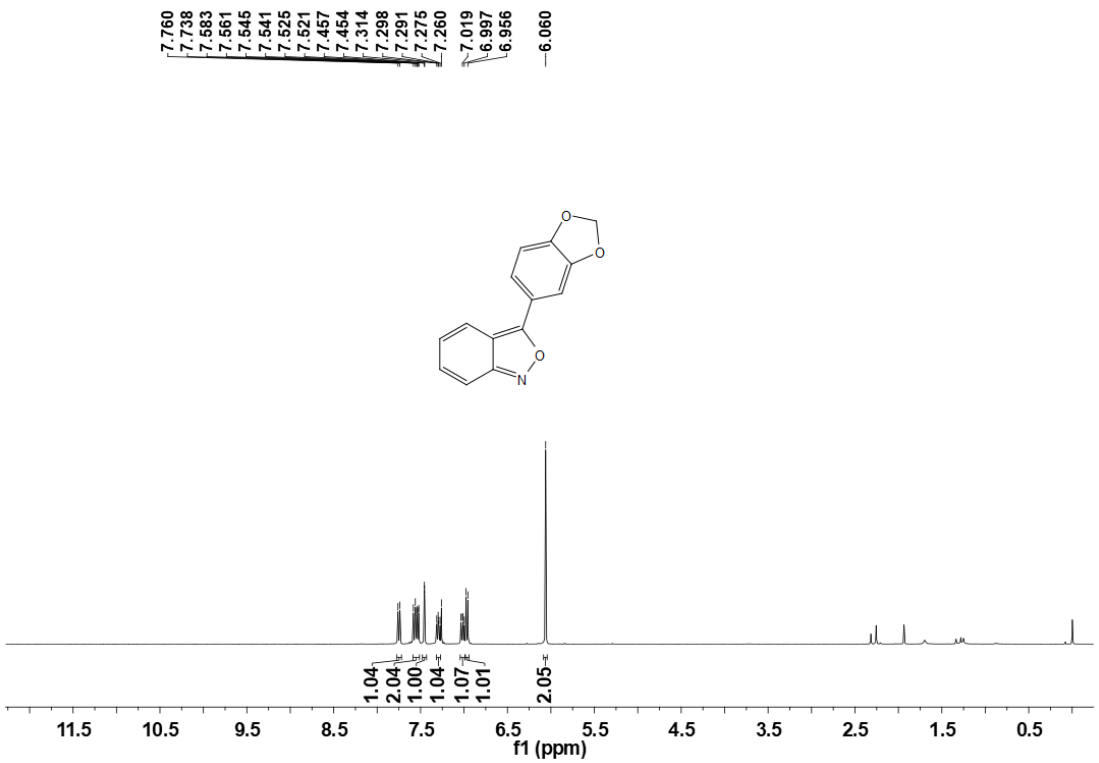


^{13}C NMR (100 MHz, $CDCl_3$)

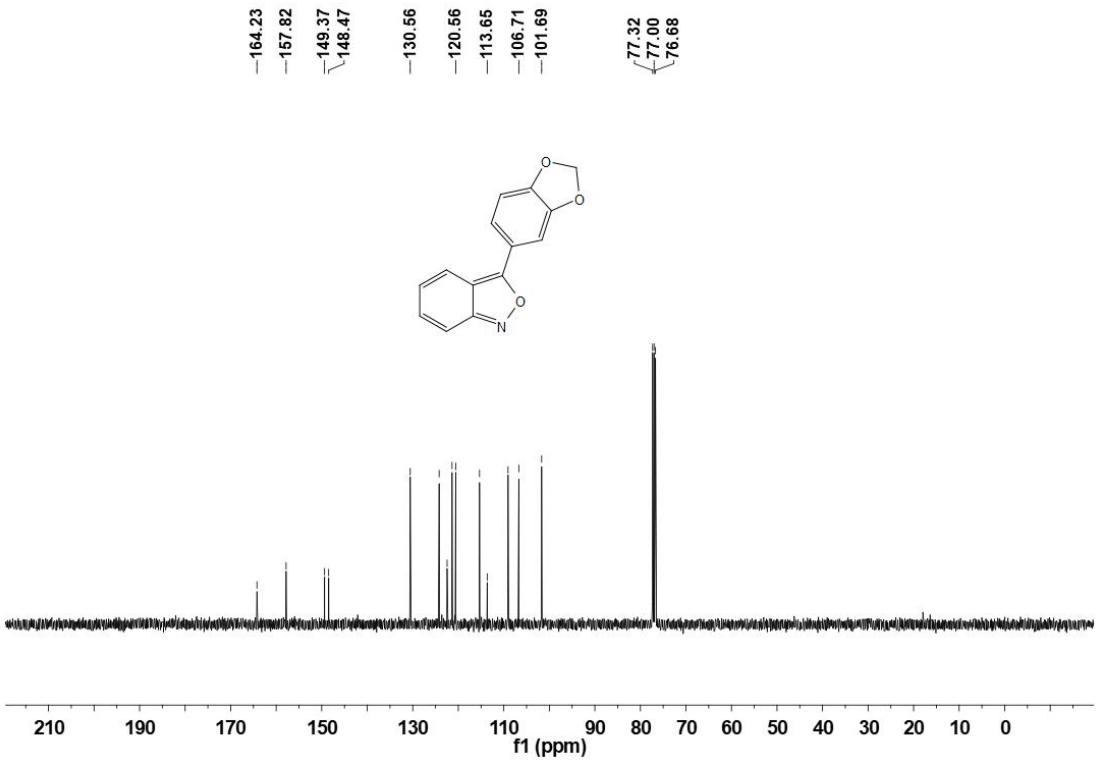


3-(Benzo[d][1,3]dioxol-5-yl)benzo[c]isoxazole (**3ab**)

^{1}H NMR (400 MHz, $CDCl_3$)

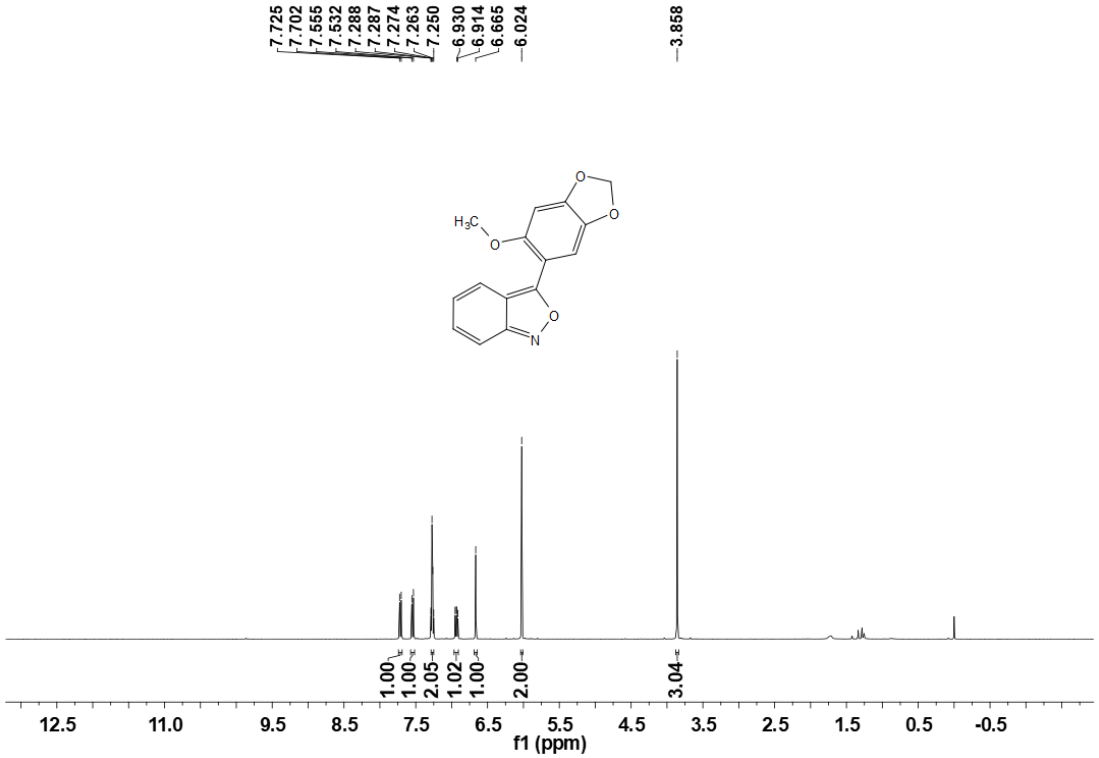


^{13}C NMR (100 MHz, $CDCl_3$)

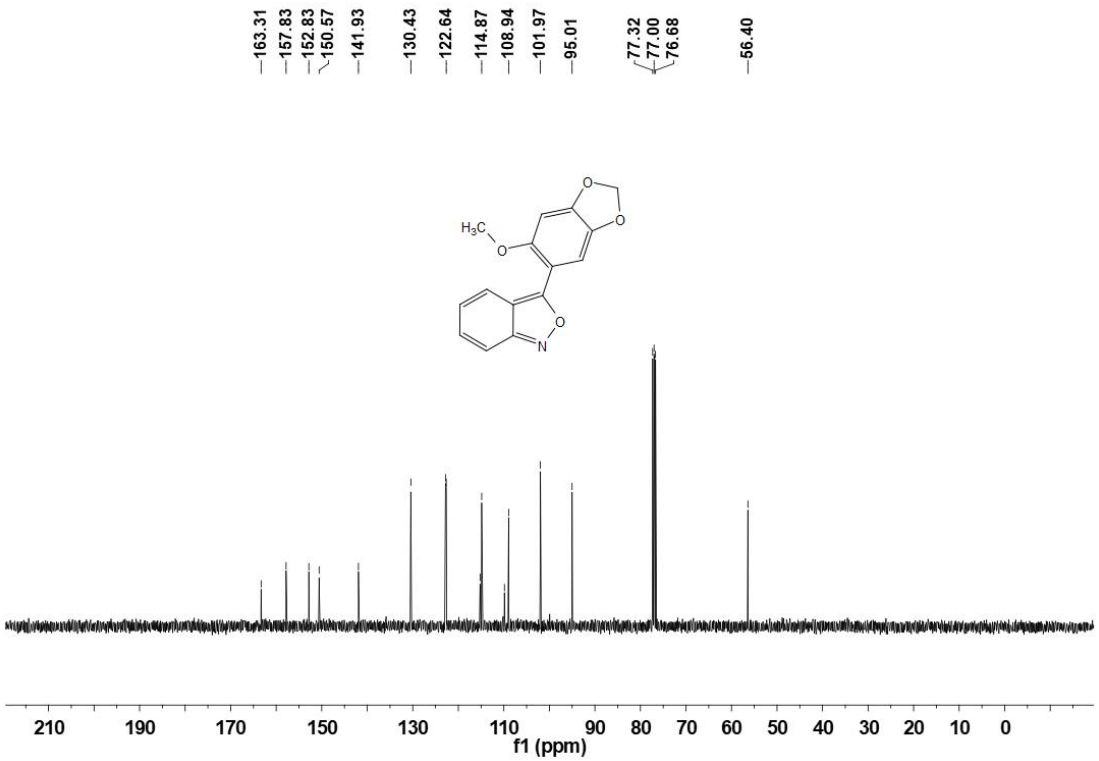


3-(6-Methoxybenzo[d][1,3]dioxol-5-yl)benzo[c]isoxazole (**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$)

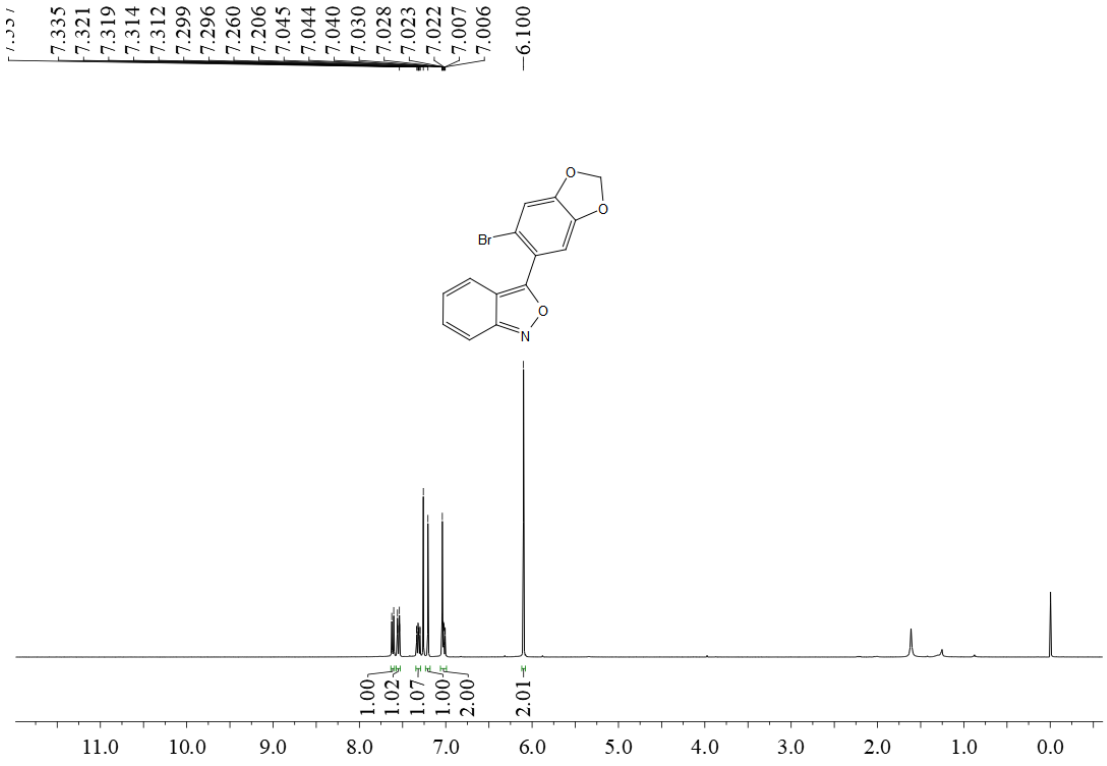


^{13}C NMR (100 MHz, $CDCl_3$)

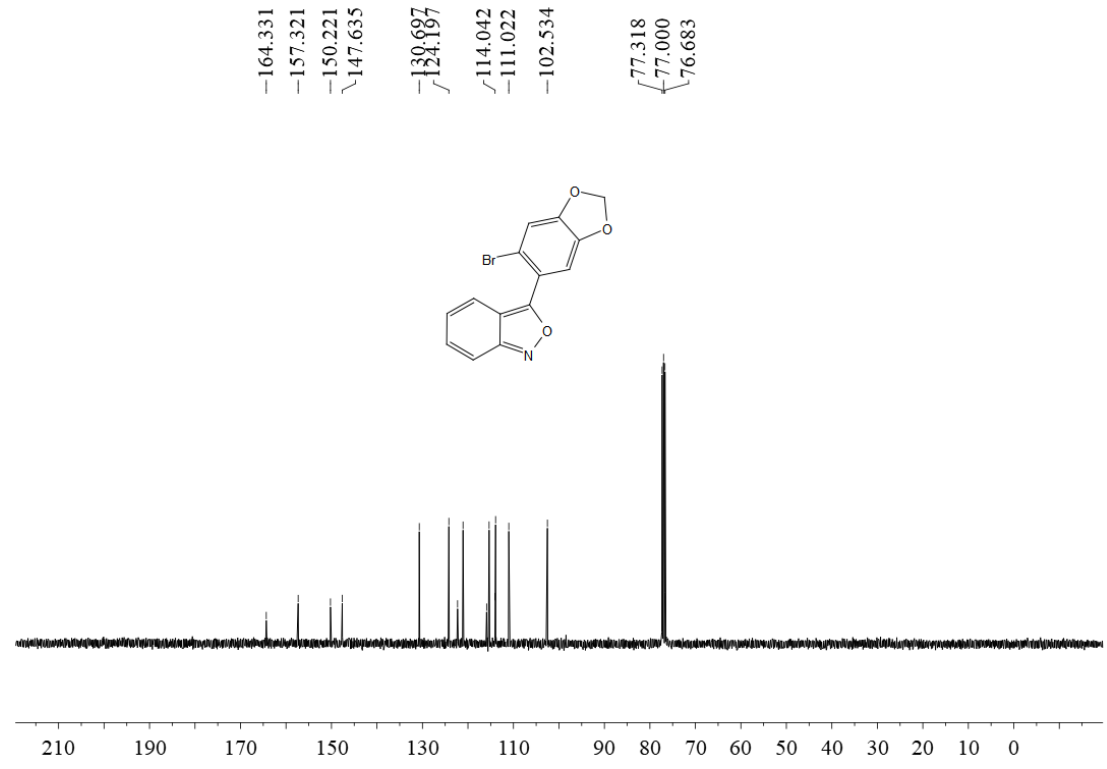


3-(6-Bromobenzo[d][1,3]dioxol-5-yl)benzo[c]isoxazole (**3ad**)

^{1}H NMR (400 MHz, $CDCl_3$)

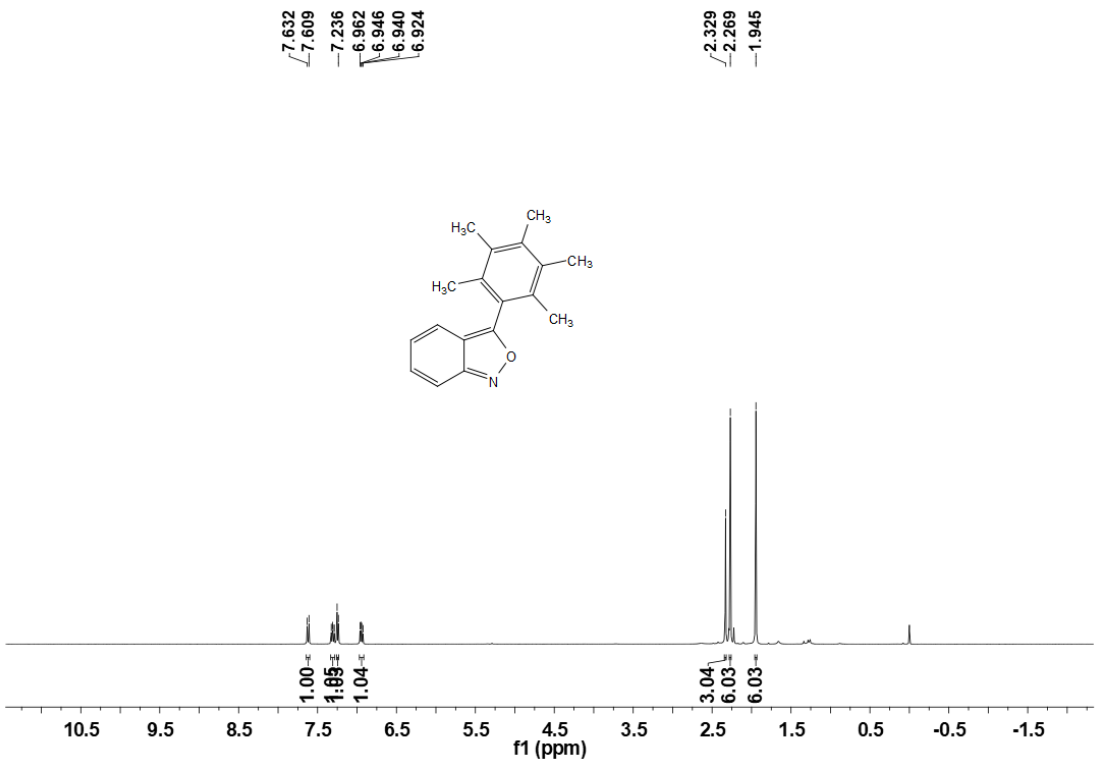


^{13}C NMR (100 MHz, $CDCl_3$)

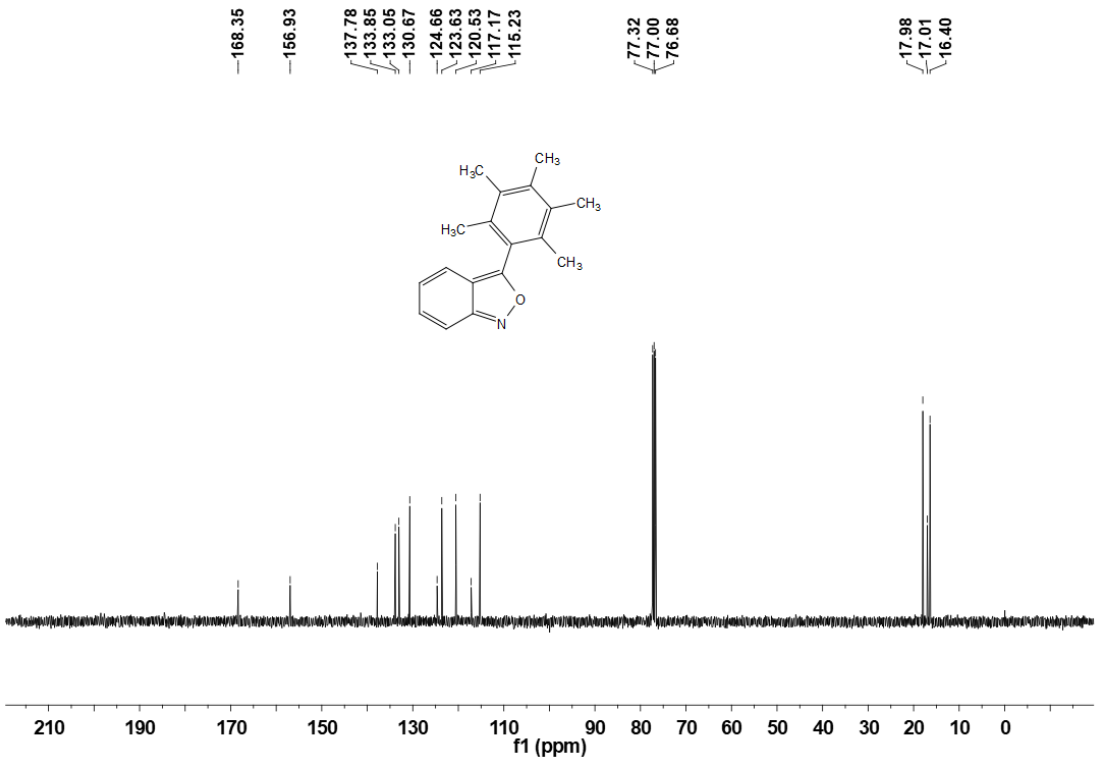


3-(2,3,4,5,6-Pentamethylphenyl)benzo[c]isoxazole (**3ae**)

^{1}H NMR (400 MHz, $CDCl_3$)

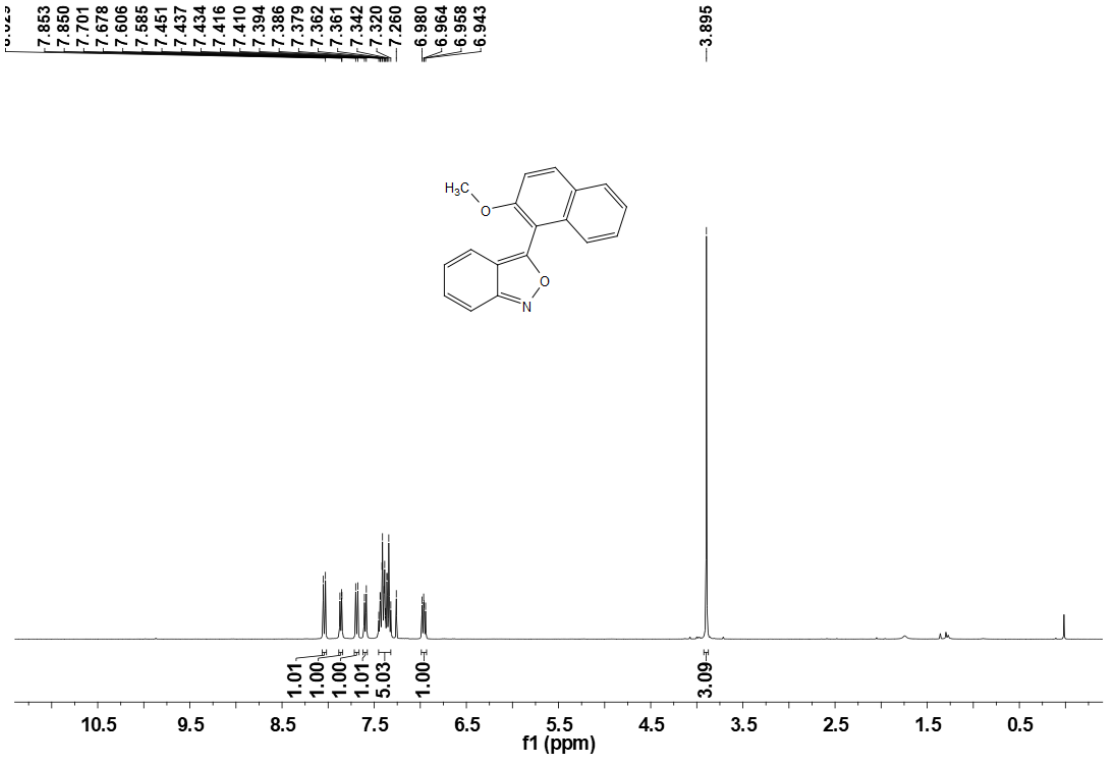


^{13}C NMR (100 MHz, $CDCl_3$)

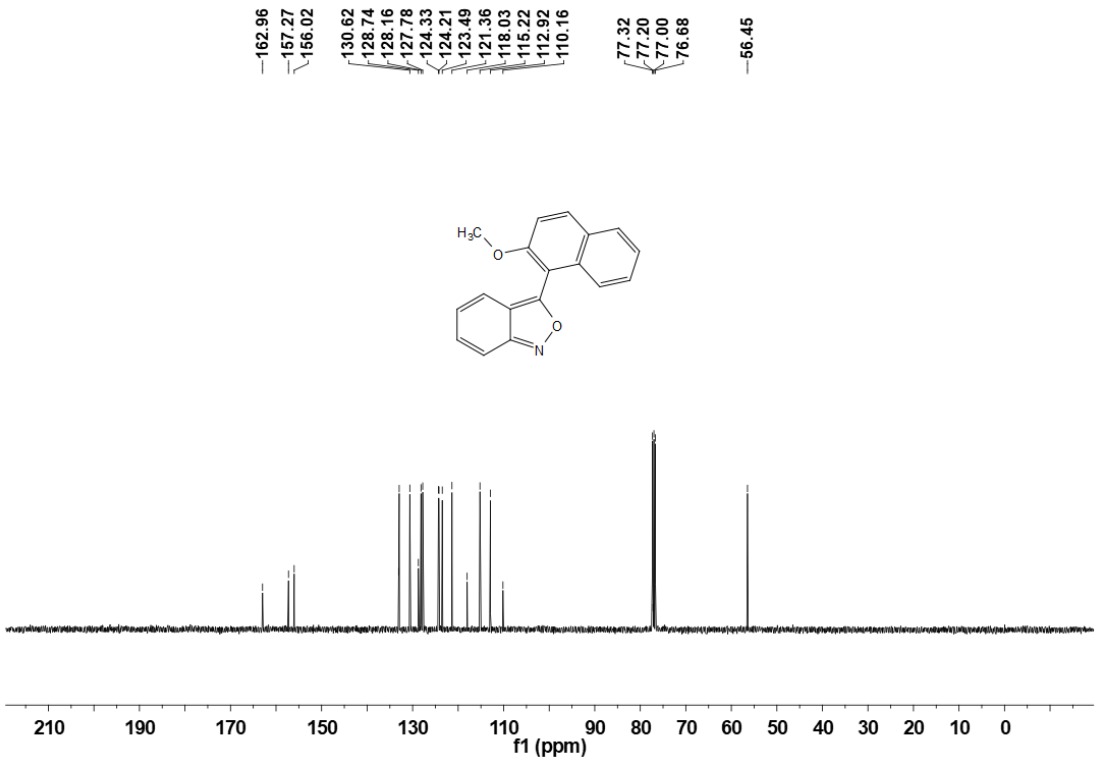


3-(2-Methoxynaphthalen-1-yl)benzo[c]isoxazole (**3af**)

^{1}H NMR (400 MHz, $CDCl_3$)

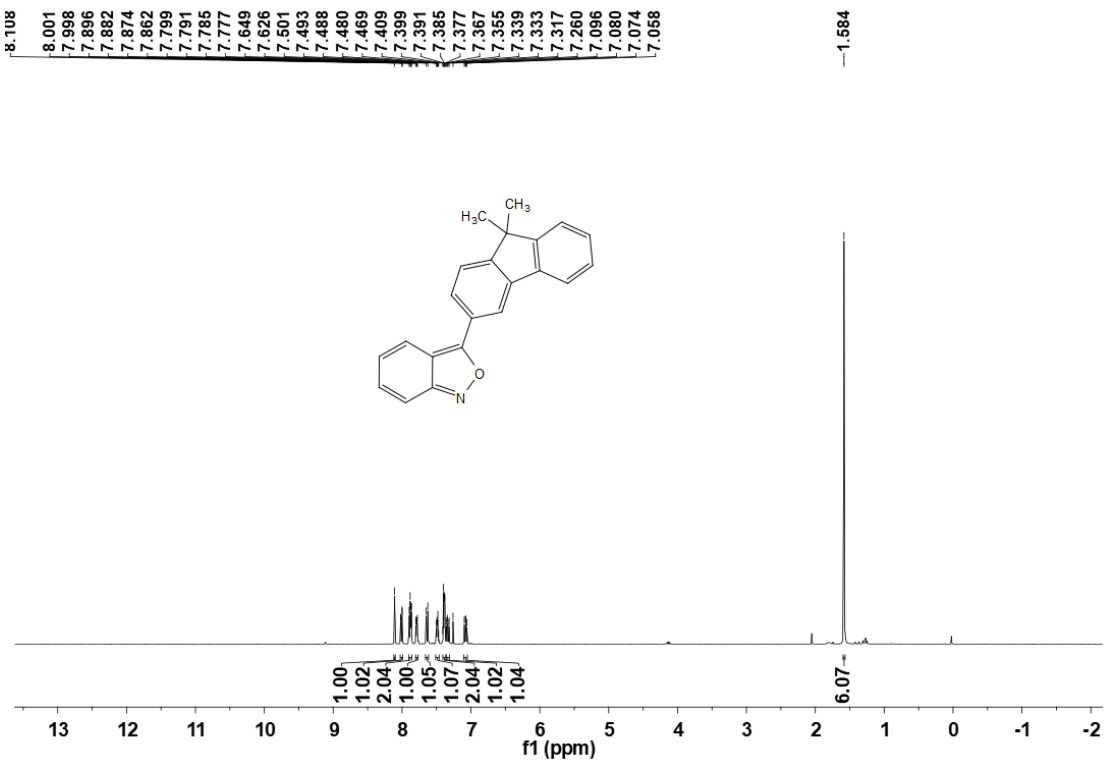


^{13}C NMR (100 MHz, $CDCl_3$)

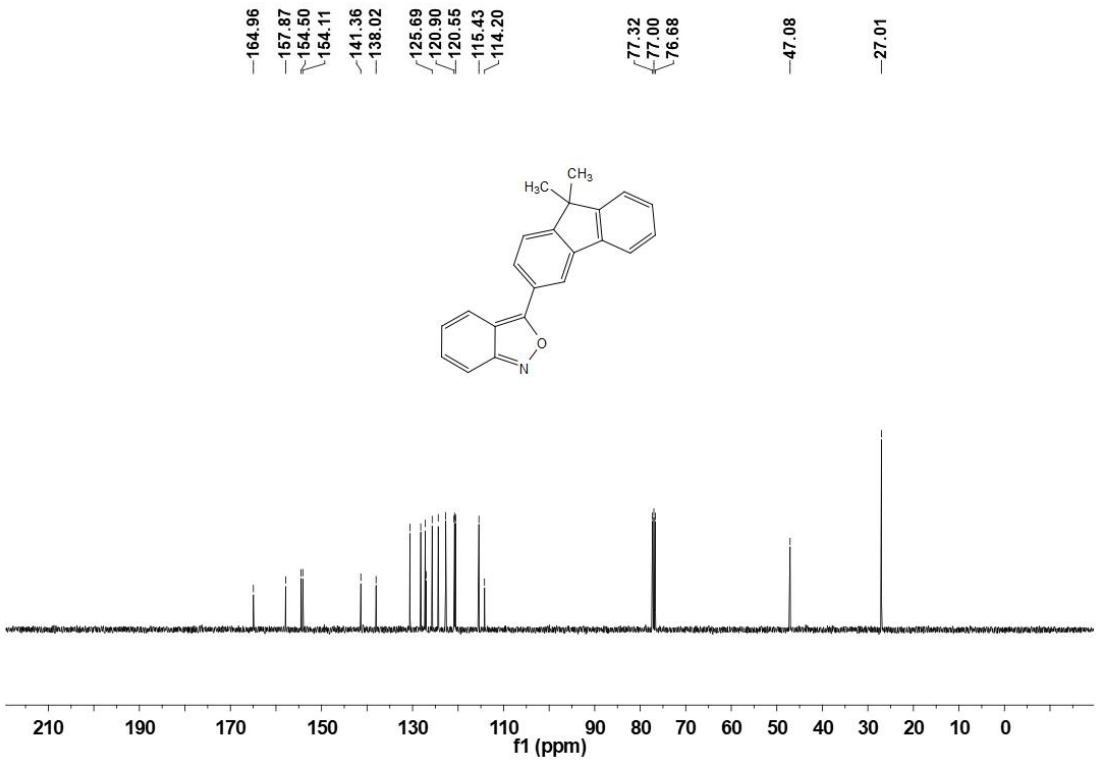


3-(9,9-Dimethyl-9H-fluoren-3-yl)benzo[c]isoxazole (**3ag**)

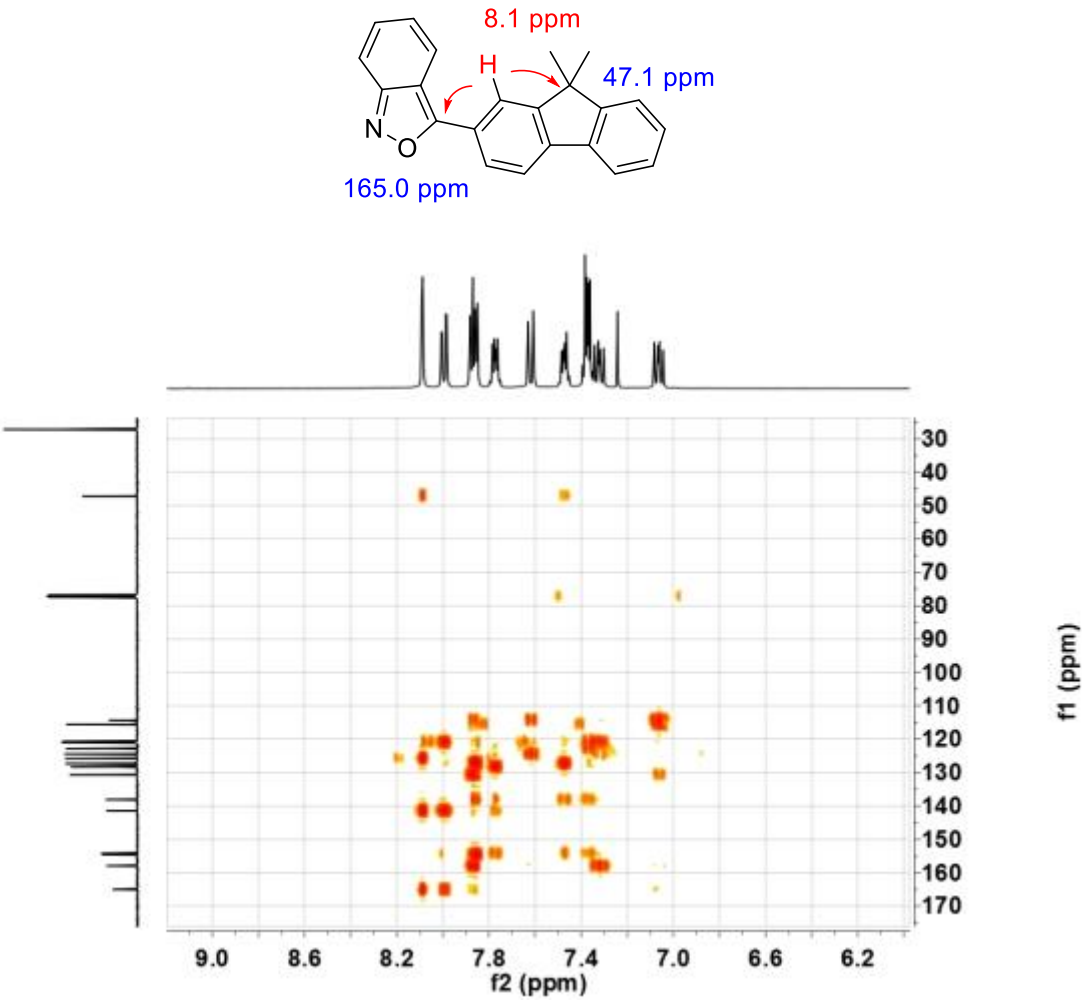
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

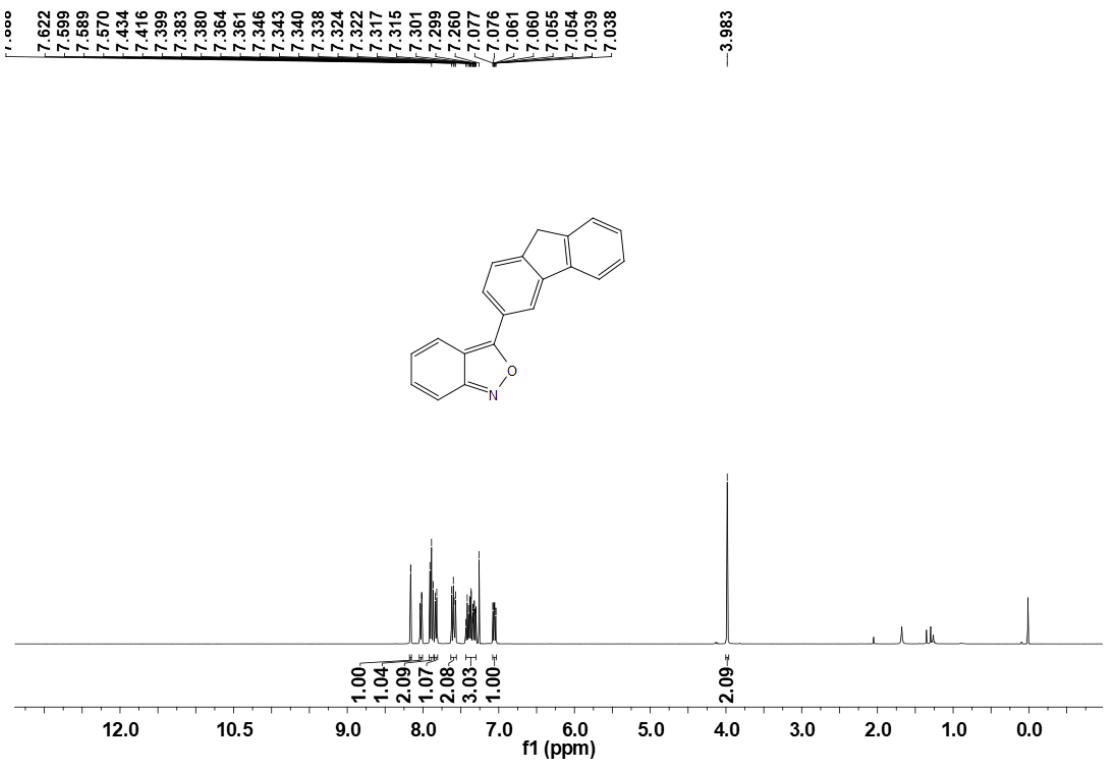


HMBC spectrum of 3ag

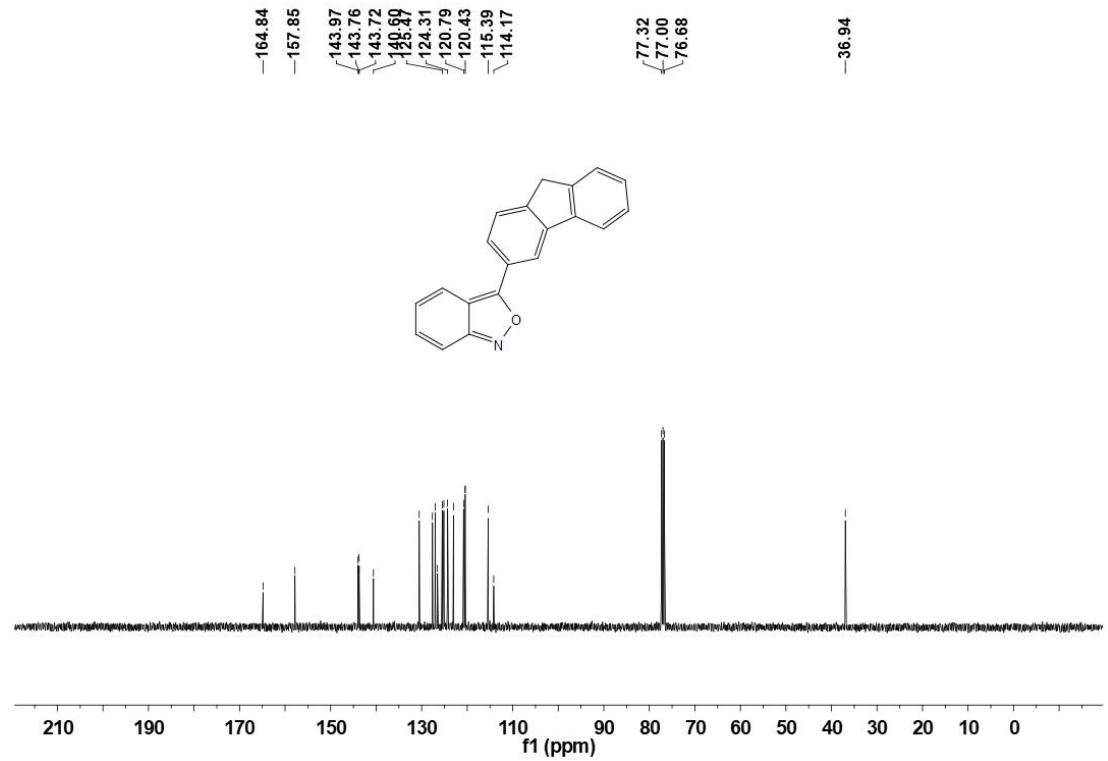


3-(9*H*-Fluoren-3-yl)benzo[c]isoxazole (**3ah**)

^{1}H NMR (400 MHz, $CDCl_3$)

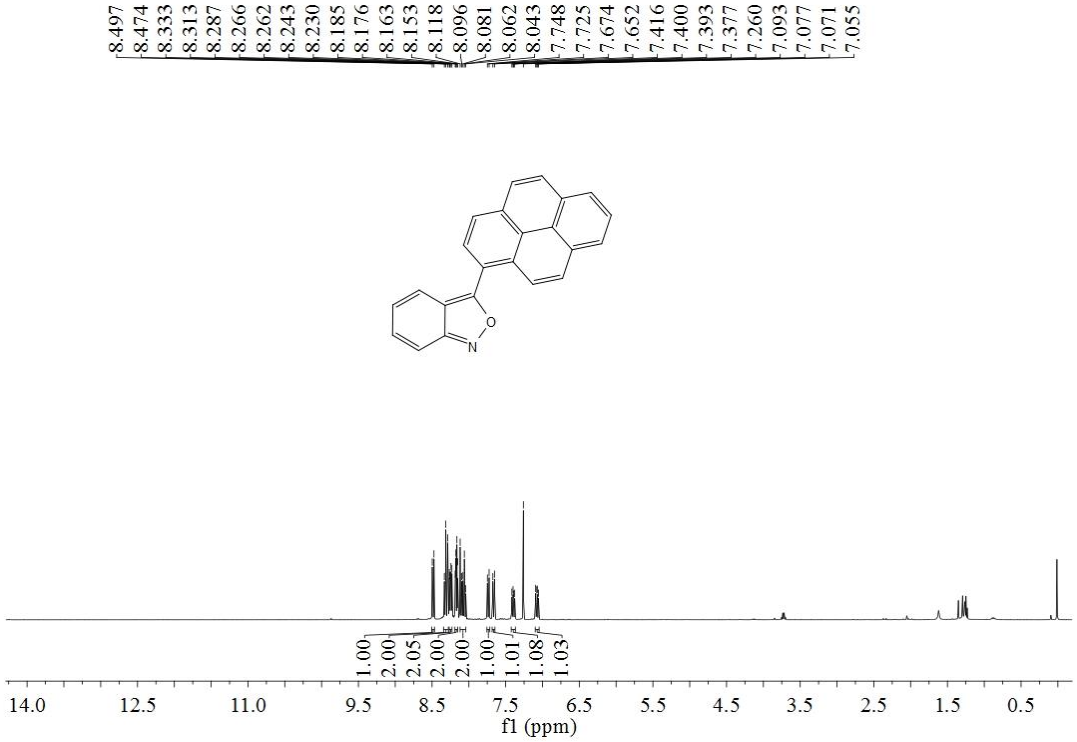


^{13}C NMR (100 MHz, $CDCl_3$)

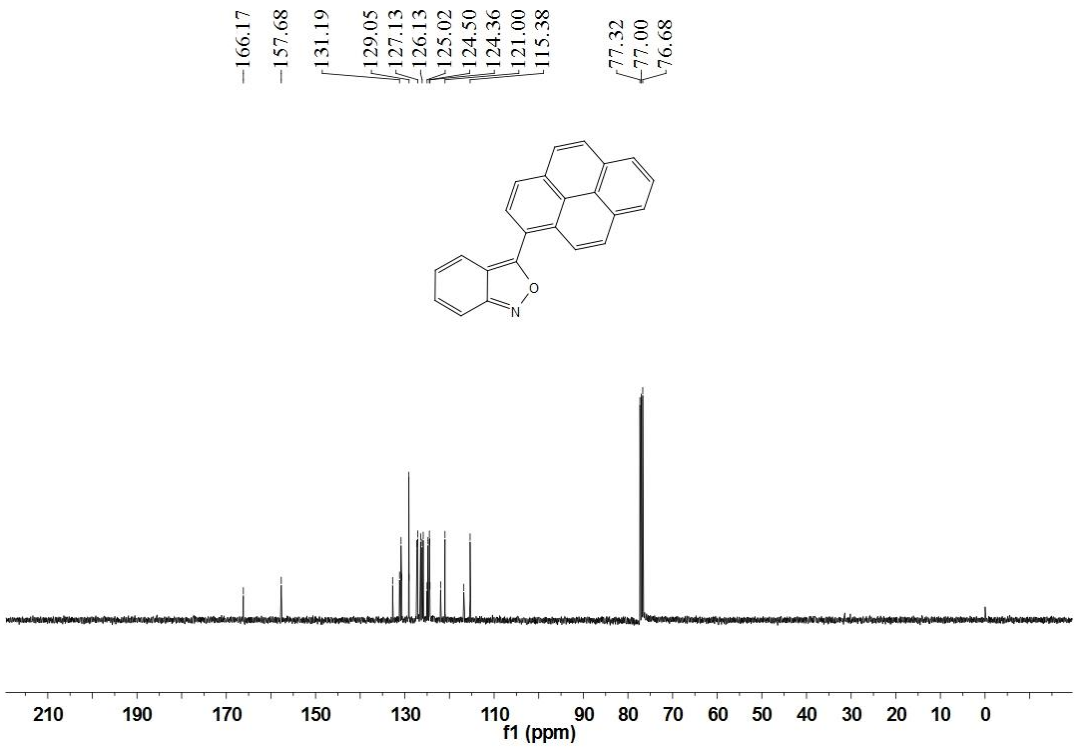


3-(Pyren-2-yl)benzo[c]isoxazole (**3ai**)

^{1}H NMR (400 MHz, $CDCl_3$)

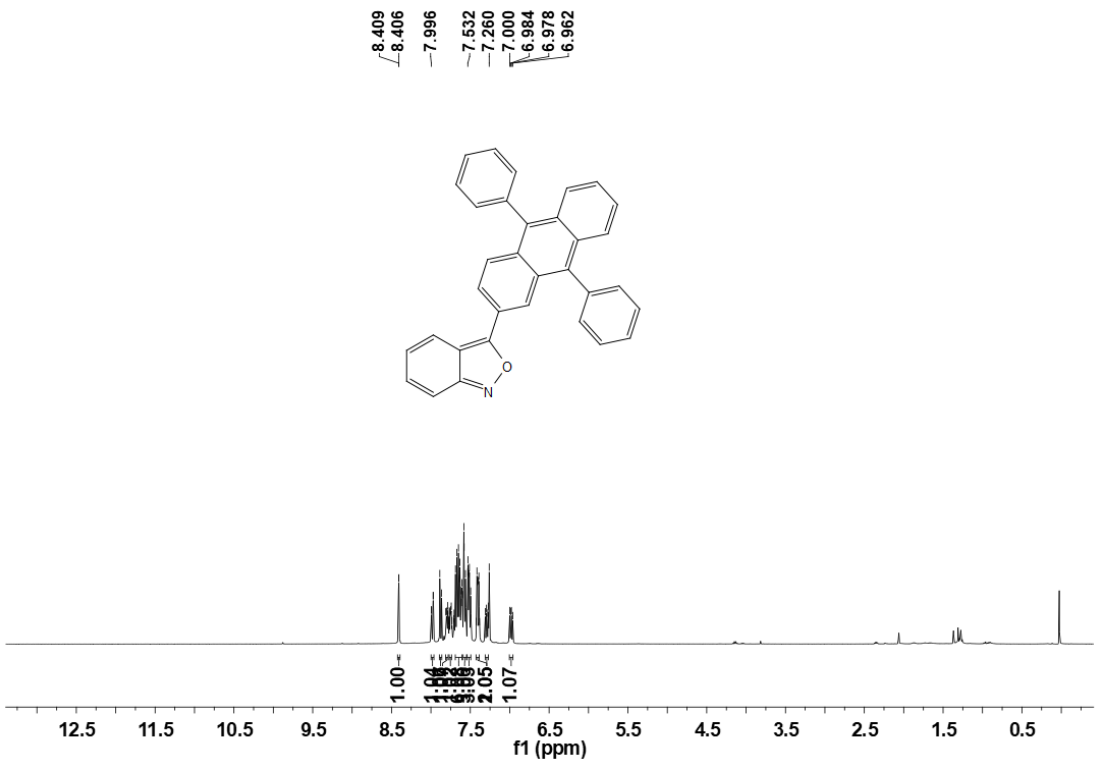


^{13}C NMR (100 MHz, $CDCl_3$)

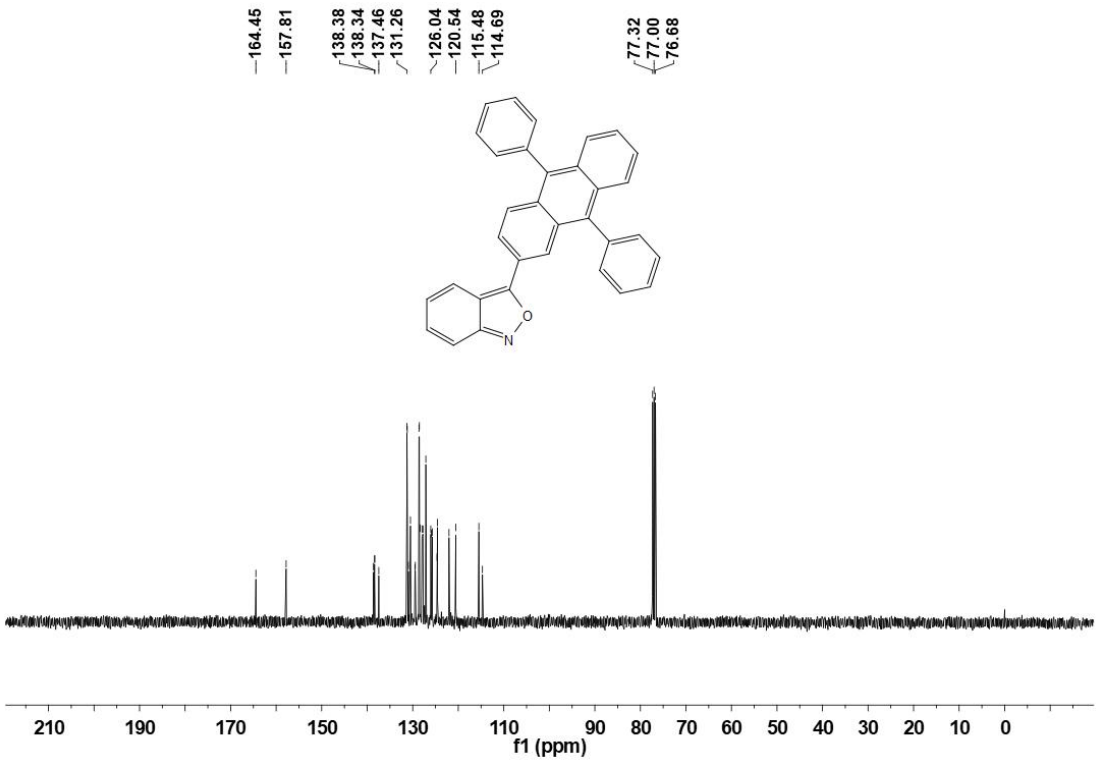


3-(9,10-Diphenylanthracen-2-yl)benzo[c]isoxazole (**3aj**)

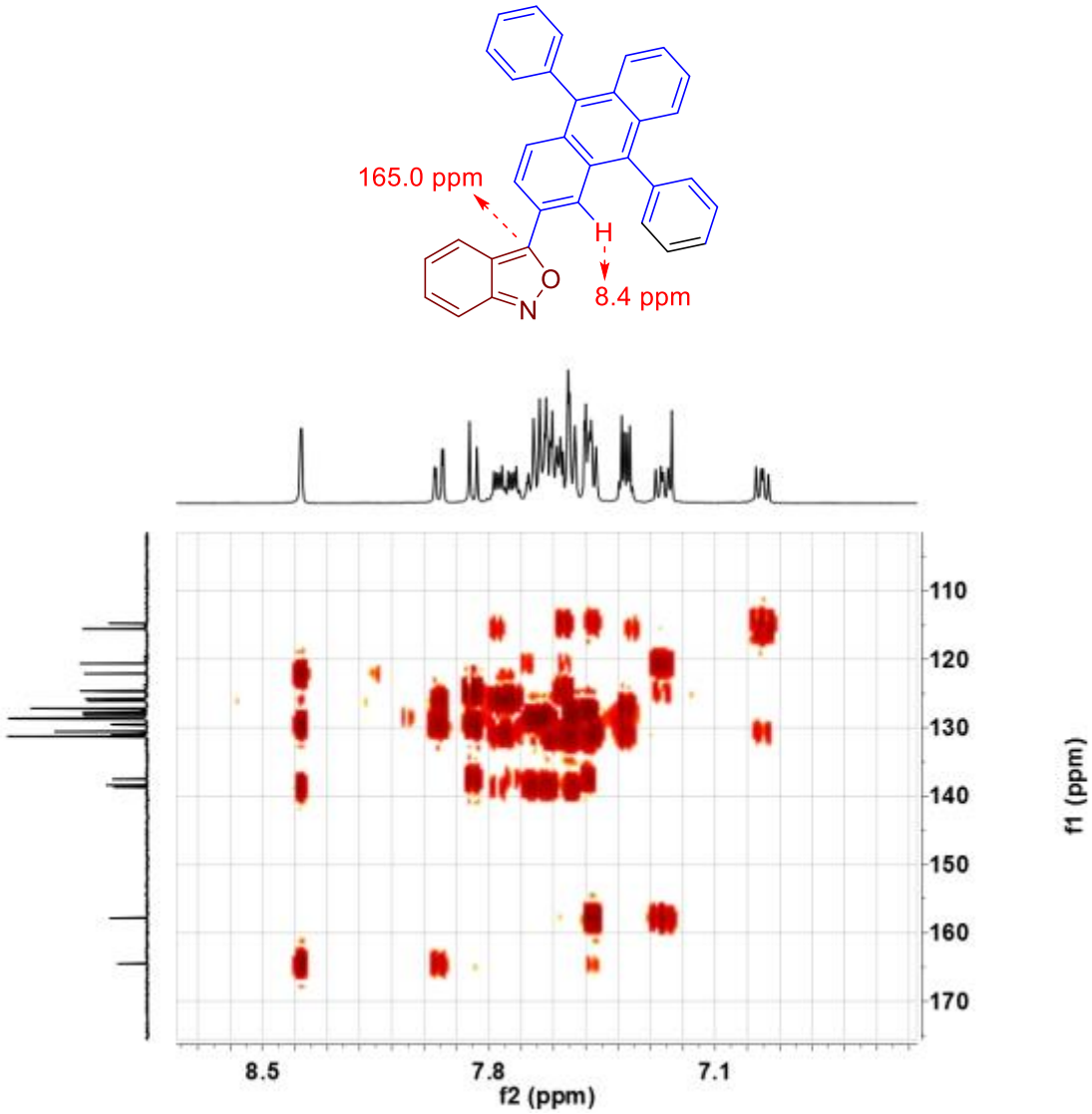
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

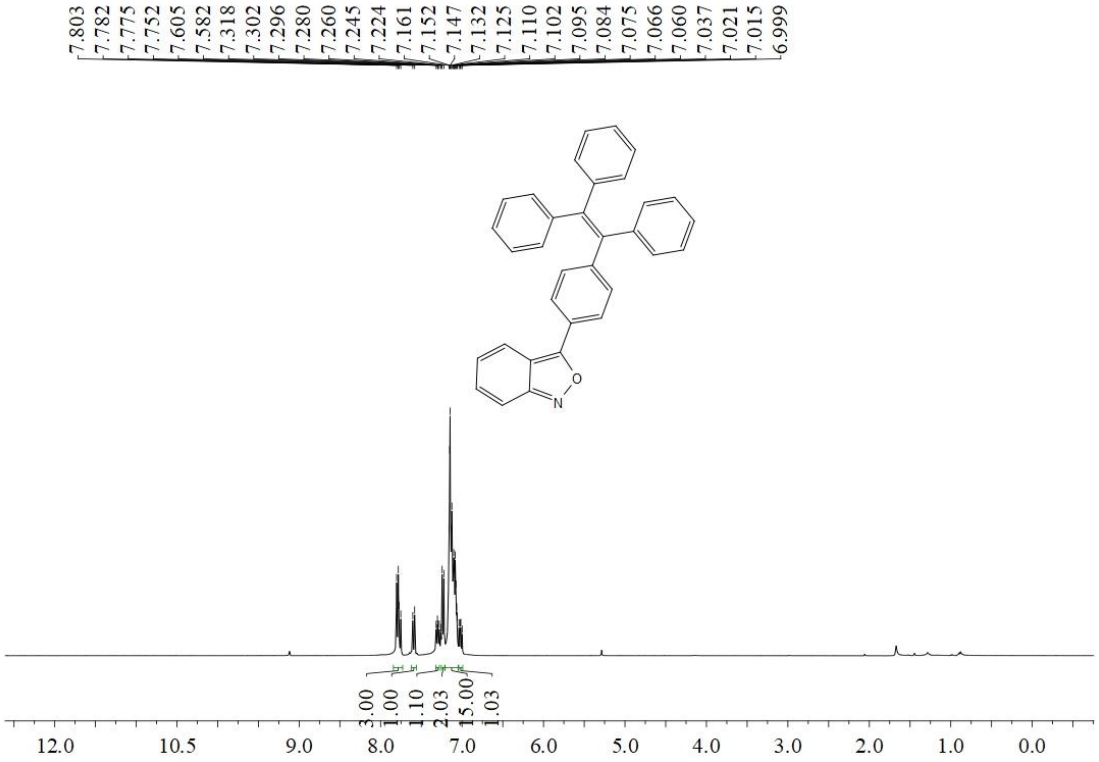


HMBC spectrum of 3aj

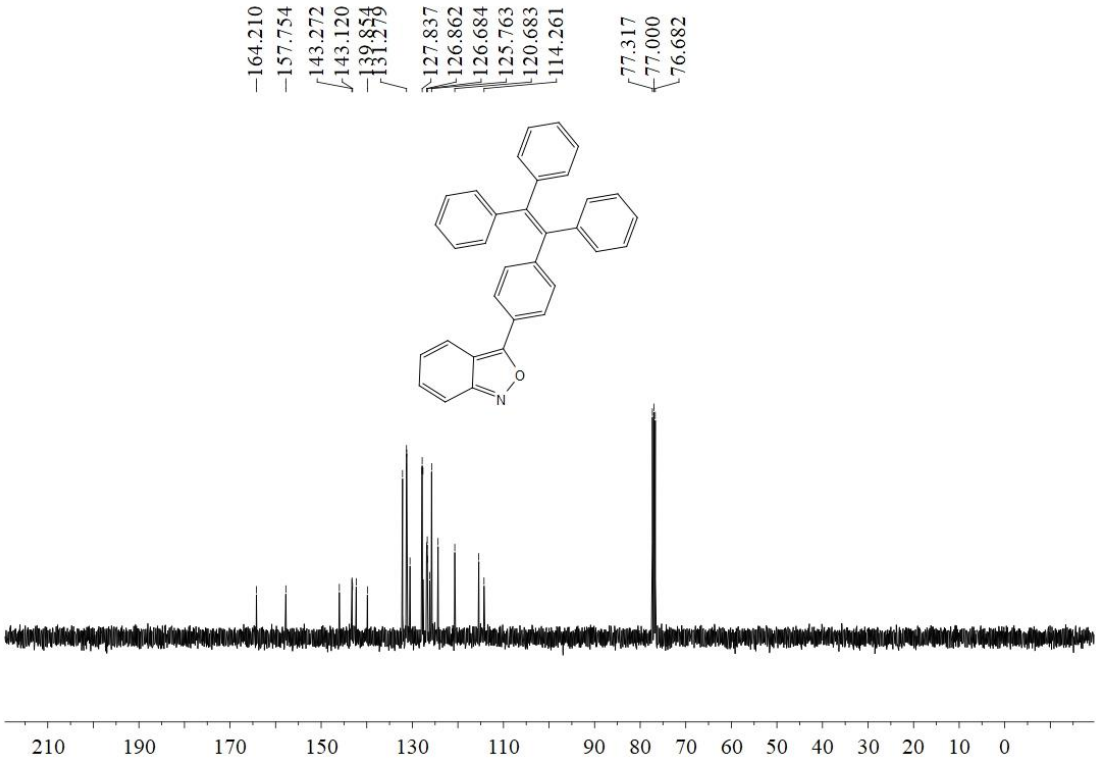


3-(4-(1,2,2-Triphenylvinyl)phenyl)benzo[c]isoxazole (3ak)

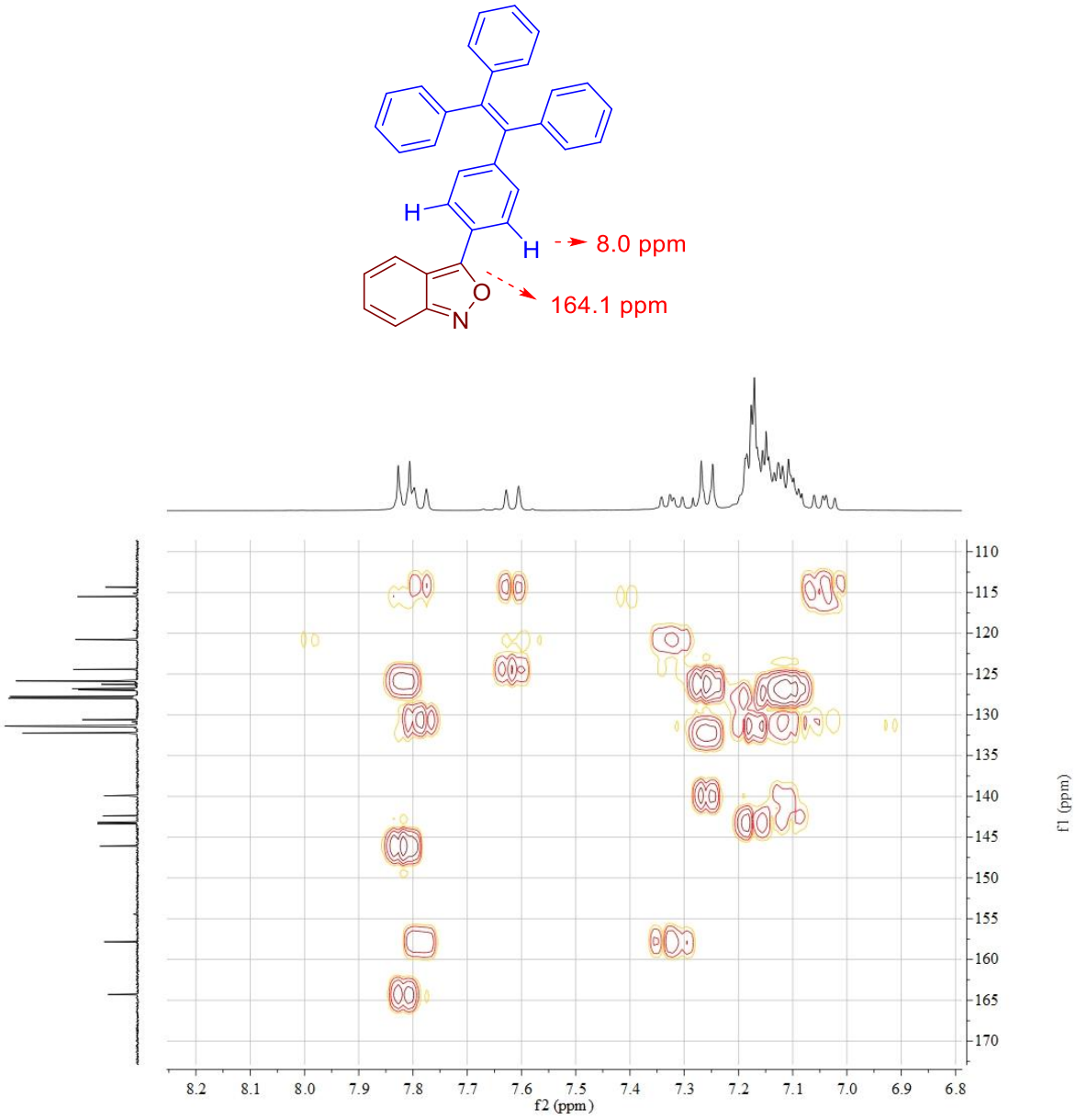
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

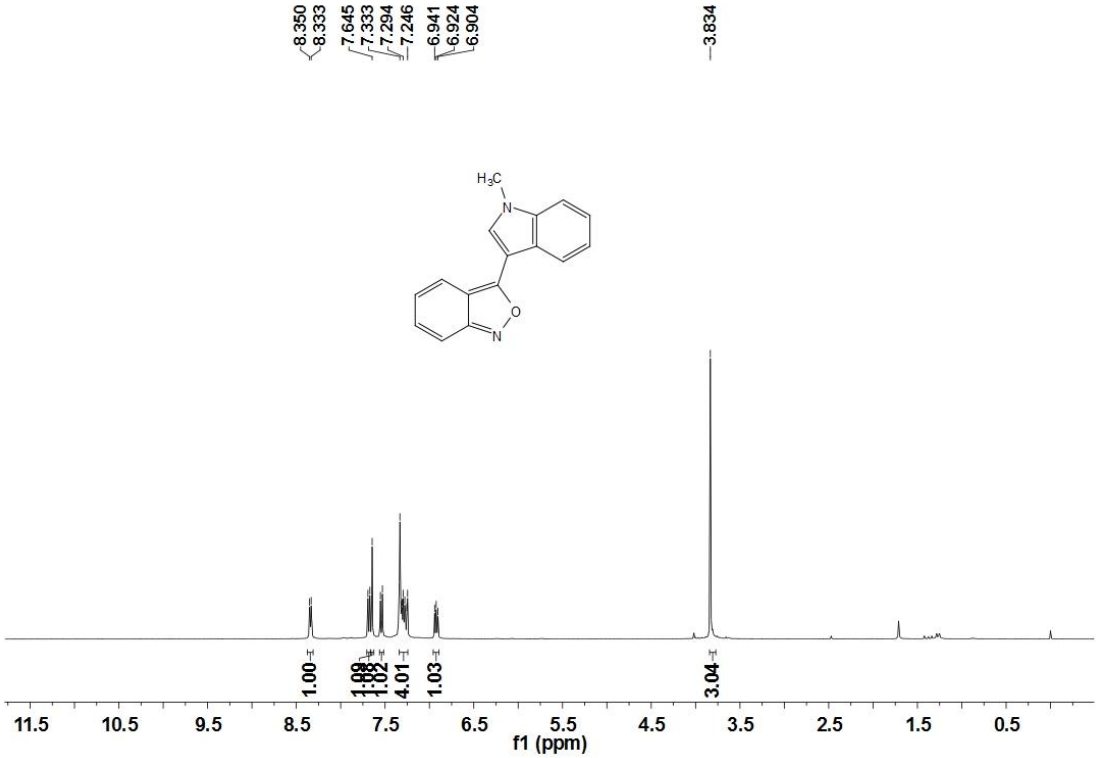


HMBC spectrum of 3ak

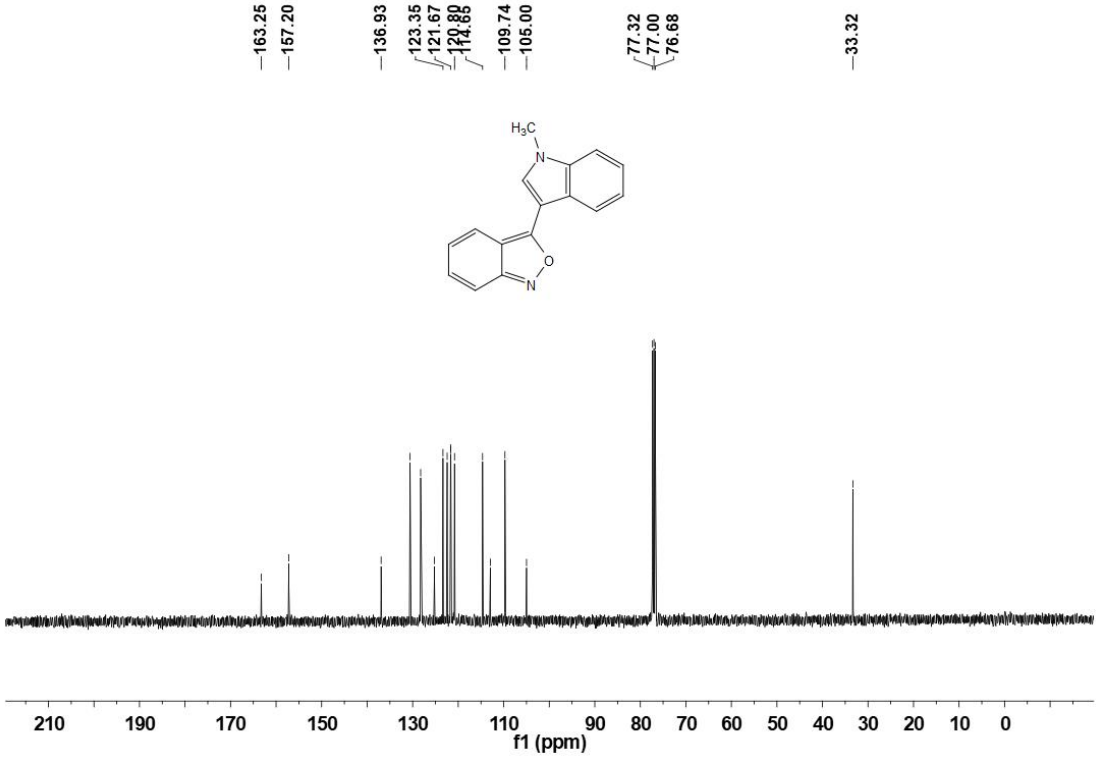


3-(1-Methyl-1H-indol-3-yl)benzo[c]isoxazole (**3al**)

^{1}H NMR (400 MHz, $CDCl_3$)

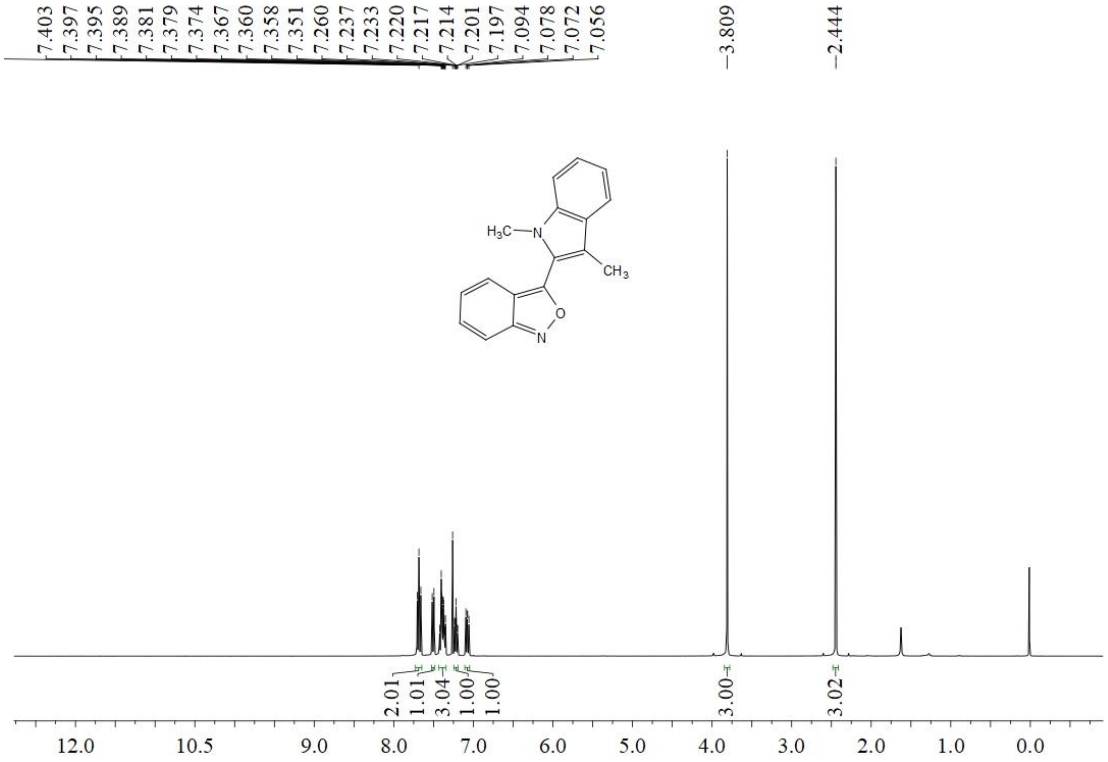


^{13}C NMR (100 MHz, $CDCl_3$)

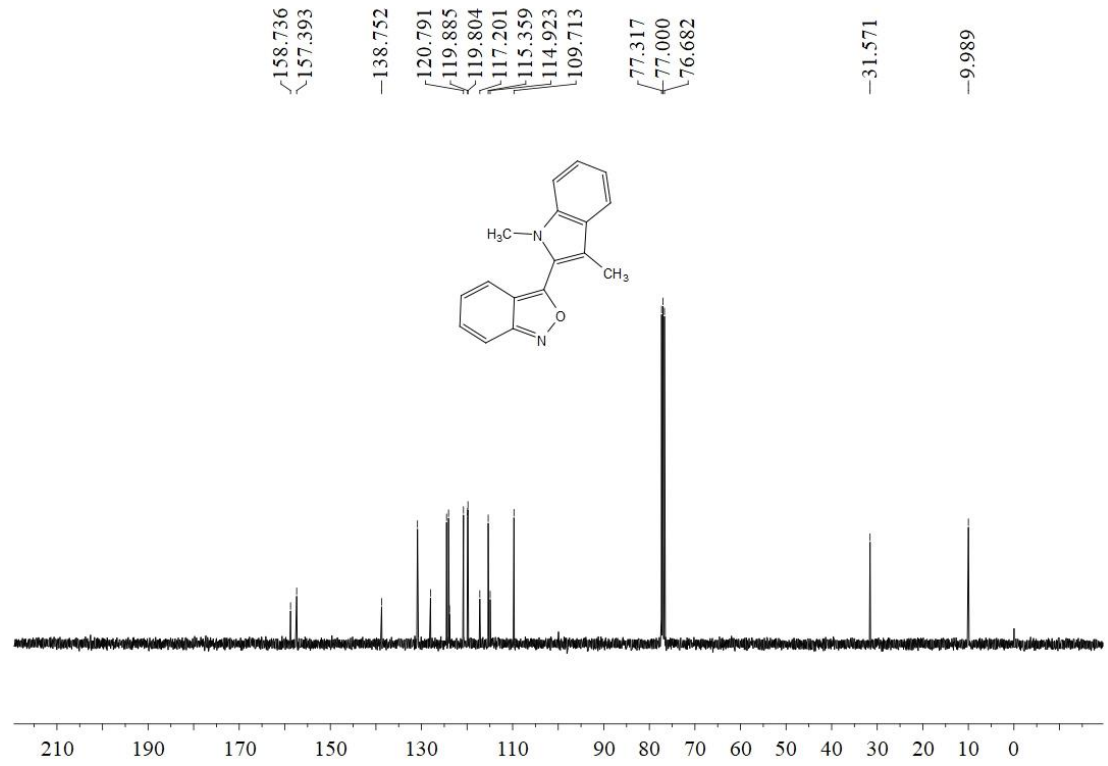


3-(1,3-Dimethyl-1H-indol-2-yl)benzo[c]isoxazole (**3am**)

^{1}H NMR (400 MHz, $CDCl_3$)

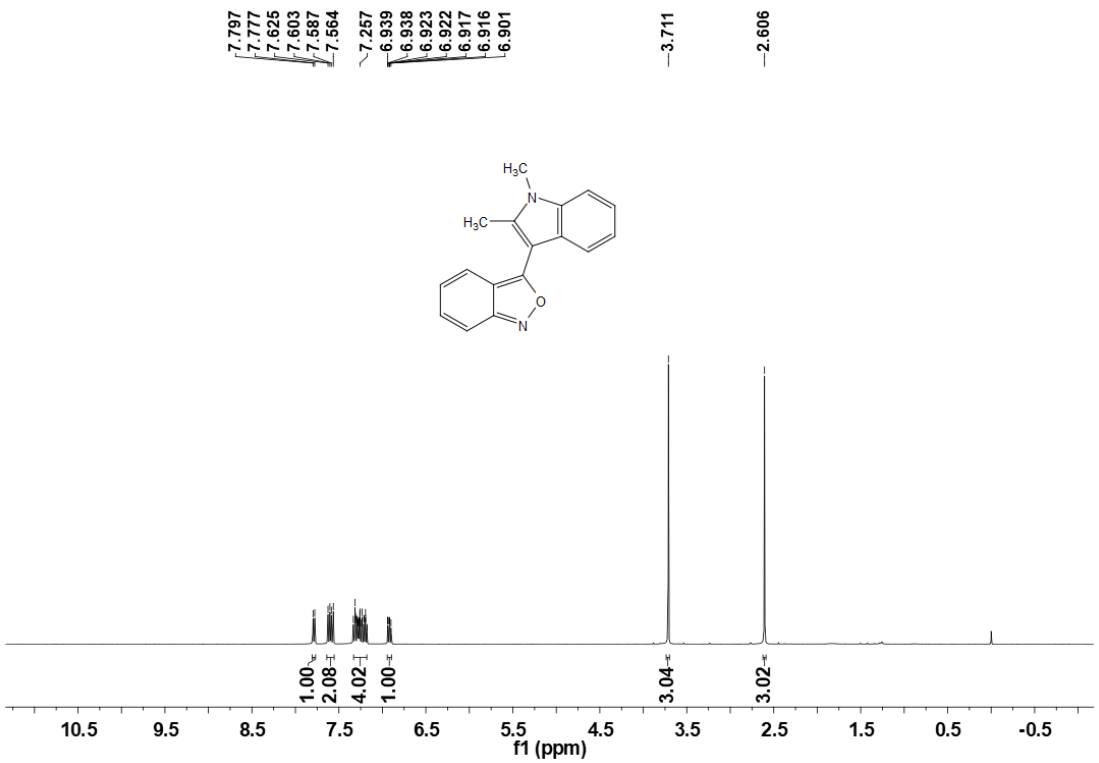


^{13}C NMR (100 MHz, $CDCl_3$)

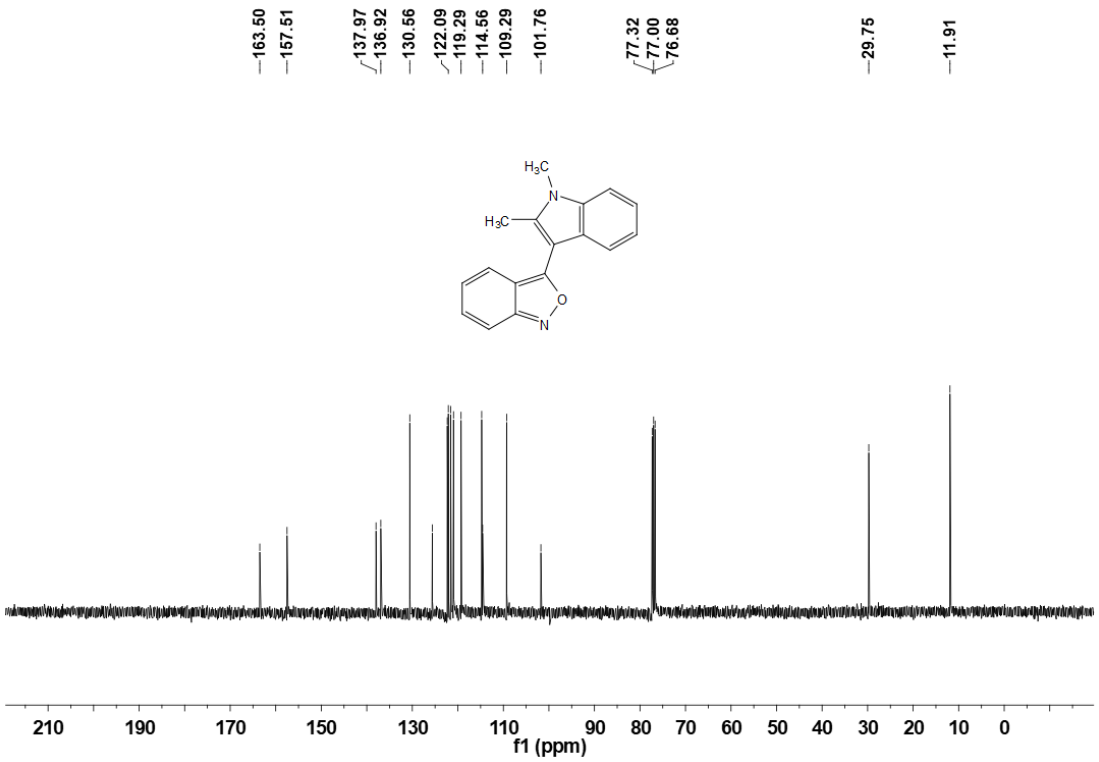


3-(1,2-Dimethyl-1H-indol-3-yl)benzo[c]isoxazole (**3an**)

^{1}H NMR (400 MHz, $CDCl_3$)

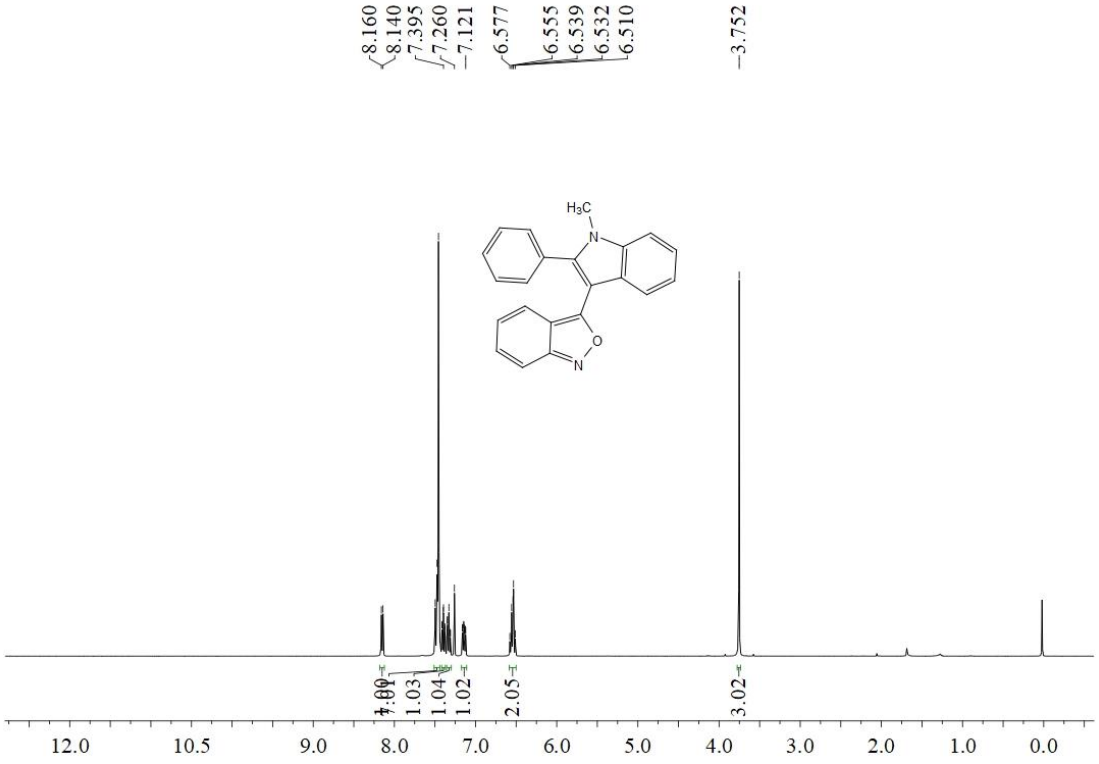


^{13}C NMR (100 MHz, $CDCl_3$)

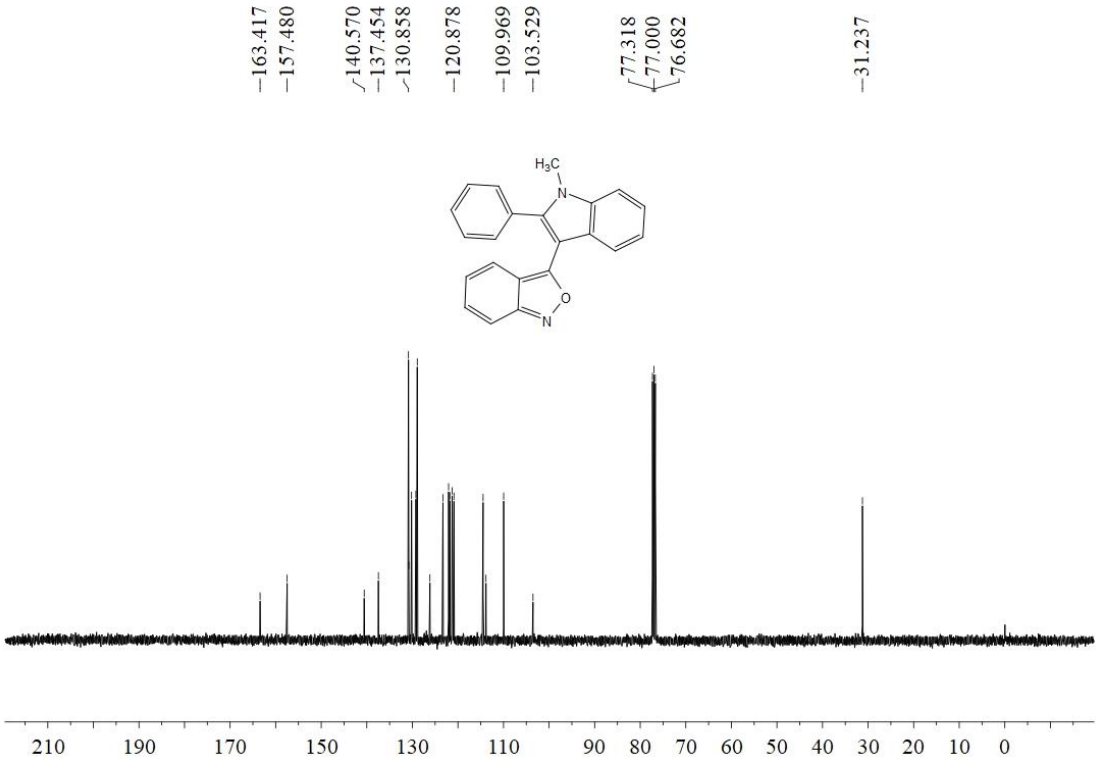


3-(1-Methyl-2-phenyl-1H-indol-3-yl)benzo[c]isoxazole (**3ao**)

^{1}H NMR (400 MHz, $CDCl_3$)

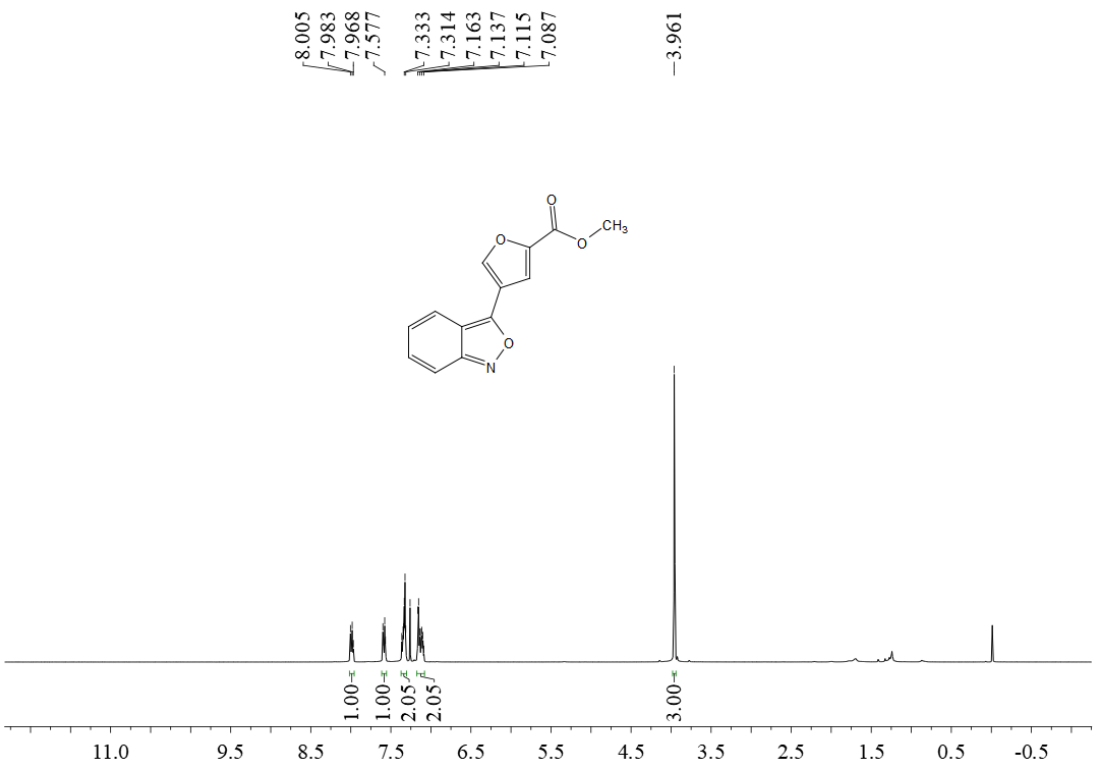


^{13}C NMR (100 MHz, $CDCl_3$)

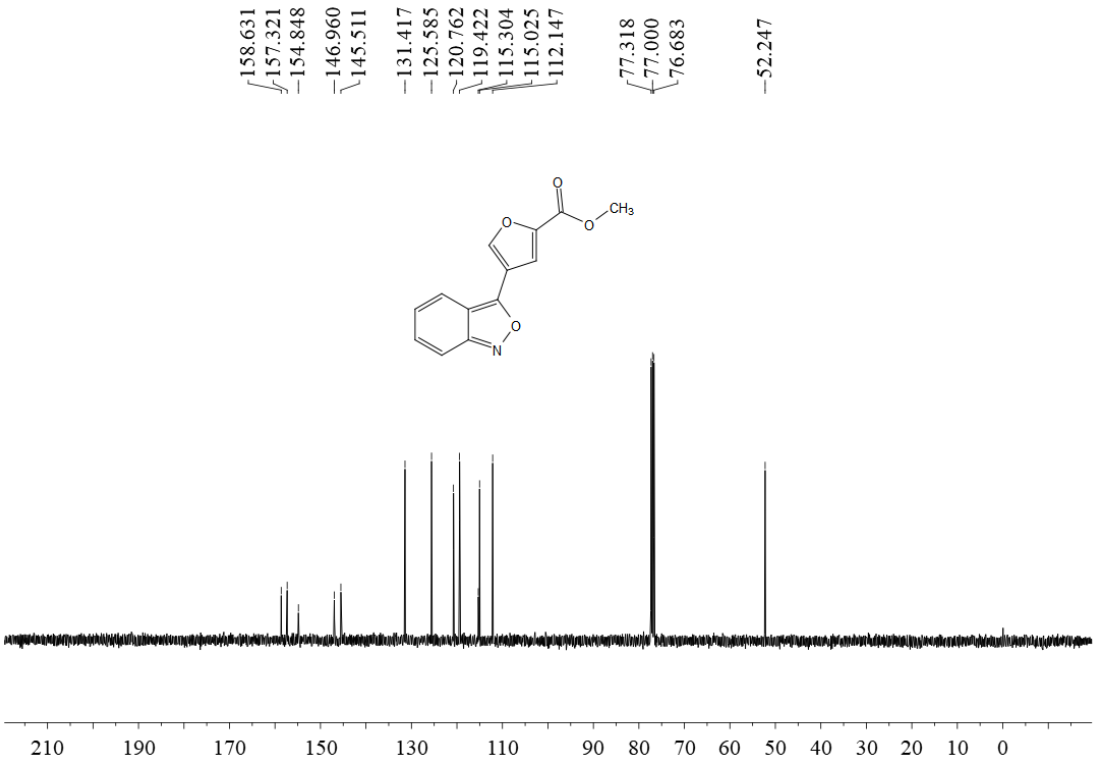


Methyl 5-(benzo[c]isoxazol-3-yl)furan-2-carboxylate (**3ap**)

^{1}H NMR (400 MHz, $CDCl_3$)

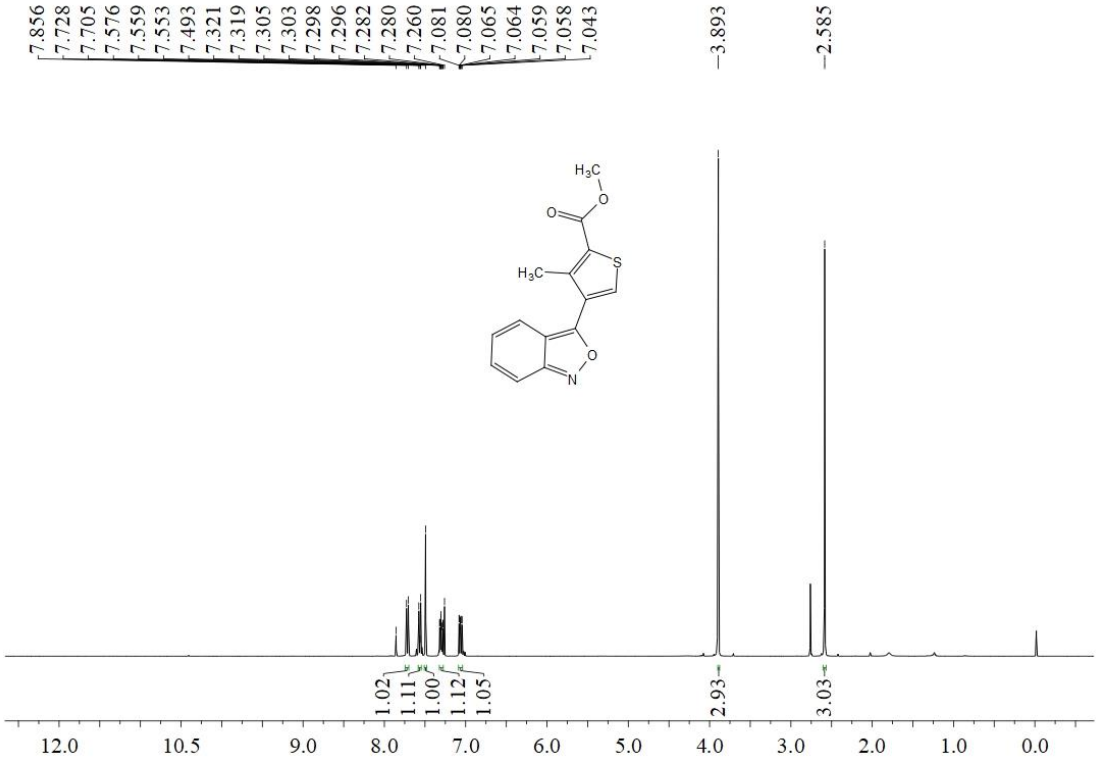


^{13}C NMR (100 MHz, $CDCl_3$)

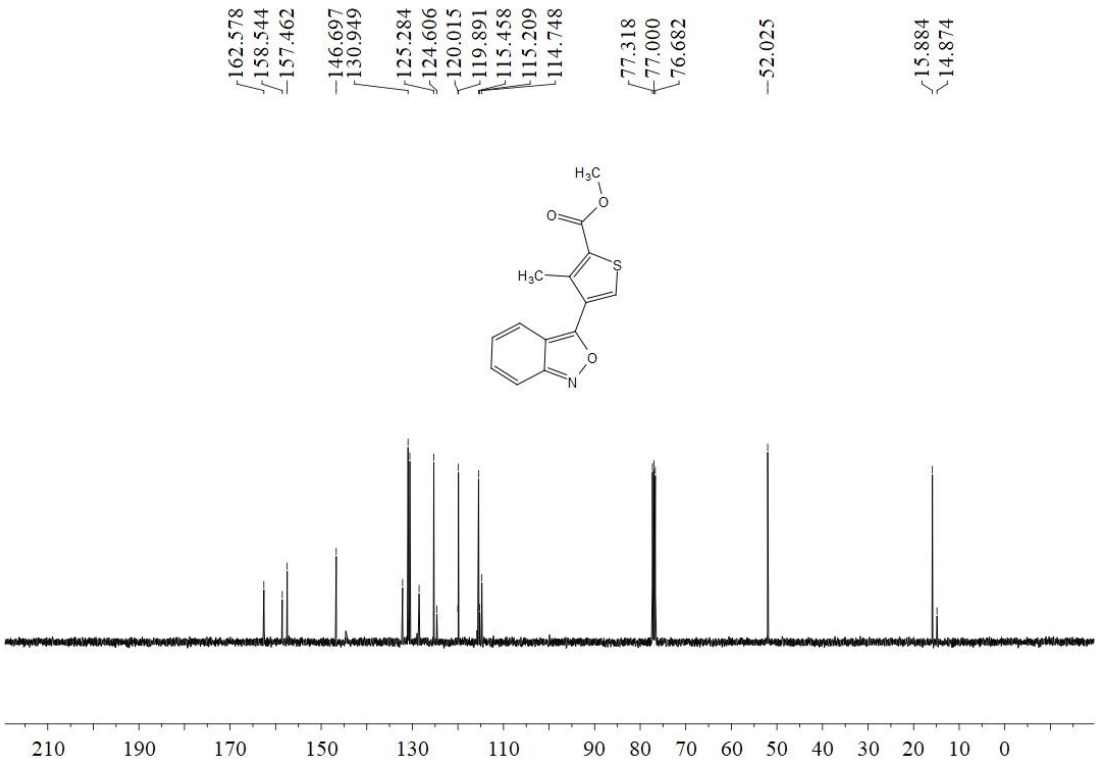


Methyl 4-(benzo[c]isoxazol-3-yl)-3-methylthiophene-2-carboxylate (**3aq**)

^{1}H NMR (400 MHz, $CDCl_3$)

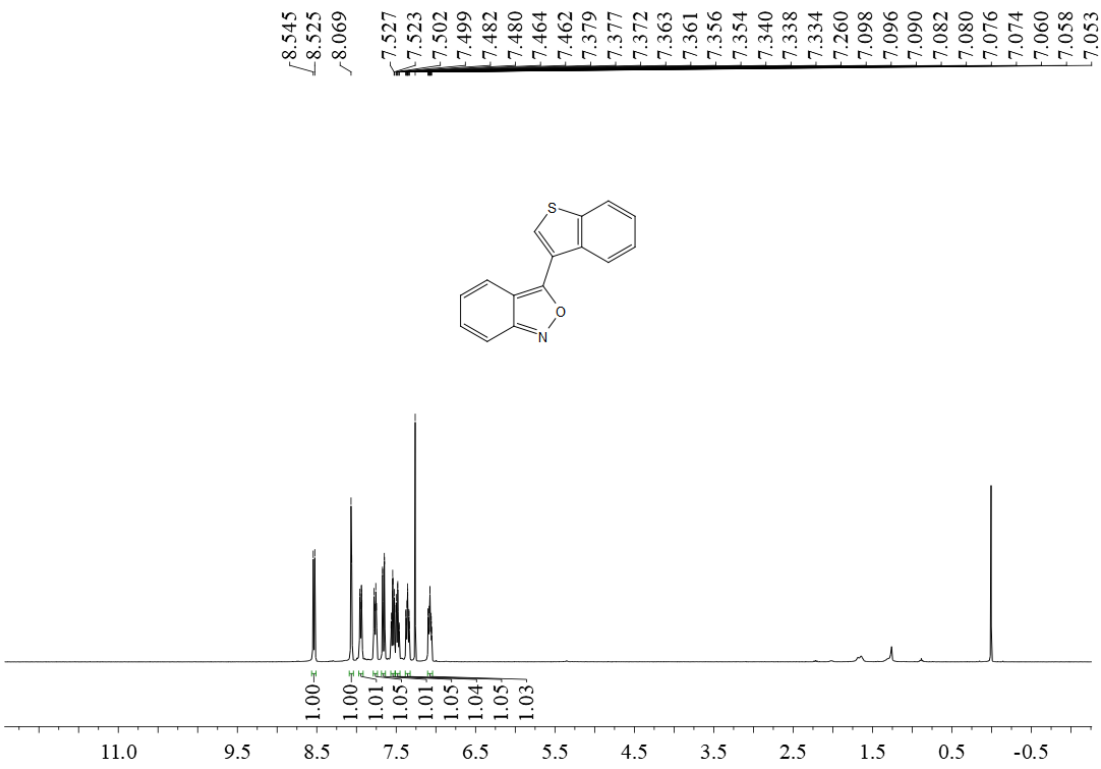


^{13}C NMR (100 MHz, $CDCl_3$)

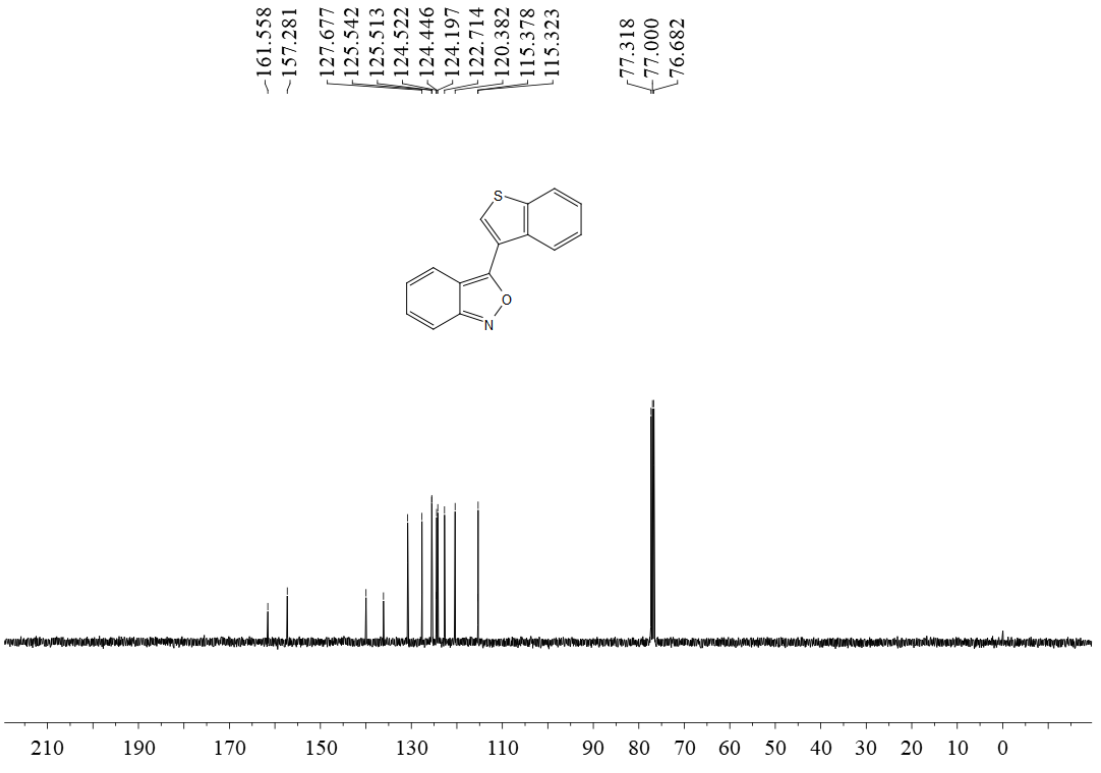


3-(Benzo[b]thiophen-2-yl)benzo[c]isoxazole (**3ar**)

^{1}H NMR (400 MHz, $CDCl_3$)

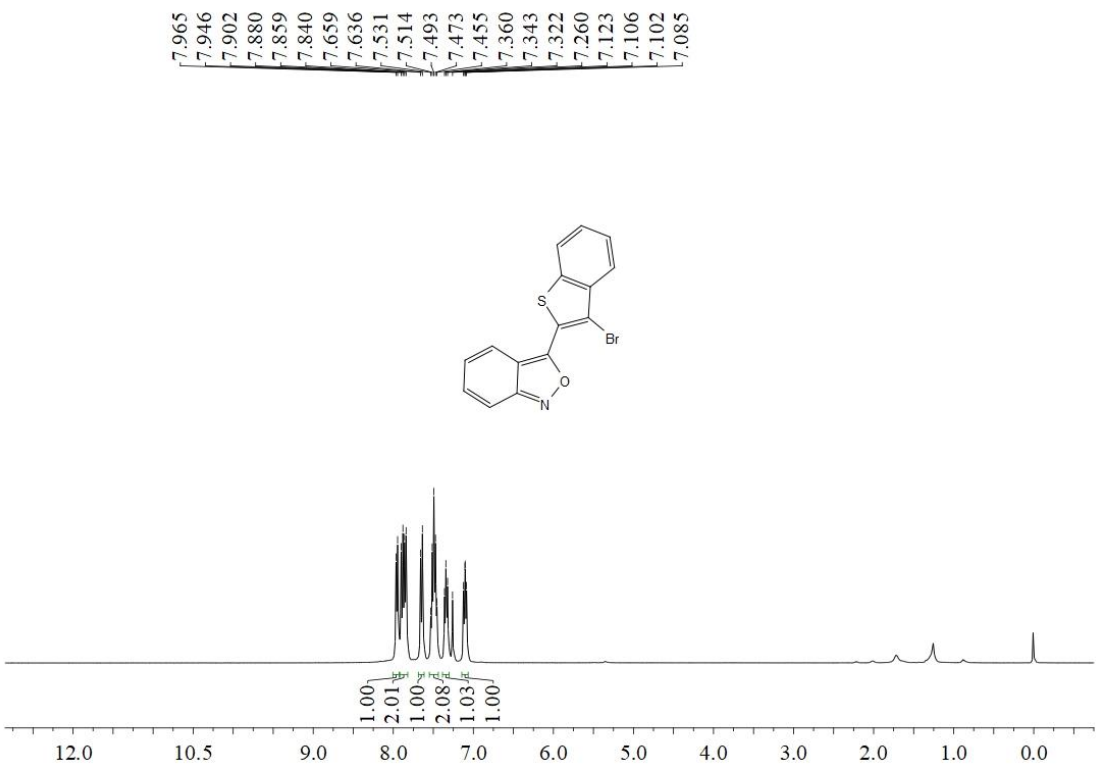


^{13}C NMR (100 MHz, $CDCl_3$)

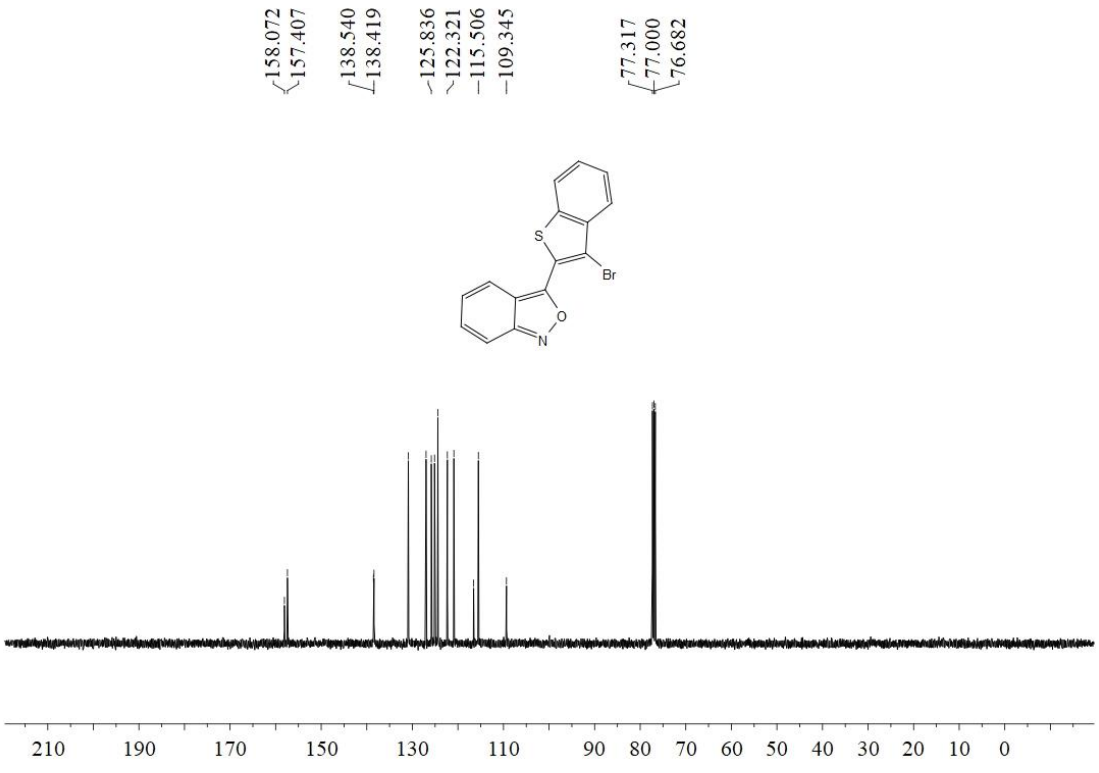


3-(3-Bromobenzo[b]thiophen-2-yl)benzo[c]isoxazole (**3as**)

^{1}H NMR (400 MHz, $CDCl_3$)

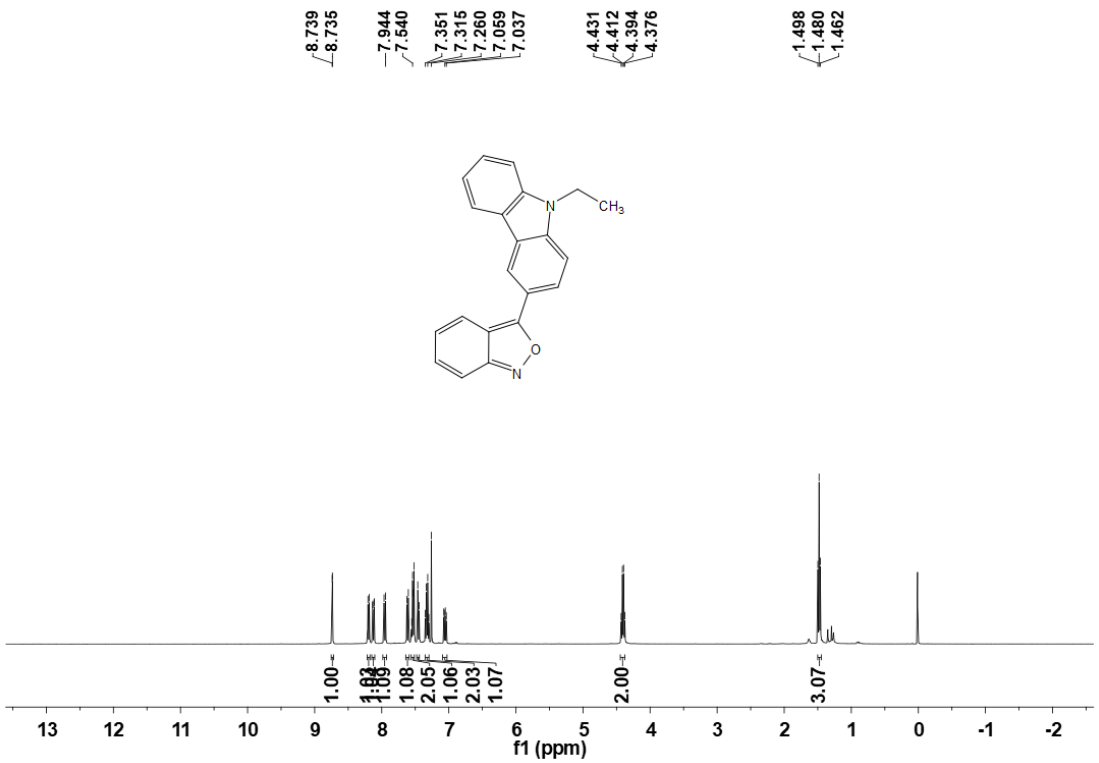


^{13}C NMR (100 MHz, $CDCl_3$)

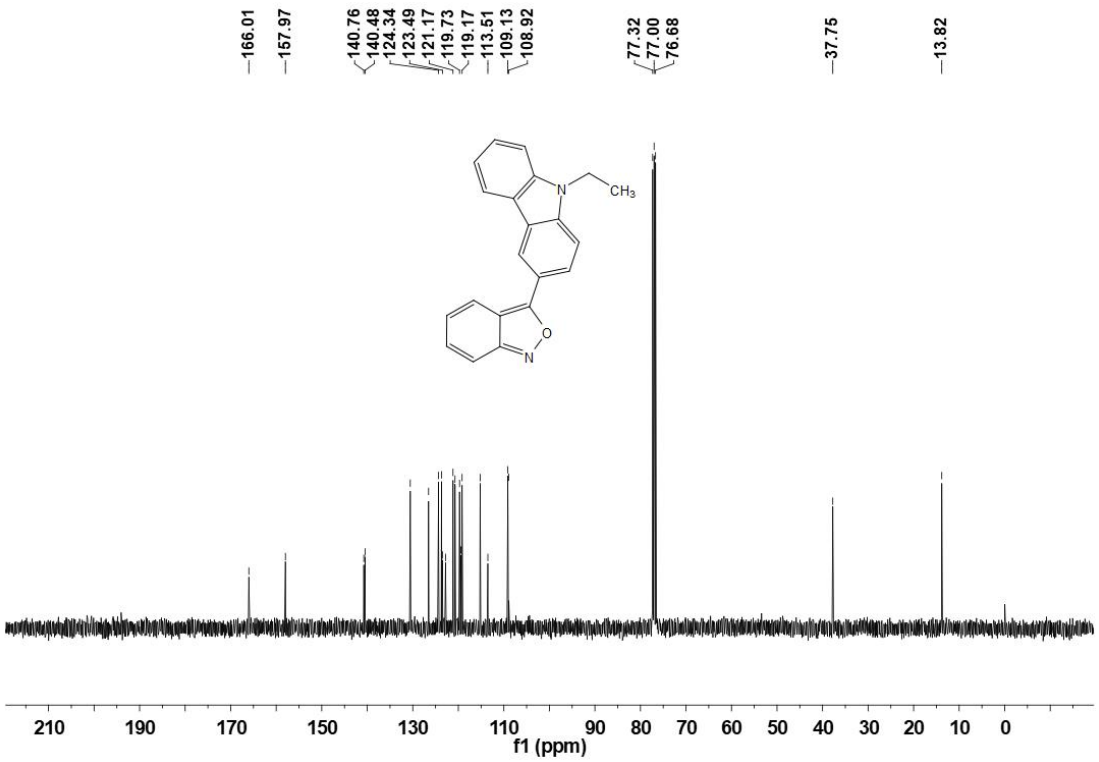


3-(9-Ethyl-9H-carbazol-3-yl)benzo[c]isoxazole (**3at**)

^{1}H NMR (400 MHz, $CDCl_3$)

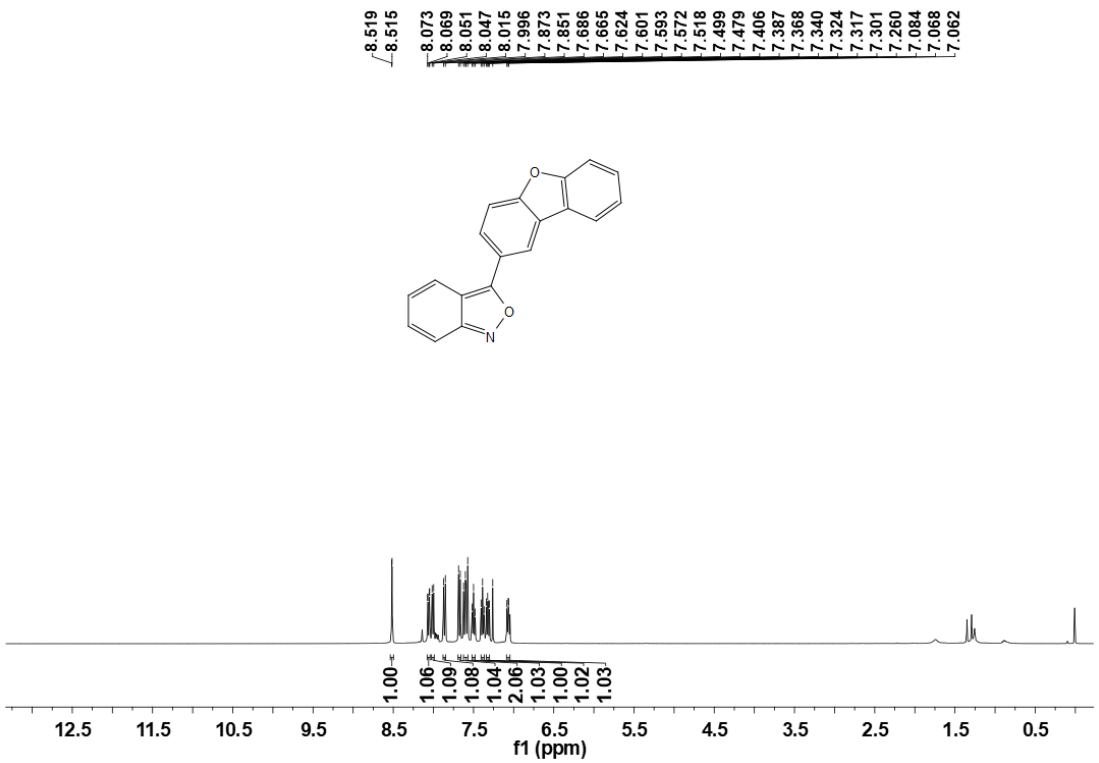


^{13}C NMR (100 MHz, $CDCl_3$)

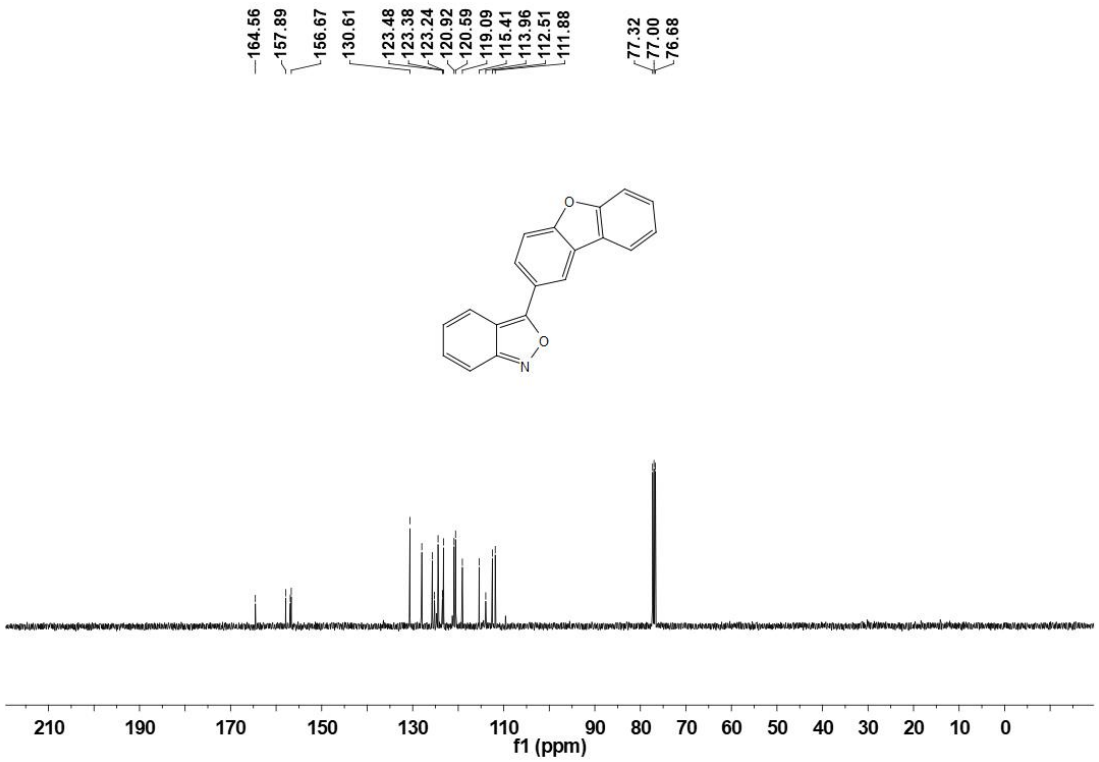


3-(Dibenzo[b,d]furan-2-yl)benzo[c]isoxazole (**3au**)

^{1}H NMR (400 MHz, $CDCl_3$)

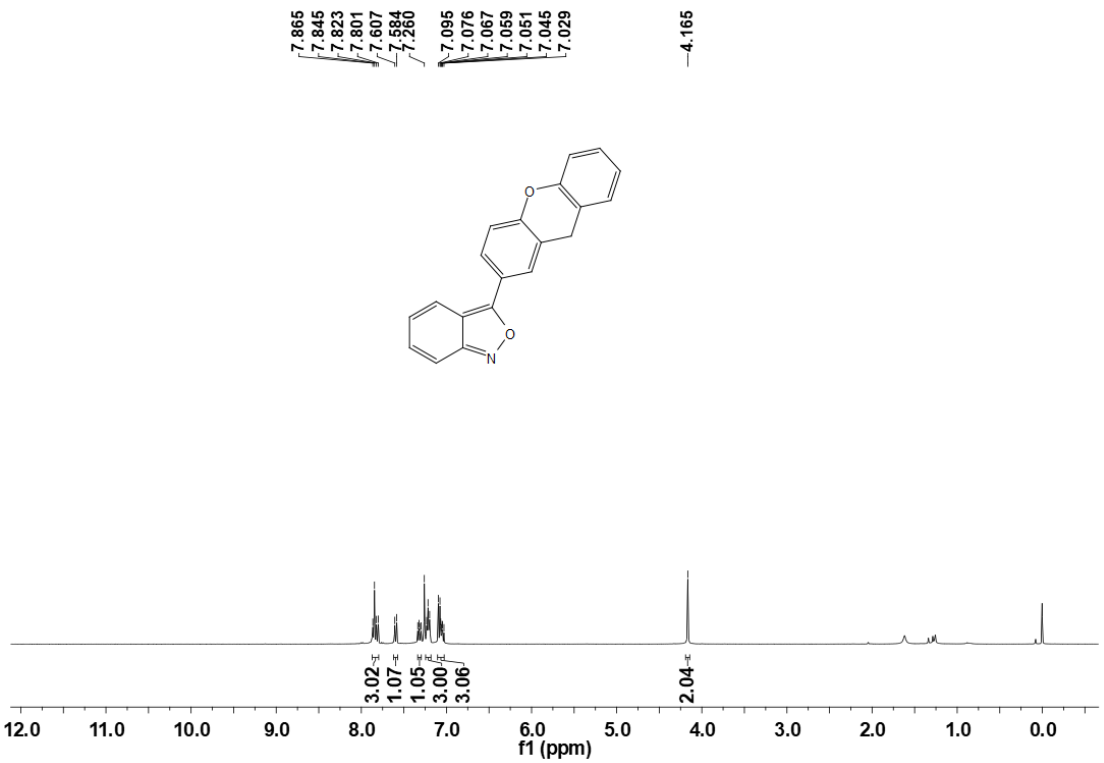


^{13}C NMR (100 MHz, $CDCl_3$)

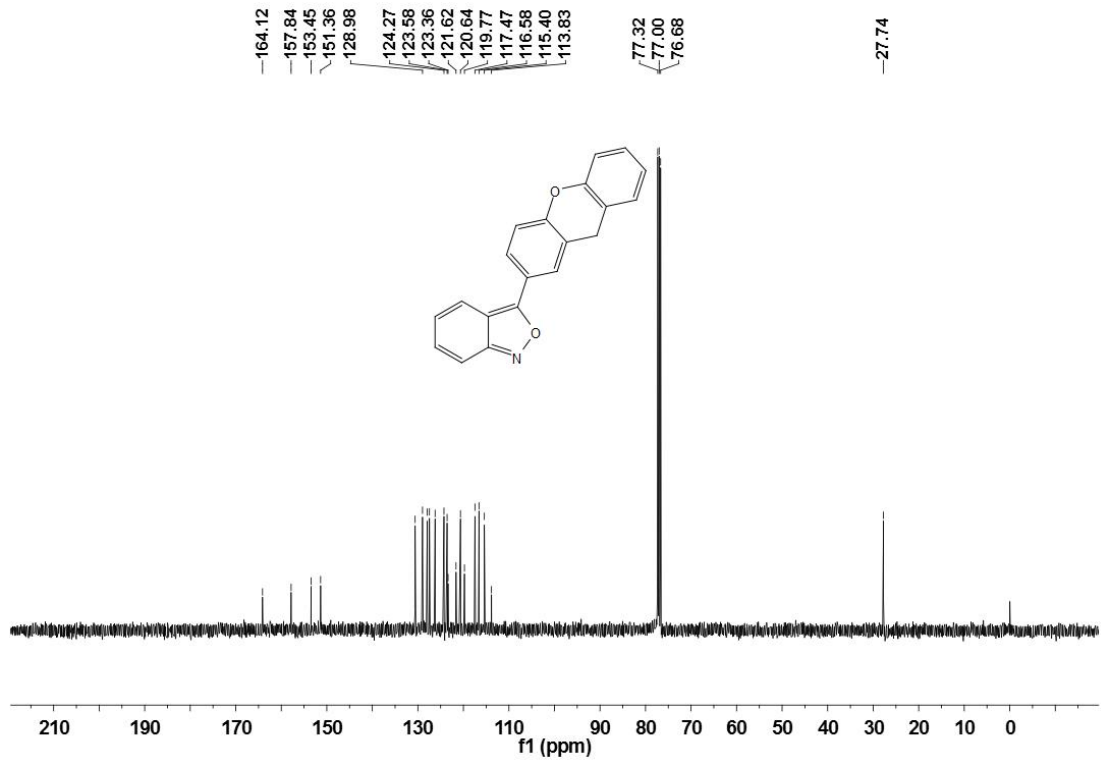


3-(9*H*-Xanthen-2-yl)benzo[c]isoxazole (**3av**)

^{1}H NMR (400 MHz, $CDCl_3$)

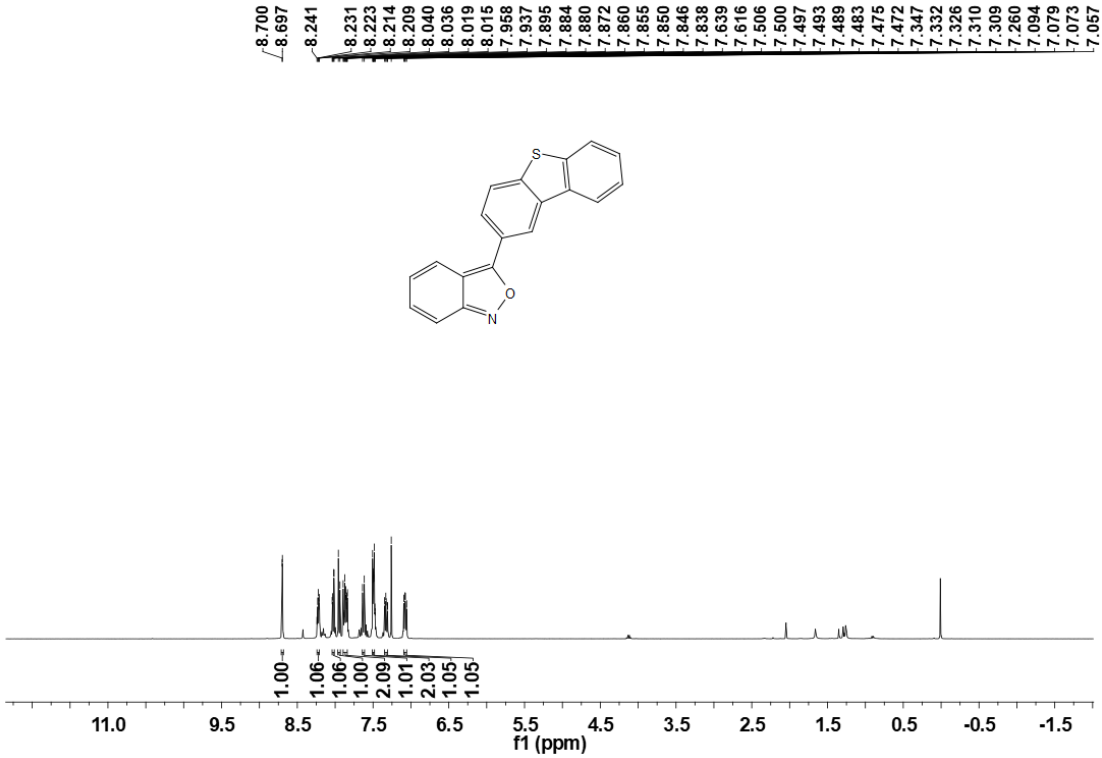


^{13}C NMR (100 MHz, $CDCl_3$)

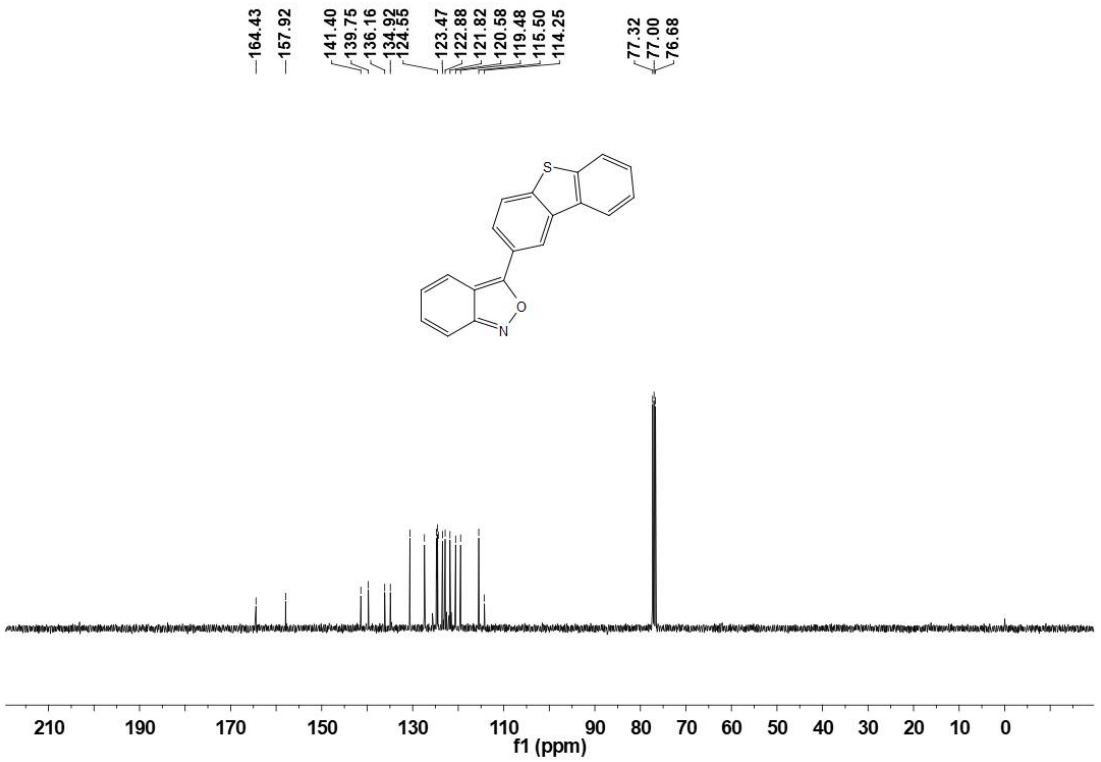


3-(Dibenzo[b,d]thiophen-2-yl)benzo[c]isoxazole (**3aw**)

^{1}H NMR (400 MHz, $CDCl_3$)

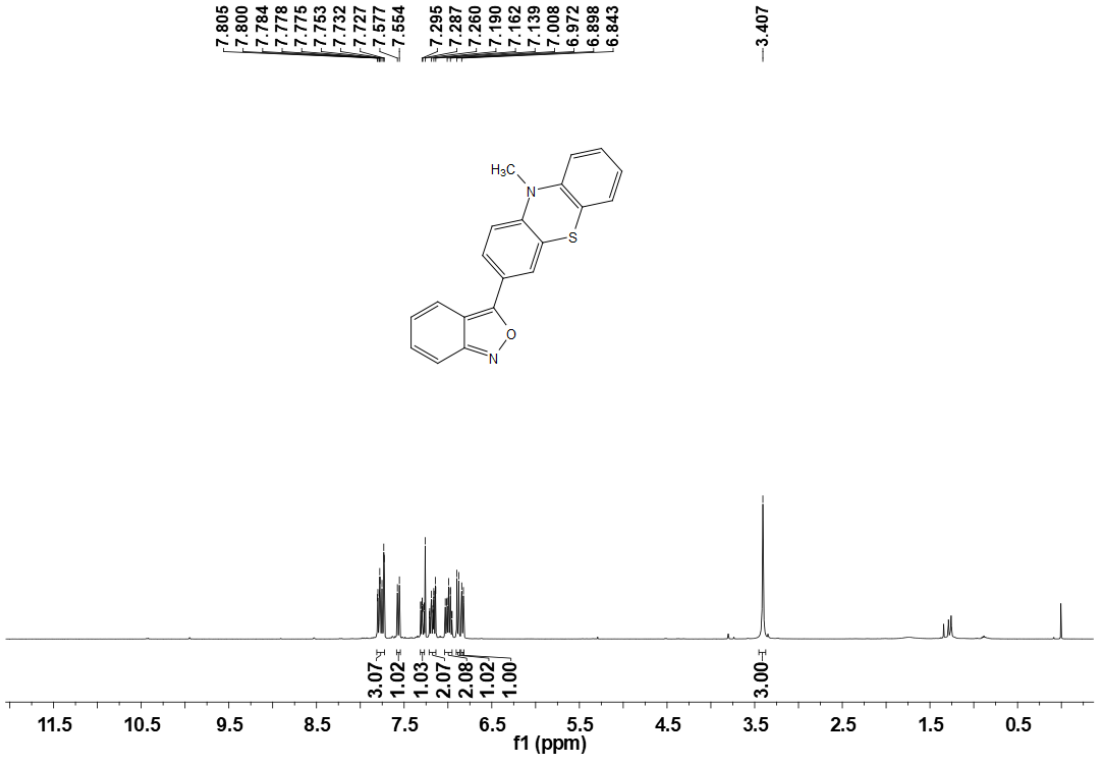


^{13}C NMR (100 MHz, $CDCl_3$)

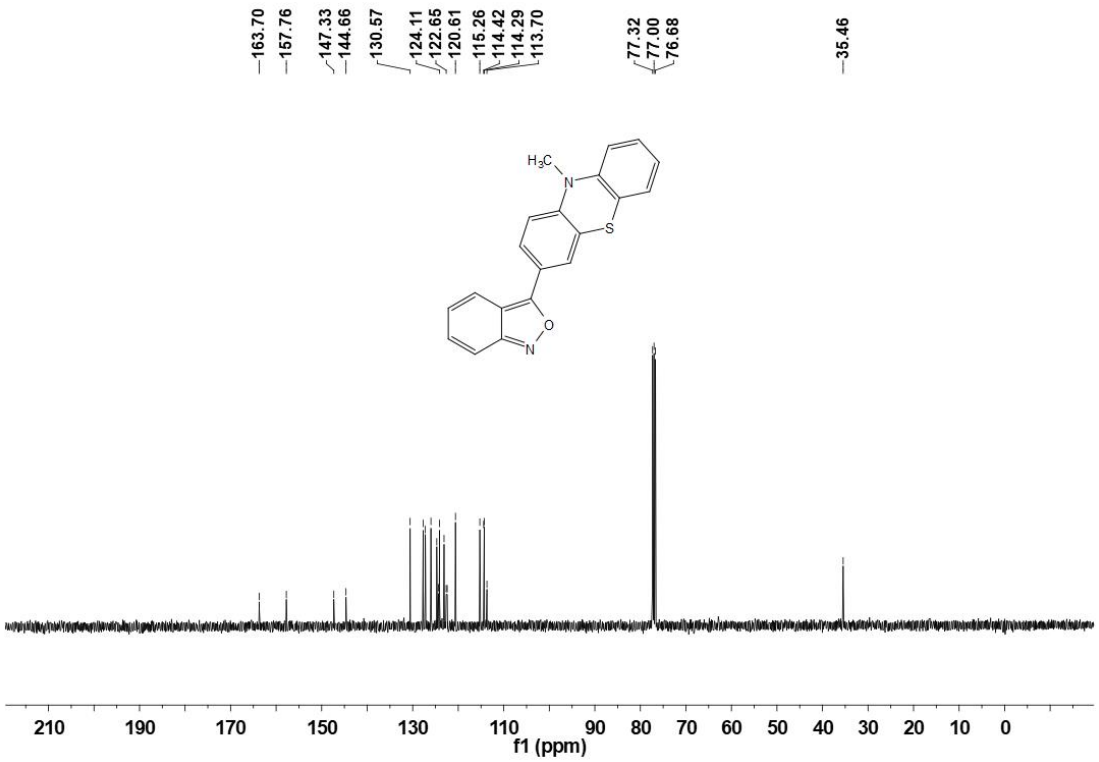


3-(10-Methyl-10H-phenothiazin-3-yl)benzo[c]isoxazole (**3ax**)

^{1}H NMR (400 MHz, $CDCl_3$)

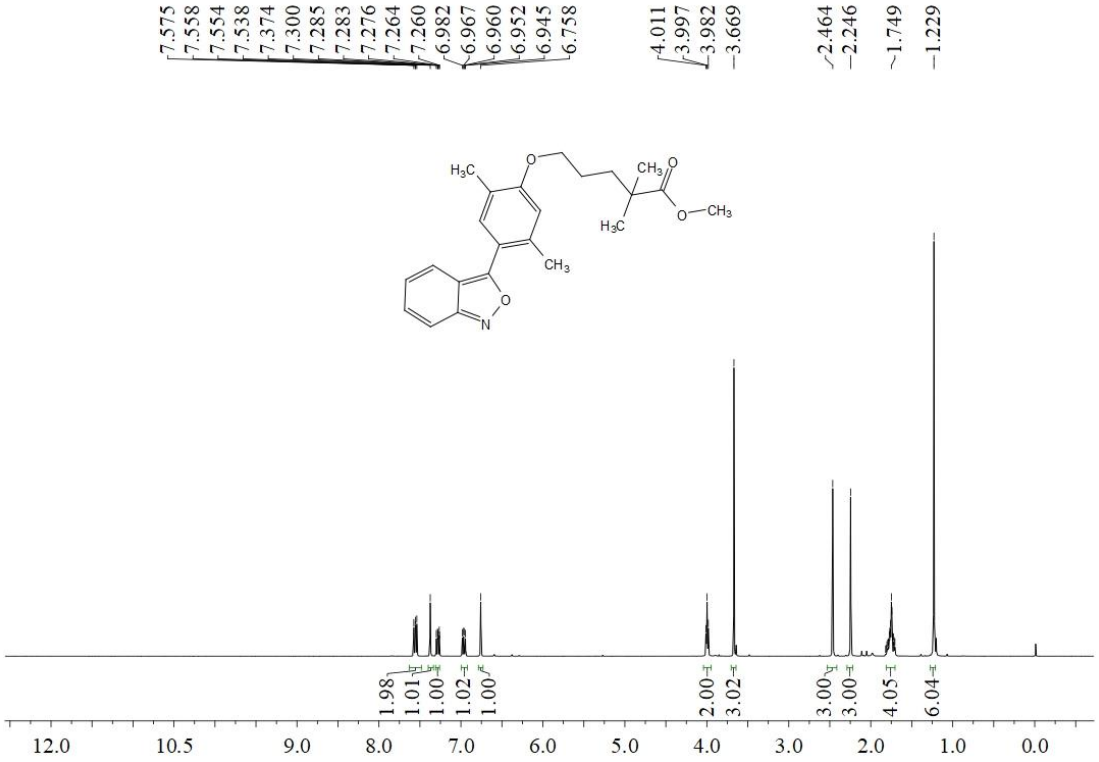


^{13}C NMR (100 MHz, $CDCl_3$)

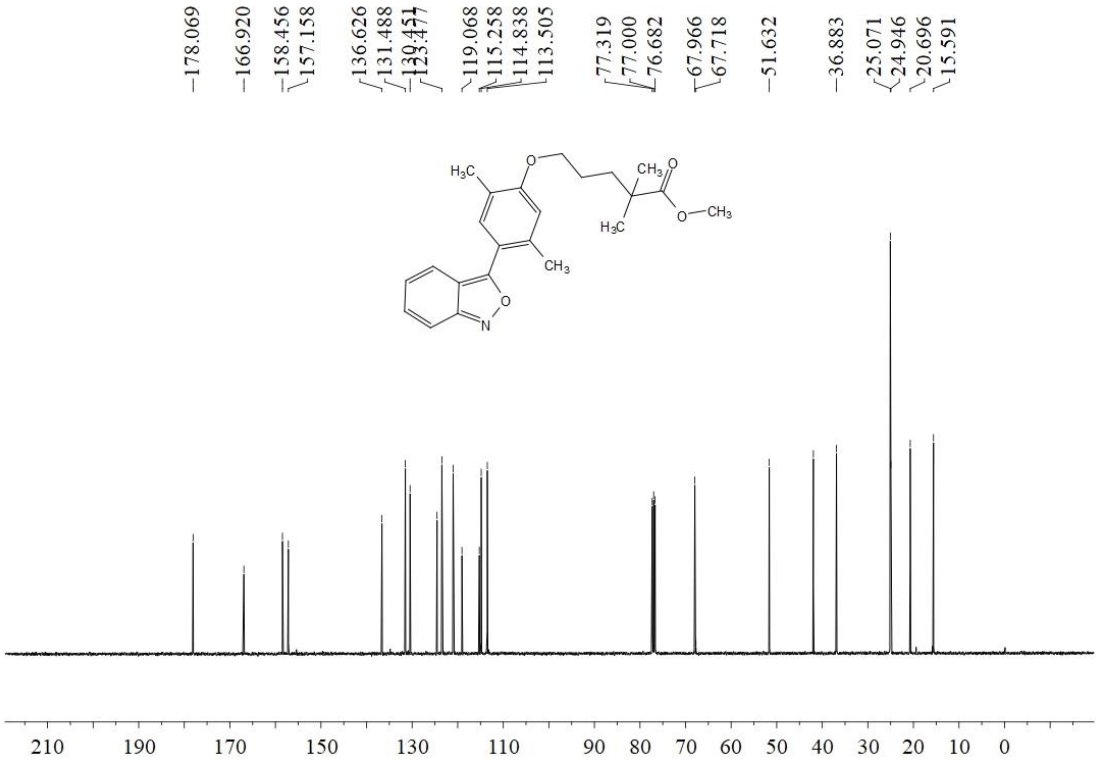


Methyl 5-(4-(benzo[c]isoxazol-3-yl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**3ay**)

^{1}H NMR (400 MHz, $CDCl_3$)

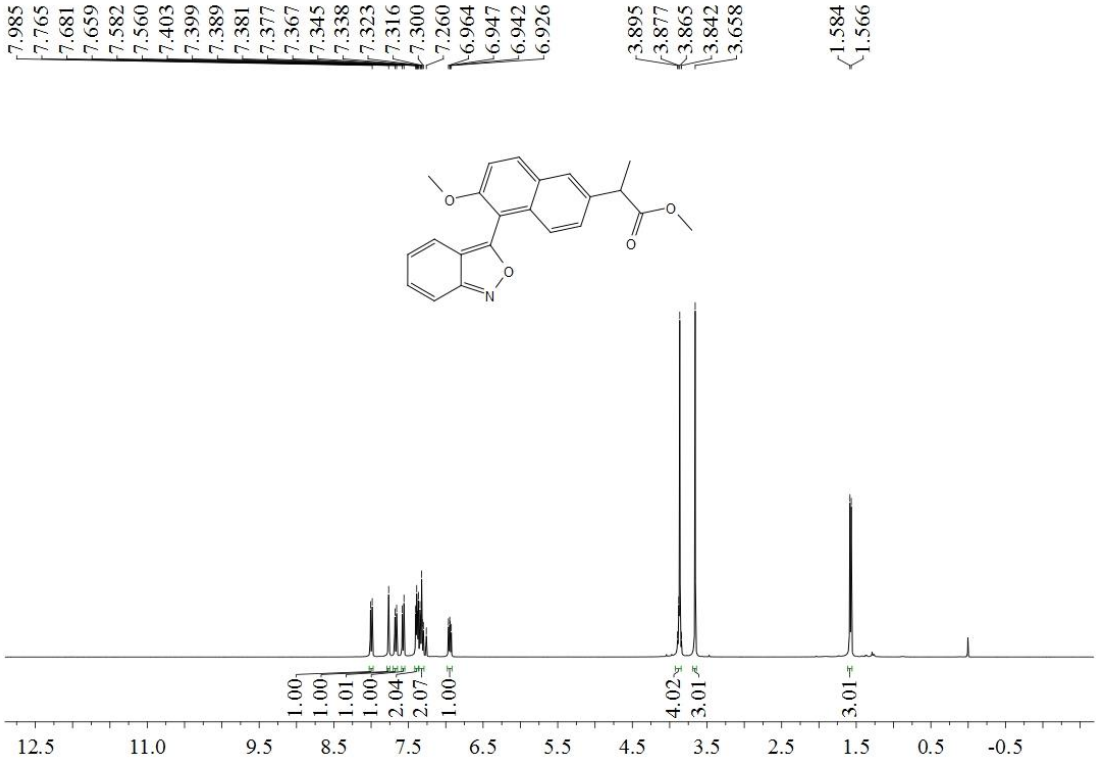


^{13}C NMR (100 MHz, $CDCl_3$)

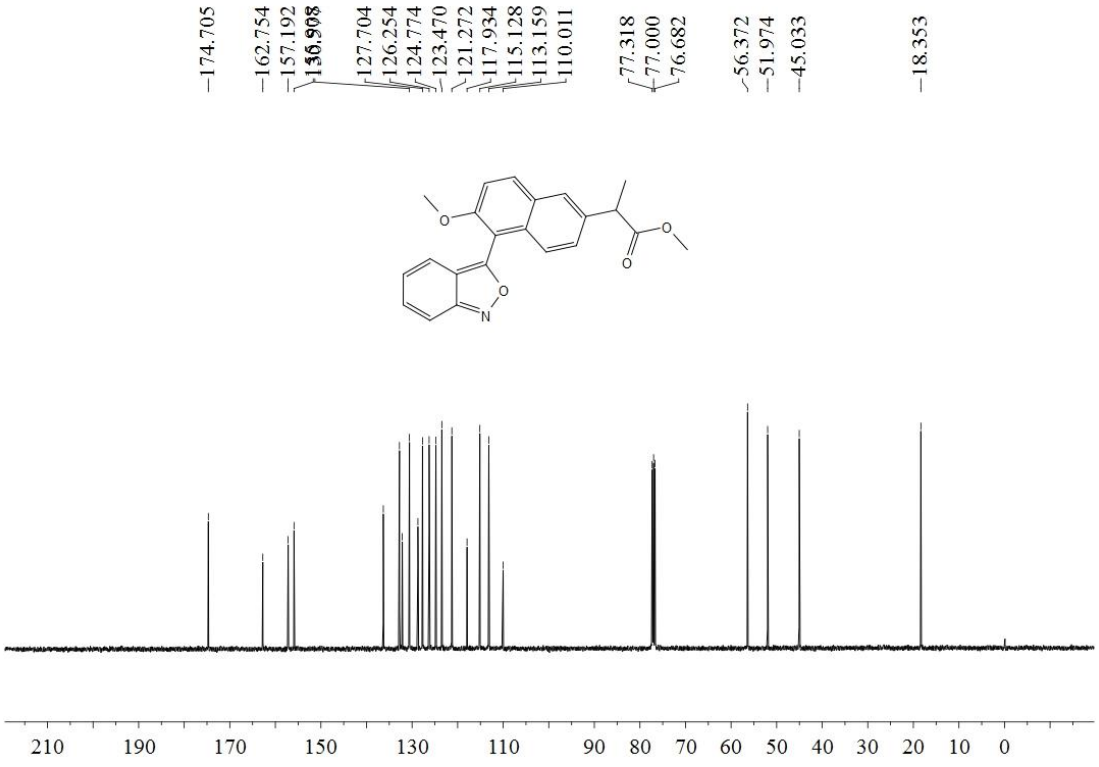


Methyl 2-(1-(benzo[c]isoxazol-3-yl)-6-methoxynaphthalen-2-yl)propanoate (**3az**)

^{1}H NMR (400 MHz, $CDCl_3$)

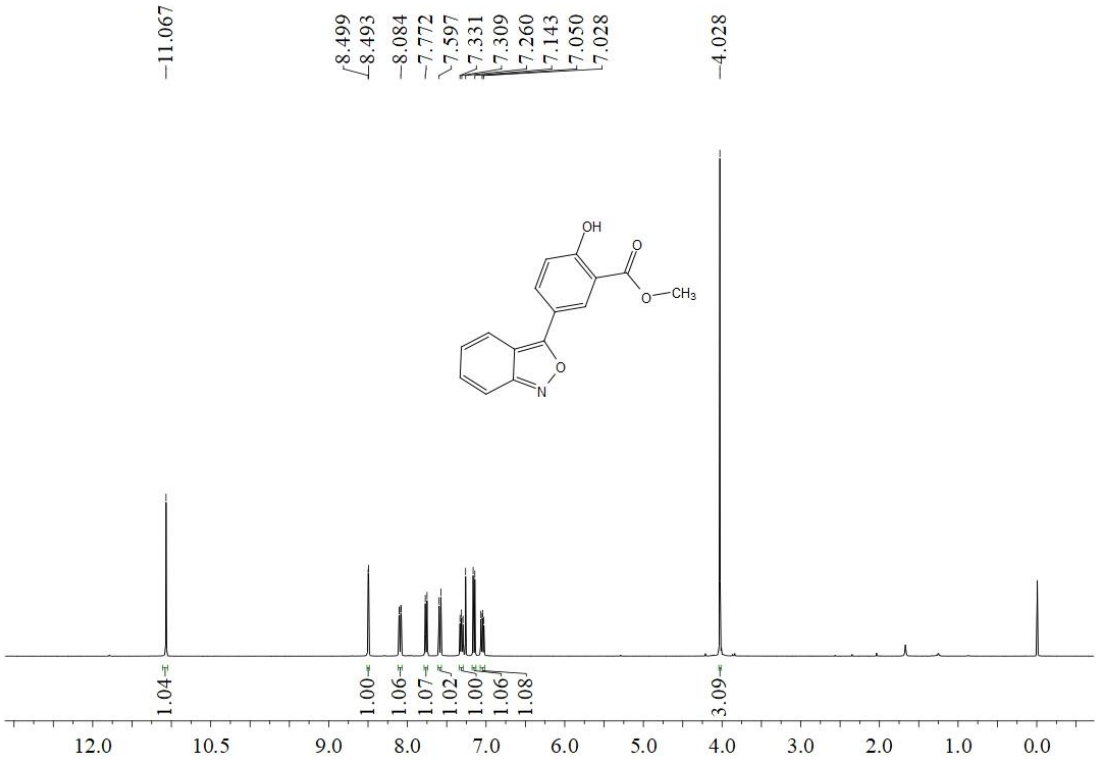


^{13}C NMR (100 MHz, $CDCl_3$)

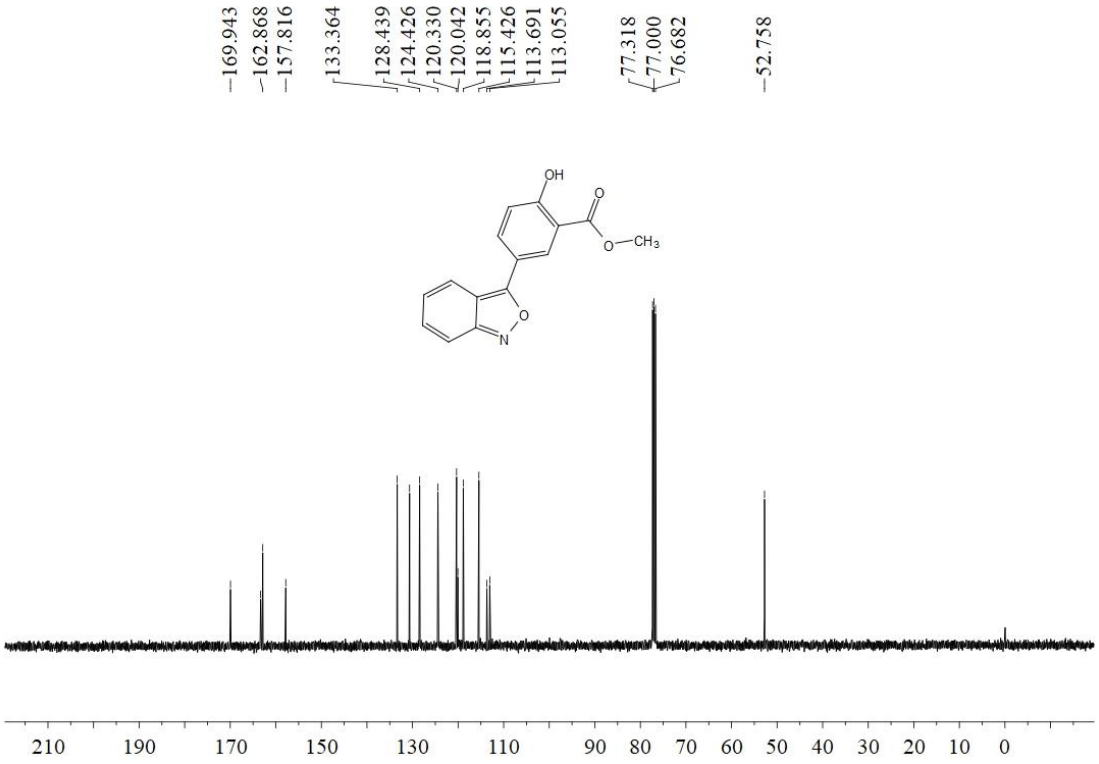


Methyl 5-(benzo[c]isoxazol-3-yl)-2-hydroxybenzoate (**3ba**)

^{1}H NMR (400 MHz, $CDCl_3$)

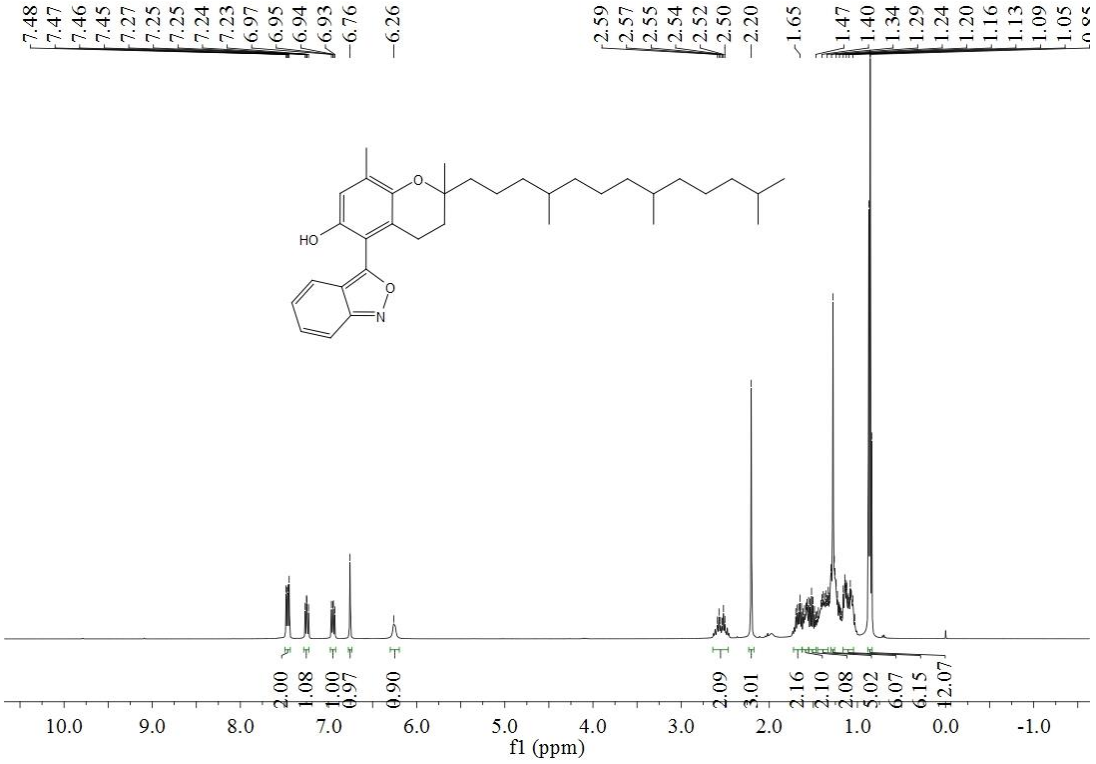


^{13}C NMR (100 MHz, $CDCl_3$)

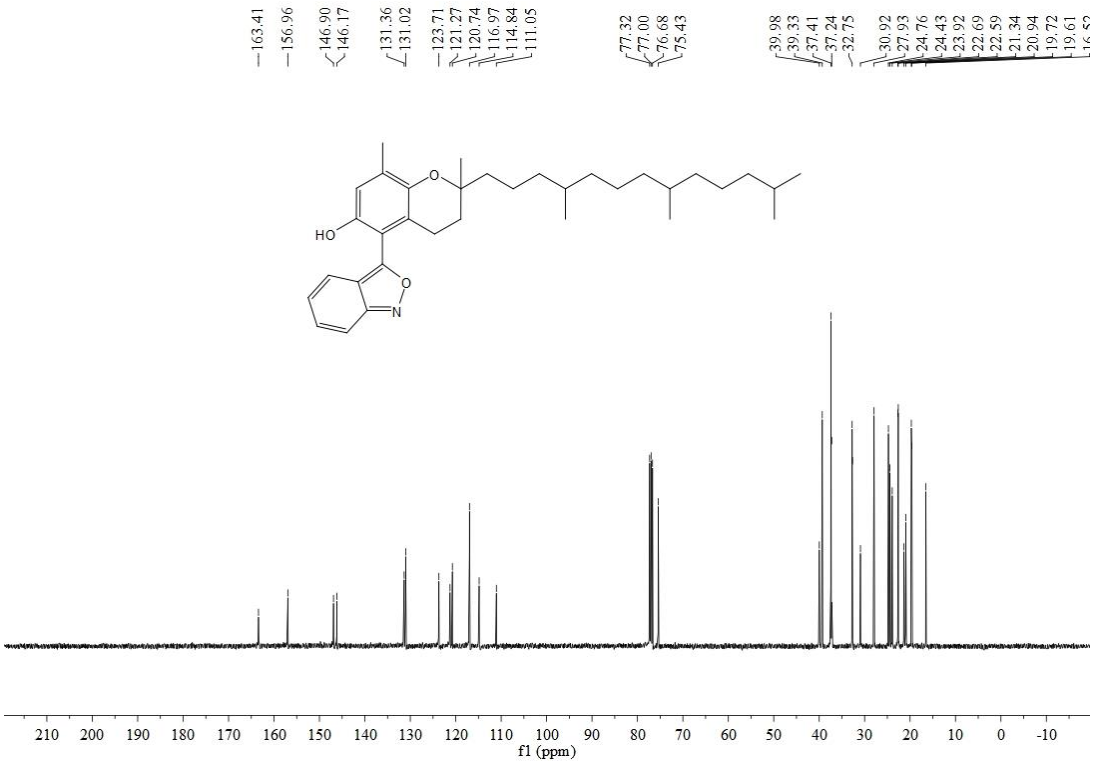


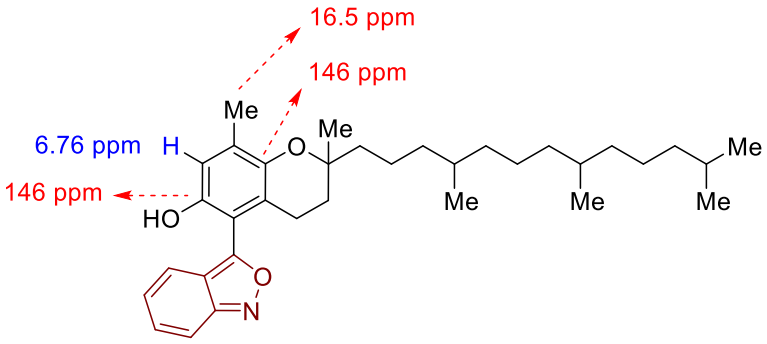
5-(Benzo[c]isoxazol-3-yl)-2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol (**3bb**)

^{1}H NMR (400 MHz, $CDCl_3$)

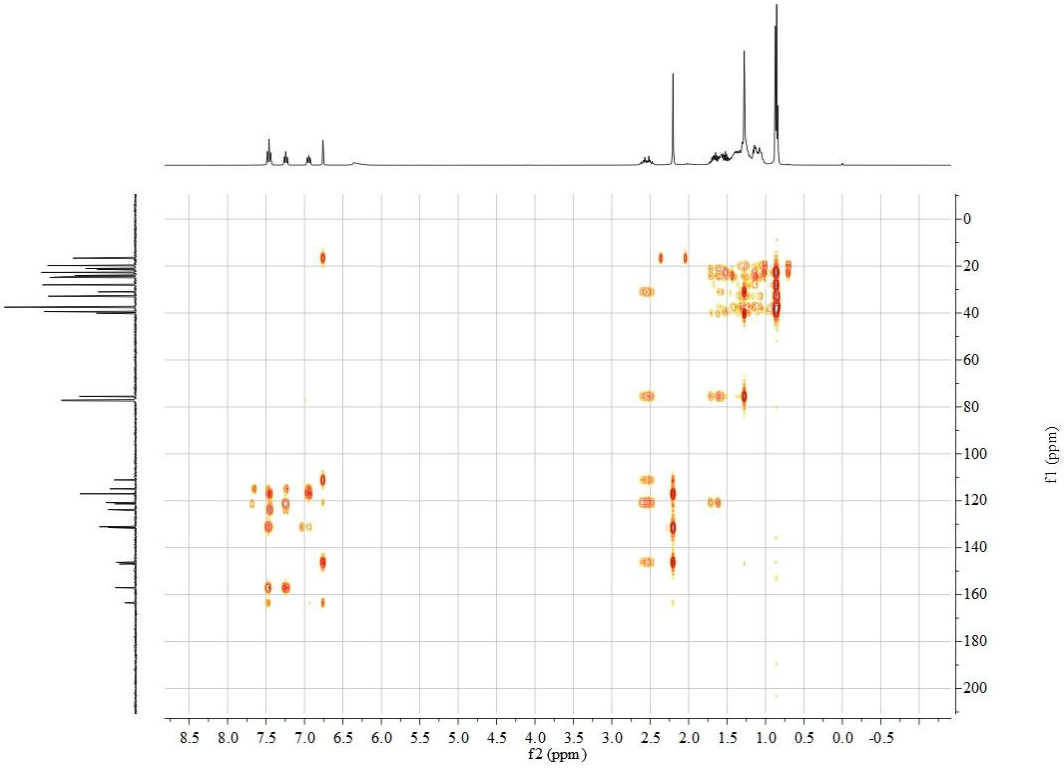


^{13}C NMR (100 MHz, $CDCl_3$)



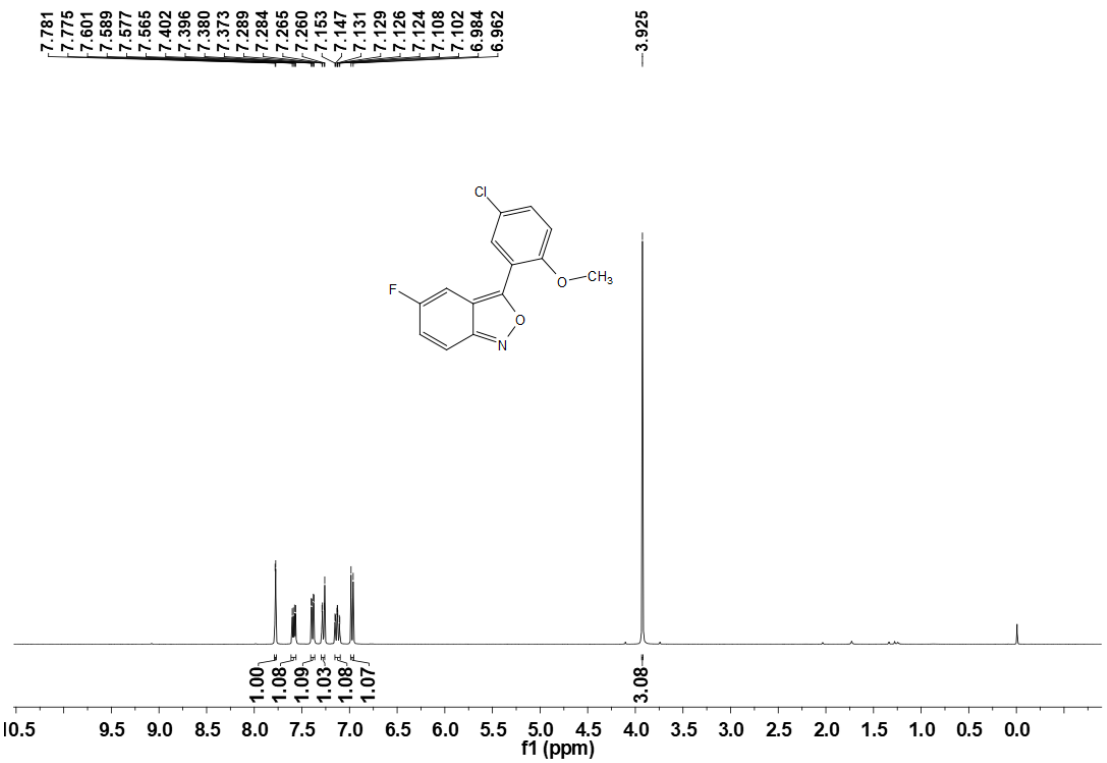


HMBC spectrum of **3bb**

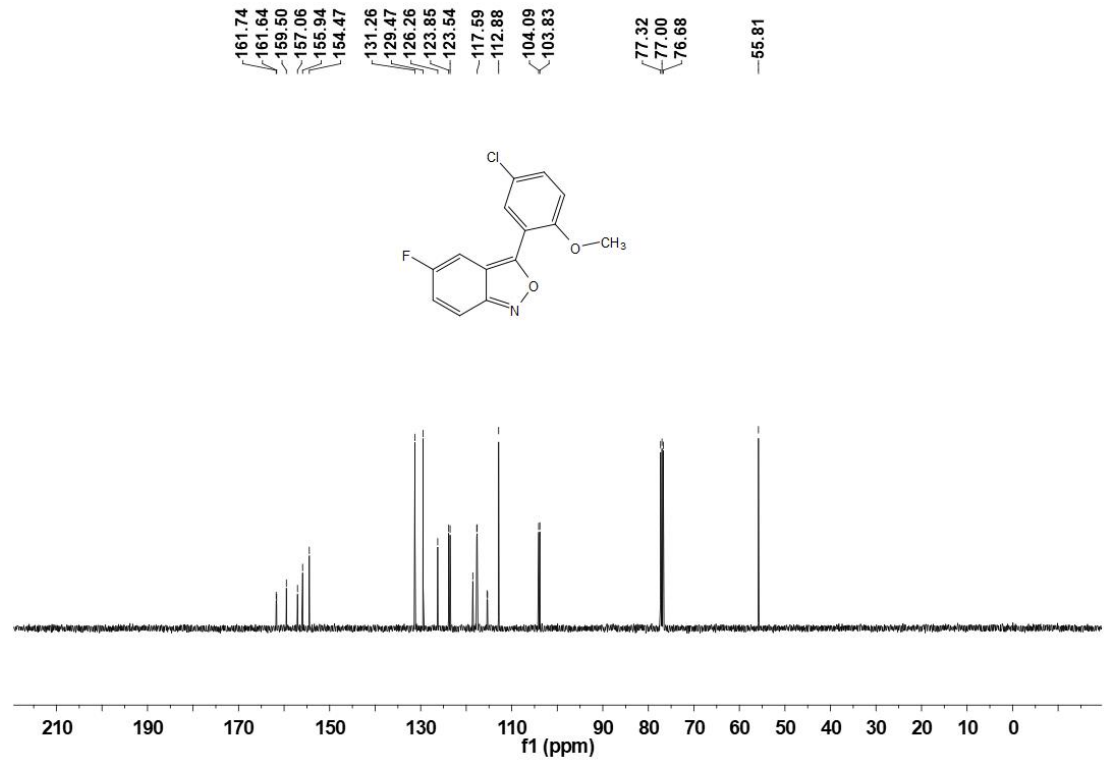


3-(5-Chloro-2-methoxyphenyl)-5-fluorobenzo[c]isoxazole (**3bc**)

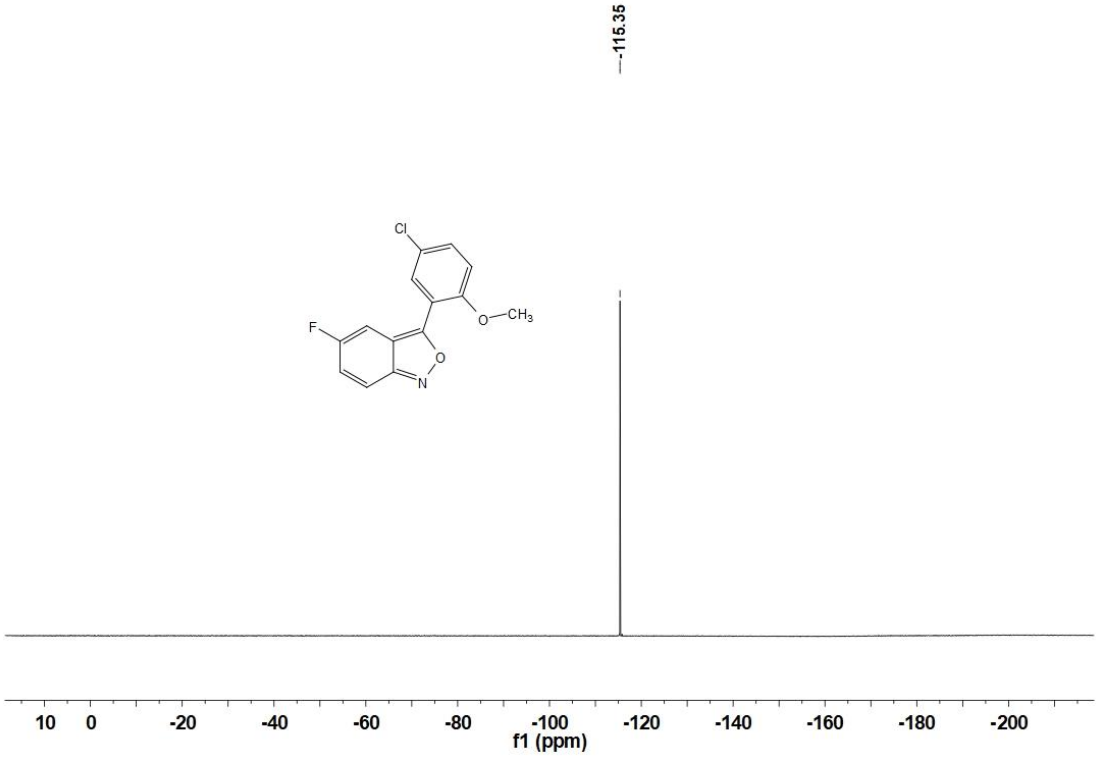
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

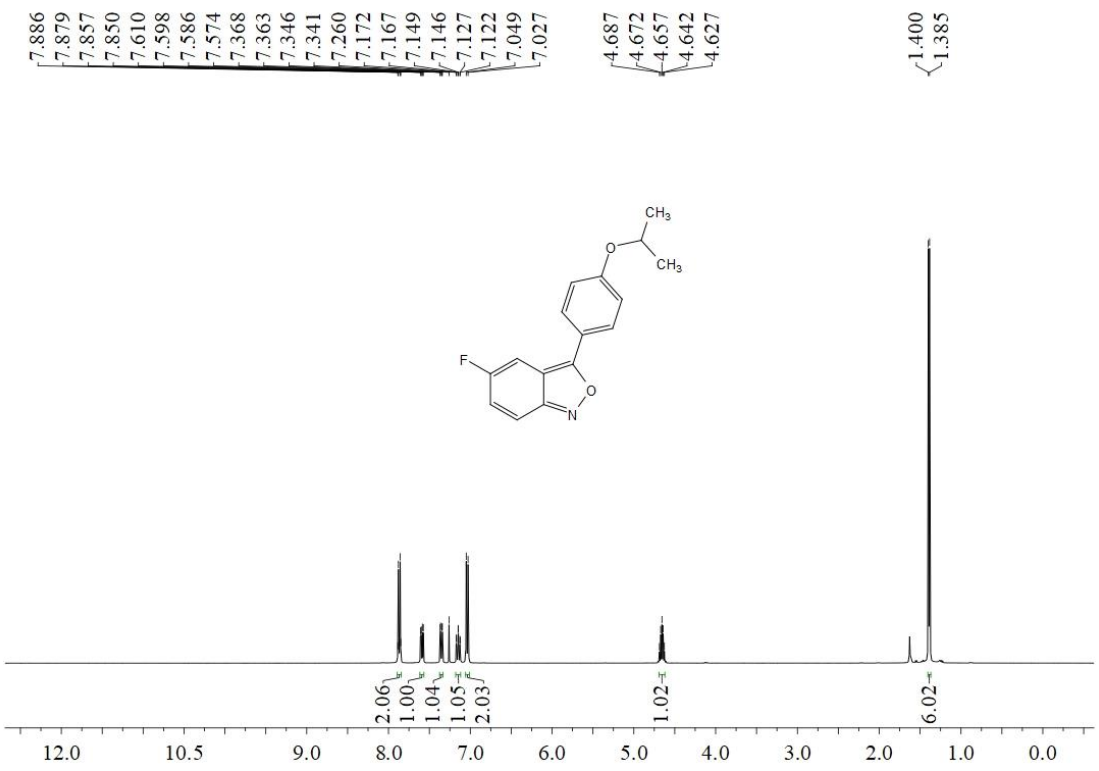


^{19}F NMR (300 MHz, $CDCl_3$)

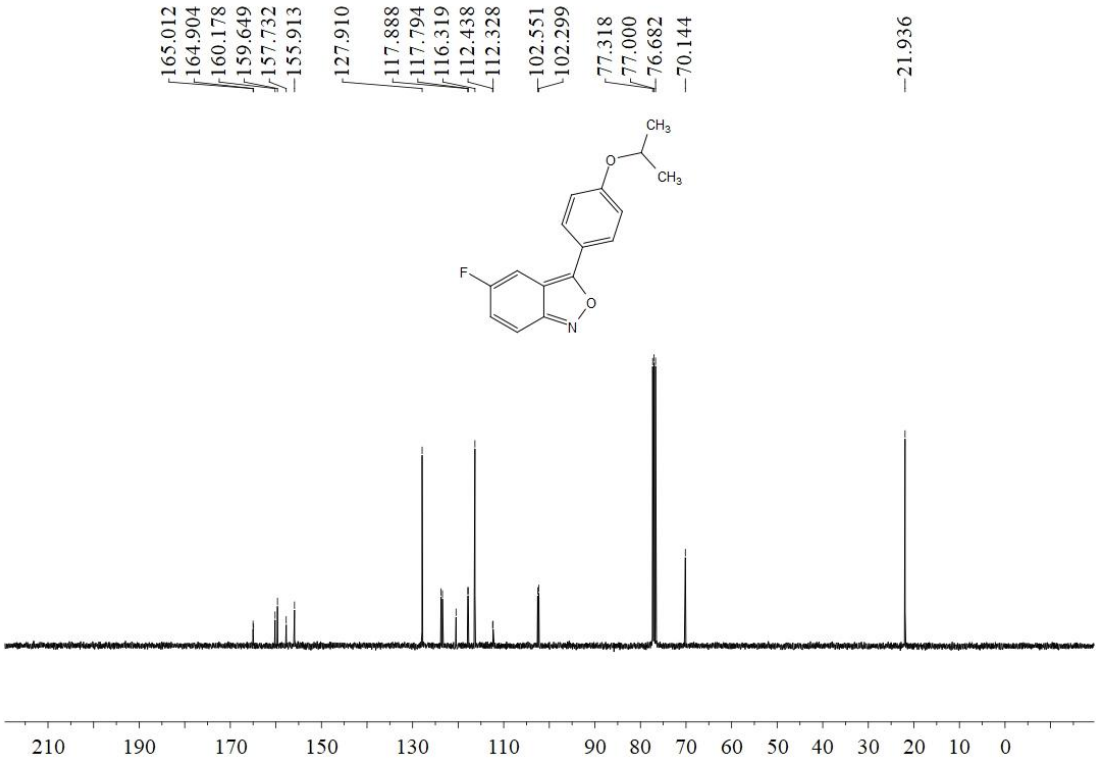

-115.35
Cl
F
O
CH3
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

5-Fluoro-3-(4-isopropoxyphenyl)benzo[c]isoxazole (**3bd**)

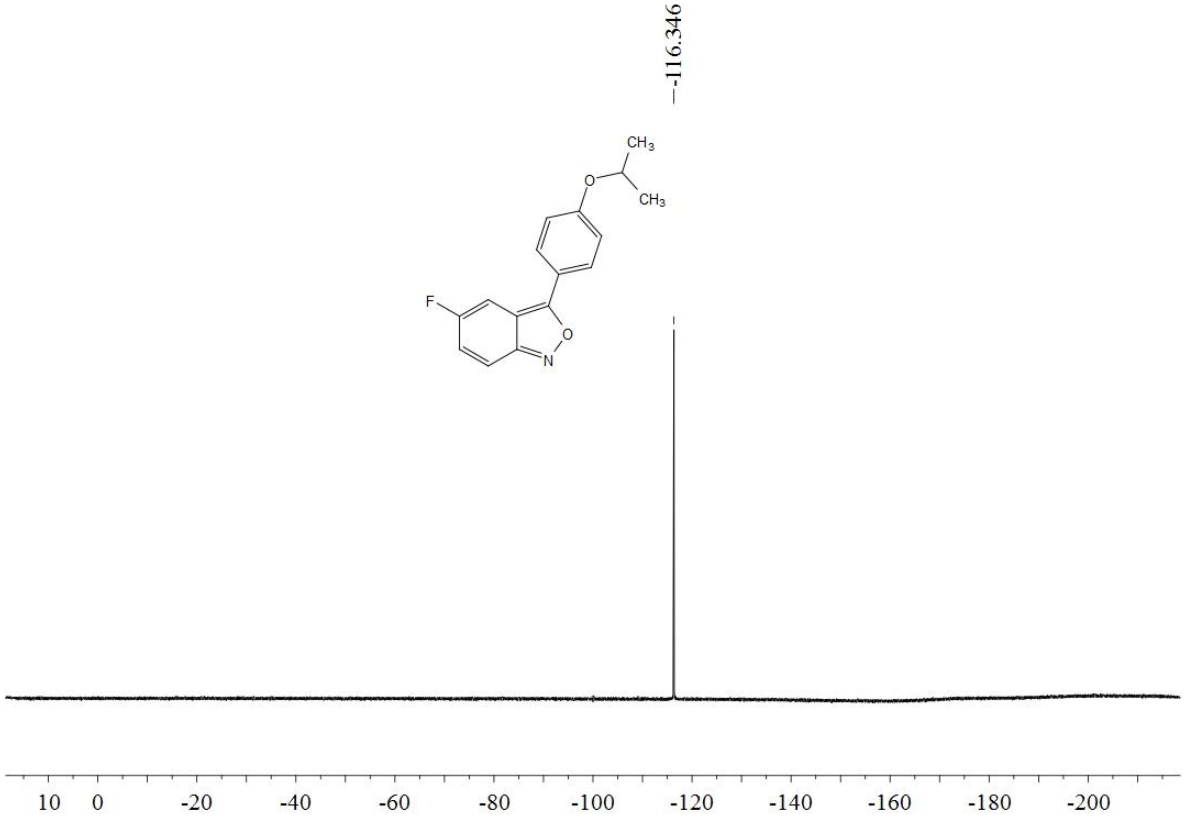
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

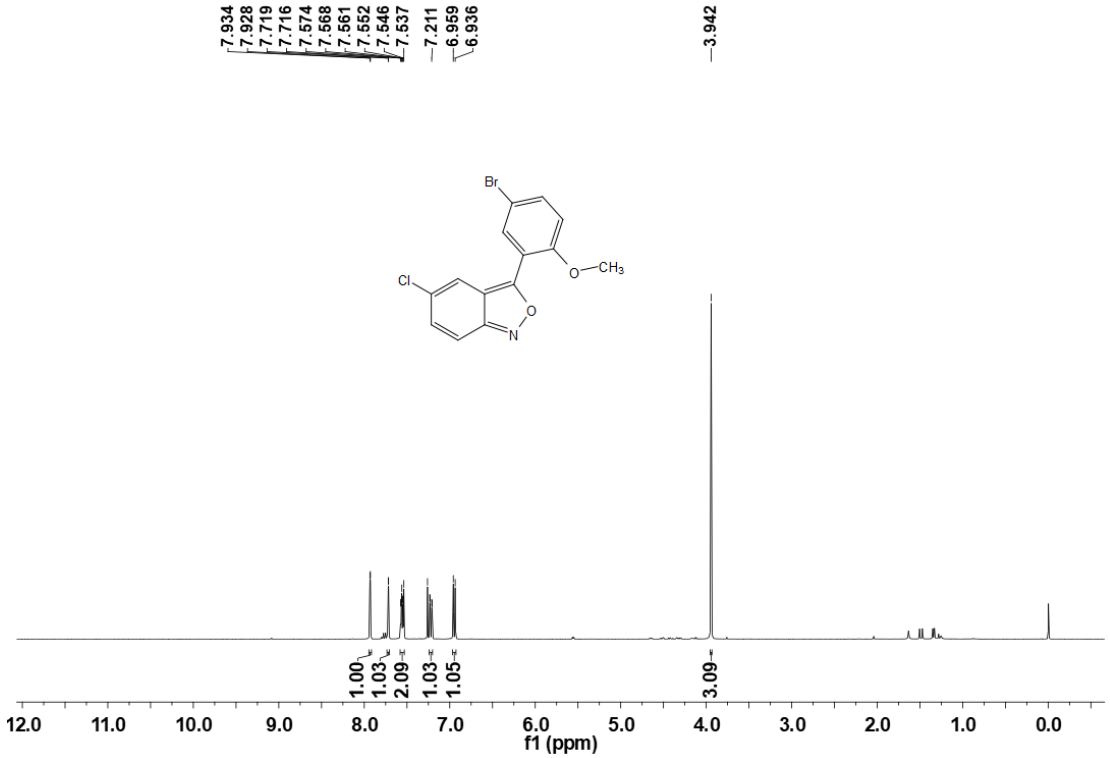


^{19}F NMR (375 MHz, $CDCl_3$)

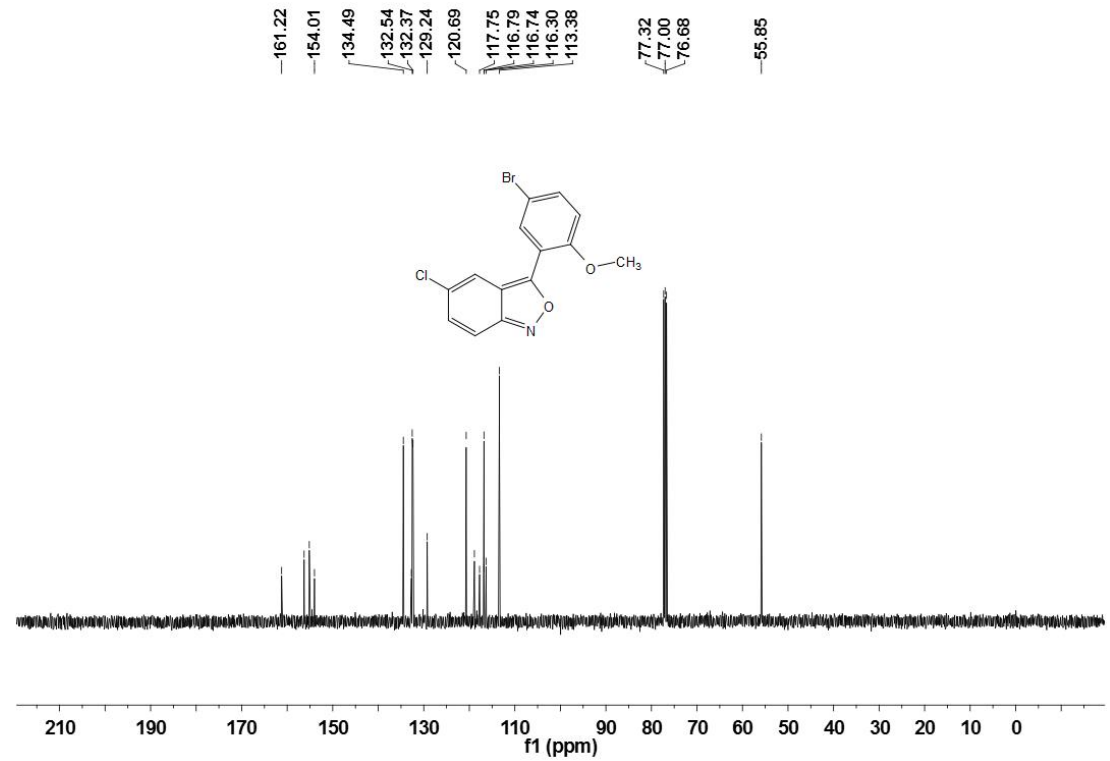

-116.346
CH3
O
CH3
F
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(5-Bromo-2-methoxyphenyl)-5-chlorobenzo[c]isoxazole (**3be**)

^{1}H NMR (400 MHz, $CDCl_3$)

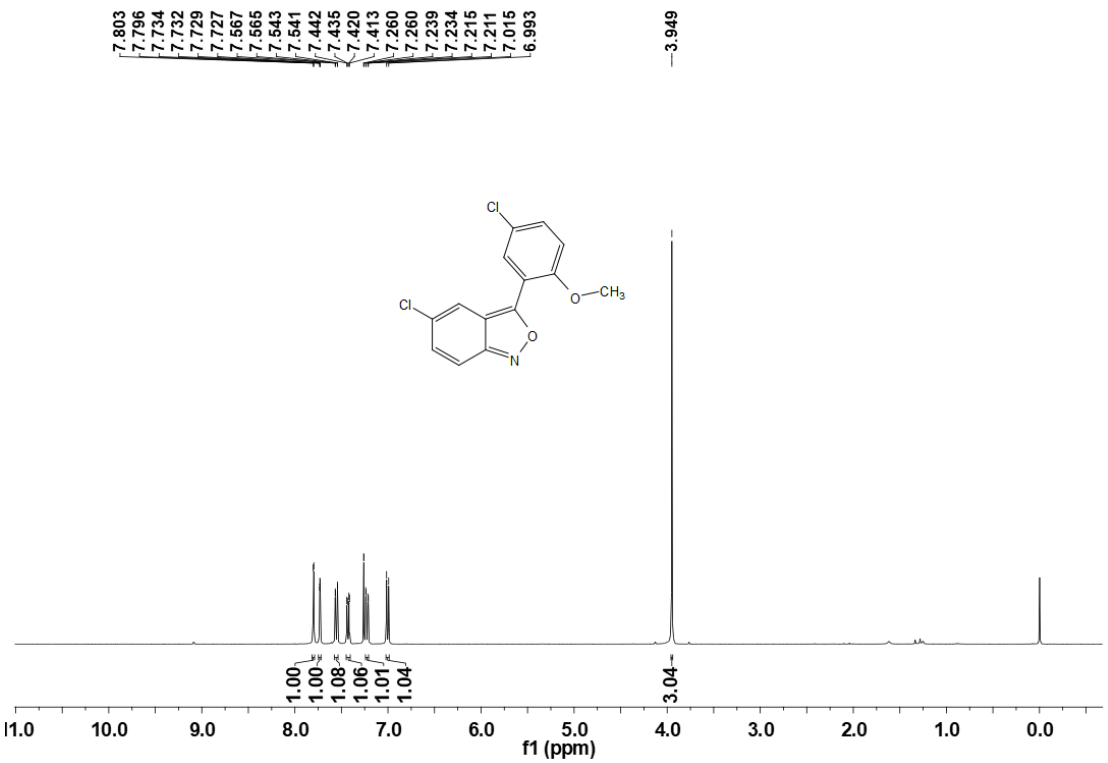


^{13}C NMR (100 MHz, $CDCl_3$)

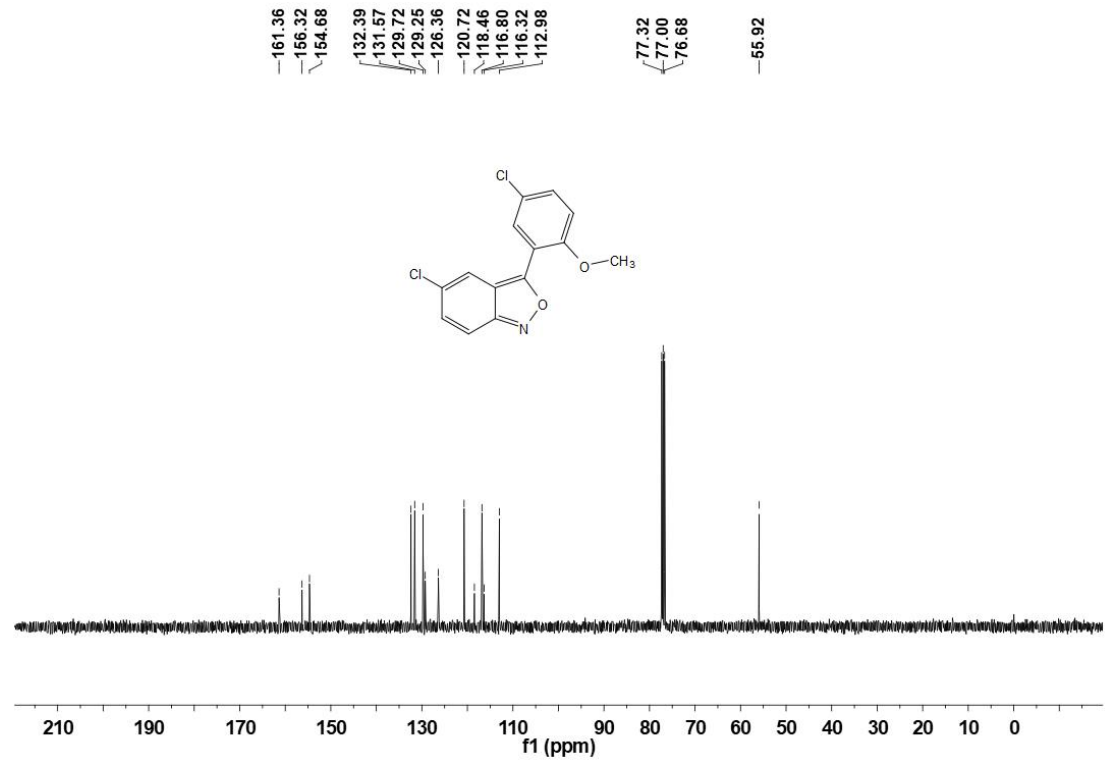


5-Chloro-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (**3bf**)

^{1}H NMR (400 MHz, $CDCl_3$)

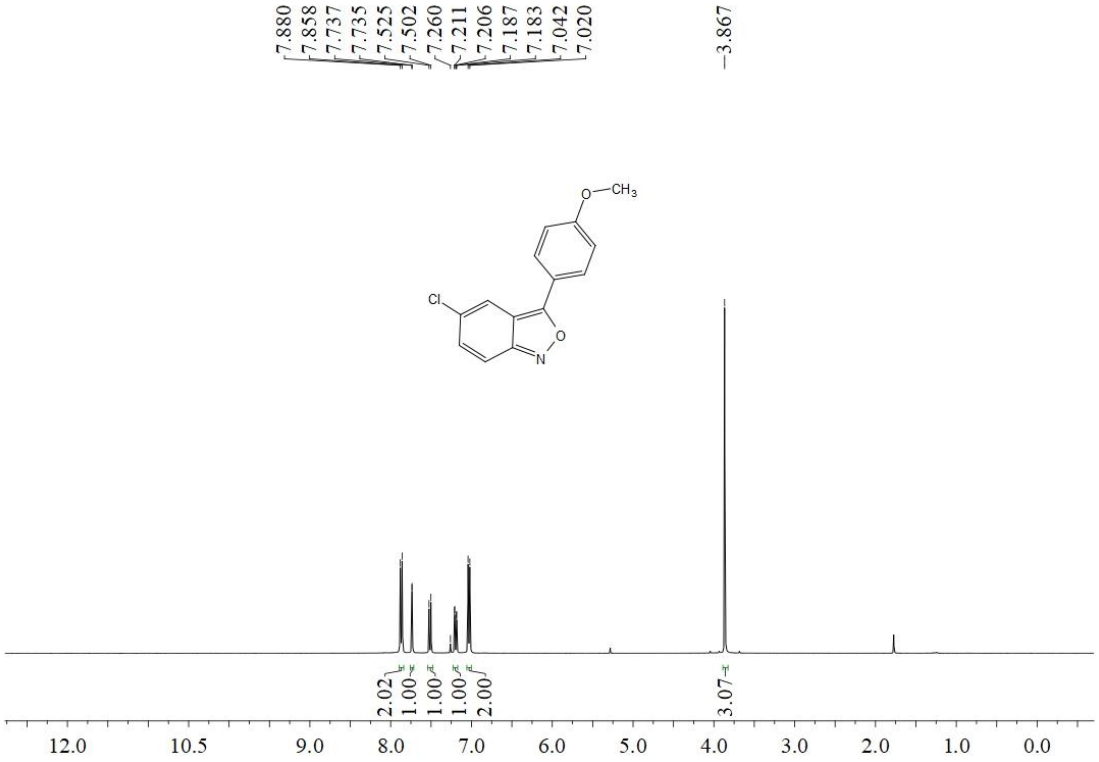


^{13}C NMR (100 MHz, $CDCl_3$)

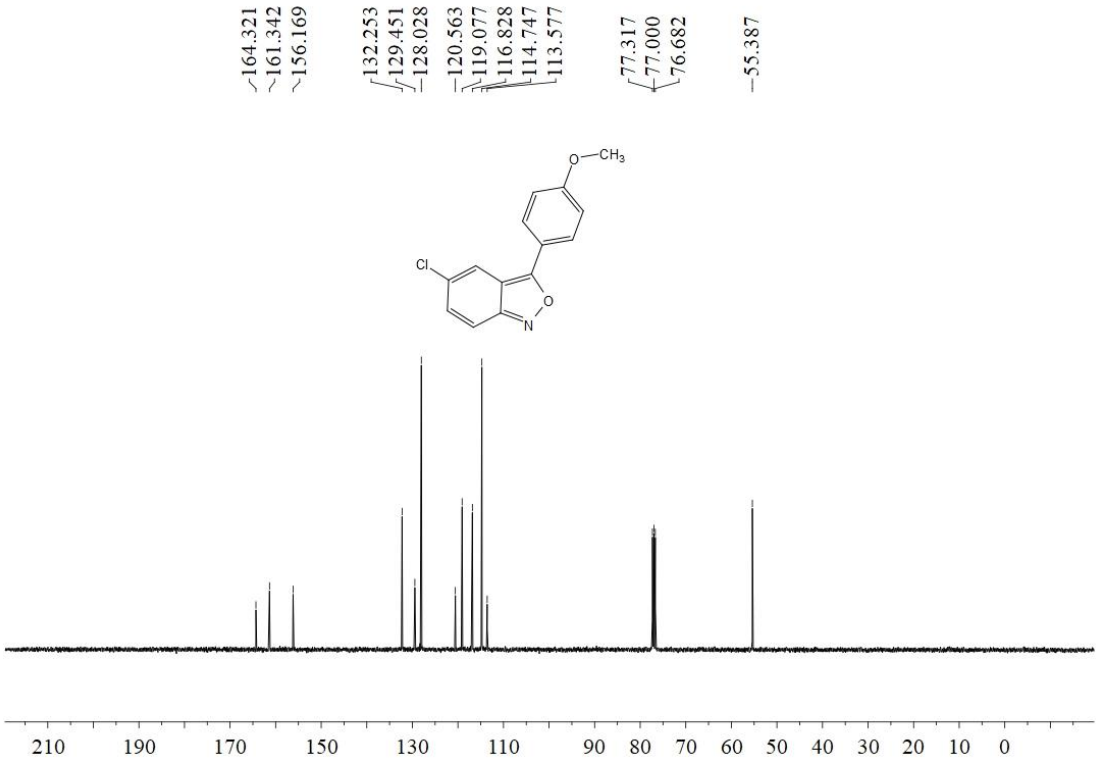


5-Chloro-3-(4-methoxyphenyl)benzo[c]isoxazole (**3bg**)

^{1}H NMR (400 MHz, $CDCl_3$)

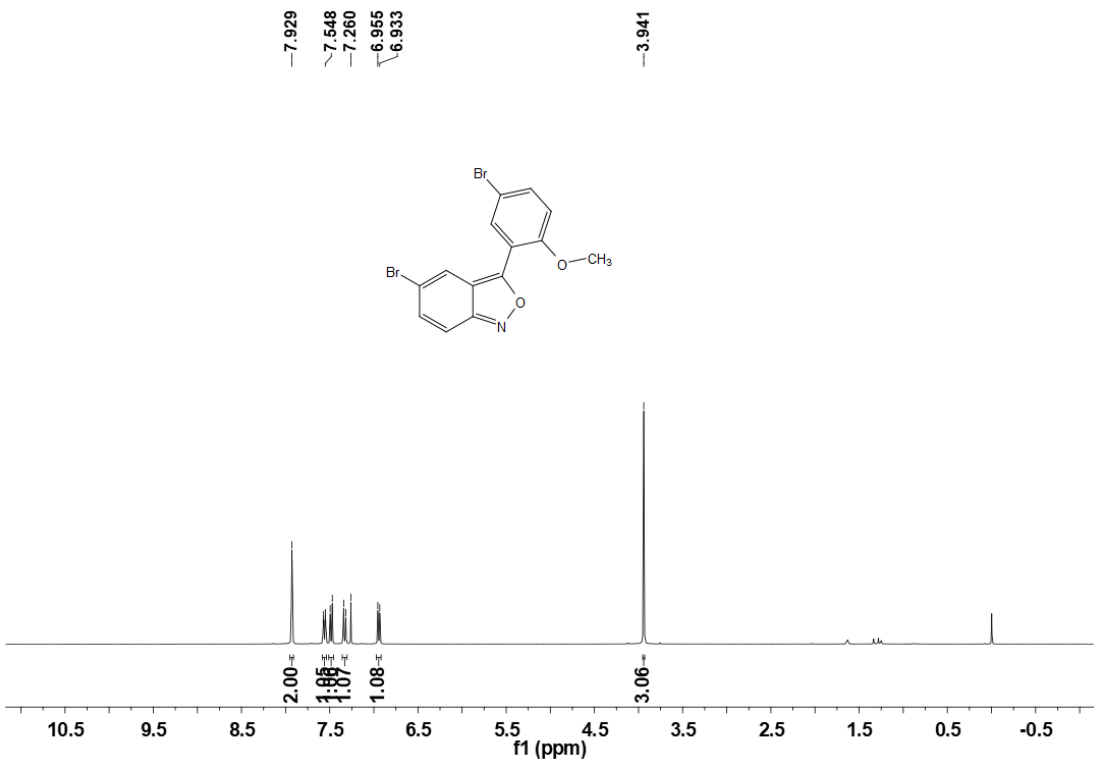


^{13}C NMR (100 MHz, $CDCl_3$)

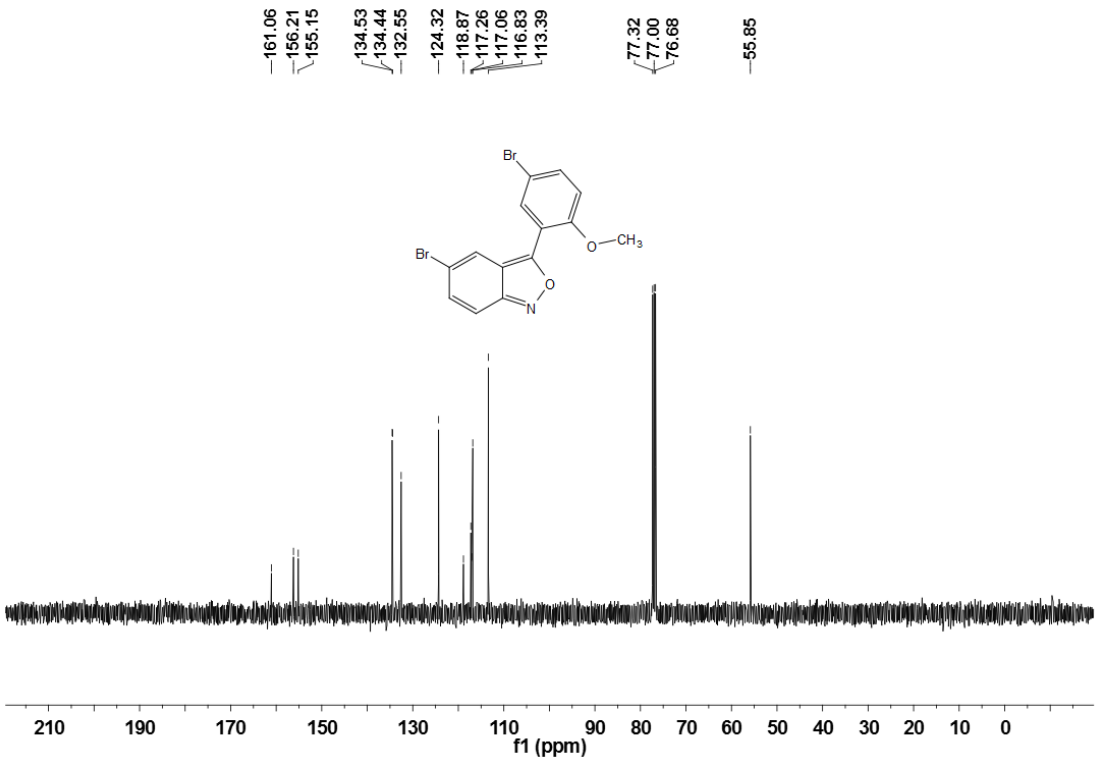


5-Bromo-3-(5-bromo-2-methoxyphenyl)benzo[c]isoxazole (**3bh**)

^{1}H NMR (400 MHz, $CDCl_3$)

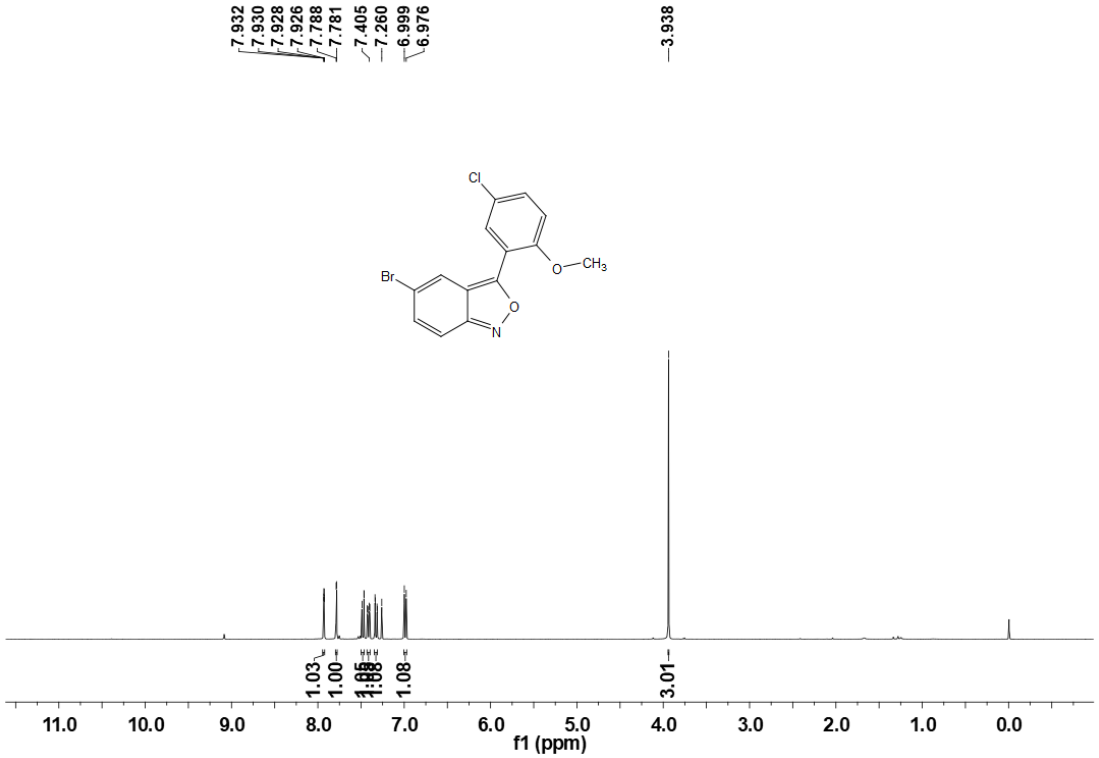


^{13}C NMR (100 MHz, $CDCl_3$)

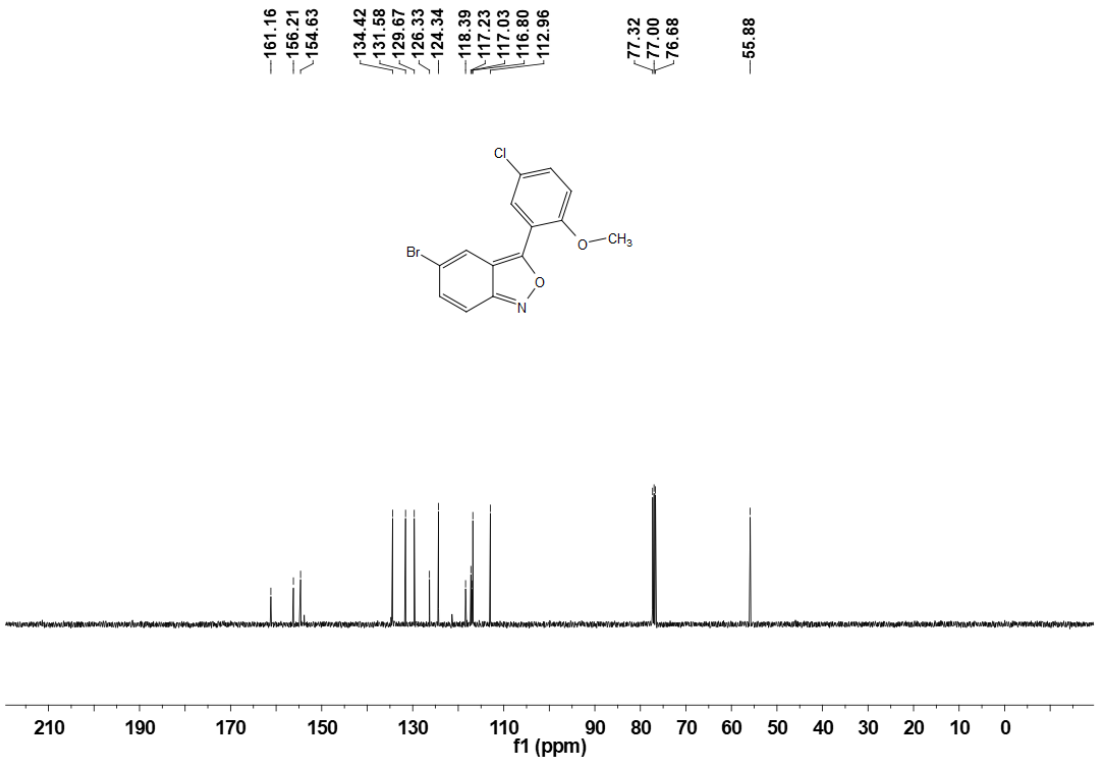


5-Bromo-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (**3bi**)

^{1}H NMR (400 MHz, $CDCl_3$)

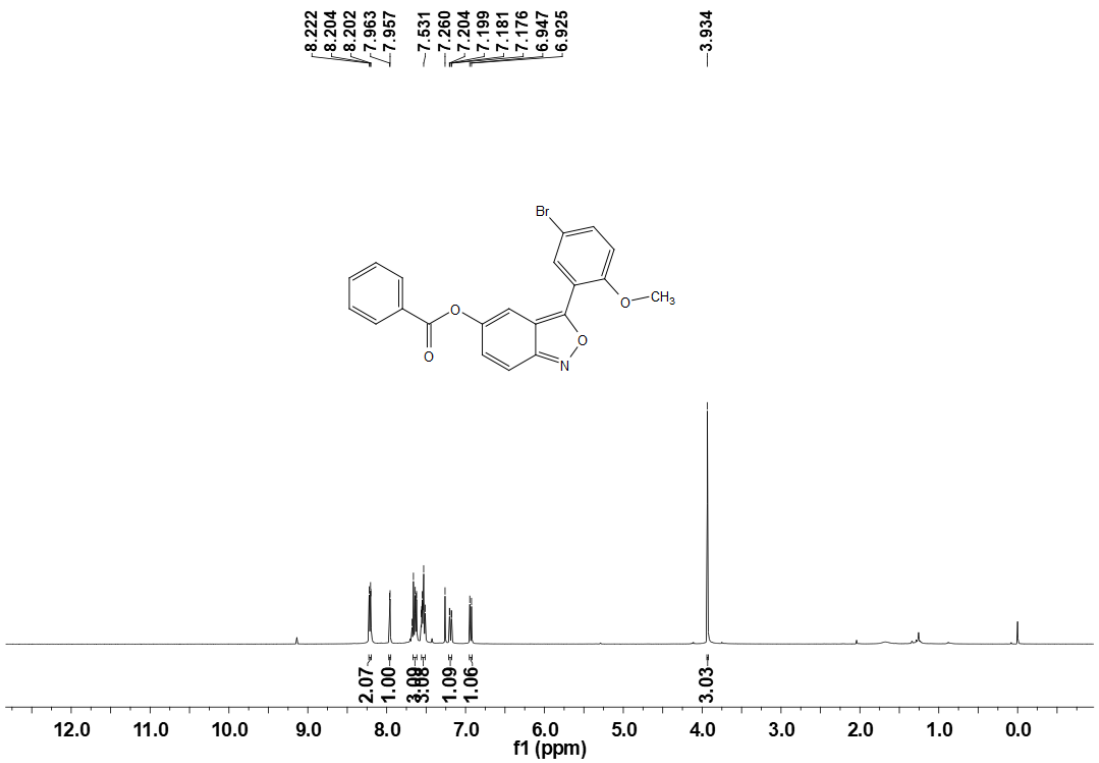


^{13}C NMR (100 MHz, $CDCl_3$)

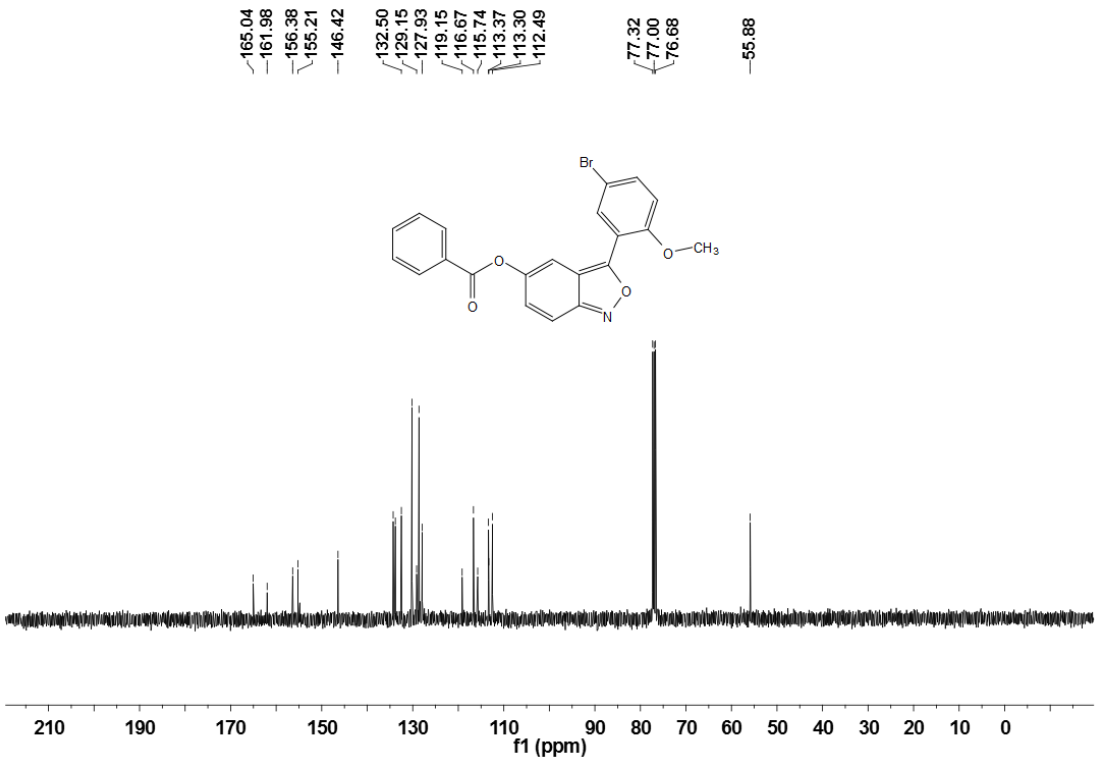


3-(5-Bromo-2-methoxyphenyl)benzo[c]isoxazol-5-yl benzoate (**3bj**)

^{1}H NMR (400 MHz, $CDCl_3$)

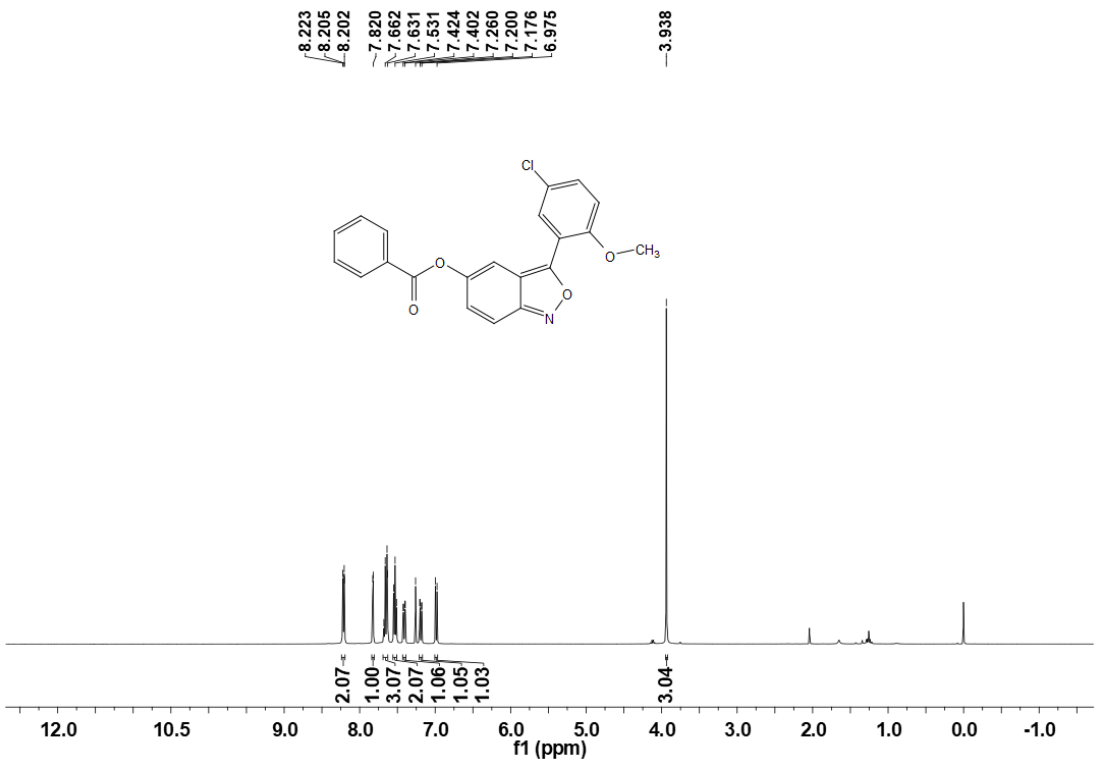


^{13}C NMR (100 MHz, $CDCl_3$)

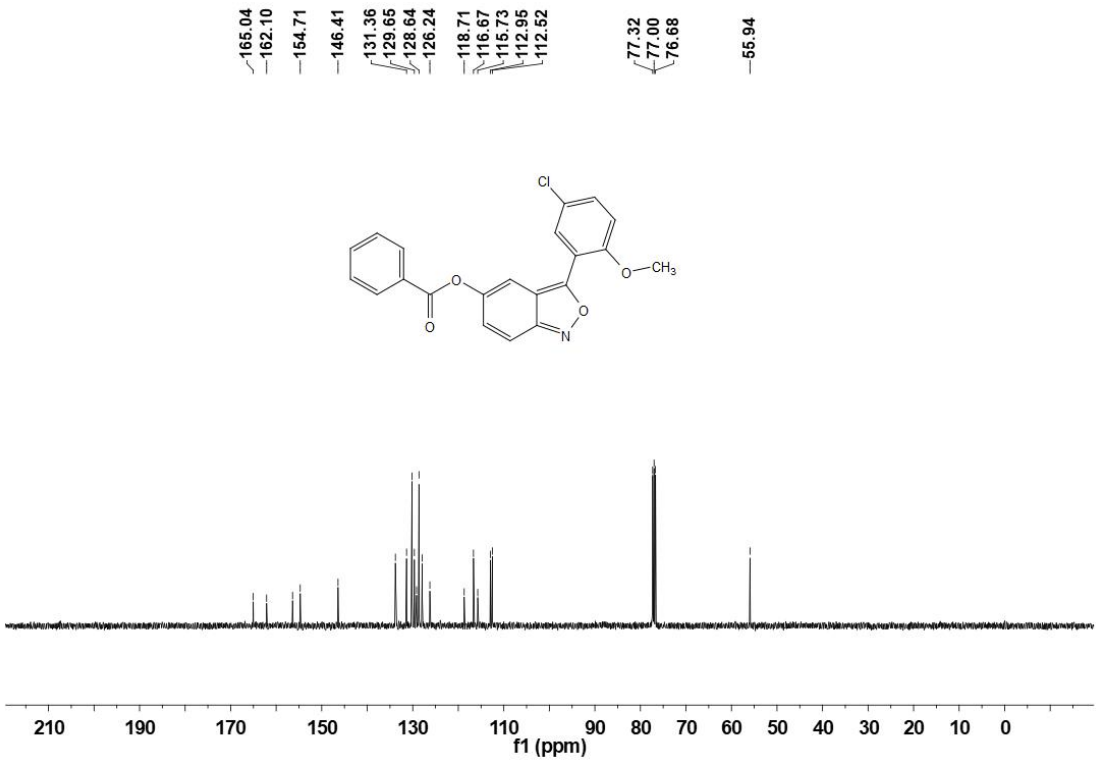


3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazol-5-yl benzoate (**3bk**)

^{1}H NMR (400 MHz, $CDCl_3$)

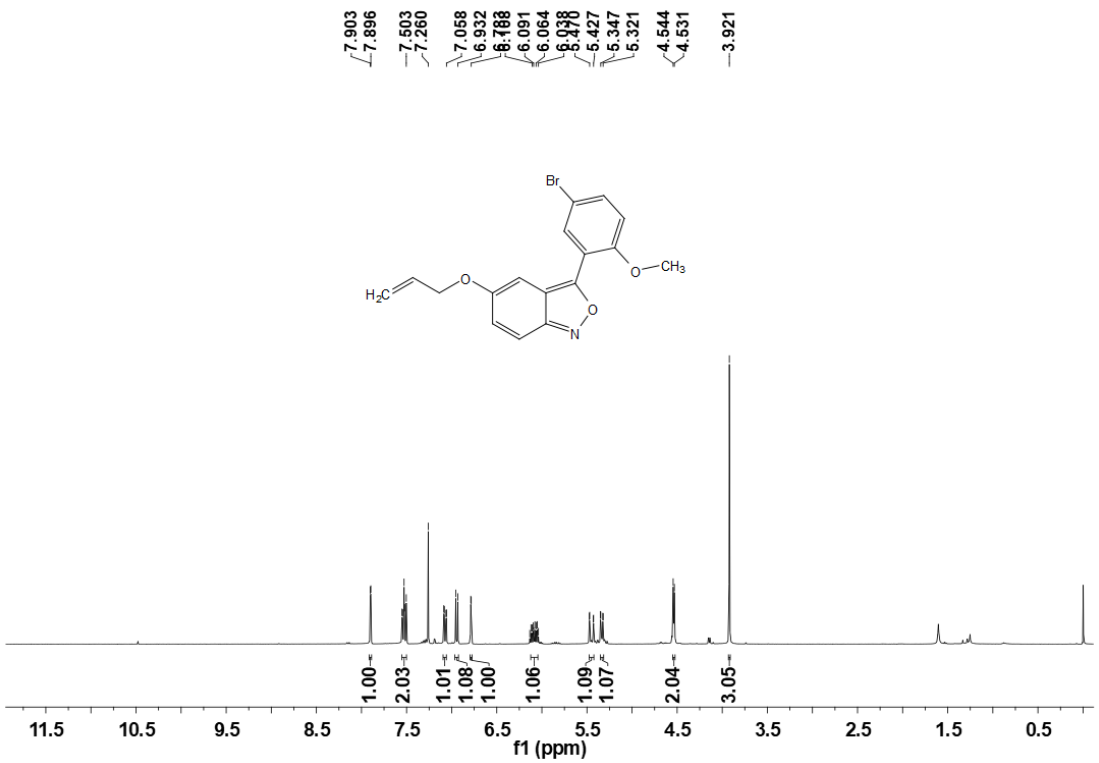


^{13}C NMR (100 MHz, $CDCl_3$)

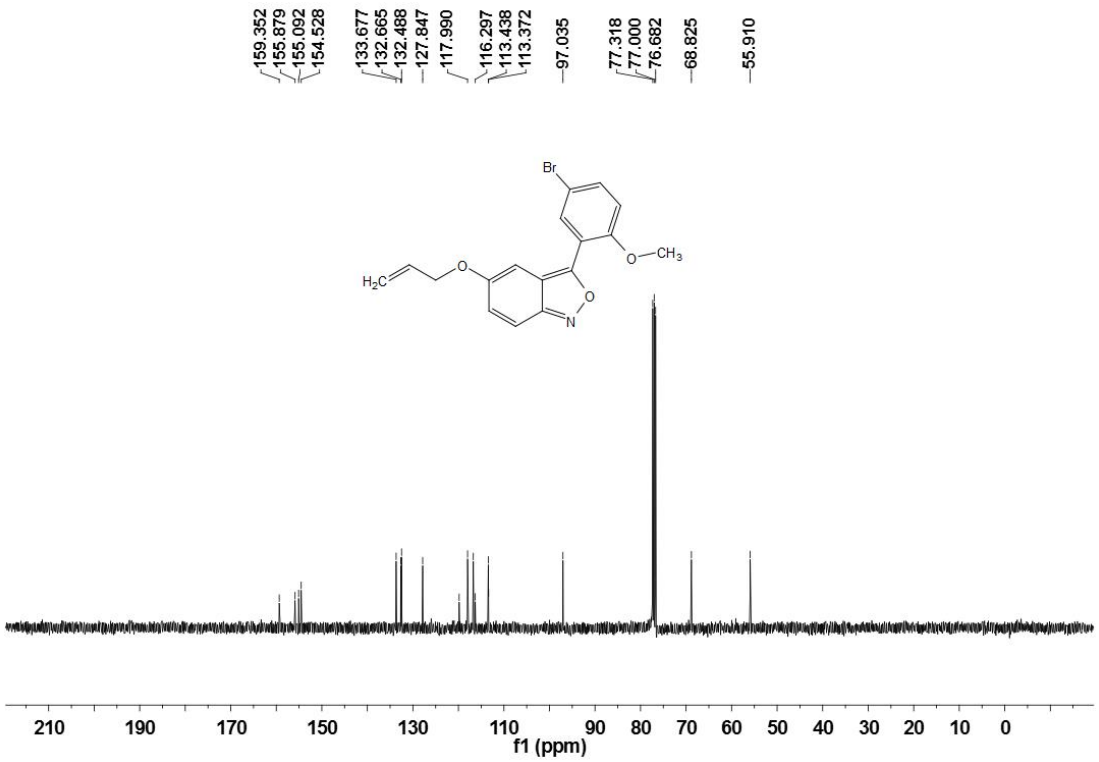


5-(Allyloxy)-3-(5-bromo-2-methoxyphenyl)benzo[c]isoxazole (**3bl**)

^{1}H NMR (400 MHz, $CDCl_3$)

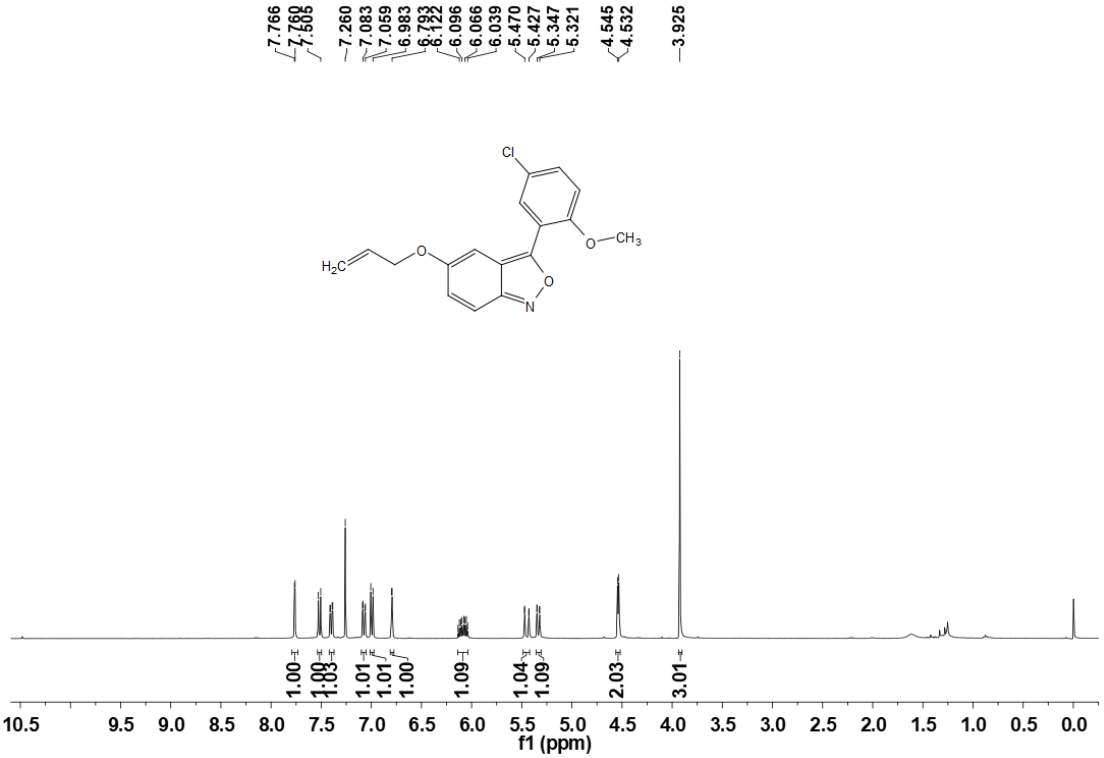


^{13}C NMR (100 MHz, $CDCl_3$)

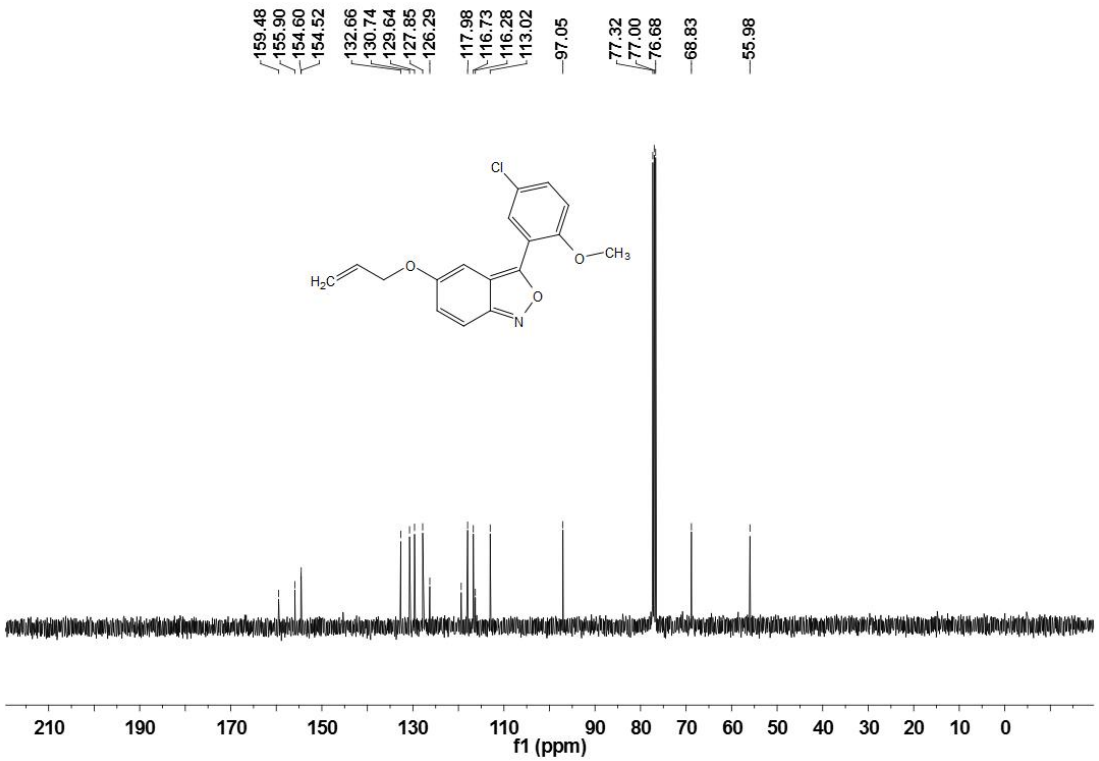


5-(Allyloxy)-3-(5-chloro-2-methoxyphenyl)benzo[c]isoxazole (**3bm**)

^{1}H NMR (400 MHz, $CDCl_3$)

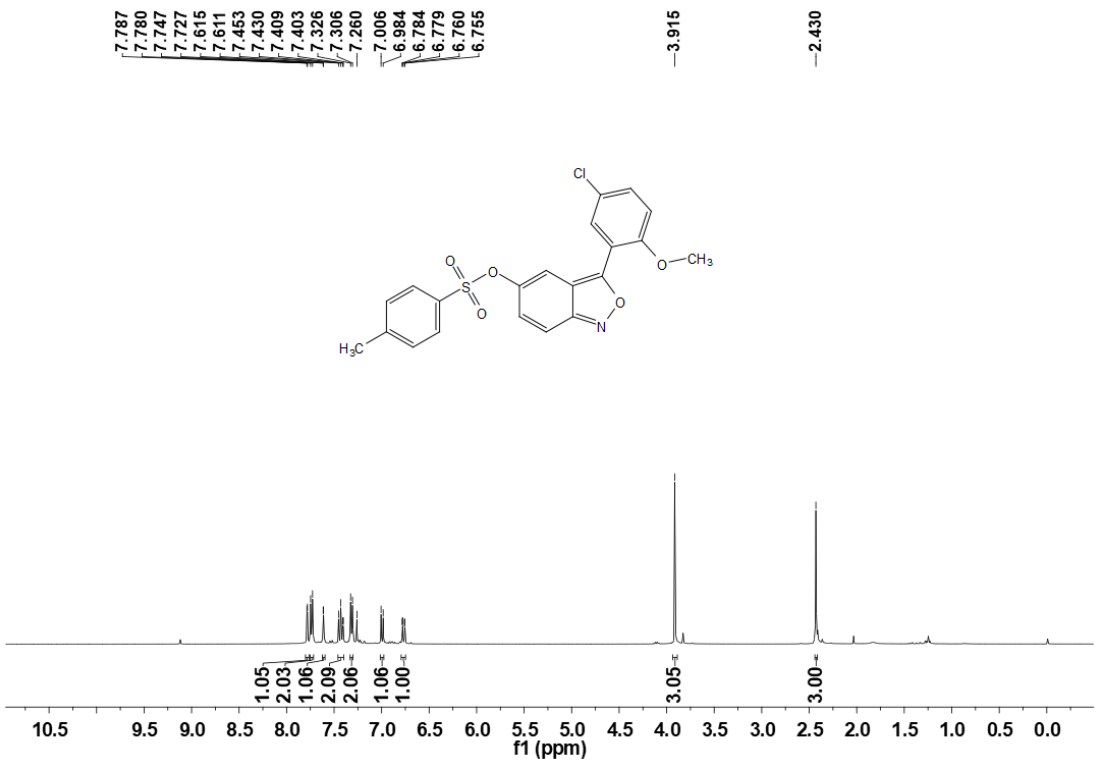


^{13}C NMR (100 MHz, $CDCl_3$)

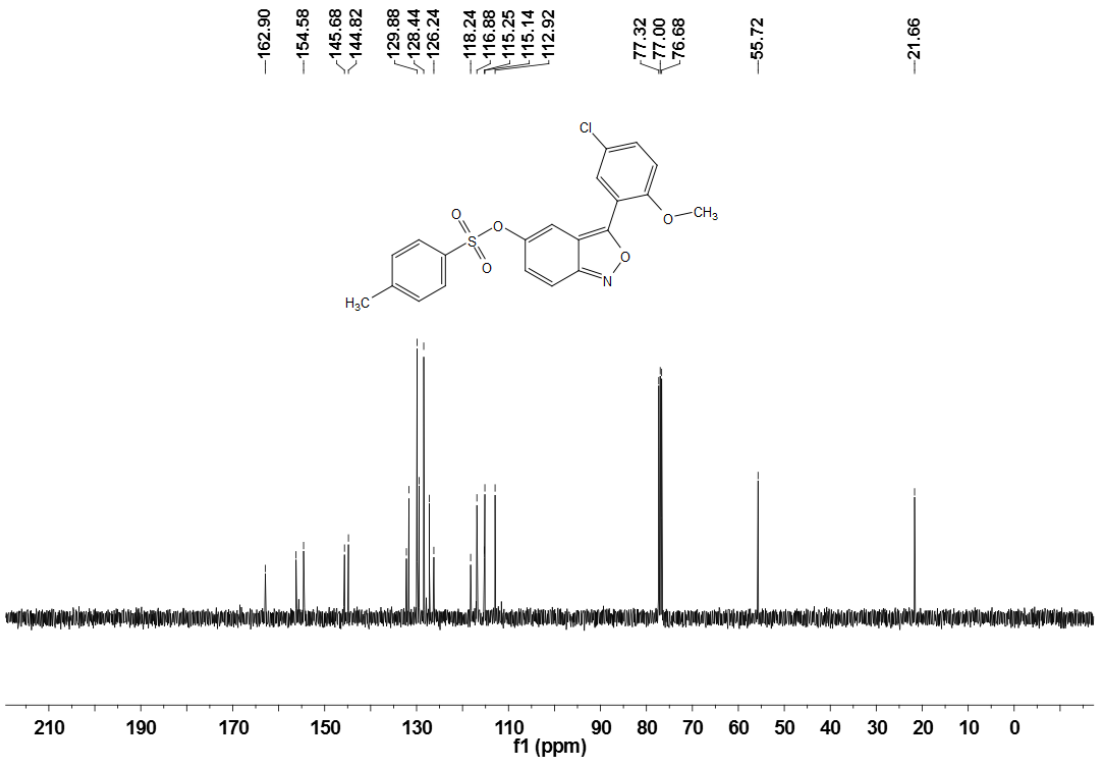


3-(5-Chloro-2-methoxyphenyl)benzo[c]isoxazol-5-yl 4-methylbenzenesulfonate (**3bn**)

^{1}H NMR (400 MHz, $CDCl_3$)

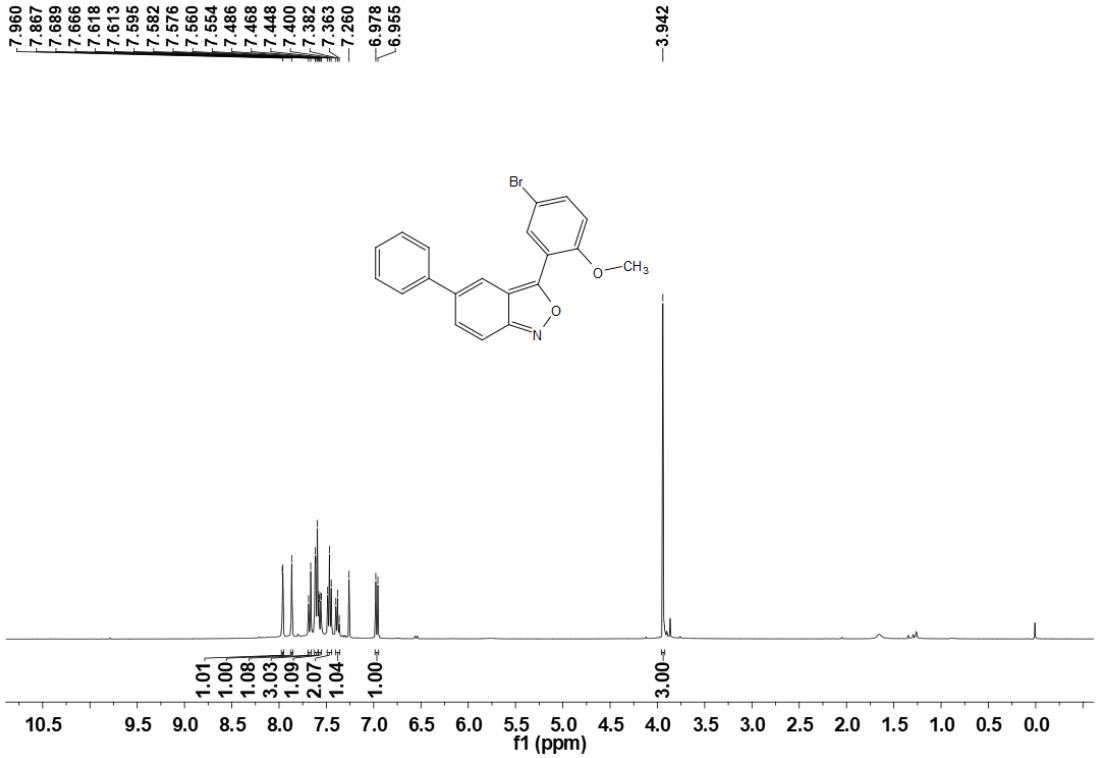


^{13}C NMR (100 MHz, $CDCl_3$)

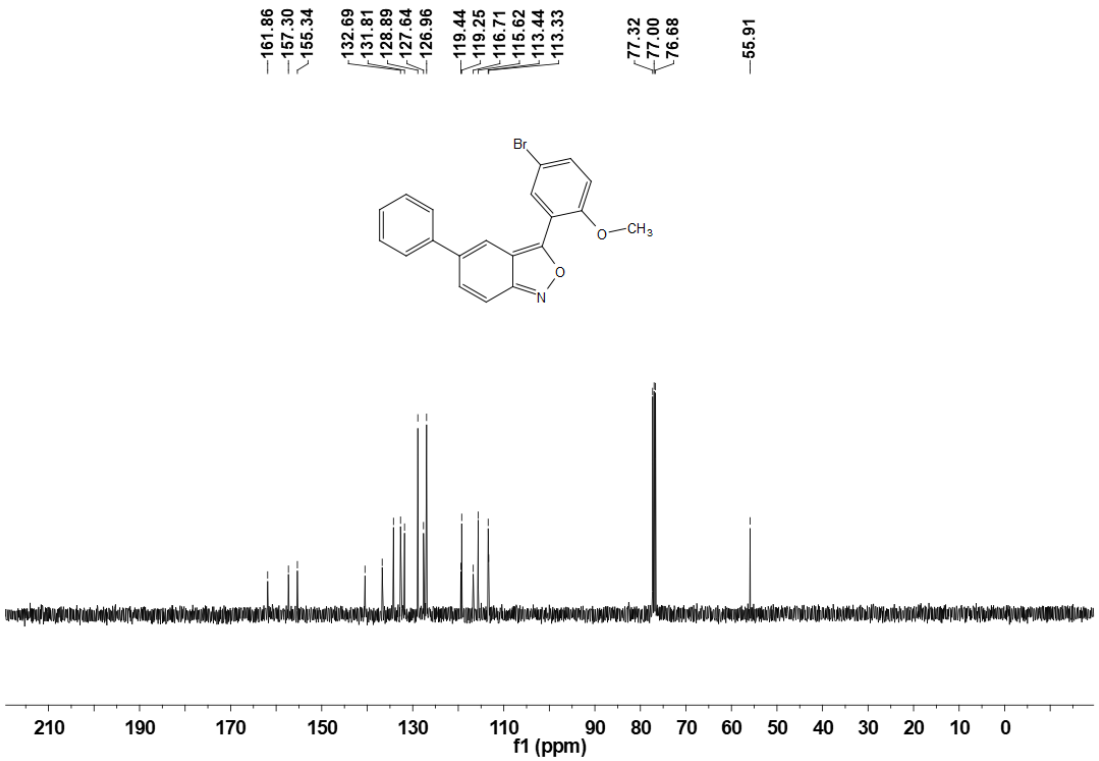


3-(5-Bromo-2-methoxyphenyl)-5-phenylbenzo[c]isoxazole (**3bo**)

^{1}H NMR (400 MHz, $CDCl_3$)

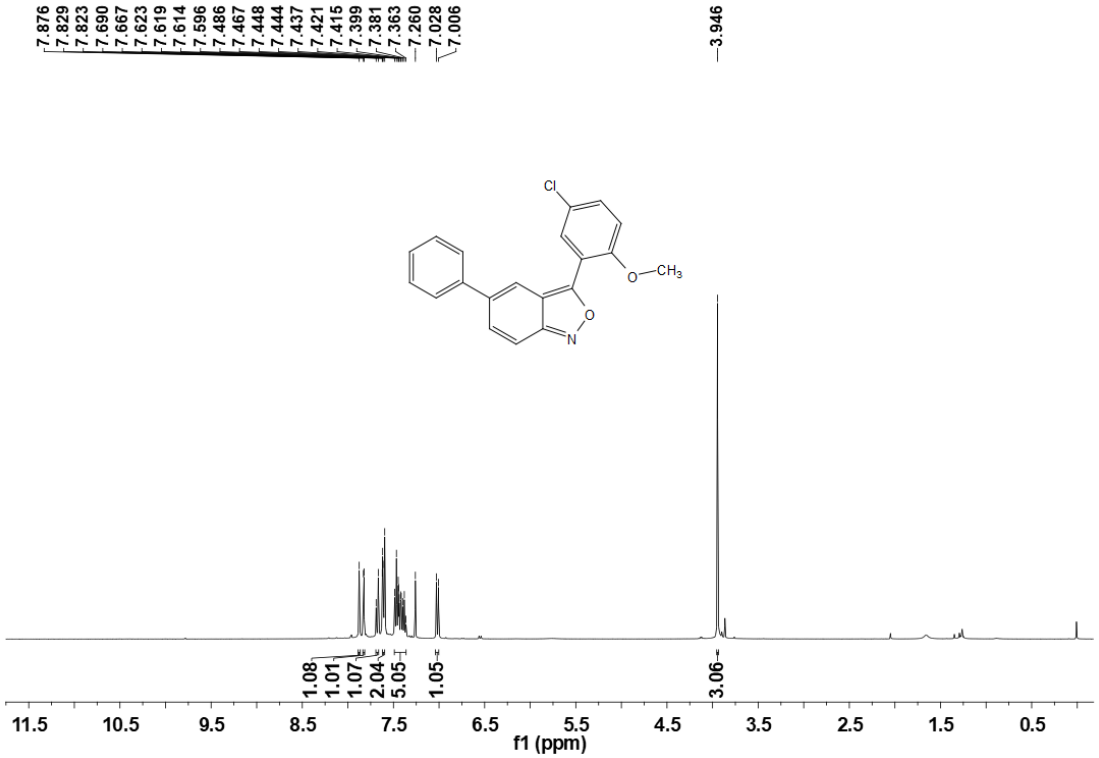


^{13}C NMR (100 MHz, $CDCl_3$)

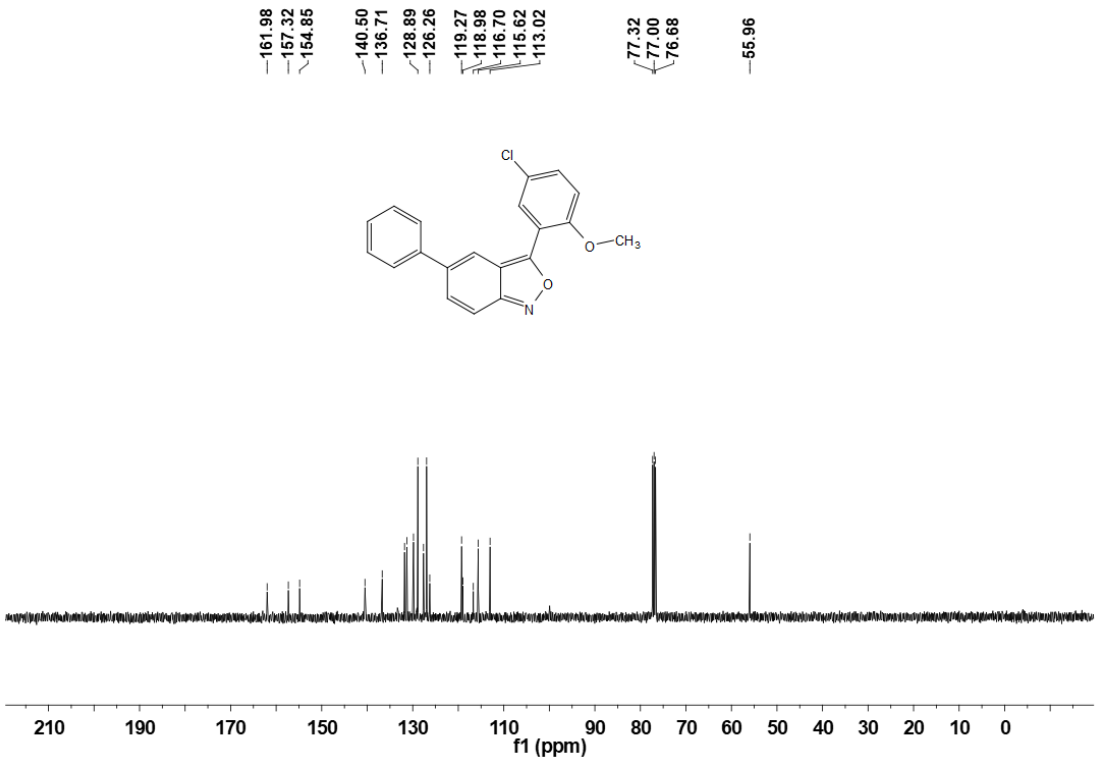


3-(5-Chloro-2-methoxyphenyl)-5-phenylbenzo[c]isoxazole (**3bp**)

^{1}H NMR (400 MHz, $CDCl_3$)

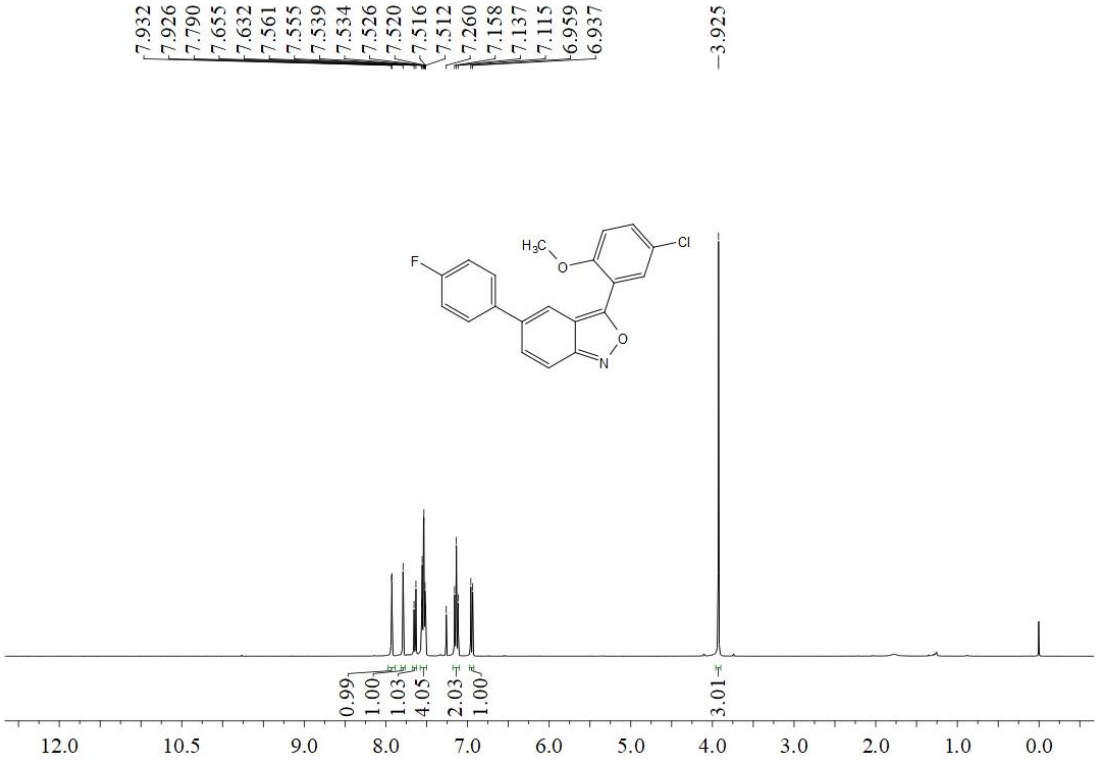


^{13}C NMR (100 MHz, $CDCl_3$)

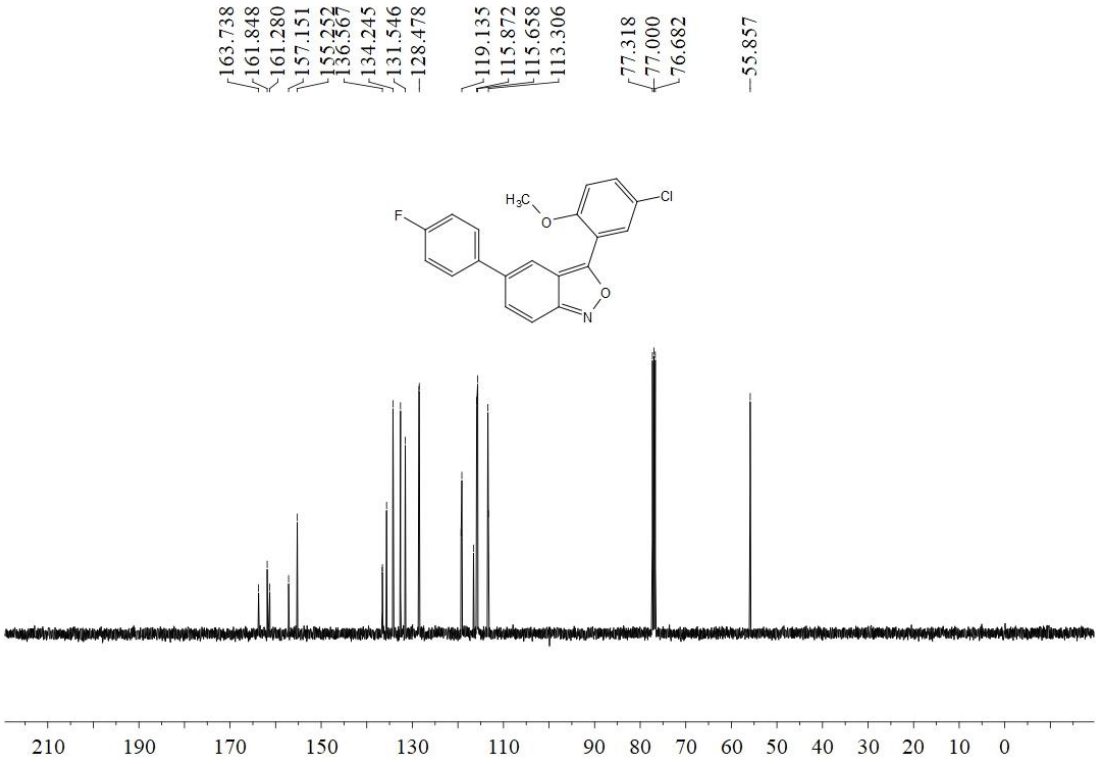


3-(5-Chloro-2-methoxyphenyl)-5-(4-fluorophenyl)benzo[c]isoxazole (**3bq**)

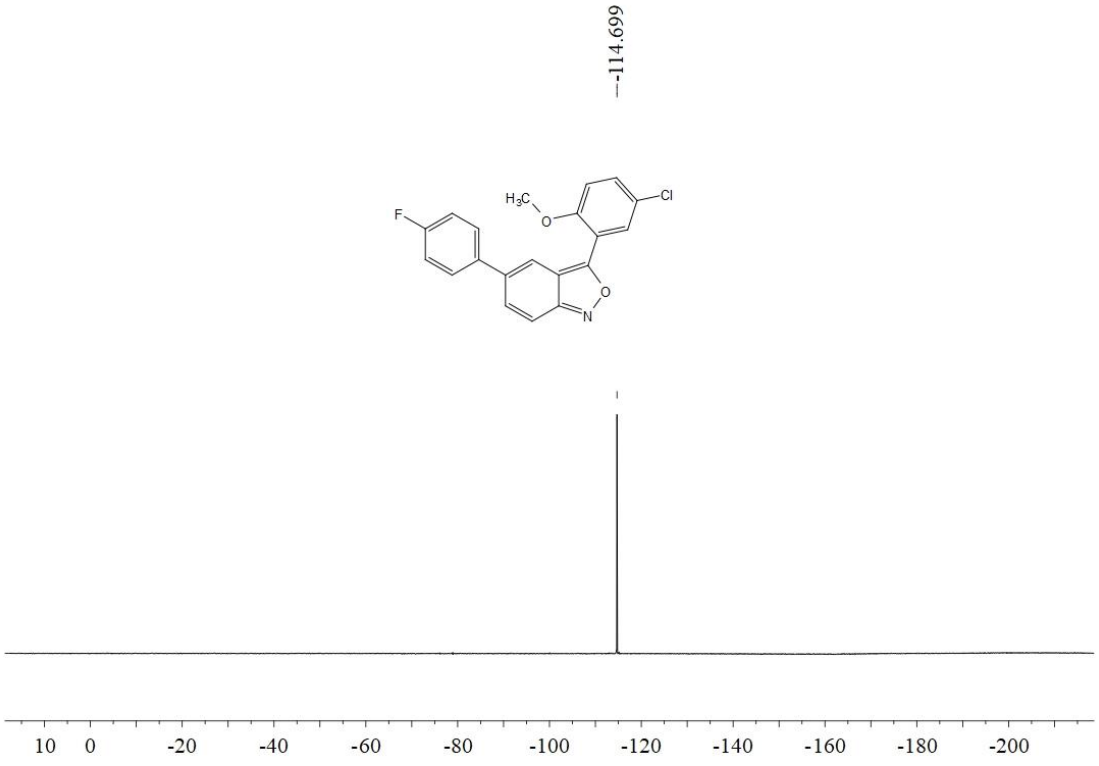
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

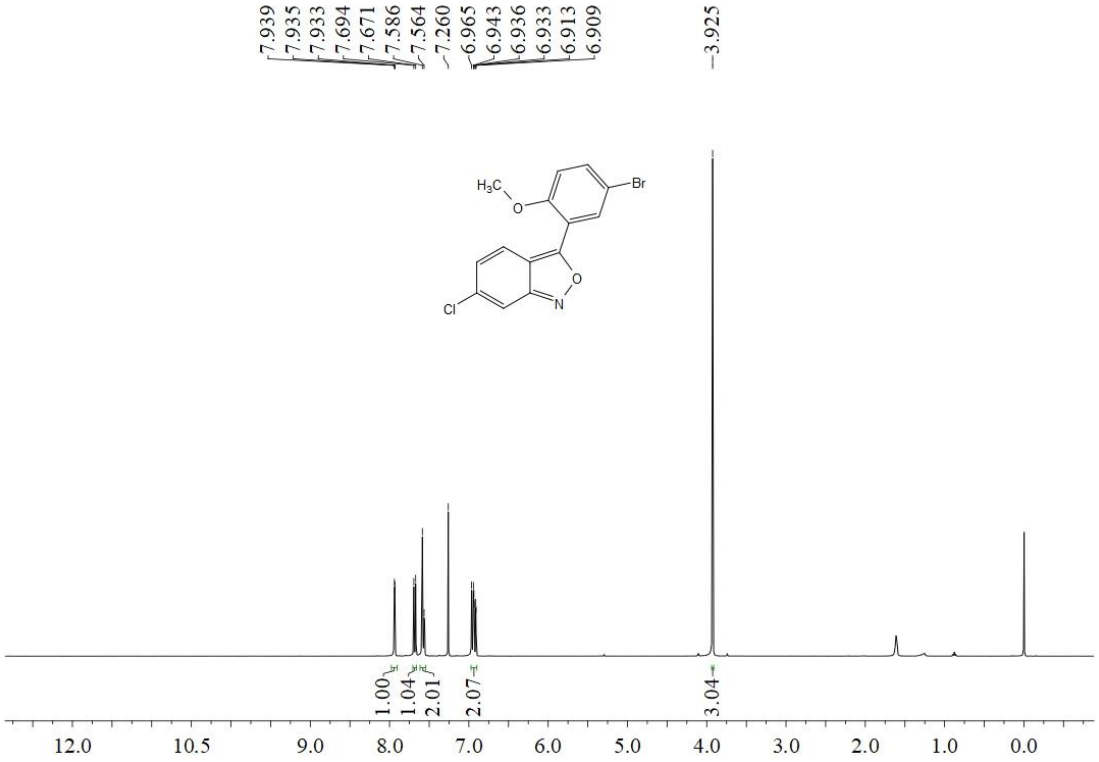


^{19}F NMR (375 MHz, $CDCl_3$)

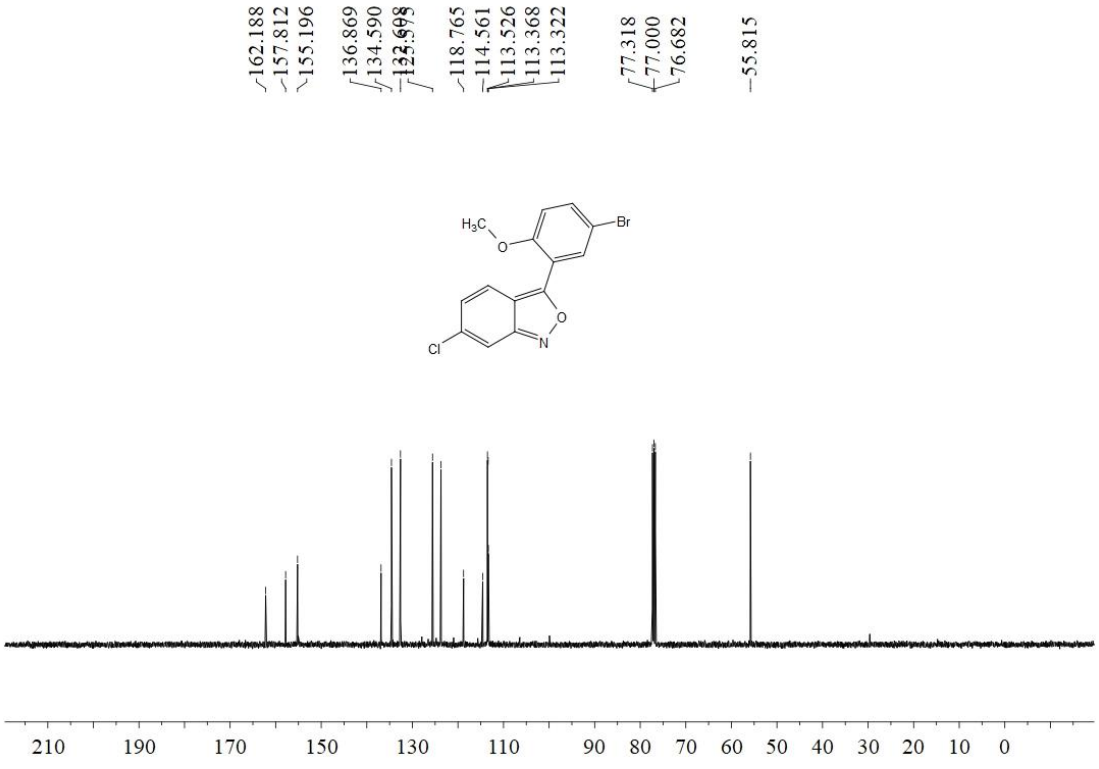

-114.699
F
H3C
O
Cl
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(5-Bromo-2-methoxyphenyl)-6-chlorobenzo[c]isoxazole (**3br**)

^{1}H NMR (400 MHz, $CDCl_3$)

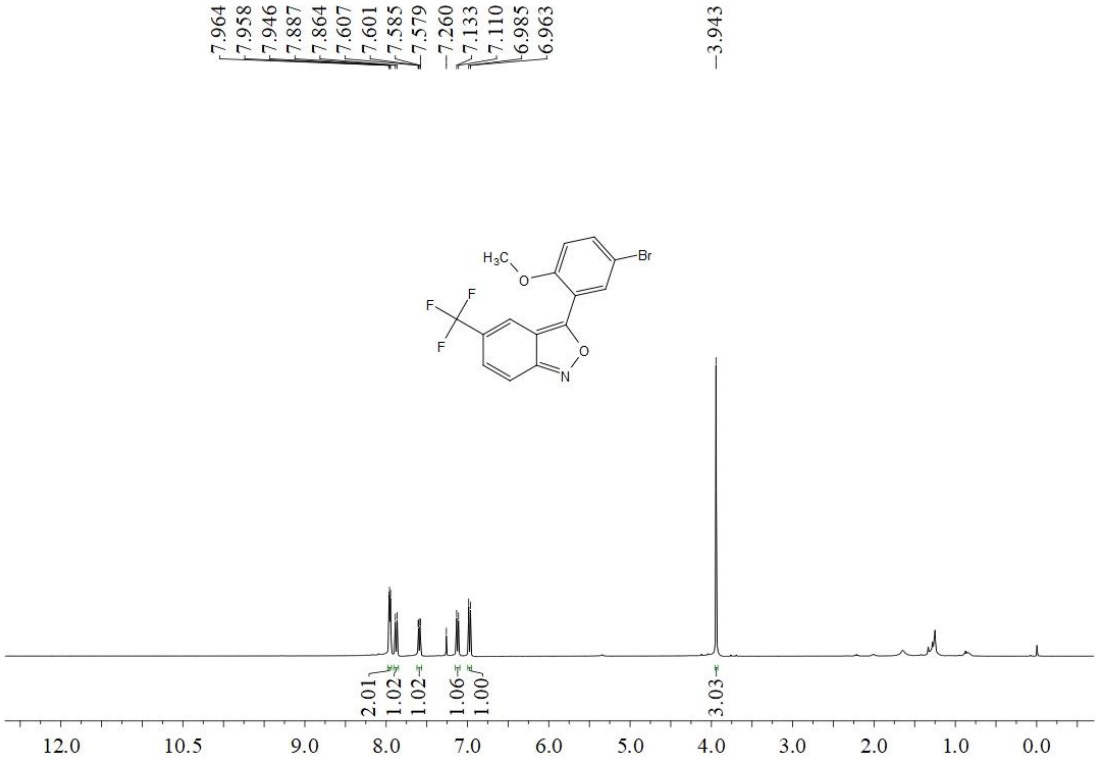


^{13}C NMR (100 MHz, $CDCl_3$)

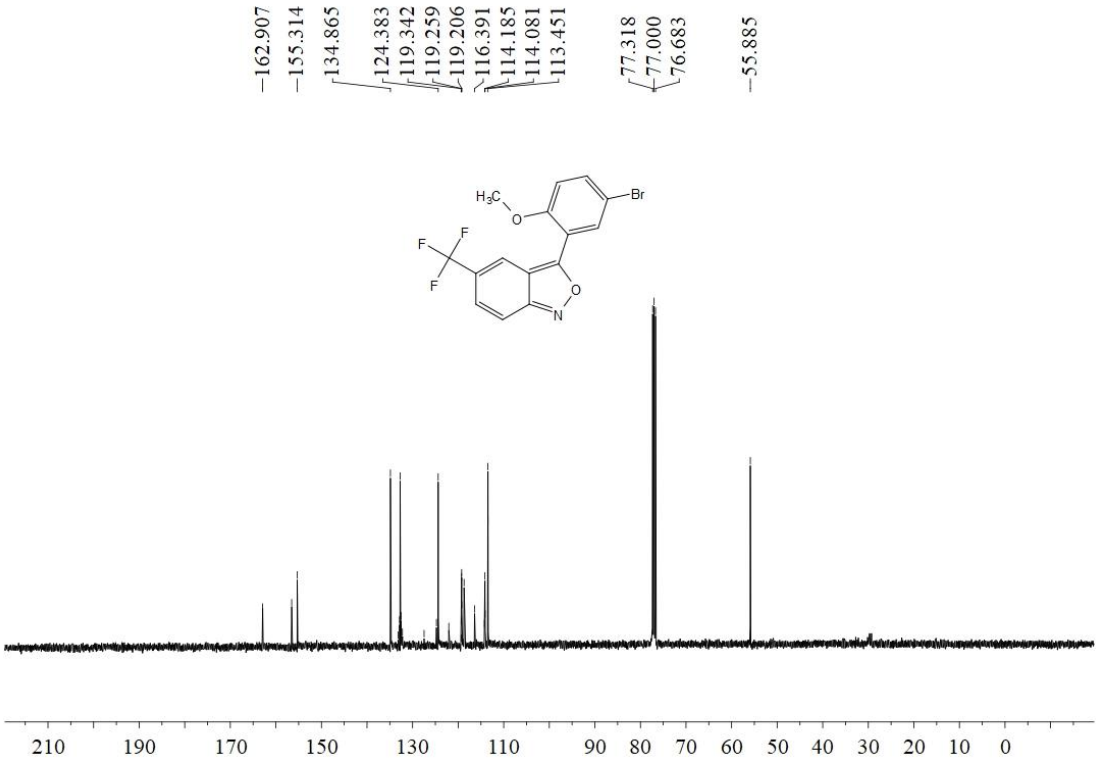


3-(5-Bromo-2-methoxyphenyl)-5-(trifluoromethyl)benzo[c]isoxazole (**3bs**)

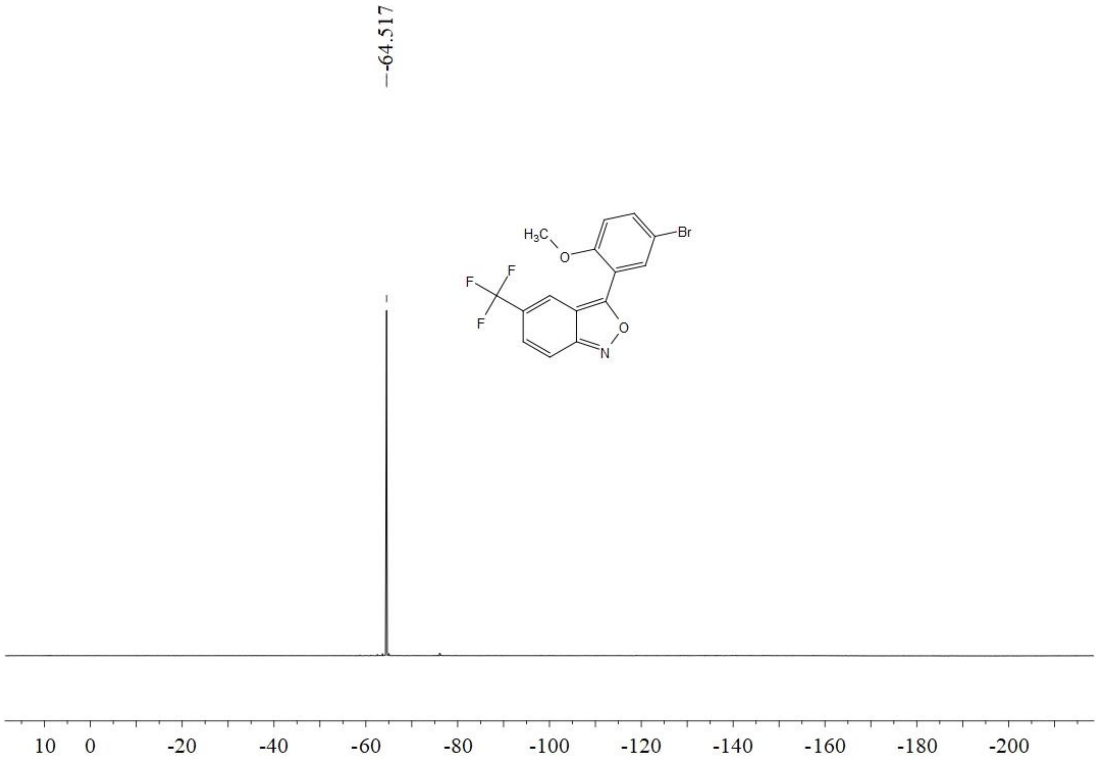
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

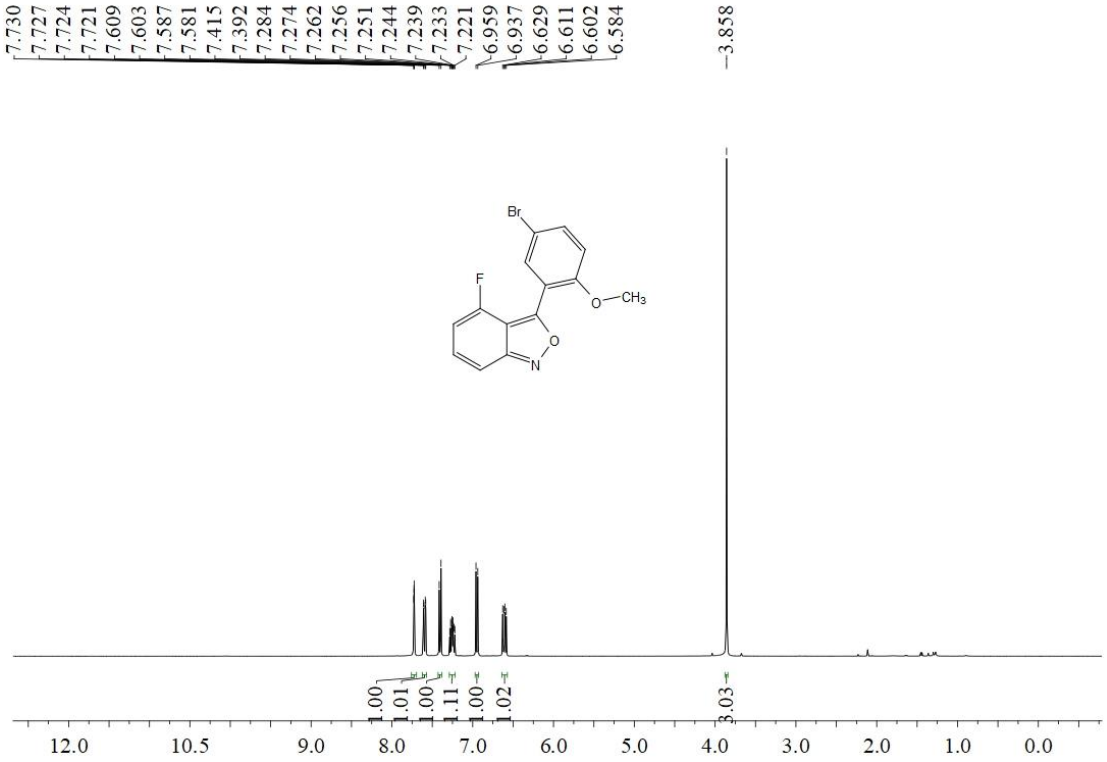


^{19}F NMR (375 MHz, $CDCl_3$)

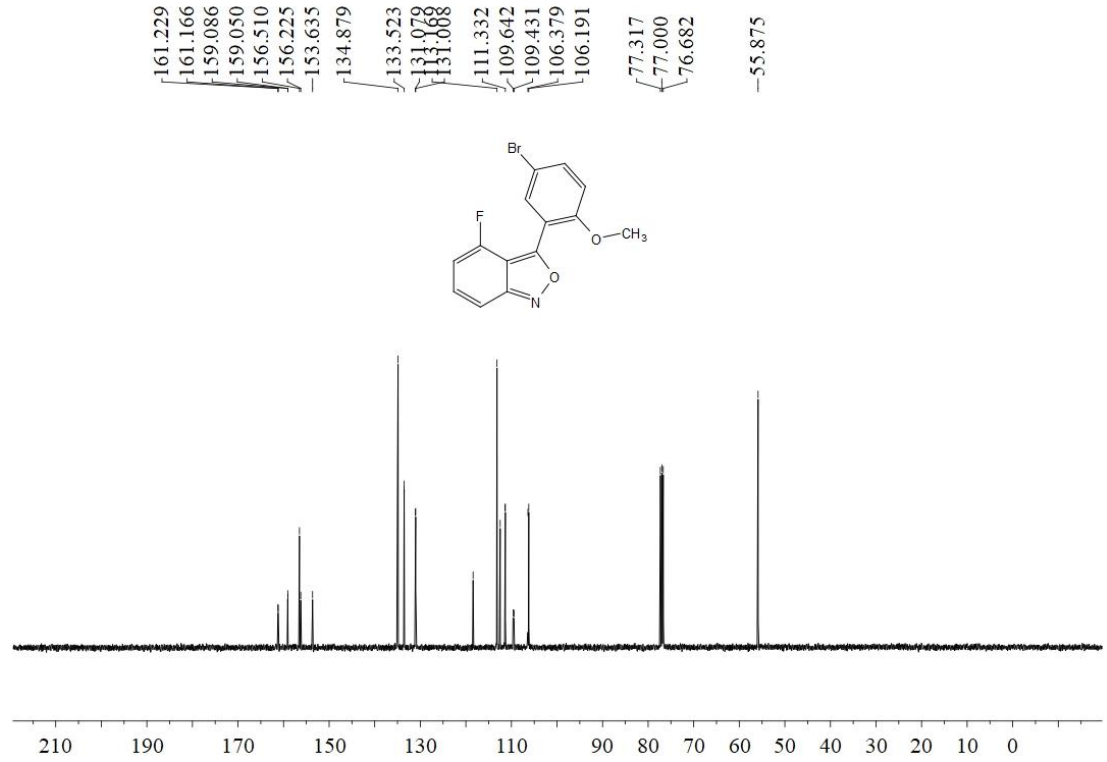

-64.517
H3C
O
Br
F
F
F
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(5-Bromo-2-methoxyphenyl)-4-fluorobenzo[c]isoxazole (**3bt**)

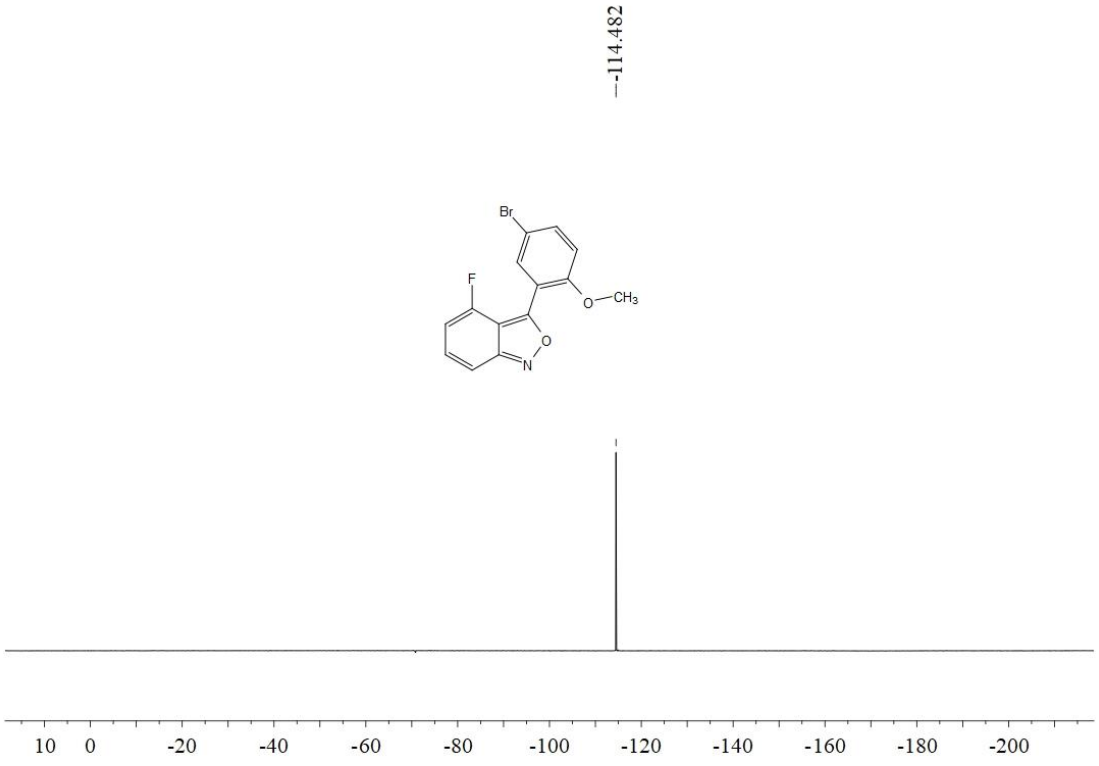
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

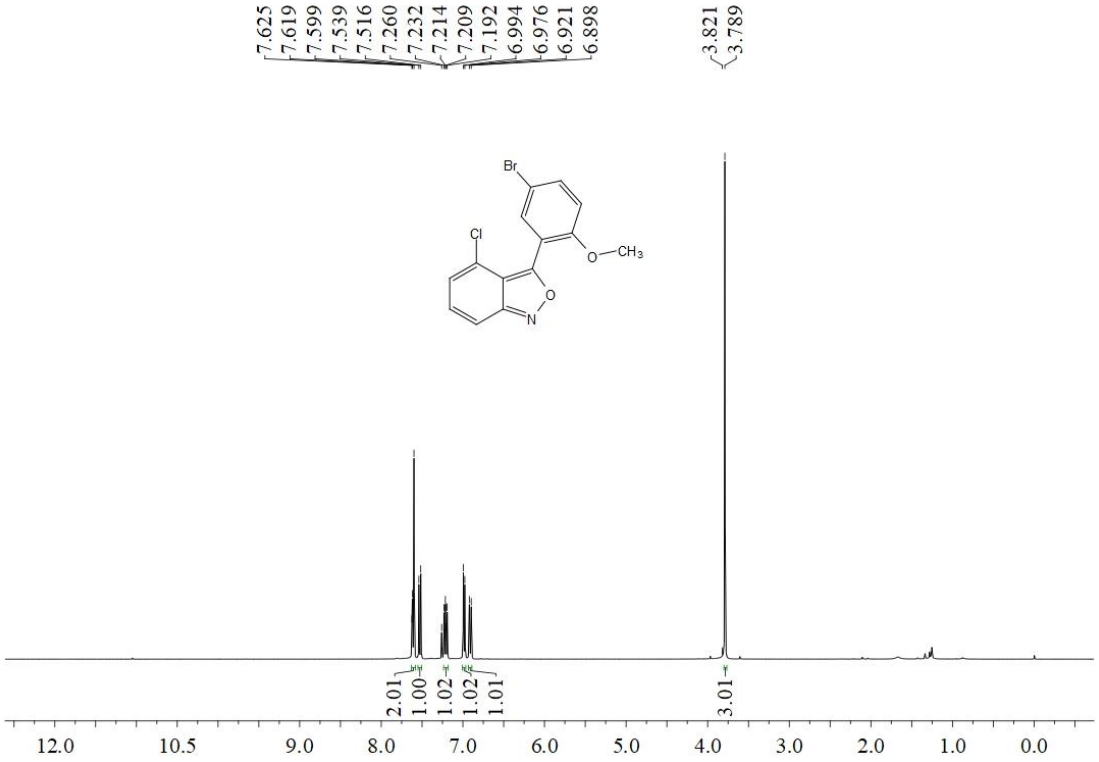


^{19}F NMR (375 MHz, $CDCl_3$)

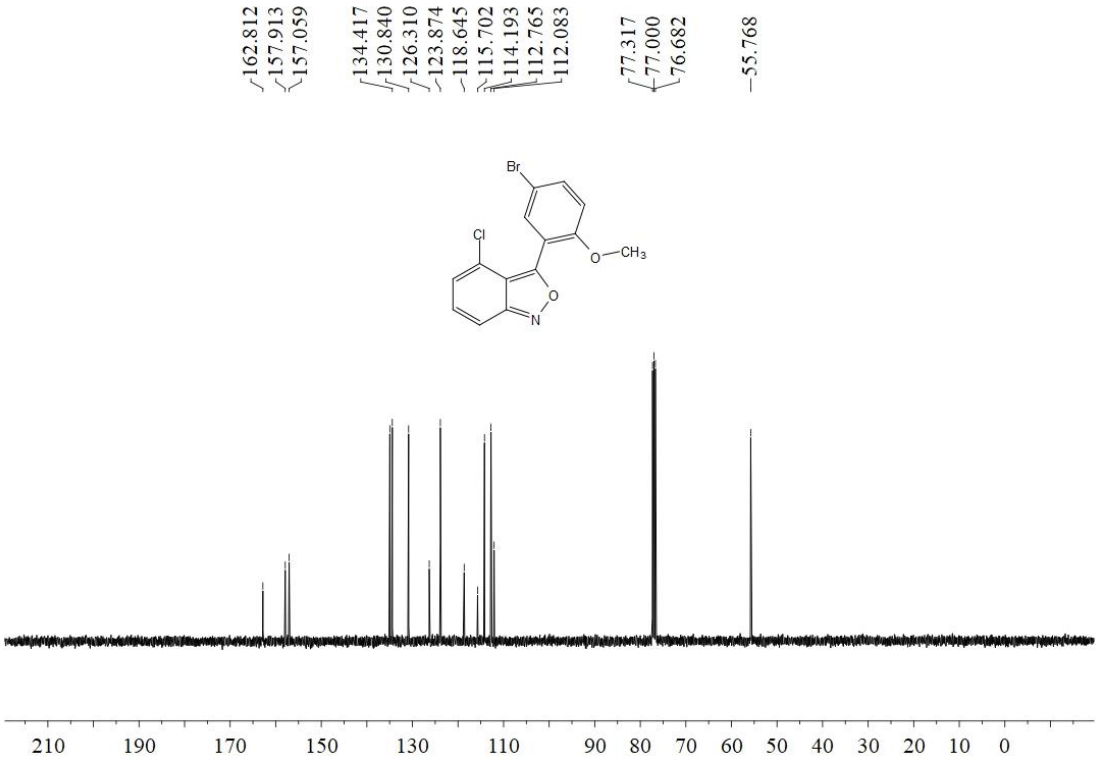

-114.482
Br
F
O
CH3
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(5-Bromo-2-methoxyphenyl)-4-chlorobenzo[c]isoxazole (**3bu**)

^{1}H NMR (400 MHz, $CDCl_3$)

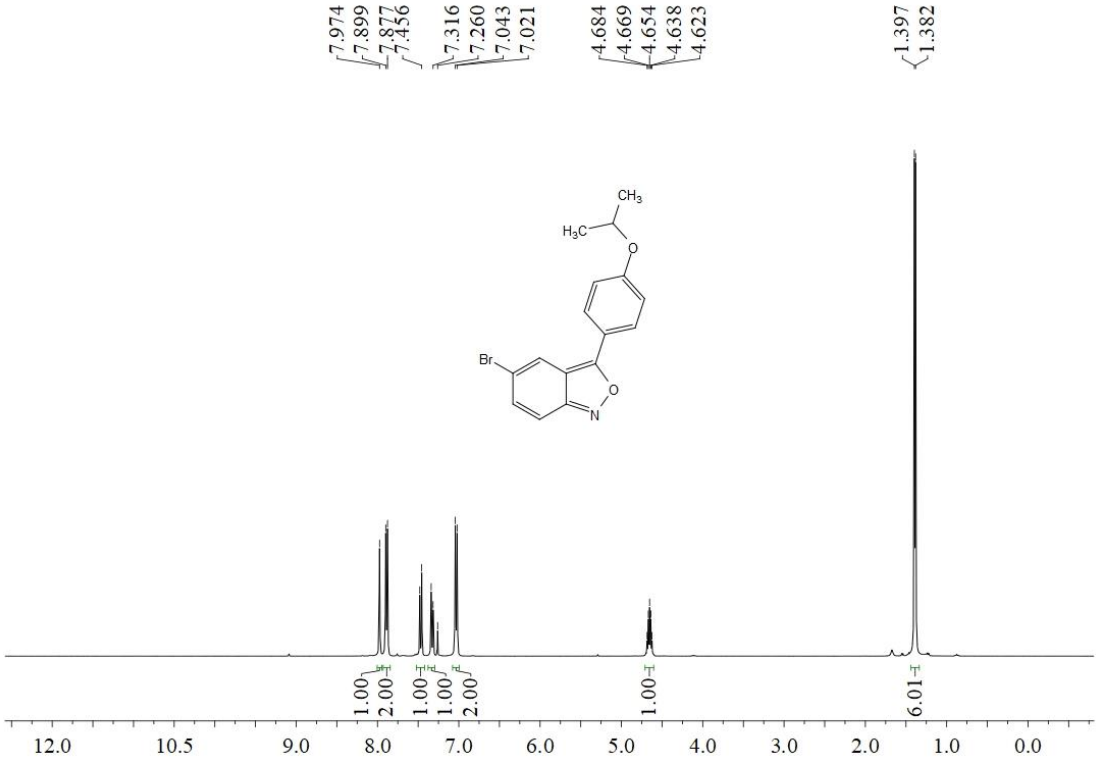


^{13}C NMR (100 MHz, $CDCl_3$)

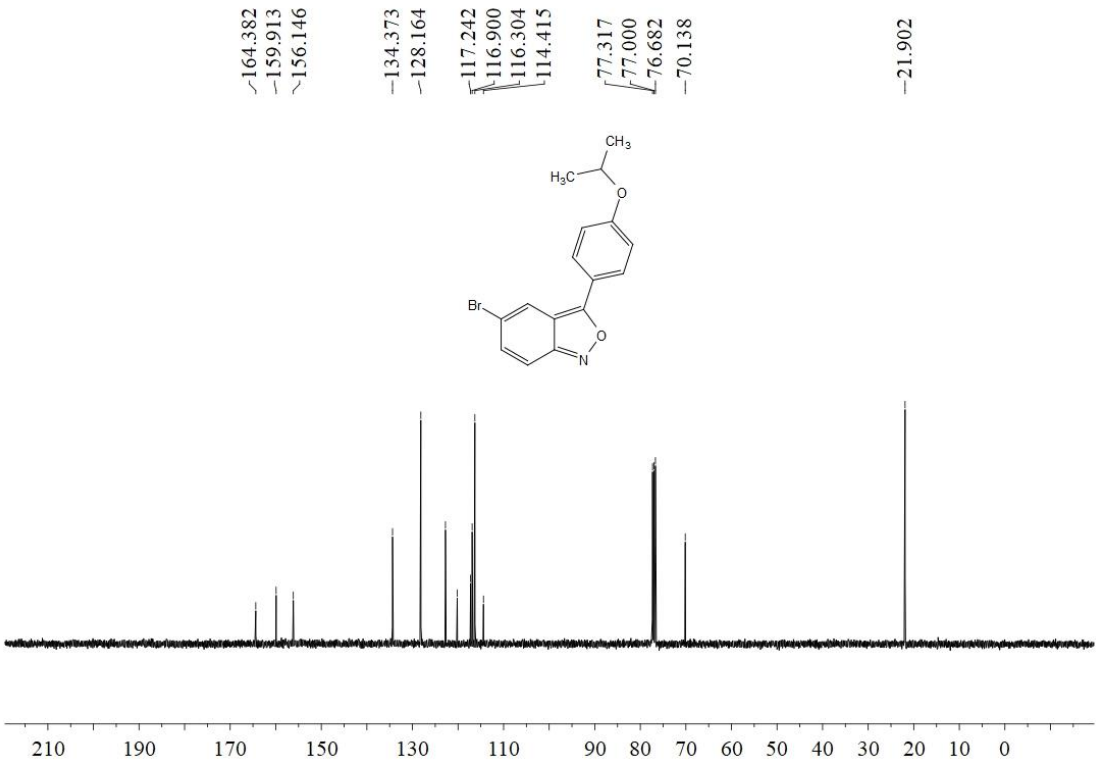


5-Bromo-3-(4-isopropoxyphenyl)benzo[c]isoxazole (**3bv**)

^{1}H NMR (400 MHz, $CDCl_3$)

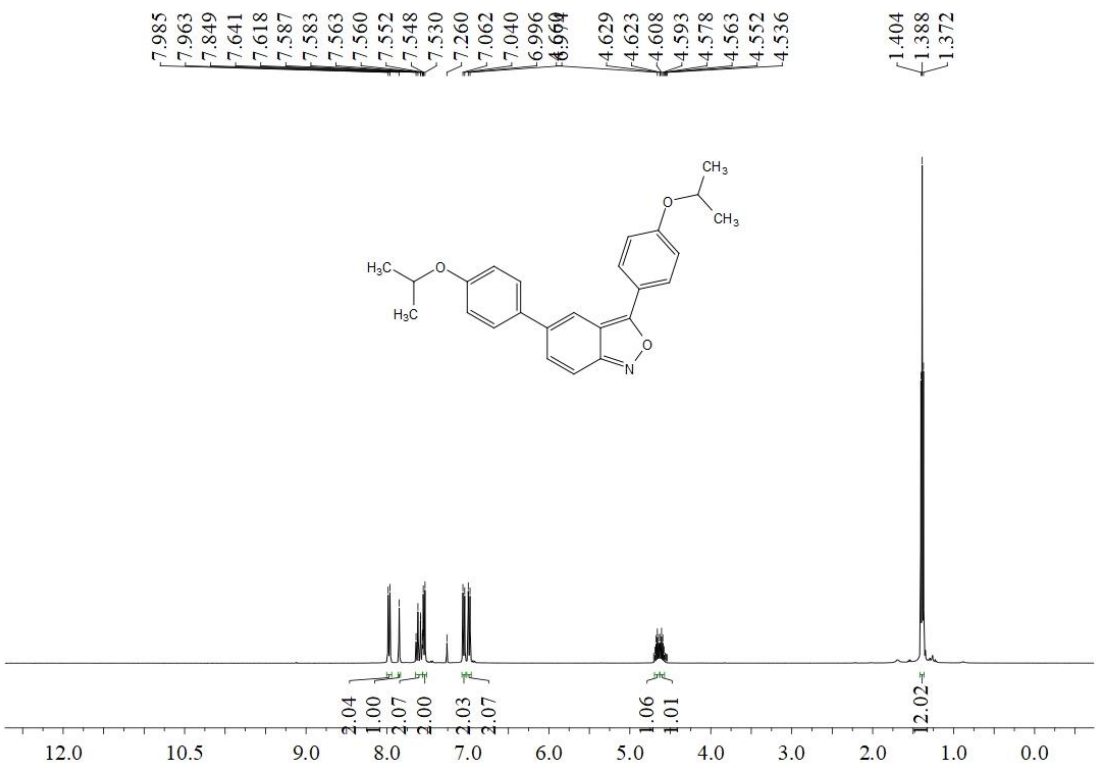


^{13}C NMR (100 MHz, $CDCl_3$)

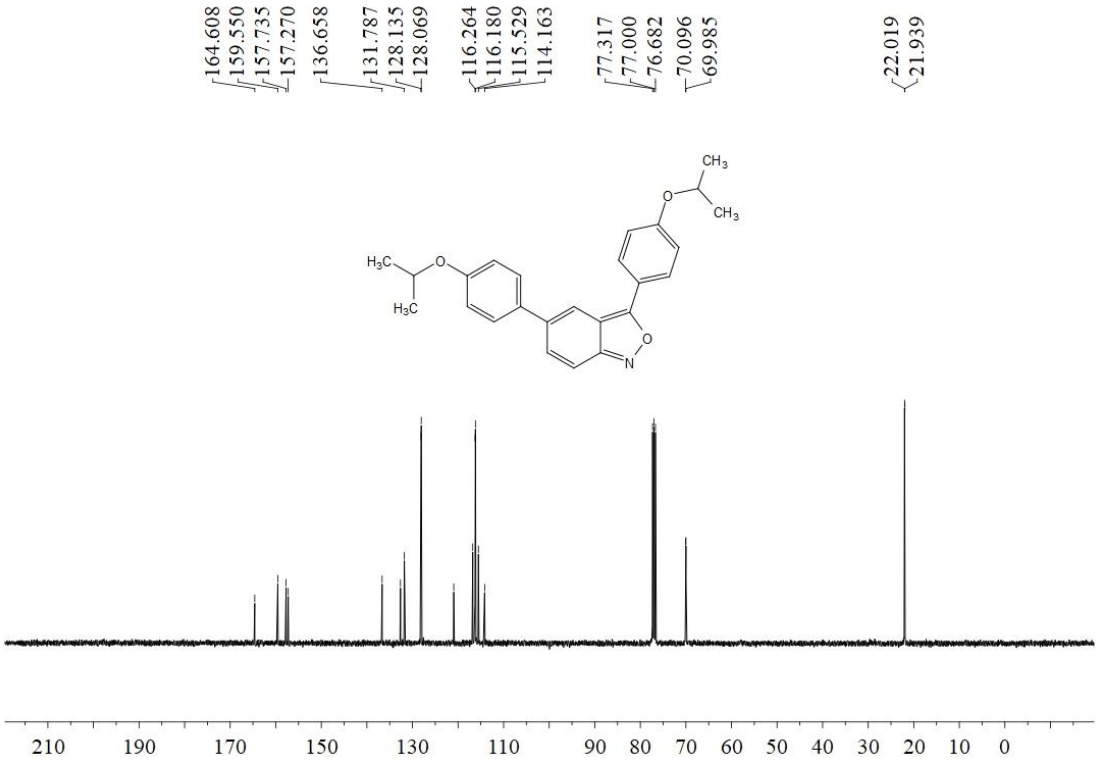


3,5-Bis(4-isopropoxyphenyl)benzo[c]isoxazole (**3bw**)

^{1}H NMR (400 MHz, $CDCl_3$)

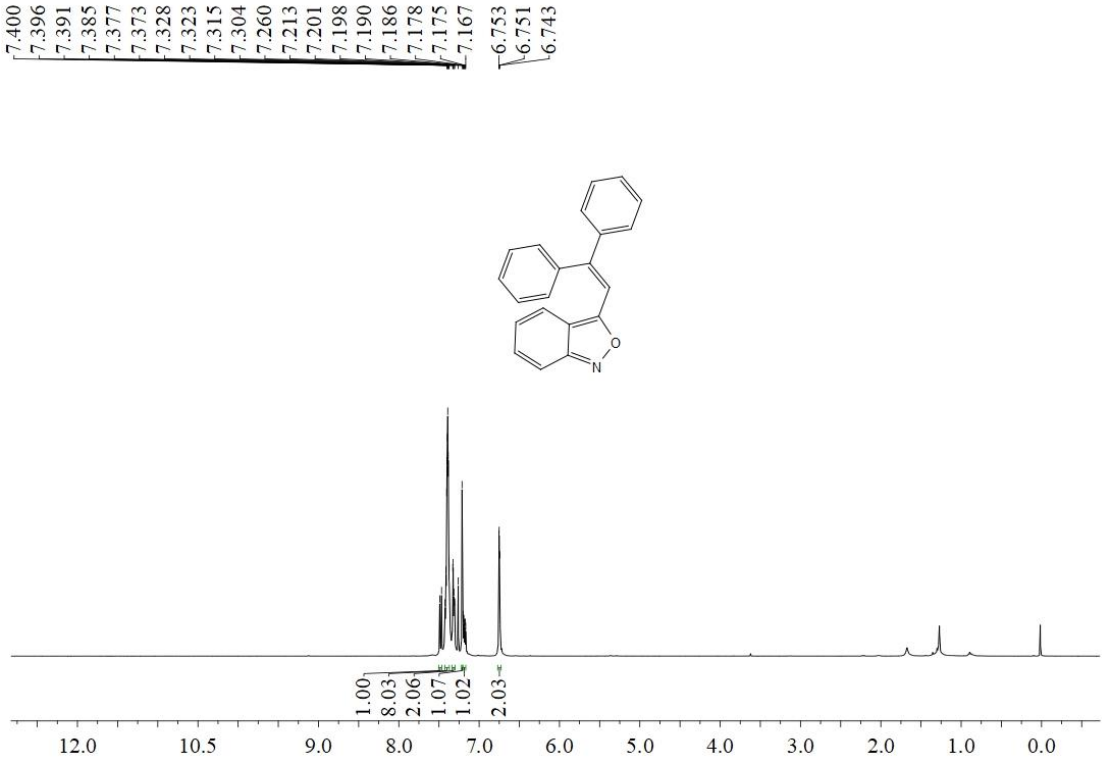


^{13}C NMR (100 MHz, $CDCl_3$)

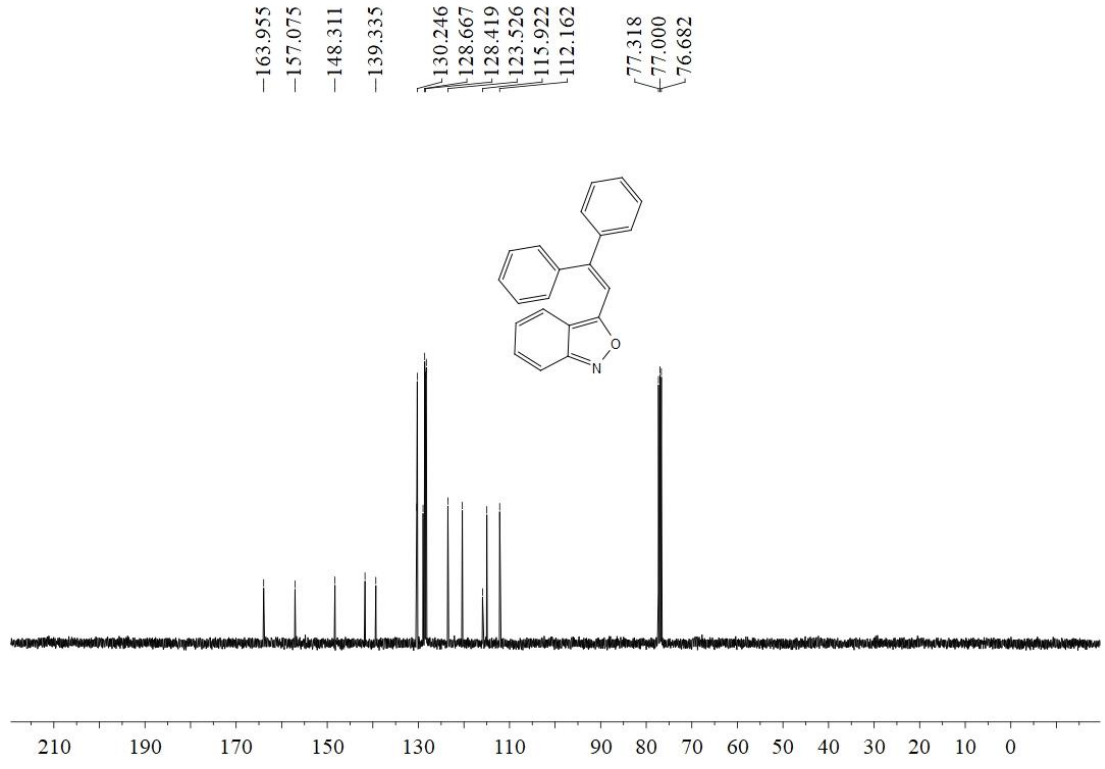


3-(2,2-Diphenylvinyl)benzo[c]isoxazole (**5a**)

^{1}H NMR (400 MHz, $CDCl_3$)

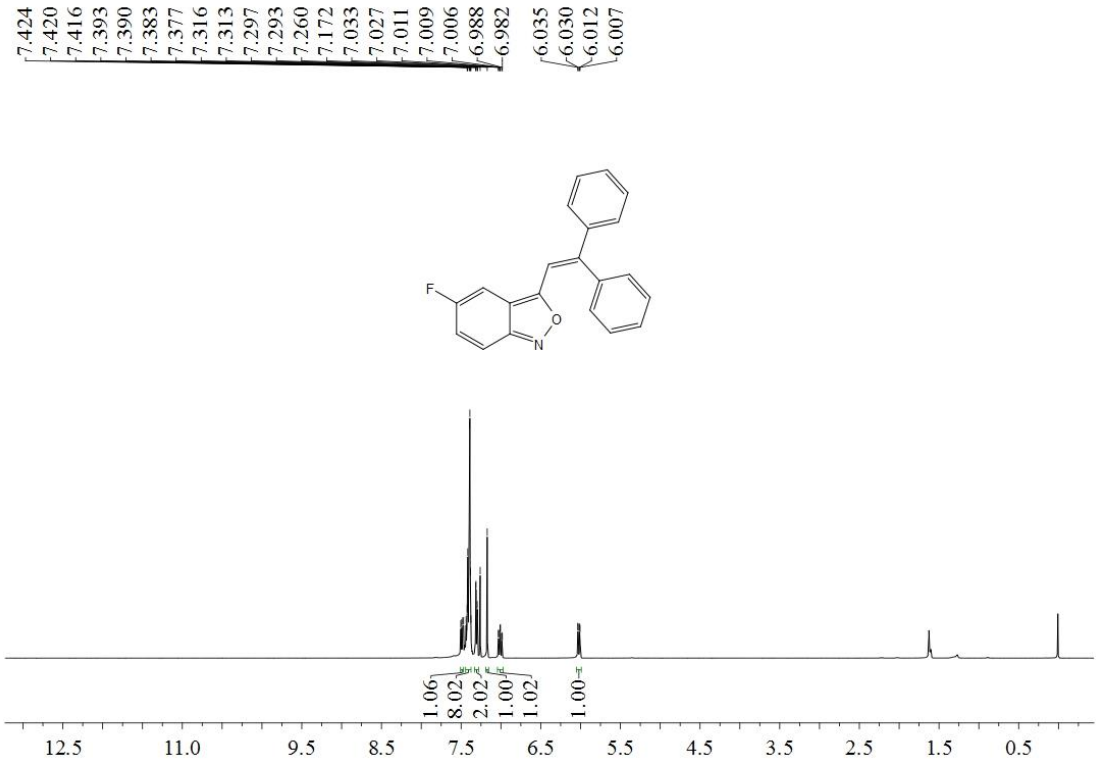


^{13}C NMR (100 MHz, $CDCl_3$)

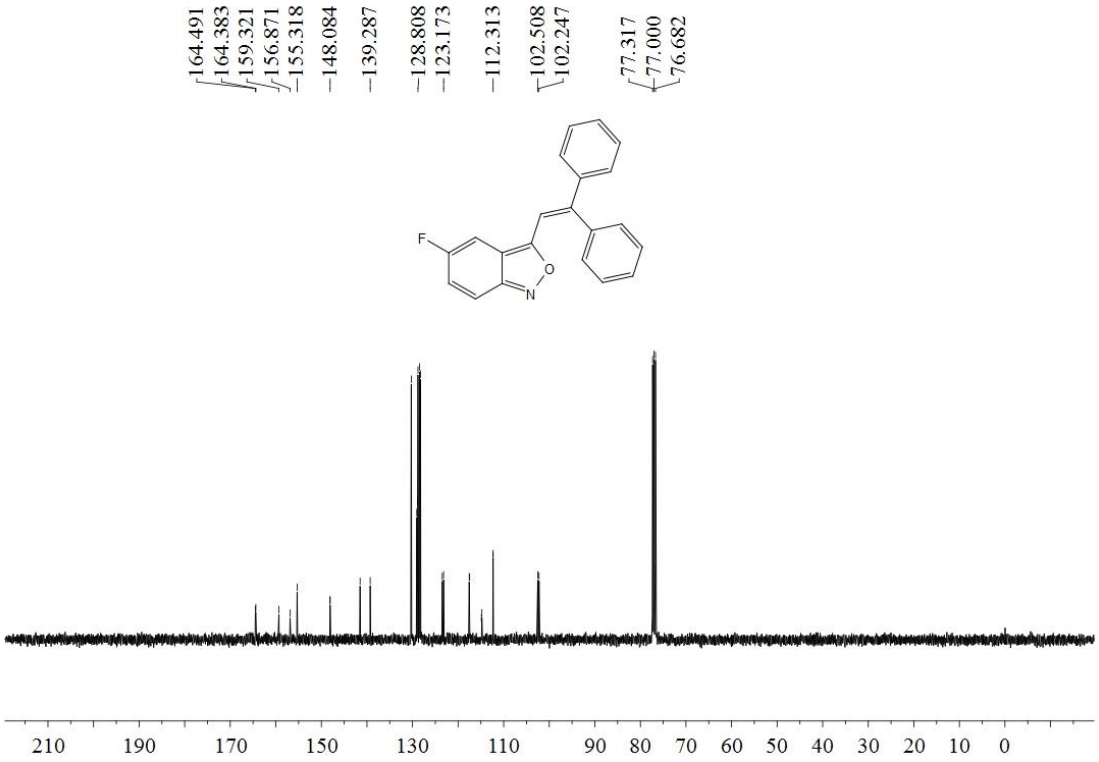


3-(2,2-Diphenylvinyl)-5-fluorobenzo[c]isoxazole (**5b**)

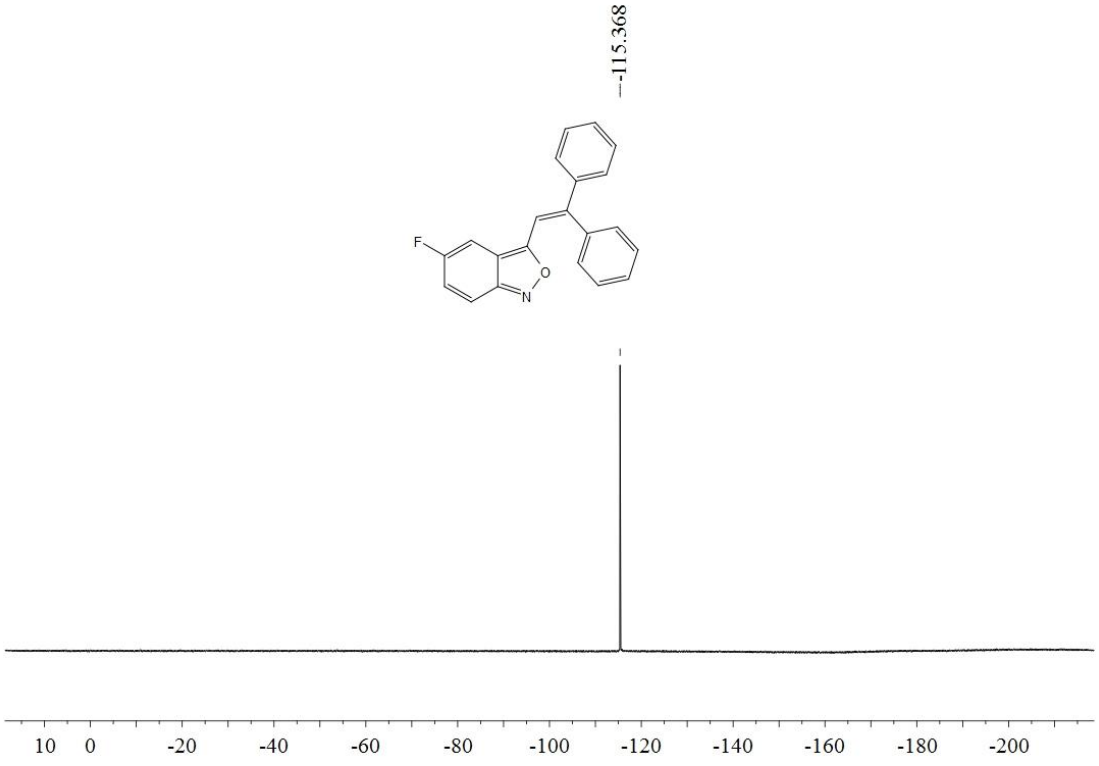
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

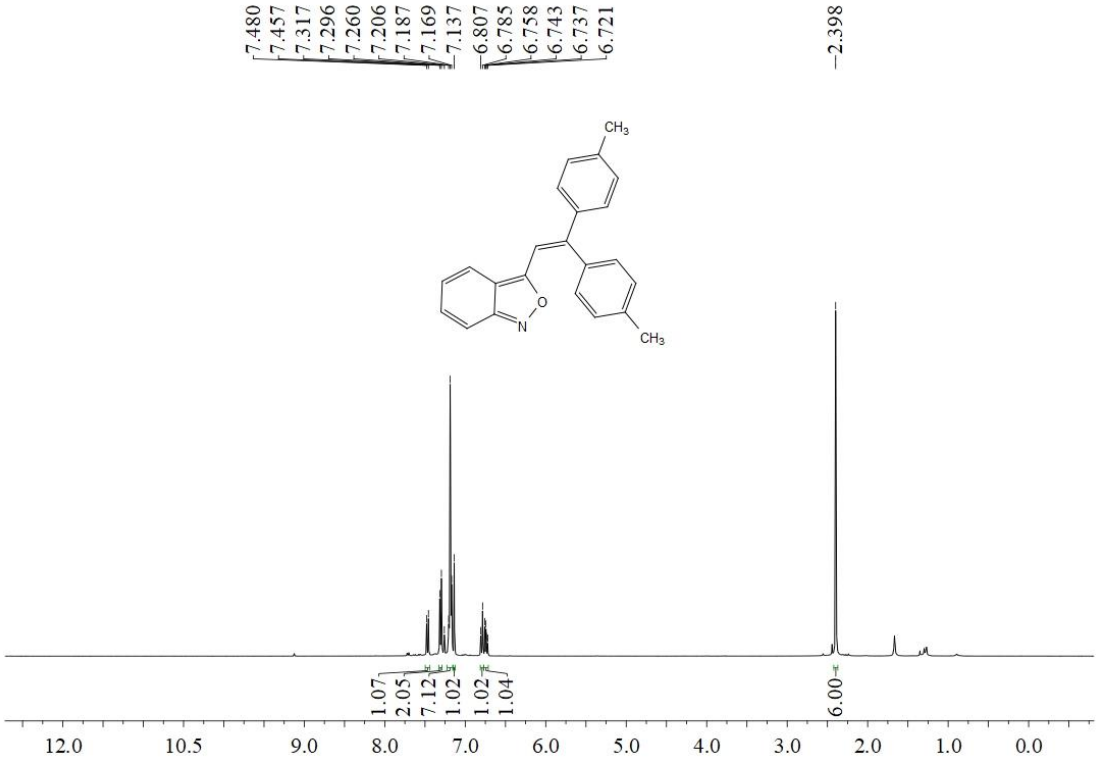


^{19}F NMR (375 MHz, $CDCl_3$)

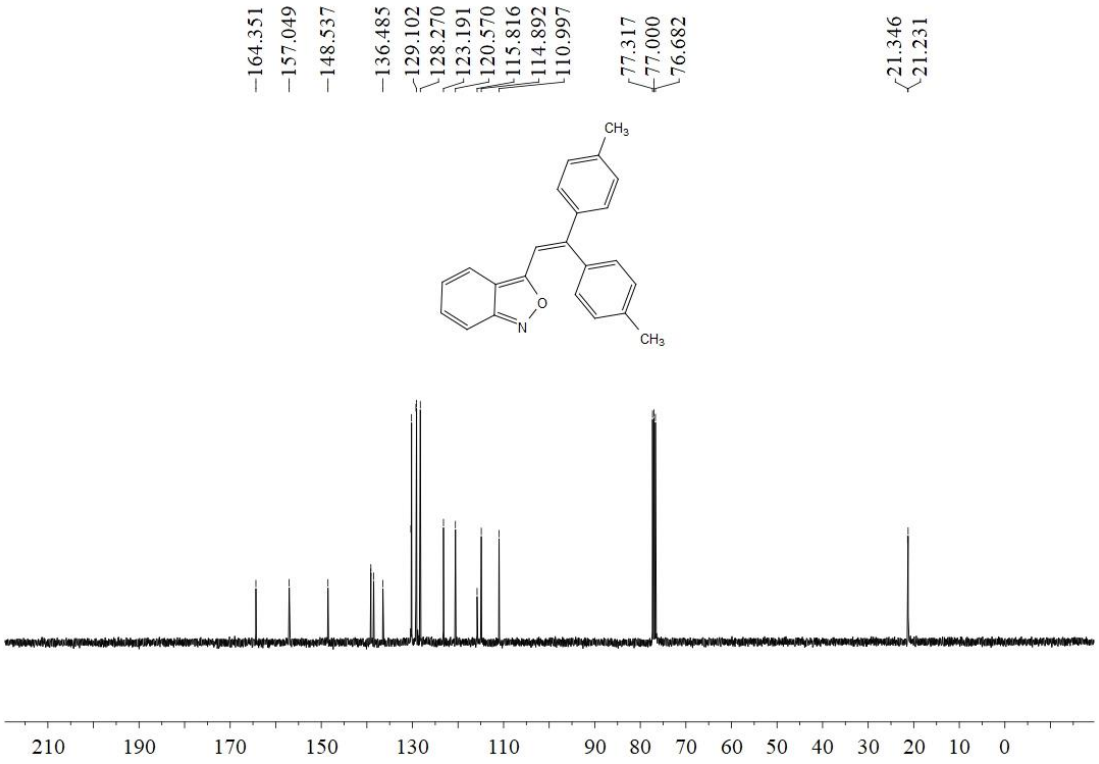

-115.368
F
O
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(2,2-Di-*p*-tolylvinyl)benzo[c]isoxazole (5c)

^{1}H NMR (400 MHz, $CDCl_3$)

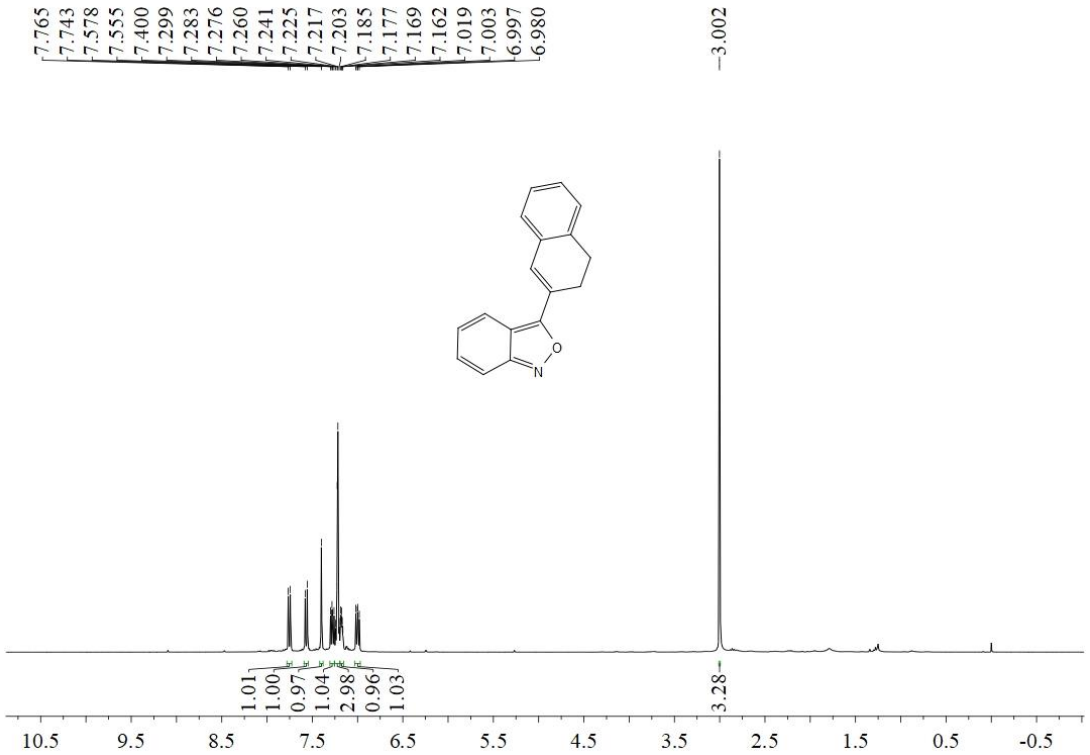


^{13}C NMR (100 MHz, $CDCl_3$)

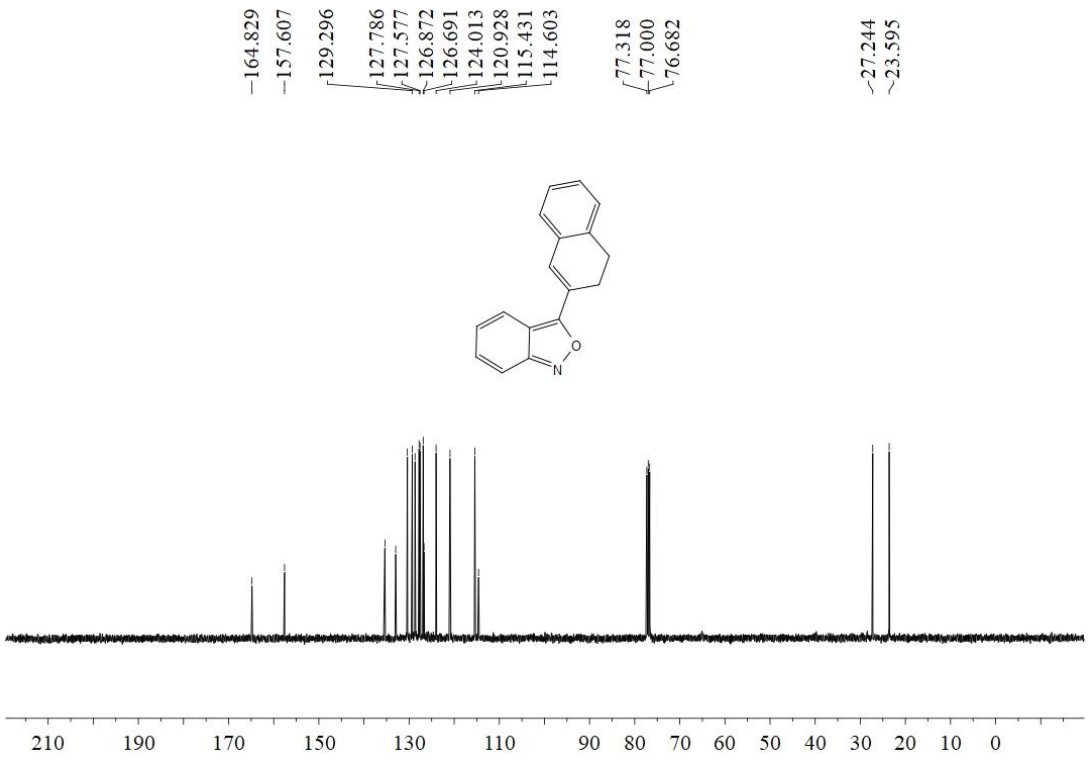


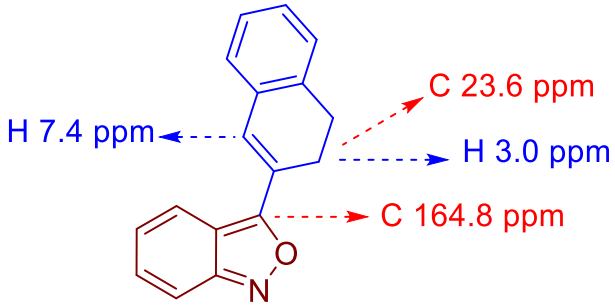
3-(3,4-Dihydronaphthalen-2-yl)benzo[c]isoxazole (**5d**)

^{1}H NMR (400 MHz, $CDCl_3$)

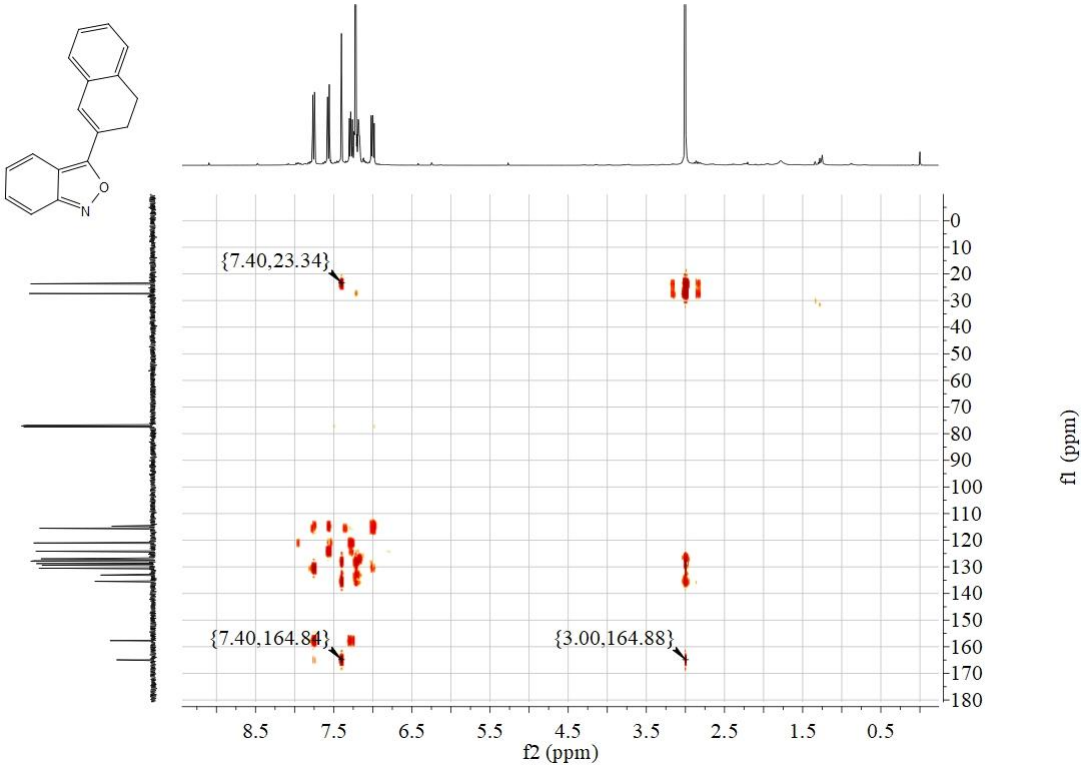


^{13}C NMR (100 MHz, $CDCl_3$)



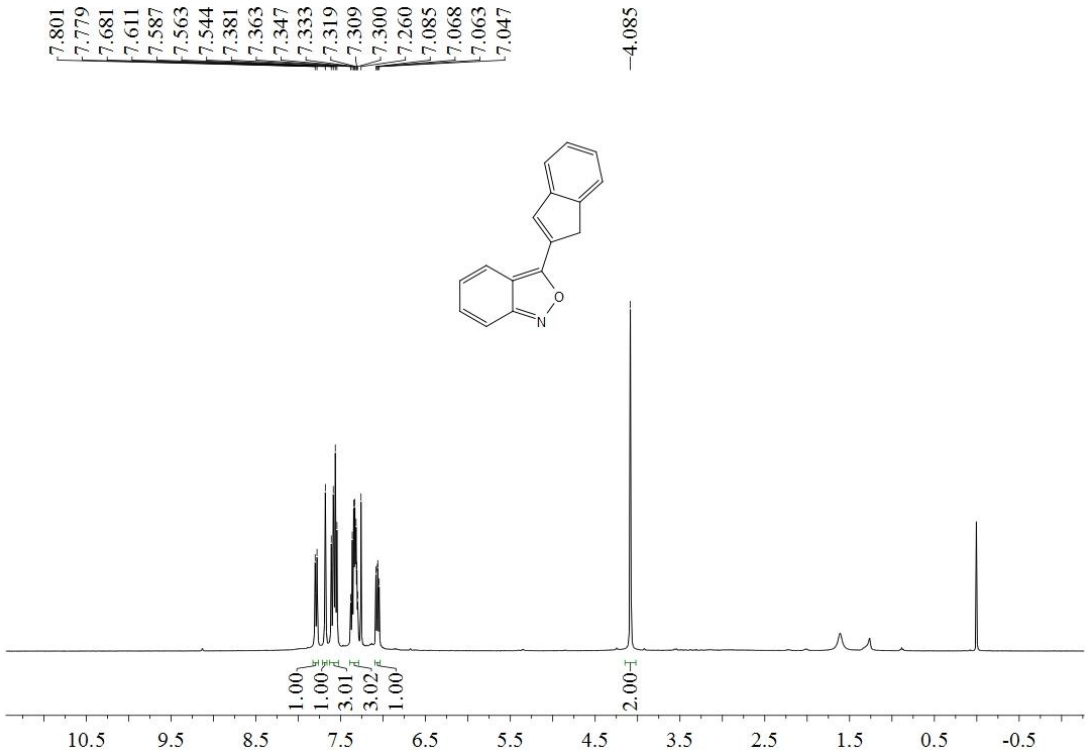


HMBC spectrum of **5d**

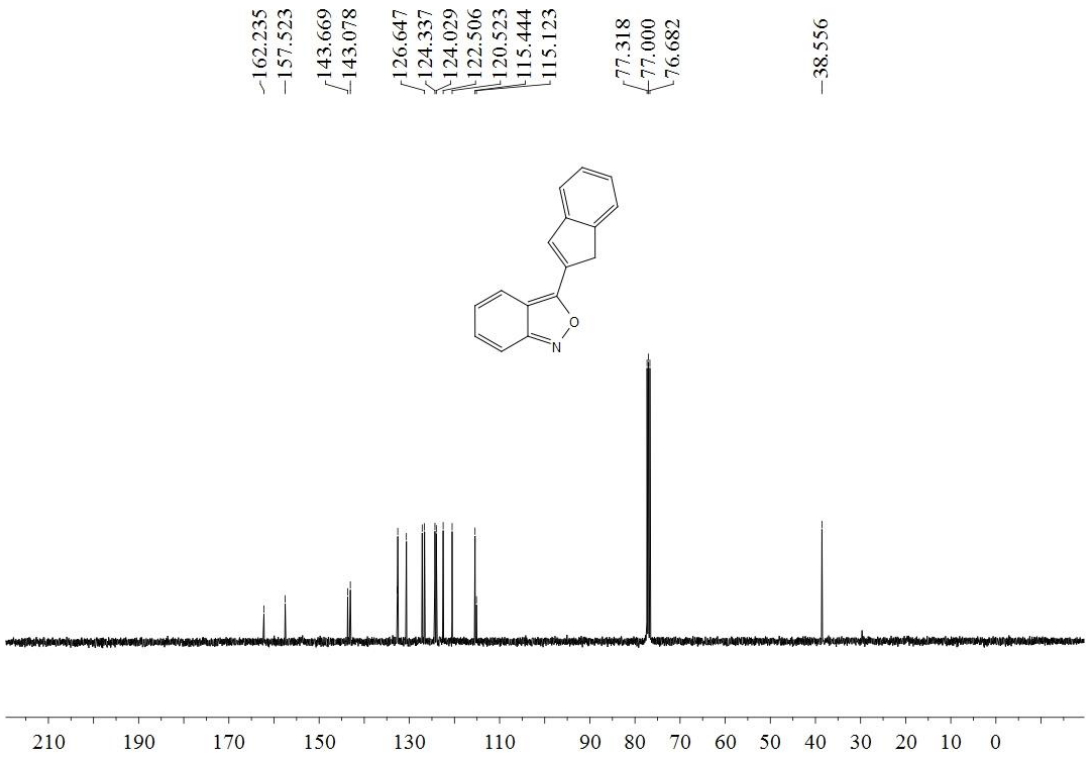


3-(1H-Inden-2-yl)benzo[c]isoxazole (**5e**)

^{1}H NMR (400 MHz, $CDCl_3$)

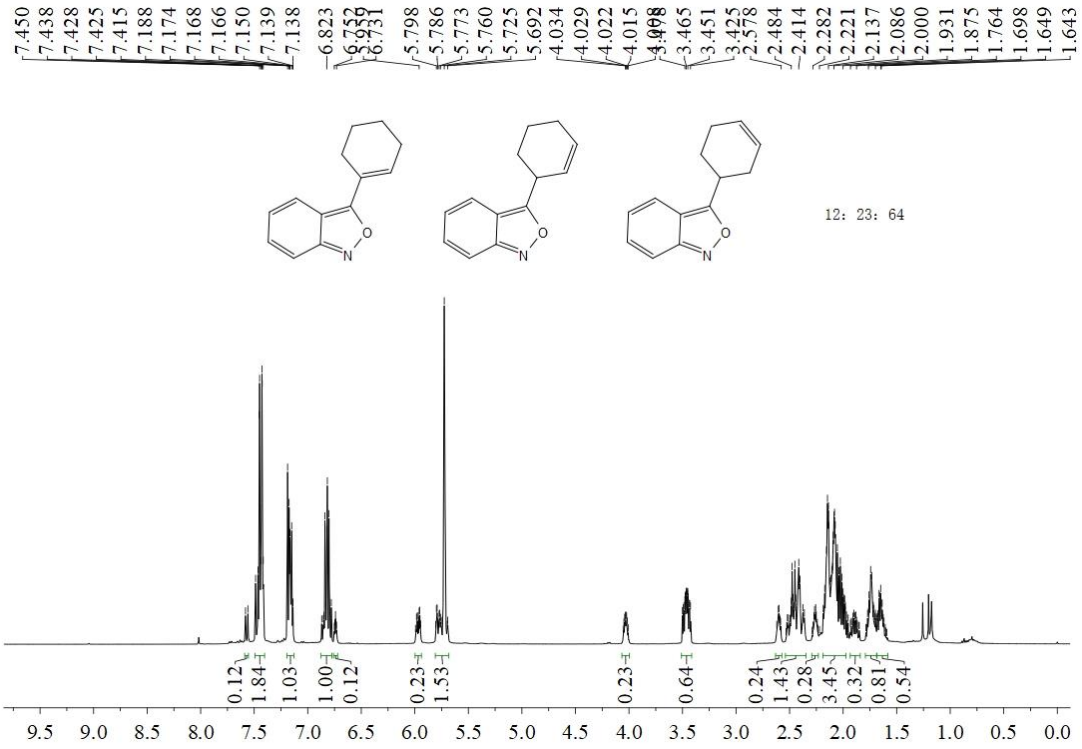


^{13}C NMR (100 MHz, $CDCl_3$)

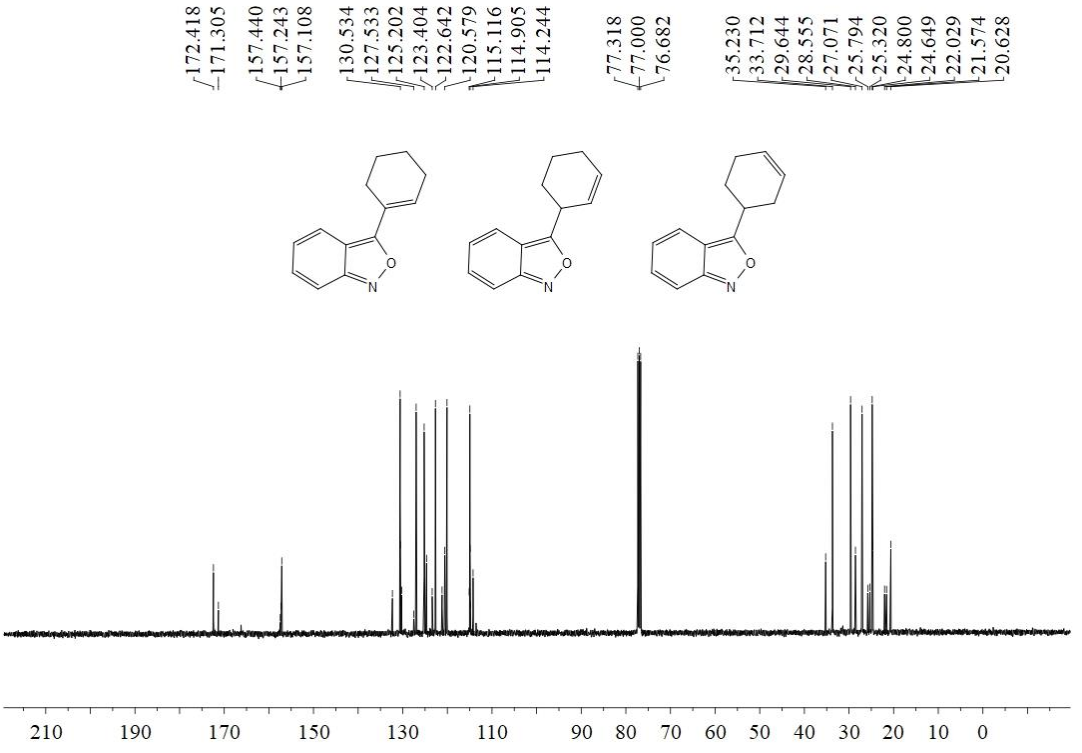


Mixture of 3-(cyclohex-1-en-1-yl)benzo[c]isoxazole, 3-(cyclohex-2-en-1-yl)benzo[c]isoxazole and 3-(cyclohex-3-en-1-yl)benzo[c]isoxazole (**5f**)

^{1}H NMR (400 MHz, $CDCl_3$)

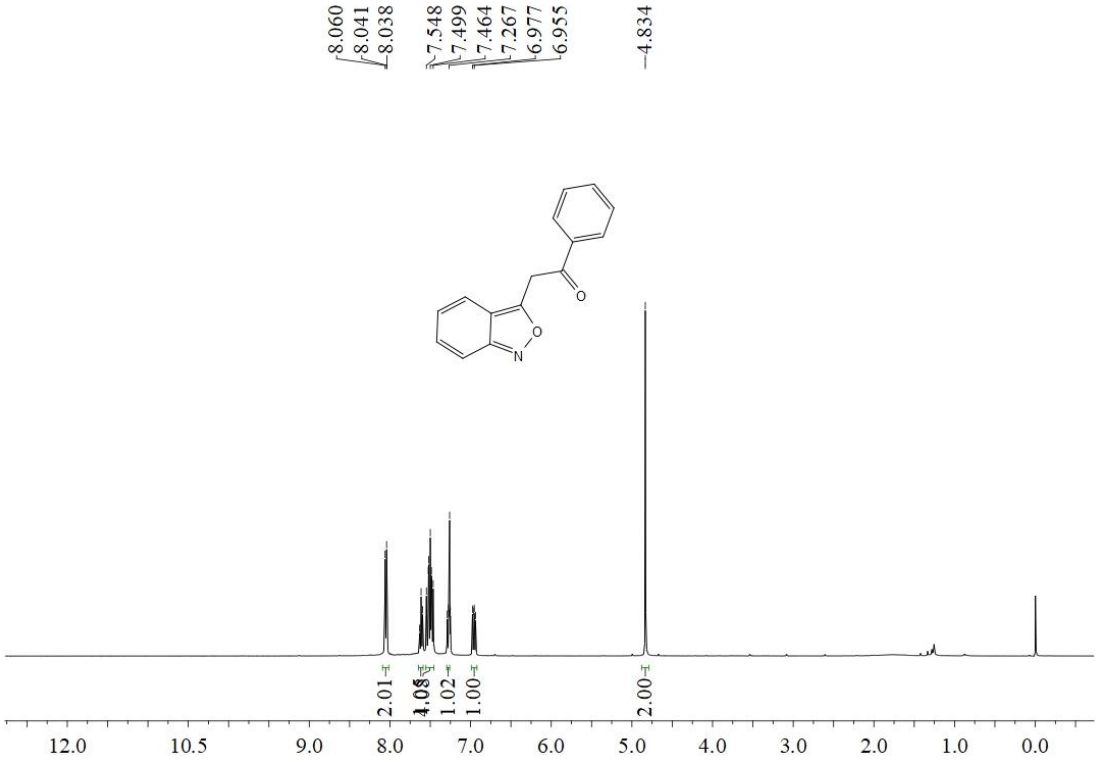


^{13}C NMR (100 MHz, $CDCl_3$)

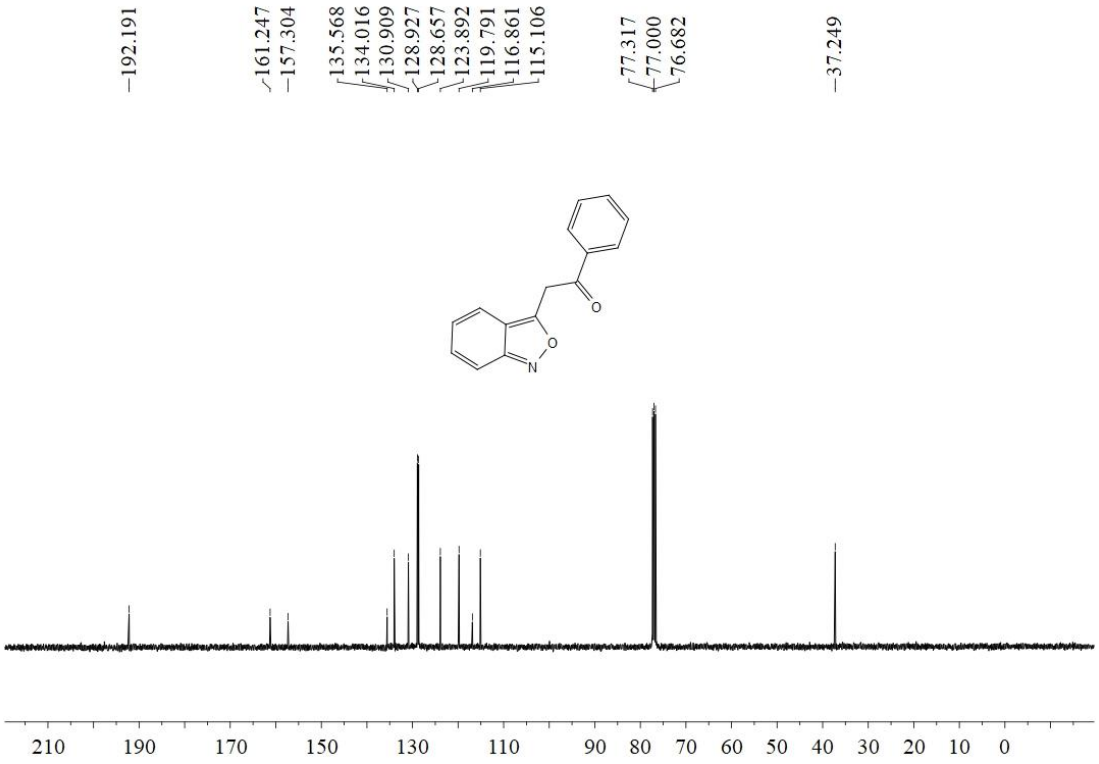


2-(Benzo[c]isoxazol-3-yl)-1-phenylethan-1-one (**7a**)

^{1}H NMR (400 MHz, $CDCl_3$)

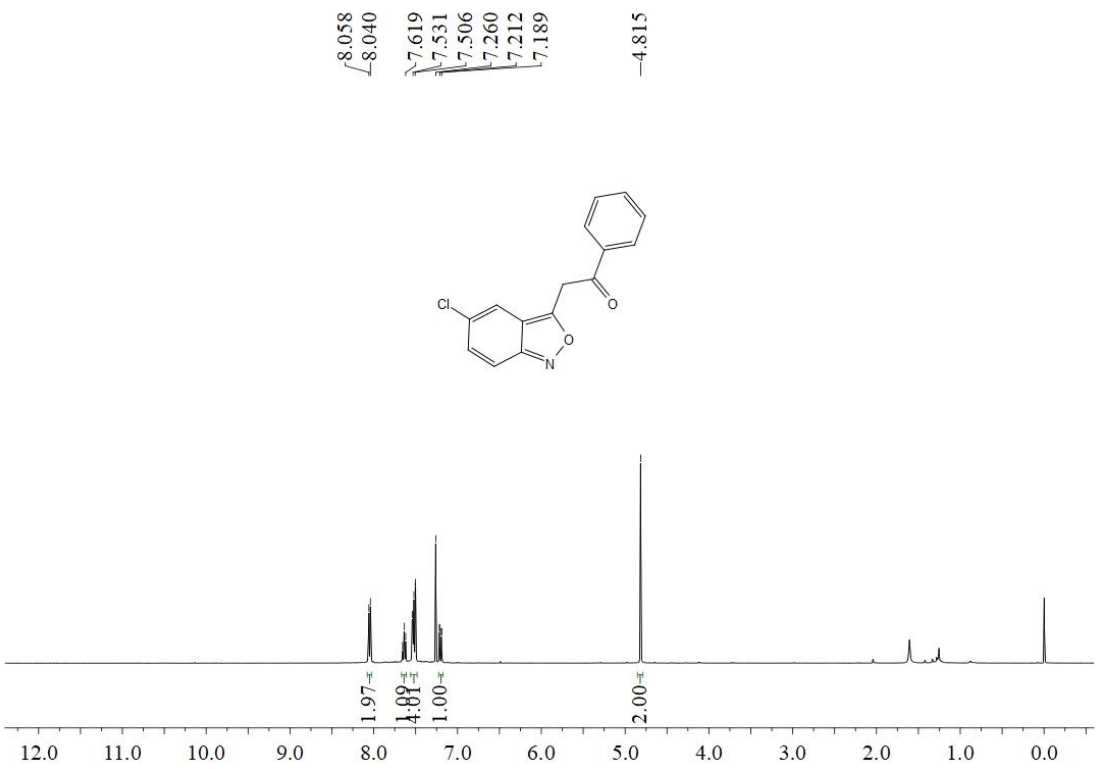


^{13}C NMR (100 MHz, $CDCl_3$)

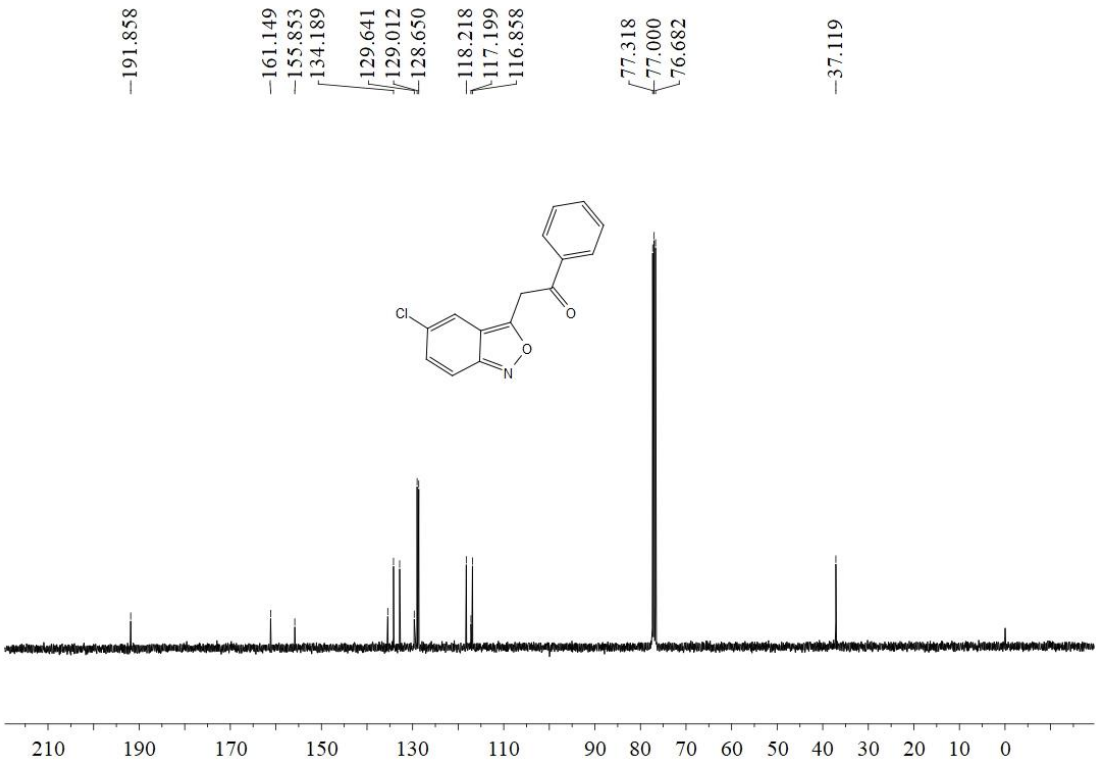


2-(5-Chlorobenzo[c]isoxazol-3-yl)-1-phenylethan-1-one (**7b**)

^{1}H NMR (400 MHz, $CDCl_3$)

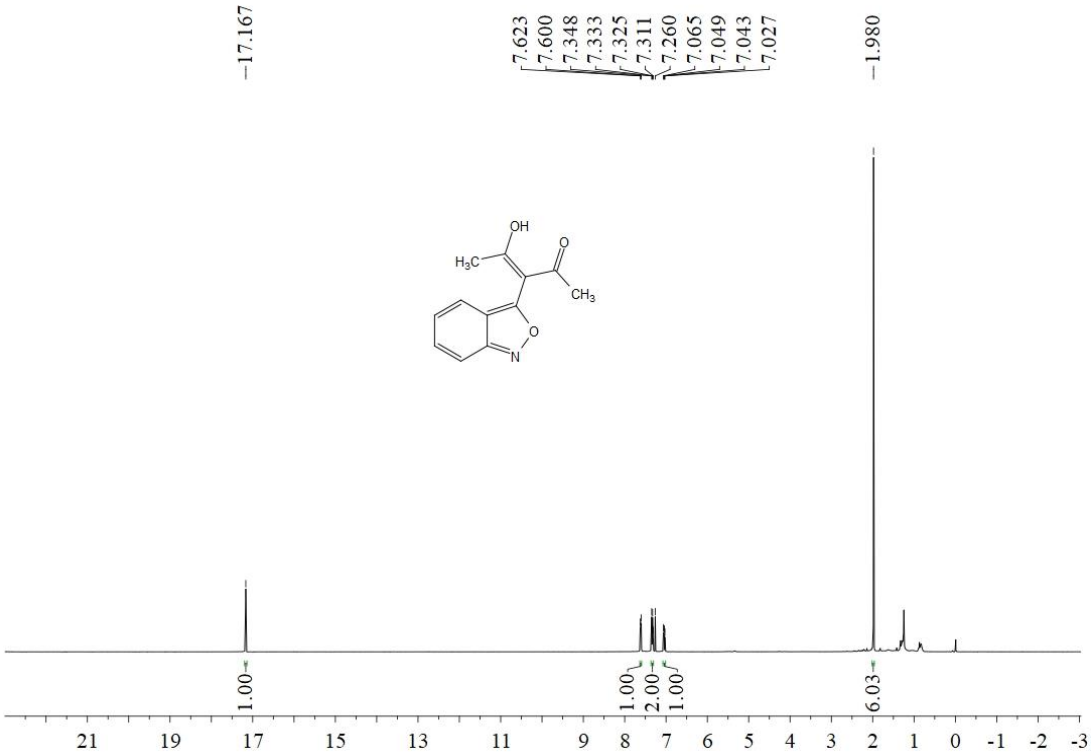


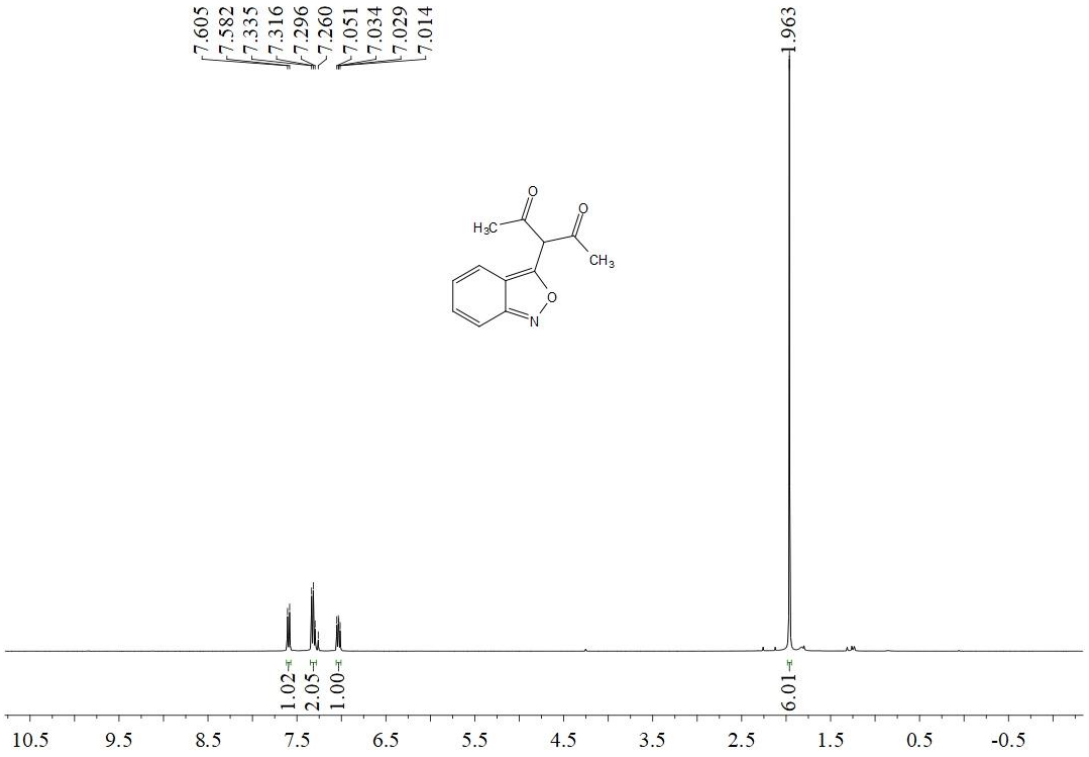
^{13}C NMR (100 MHz, $CDCl_3$)



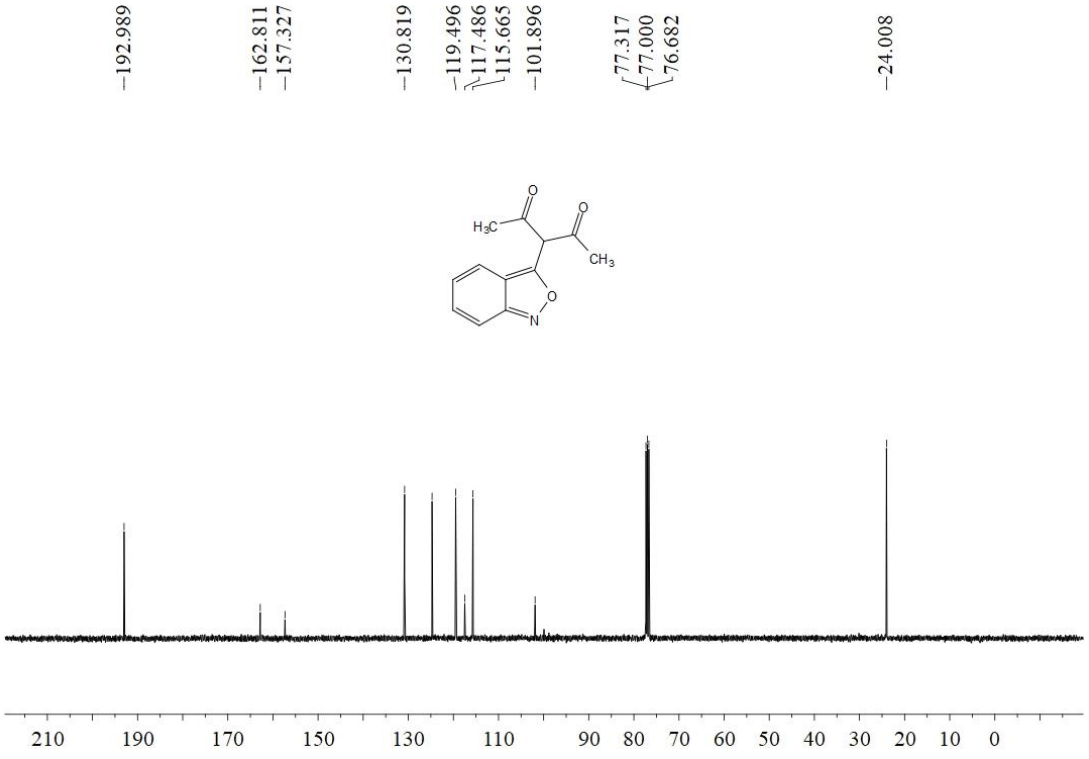
3-(Benzo[c]isoxazol-3-yl)pentane-2,4-dione (**7c**)

^{1}H NMR (400 MHz, $CDCl_3$)



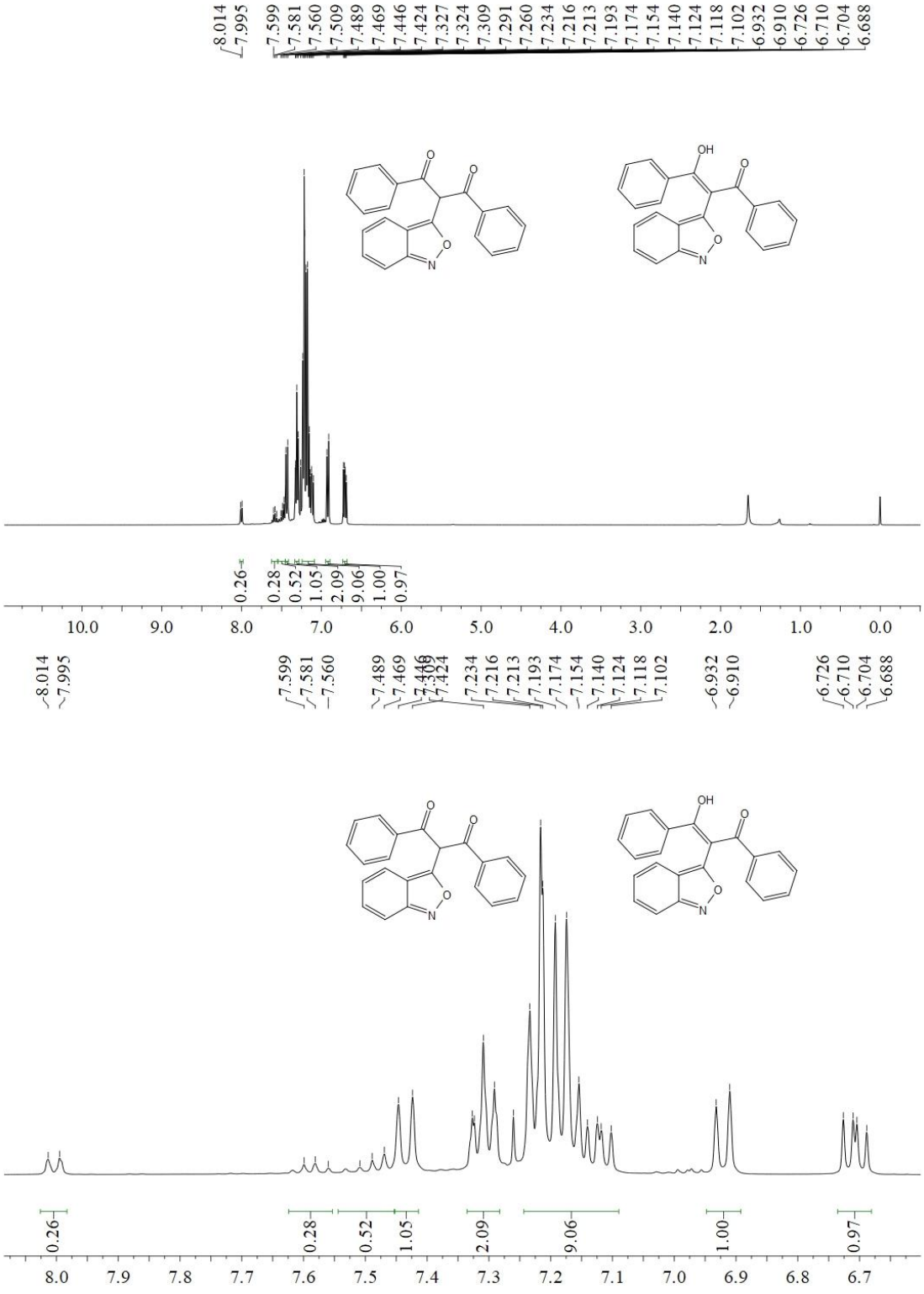


^{13}C NMR (100 MHz, $CDCl_3$)

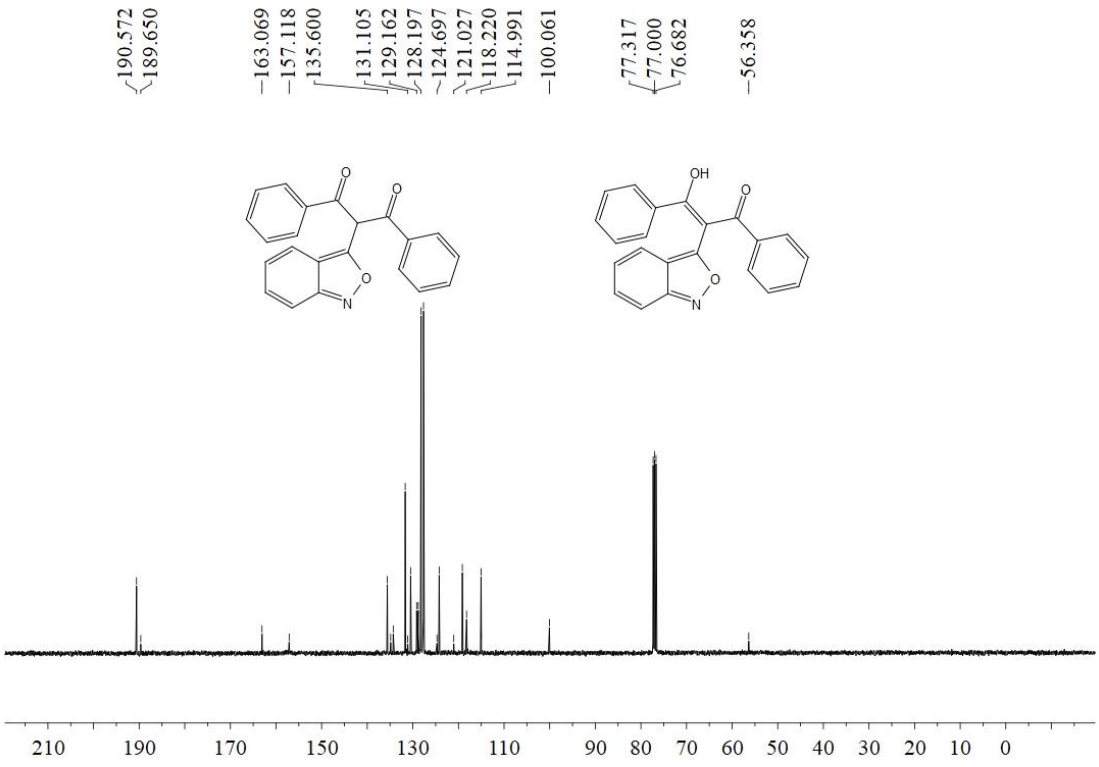

192.989
162.811
157.327
130.819
119.496
117.486
115.665
101.896
77.317
77.000
76.682
24.008
O
H3C
O
CH3
O
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

2-(Benzo[c]isoxazol-3-yl)-1,3-diphenylpropane-1,3-dione (**7d**)

^{1}H NMR (400 MHz, $CDCl_3$)

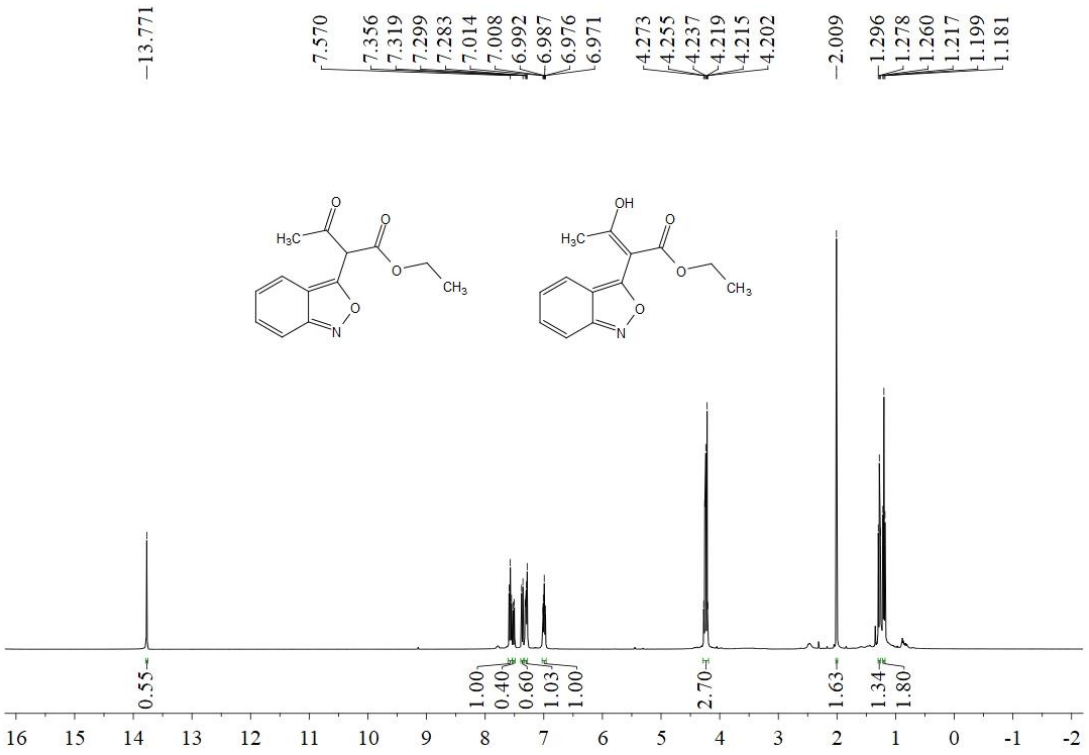


^{13}C NMR (100 MHz, $CDCl_3$)

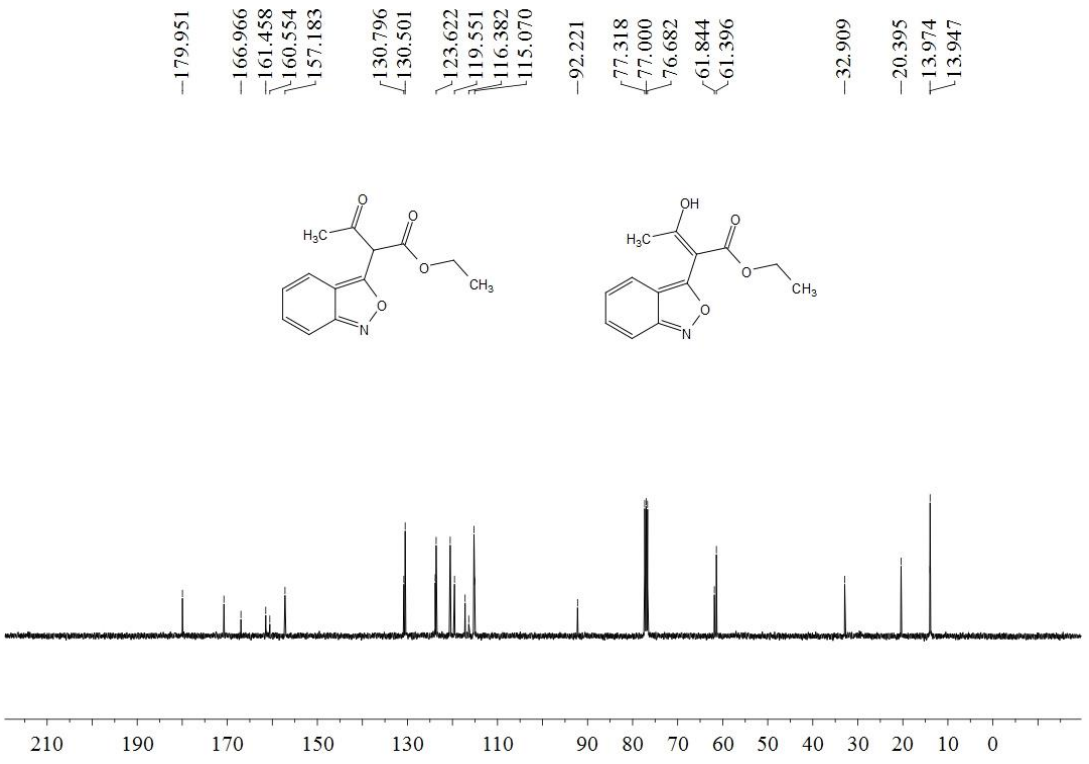

190.572
189.650
163.069
157.118
135.600
131.105
129.162
128.197
124.697
121.027
118.220
114.991
100.061
77.317
77.000
76.682
56.358
O
O
OH
O
N
O
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

Ethyl 2-(benzo[c]isoxazol-3-yl)-3-oxobutanoate (**7e**)

^{1}H NMR (400 MHz, $CDCl_3$)

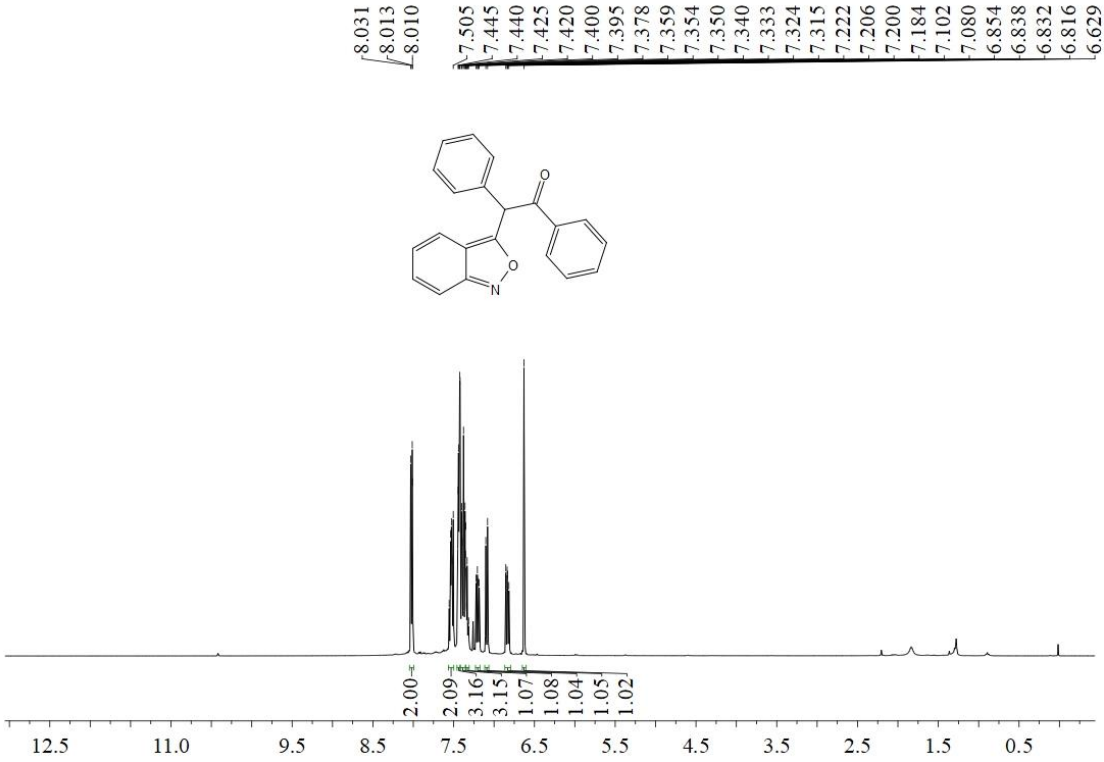


^{13}C NMR (100 MHz, $CDCl_3$)

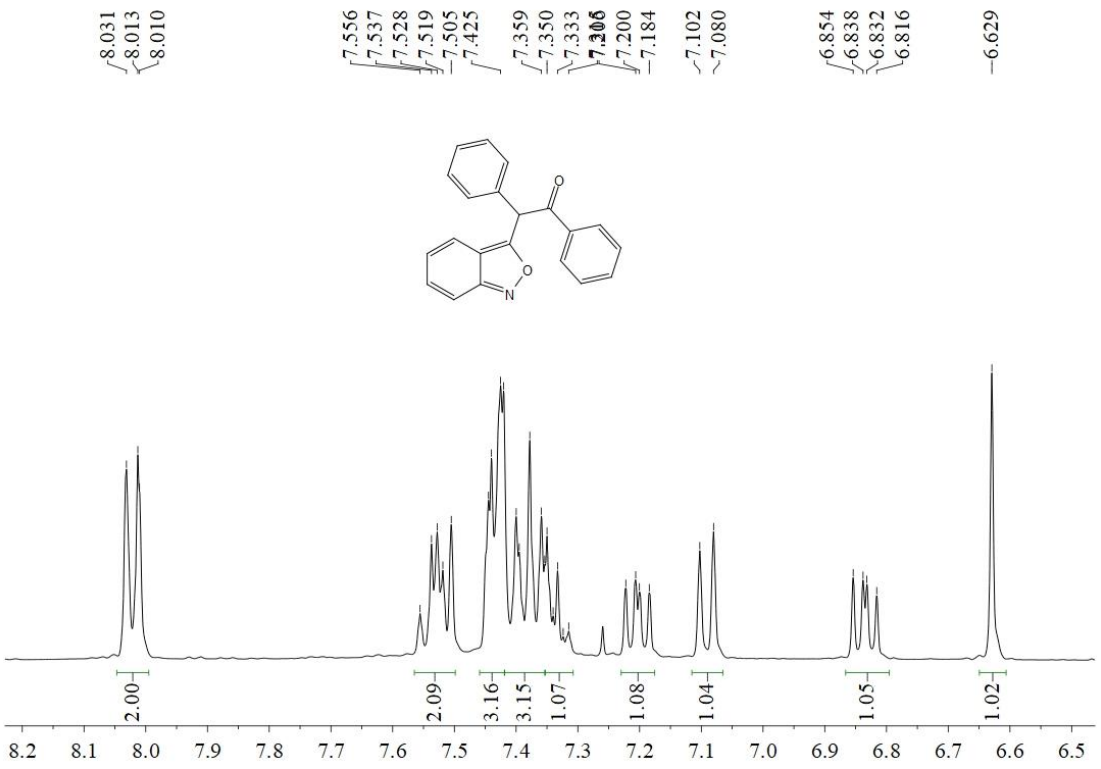


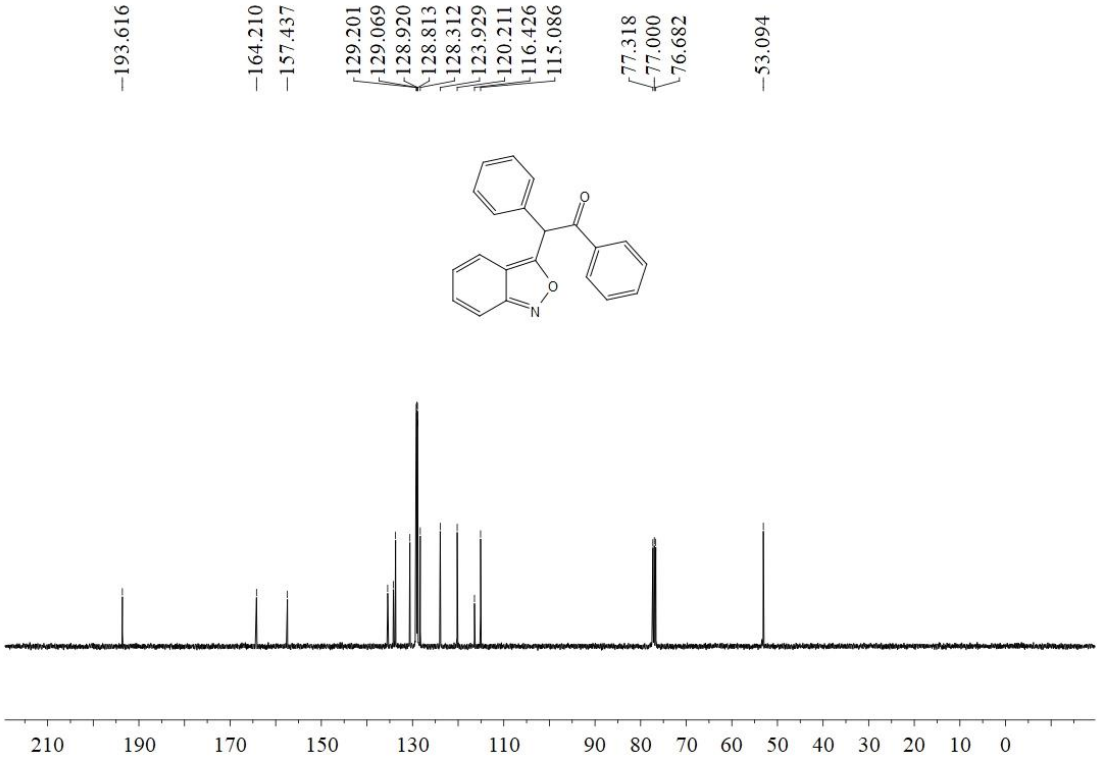
2-(Benzo[c]isoxazol-3-yl)-1,2-diphenylethan-1-one (**7f**)

^{1}H NMR (400 MHz, $CDCl_3$)



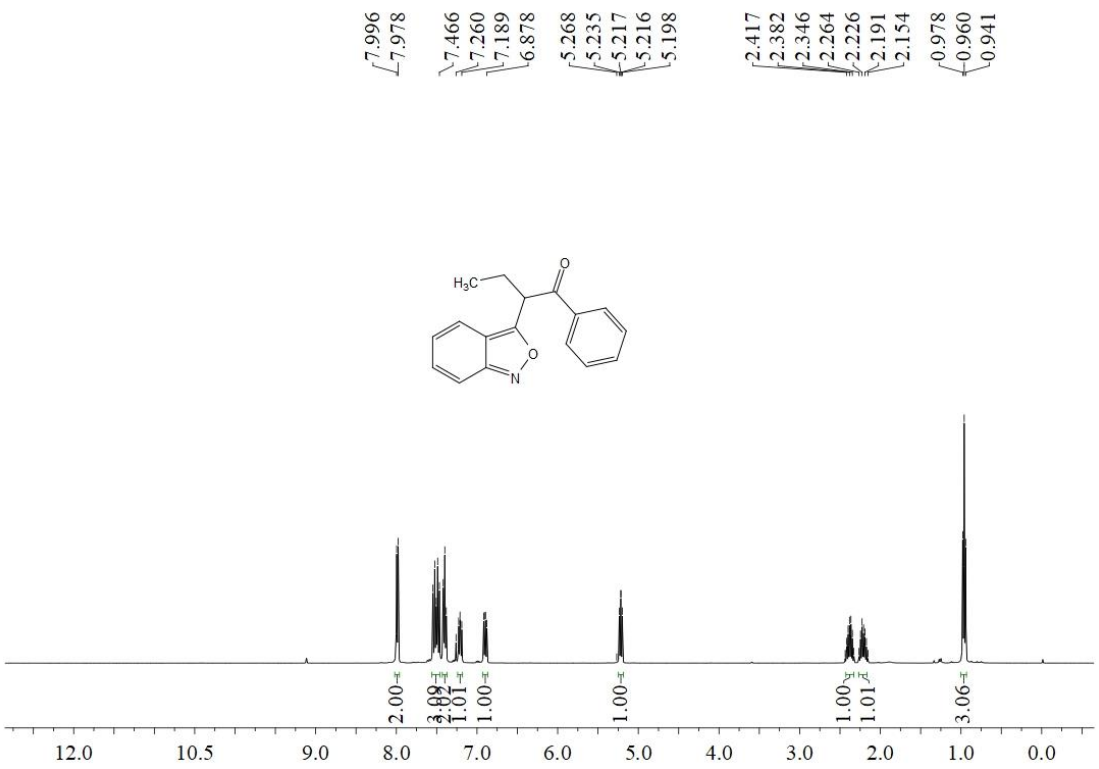
^{13}C NMR (100 MHz, $CDCl_3$)



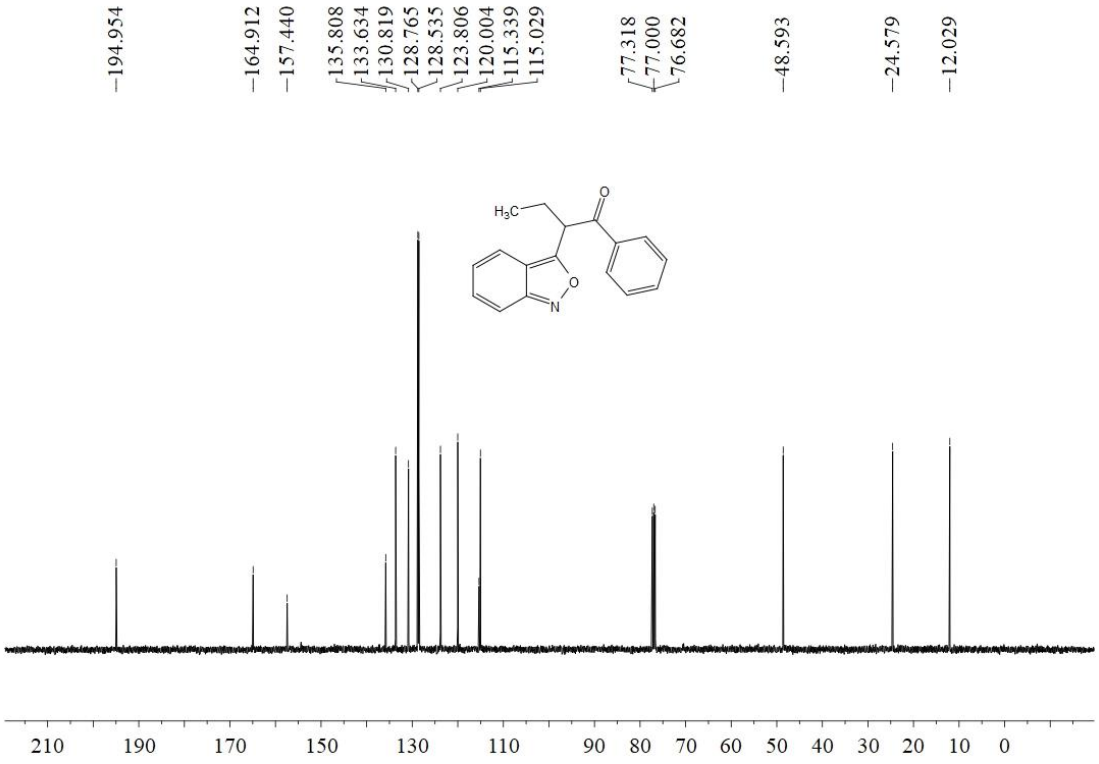

193.616
164.210
157.437
129.201
129.069
128.920
128.813
128.312
123.929
120.211
116.426
115.086
77.318
77.000
76.682
53.094
O
O
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

2-(Benzo[c]isoxazol-3-yl)-1-phenylbutan-1-one (**7g**)

^{1}H NMR (400 MHz, $CDCl_3$)

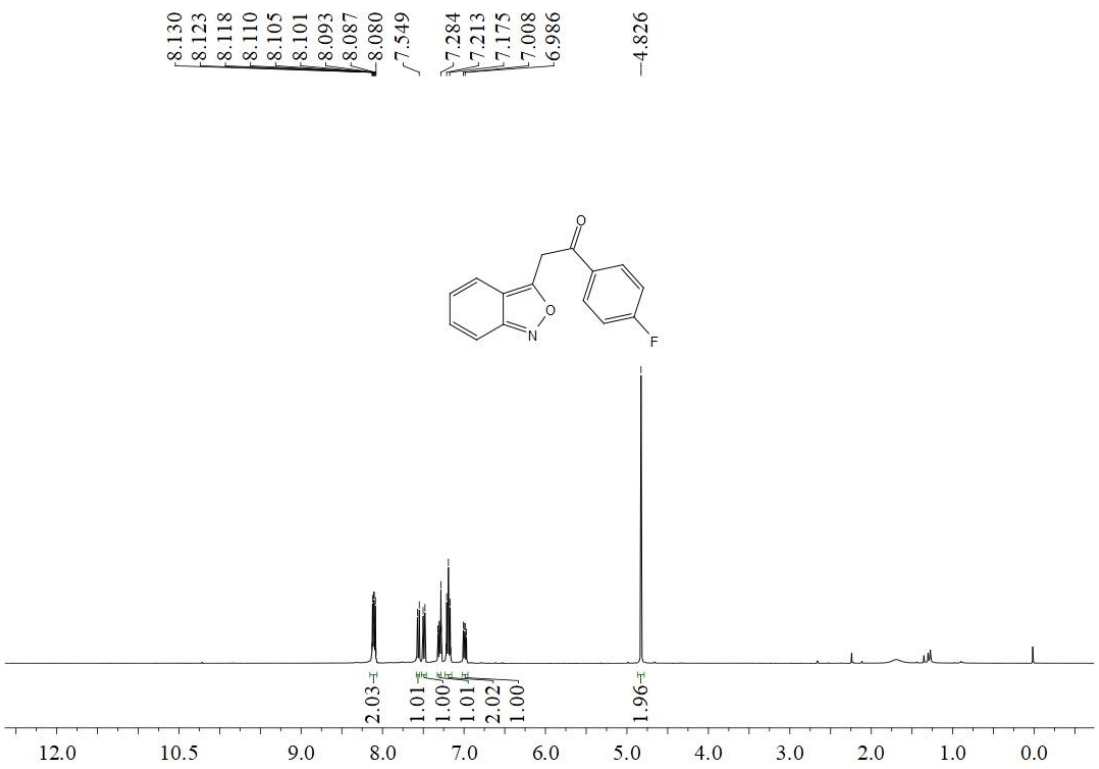


^{13}C NMR (100 MHz, $CDCl_3$)

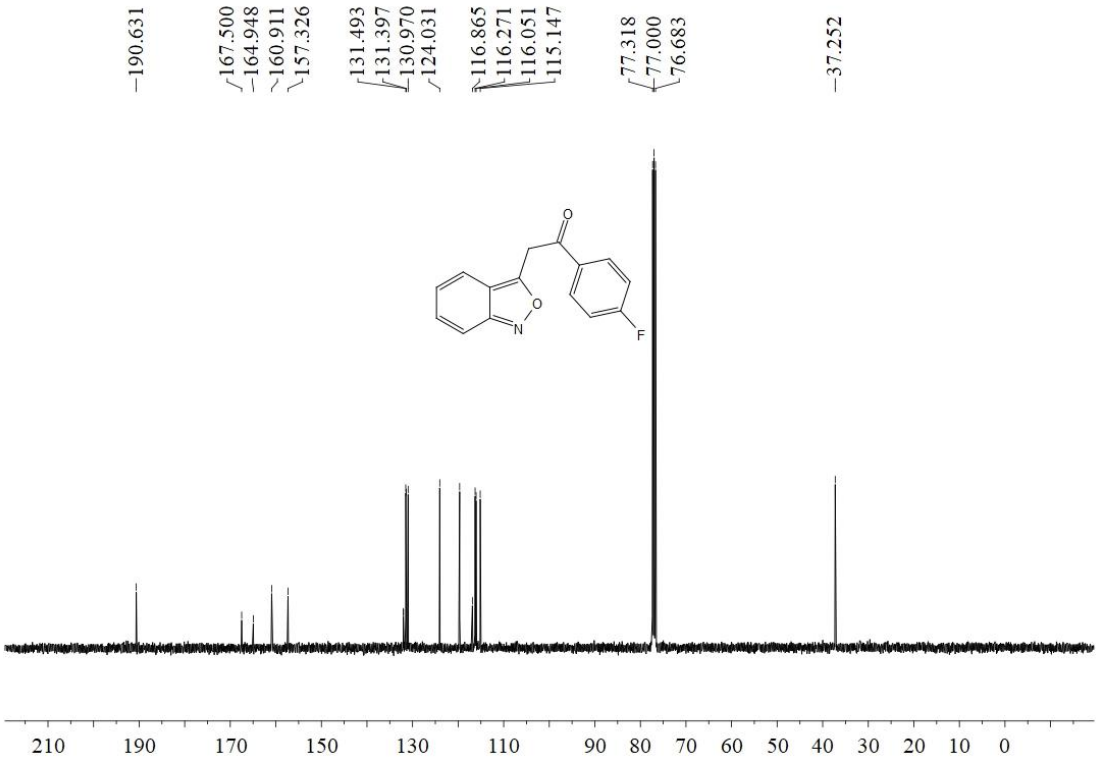


2-(Benzo[c]isoxazol-3-yl)-1-(4-fluorophenyl)ethan-1-one (**7h**)

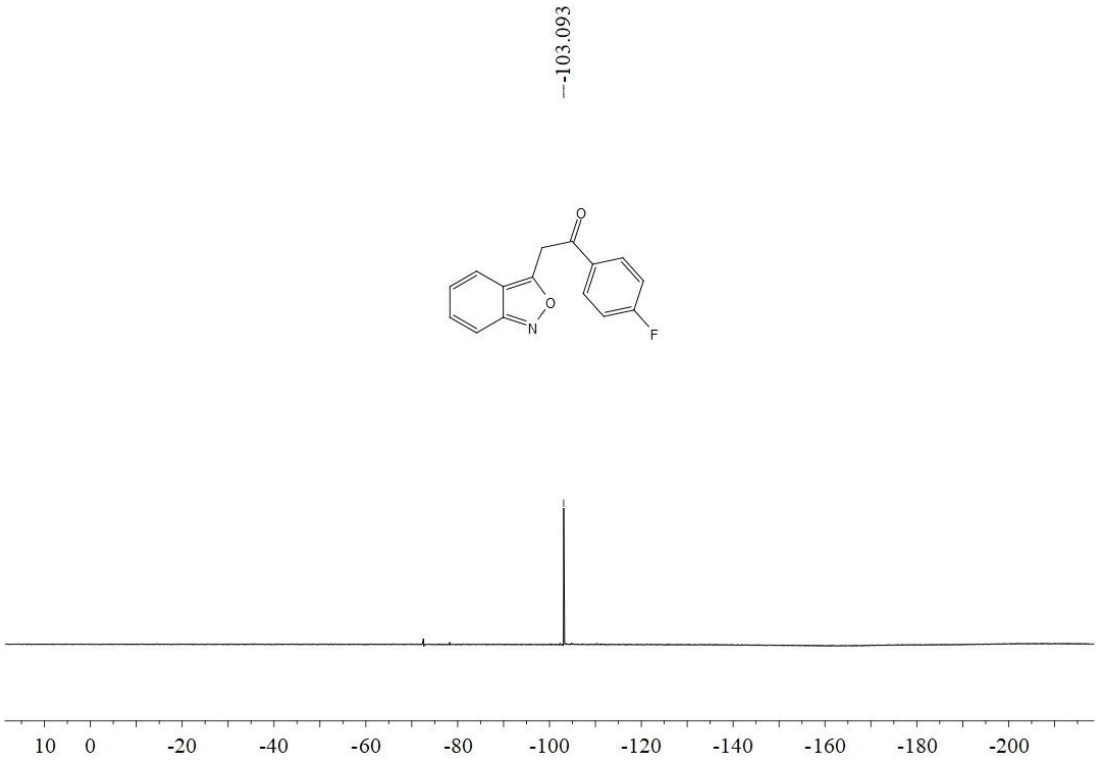
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

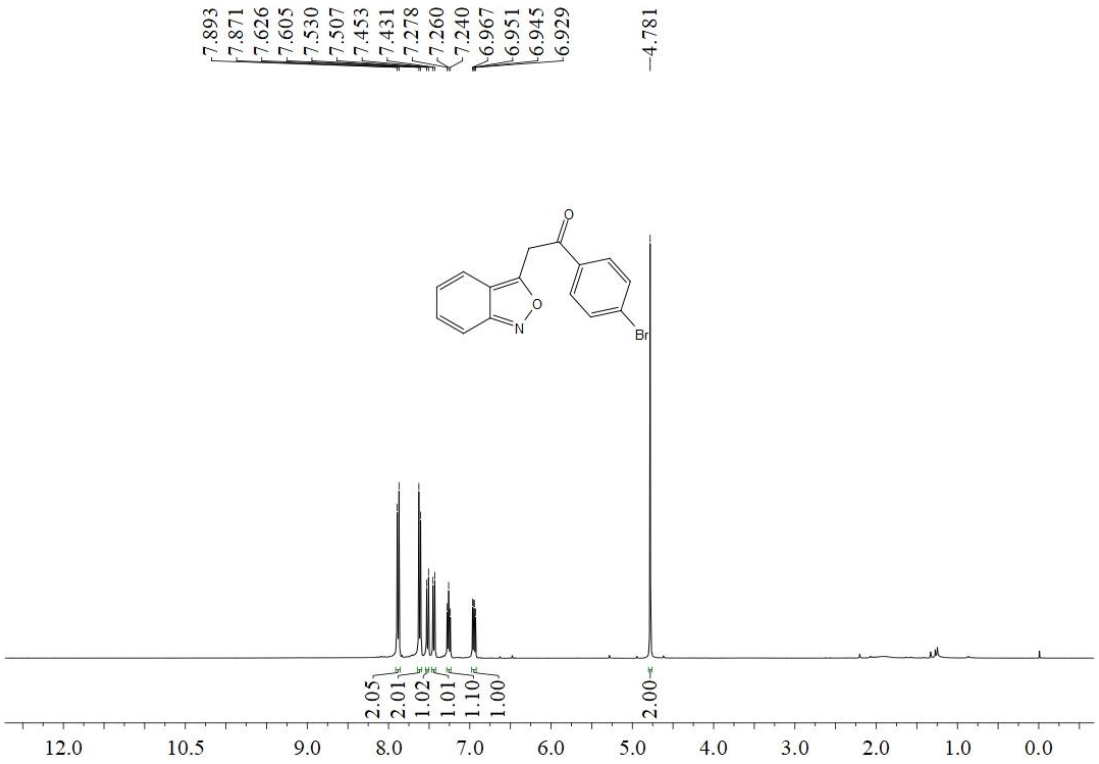


^{19}F NMR (375 MHz, $CDCl_3$)

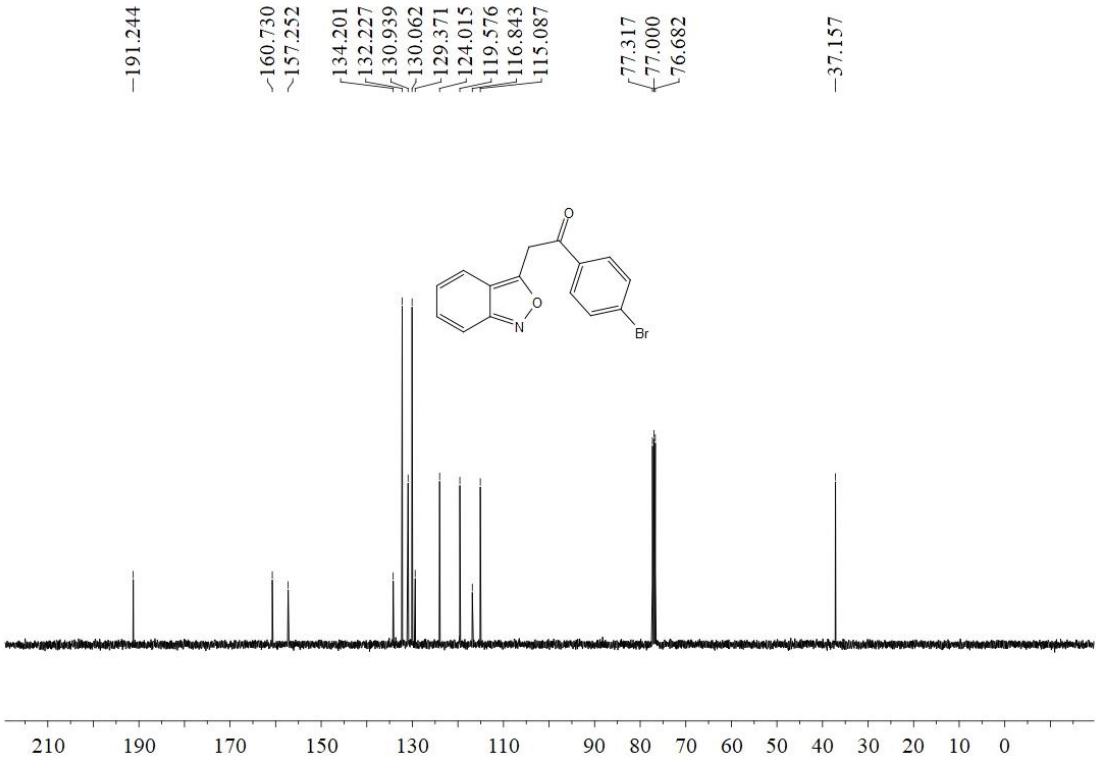

-103.093
O
O
N
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

2-(Benzo[c]isoxazol-3-yl)-1-(4-bromophenyl)ethan-1-one (**7i**)

^{1}H NMR (400 MHz, $CDCl_3$)

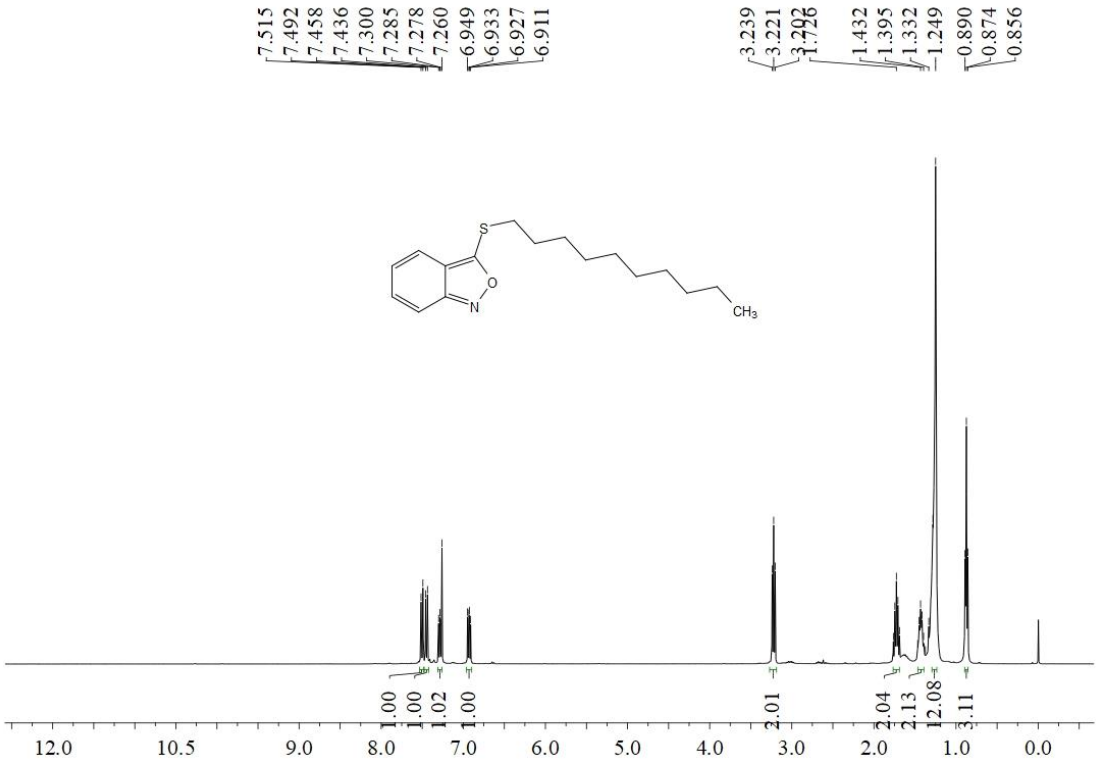


^{13}C NMR (100 MHz, $CDCl_3$)

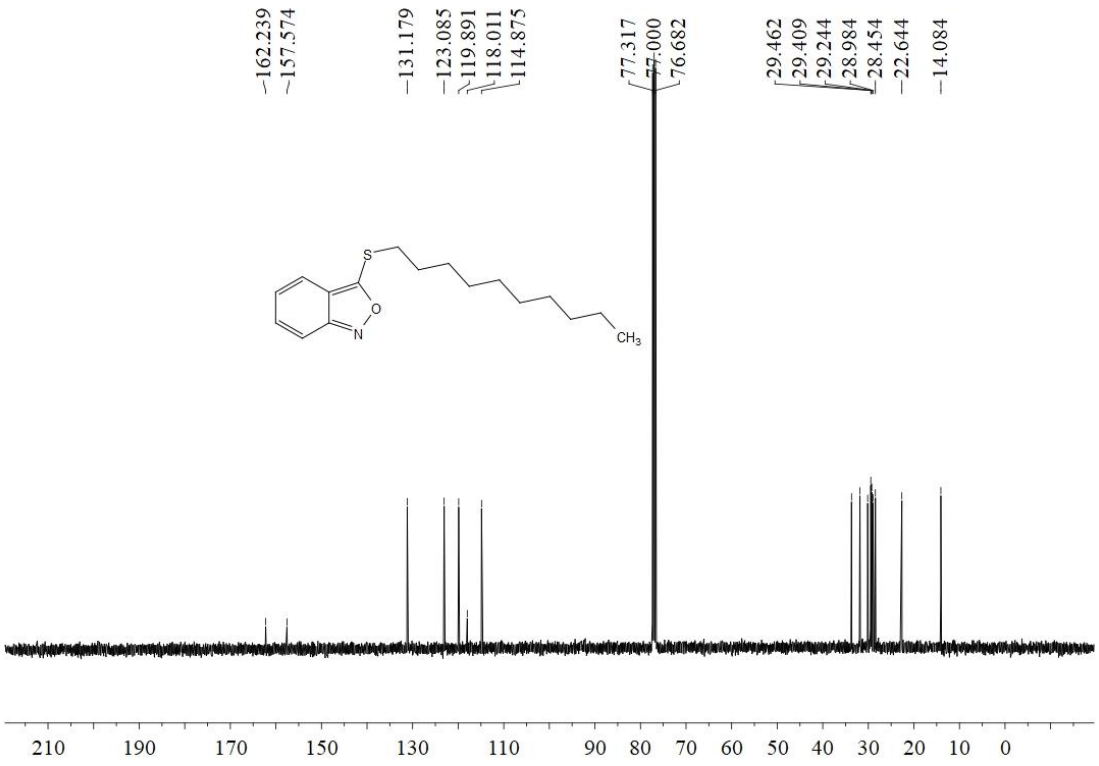


3-(Decylthio)benzo[c]isoxazole (**9a**)

^{1}H NMR (400 MHz, $CDCl_3$)

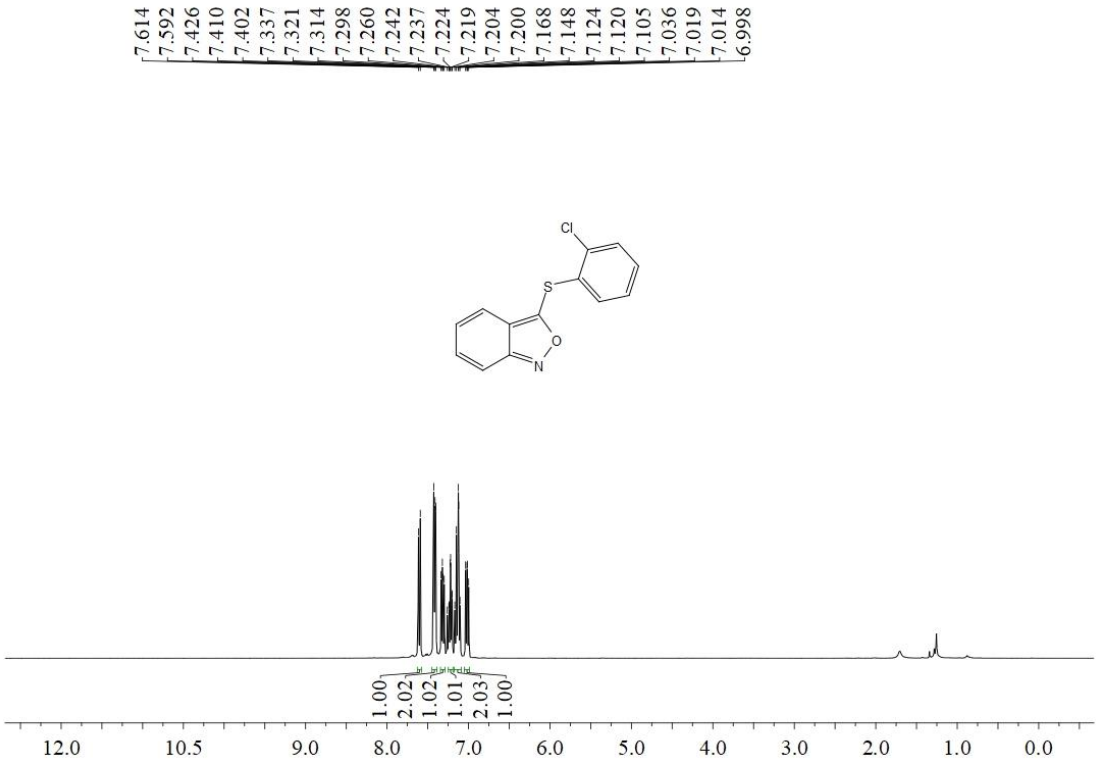


^{13}C NMR (100 MHz, $CDCl_3$)

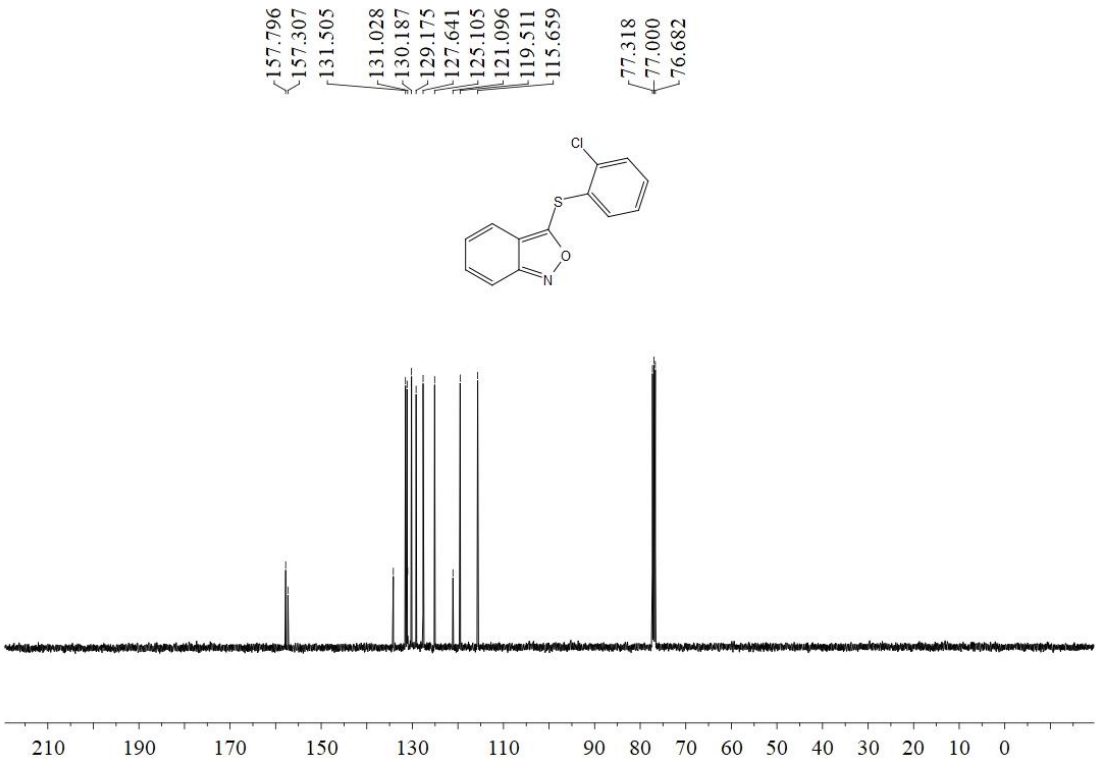


3-((2-Chlorophenyl)thio)benzo[c]isoxazole (**9b**)

^{1}H NMR (400 MHz, $CDCl_3$)

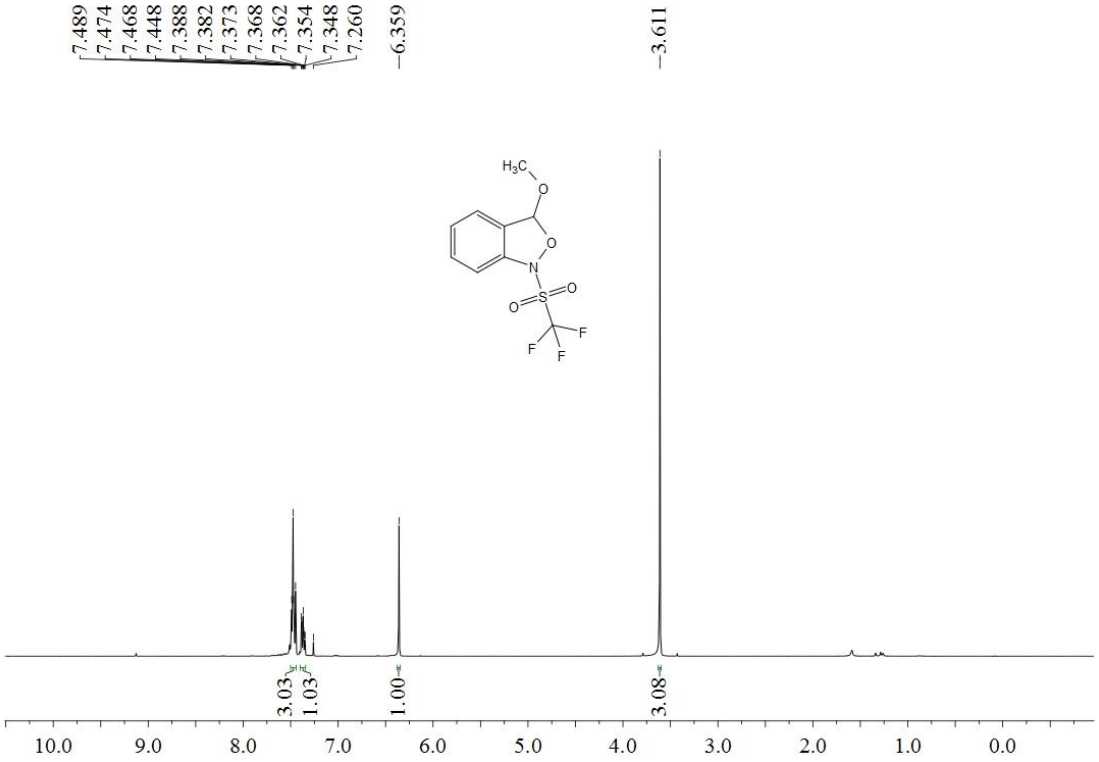


^{13}C NMR (100 MHz, $CDCl_3$)

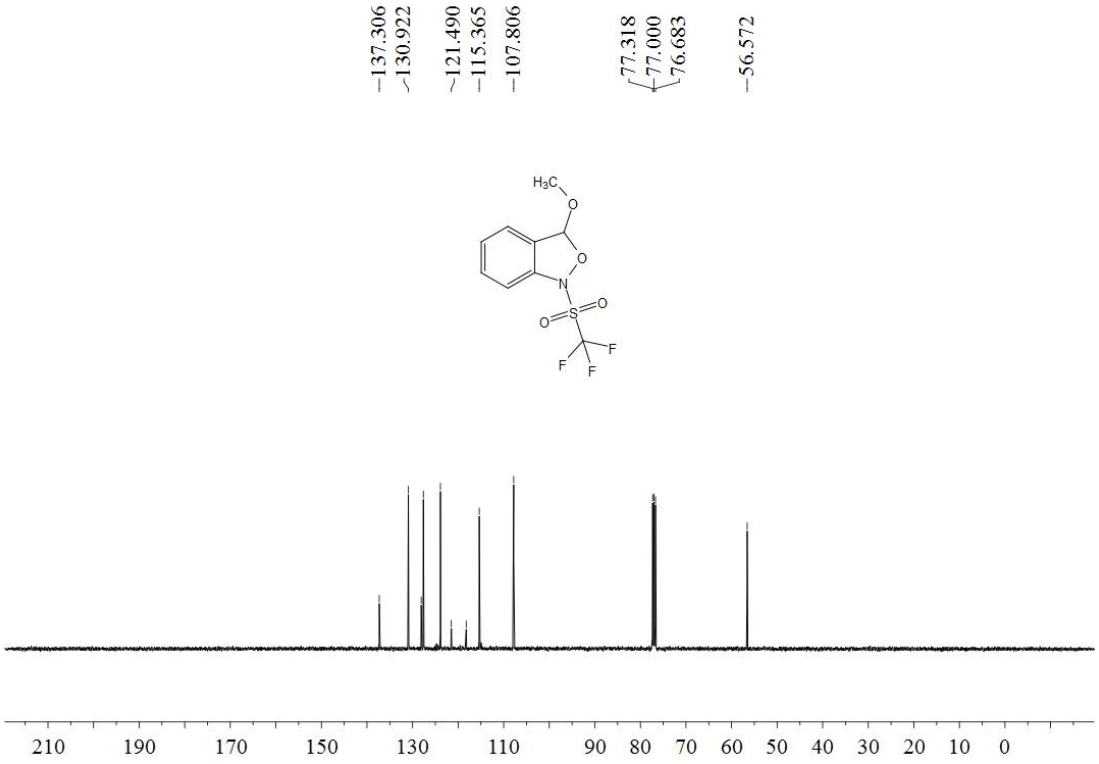


3-Methoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (**9c**)

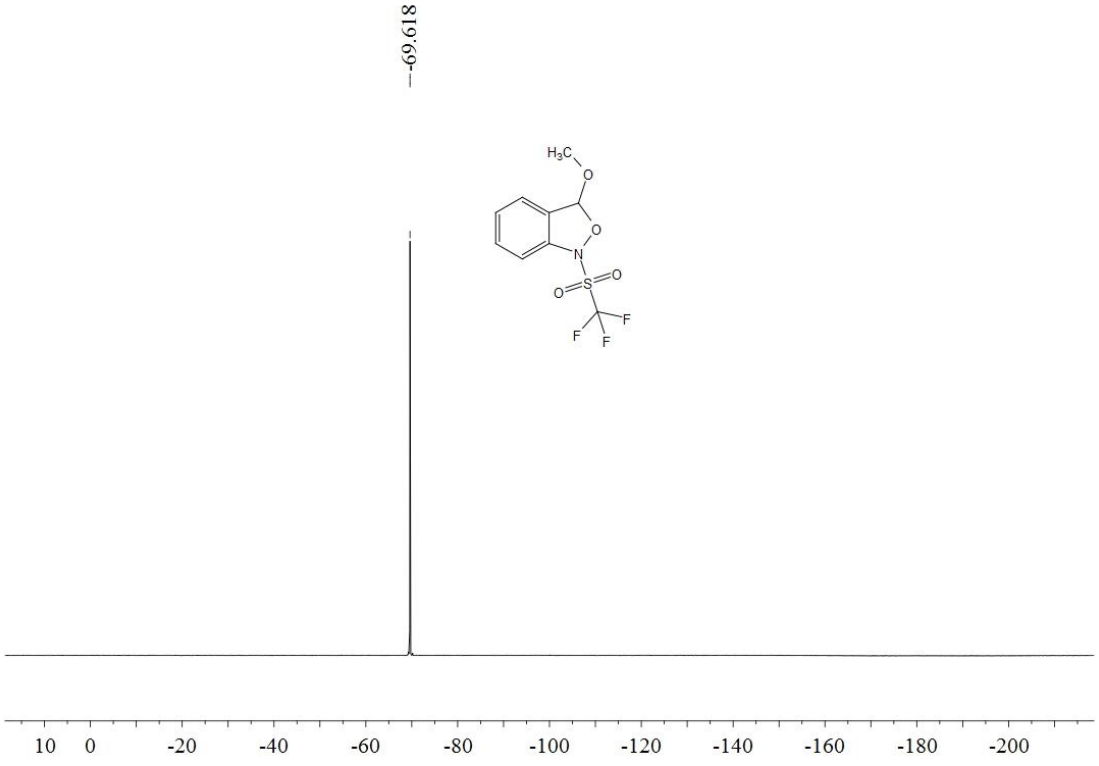
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

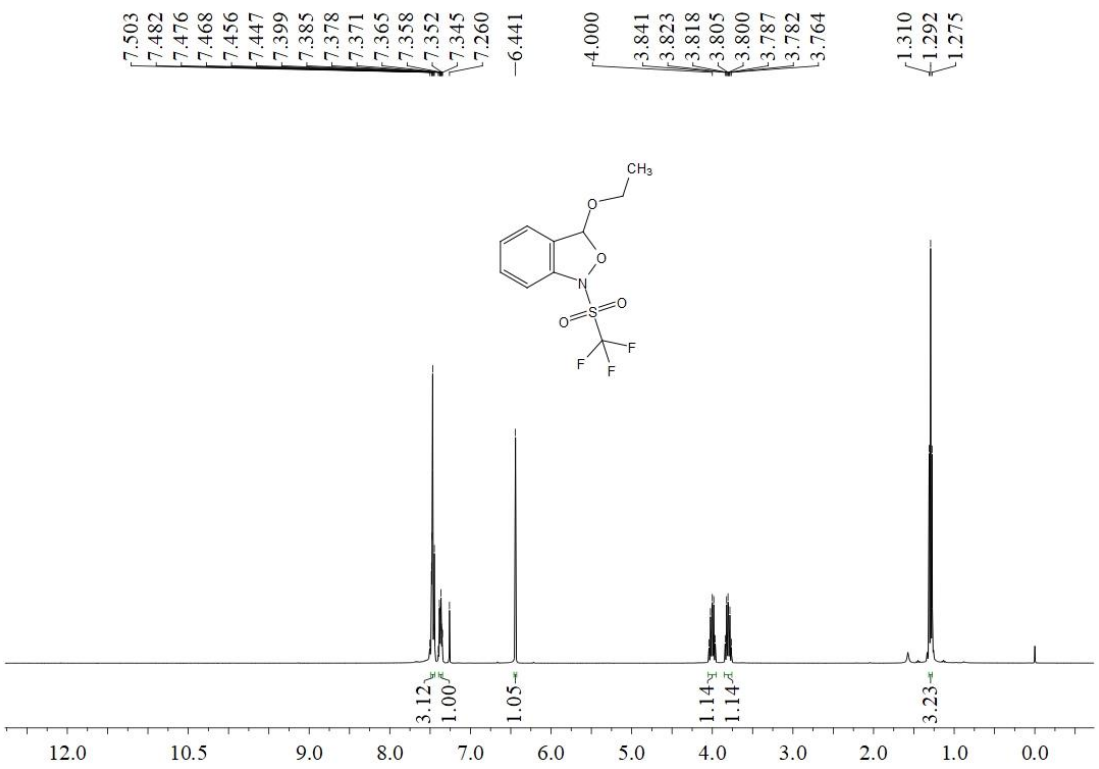


^{19}F NMR (376 MHz, $CDCl_3$)

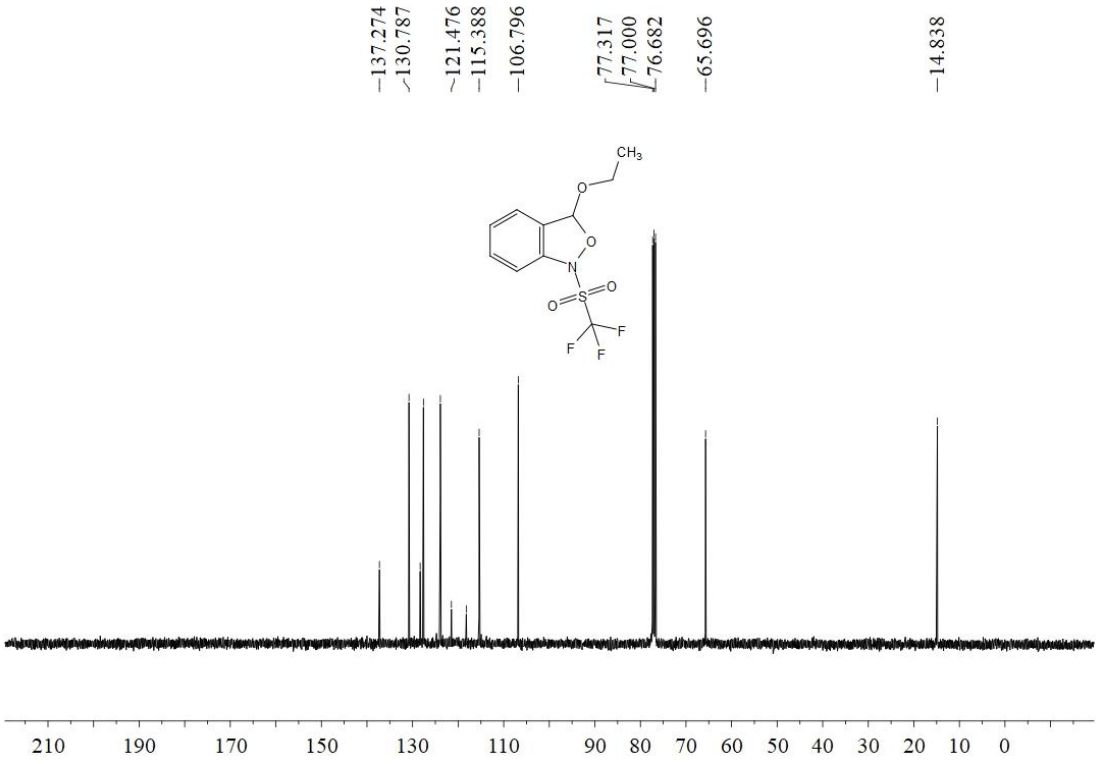

-69.618
H3C
O
O
N
O
S
O
O
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-Ethoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (**9d**)

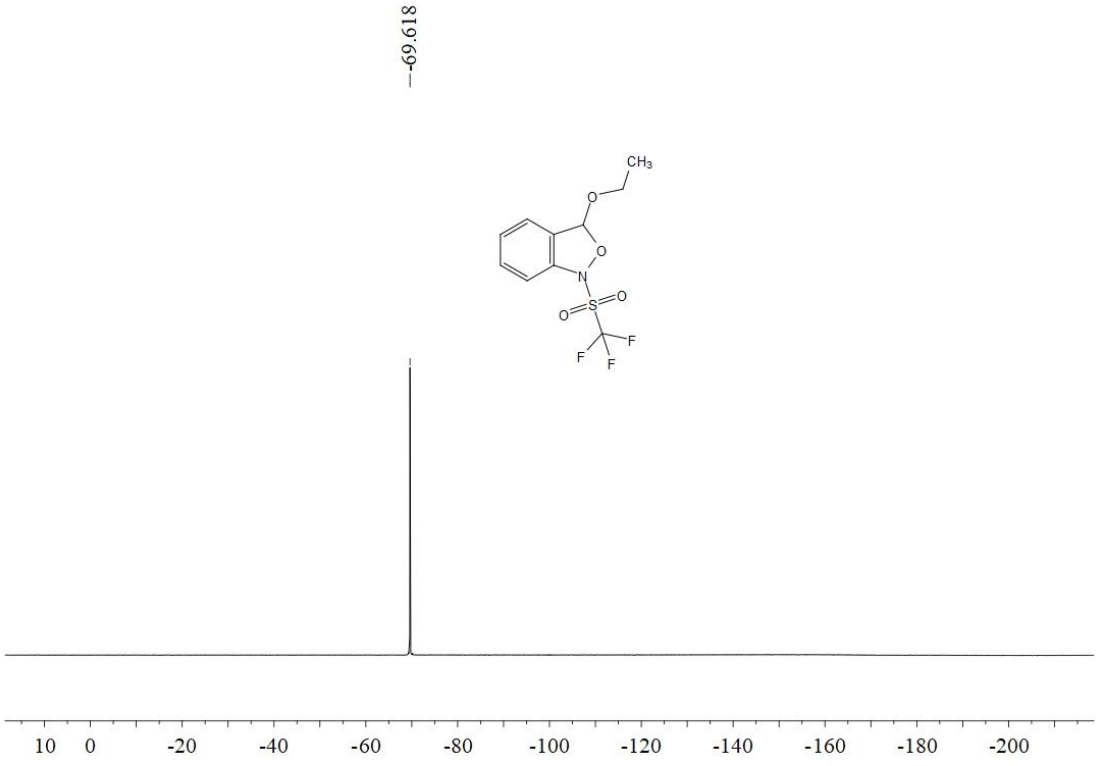
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

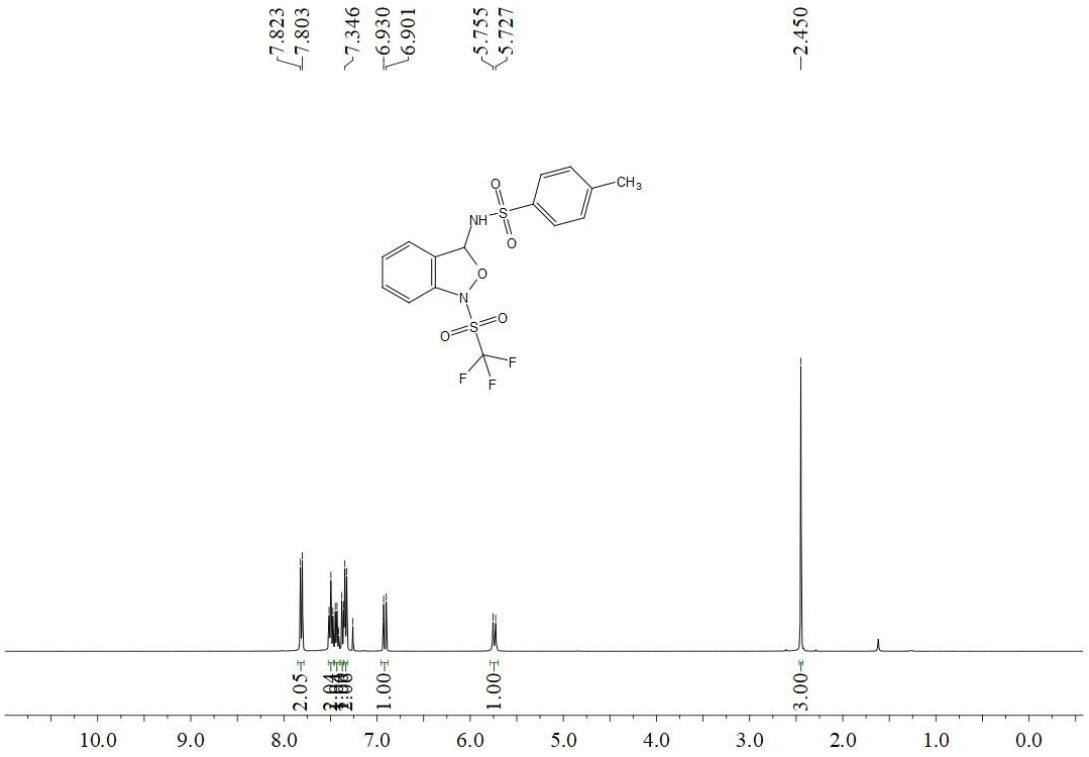


^{19}F NMR (375 MHz, $CDCl_3$)

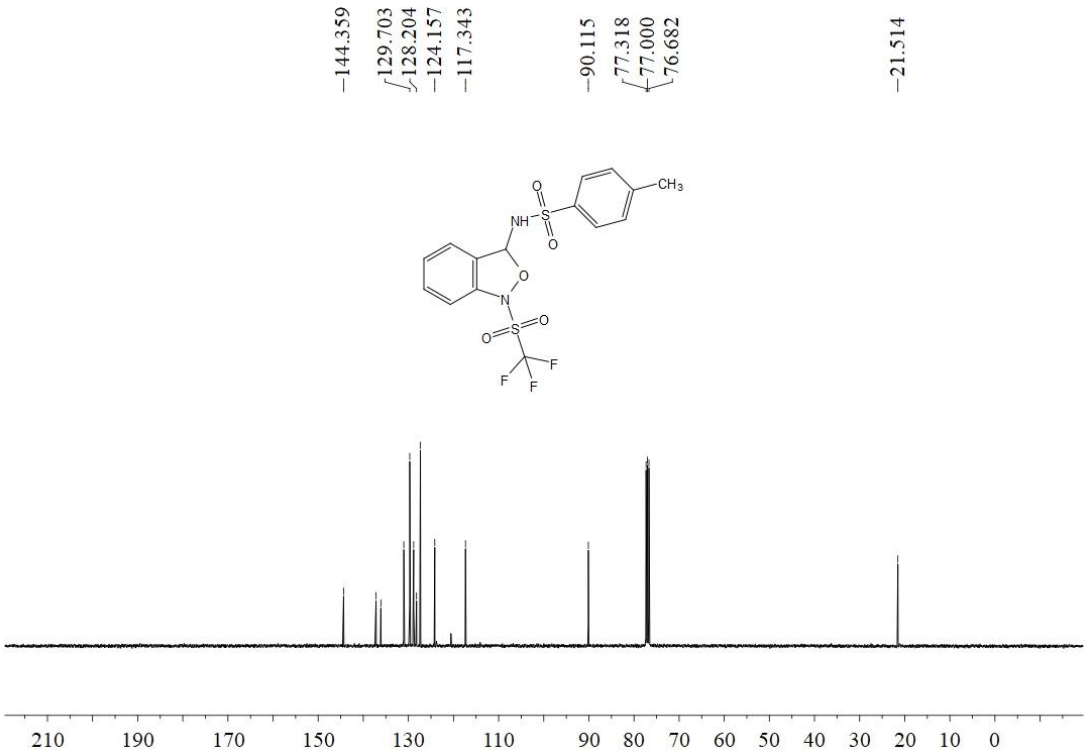

-69.618
CH3
O
O
N
S
O
O
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

4-Methyl-N-(1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazol-3-yl)benzenesulfonamide (**9e**)

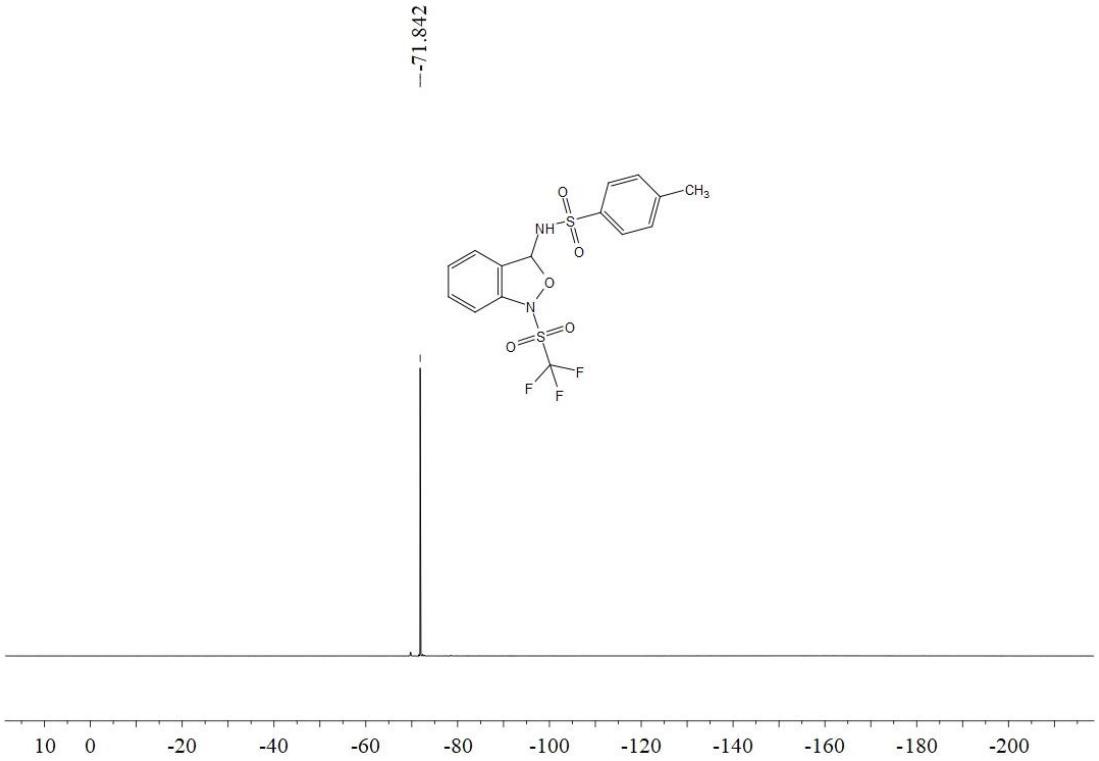
^{1}H NMR (400 MHz, $CDCl_3$)



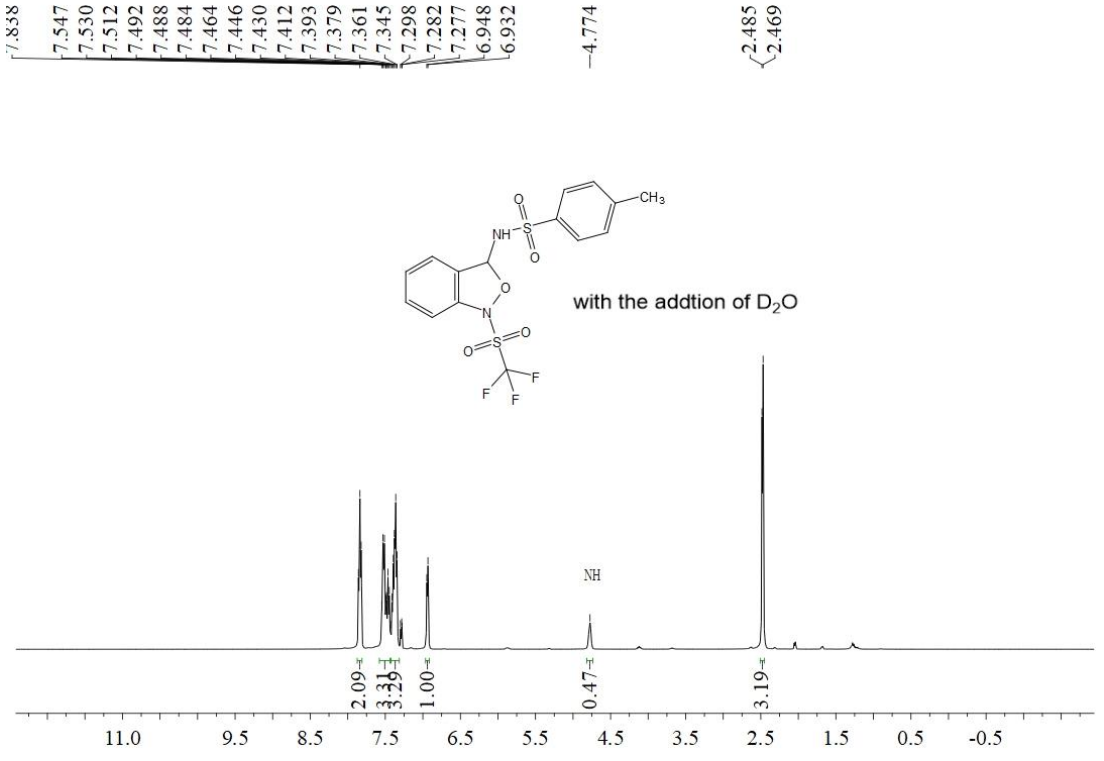
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (375 MHz, $CDCl_3$)

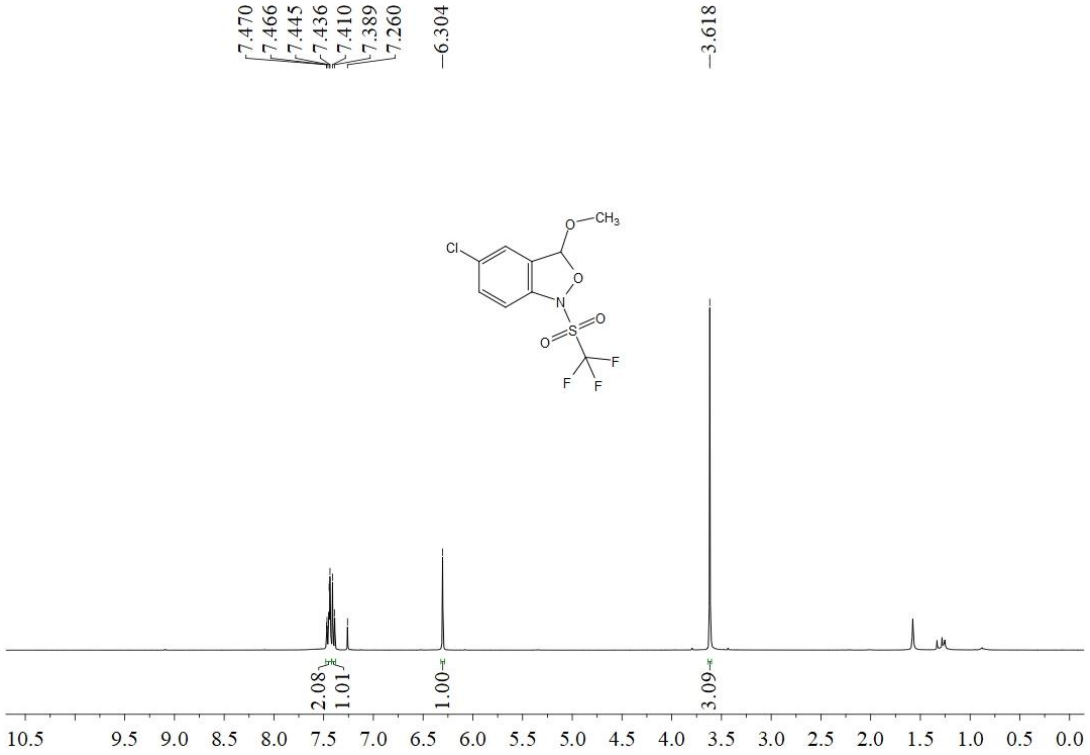


^{1}H NMR (400 MHz, $CDCl_3$) with the addition of a drop of D_2O

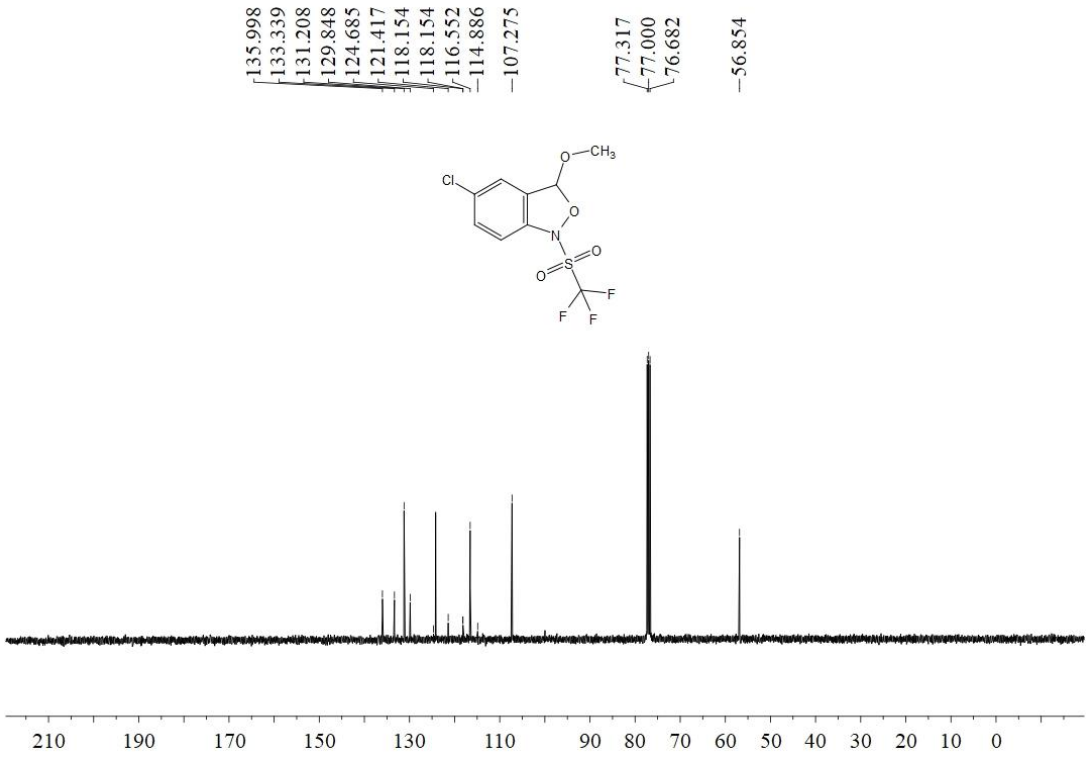


5-Chloro-3-methoxy-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (**9f**)

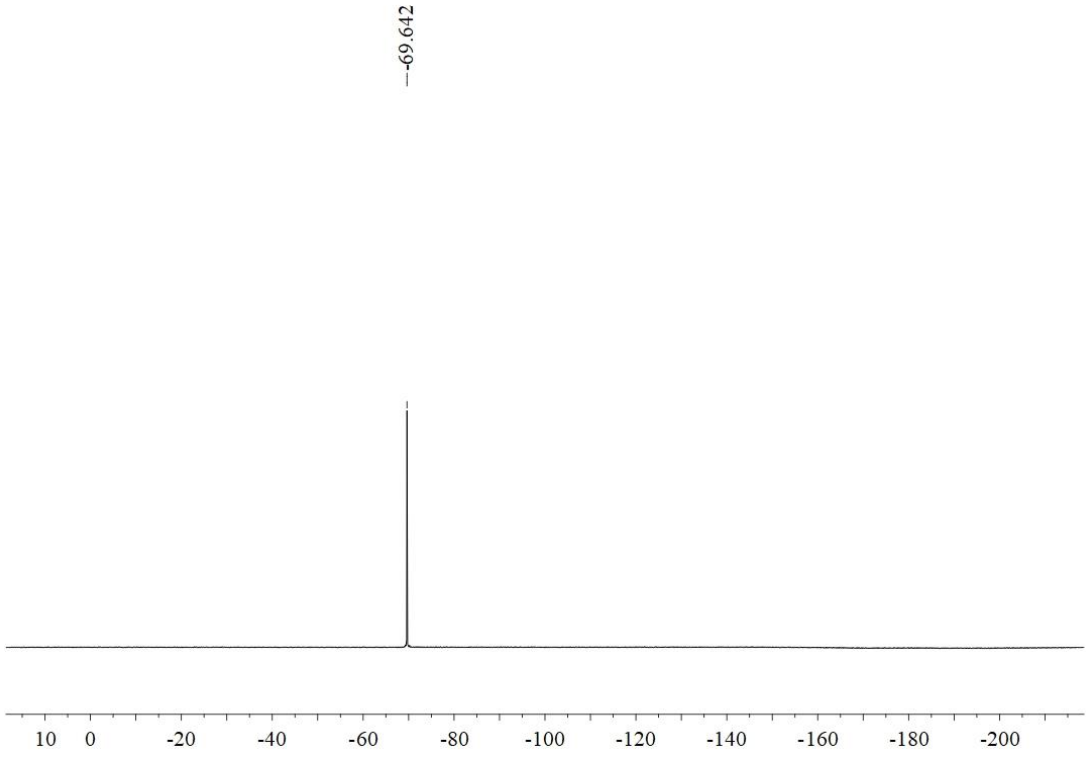
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

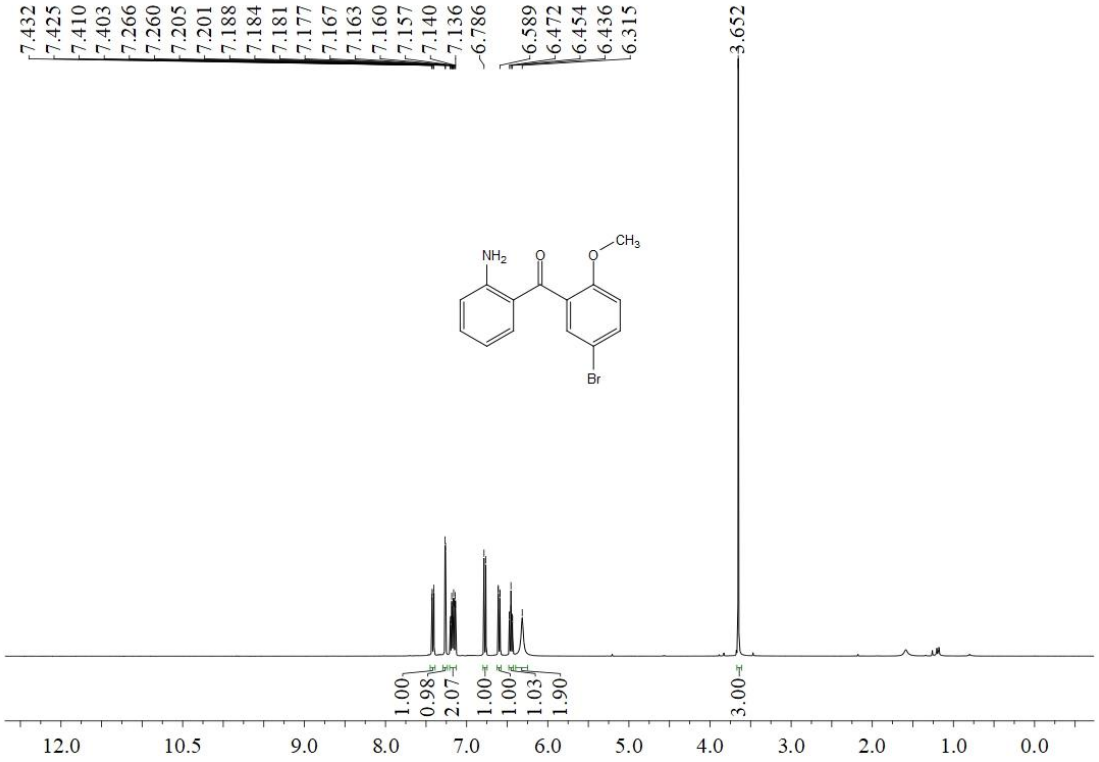


^{19}F NMR (376 MHz, $CDCl_3$)

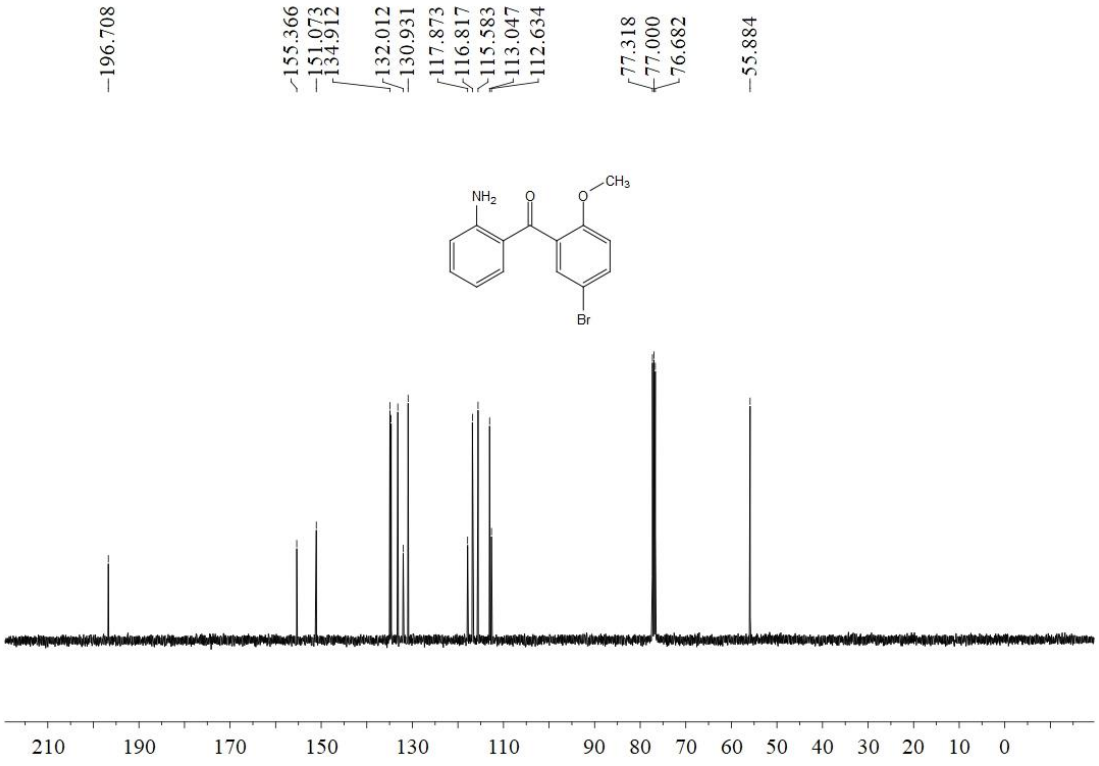

-69.642
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

(2-Aminophenyl)(5-bromo-2-methoxyphenyl)methanone (**11a**)

^{1}H NMR (400 MHz, $CDCl_3$)

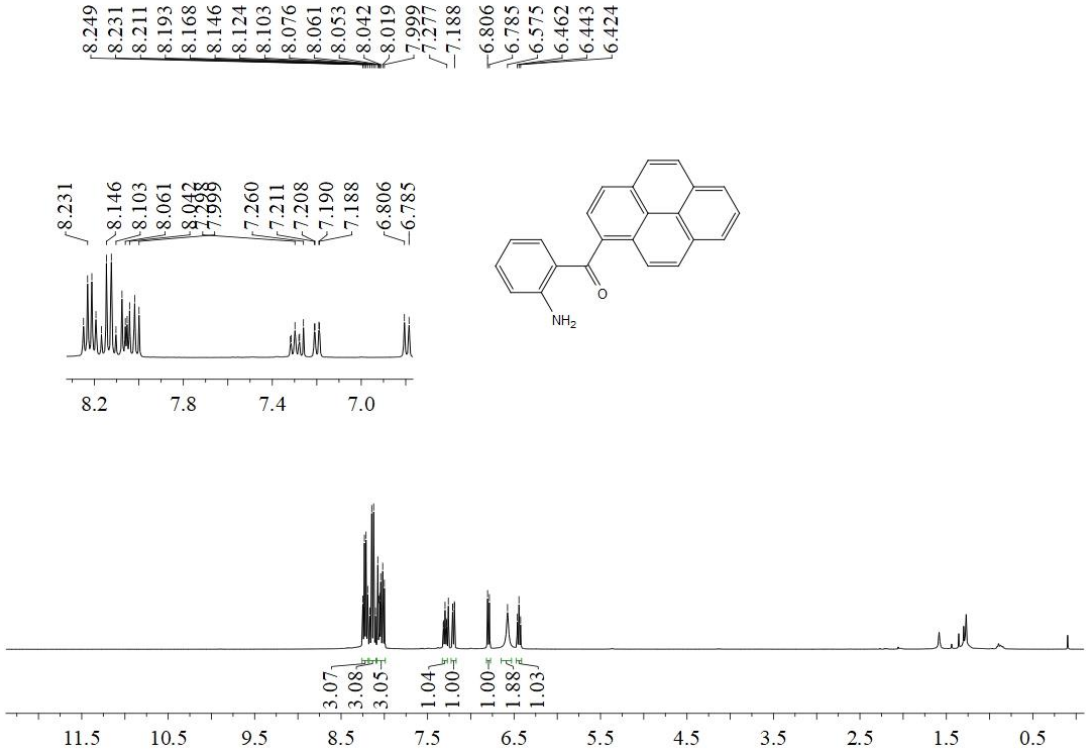


^{13}C NMR (100 MHz, $CDCl_3$)

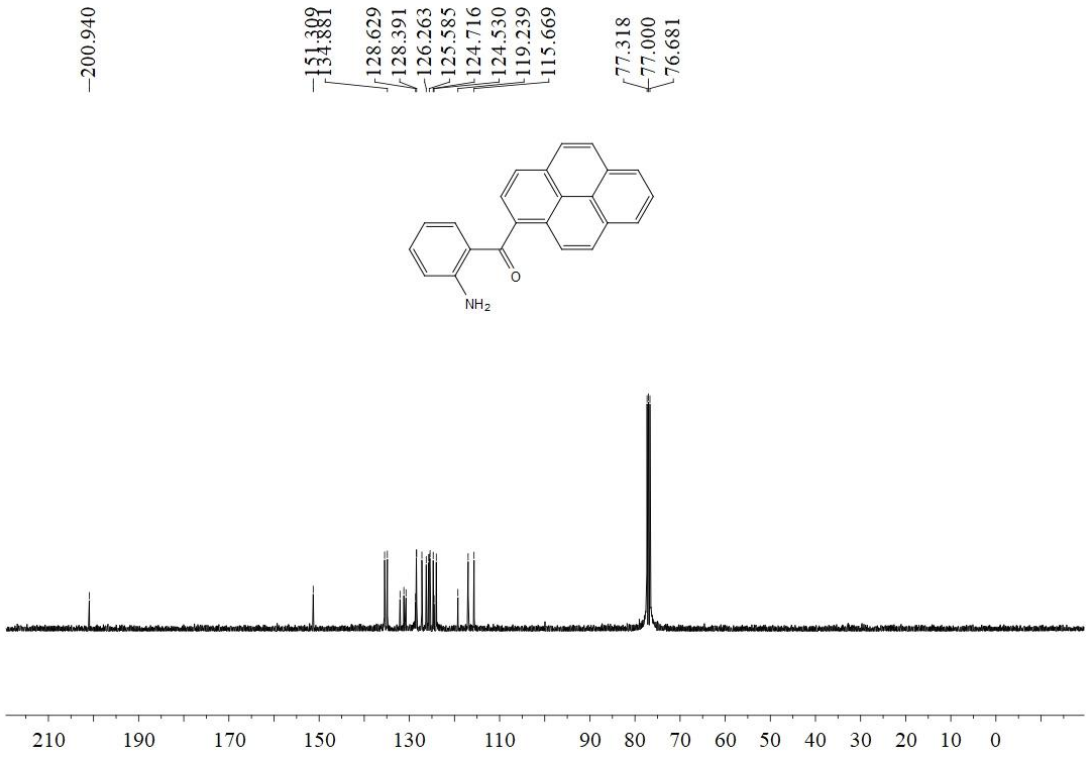


(2-Aminophenyl)(pyren-1-yl)methanone (**11b**)

^{1}H NMR (400 MHz, $CDCl_3$)

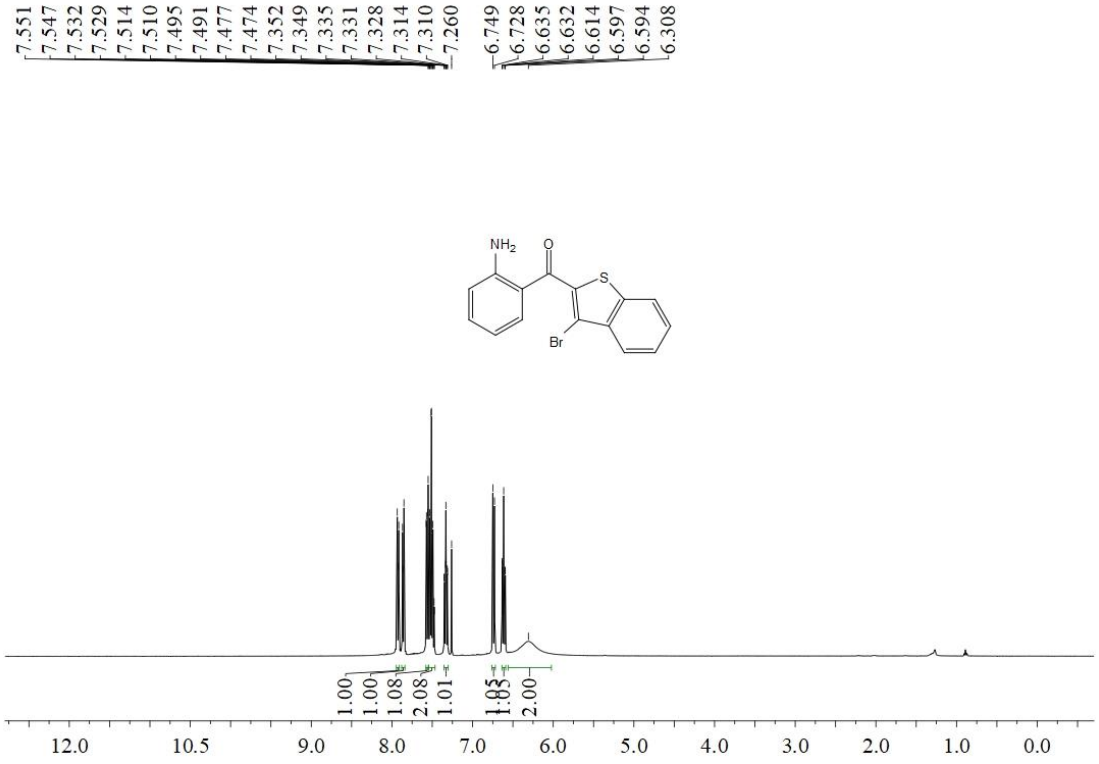


^{13}C NMR (100 MHz, $CDCl_3$)

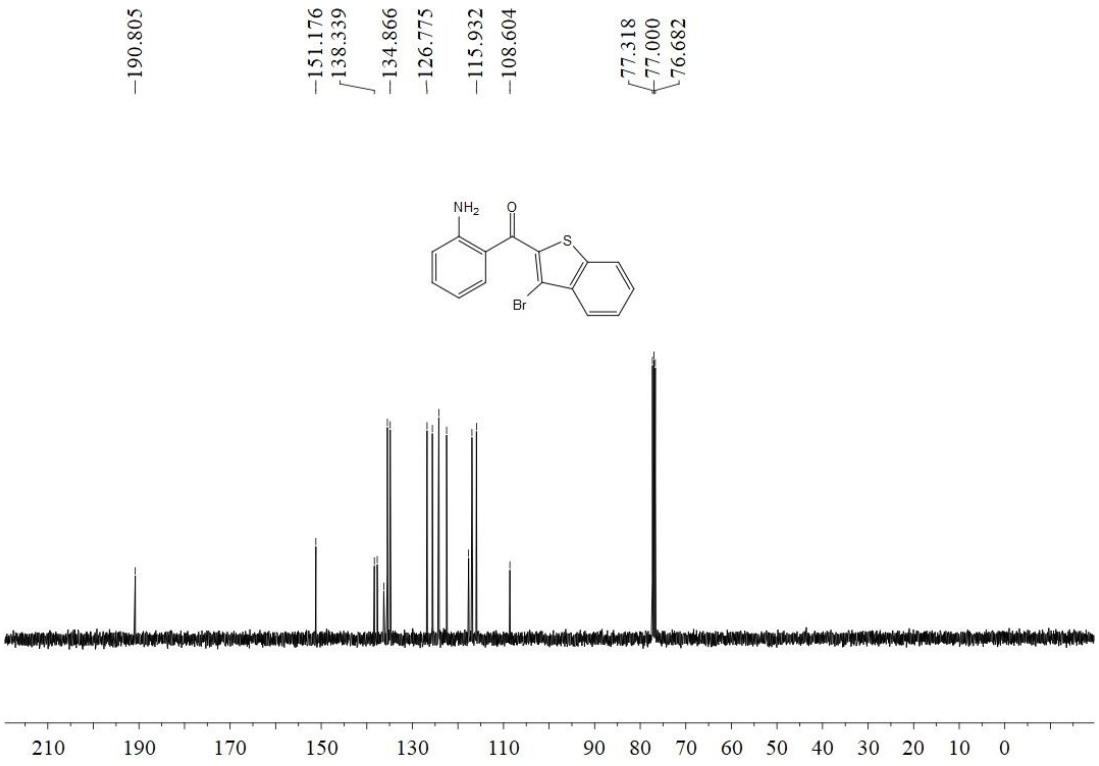


(2-Aminophenyl)(3-bromobenzo[b]thiophen-2-yl)methanone (**11c**)

^{1}H NMR (400 MHz, $CDCl_3$)

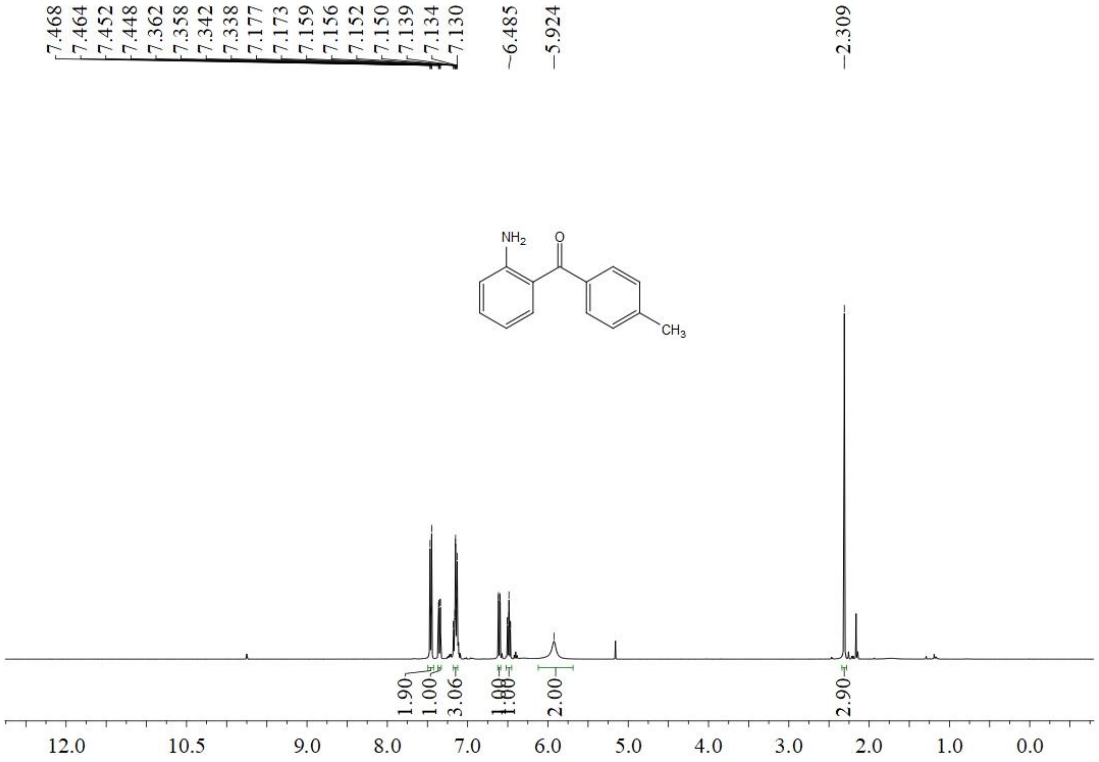


^{13}C NMR (100 MHz, $CDCl_3$)

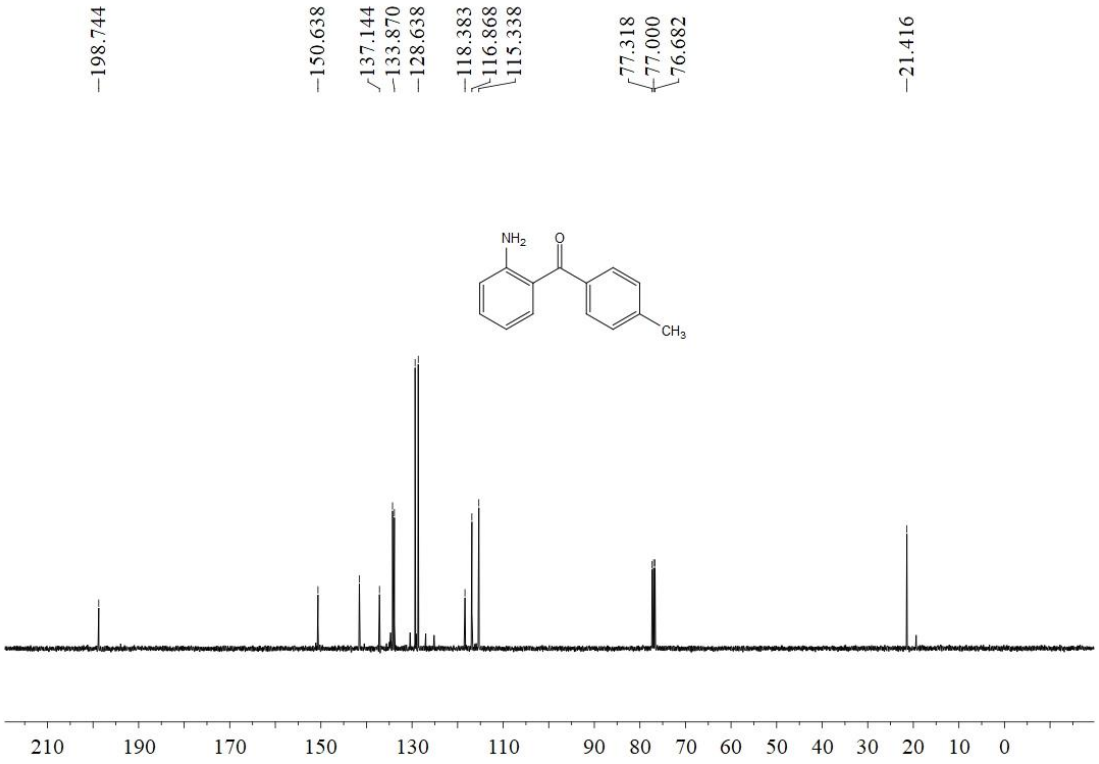


(2-Aminophenyl)(*p*-tolyl)methanone (**11d**)

^{1}H NMR (400 MHz, $CDCl_3$)

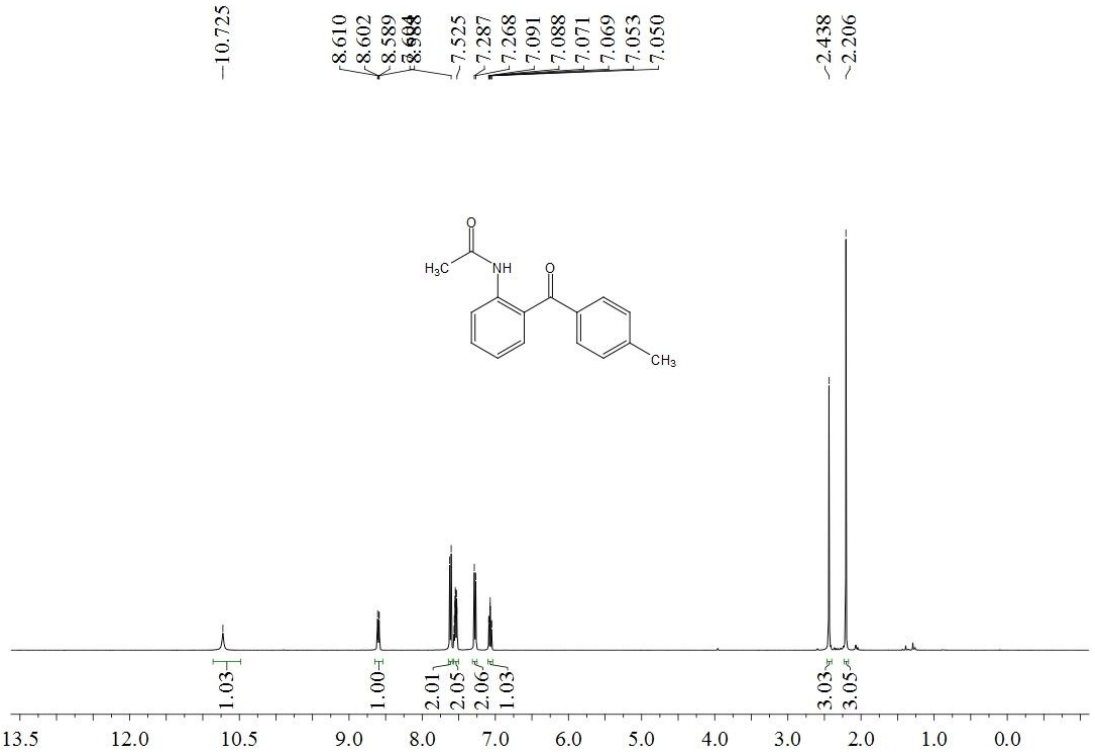


^{13}C NMR (100 MHz, $CDCl_3$)

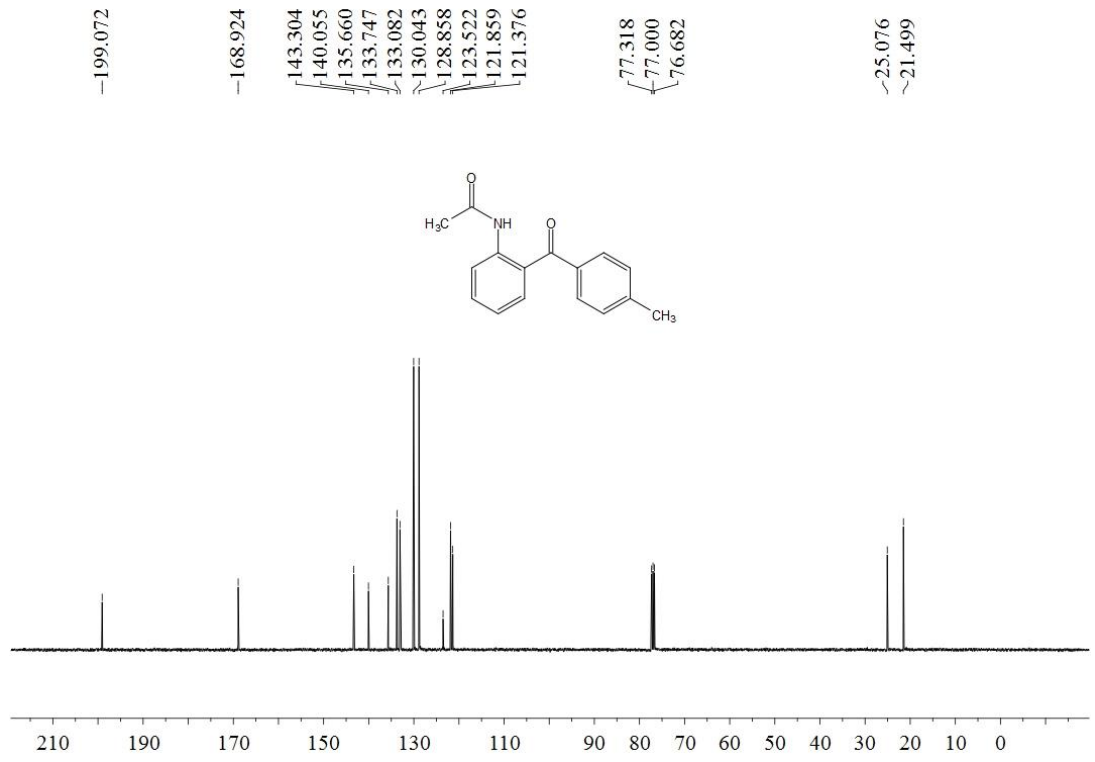


2-Chloro-N-(2-(4-methylbenzoyl)phenyl)acetamide (**11e**)

^{1}H NMR (400 MHz, $CDCl_3$)

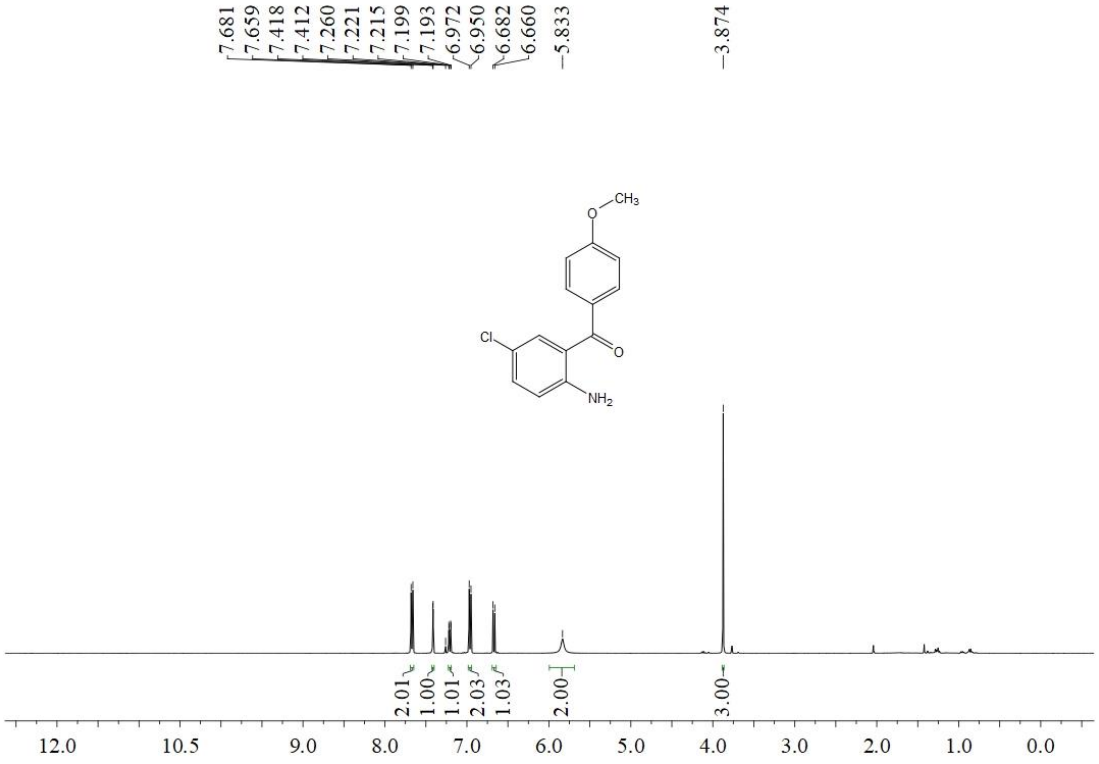


^{13}C NMR (100 MHz, $CDCl_3$)

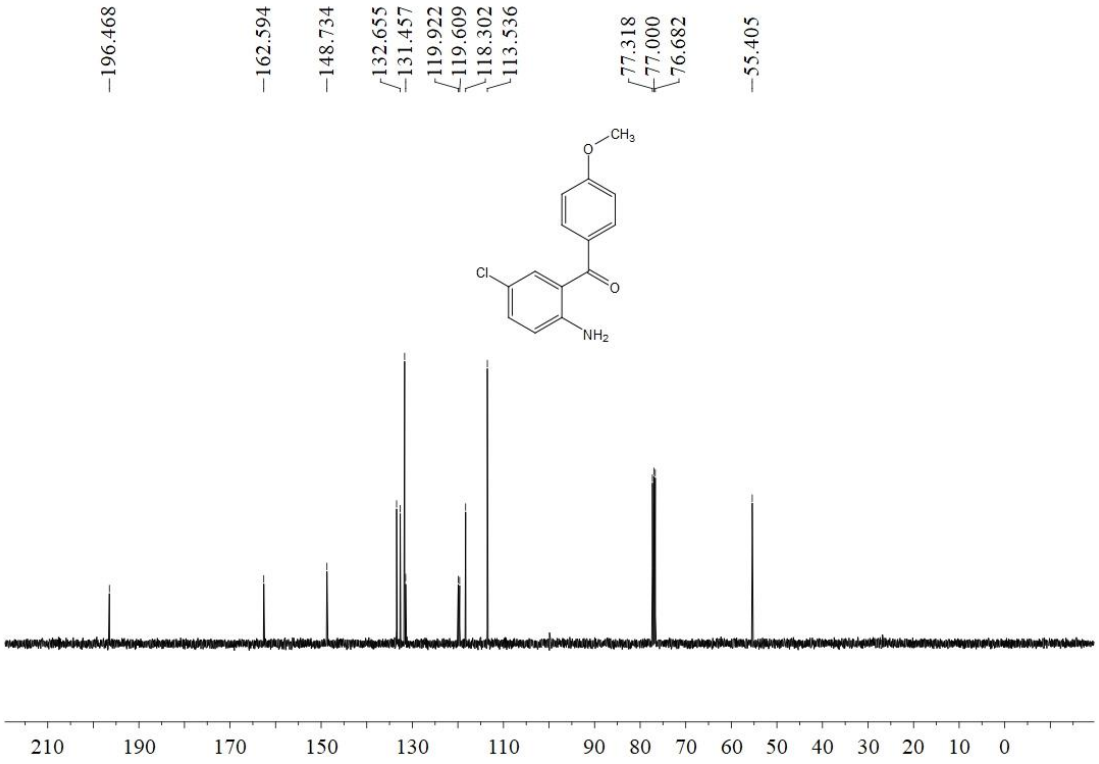


(2-Amino-5-chlorophenyl)(4-methoxyphenyl)methanone (**11f**)

^{1}H NMR (400 MHz, $CDCl_3$)

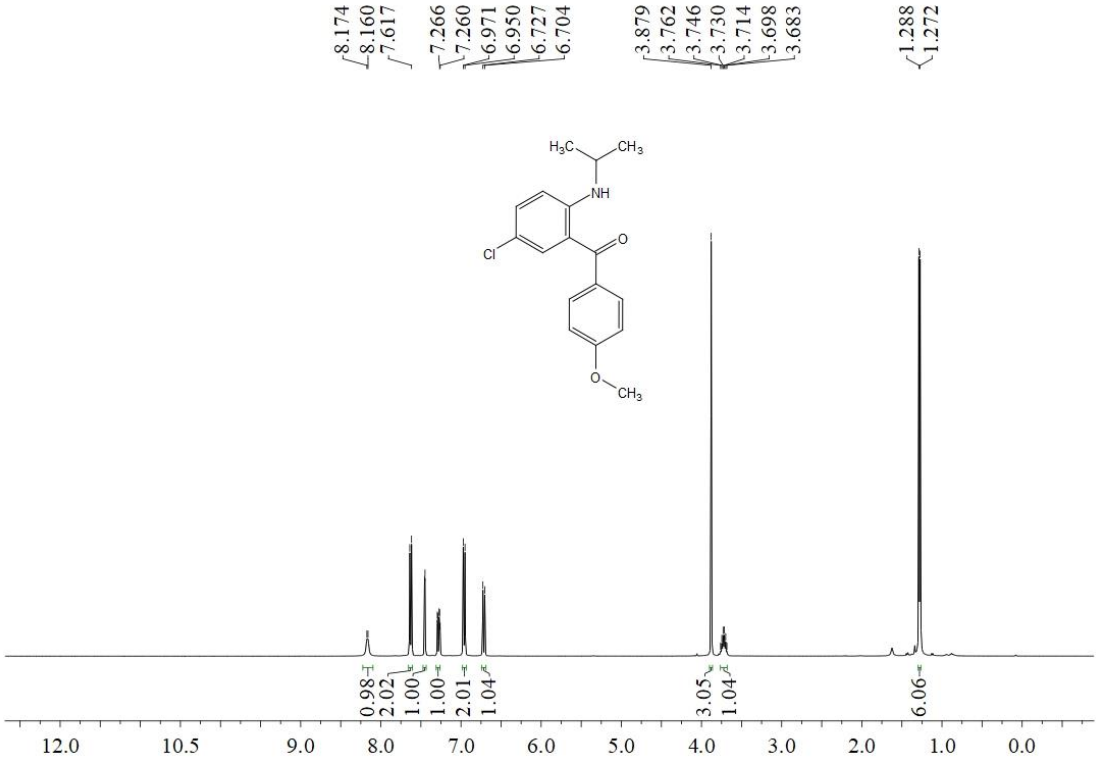


^{13}C NMR (100 MHz, $CDCl_3$)

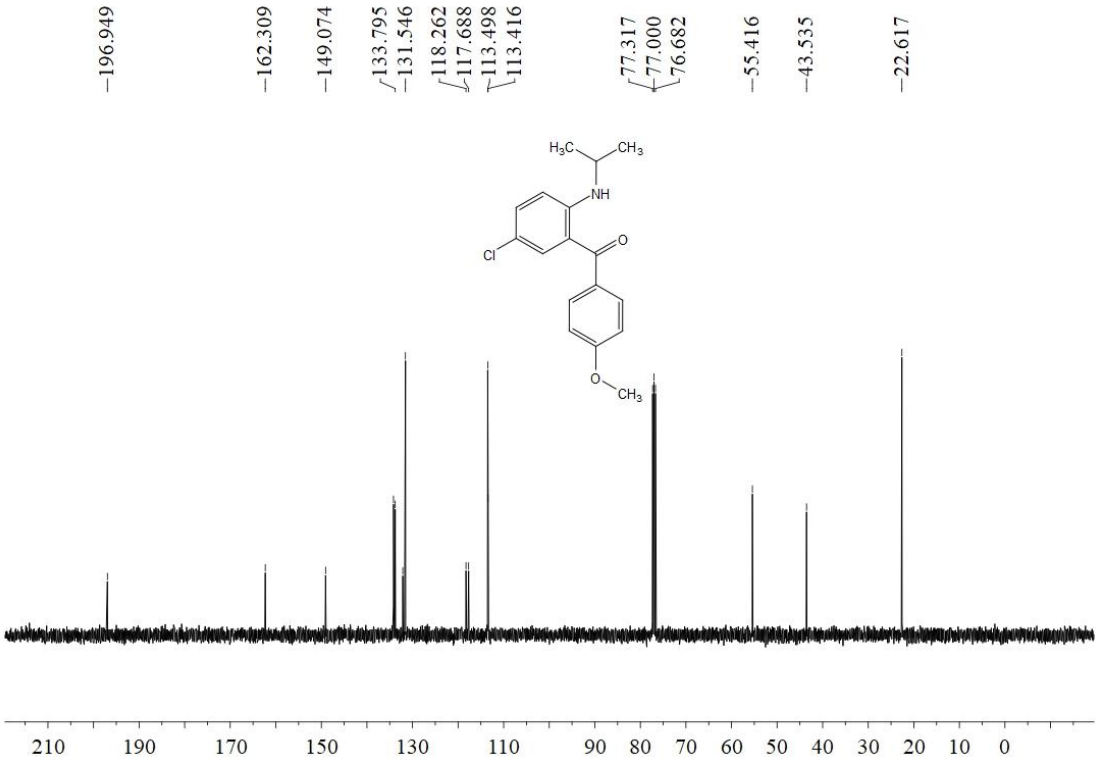


(5-Chloro-2-(isopropylamino)phenyl)(4-methoxyphenyl)methanone (**11g**)

^{1}H NMR (400 MHz, $CDCl_3$)

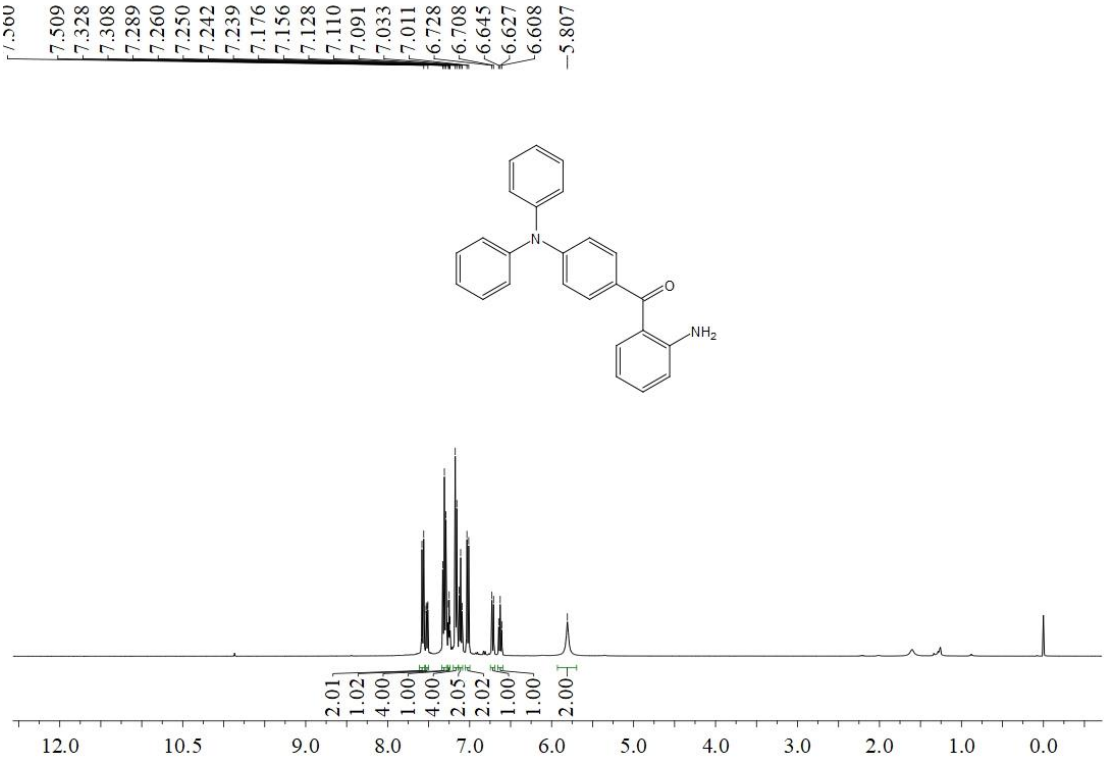


^{13}C NMR (100 MHz, $CDCl_3$)

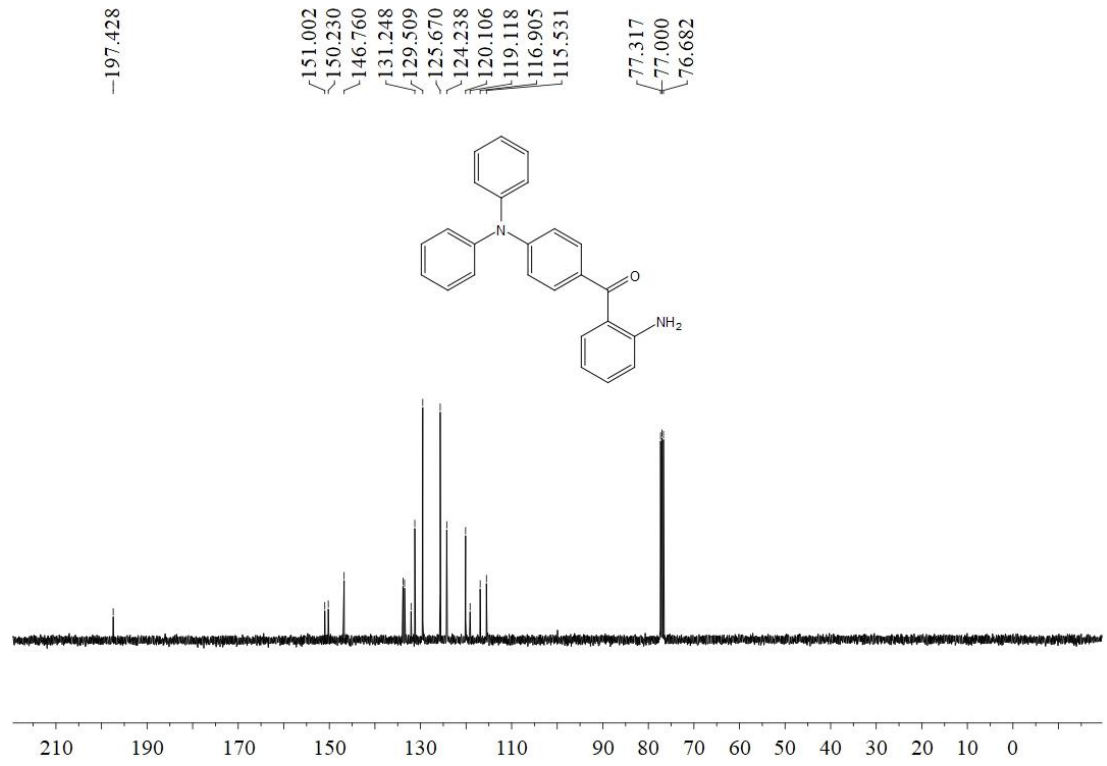


(2-Aminophenyl)(4-(diphenylamino)phenyl)methanone (**11h**)

^{1}H NMR (400 MHz, $CDCl_3$)

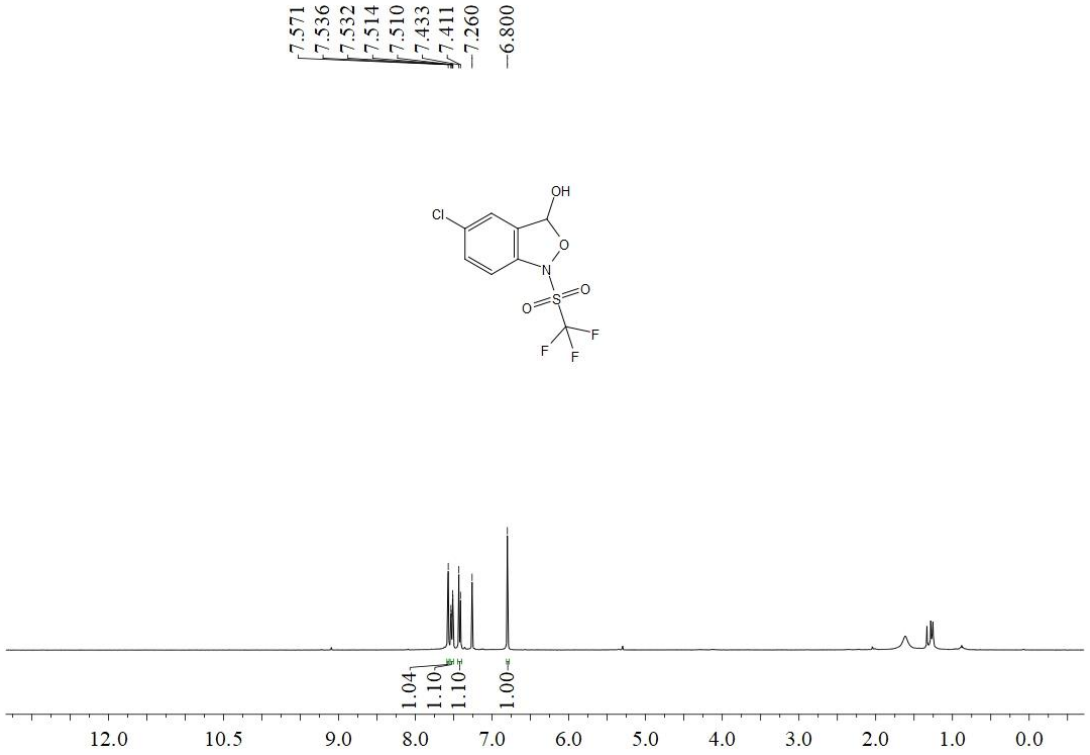


^{13}C NMR (100 MHz, $CDCl_3$)

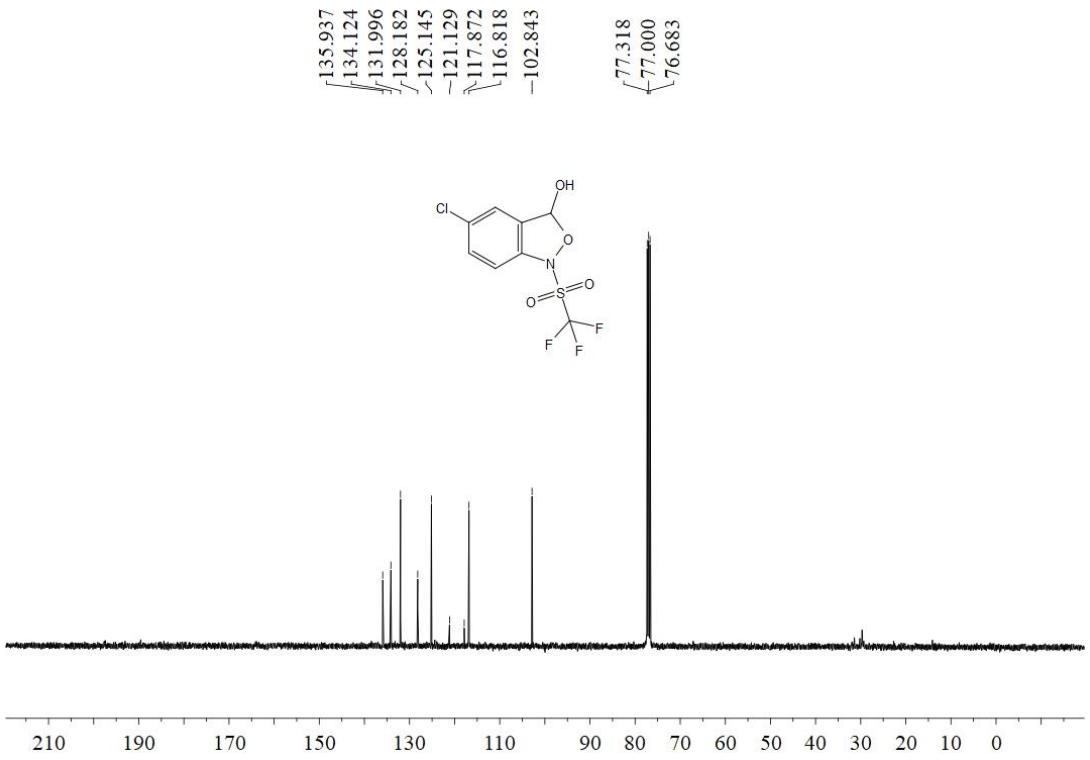


5-Chloro-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazol-3-ol (**12**)

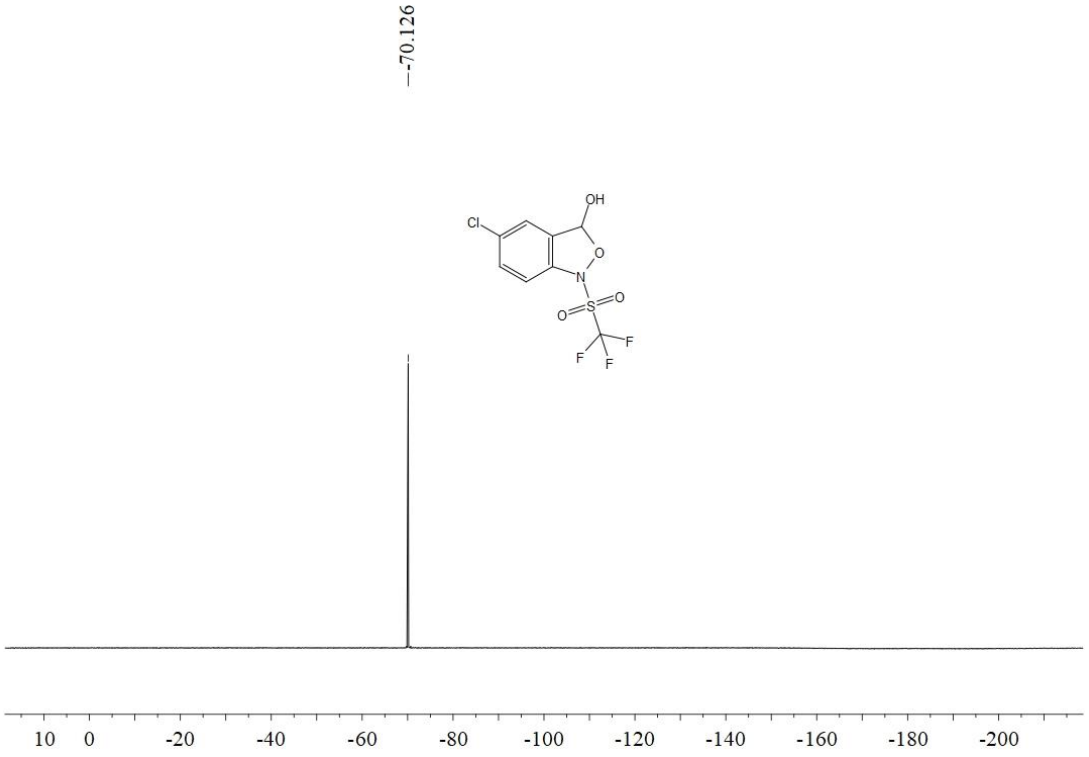
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

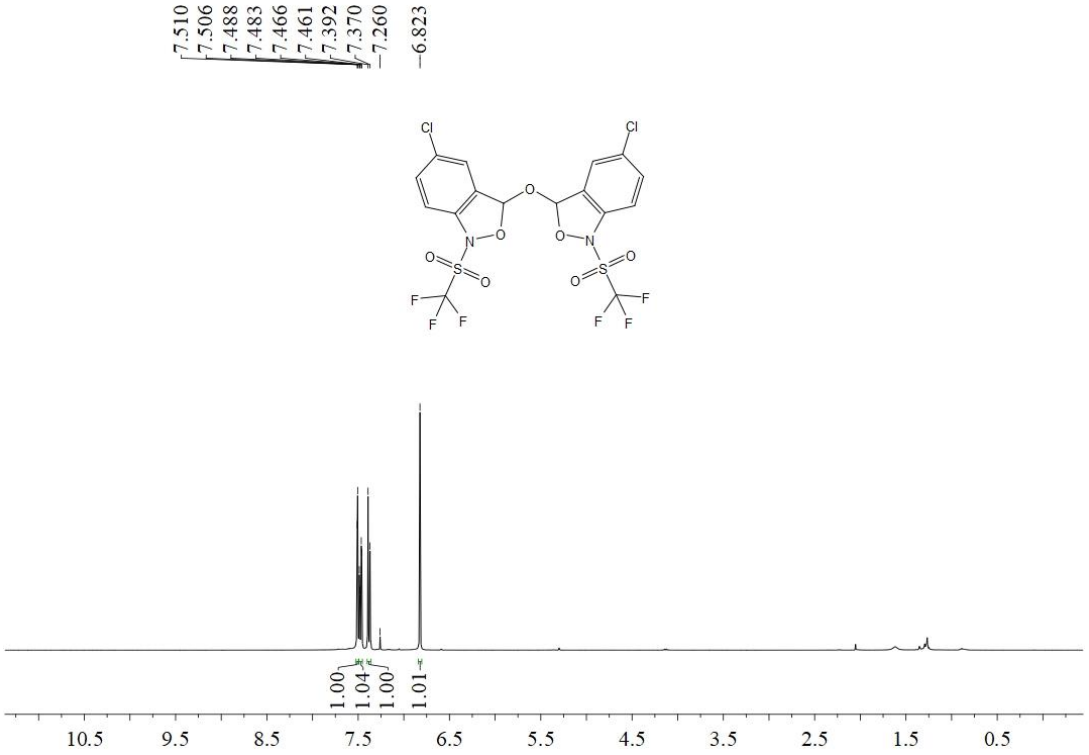


^{19}F NMR (376 MHz, $CDCl_3$)

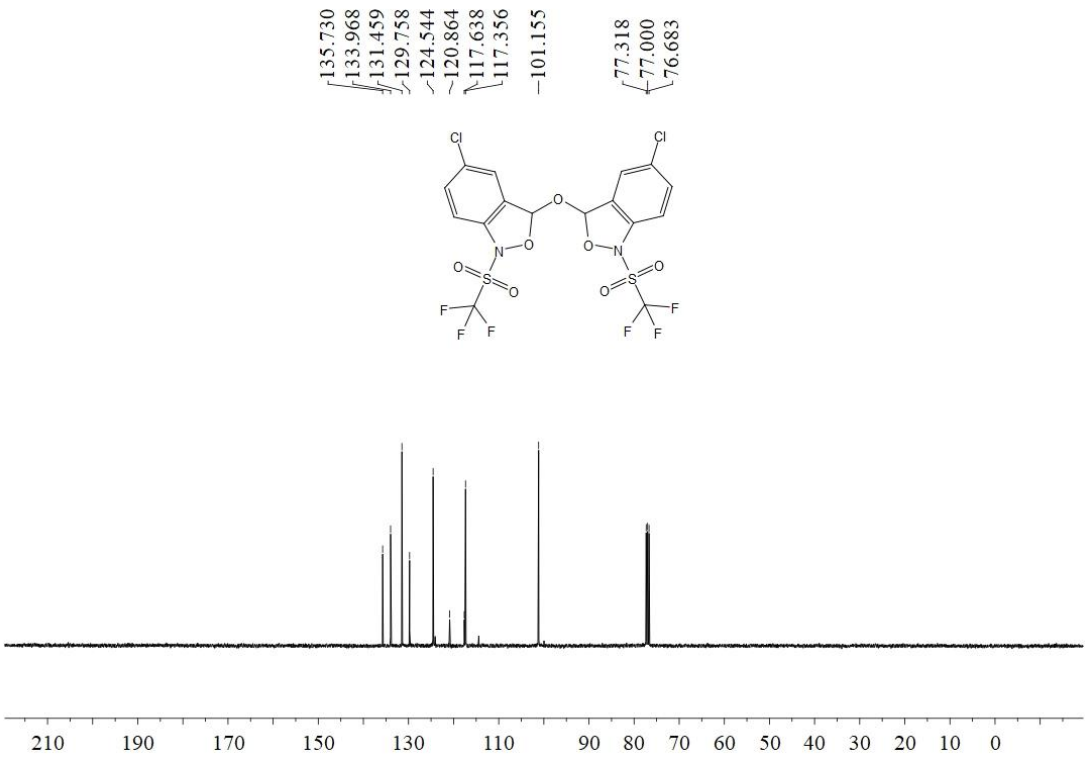

-70.126
OH
Cl
O
N
S
O
O
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3,3'-Oxybis(5-chloro-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole) (**13**)

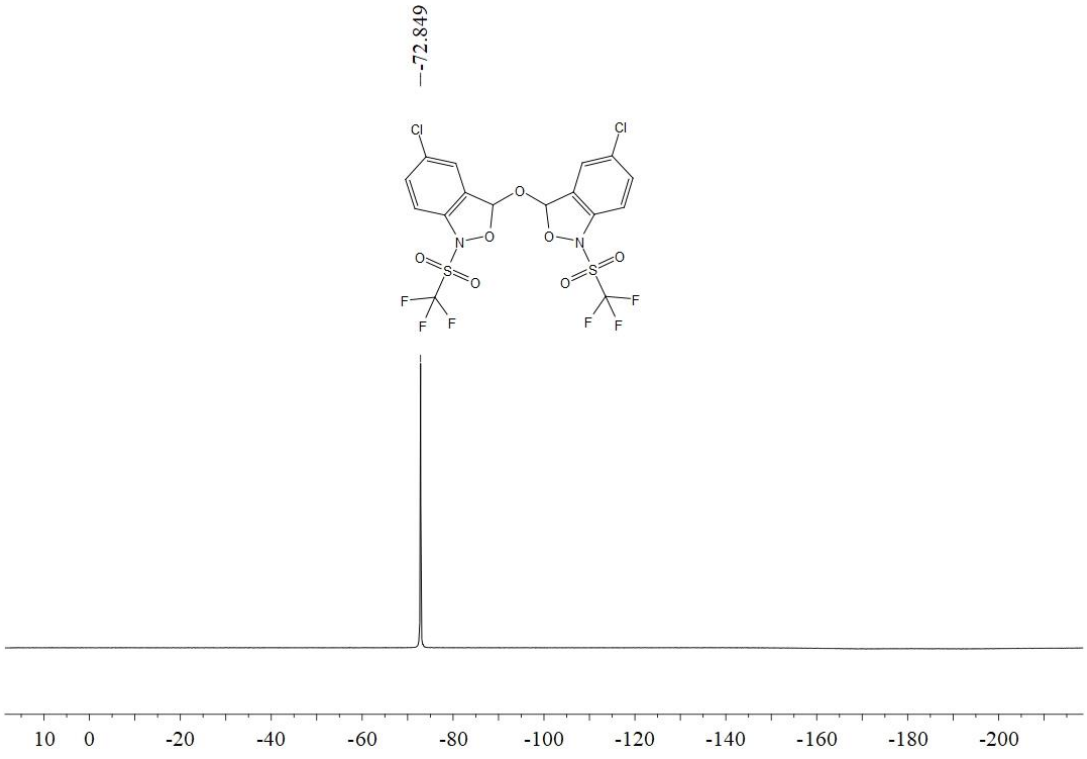
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

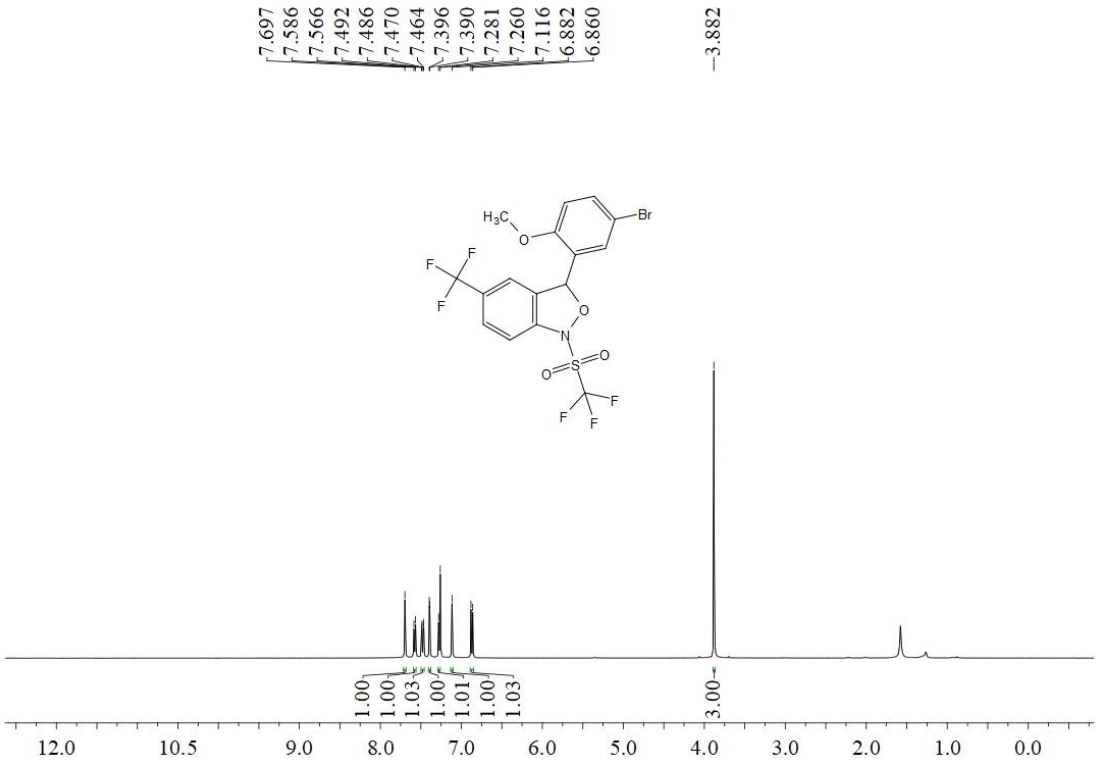


^{13}C NMR (100 MHz, $CDCl_3$)

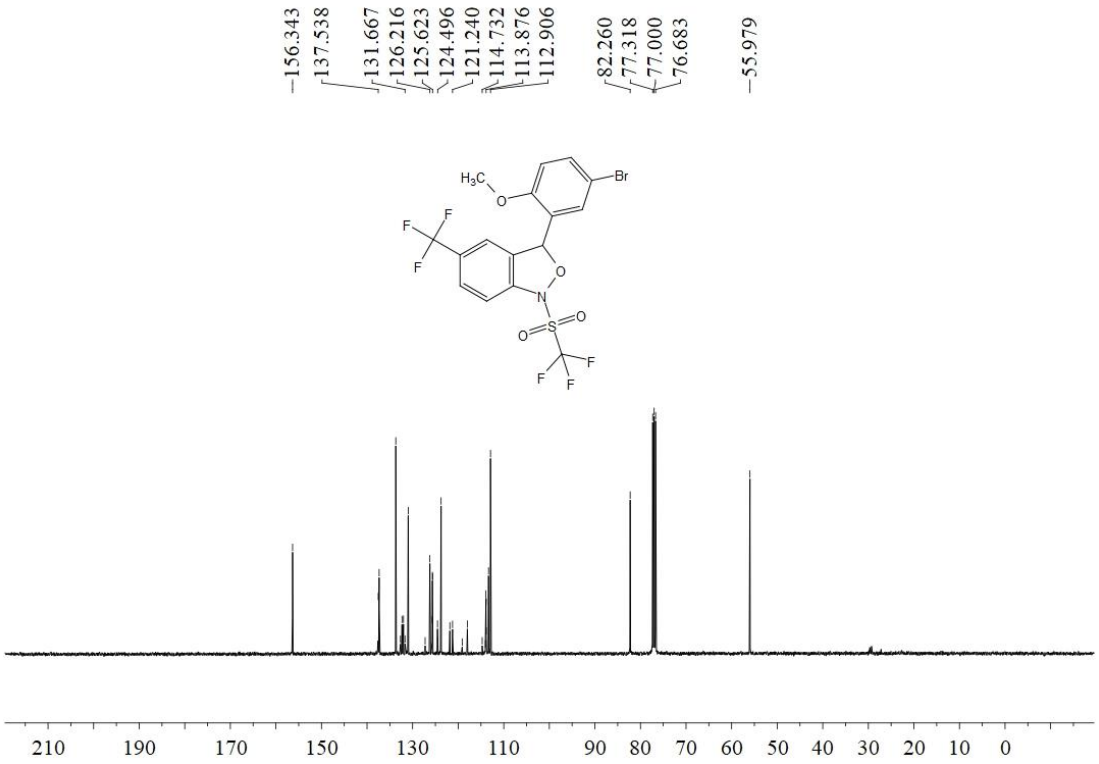

-72.849
Cl
Cl
O
N
O
O
N
O
S
O
O
S
O
F
F
F
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

3-(5-Bromo-2-methoxyphenyl)-5-(trifluoromethyl)-1-((trifluoromethyl)sulfonyl)-1,3-dihydrobenzo[c]isoxazole (**14**)

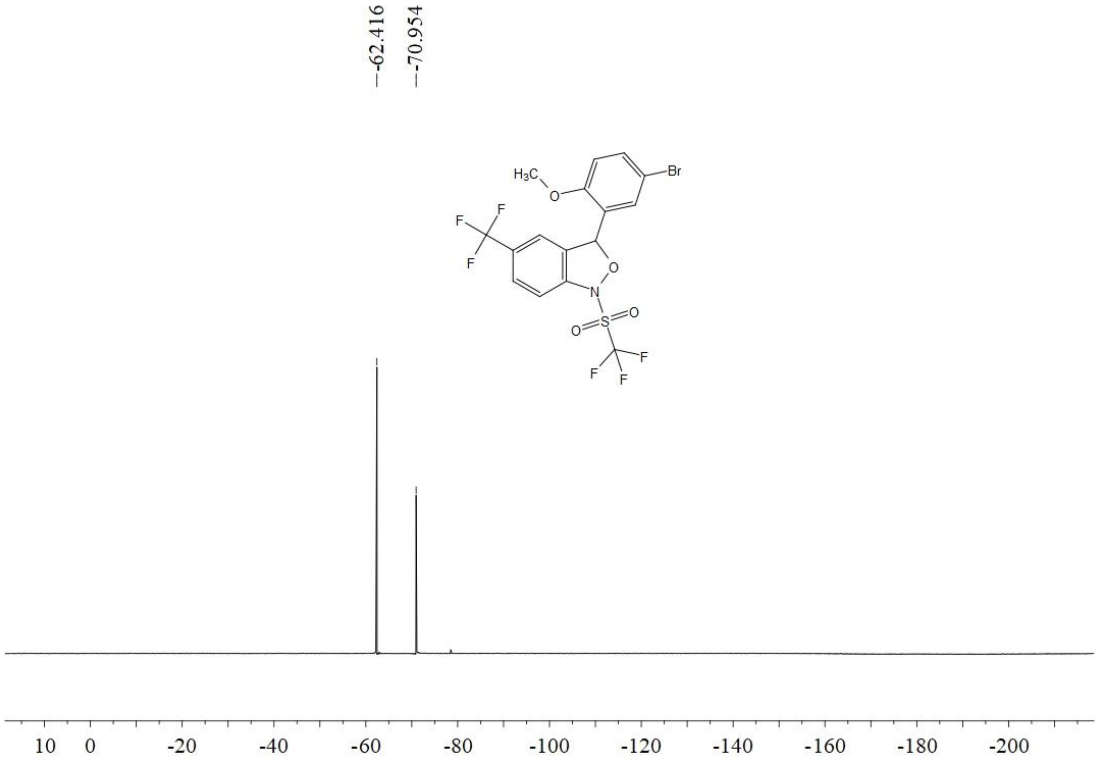
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

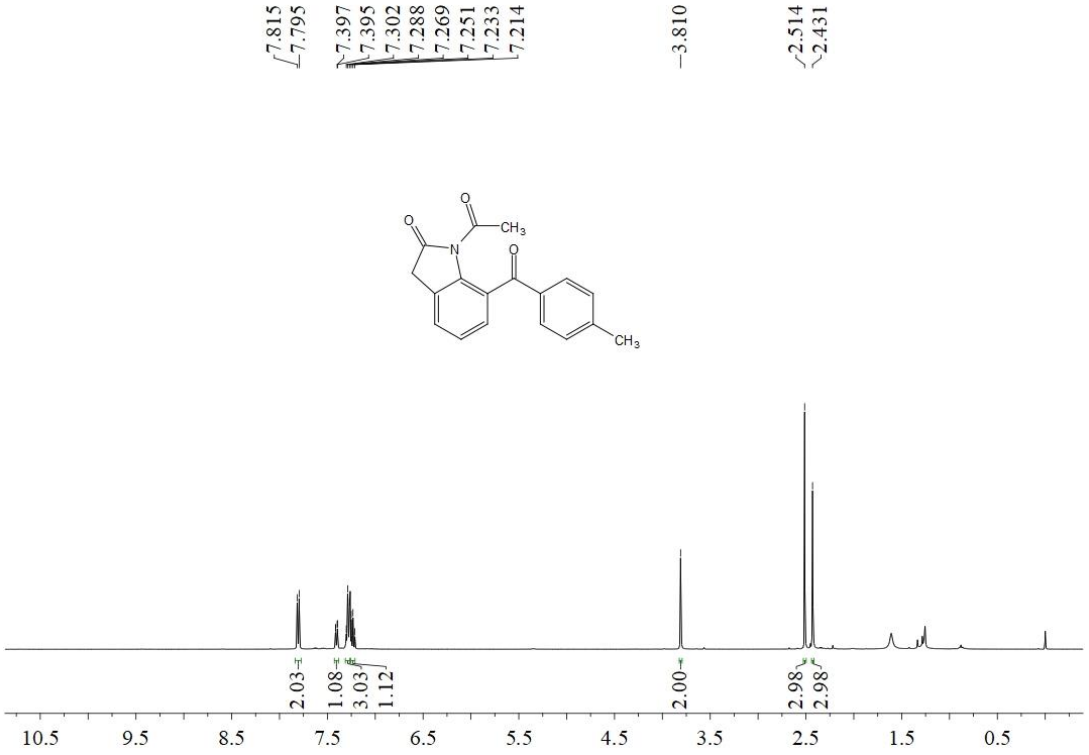


^{19}F NMR (375 MHz, $CDCl_3$)

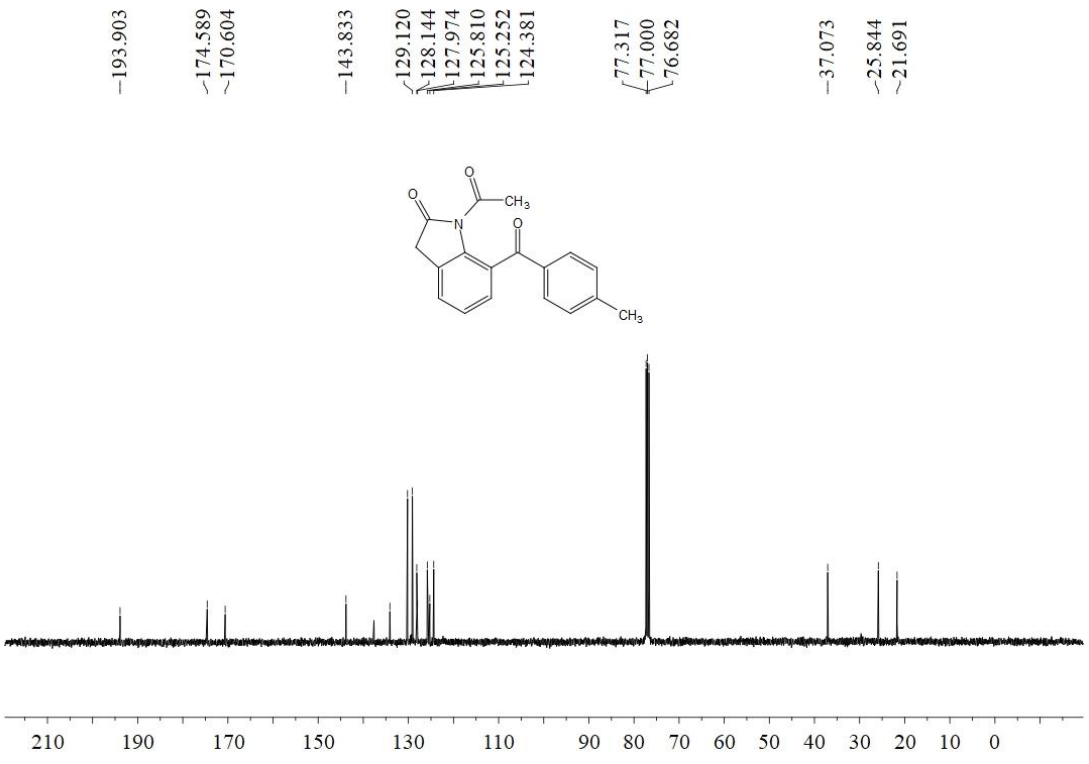

-62.416
-70.954
H3C
O
Br
F
F
F
O
N
O
S
O
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

1-Acetyl-7-(4-methylbenzoyl)indolin-2-one (**15**)

^{1}H NMR (400 MHz, $CDCl_3$)

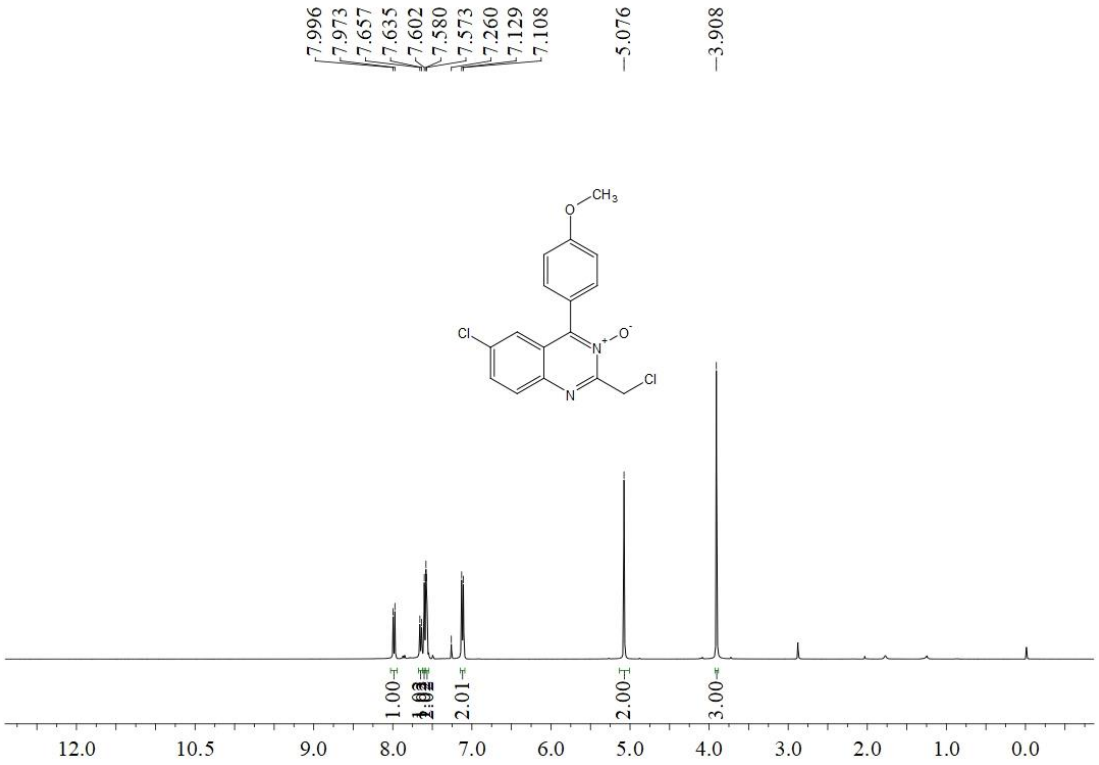


^{13}C NMR (100 MHz, $CDCl_3$)

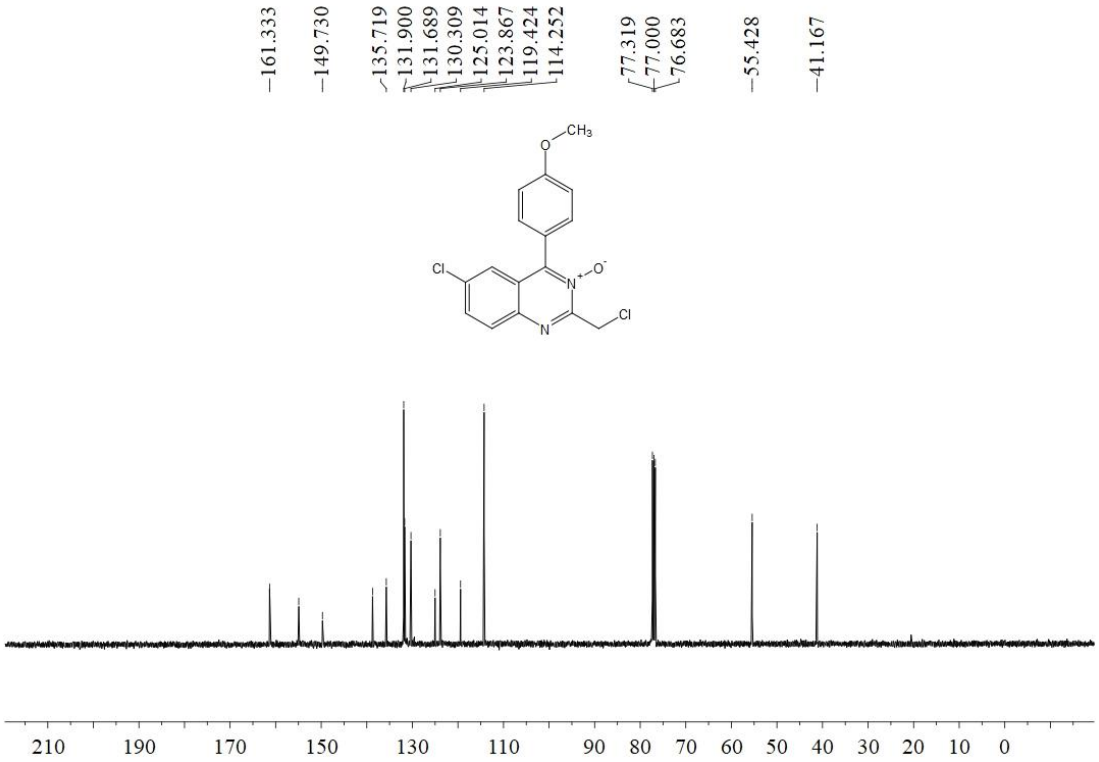


6-Chloro-2-(chloromethyl)-4-(4-methoxyphenyl)quinazoline 3-oxide (**18**)

^{1}H NMR (400 MHz, $CDCl_3$)

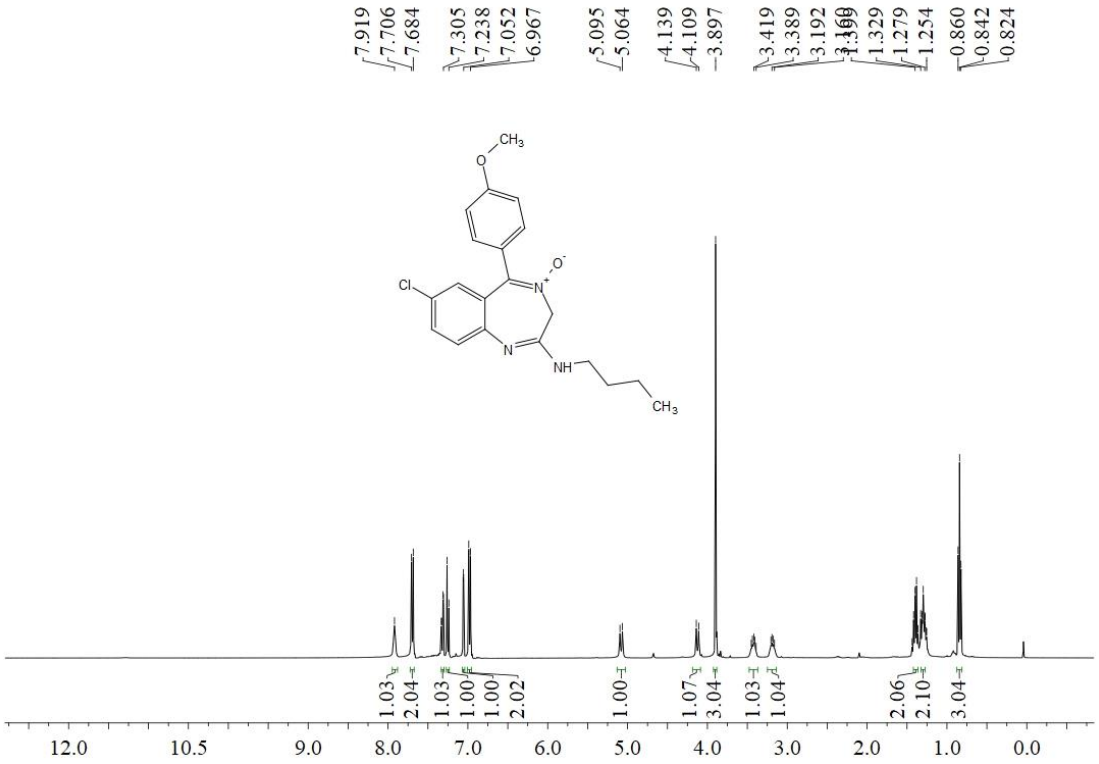


^{13}C NMR (100 MHz, $CDCl_3$)

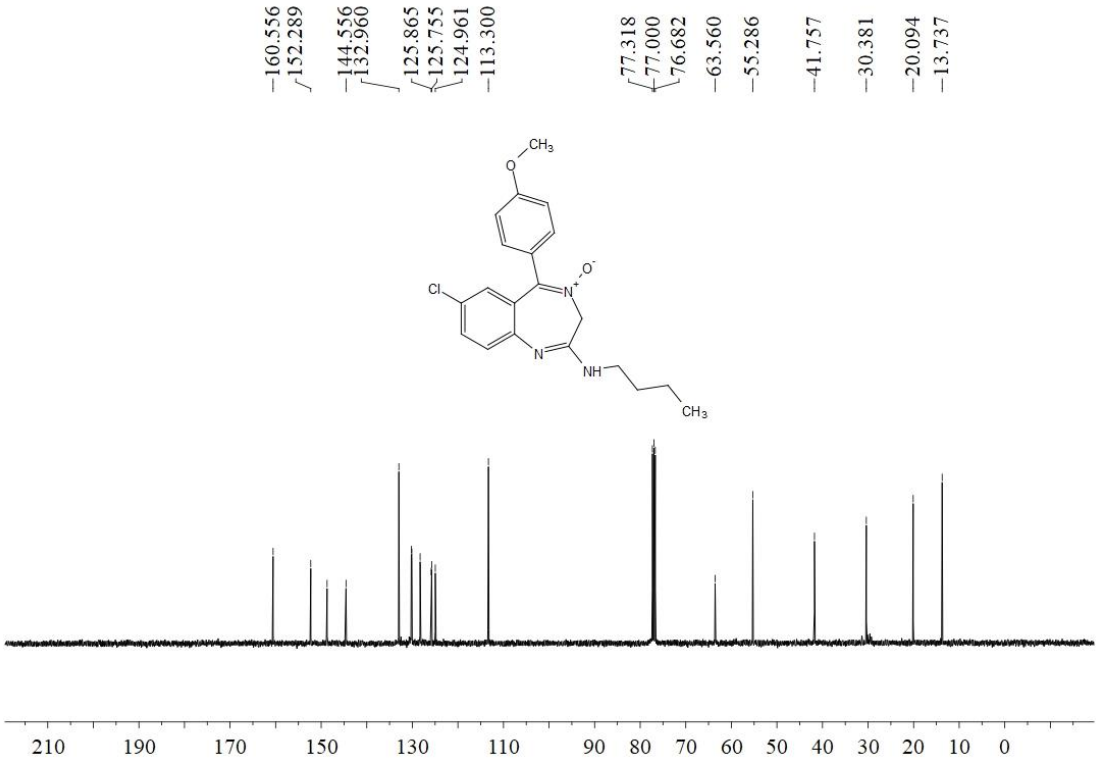


2-(Butylamino)-7-chloro-5-(4-methoxyphenyl)-3H-benzo[e][1,4]diazepine 4-oxide (**19**)

^{1}H NMR (400 MHz, $CDCl_3$)

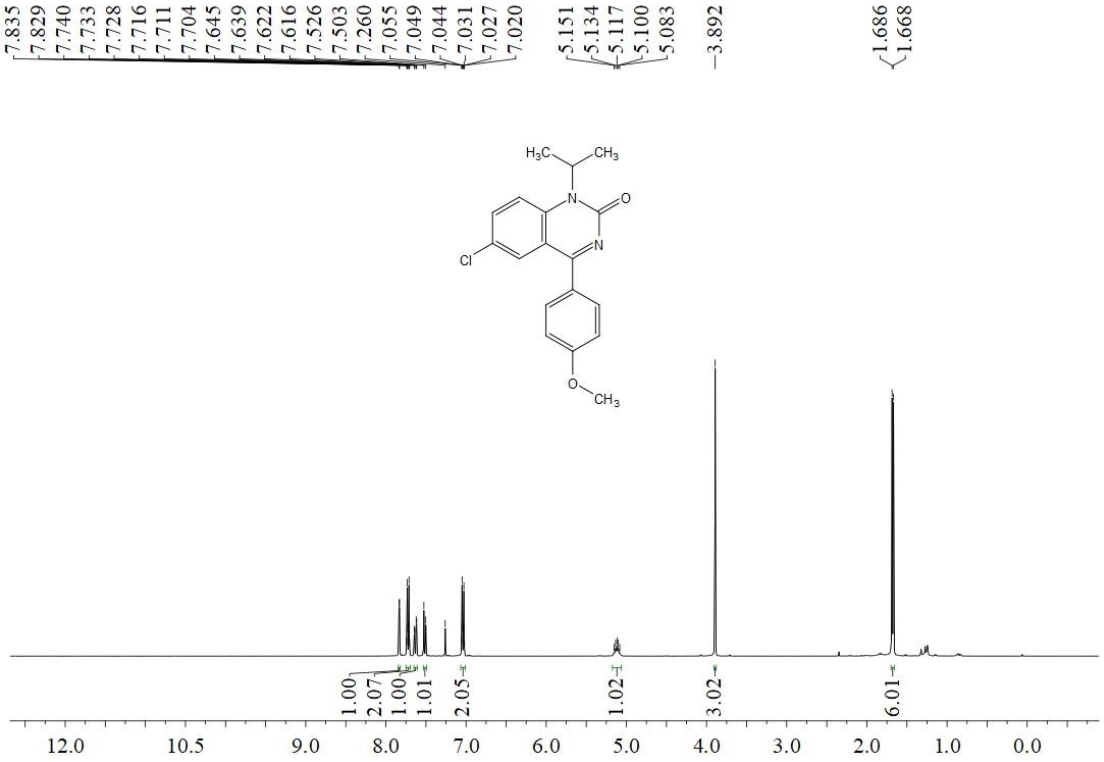


^{13}C NMR (100 MHz, $CDCl_3$)

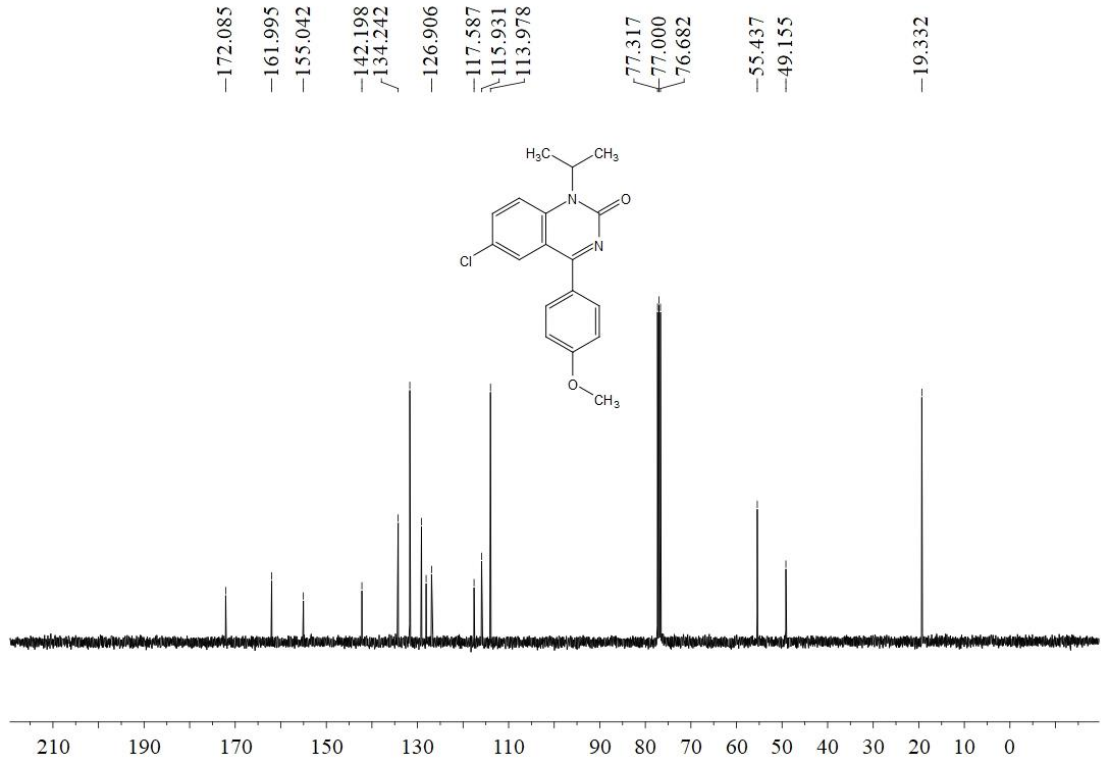


6-Chloro-1-isopropyl-4-(4-methoxyphenyl)quinazolin-2(1H)-one (**20**)

^{1}H NMR (400 MHz, $CDCl_3$)

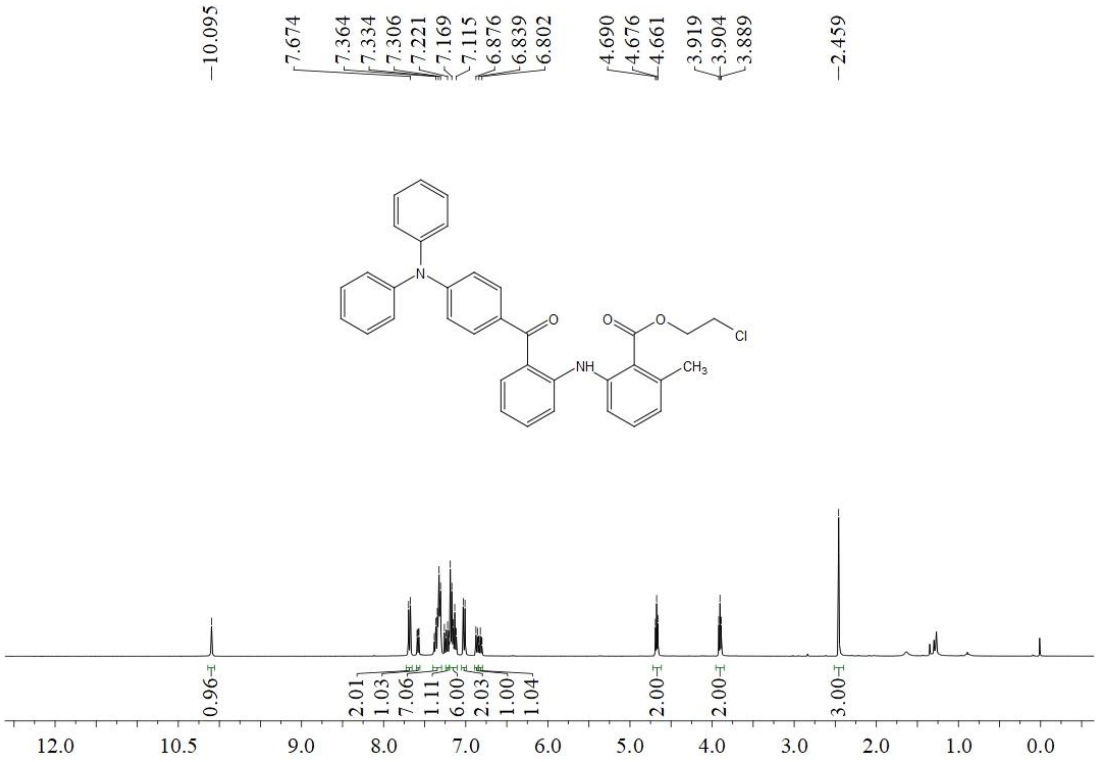


^{13}C NMR (100 MHz, $CDCl_3$)

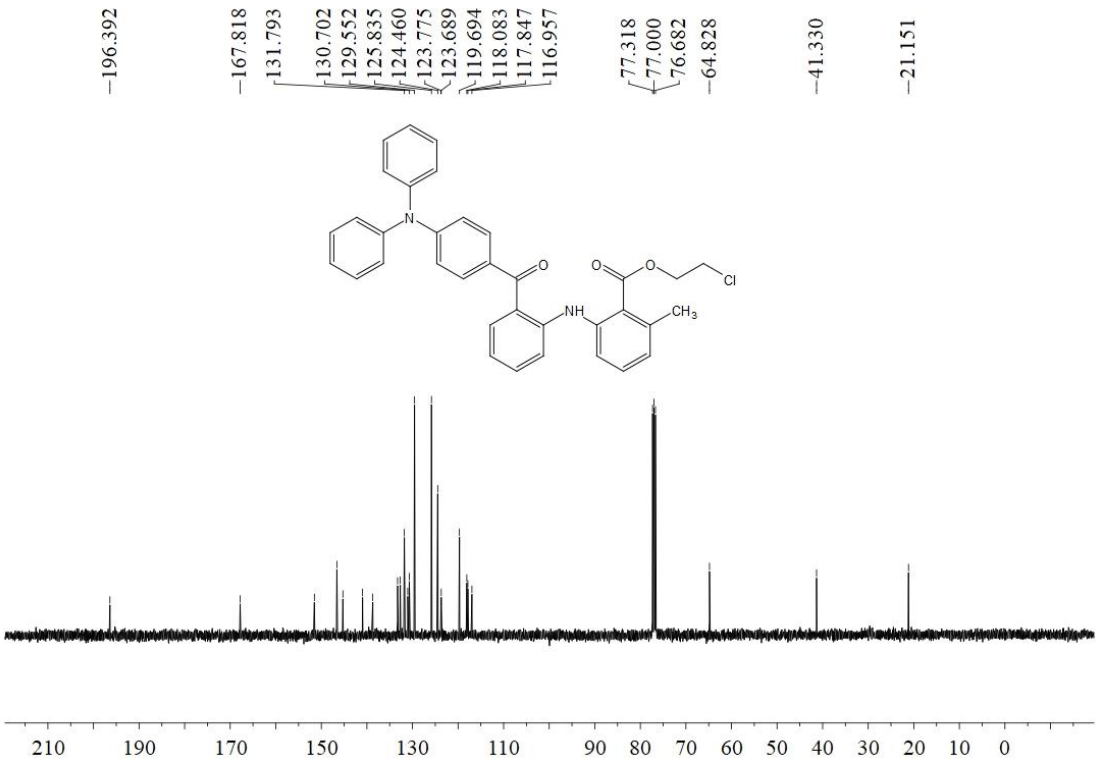


2-Chloroethyl 2-((2-(4-(diphenylamino)benzoyl)phenyl)amino)-6-methylbenzoate (**21**)

^{1}H NMR (400 MHz, $CDCl_3$)

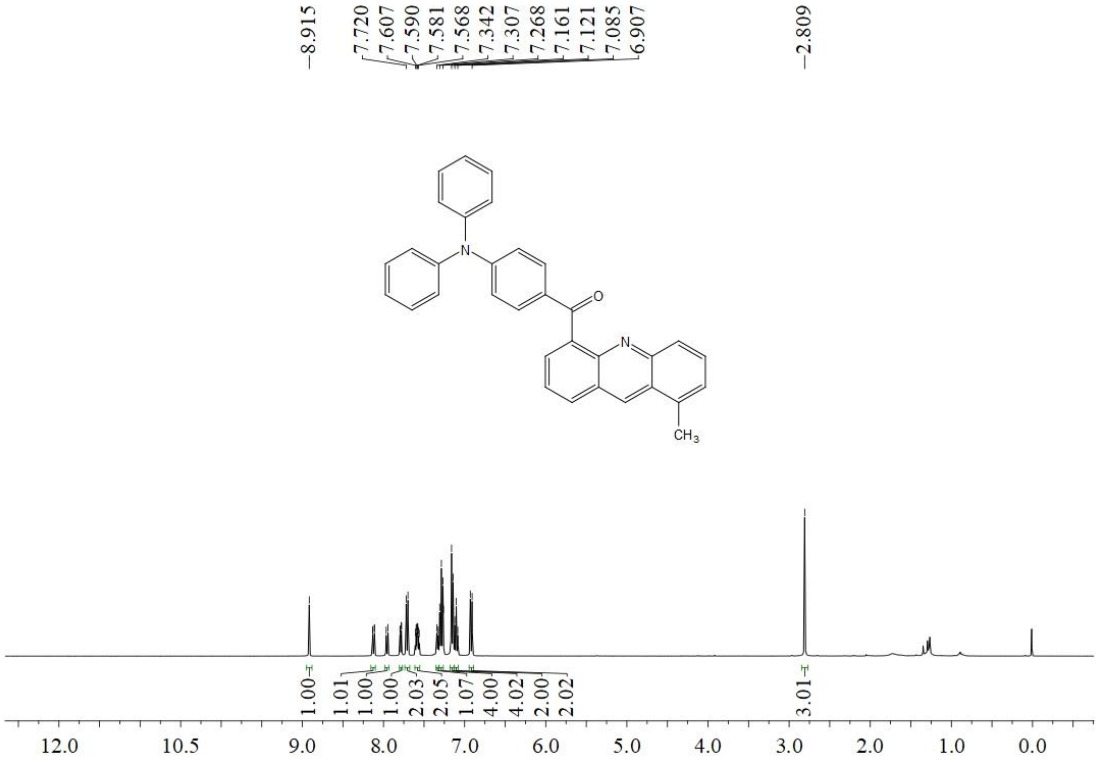


^{13}C NMR (100 MHz, $CDCl_3$)

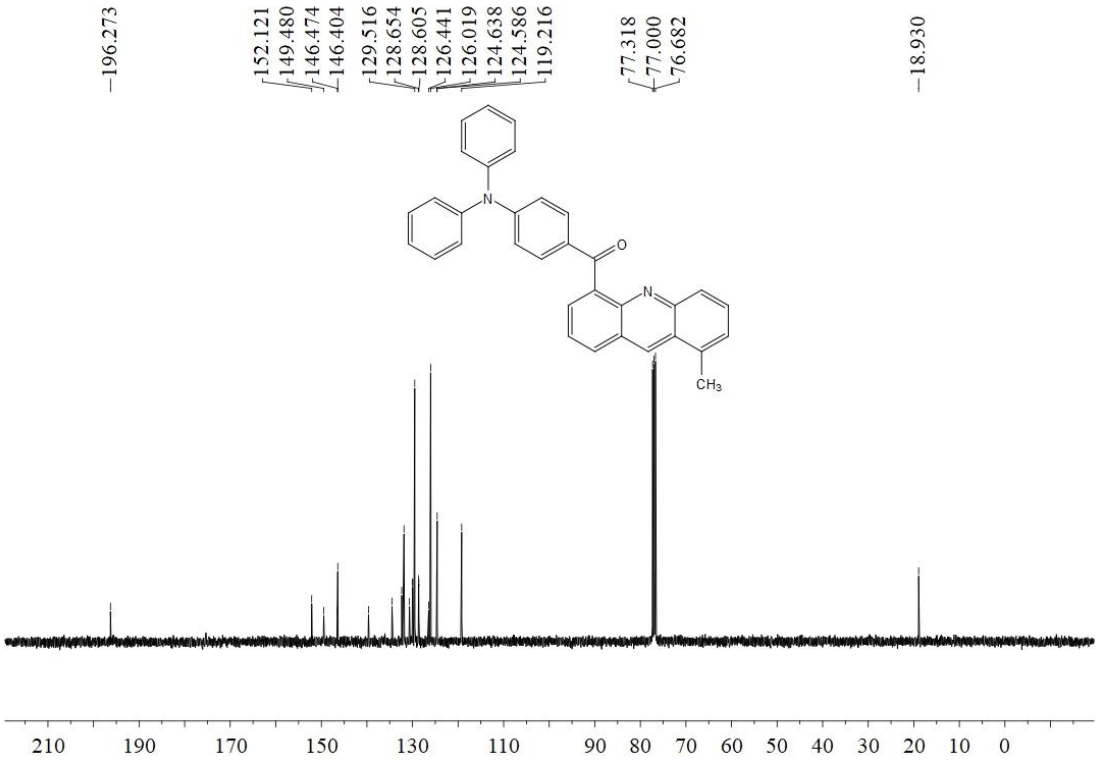


(4-(Diphenylamino)phenyl)(8-methylacridin-4-yl)methanone (**22**)

^{1}H NMR (400 MHz, $CDCl_3$)

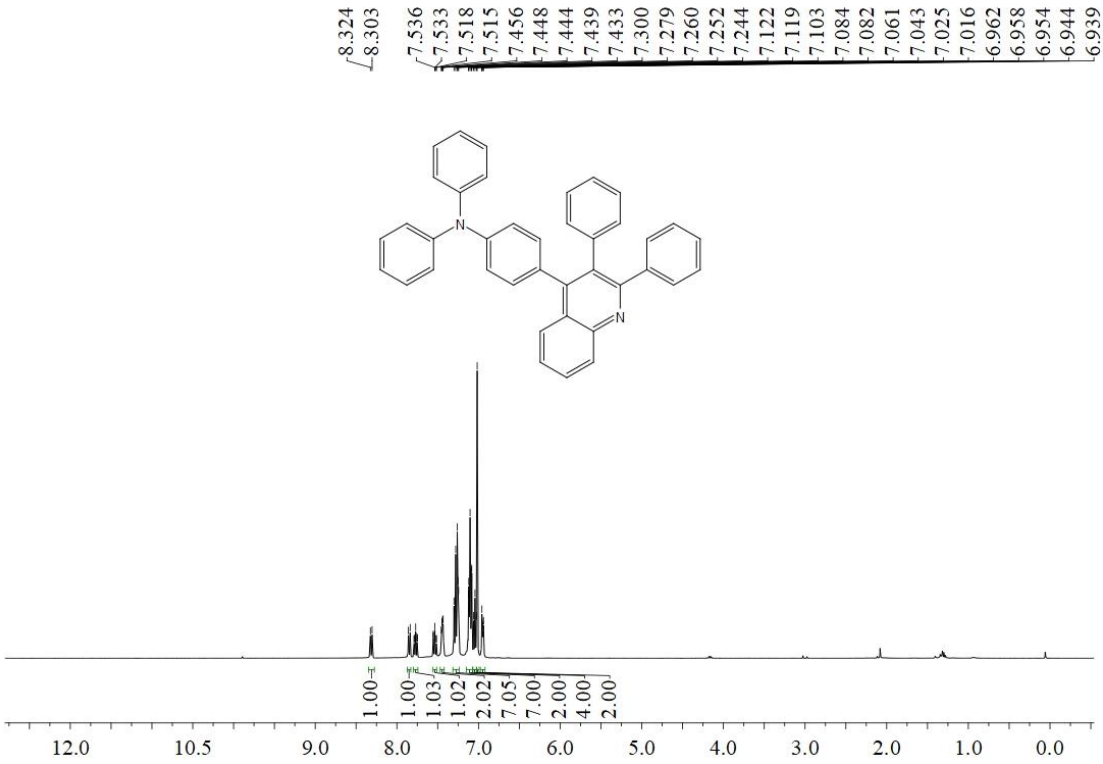


^{13}C NMR (100 MHz, $CDCl_3$)

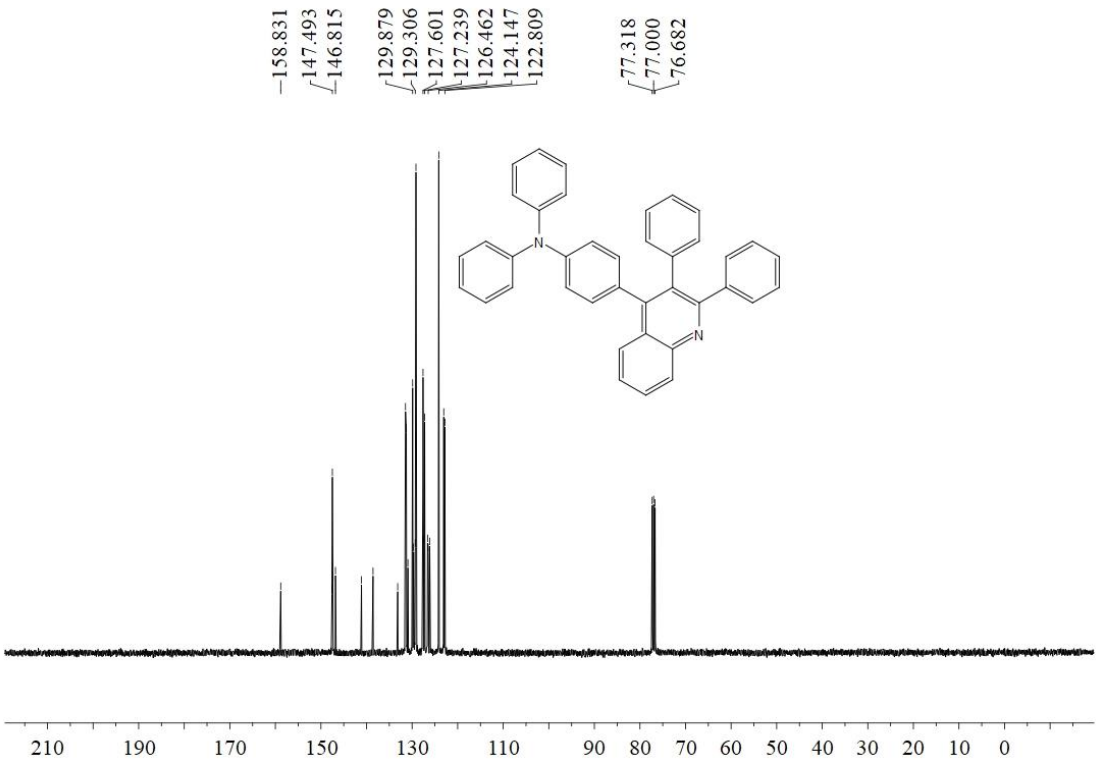


4-(2,3-Diphenylquinolin-4-yl)-N,N-diphenylaniline (**23**)

^{1}H NMR (400 MHz, $CDCl_3$)

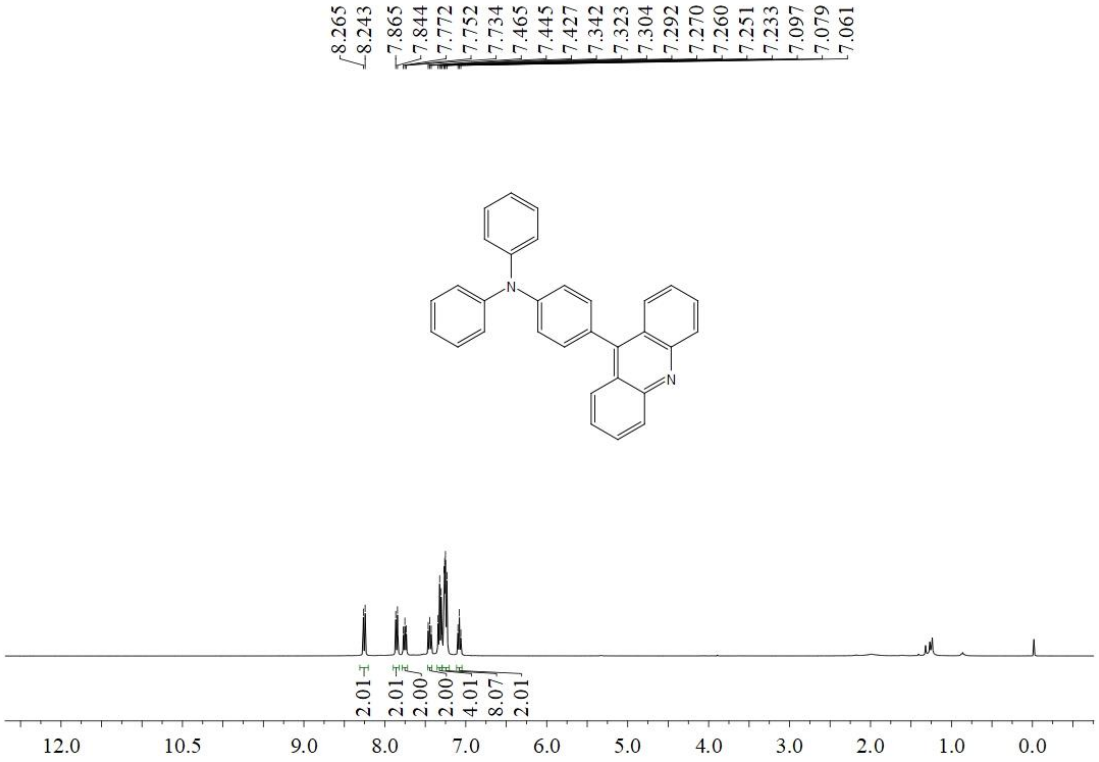


^{13}C NMR (100 MHz, $CDCl_3$)

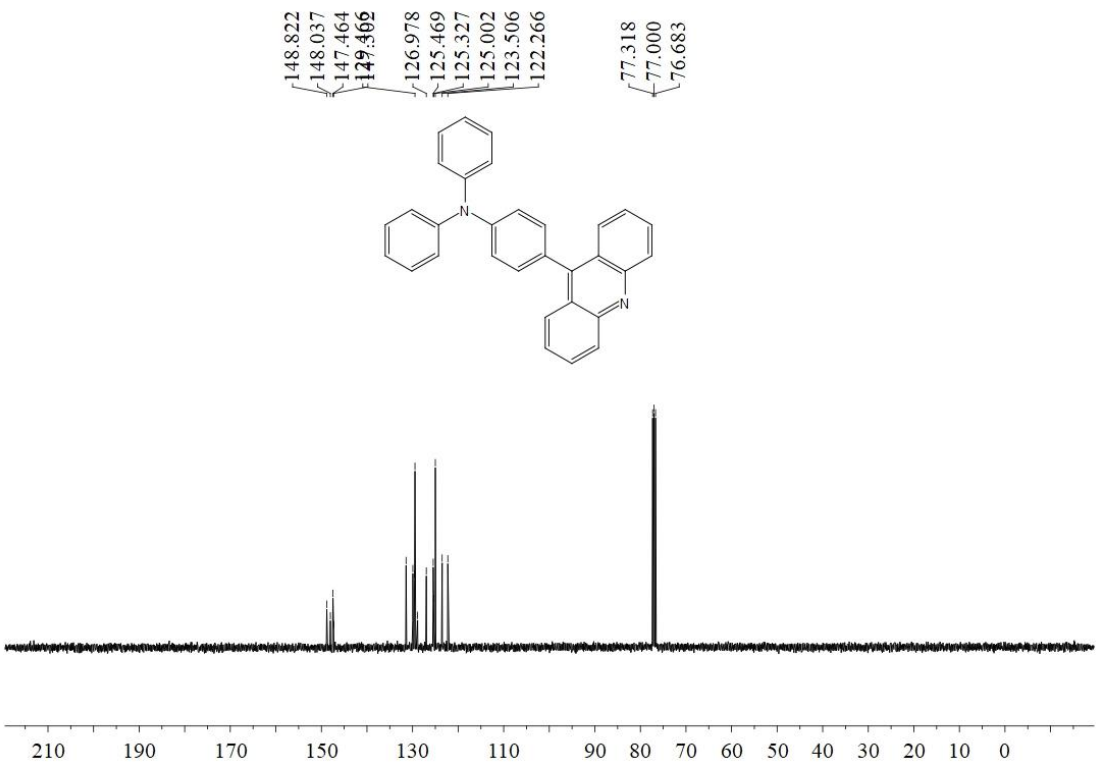


4-(Acridin-9-yl)-N,N-diphenylaniline (**24**)

^{1}H NMR (400 MHz, $CDCl_3$)

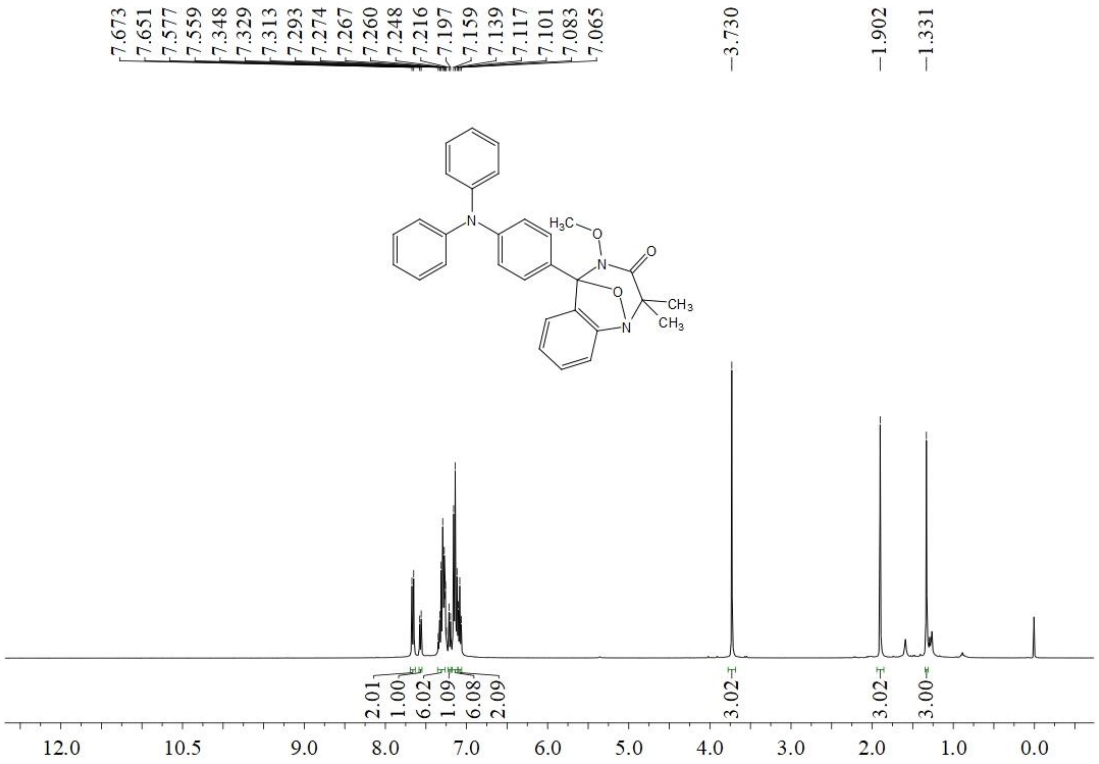


^{13}C NMR (100 MHz, $CDCl_3$)



5-(4-(Diphenylamino)phenyl)-4-methoxy-2,2-dimethyl-4,5-dihydro-1,5-epoxybenzo[e][1,4]diazepin-3(2H)-one (**25**)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)