Copper-Catalyzed Difluoromethylenation of C (sp^2) -H Bonds of Alkenes

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Contents

1. General information

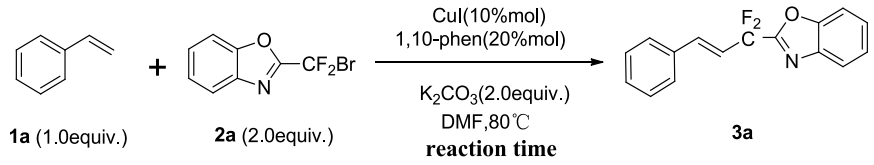
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 and AM500 spectrometer. ^{19}F NMR was recorded on a Bruker AM400 spectrometer ($CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using trifluorotoluene as an internal standard before working up the reaction. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm-1. Melting points were obtained on a X-4 digital melting point apparatus without correction. High-resolution mass spectra (HRMS) were measured with JEOL JMX-SX 102A spectrometer (FAB) and electrospray (ESI). Some associative experiments were performed on a Varian Saturn 2200 GC-MS system.

Materials: All reagents were used as received from commercial sources.

2. Optimization of the reaction conditions

2.1 Optimization of reaction time

Table S1. Optimization of reaction time



1a (1.0equiv.) **2a** (2.0equiv.) **3a**

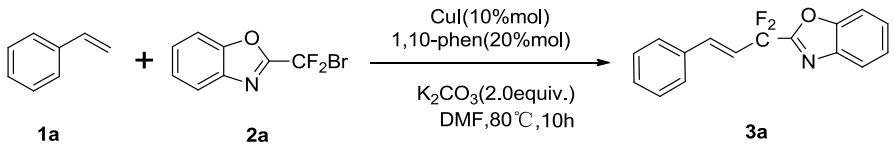
Entry	Reaction time (h)	**3a** Yield (%)[a]
1	8	67
2	10	89
3	19	88
4	24	91

[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Conclusion: From above, the yield of desired product obviously increased when the reaction time changed from 8 hours to 10 hours. However, the yield was almost constant when the time prolonged from 10 h, 19 h to 24 h. Therefore, the reaction time was selected 10 h.

2.2 Optimization of the substrate ratio

Table S2. Optimization of the substrate ratio



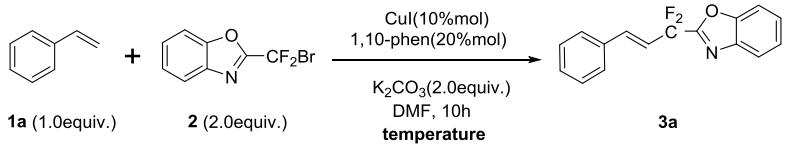
Entry	**2a** (equiv.)	**1a** (equiv.)	**3a** Yield (%)[a]
1	1.5	1.0	56
2	2.0	1.0	67
3	3.0	1.0	90
4	5.0	1.0	87

[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Conclusion: From above, the yields of product **3a** have obvious change when the amount of the substrate **2a** increased from 2.0 to 3.0 equiv. Continue to increase the amount of substrate **2a** to 5.0 equiv, the yield was slightly lower. Therefore, the substrate ratio (**2**/**1a**) = 2:1 was selected in the optimized reaction condition.

2.3 Optimization of reaction temperature

Table S3. Optimization of reaction temperature



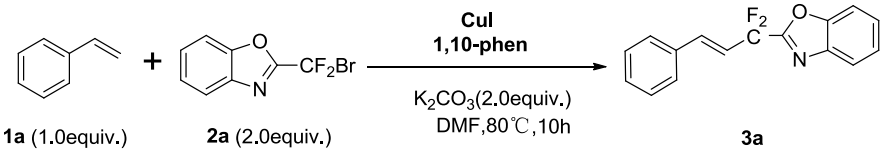
Entry	temperature (℃)	Yield (%)[a]
1	60	54
2	80	90
3	100	87
4	120	68

[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Conclusion: From above, the lower yield was observed when the reaction was carried at 120℃. Therefore, the 80℃ was selected as the best reaction temperature.

2.4 Optimization of ratio between catalyst and ligand

Table S4. Optimization of ratio between catalyst and ligand



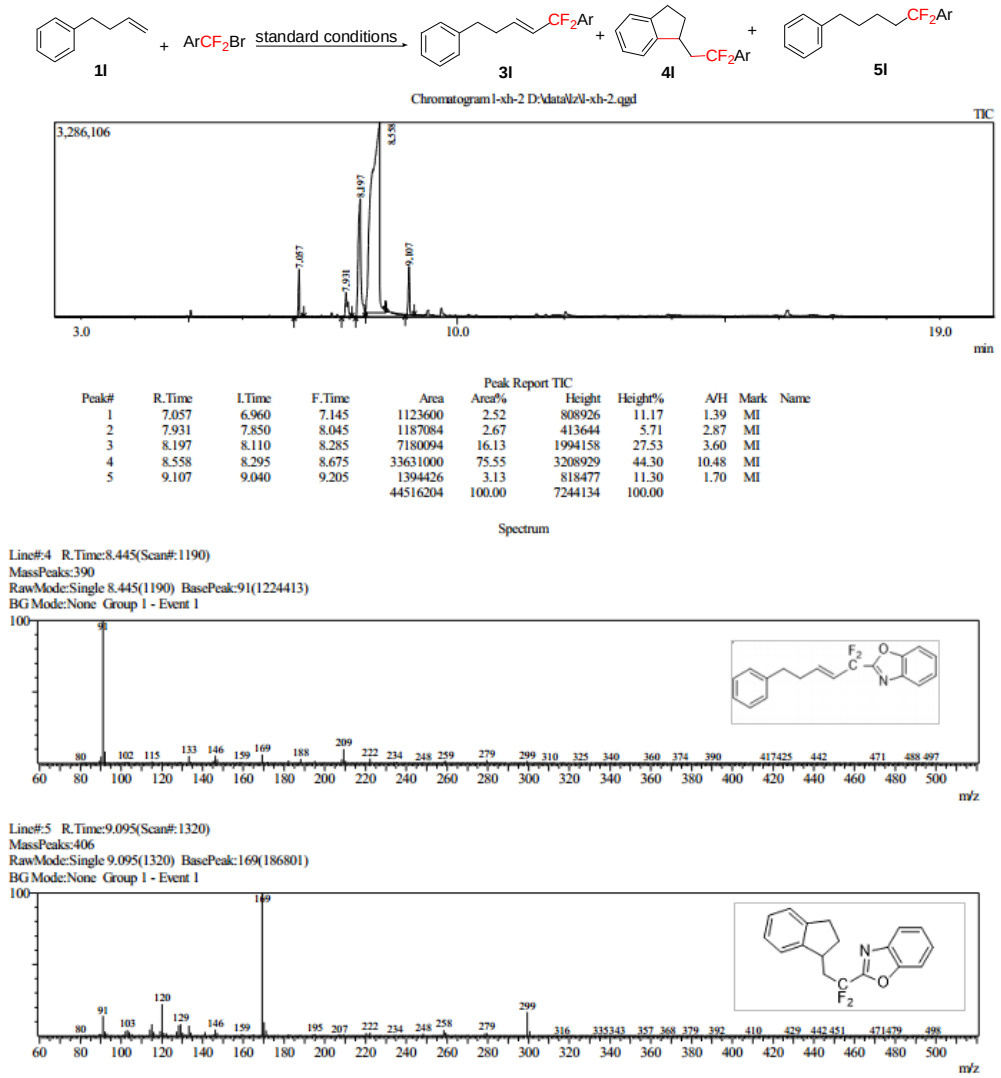
Entry	CuI (equiv)	1,10-phen (equiv)	Yield (%)[a]
1	0.005	0.012	38
2	0.01	0.02	88
3	0.01	0.015	49
4	0.01	0.01	42
5	0.01	0.03	90

[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Conclusion: From table S4, the combination of 0.01 equiv. CuI and 0.02 equiv. 1,10-phen was selected as the optimized reaction condition.

3. Monitored the *gem*-difluoromethylenation reaction by GC-MS

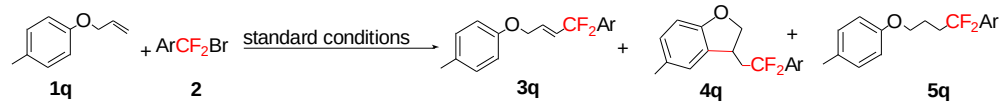
3.1 Exploring the reactions of **1l** and **2a** by GC-MS



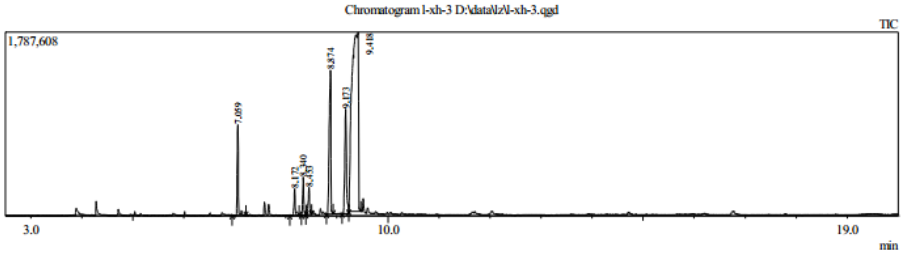
Scheme S1. The results of the reaction of **1l** and **2a** by GC-MS

Conclusion: From scheme S1, the peak at 8.445 min is attributed to the main product **3l**, and the peak at 9.095 min is that of **4l**.

3.2 Exploring the reaction of **1q** and **2a** by GC-MS



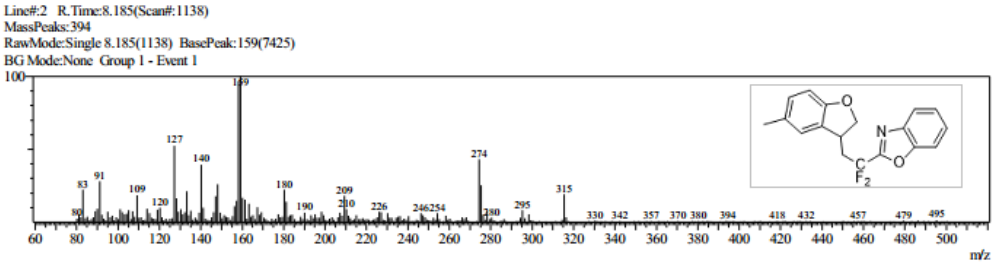
1q **2** **3q** **4q** **5q**

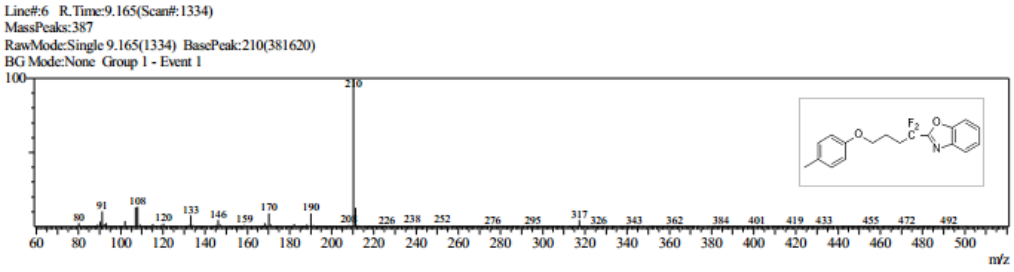


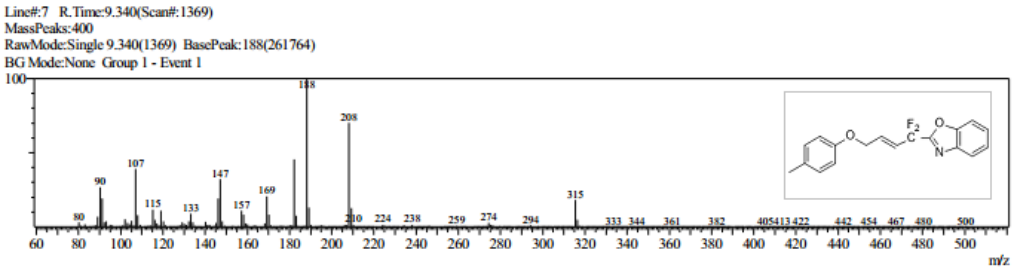
Peak Report TIC

Peak#	R.Time	LTime	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.059	6.950	7.220	1280989	5.39	882737	14.86	1.45	MI	
2	8.172	8.080	8.260	406274	1.71	262307	4.42	1.55	MI	
3	8.340	8.300	8.400	540535	2.27	367370	6.18	1.47	MI	
4	8.453	8.390	8.505	492510	2.07	268085	4.51	1.84	MI	
5	8.874	8.795	8.930	3152420	13.27	1399733	23.56	2.25	MI	
6	9.173	9.105	9.235	2337858	9.84	1016833	17.12	2.30	MI	
7	9.418	9.235	9.470	15550987	65.45	1743415	29.35	8.92	MI	
				23761573	100.00	5940480	100.00			

Spectrum



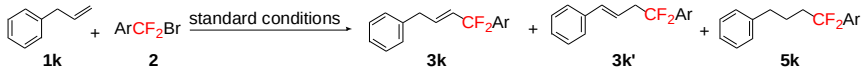


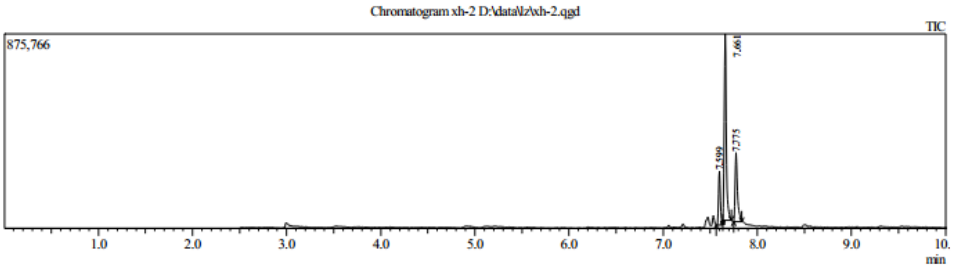


Scheme S2. The results of the reaction of **1q** and **2a** by GC-MS

Conclusion: The desired product **3q**, the peak at 9.340 min, was obtained in 35% isolated yield. The product **5q** (GC-MS at 9.165 min) was formed through the active radical abstracting H. The product **4q**, detected by ^{19}F NMR and GC-MS (8.185 min), was a *gem*-difluoromethylenation/cyclizaion cascade product.

3.3 Exploring the reaction of **2a** and **1k** by GC-MS

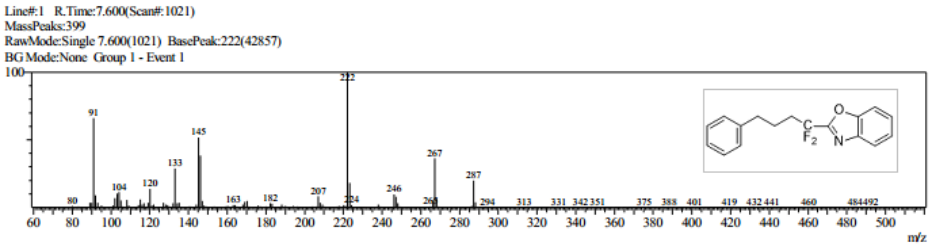


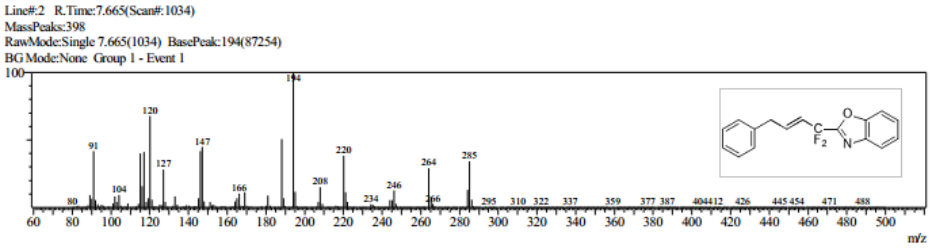


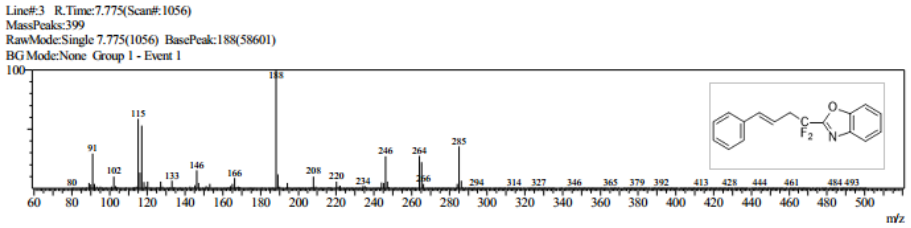
Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.599	7.565	7.635	331378	15.70	242985	17.42	1.36	MI	
2	7.661	7.635	7.725	1246693	59.06	839201	60.17	1.49	MI	
3	7.775	7.750	7.835	532776	25.24	312438	22.40	1.71	MI	
				2110847	100.00	1394624	100.00			

Spectrum







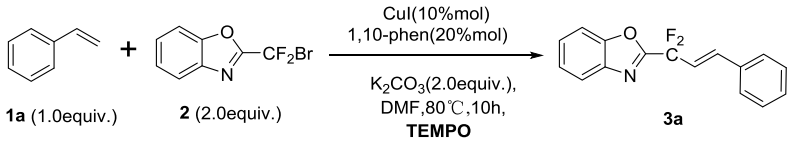
Scheme S3. The results of the reaction of **2** and **1k** by GC-MS

Conclusion: The alkane **5k** (GC-MS 7.600 min) arisen from radical abstracting hydrogen atom. The formation of **5k** was deduced that this reaction was to undergo a free radical process. The product **3k'** was isolated and detected by ^{19}F NMR and GC-MS (7.775 min).

4. Preliminary mechanistic study

4.1 The effect of TEMPO on the standard reaction

Table S5. The effect of TEMPO on the standard reaction

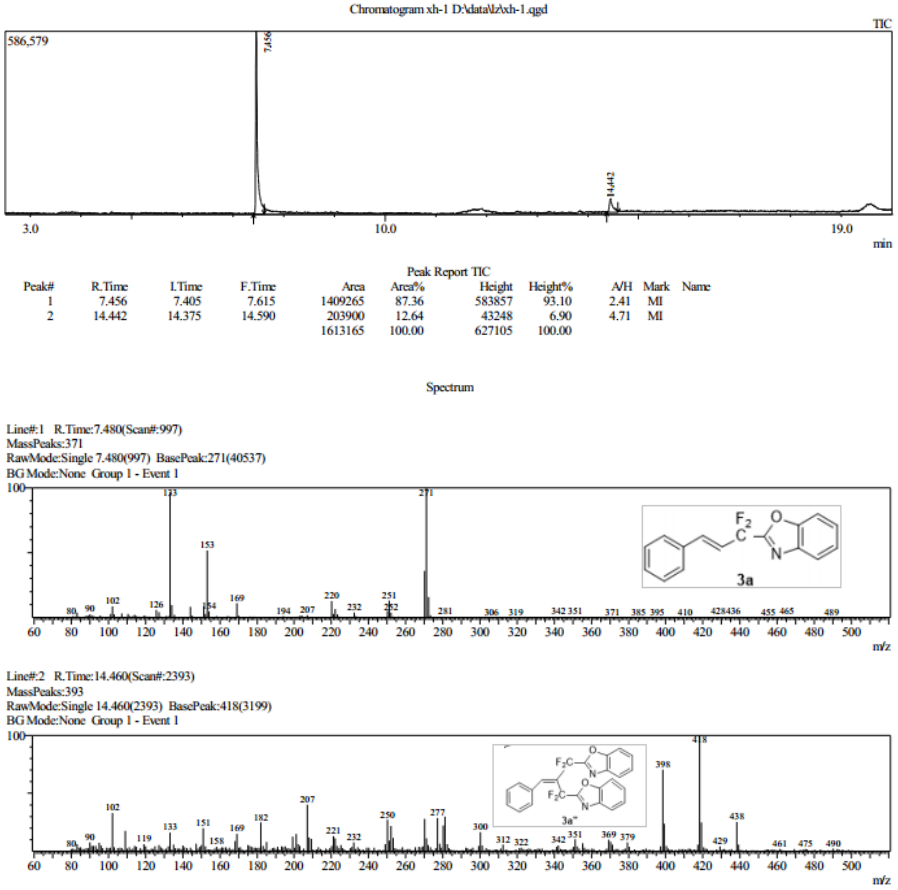


Entry	TEMPO (equiv)	Yield (%)[a]
1	—	94
2	1.0	51
3	2.0	trace

[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Conclusion: The yield of the desired product **3a** was decreased from 94% to 51% when 1 equivalent TEMPO was added in the standard reaction system. Additionally, when 2 equivalents TEMPO was added, **3a** was hardly observed. The results implied that the reaction could involve in a radical process.

4.2 The results of standard reaction by GC-MS

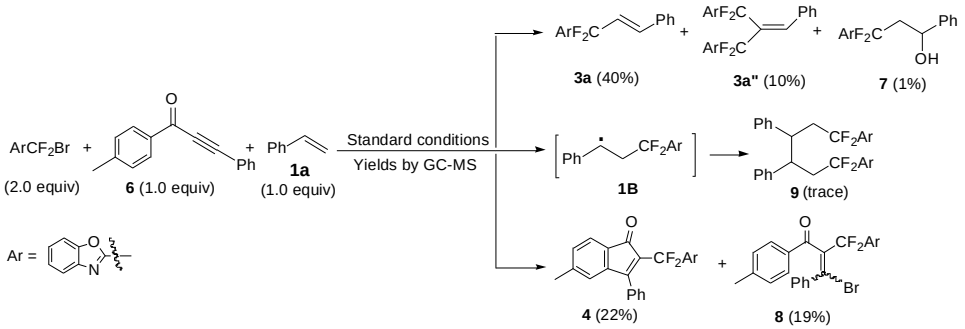


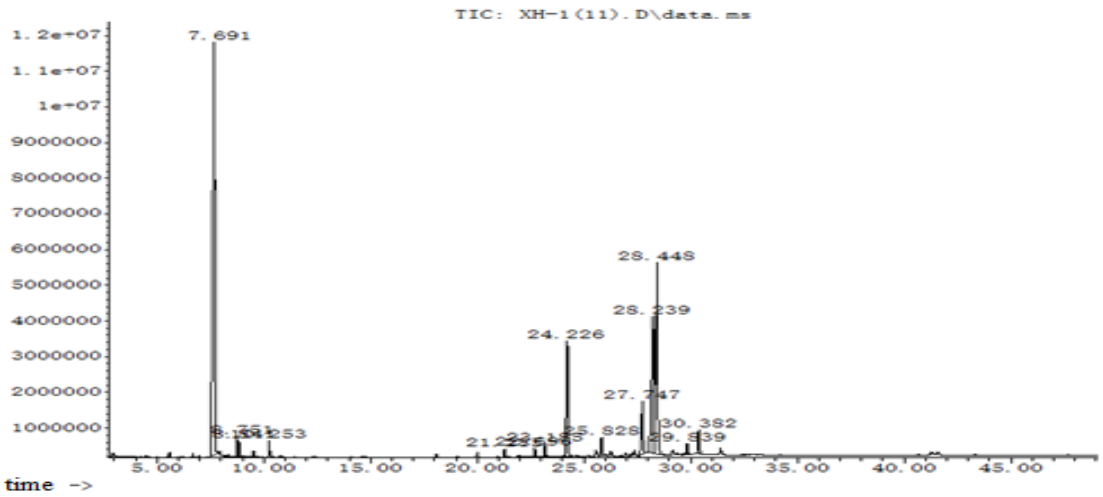
Scheme S4. The results of standard reaction by GC-MS

Conclusion: The product **3a''** was obtained in 8% isolated yields which was formed through the radical $ArCF_2\cdot$ adding to **3a**. Evidences of the formation of **3a** and **3a''** further confirmed that the difluoromethylenation of alkenes was *via* intermediate difluoromethylene radical.

4.3 The results of the reaction of **1a**, **2a** and alkyne **6** by GC-MS

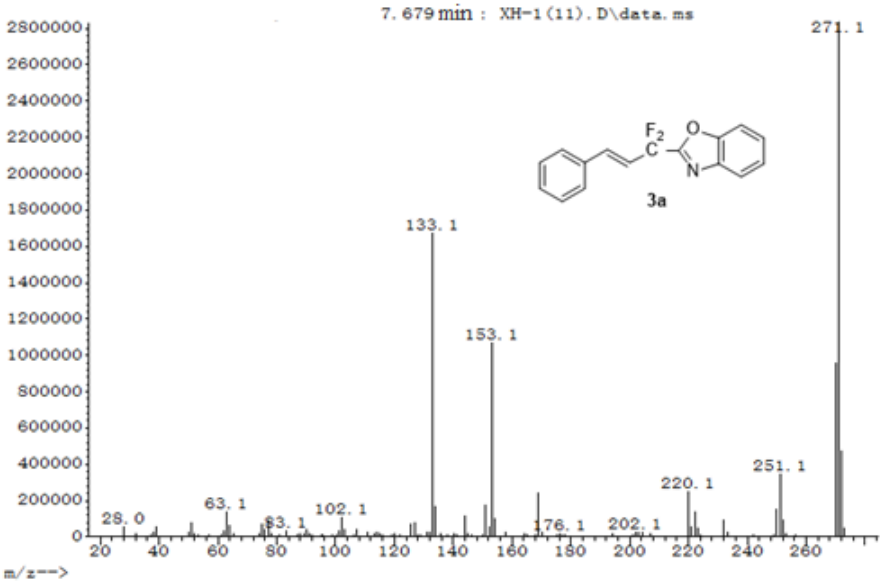
The mixture sample was prepared through the reaction of **6**, **1a**, and **2a** under the standard conditions, then tested by the Instrument model Agilent 7890A-5975C. Gradient temperature was 190-280℃ (increasing speed: 3℃/min), and the volume injected was 1μL. The results see Scheme S5.

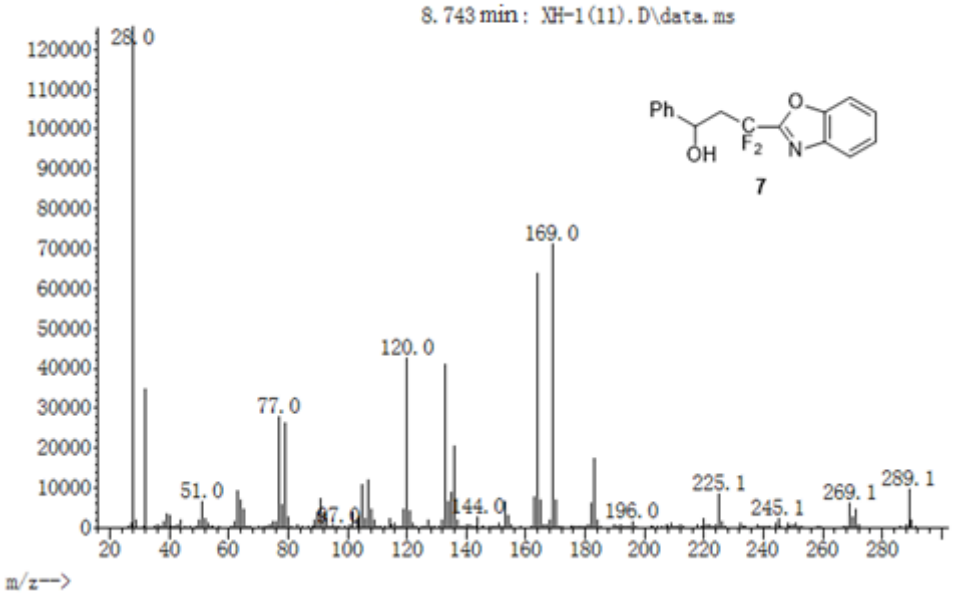


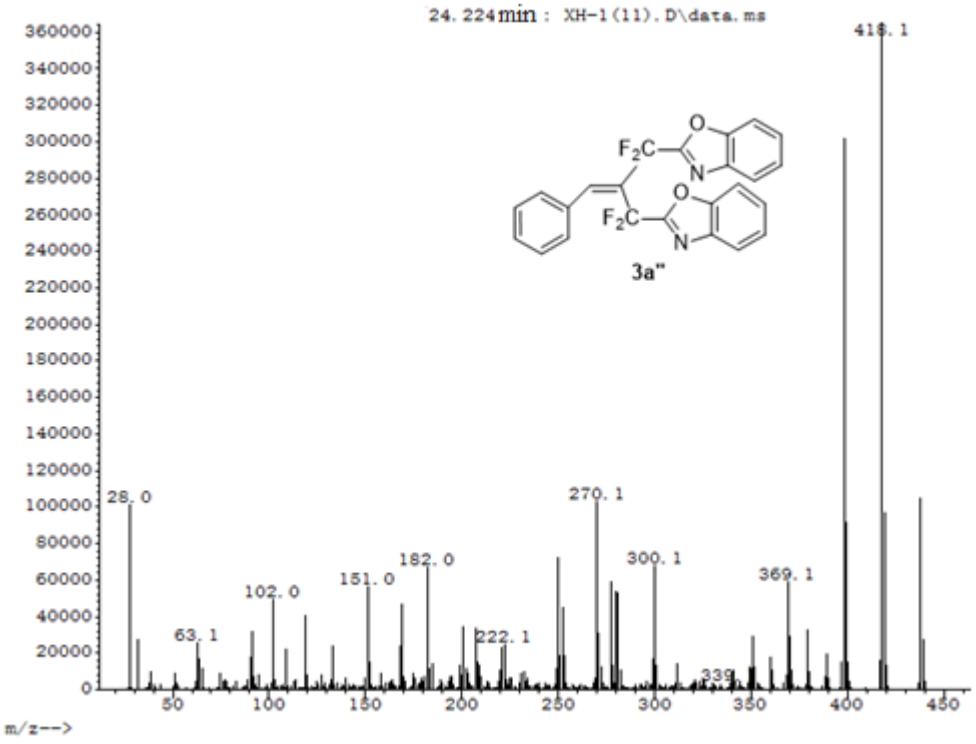


1	2.640	3	7	21	BB	497157	8273569	1.20%	0.474%
2	7.691	598	628	646	BV	11507172	688836802	100.00%	39.503%
3	8.751	744	759	765	BV	569303	18018062	2.62%	1.033%
4	8.841	765	770	786	VV	435109	14735273	2.14%	0.845%
5	10.253	927	944	962	BB 2	462945	16263471	2.36%	0.933%
6	21.285	2284	2302	2320	BB	232682	9930168	1.44%	0.569%
7	22.696	2460	2476	2494	BB 2	236102	10554252	1.53%	0.605%
8	23.185	2517	2536	2557	BB	361158	16545361	2.40%	0.949%
9	24.226	2636	2664	2695	BV	3226750	169397785	24.59%	9.715%
10	25.828	2849	2861	2874	BV 2	513389	23800239	3.46%	1.365%
11	27.747	3072	3098	3114	BB	1460288	85308936	12.38%	4.892%

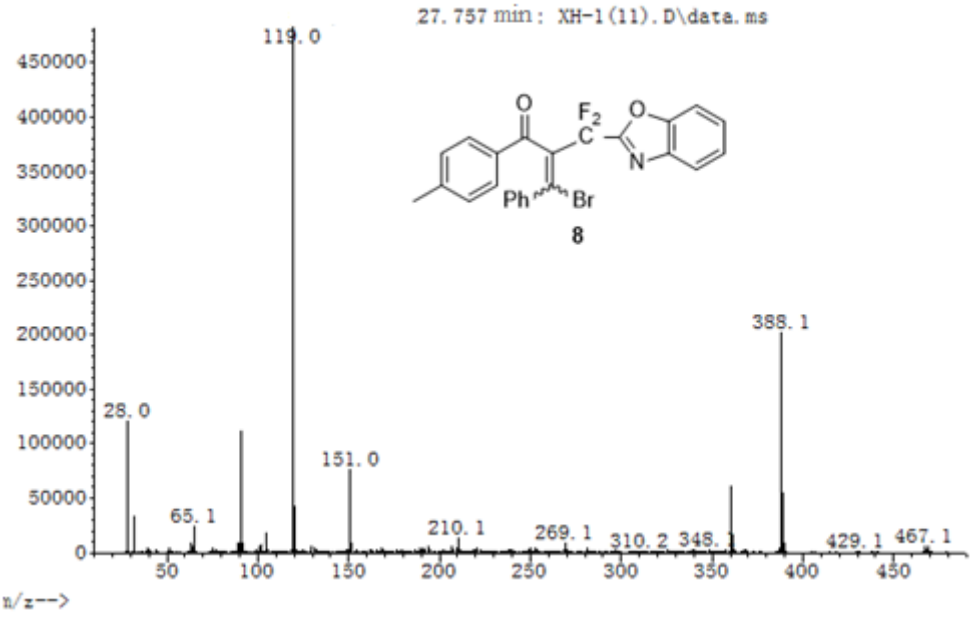
12	28.239	3124	3158	3164	BV	3829143	253307010	36.77%	14.526%
13	28.448	3164	3184	3225	VB	5323266	380967097	55.31%	21.847%
14	29.839	3344	3355	3379	VV 2	308099	14281667	2.07%	0.819%
15	30.382	3404	3422	3451	BB	658582	33541657	4.87%	1.924%



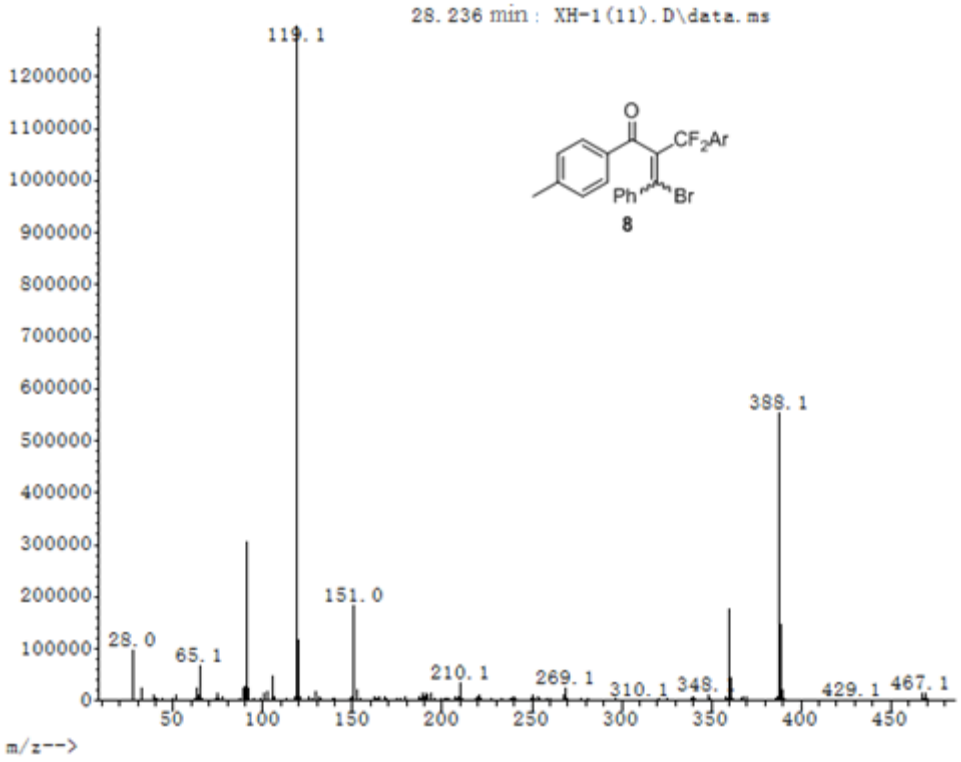



24.224min : XH-1(11).D\data.ms
418.1
28.0
270.1
300.1
182.0
151.0
102.0
369.1
63.1
222.1
339
m/z-->

3a''


27.757 min : XH-1(11).D\data.ms
119.0
388.1
28.0
151.0
65.1
210.1
269.1
310.2
348.1
429.1
467.1
m/z-->

8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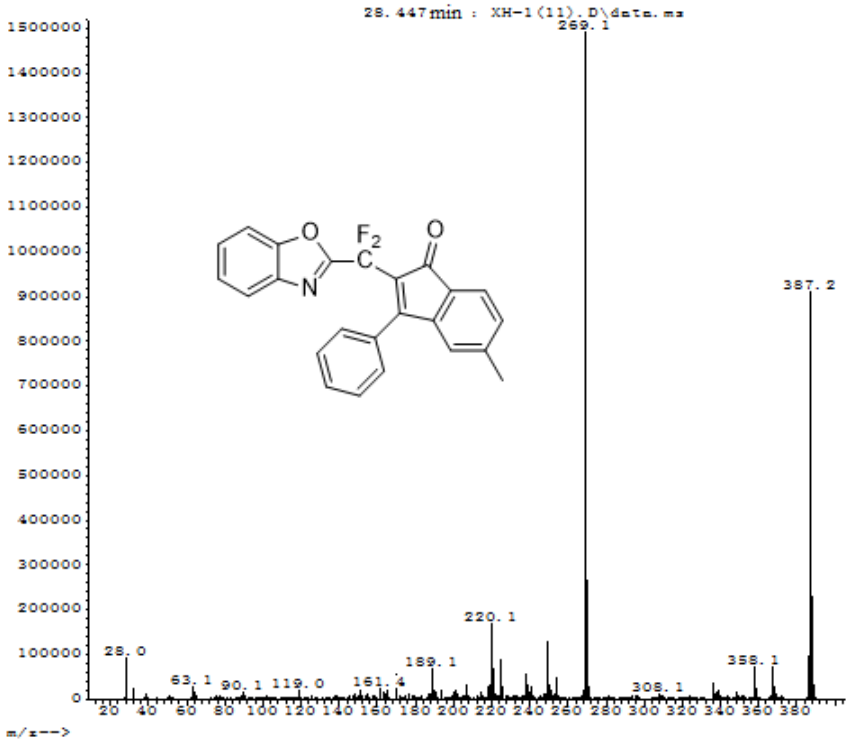
348.1
429.1
467.1
m/z-->

8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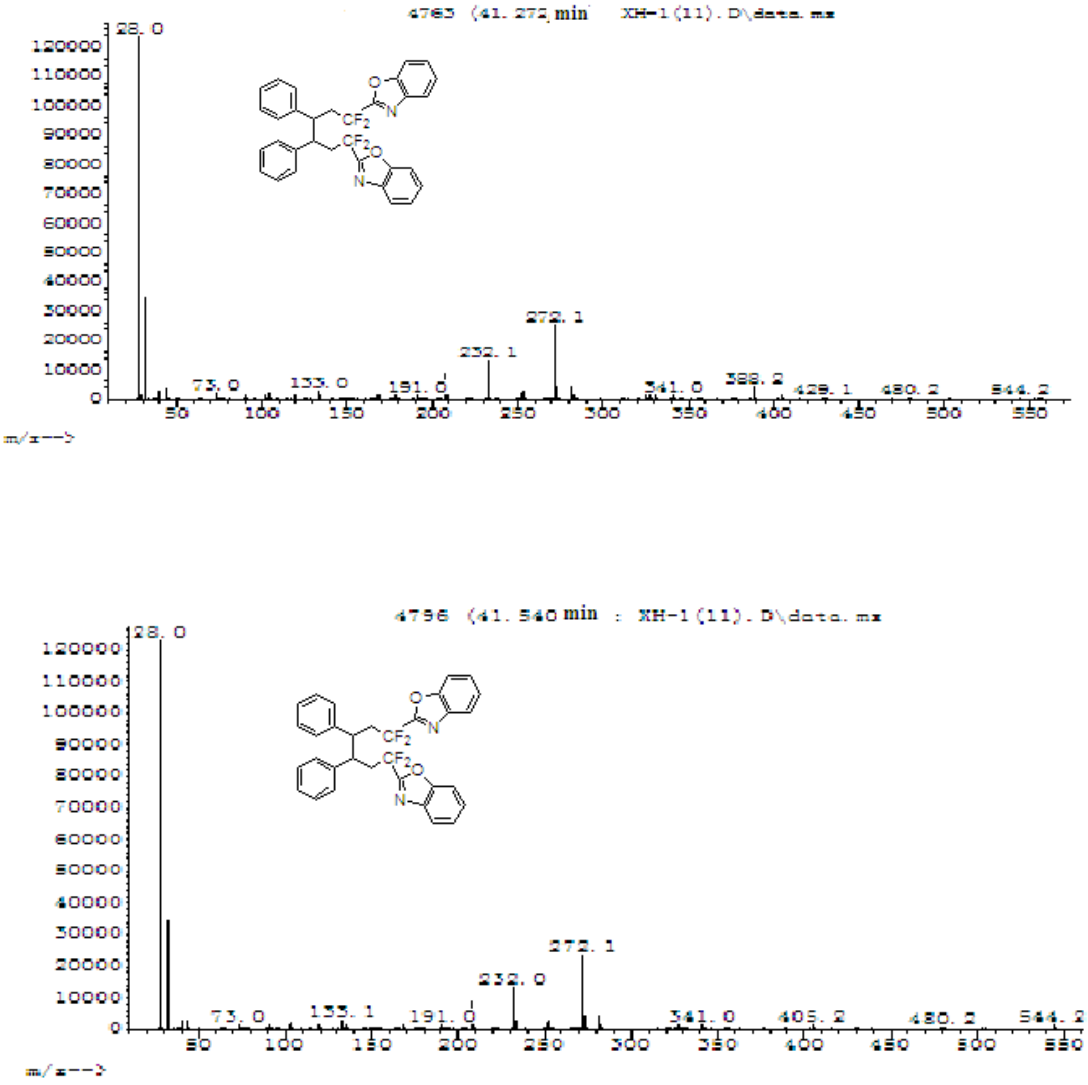
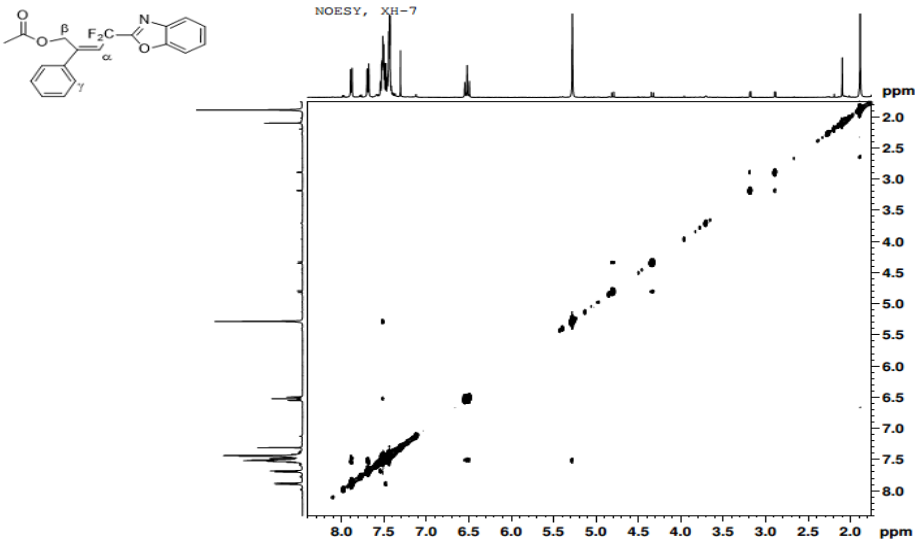
90.1
119.0
161.4
308.1
m/z-->



Scheme S5. The results of the reaction of **1a**, **2a** and alkyne **6** by GC-MS

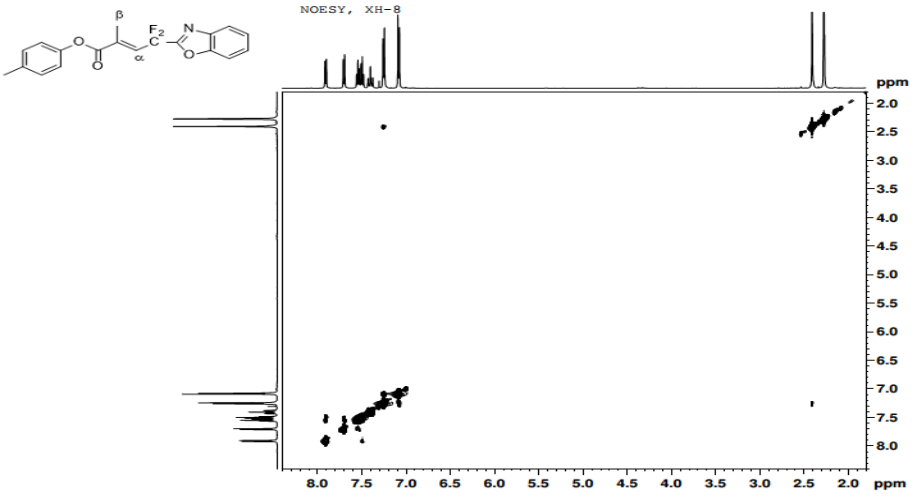
Conclusion: Besides the products **3a** and **3a''**, the product **4,** which formed by capturing radical A, was also isolated. The formation of those products further supported the speculated mechanism. The formation of hydroxyl adducts **7** and **8** (GC-MS 27.757 min and 28.236min) could be further inferred that the carbocation was involved in this reaction. The product **9** observed through GC-MS monitoring of the reaction mixture after 8 hours was homo-coupled product of radical **1B**

5. ^{1}H NOESY experiments of 3j and 3t



Scheme S6 ^{1}H, ^{1}H NOESY spectrum of **3j**

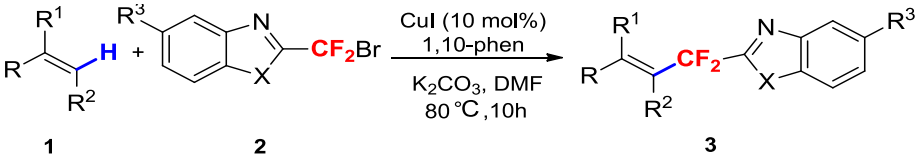
From the NOESY spectrum, the α-H ($\delta_{6.50}$) coupled with γ-H (an aromatic H), while the β-H ($\delta_{5.26}$) (displaying a single peak) had no couple with α-H. These results deduced that the geometric configuration for the double bonds of **3j** is indicated as *Z*.



Scheme S7 ^{1}H, ^{1}H NOESY spectrum of **3t**

The NOESY spectrum showed that the α-H ($\delta_{7.37}$, td) had no couple with β-H ($\delta_{2.39}$, s). Therefore, the geometric configuration for the double bonds of **3t** is indicated as *E*.

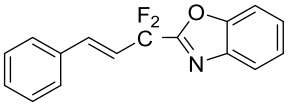
6. New compounds characterization



1 2 3

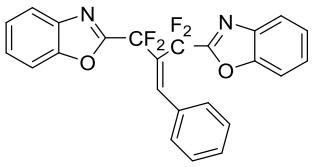
A 25 mL round-bottom flask was charged with CuI (10 mol %), 1,10-phen (20 mol %), K_2CO_3 (2.0 equiv). **2** (0.6 mmol, 2.0 equiv), **1** (0.3 mmol) and DMF (2.5 mL) under air. The reaction mixture was stirred at 80 ℃ (oil bath) for 10 h. Then the reaction mixture was cooled to room temperature. The crude product was purified with silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to give product **3**.

(*E*)-2-(1,1-difluoro-3-phenylallyl)benzo[*d*]oxazole (3a)



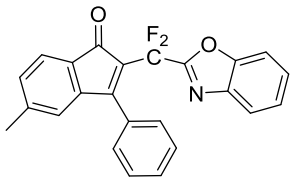
Light yellow solid, 86%, mp: 52-54℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.85 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.45 (td, *J* = 7.4, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.39-7.32 (m, 3H), 7.22 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.67 (dt, *J* = 16.2, 11.0 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.63 (dd, *J* = 11.0, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0 (t, $^2J_{C\text{-}F}$ = 36.0 Hz), 150.7, 140.1, 136.8 (t, $^3J_{C\text{-}F}$ = 9.0 Hz), 134.1, 129.7, 128.9, 127.6, 126.9, 125.4, 121.3, 119.5 (t, $^2J_{C\text{-}F}$ = 25.1 Hz), 113.5 (t, $^1J_{C\text{-}F}$ = 239.7 Hz), 111.4. IR: 3060, 1652, 1610, 1443, 1193, 1054, 977, 749cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{12}F_2NO$ $[M+H]^+$ 272.0887, found: 272.0890.

2,2'-(2-benzylidene-1,1,3,3-tetrafluoropropane-1,3-diyl)bis(benzo[*d*]oxazole) (3a'')



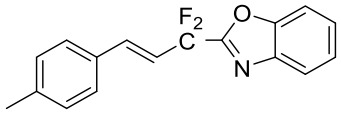
Colorless solid, 8%, mp: 109-110℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.54-7.44 (m, 3H), 7.43-7.38 (m, 1H), 7.38-7.30 (m, 3H), 7.21-7.08 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -88.26 (t, *J* = 7.4 Hz), -93.56 (t, *J* = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5 (t, $^2J_{C\text{-}F}$ = 35.2 Hz), 156.5 (t, $^2J_{C\text{-}F}$ = 33.5 Hz), 150.7, 150.3, 143.6-142.6 (m), 140.2, 139.8, 131.9, 129.2, 128.7, 127.9, 126.9, 126.9, 125.3, 125.2, 121.5, 121.3, 112.8 (t, $^1J_{C\text{-}F}$ = 246.8 Hz), 112.6(t, $^1J_{C\text{-}F}$ = 246.8 Hz)111.5, 111.2. IR: 3024, 1651, 1449, 1184, 1082, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{15}F_4N_2O_2$ $[M+H]^+$ 438.0991, found: 438.0989.

2-(benzo[*d*]oxazol-2-yldifluoromethyl)-5-methyl-3-phenyl-1H-inden-1-one (4)



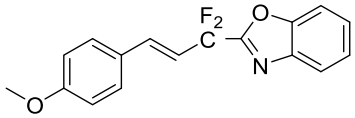
Yellow solid, 16%, mp: 164-166℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.44 (m, 6H), 7.19 (d, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 2.36 (s, 3H).^{19}F NMR (470 MHz, $CDCl_3$) δ -91.51 (s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9 (t, $^{3}J_{C\text{-}F}$ = 2.4 Hz), 162.9 (t, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 157.4 (t, $^{2}J_{C\text{-}F}$ = 34.3 Hz), 150.6, 145.1, 144.3, 140.1, 130.9, 130.8, 129.9, 128.3, 127.9, 126.7, 125.8, 125.2, 124.9 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz), 124.6, 123.6, 121.5, 121.3, 112.4 (t, $^{1}J_{C\text{-}F}$ = 241.6 Hz), 111.4, 22.0. IR: 3037, 2926, 1711, 1606, 1514, 1194, 1034, 743 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{16}F_2NO_2$ $[M+H]^+$ 388.1149, found: 388.1153.

(*E*)-2-(1,1-difluoro-3-(*p*-tolyl)allyl)benzo[*d*]oxazole (3b)



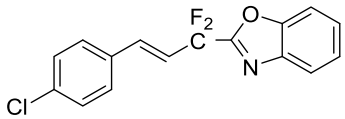
Light yellow solid, 61%, mp: 38-40℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.85 (m, 1H), 7.67-7.64 (m, 1H), 7.51-7.41 (m, 4H), 7.23-7.17 (m, 3H), 6.62 (dt, *J* = 16.1, 11.0 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.24 (d, *J* = 11.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (t, $^{2}J_{C\text{-}F}$ = 36.1 Hz), 150.7, 140.1, 139.9, 136.7 (t, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 131.3, 129.6, 127.6, 126.8, 125.3, 121.3, 118.3 (t, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 113.6 (t, $^{1}J_{C\text{-}F}$ = 239.5 Hz), 111.4, 21.4. IR: 3013, 2916, 1609, 1448, 1190, 1043, 980, 748 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1043, found: 286.1041.

(*E*)-2-(1,1-difluoro-3-(4-methoxyphenyl)allyl)benzo[*d*]oxazole (3c)



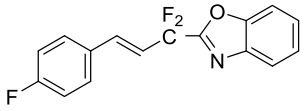
Yellow solid, 74%; mp: 81-82℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.52-7.41 (m, 4H), 7.16 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.96-6.89 (m, 2H), 6.52 (dt, *J* = 16.1, 11.0 Hz, 1H), 3.85 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.88 (dd, *J* = 11.0, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 158.3 (t, $^{2}J_{C\text{-}F}$ = 36.4 Hz), 150.7, 140.1, 136.2 (t, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 129.1, 126.8, 125.3, 121.3, 117.0 (t, $^{2}J_{C\text{-}F}$ = 25.1 Hz), 114.2, 113.7 (t, $^{1}J_{C\text{-}F}$ = 239.5 Hz), 111.4, 55.4. IR: 3029, 2964, 1605, 1511, 1216, 1037, 969, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{14}F_2NO_2$ $[M+H]^+$ 302.0993, found: 302.0995.

(*E*)-2-(3-(4-chlorophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3d)



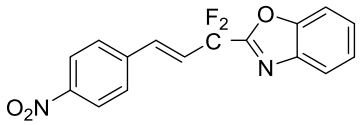
Light yellow solid, 89%, mp: 89-91℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.54-7.41 (m, 4H), 7.37 (m, 2H), 7.18 (dt, *J* = 16.1, 2.2 Hz, 1H), 6.65 (dt, *J* = 16.1, 10.9 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.66 (d, *J* = 10.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8 (t, $^{2}J_{C\text{-}F}$ = 35.8 Hz), 150.7, 140.0, 135.6, 135.4 (t, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 132.6, 129.1, 128.8, 127.0, 125.4, 121.3, 120.0 (t, $^{2}J_{C\text{-}F}$ = 25.3 Hz), 113.3 (t, $^{1}J_{C\text{-}F}$ = 240.1 Hz), 110.4. IR: 3035, 1658, 1489, 1189, 1077, 1044, 970, 811, 745cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}ClF_2NO$ $[M+H]^+$ 306.0497, found: 306.0495.

(*E*)-2-(1,1-difluoro-3-(4-fluorophenyl)allyl)benzo[*d*]oxazole (3e)



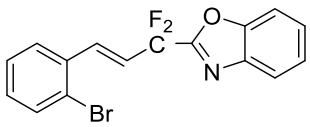
Light yellow solid, 83%, mp: 67-68℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59-7.34 (m, 4H), 7.19 (dt, *J* = 16.2, 2.3 Hz, 1H), 7.11-7.06 (m, 2H), 6.60 (dt, *J* = 16.2, 11.0 Hz, 1H). ^{19}F NMR (470 MHz,$CDCl_3$) δ -94.41 (dd, *J* = 11.0, 2.3 Hz), -110.72 (ddd, *J* = 13.6, 8.5, 5.0 Hz). ^{13}C NMR (125 MHz,$CDCl_3$) δ 163.5 (d, $^{1}J_{C\text{-}F}$ = 250.1 Hz), 157.9 (t, $^{2}J_{C\text{-}F}$ = 35.9 Hz), 150.7, 140.0, 135.5 (t, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 130.3, 129.4 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 126.9, 125.4, 121.3, 119.2 (t, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 112.4 (t, $^{1}J_{C\text{-}F}$ = 239.9 Hz), 111.4. IR: 3040, 1605, 1059, 1223, 1161, 1044, 970, 746 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}F_3NO$ $[M+H]^+$ 290.0793, found: 290.0798.

(*E*)-2-(1,1-difluoro-3-(4-nitrophenyl)allyl)benzo[*d*]oxazole (3f)



Light yellow solid, 49%, mp: 151-152℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.67 (m, 3H), 7.56-7.39 (m, 2H), 7.31 (dt, *J* = 16.1, 2.3 Hz,1H), 6.84 (dt, *J* = 16.1, 10.7 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.37 (dd, *J* = 10.7, 2.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3 (t, $^{2}J_{C\text{-}F}$ = 35.2 Hz), 150.7, 148.3, 140.2, 139.9, 134.4 (t, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 128.3, 127.2, 125.5, 124.1, 123.8 (t, $^{2}J_{C\text{-}F}$ = 25.1 Hz), 121.4, 112.8 (t, $^{1}J_{C\text{-}F}$ = 240.4 Hz), 111.5. IR: 3024, 1602, 1518, 1343, 1192, 1061, 974, 747cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}F_2N_2O_3$ $[M+H]^+$ 317.0738, found: 317.0741.

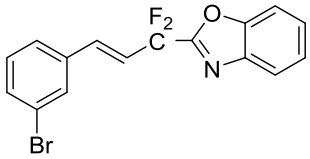
(*E*)-2-(3-(2-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3g)



Light yellow solid, 67%, mp: 68-69℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.5, 1.0 Hz, 1H),

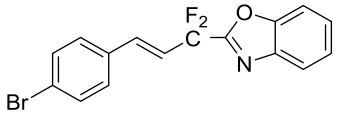
7.67 - 7.61 (m, 3H), 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.47 (td, *J* = 7.5, 1.2 Hz, 1H), 7.43 (td, *J* = 7.6, 1.1 Hz, 1H), 7.32 (td, *J* = 7.2, 0.5 Hz, 1H), 7.20 (td, *J* = 7.9, 1.5 Hz, 1H), 6.65 (dt, *J* = 16.0, 10.9 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.82 (dd, *J* = 10.9, 2.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (t, $^2J_{C\text{-}F}$ = 35.6 Hz), 150.7, 140.0, 135.5 (t, $^3J_{C\text{-}F}$ = 9.2 Hz), 134.1, 133.3, 130.8, 127.7, 127.7, 122.1 (t, $^2J_{C\text{-}F}$ = 24.9 Hz), 121.3, 113.1 (t, $^1J_{C\text{-}F}$ = 240.5 Hz), 111.4. IR: 3023, 1610, 1457, 1193, 1049, 960, 752, 658cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}BrF_2NO$ $[M+H]^+$ 349.9992, found: 349.9996.

(*E*)-2-(3-(3-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3h)



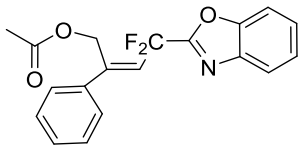
Yellow oil, 54%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.67–7.61 (m, 2H), 7.51–7.46 (m, 2H), 7.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.1 Hz,1H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.15 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.68 (dt, *J* = 16.1, 10.8 Hz, 1H).^{19}F NMR (470 MHz, $CDCl_3$) δ -94.77 (dd, *J* = 10.8, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (t, $^2J_{C\text{-}F}$ = 35.7 Hz), 150.7, 140.0, 136.1, 135.2 (t, $^3J_{C\text{-}F}$ = 9.0 Hz), 132.6, 130.3, 127.0, 126.3 , 125.4, 123.0, 121.4, 121.0 (t, $^2J_{C\text{-}F}$ = 25.1 Hz), 113.1 (t, $^1J_{C\text{-}F}$ =240.21 Hz),111.5. IR: 3023, 1659, 1565, 1195, 1038, 968, 747, 675 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}BrF_2NO$ $[M+H]^+$ 349.9992, found: 349.9987.

(*E*)-2-(3-(4-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3i)



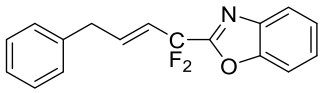
Yellow solid, 62%, mp: 111-112℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.57–7.52 (m, 2H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 1.1 Hz, 1H), 7.39 (m, 2H), 7.17 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.67 (dt, *J* = 16.1, 10.9 Hz, 1H).^{19}F NMR (470 MHz, $CDCl_3$) δ -94.73 (dd, *J* = 10.9, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (t, $^2J_{C\text{-}F}$ = 35.9 Hz), 150.7, 140.0, 135.5 (t, $^3J_{C\text{-}F}$ = 9.0 Hz), 133.0, 132.1, 129.1, 127.0 , 125.4, 123.9, 121.4 , 120.2 (t, $^2J_{C\text{-}F}$ = 25.2 Hz), 113.2 (t, $^1J_{C\text{-}F}$ = 239.7 Hz),111.5. IR: 3037, 1652, 1567, 1187, 1045, 969, 744, 562cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{11}BrF_2NO$ $[M+H]^+$ 349.9992, found: 349.9993.

(*Z*)-4-(benzo[*d*]oxazol-2-yl)-4,4-difluoro-2-phenylbut-2-en-1-yl acetate (3j)



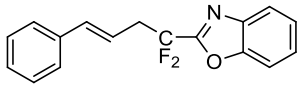
Light yellow solid, 51%, mp: 127-129℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.51-7.46 (m, 3H), 7.47-7.39 (m, 4H), 6.50 (t, *J* = 13.7 Hz, 1H), 5.26 (s, 2H), 1.86 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -88.19 (d, *J* = 13.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 157.8 (t, $^{2}J_{C\text{-}F}$ = 35.4 Hz), 150.8, 146.4 (t, $^{3}J_{C\text{-}F}$ = 6.1 Hz), 140.0, 138.0, 129.2, 128.6, 127.0, 126.9, 125.4, 123.0 (t, $^{2}J_{C\text{-}F}$ = 26.9 Hz), 121.4, 113.0 (t, $^{1}J_{C\text{-}F}$ = 240.2 Hz), 111.5, 60.8 (t, $^{4}J_{C\text{-}F}$ = 2.4 Hz), 20.5. IR: 3012, 2925, 1743, 1646, 1514, 1231, 1034, 745, 696cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}F_2NO$ $[M+H]^+$ 344.1098, found: 344.1201.

(*E*)-2-(1,1-difluoro-4-phenylbut-2-en-1-yl)benzo[*d*]oxazole (3k)



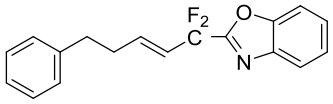
Colorless oil, 40%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.48 (td, *J* = 7.2, 1.2 Hz, 1H), 7.44 (td, *J* = 7.5, 1.1 Hz, 1H),7.40-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.26-7.21 (m, 2H), 6.58 (dtt, *J* = 15.7, 6.9, 2.4 Hz,1H), 6.08 (dtt, *J* = 15.7, 10.6, 1.5 Hz, 1H), 3.66-3.49 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.45 (dd, *J* = 10.6, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (t, $^{2}J_{C\text{-}F}$ = 35.6 Hz), 150.7, 140.0, 138.3 (t, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 137.7, 128.8, 128.7, 126.8, 126.7, 125.3, 122.9 (t, $^{2}J_{C\text{-}F}$ = 25.3 Hz), 121.3, 113.0 (t, $^{1}J_{C\text{-}F}$ = 239.2 Hz), 111.4, 38.1. IR: 3030, 2910, 1610, 1491, 1210, 1041, 975, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1043, found: 286.1041.

(*E*)-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3k')



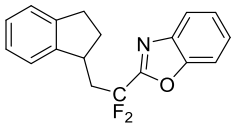
Light yellow oil, 15%; ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.64 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.46 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.25 (m, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.35 (td, *J* = 15.9, 7.2 Hz, 1H), 3.47 (td, *J* = 16.0, 7.2 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.22 (t, *J* = 16.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.85 (t, $^{2}J_{C\text{-}F}$ = 33.5 Hz), 150.67 , 140.05 , 136.76 , 136.53 , 128.61 , 127.97 , 126.90 , 126.50 , 125.33 , 121.33 , 118.19 (t, $^{3}J_{C\text{-}F}$ = 4.8 Hz), 115.91 (t, $^{1}J_{C\text{-}F}$ = 242.2 Hz), 111.44 , 39.80 (t, $^{2}J_{C\text{-}F}$ = 24.3 Hz). IR: 3008, 1606, 1485, 1206, 1030, 968,746 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1043, found: 286.1047.

(*E*)-2-(1,1-difluoro-5-phenylpent-2-en-1-yl)benzo[*d*]oxazole (3l)



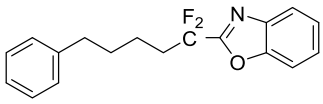
Light red oil, 58%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.4, 1.5 Hz,1H), 7.67-7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52-7.43 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.21 (m, 3H), 6.51 (dtt, *J* = 15.8, 6.7, 2.3 Hz, 1H), 6.13 (dt, *J* = 15.8, 10.5 Hz, 1H), 2.89-2.81 (m, 2H), 2.64-2.52 (m, 2H).^{19}F NMR (470 MHz, $CDCl_3$) δ -94.77 (dd, *J* = 10.9, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (t, $^{2}J_{C\text{-}F}$ = 35.9 Hz), 150.7, 140.8, 140.1, 138.9 (t, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 128.5, 126.8, 126.2, 125.3, 122.4 (t, $^{2}J_{C\text{-}F}$ = 25.1 Hz), 121.3, 113.1 (t, $^{1}J_{C\text{-}F}$ = 239.1 Hz), 111.4, 34.6, 33.7. IR: 3029, 2931, 1676, 1448, 1213, 1032, 969, 749 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{16}F_2NO$ $[M+H]^+$ 300.1200, found: 300.1205.

2-(2-(2,3-dihydro-1H-inden-1-yl)-1,1-difluoroethyl)benzo[d]oxazole (4l)



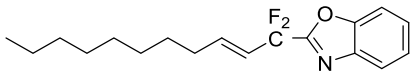
Light yellow oil, 7%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.49 (dtd, *J* = 22.0, 7.8, 1.1 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.22 (m, 3H), 4.32 (dtd, *J* = 9.9, 6.7, 4.0 Hz, 1H), 3.25 (qd, *J* = 15.9, 7.2 Hz, 1H), 3.17 – 3.04 (dtd, *J* = 17.8, 12.1, 6.0 Hz, 1H), 2.96 (ddd, *J* = 14.0, 9.1, 5.0 Hz, 1H), 2.82 (ddd, *J* = 16.0, 9.0, 2.0 Hz, 1H), 2.37 – 2.17 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.89 (ddd, *J* = 278.2, 17.3, 12.1 Hz), -99.19 (dt, *J* = 278.2, 16.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.11 (t, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 150.58 , 140.21 , 139.90 , 128.53 , 128.49 , 127.02 , 126.25 , 125.41 , 121.36 , 115.51 (t, $^{1}J_{C\text{-}F}$ = 243.1 Hz), 111.48 , 45.40 (t, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 45.02 (t, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 40.60 , 33.32 . IR: 3022, 2927, 1688, 1469, 1223, 1068, 978, 747 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{16}F_2NO$ $[M+H]^+$ 300.1200, found: 300.1204.

2-(1,1-difluoro-5-phenylpentyl)benzo[d]oxazole (5l)



Light yellow oil, 9%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.31 – 7.27 (m, 2H), 7.20 (t, *J* = 7.8 Hz, 3H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.58 – 2.44 (m, 2H), 1.77 (m, 2H), 1.69 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.20 (t, *J* = 16.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.17 (t, $^{2}J_{C\text{-}F}$ = 33.9 Hz), 150.57 , 141.87 , 139.98 , 128.35 , 126.77 , 125.85 , 125.26 , 121.24 , 116.88 (t, $^{1}J_{C\text{-}F}$ = 241.2 Hz), 114.56 , 111.40 , 35.77 (t, ^{2}J = 23.5 Hz), 35.55 , 30.91 , 21.37 (t, ^{3}J = 3.9 Hz). IR: 3021, 2918, 1648, 1490, 1212, 1049, 972,750 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{18}F_2NO$ $[M+H]^+$ 302.1356, found: 302.1360.

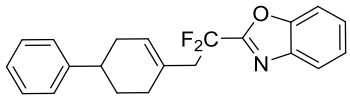
(*E*)-2-(1,1-difluoroundec-2-en-1-yl)benzo[*d*]oxazole (3m)



Yellow oil, 94%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.63-7.60 (m, 1H),

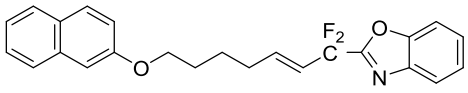
7.49-7.37 (m, 2H), 6.46-6.34 (m, 1H), 6.09-5.98 (m, 1H), 2.28-2.16 (m, 2H), 1.47 (p, *J* = 7.4 Hz, 2H), 1.39-1.19 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.32 (dd, *J* = 10.6, 2.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (t, $^2J_{C\text{-}F}$ = 36.4 Hz), 150.6, 140.06, 139.8 (t, $^3J_{C\text{-}F}$ = 7.7 Hz) , 126.6, 125.1, 121.6 (t, $^2J_{C\text{-}F}$ = 25.0 Hz), 121.2, 113.0 (t, $^1J_{C\text{-}F}$ = 238.9 Hz), 111.2, 31.9, 31.8, 29.3, 29.2, 29.1, 28.1, 22.6, 14.0. IR: 3032, 2926, 1676, 1457, 1228, 1040, 972, 749 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{24}F_2NO$ $[M+H]^+$ 308.1826, found: 308.1832.

2-(1,1-difluoro-2-(4-phenylcyclohexylidene)ethyl)benzo[*d*]oxazole (3n)



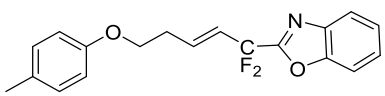
Light yellow solid, 95%, mp: 99-101℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.50 (td, *J* = 7.6, 1.3 Hz, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34–7.28 (m, 2H), 7.25–7.19 (m, 3H), 5.77 (s, 1H), 3.18 (t, *J* = 17.0 Hz, 2H), 2.84–2.69 (m, 1H), 2.39–2.26 (m, 2H), 2.25–2.10 (m, 2H), 2.00–1.93 (m, 1H), 1.87–1.73 (m, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.75 (td, *J* = 17.0, 3.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3 (t, $^2J_{C\text{-}F}$ = 33.9 Hz), 150.6, 146.6, 140.1, 128.4, 128.3 (t, $^3J_{C\text{-}F}$ = 2.8 Hz), 126.8, 126.7, 126.1, 125.3, 121.3, 116.4 (t, $^1J_{C\text{-}F}$ = 243.8 Hz), 111.4, 44.0 (t, $^2J_{C\text{-}F}$ = 23.7 Hz), 39.4, 33.6, 30.0, 29.9. IR: 3026, 2918, 1609, 1489, 1445, 1198, 1022, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}F_2NO$ $[M+H]^+$ 340.1513, found: 340.1515.

(*E*)-2-(1,1-difluoro-7-(naphthalen-2-yloxy)hept-2-en-1-yl)benzo[*d*]oxazole (3o)



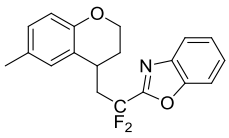
Light yellow solid, 52%, mp: 70-72℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.83-7.73 (m, 3H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.52-7.42 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.22-7.12 (m, 2H), 6.48 (dt, *J* = 15.7, 6.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 10.7 Hz, 1H), 4.12 (t, *J* = 6.4Hz, 2H), 2.39-2.33 (m, 2H), 1.93 (m, 2H), 1.75 (m, 2H).^{19}F NMR (470 MHz, $CDCl_3$) δ -94.79 (dd, *J* = 10.8, 2.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (t, $^2J_{C\text{-}F}$ = 36.0 Hz), 157.0, 150.7, 140.1, 139.4 (t, $^3J_{C\text{-}F}$ = 8.5 Hz), 134.6, 129.4, 129.0, 127.7, 126.8, 126.8, 126.4, 125.3, 123.6, 122.1 (t, $^2J_{C\text{-}F}$ = 25.0 Hz), 121.3, 119.0, 113.1 (t, $^1J_{C\text{-}F}$ = 238.7 Hz), 111.4, 106.6, 67.5, 31.7, 28.7, 24.9. IR: 3024, 2939, 1625, 1508, 1176, 1132, 1059,970, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{22}F_2NO_2$ $[M+H]^+$ 394.1619, found: 394.1621.

(*E*)-2-(1,1-difluoro-5-(*p*-tolyloxy)pent-2-en-1-yl)benzo[*d*]oxazole (3p)



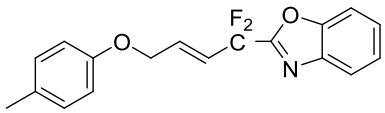
Yellow oil, 44%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.49 (td, *J* = 7.8, 1.4 Hz, 1H), 7.45 (td, *J* = 7.8, 1.4 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.84-6.82 (m, 2H), 6.54 (dtt, *J* = 15.8, 6.8, 2.3 Hz, 1H), 6.22 (dt, *J* = 15.8, 10.6 Hz,1H), 4.09 (t, *J* = 6.4 Hz, 2H), 2.87-2.61 (m, 2H), 2.32 (s, 3H).^{19}F NMR (470 MHz, $CDCl_3$) δ -94.90 (d, *J* = 10.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0 (t, $^{2}J_{C\text{-}F}$ = 35.7 Hz), 156.5, 150.7, 140.0, 135.7 (t, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 130.2, 129.9, 126.9, 125.3, 123.8 (t, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 121.3, 114.5, 112.9 (t, $^{1}J_{C\text{-}F}$ = 239.3 Hz), 111.4, 66.2, 31.9, 20.5. IR: 3024, 2924, 1681, 1513, 1237, 1039, 968, 745 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}F_2NO_2$ $[M+H]^+$ 330.1306, found: 330.1311.

2-[1,1-Difluoro-2-(6-methyl-chroman-4-yl)-ethyl]-benzooxazole (4p)



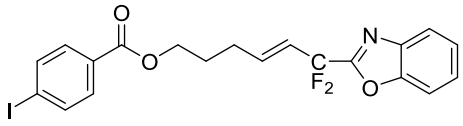
Yellow oil, 14%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.51 (td, 1H), 7.47 (td, *J* = 7.4, 1.1 Hz, 1H), 7.01 (s, 1H), 6.93 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 4.26–4.15 (m, 2H), 3.42–3.30 (m, 1H), 3.01 (dtd, *J* = 22.3, 15.8, 2.9 Hz, 1H), 2.74 (m, 1H), 2.27 (s, 3H), 2.26–2.19 (m, 1H), 2.11–2.00 (m, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.22 (ddd, *J* = 276.2, 22.4, 10.9 Hz), -98.61 (ddd, *J* = 276.1, 21.2, 16.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9 (t, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 152.4, 150.6, 139.9, 129.7, 129.3, 128.7, 127.0, 125.4, 123.9, 121.3, 116.9, 116.8 (t, $^{1}J_{C\text{-}F}$ = 242.9 Hz), 111.4, 62.9, 42.6 (t, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 28.2 (t, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 27.8, 20.6. IR: 3012, 2929, 1691, 1502, 1229, 1098, 1046, 745 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}F_2NO_2$ $[M+H]^+$ 330.1306, found: 330.1310.

(*E*)-2-(1,1-difluoro-4-(*p*-tolyloxy)but-2-en-1-yl)benzo[*d*]oxazole (3q)



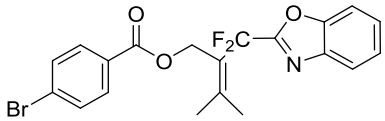
Light yellow solid, 35%, mp: 76-78℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.45 (td, *J* = 7.7, 1.2 Hz, 1H), 7.15–7.10 (m, 2H), 6.90–6.83 (m, 2H), 6.68–6.60 (m, 1H), 6.49 (dtt, *J* = 15.8, 10.4, 1.5 Hz, 1H), 4.78–4.56 (m, 2H), 2.32 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.52 (dd, *J* = 10.4, 3.1 Hz).^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (t, $^{2}J_{C\text{-}F}$ = 35.4 Hz), 156.0, 150.7, 140.0, 134.2 (t, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 130.7, 130.0, 126.9, 125.4, 122.7 (t, $^{2}J_{C\text{-}F}$ = 25.5 Hz), 121.3, 114.6, 112.9 (t, $^{1}J_{C\text{-}F}$ = 239.7 Hz), 111.4, 66.3, 20.5. IR: 3025, 2918, 1609, 1488, 1197, 1058, 1022, 936, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{16}F_2NO_2$ $[M+H]^+$ 316.1149, found: 316.1152.

(*E*)-6-(benzo[*d*]oxazol-2-yl)-6,6-difluorohex-4-en-1-yl 4-iodobenzoate (3r)



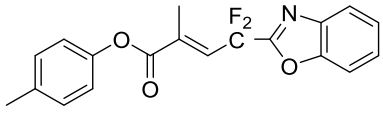
Yellow oil, 96%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz,1H), 7.78–7.68 (m, 4H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.3 Hz,1H), 7.40 (t, *J* = 7.5 Hz,1H), 6.45 (dtt, *J* = 15.8, 6.8, 2.4 Hz, 1H), 6.11 (dt, *J* = 15.8, 10.6 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 2H), 2.43 – 2.33 (m, 2H), 2.01 – 1.92 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.28 (dd, *J* = 10.6, 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 158.0 (t, $^{2}J_{C\text{-}F}$ = 35.7 Hz), 150.6, 139.9, 138.3 (t, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 137.7, 131.7 , 131.0, 129.6, 126.9, 125.3, 122.5 (t, $^{2}J_{C\text{-}F}$ = 24.9 Hz), 121.3, 112.8 (t, $^{1}J_{C\text{-}F}$ = 238.8 Hz), 111.4, 100.8, 64.4, 28.6, 27.3. IR: 3015, 2954, 1720, 1678, 1583, 1182, 1040, 972, 751 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{17}F_2INO_3$ $[M+H]^+$ 484.0221, found: 484.0225.

2-(benzo[*d*]oxazol-2-yldifluoromethyl)-3-methylbut-2-en-1-yl 4-bromobenzoate (3s)



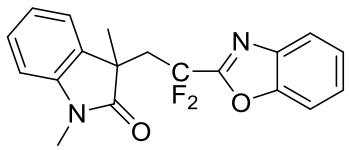
Yellow oil, 46%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.82 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.53-7.47 (m, 3H), 7.46-7.36 (m, 2H), 5.18 (s, 2H), 2.08 (s, 3H), 1.94 (s, 3H).^{19}F NMR (470 MHz, $CDCl_3$) δ -90.94 (s).^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 158.66 (t, $^{2}J_{C\text{-}F}$ = 36.7 Hz), 150.6, 149.0 (t, $^{3}J_{C\text{-}F}$ = 4.9 Hz), 140.0, 131.6, 131.2, 129.0, 128.0, 126.8, 125.3, 122.7 (t, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 121.3, 114.8 (t, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 111.3, 60.6 (t, $^{3}J_{C\text{-}F}$ = 4.5 Hz), 22.9, 22.4 (t, $^{4}J_{C\text{-}F}$ = 2.7 Hz). IR: 3027, 2924, 1723, 1659, 1514, 1271, 1182, 1097, 751, 697 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{17}BrF_2NO_3$ $[M+H]^+$ 436.0360, found: 436.0358.

(*E*)-*p*-tolyl -4-(benzo[*d*]oxazol-2-yl)-4,4-difluoro-2-methylbut-2-enoate (3t)



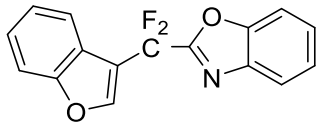
Yellow oil, 51%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.53 (td, *J* = 7.8, 1.2 Hz, 1H), 7.48 (td, *J* = 7.8, 1.1 Hz, 1H), 7.37 (td, *J* = 13.0, 1.3 Hz, 1H), 7.23 (d, *J* = 8.3Hz, 2H), 7.10–7.04 (m, 2H), 2.39 (s, 3H), 2.25 (dd, *J* = 4.4, 2.9 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.97 (d, *J* = 13.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 157.1 (t, $^{2}J_{C\text{-}F}$ =33.9 Hz), 150.8, 148.4, 139.9, 138.4 (t, $^{3}J_{C\text{-}F}$ = 5.8 Hz), 135.9, 131.0 (t, $^{2}J_{C\text{-}F}$ =27.1 Hz), 130.1, 127.2, 125.5, 121.5, 121.1, 113.0 (t, $^{1}J_{C\text{-}F}$ =241.2 Hz), 111.5, 20.9, 14.1. IR: 3019, 2927, 1741, 1659, 1510, 1192, 1038, 985, 745 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}F_2NO_3$ $[M+H]^+$ 344.1098, found: 344.1101.

3-(2-(benzo[*d*]oxazol-2-yl)-2,2-difluoroethyl)-1,3-dimethylindolin-2-one (4u)



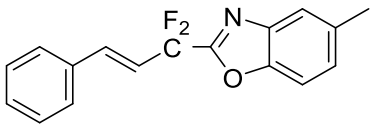
Light yellow solid, 96%, mp: 167-168℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.04 (td, *J* = 7.7, 1.1 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.57 (td, *J* = 7.5, 0.8 Hz, 1H), 3.25 (td, *J* = 15.5, 11.5 Hz, 1H), 3.19 (s, 3H), 3.09 (dt, *J* = 20.9, 14.3 Hz, 1H), 1.42 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -90.46 (dt, *J* = 277.6, 12.4 Hz), -101.16 (ddd, *J* = 277.6, 20.9, 16.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 157.3 (t, $^{2}J_{C\text{-}F}$ =33.5 Hz), 150.4, 142.9, 139.9, 130.6, 128.1, 126.6, 125.1, 123.2, 121.9, 121.0, 115.4 (t, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 111.2, 108.3, 44.6, 43.1 (t, $^{2}J_{C\text{-}F}$ =24.1 Hz), 26.4, 25.6. IR: 3021, 2928, 1708, 1610, 1483, 1190, 1047, 748 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}F_2N_2O_2$ $[M+H]^+$ 343.1258, found: 343.1261.

2-(benzofuran-3-yldifluoromethyl)benzo[*d*]oxazole (3v)



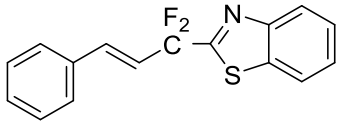
Light yellow solid, 48%, mp: 97-99℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.4, 0.9 Hz,1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.3, 0.8 Hz,1H), 7.51 (m, 1H), 7.46 (m, 1H), 7.44–7.40 (m, 1H), 7.36–7.31 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.10 (d, *J* = 4.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4 (t, $^{2}J_{C\text{-}F}$ = 34.8 Hz), 155.6, 150.8, 146.7 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 140.1, 127.2, 126.6, 126.51 , 125.5, 123.8, 122.4, 121.6, 112.1, 111.5, 109.9 (t, $^{1}J_{C\text{-}F}$ = 240.8 Hz), 108.6 (t, $^{3}J_{C\text{-}F}$ = 3.7 Hz). IR: 3015, 1609, 1447, 1158, 1004, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{10}F_2NO_2$ $[M+H]^+$ 286.0680, found: 286.0677.

(*E*)-2-(1,1-difluoro-3-phenylallyl)-5-methylbenzo[d]oxazole (3w)



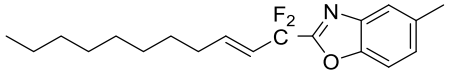
Light yellow solid, 85%, mp: 71-73℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.55-7.49 (m, 3H), 7.44-7.34 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 16.1 Hz, 1H), 6.67 (dt, *J* = 16.1, 10.8 Hz, 1H), 2.52 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.44 (d, *J* = 10.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (t, $^{2}J_{C\text{-}F}$ = 35.7 Hz), 149.0, 140.3, 136.7 (t, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 135.3, 134.1, 129.7, 128.8, 128.1, 127.6, 121.0, 119.6 (t, $^{2}J_{C\text{-}F}$ = 25.3 Hz), 113.5 (t, $^{1}J_{C\text{-}F}$ = 239.4 Hz), 110.8, 21.5. IR: 3010, 1661, 1612, 1453, 1214, 1067, 979 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1043, found: 286.1047.

(*E*)-2-(1,1-difluoro-3-phenylallyl)benzo[d]thiazole (3x)



Yellow oil, 49%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.59 (m, 1H), 7.55-7.49 (m, 3H), 7.43-7.36 (m, 3H), 7.21 (dt, *J* = 16.1, 2.5 Hz, 1H), 6.75 (dt, *J* = 16.1, 11.0 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -86.68 (dd, *J* = 11.0, 2.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6 (t, $^{2}J_{C\text{-}F}$ = 36.4 Hz), 152.8, 135.9 (t, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 135.0, 134.4, 129.5, 128.8, 127.6, 126.8, 126.6, 124.4, 122.0, 120.9 (t, $^{2}J_{C\text{-}F}$ = 26.2 Hz), 116.6 (t, $^{1}J_{C\text{-}F}$ = 239.9 Hz). IR: 3011, 1647, 1598, 1436, 1186, 1029, 974, 741cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{12}F_2NS$ $[M+H]^+$ 288.0659, found: 288.0663.

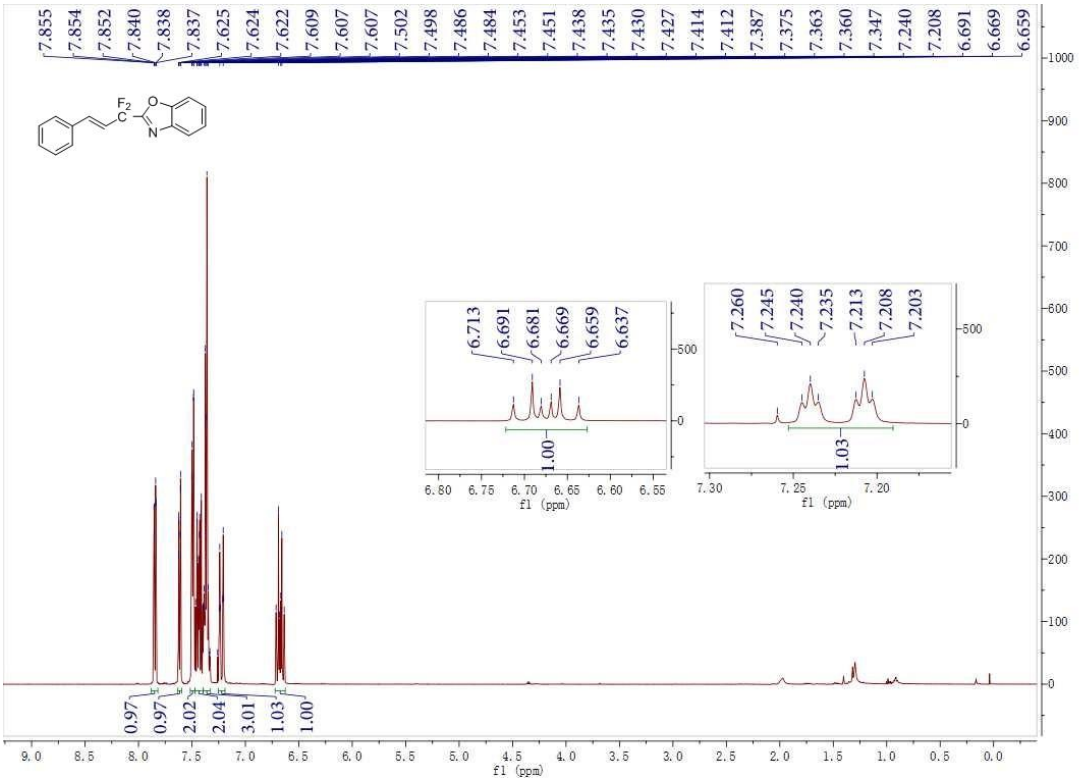
(*E*)-2-(1,1-difluoroundec-2-en-1-yl)-5-methylbenzo[*d*]oxazole (3y)

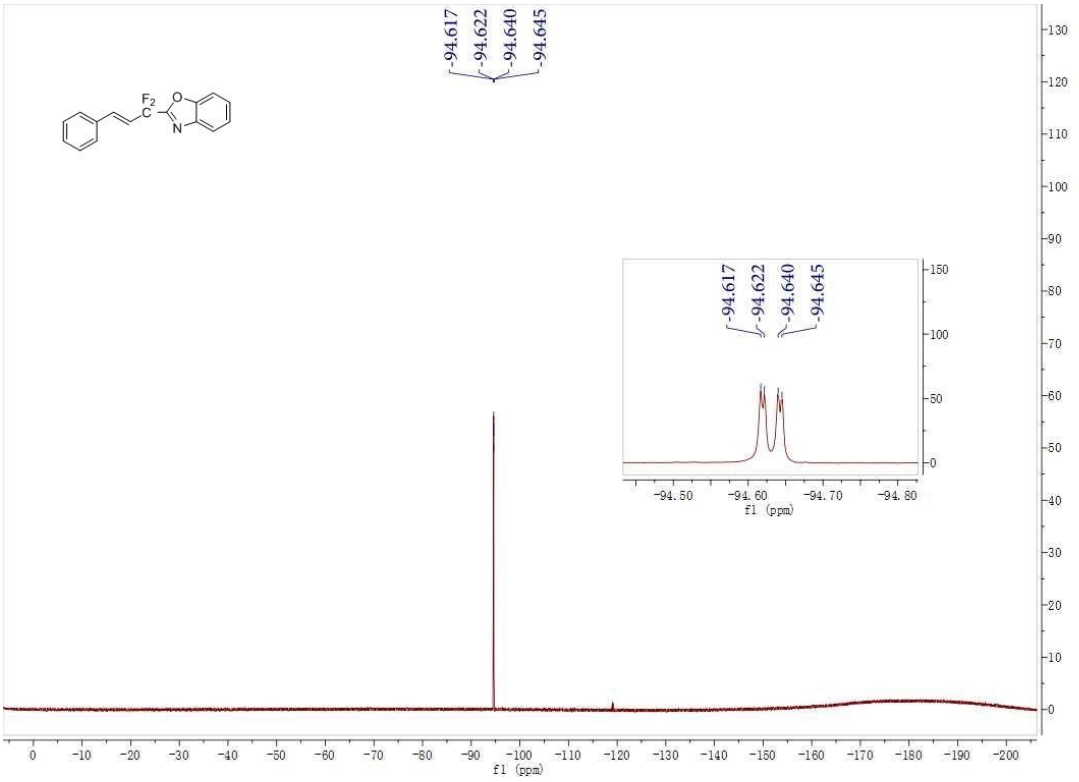


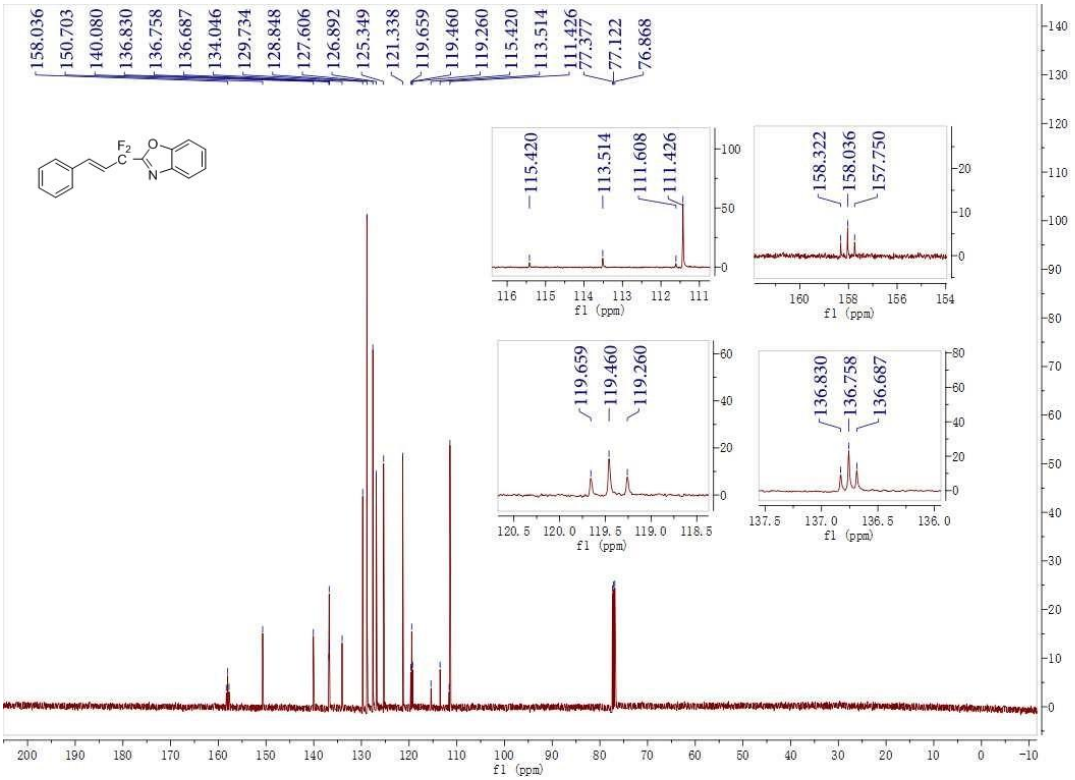
Yellow oil, 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.26 (dd, *J* = 8.5, 1.2 Hz,1H), 6.39 (dtt, *J* = 15.7, 6.9, 2.5 Hz, 1H), 6.02 (dtt, *J* = 15.7, 10.6, 1.5 Hz,1H), 2.50 (s, 3H), 2.27-2.18 (m, 2H), 1.52-1.43 (m, 2H), 1.37-1.23 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.23 (dd, *J* = 10.6, 2.9 Hz).^{13}C NMR (125 MHz, $CDCl_3$)δ 158.3 (t, $^{2}J_{C\text{-}F}$ = 35.7 Hz), 148.93, 140.3, 139.9 (t, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 135.2 , 127.9, 121.7 (t, $^{2}J_{C\text{-}F}$ = 25.1 Hz), 121.0 , 113.1 (t, $^{1}J_{C\text{-}F}$ = 238.8 Hz), 110.7, 31.9, 31.8, 29.3, 29.2, 29.1, 28.1, 22.7, 21.43 , 14.1. IR: 3018, 2930, 1679, 1461, 1232, 1044, 975, 953 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}F_2NO$ $[M+H]^+$ 322.1982, found: 322.1986.

7. Copies of ^{1}H NMR, ^{19}F NMR, ^{13}C NMR spectra of product 3, 4

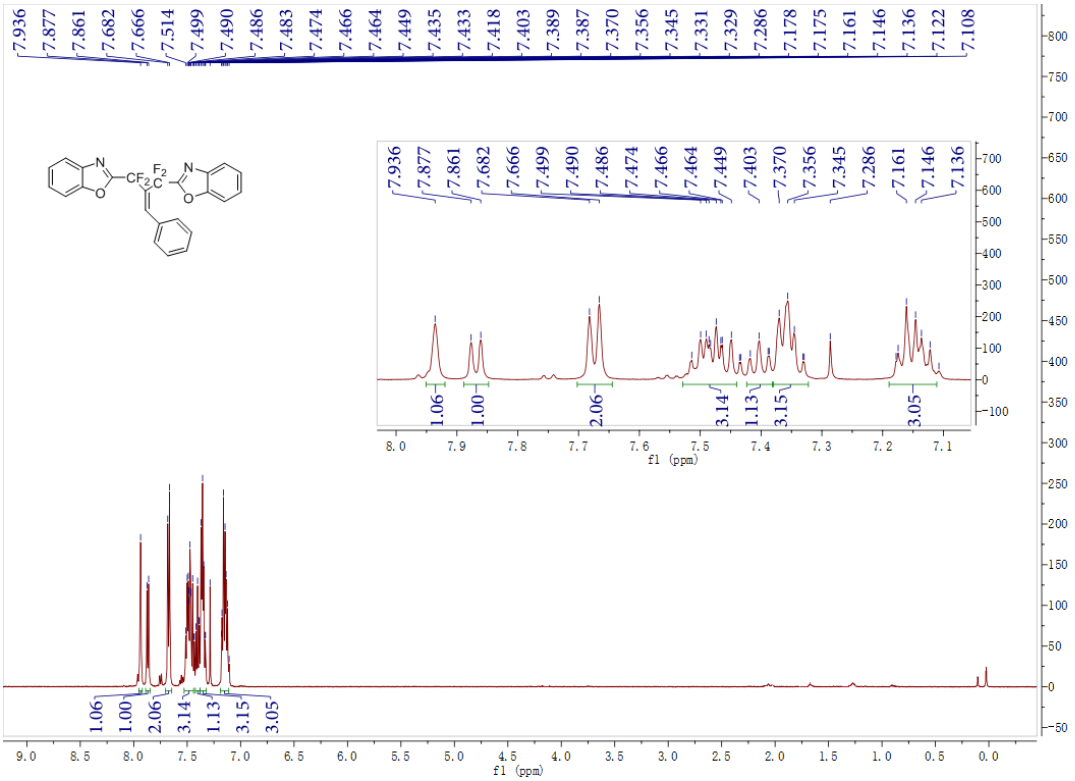
(*E*)-2-(1,1-difluoro-3-phenylallyl)benzo[*d*]oxazole (3a)

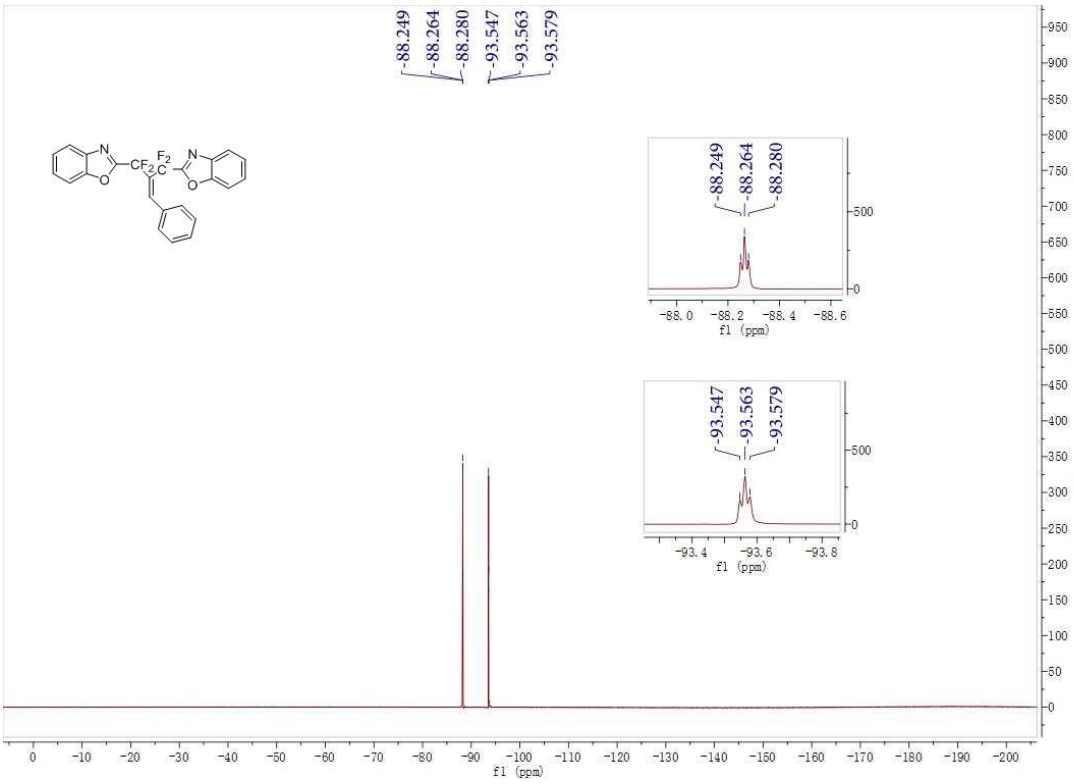


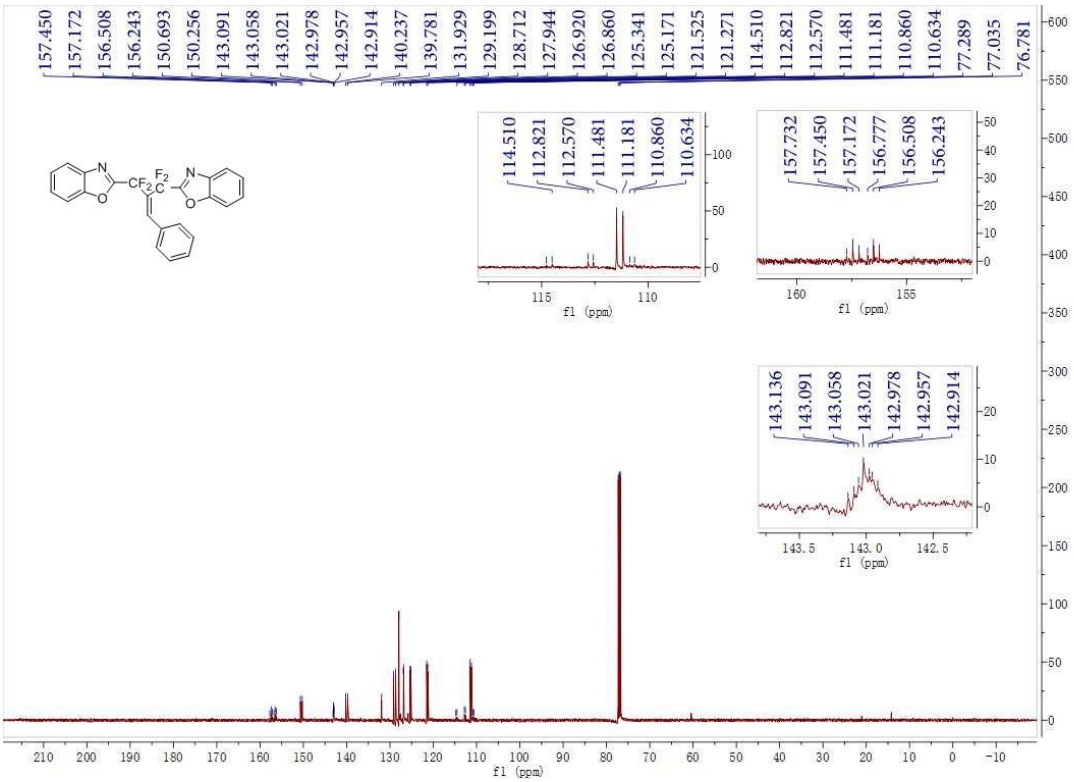




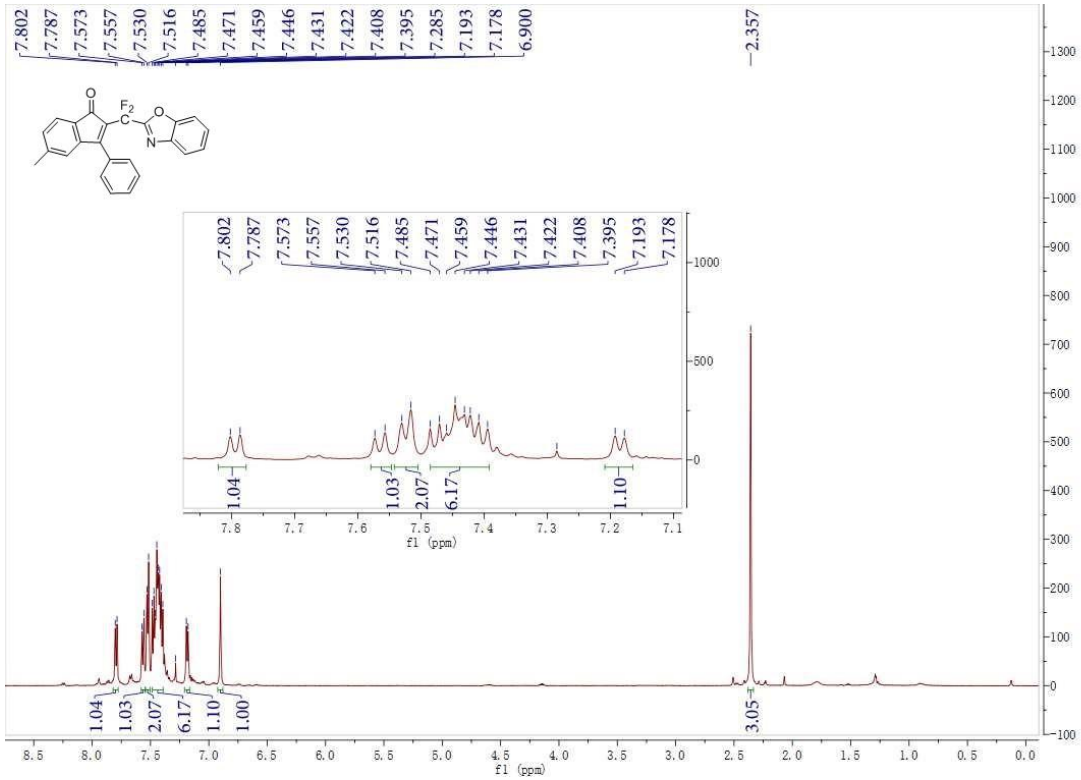
2,2'-(2-benzylidene-1,1,3,3-tetrafluoropropane-1,3-diyl)bis(benzo[*d*]oxazole) (3a'')

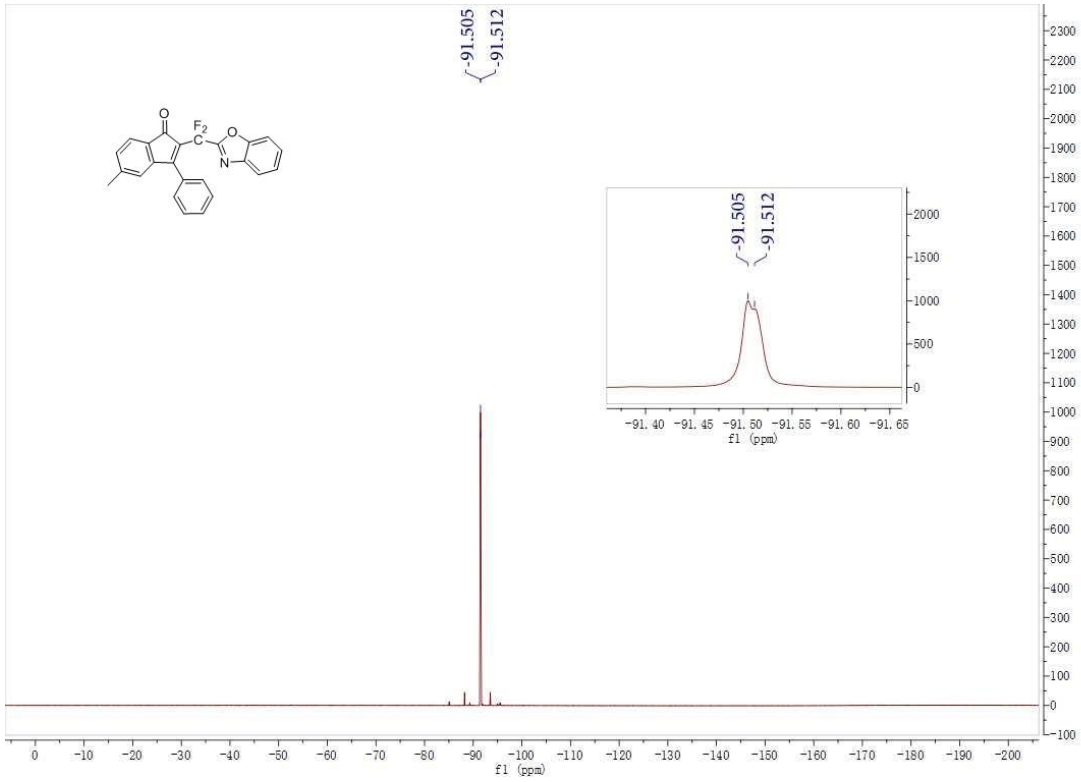


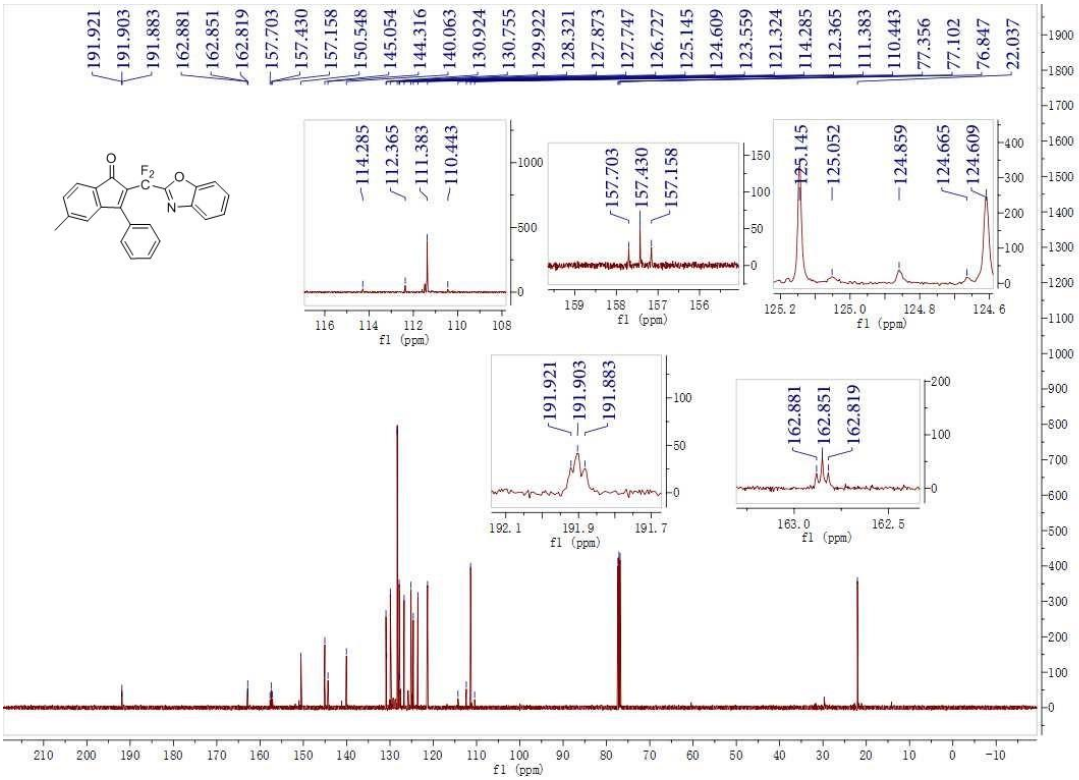

-88.249
-88.264
-88.280
-93.547
-93.563
-93.579
f1 (ppm)


157.450
157.172
156.508
156.243
150.693
150.256
143.091
143.058
143.021
142.978
142.957
142.914
140.237
139.781
131.929
129.199
128.712
127.944
126.920
126.860
125.341
125.171
121.525
121.271
114.510
112.821
112.570
111.481
111.181
110.860
110.634
77.289
77.035
76.781
f1 (ppm)

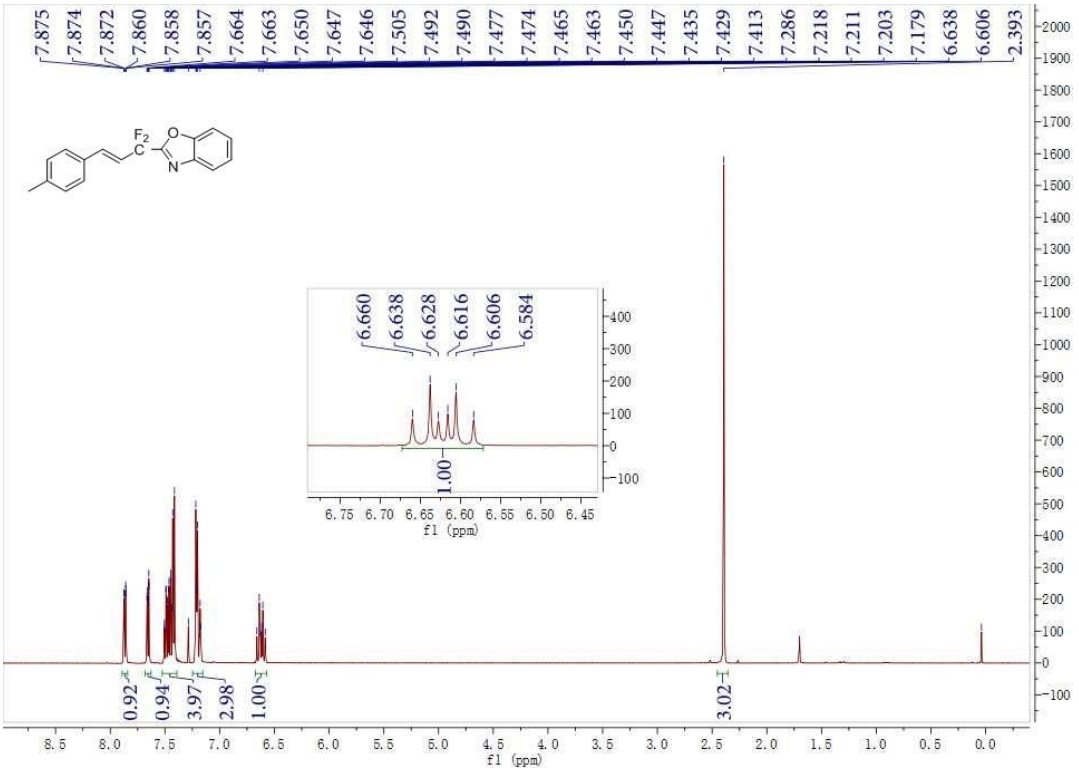
2-(benzo[*d*]oxazol-2-yldifluoromethyl)-5-methyl-3-phenyl-1H-inden-1-one (4)

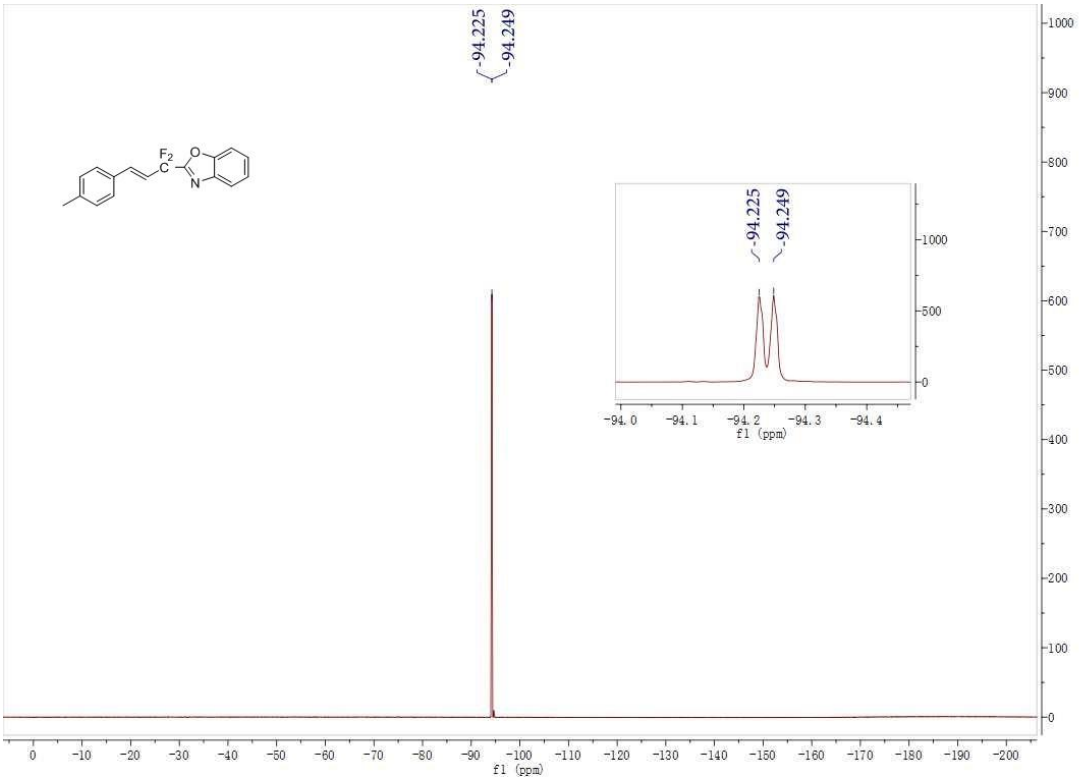


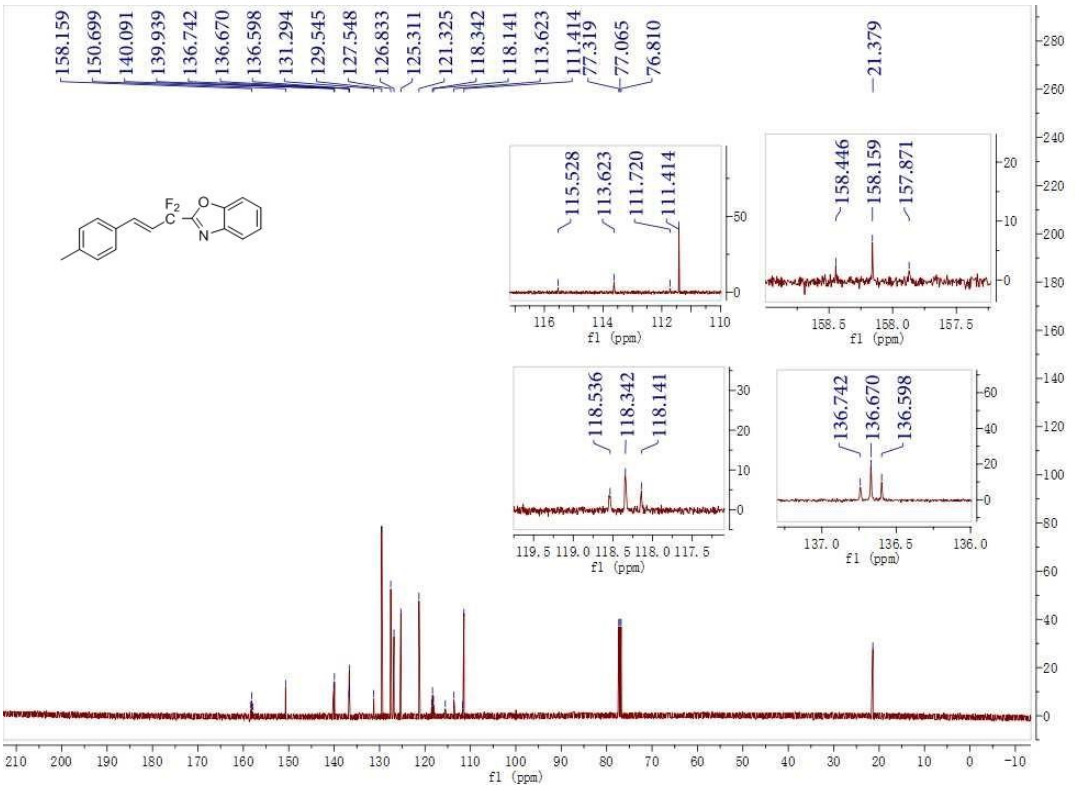




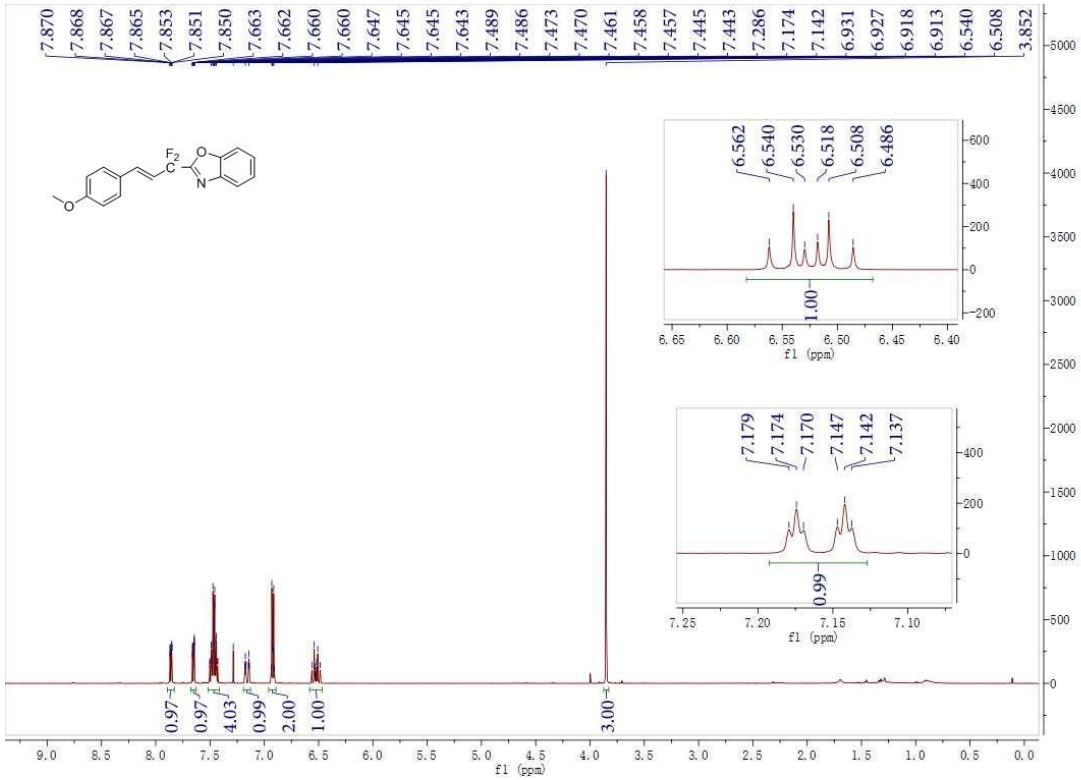
(*E*)-2-(1,1-difluoro-3-(*p*-tolyl)allyl)benzo[*d*]oxazole (3b)

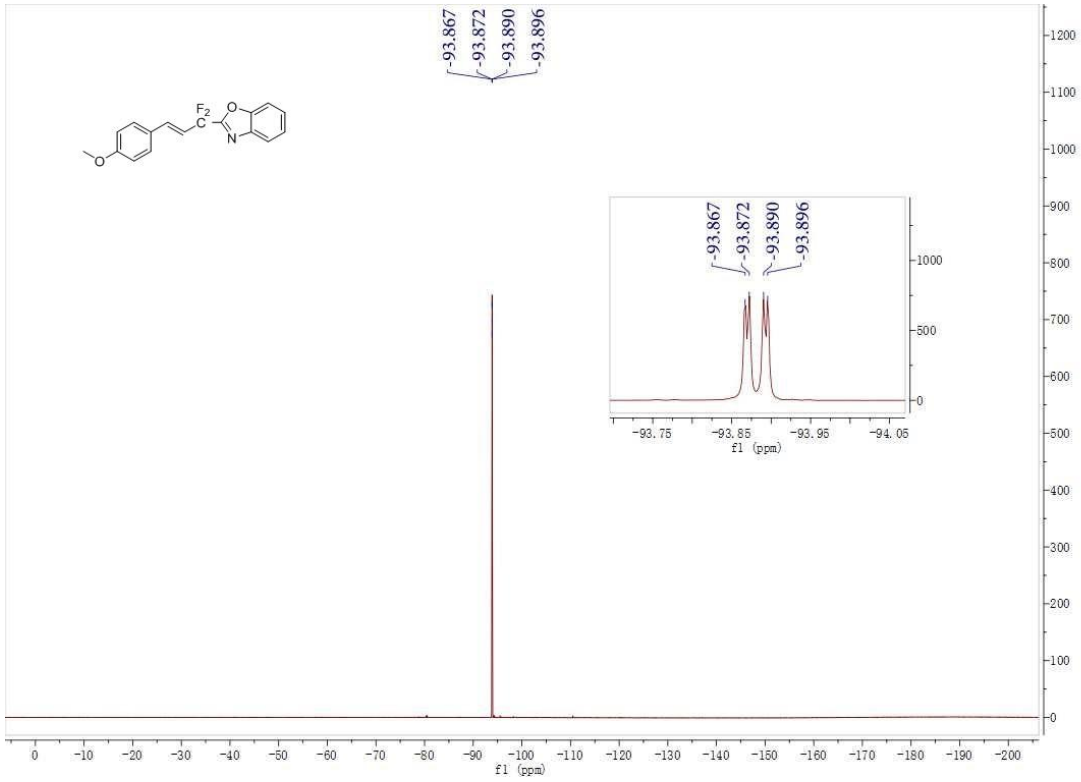


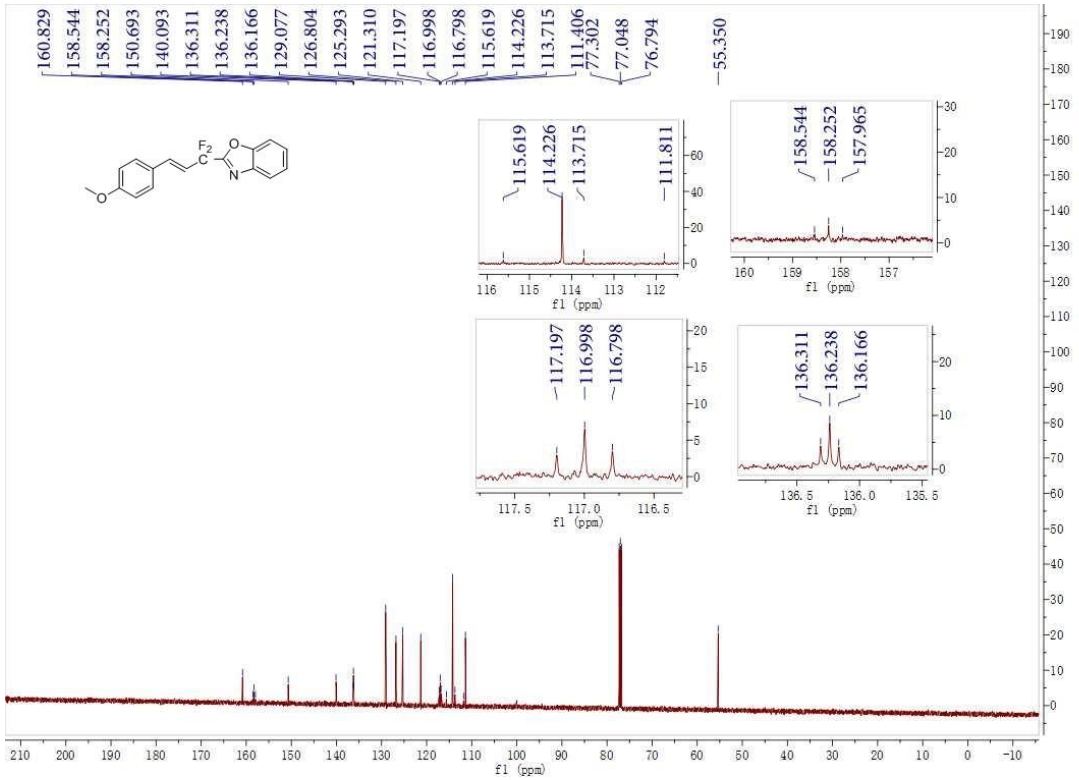

-94.225
-94.249
F2
C
O
N
-94.225
-94.249
f1 (ppm)


158.159
150.699
140.091
139.939
136.742
136.670
136.598
131.294
129.545
127.548
126.833
125.311
121.325
118.342
118.141
113.623
111.414
77.319
77.065
76.810
21.379
F2
C
O
N
115.528
113.623
111.720
111.414
158.446
158.159
157.871
118.536
118.342
118.141
136.742
136.670
136.598
f1 (ppm)

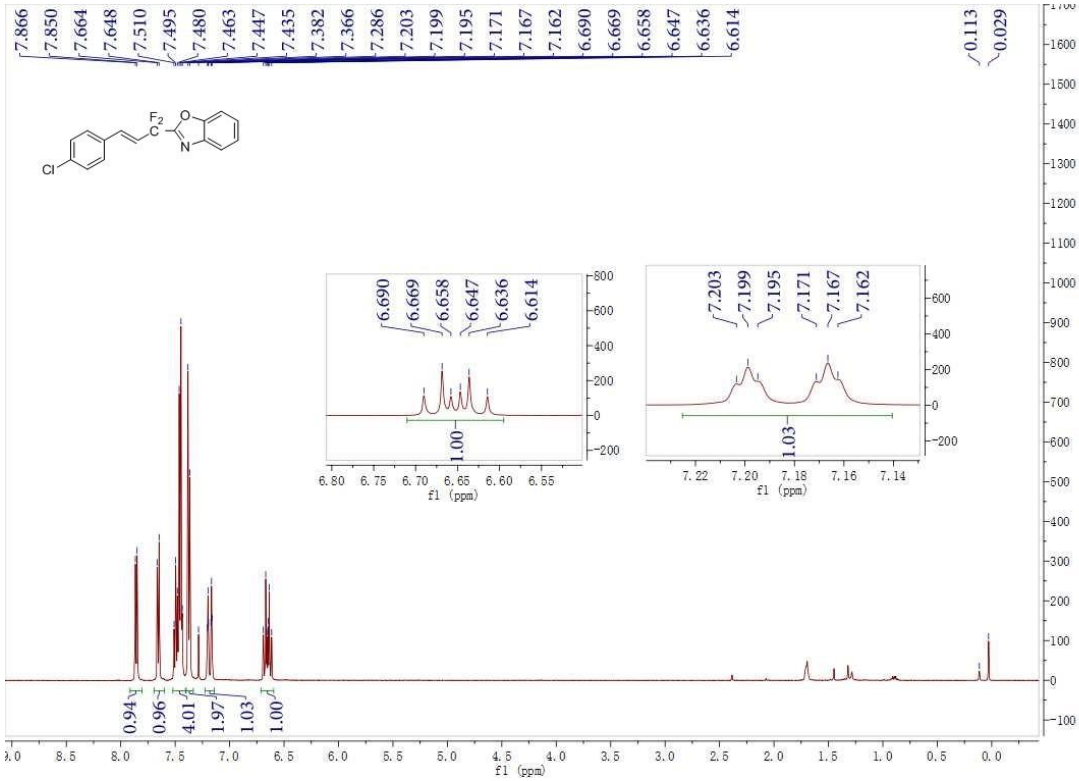
(*E*)-2-(1,1-difluoro-3-(4-methoxyphenyl)allyl)benzo[*d*]oxazole (3c)

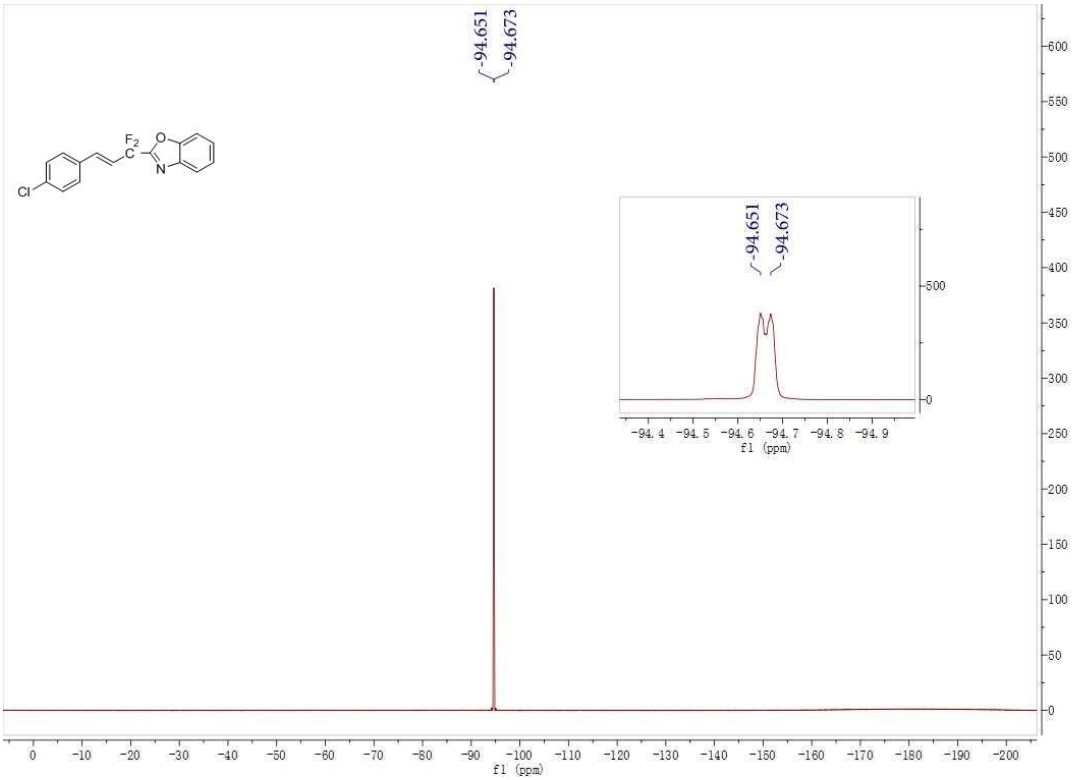


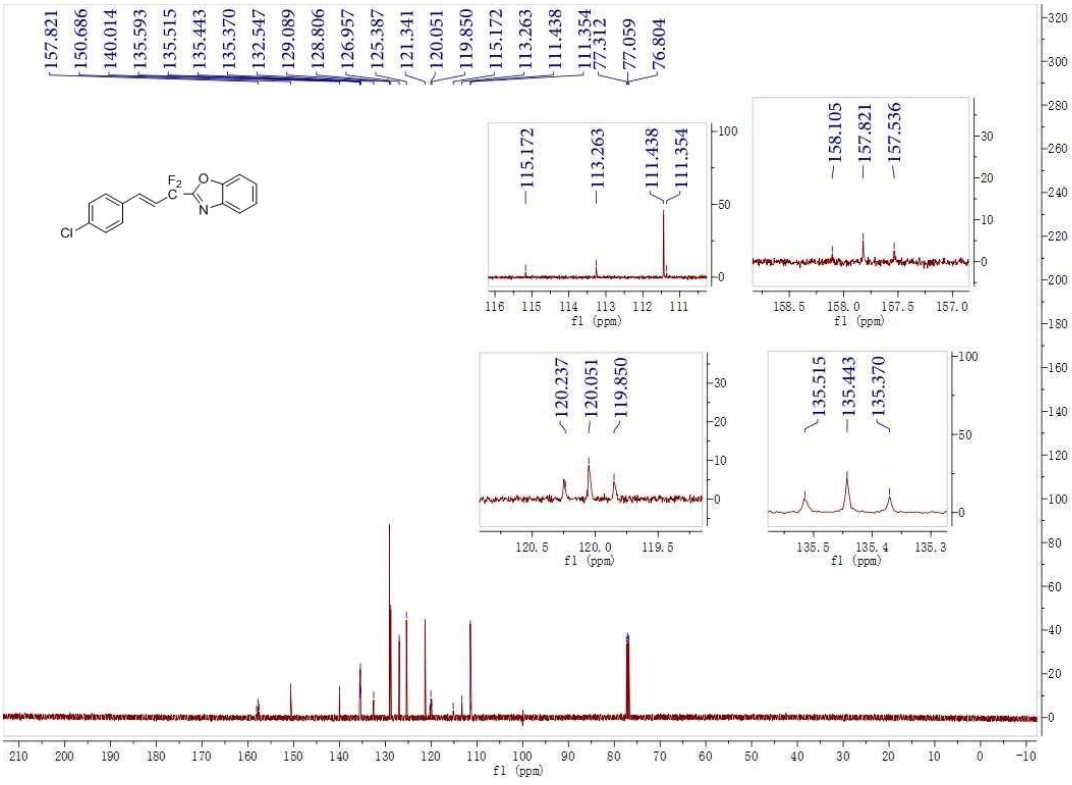




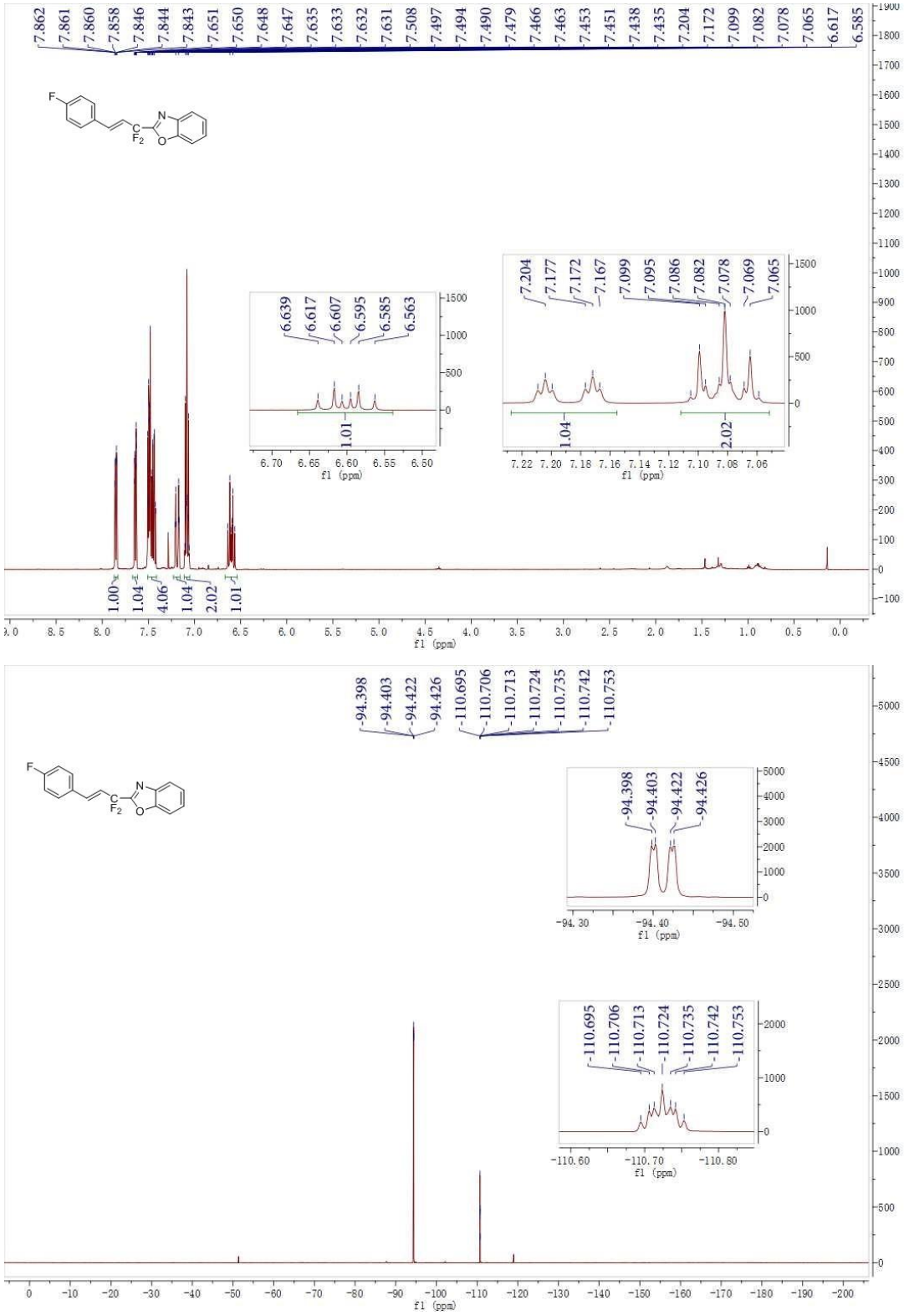
(*E*)-2-(3-(4-chlorophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3d)

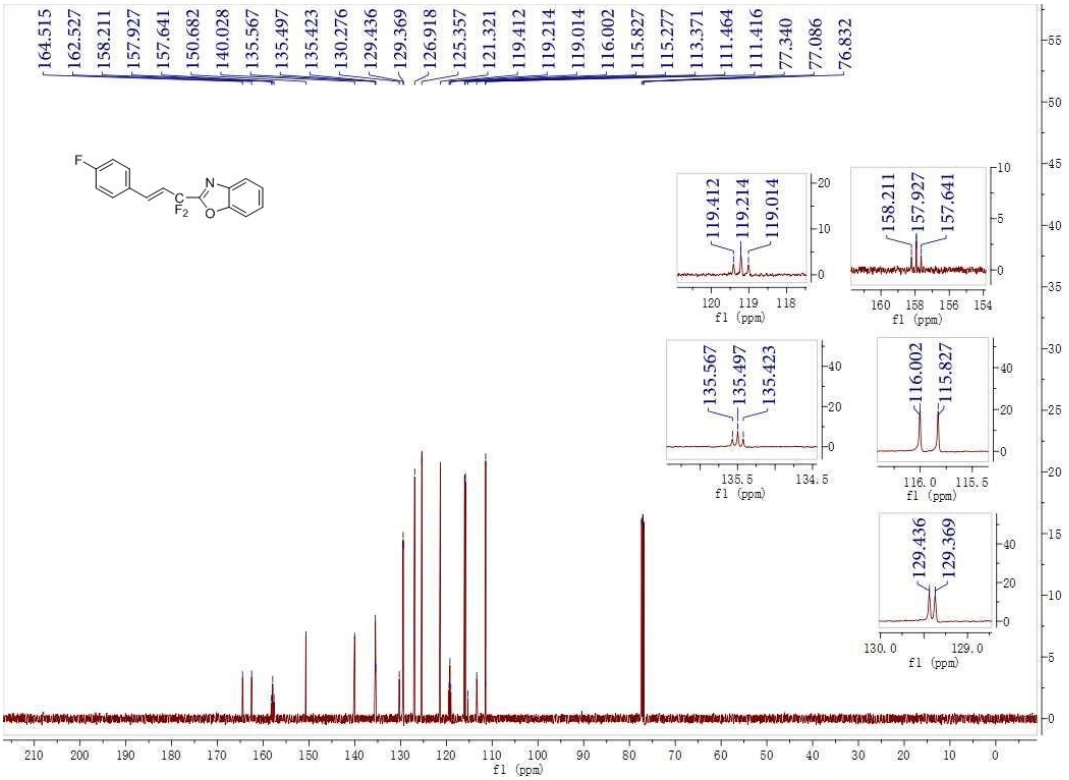



-94.651
-94.673
F2
C
O
N
Cl
f1 (ppm)

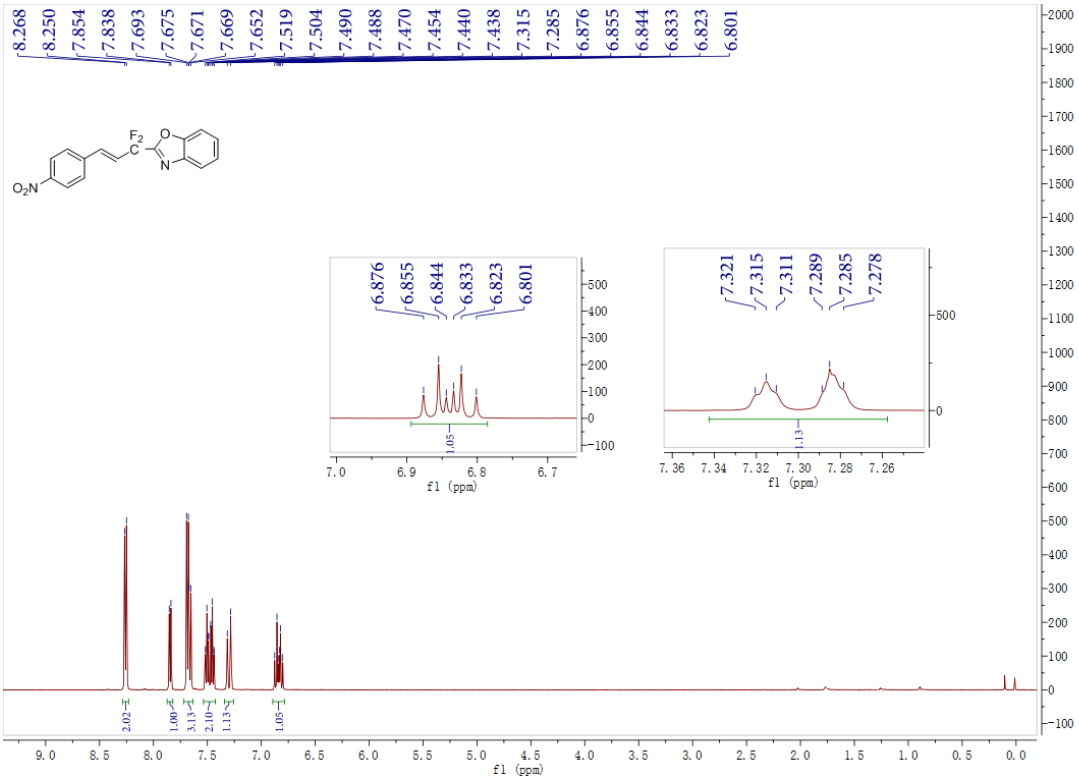

157.821
150.686
140.014
135.593
135.515
135.443
135.370
132.547
129.089
128.806
126.957
125.387
121.341
120.051
119.850
115.172
113.263
111.438
111.354
77.312
77.059
76.804
F2
C
O
N
Cl
158.105
157.821
157.536
120.237
120.051
119.850
135.515
135.443
135.370
f1 (ppm)

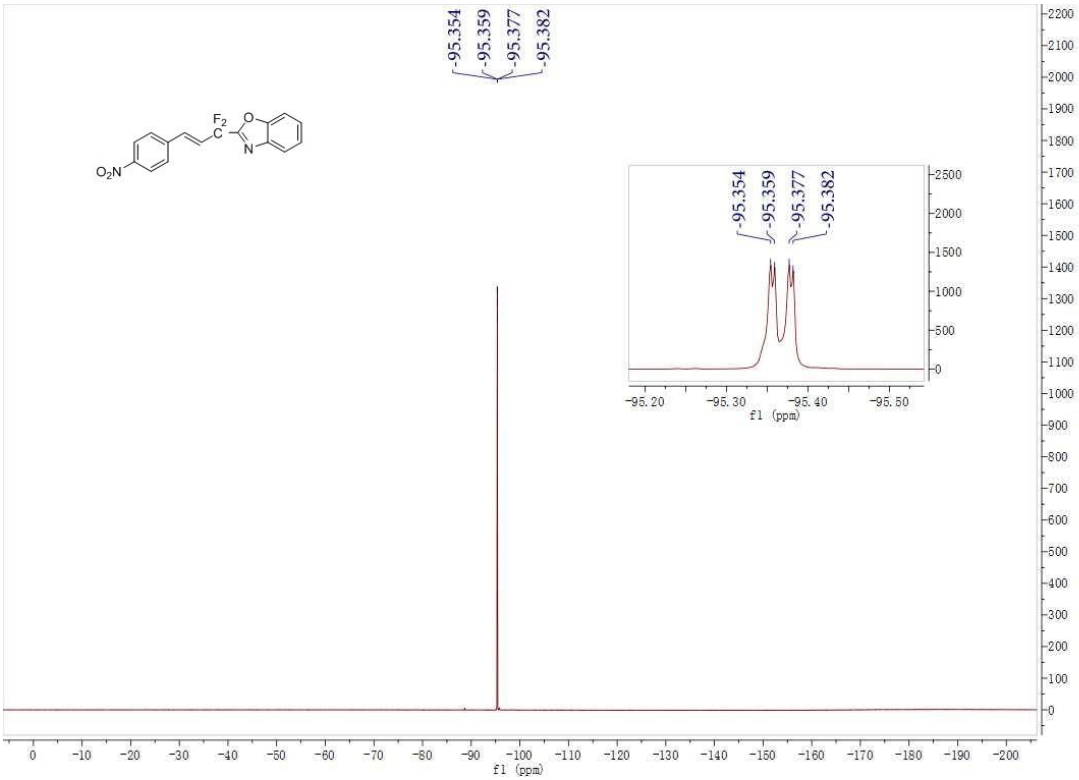
(*E*)-2-(1,1-difluoro-3-(4-fluorophenyl)allyl)benzo[*d*]oxazole (3e)

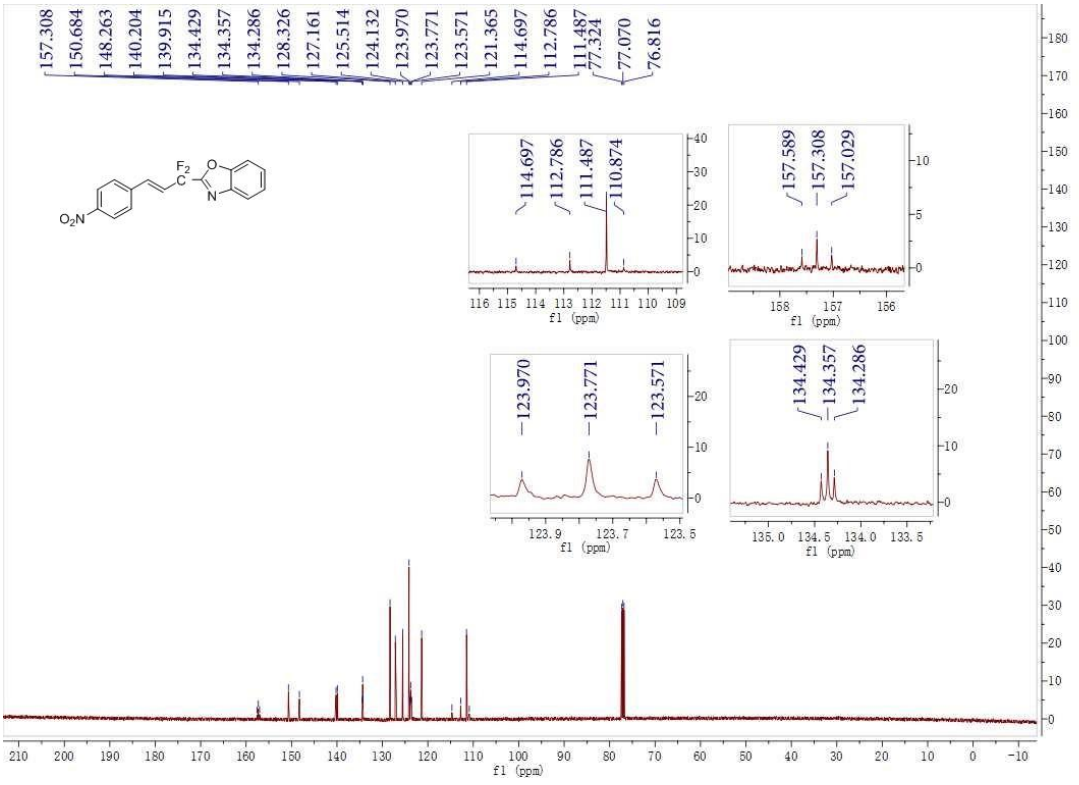




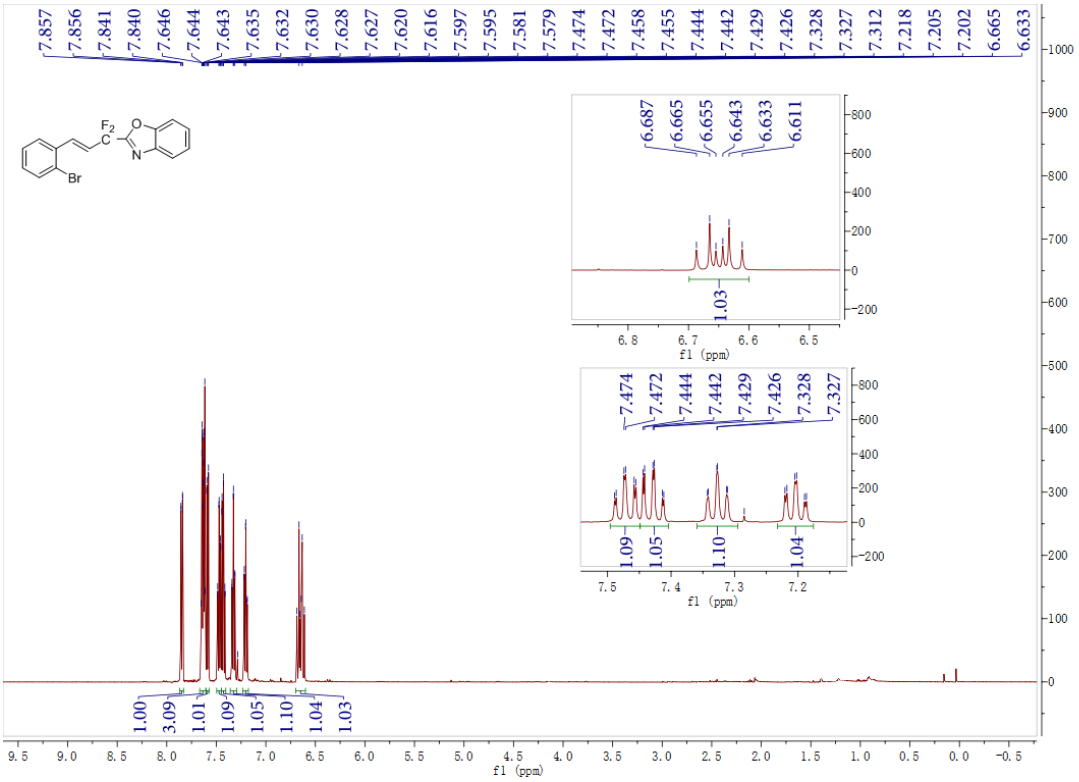
(*E*)-2-(1,1-difluoro-3-(4-nitrophenyl)allyl)benzo[*d*]oxazole (3f)

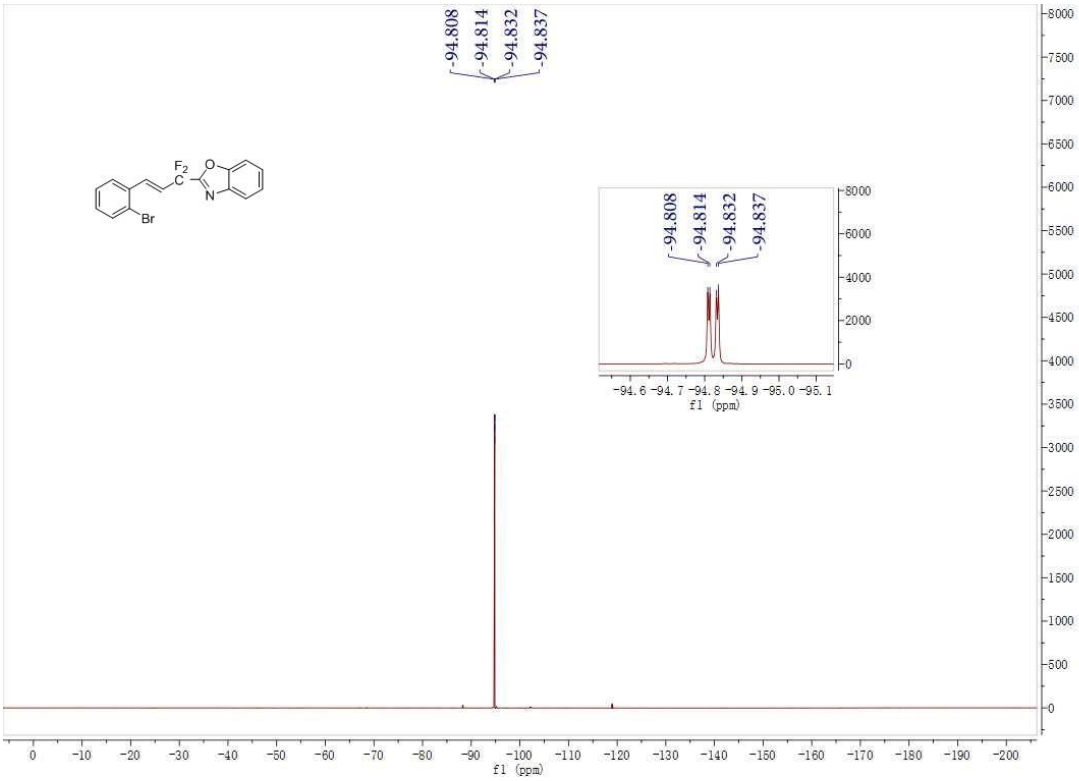


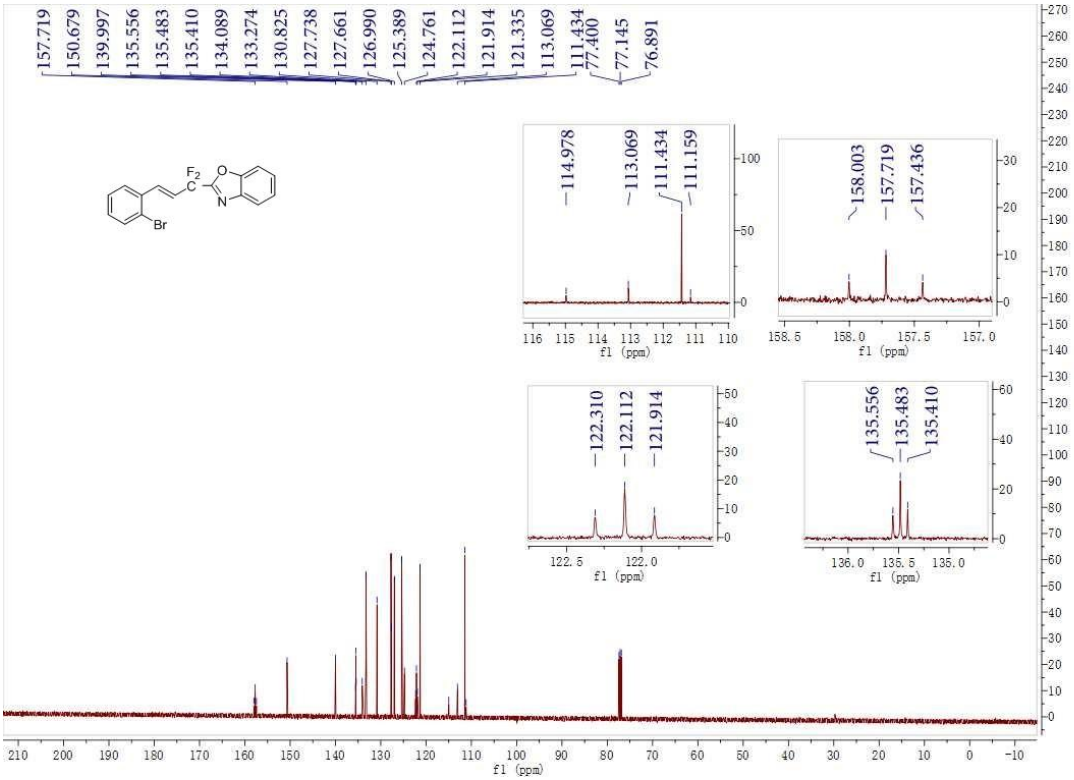

-95.354
-95.359
-95.377
-95.382
F2
O
N
O2N
f1 (ppm)


157.308
150.684
148.263
140.204
139.915
134.429
134.357
134.286
128.326
127.161
125.514
124.132
123.970
123.771
123.571
121.365
114.697
112.786
111.487
77.324
77.070
76.816
F2
O
N
O2N
114.697
112.786
111.487
110.874
157.589
157.308
157.029
123.970
123.771
123.571
134.429
134.357
134.286
f1 (ppm)

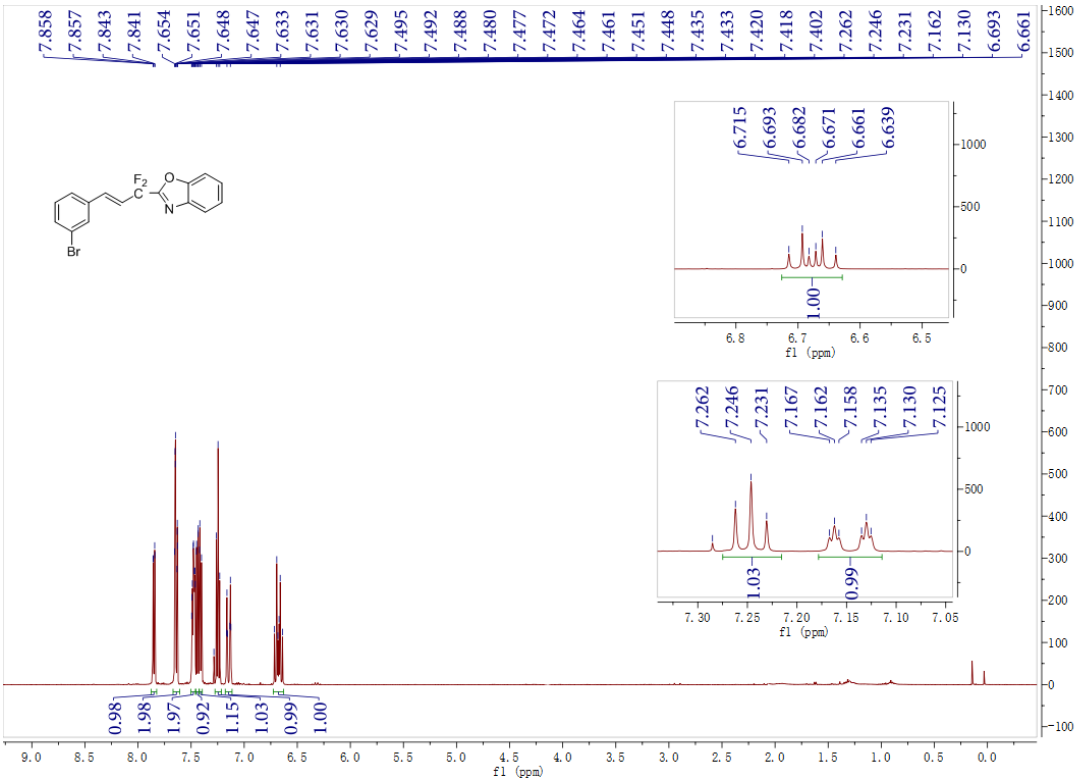
(*E*)-2-(3-(2-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3g)

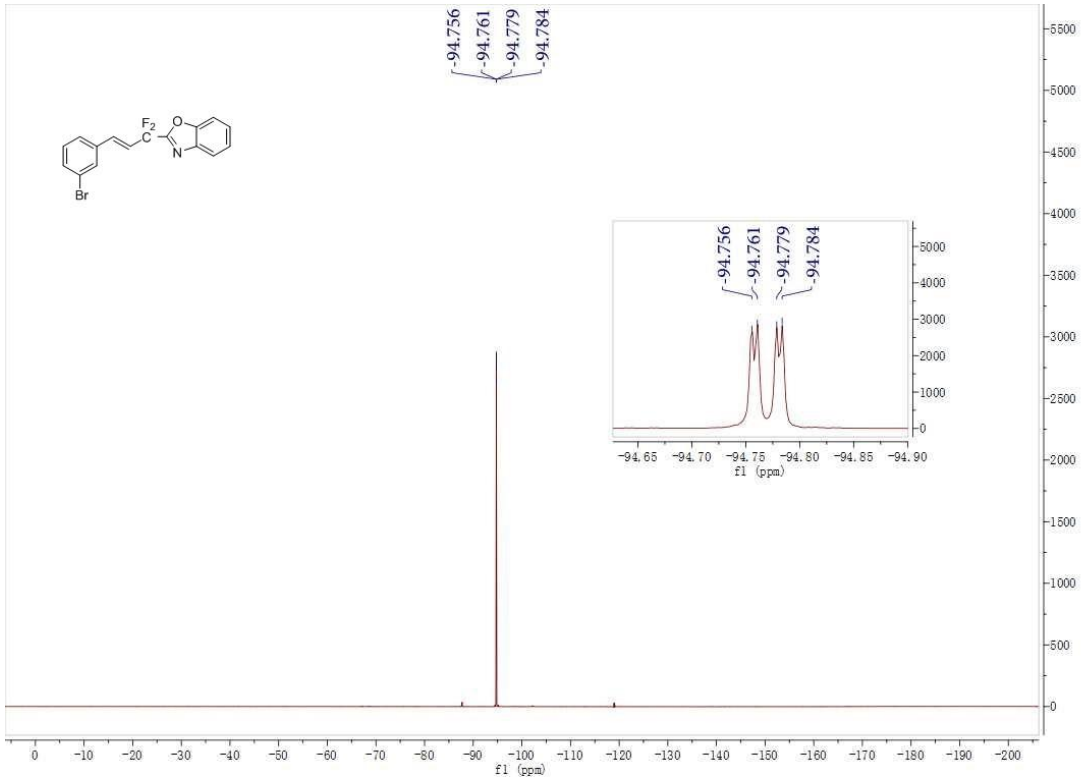


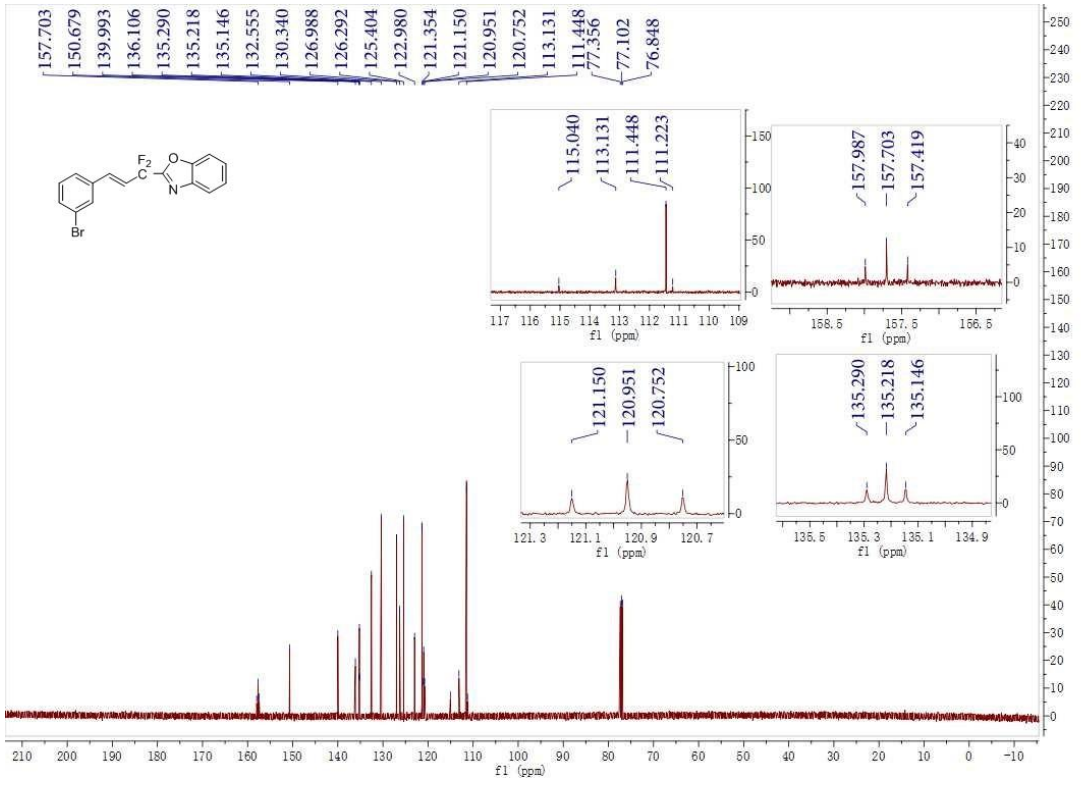




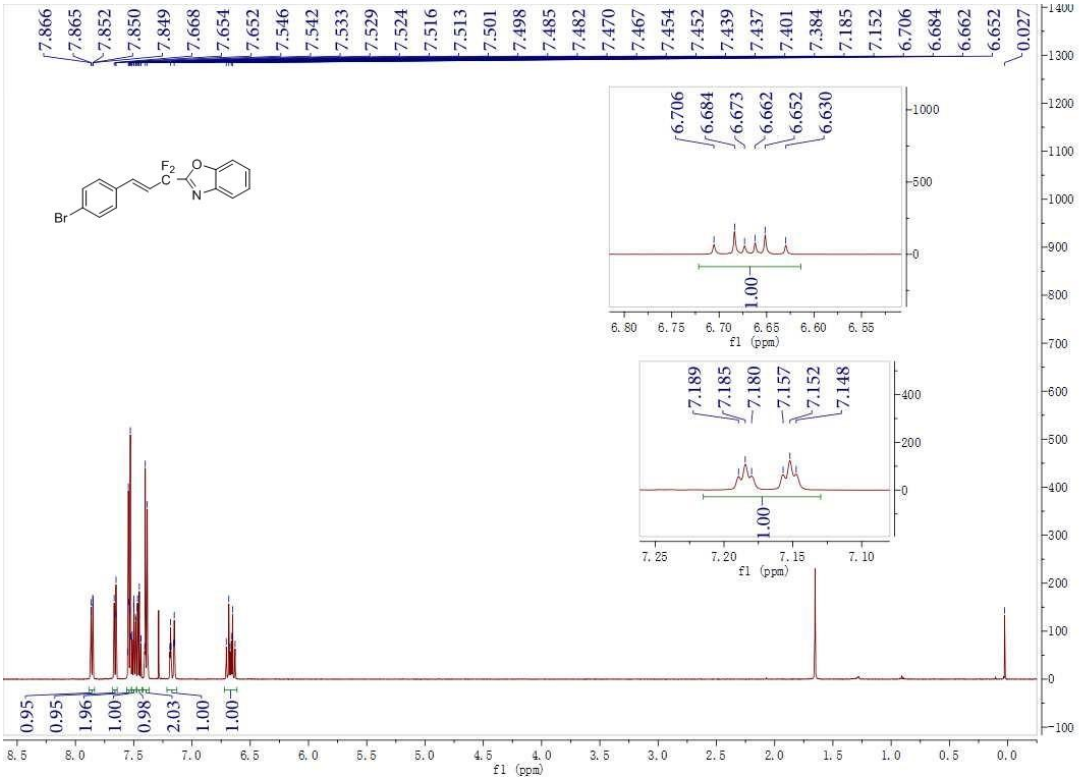
(*E*)-2-(3-(3-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3h)

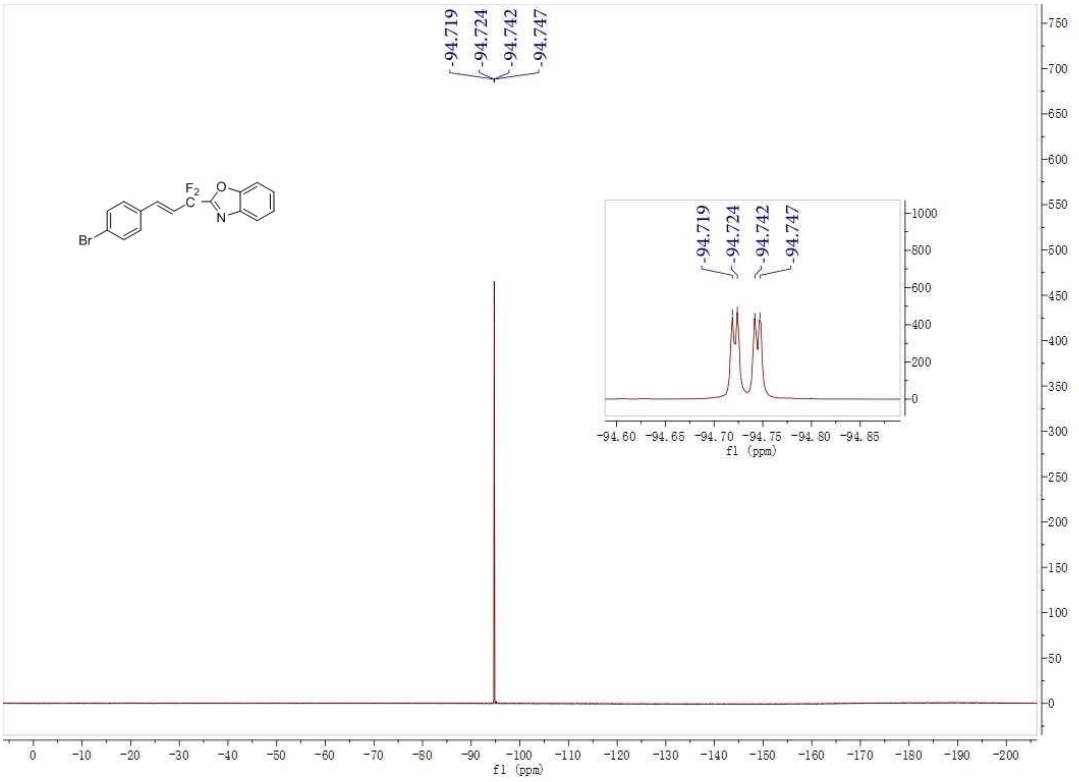


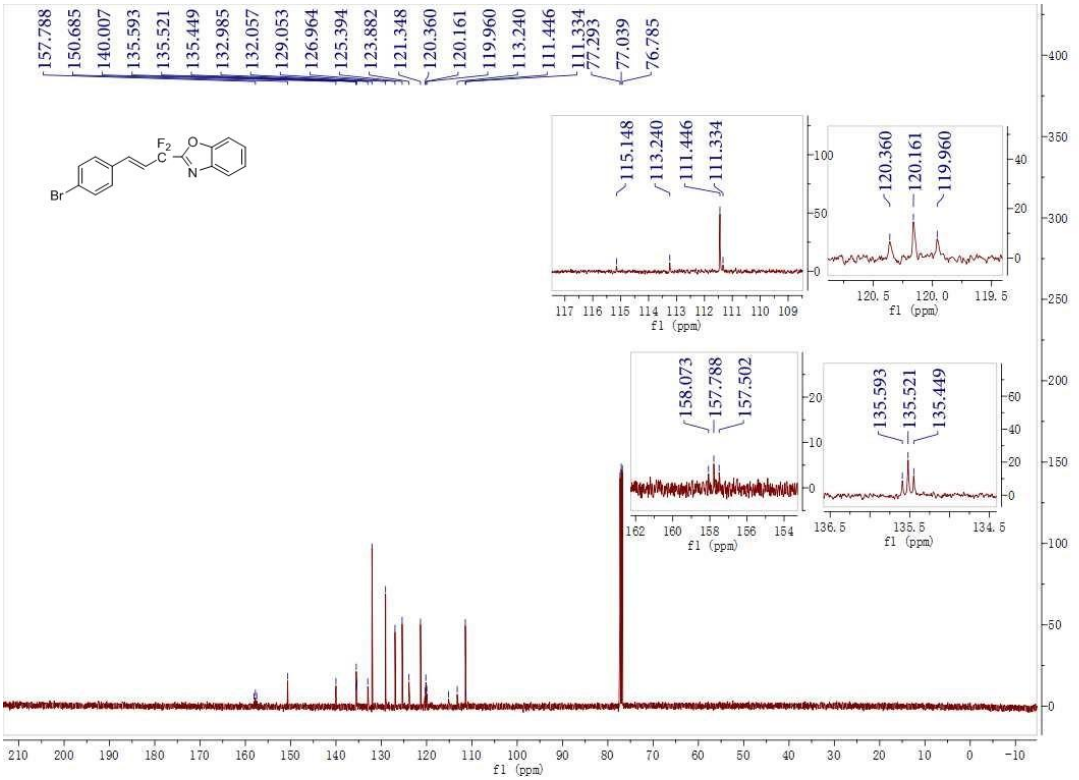

-94.756
-94.761
-94.779
-94.784
F2
C
O
N
Br
f1 (ppm)


157.703
150.679
139.993
136.106
135.290
135.218
135.146
132.555
130.340
126.988
126.292
125.404
122.980
121.354
121.150
120.951
120.752
113.131
111.448
77.356
77.102
76.848
115.040
113.131
111.448
111.223
157.987
157.703
157.419
121.150
120.951
120.752
135.290
135.218
135.146
F2
C
O
N
Br
f1 (ppm)

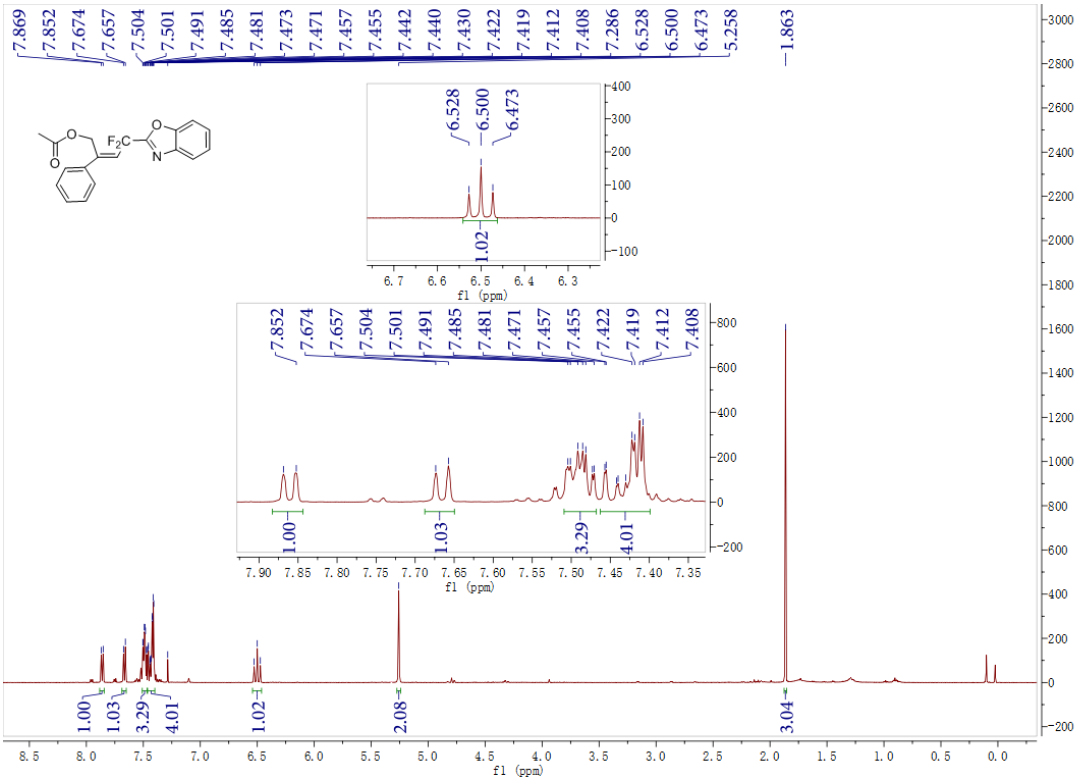
(*E*)-2-(3-(4-bromophenyl)-1,1-difluoroallyl)benzo[*d*]oxazole (3i)

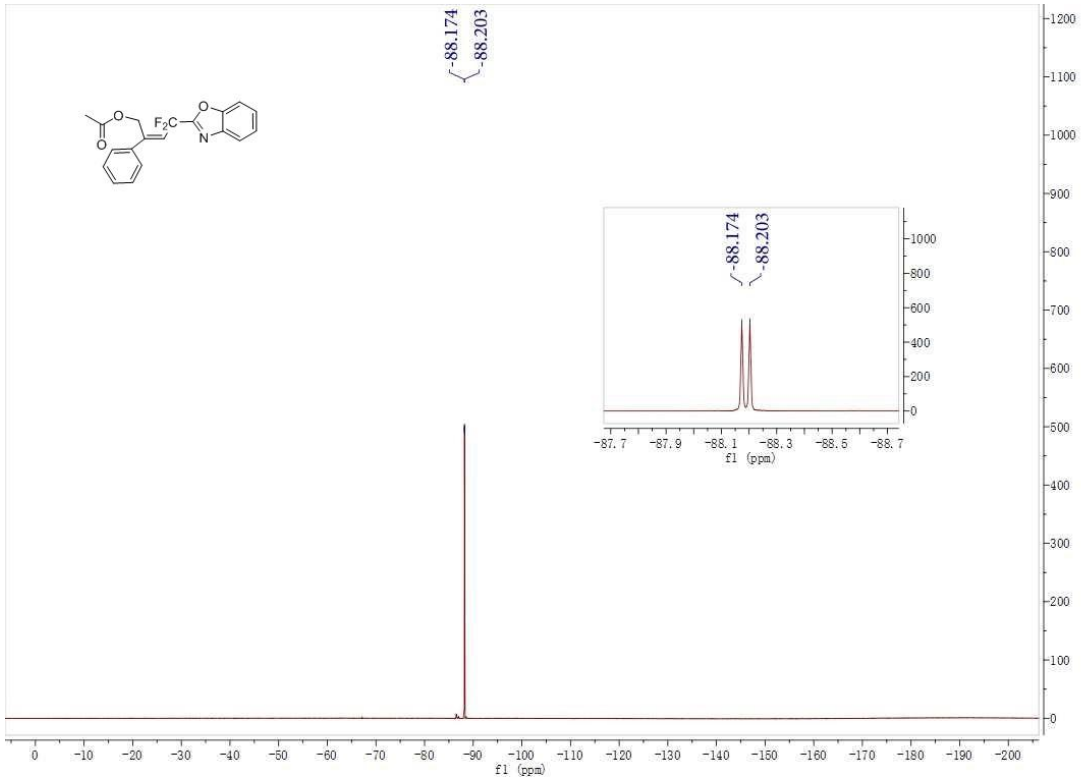


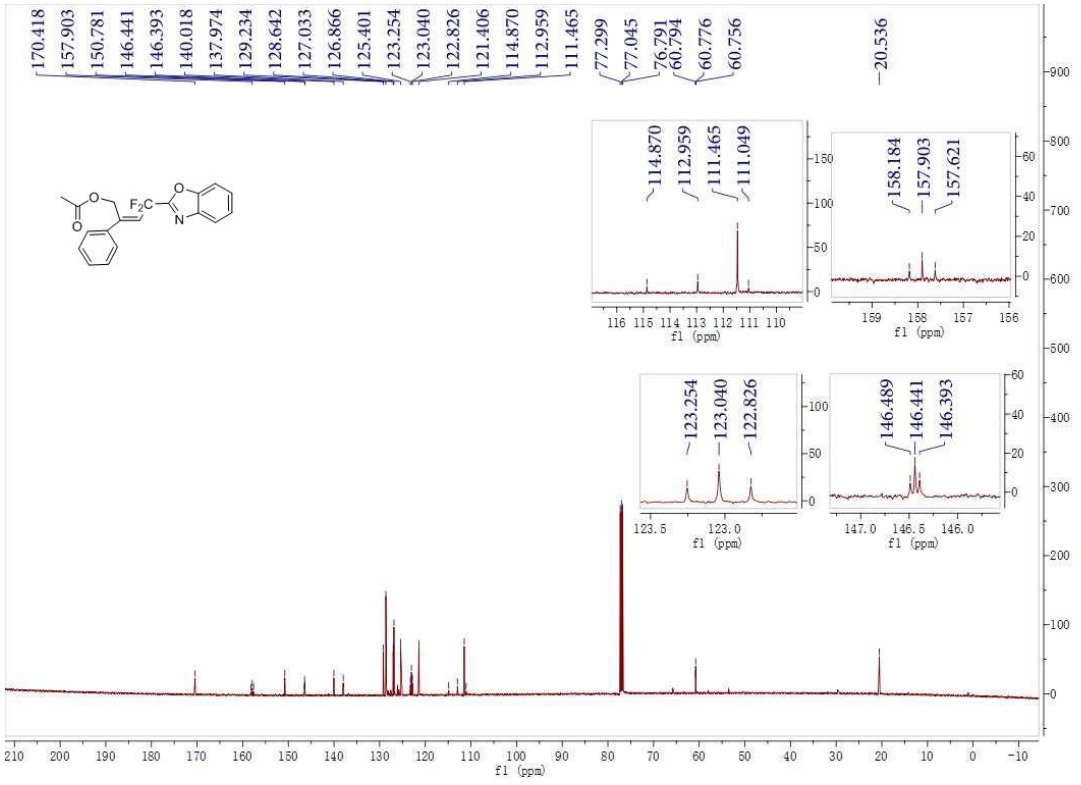




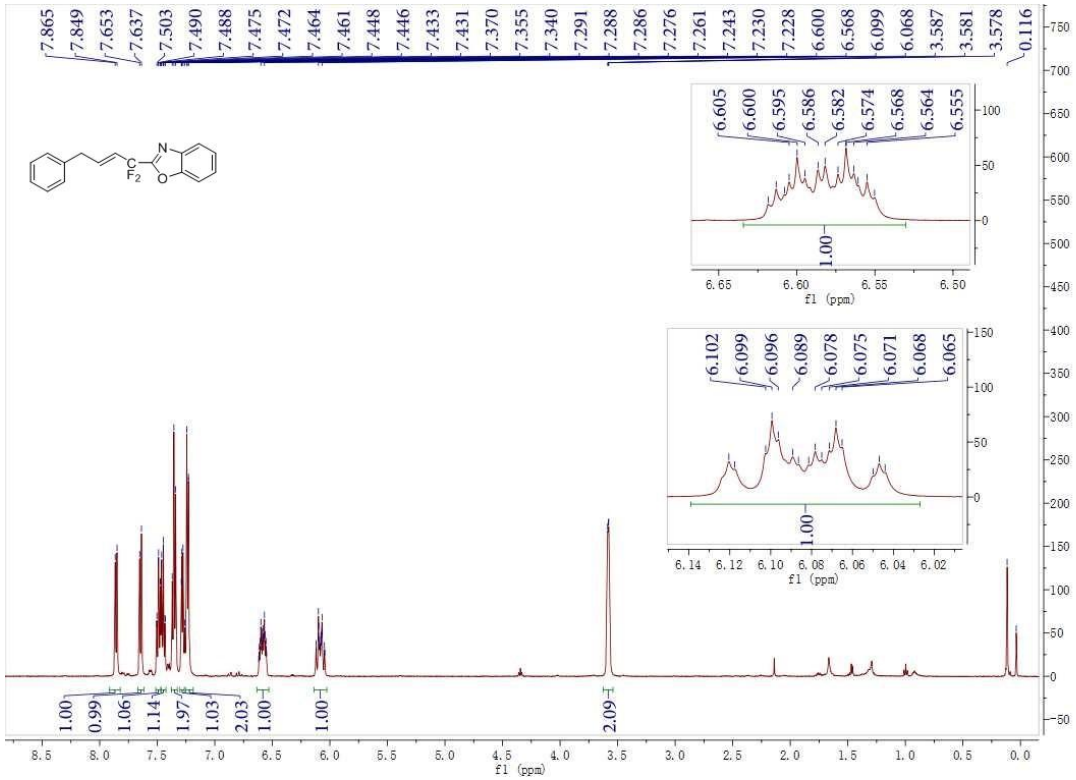
(*Z*)-4-(benzo[*d*]oxazol-2-yl)-4,4-difluoro-2-phenylbut-2-en-1-yl acetate (3j)

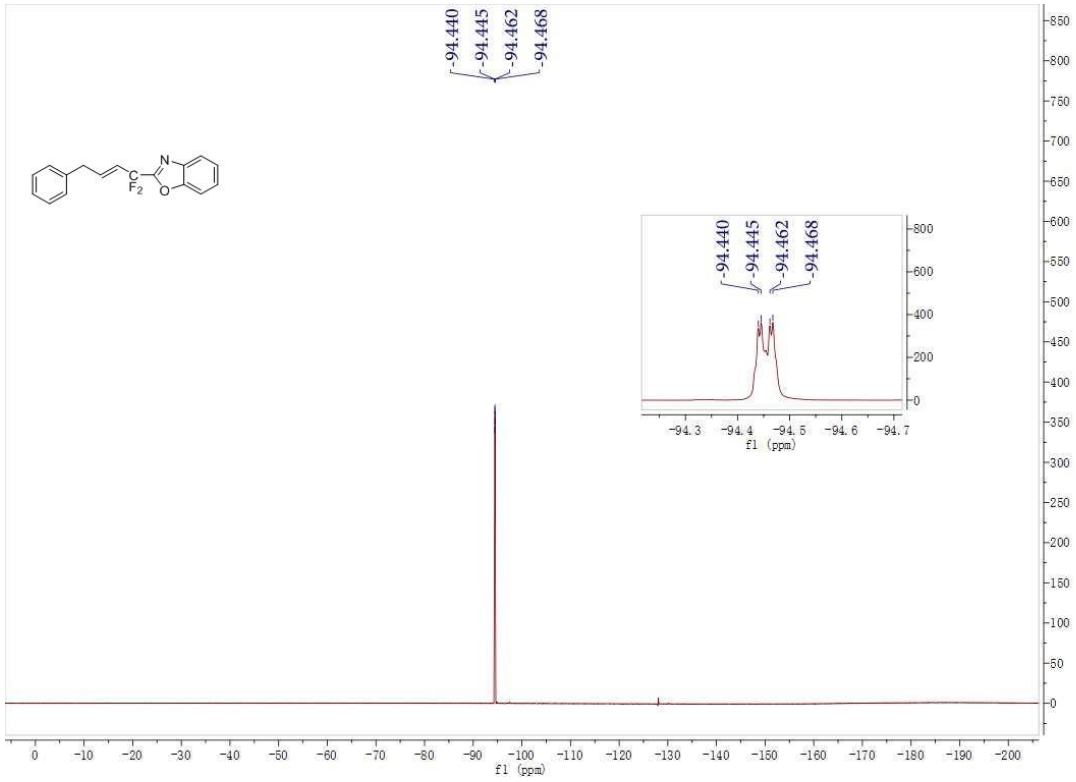


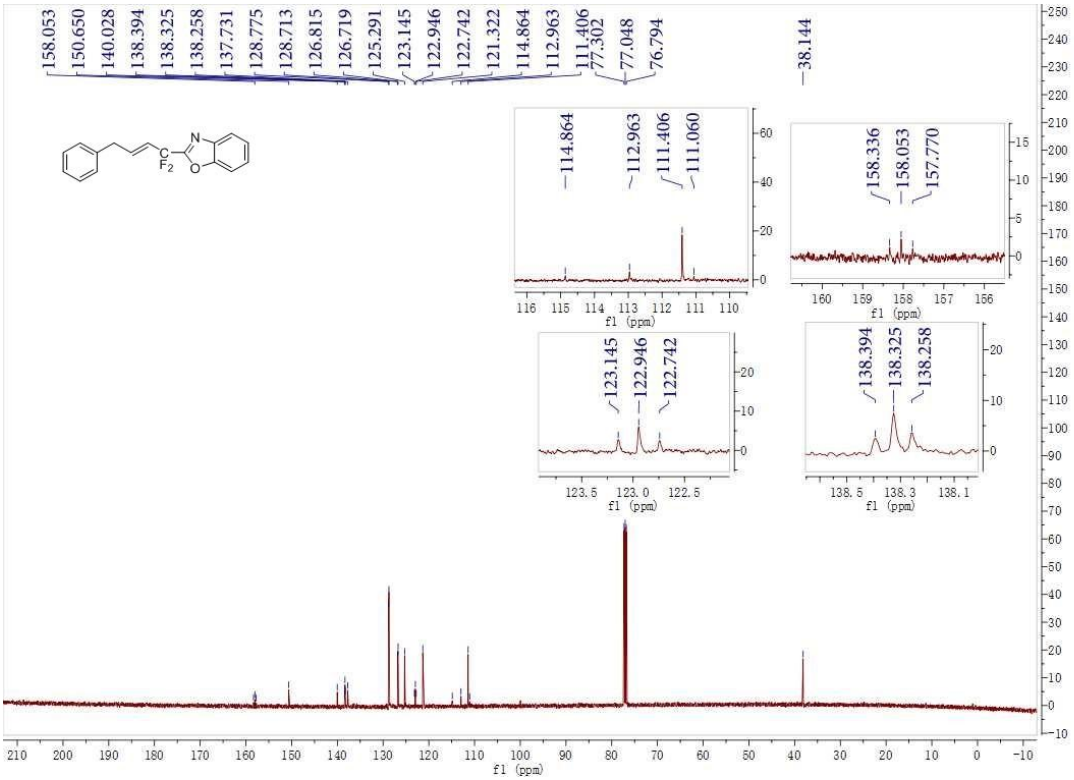

-88.174
-88.203
f1 (ppm)


170.418
157.903
150.781
146.441
146.393
140.018
137.974
129.234
128.642
127.033
126.866
125.401
123.254
123.040
122.826
121.406
114.870
112.959
111.465
77.299
77.045
76.791
60.794
60.776
60.756
20.536
f1 (ppm)

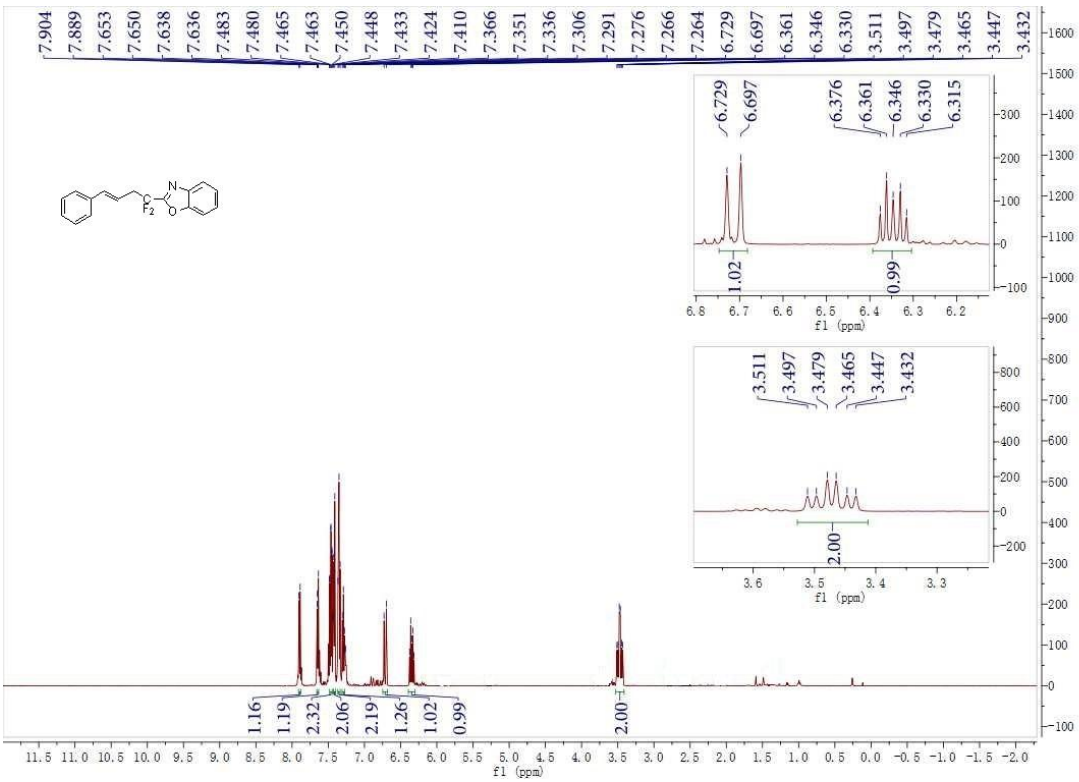
(*E*)-2-(1,1-difluoro-4-phenylbut-2-en-1-yl)benzo[*d*]oxazole (3k)

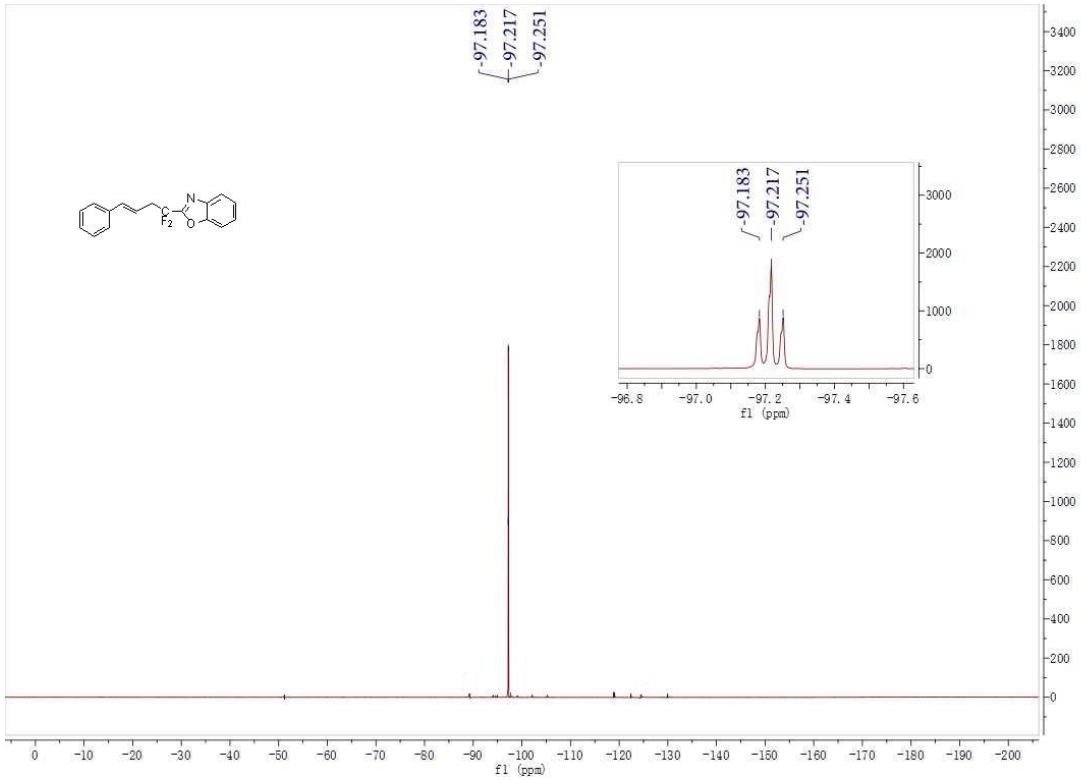


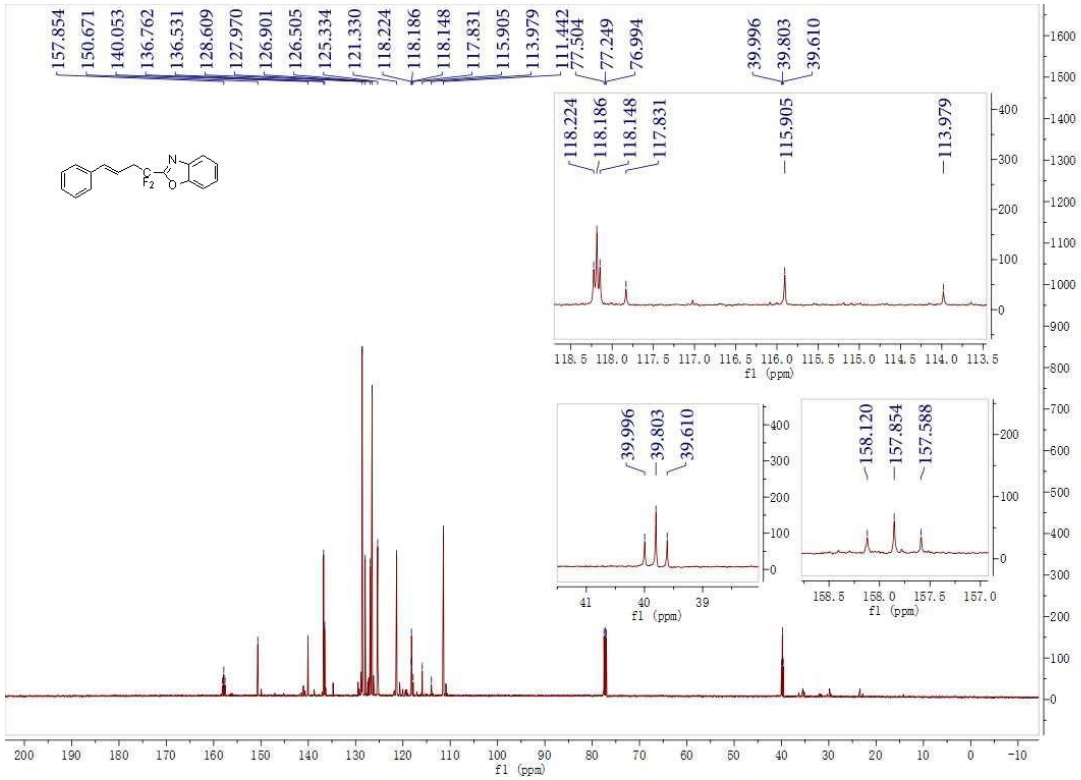




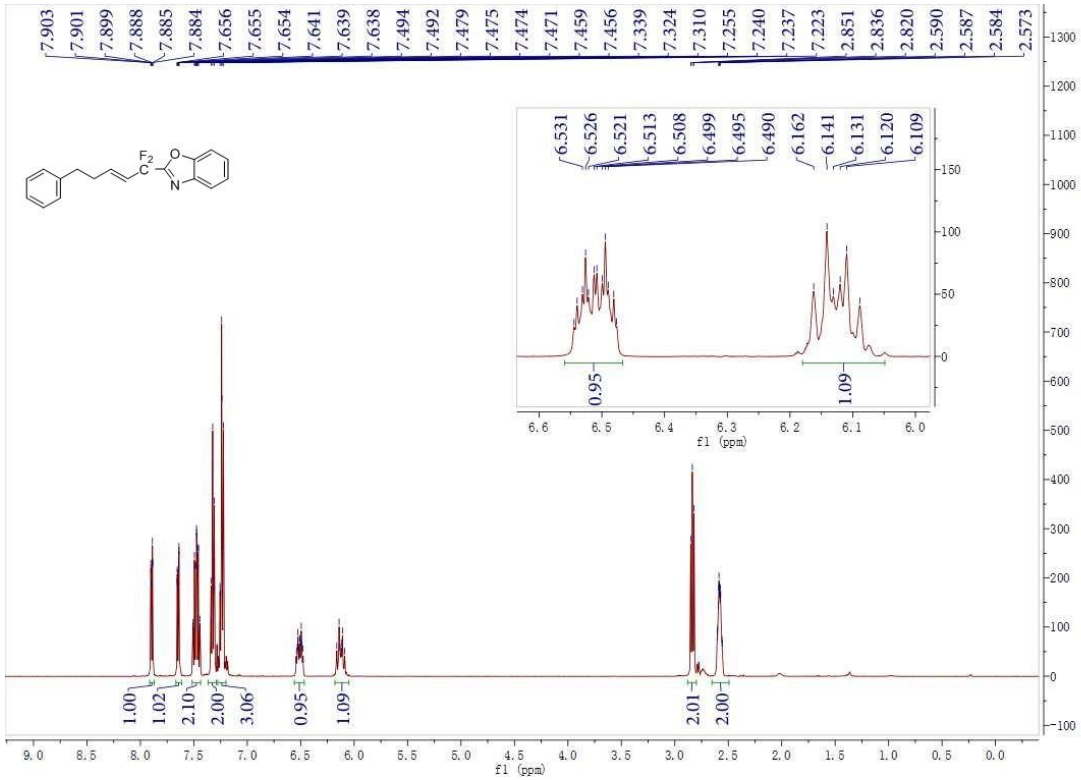
(*E*)-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3k')

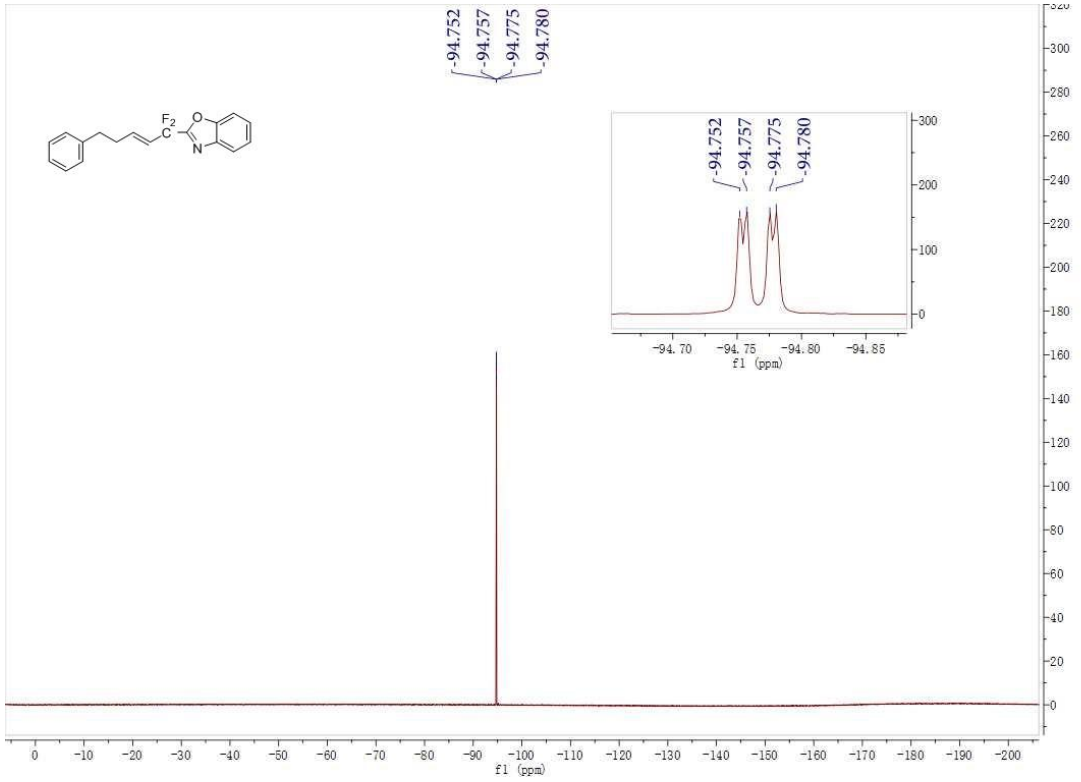


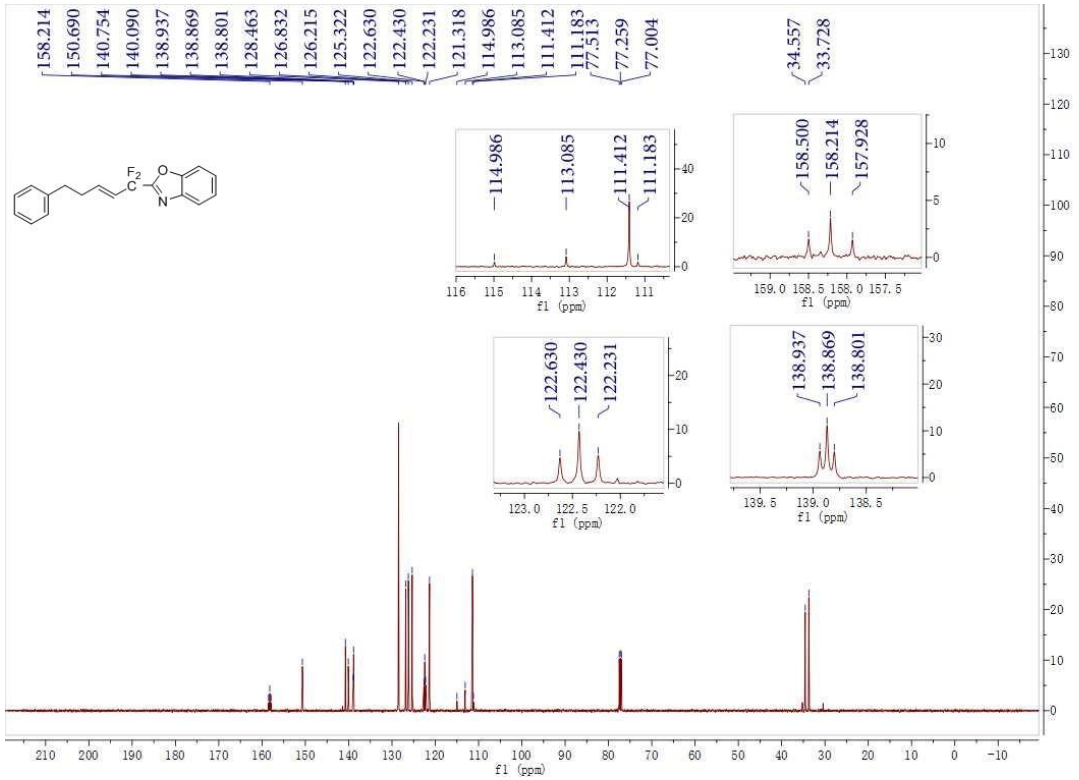

-97.183
-97.217
-97.251
f1 (ppm)


157.854
150.671
140.053
136.762
136.531
128.609
127.970
126.901
126.505
125.334
121.330
118.224
118.186
118.148
117.831
115.905
113.979
111.442
77.504
77.249
76.994
39.996
39.803
39.610
f1 (ppm)

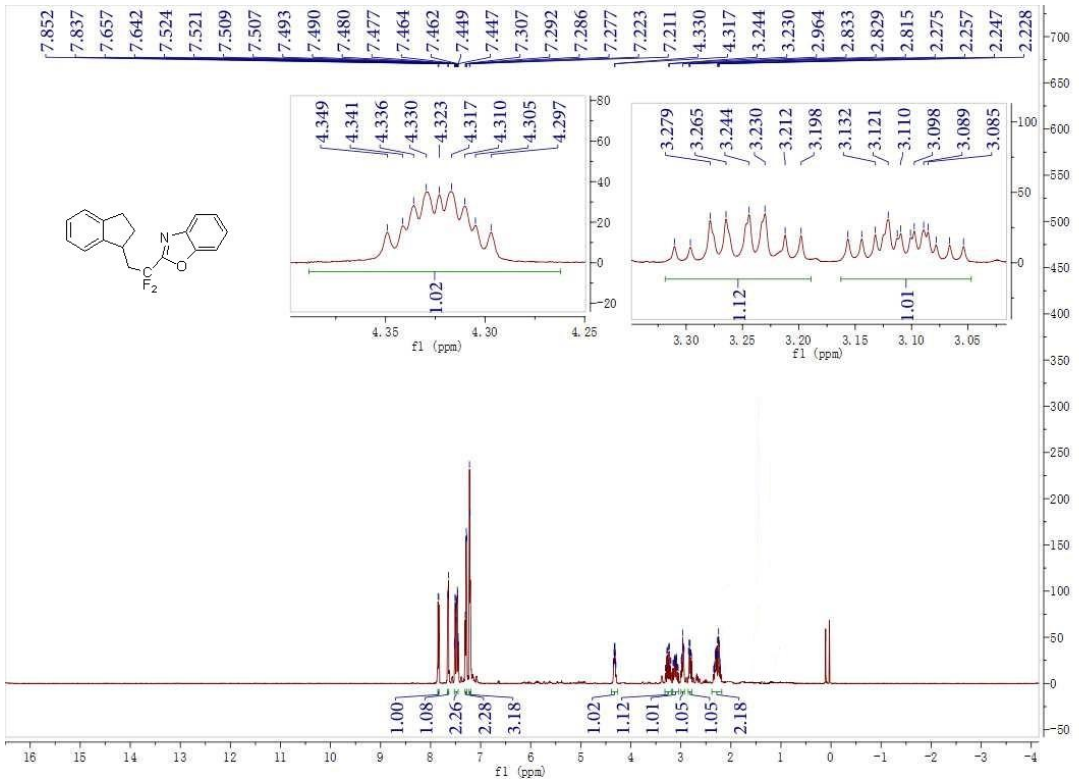
(*E*)-2-(1,1-difluoro-5-phenylpent-2-en-1-yl)benzo[*d*]oxazole (3l)

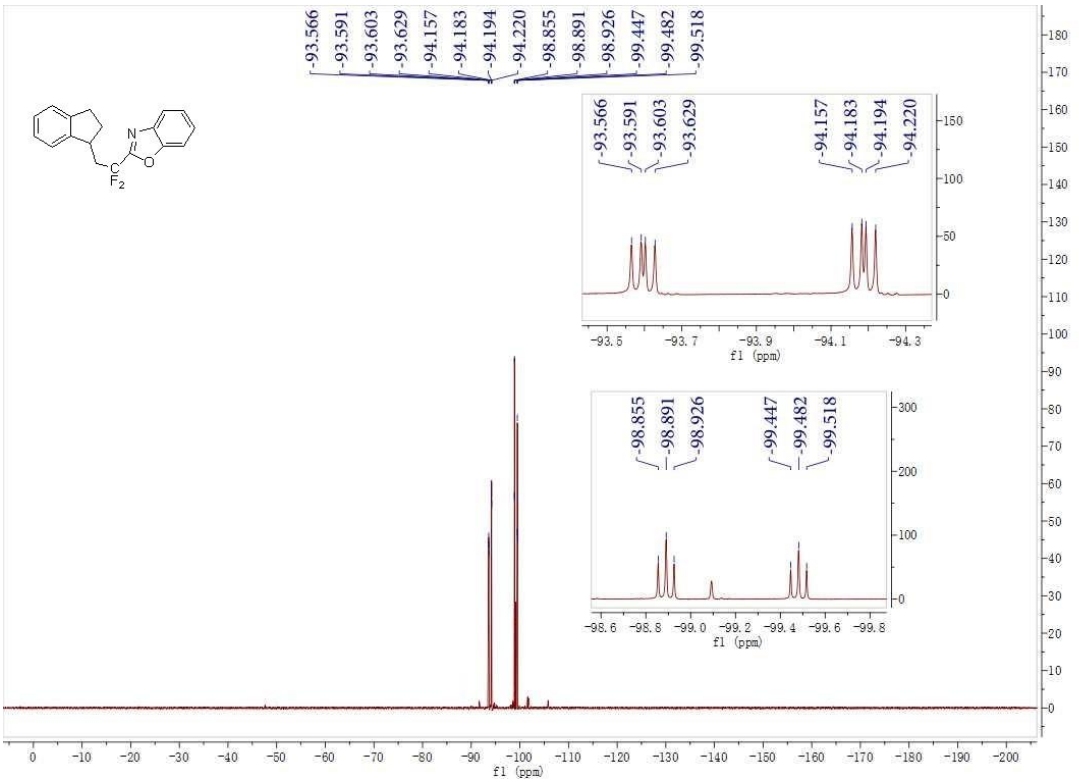


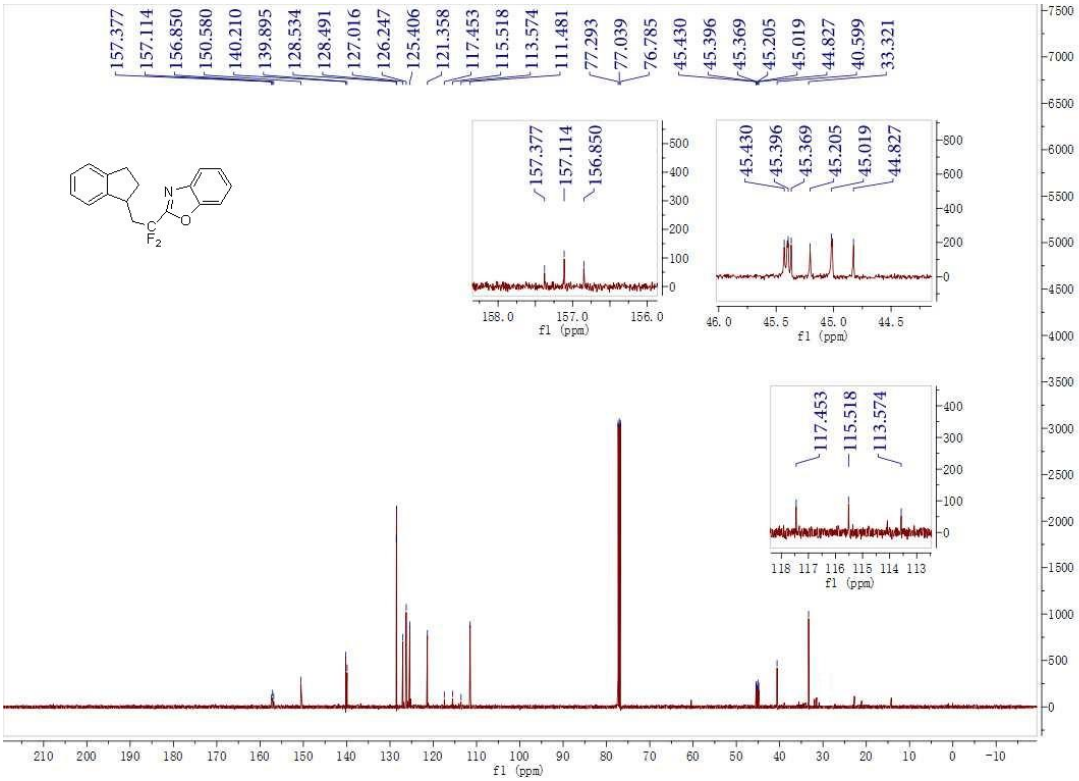




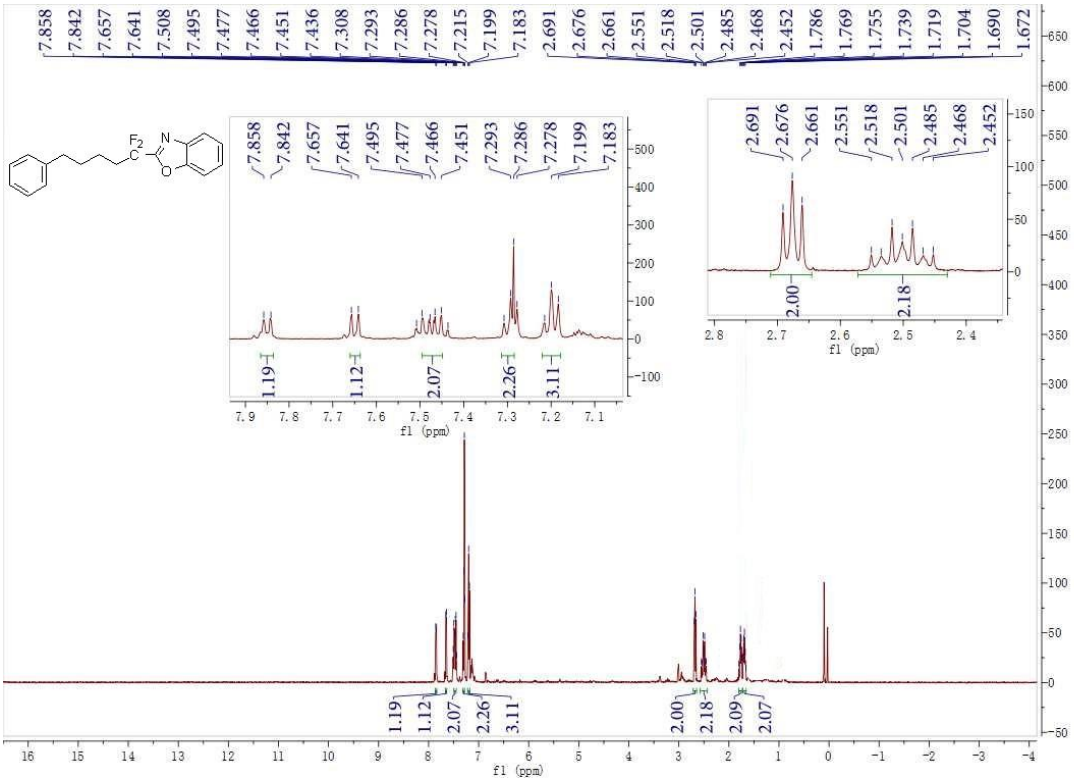
2-(2-(2,3-dihydro-1H-inden-1-yl)-1,1-difluoroethyl)benzo[d]oxazole (4l)

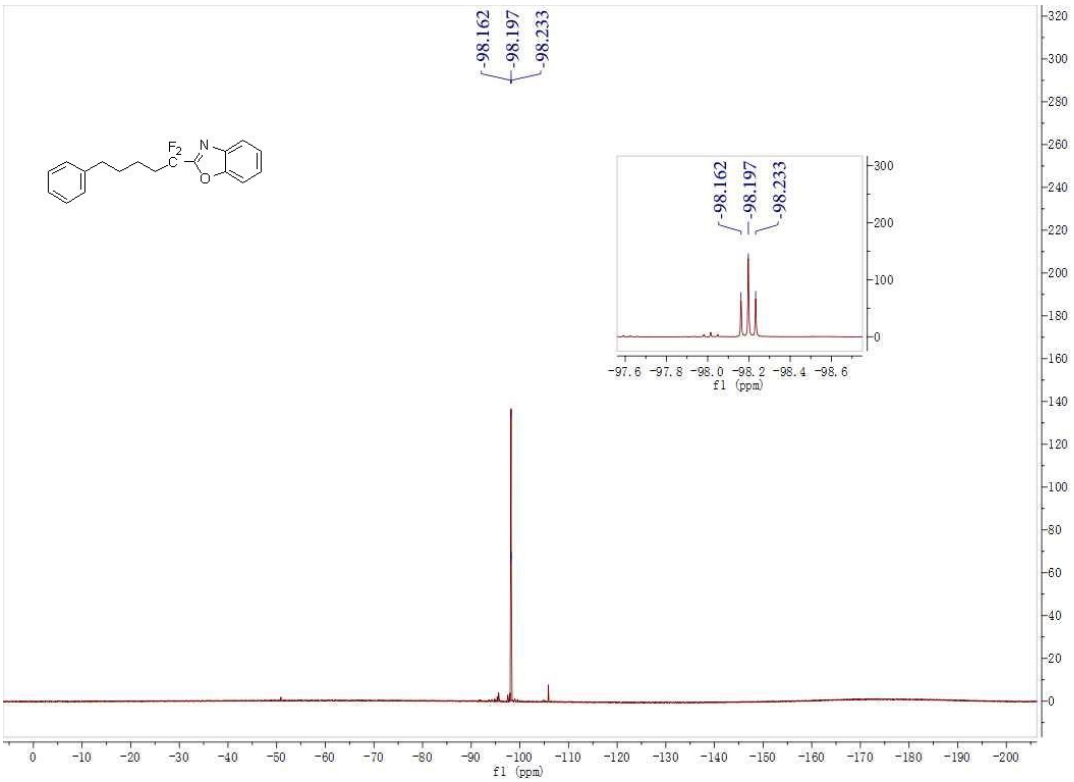


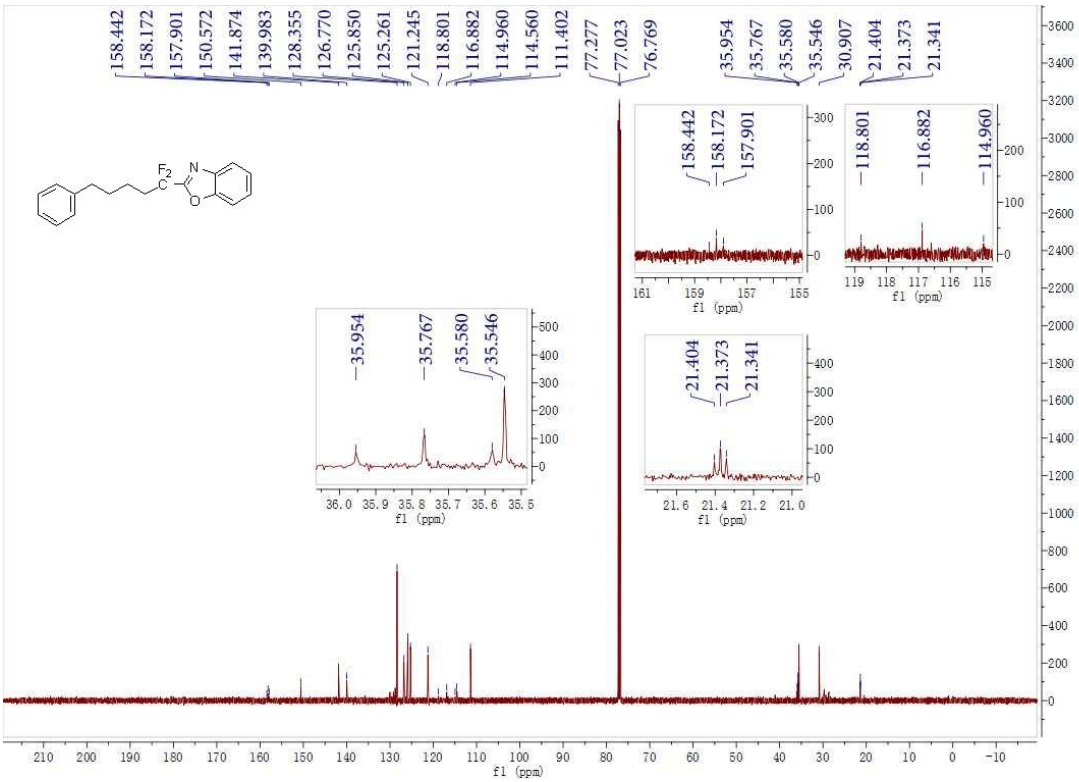

-93.566
-93.591
-93.603
-93.629
-94.157
-94.183
-94.194
-94.220
-98.855
-98.891
-98.926
-99.447
-99.482
-99.518
f1 (ppm)


157.377
157.114
156.850
150.580
140.210
139.895
128.534
128.491
127.016
126.247
125.406
121.358
117.453
115.518
113.574
111.481
77.293
77.039
76.785
45.430
45.396
45.369
45.205
45.019
44.827
40.599
33.321
f1 (ppm)

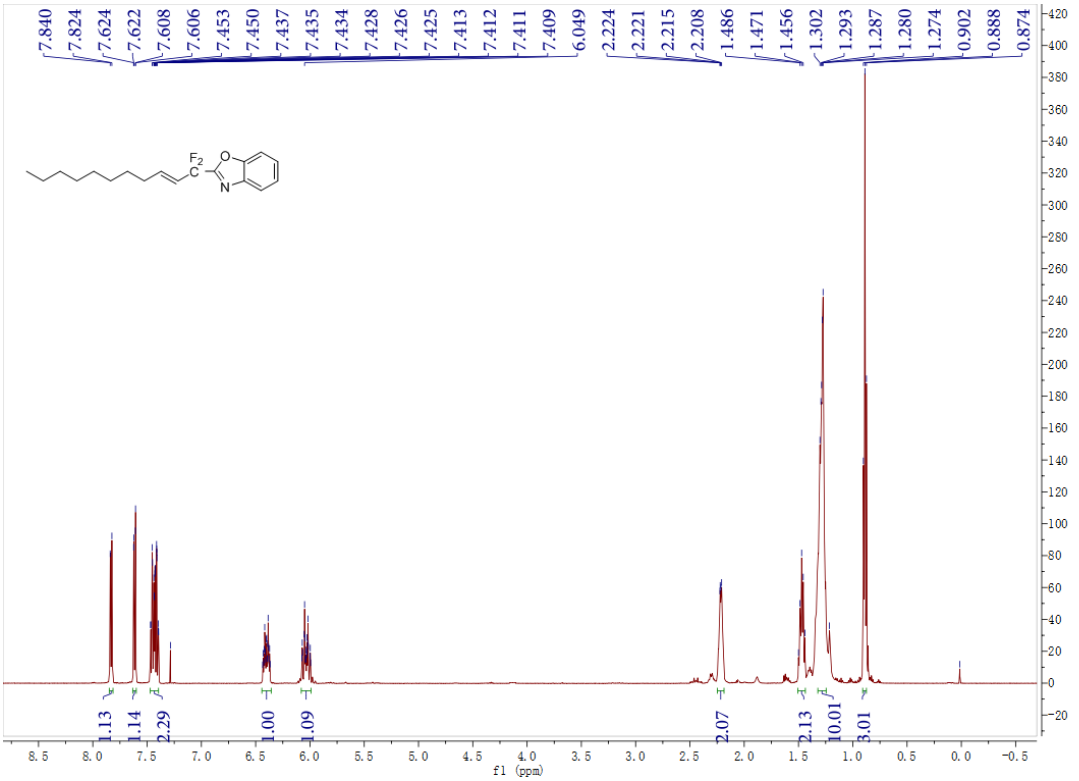
2-(1,1-difluoro-5-phenylpentyl)benzo[d]oxazole (5l)

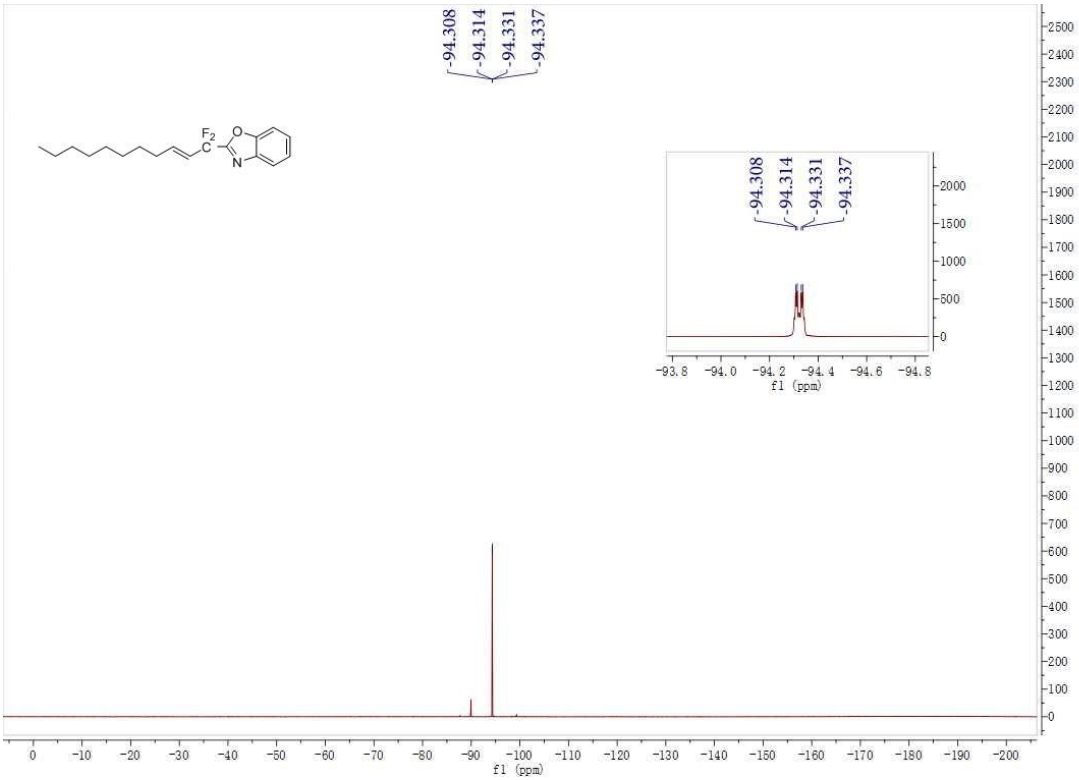


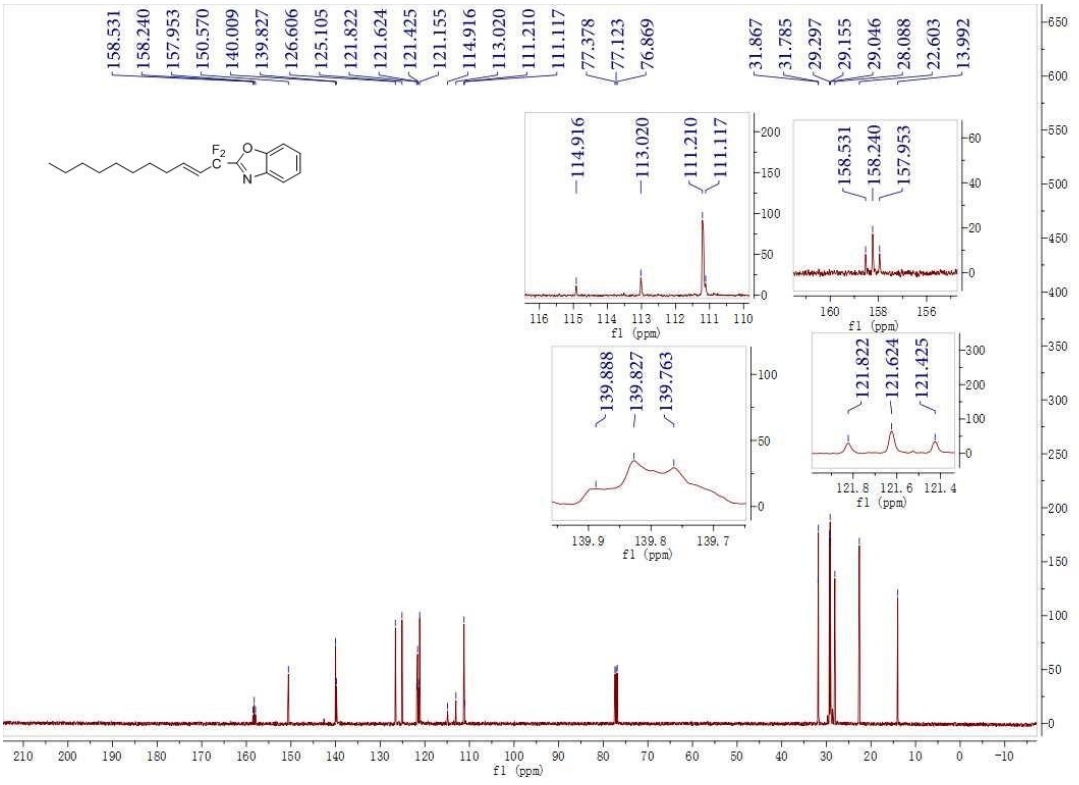




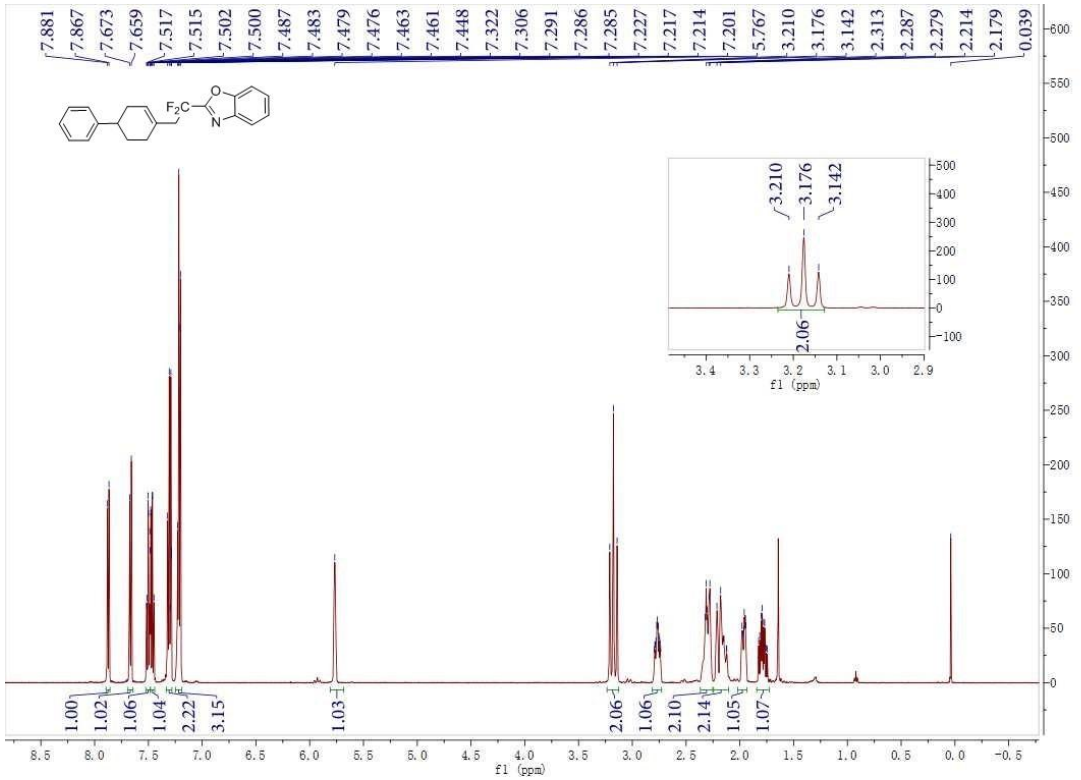
(*E*)-2-(1,1-difluoroundec-2-en-1-yl)benzo[*d*]oxazole (3m)

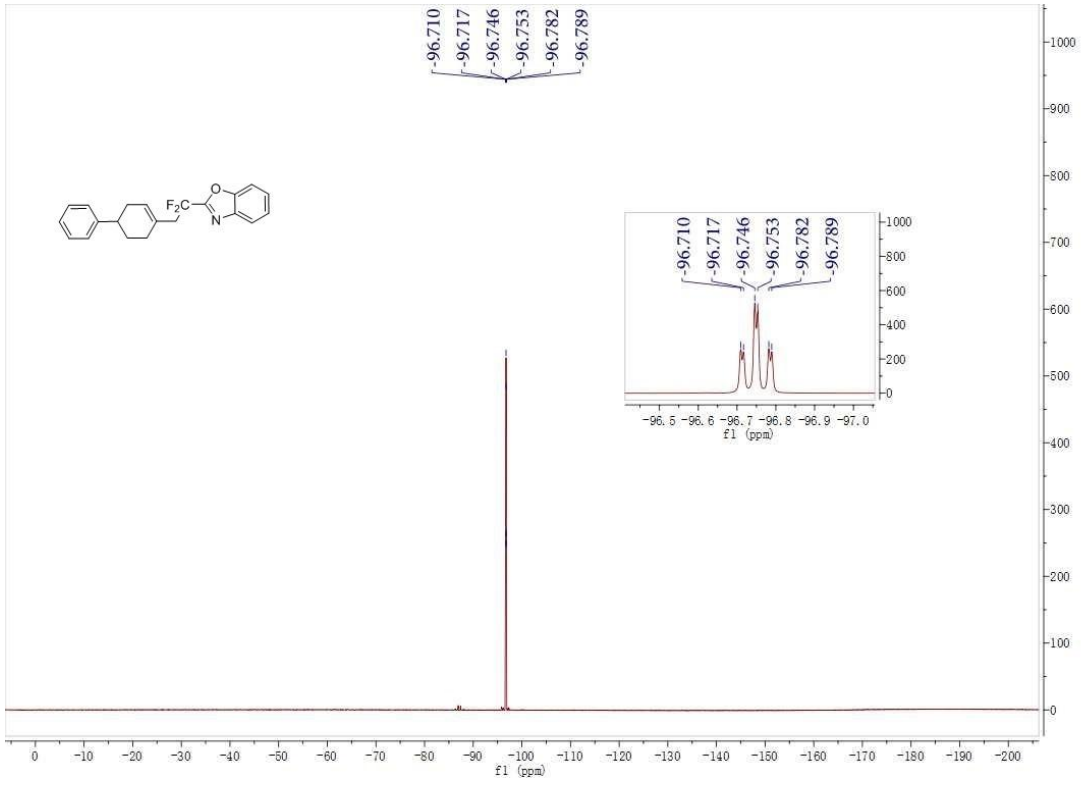


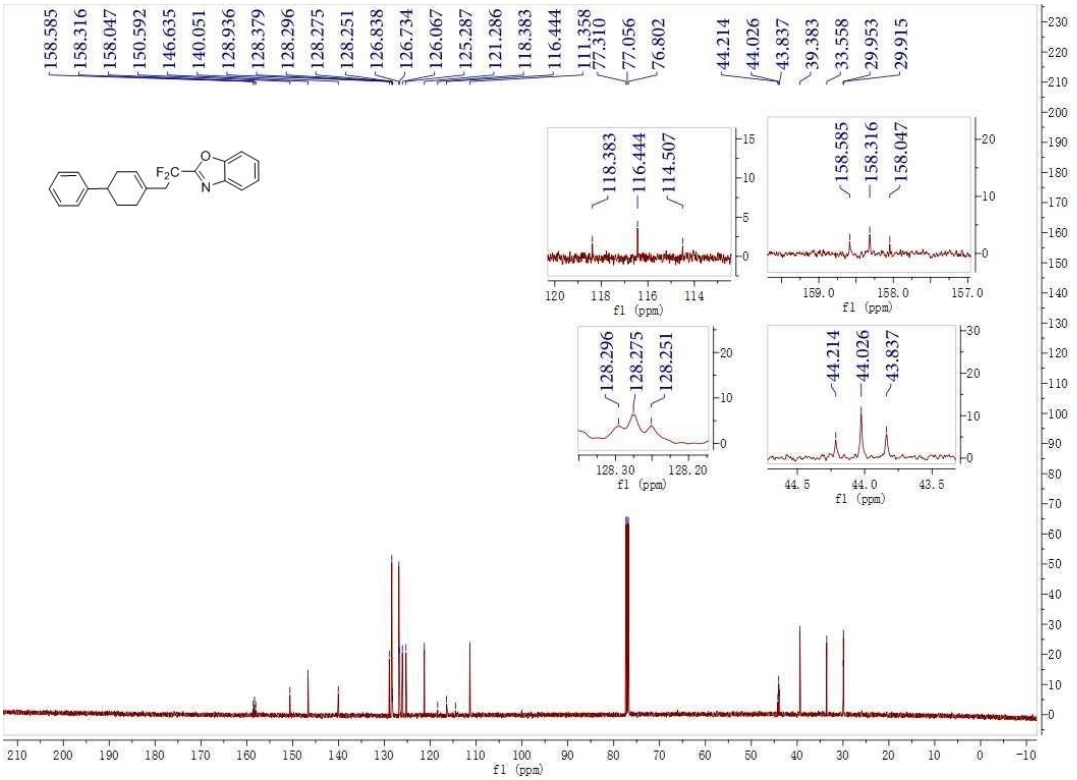




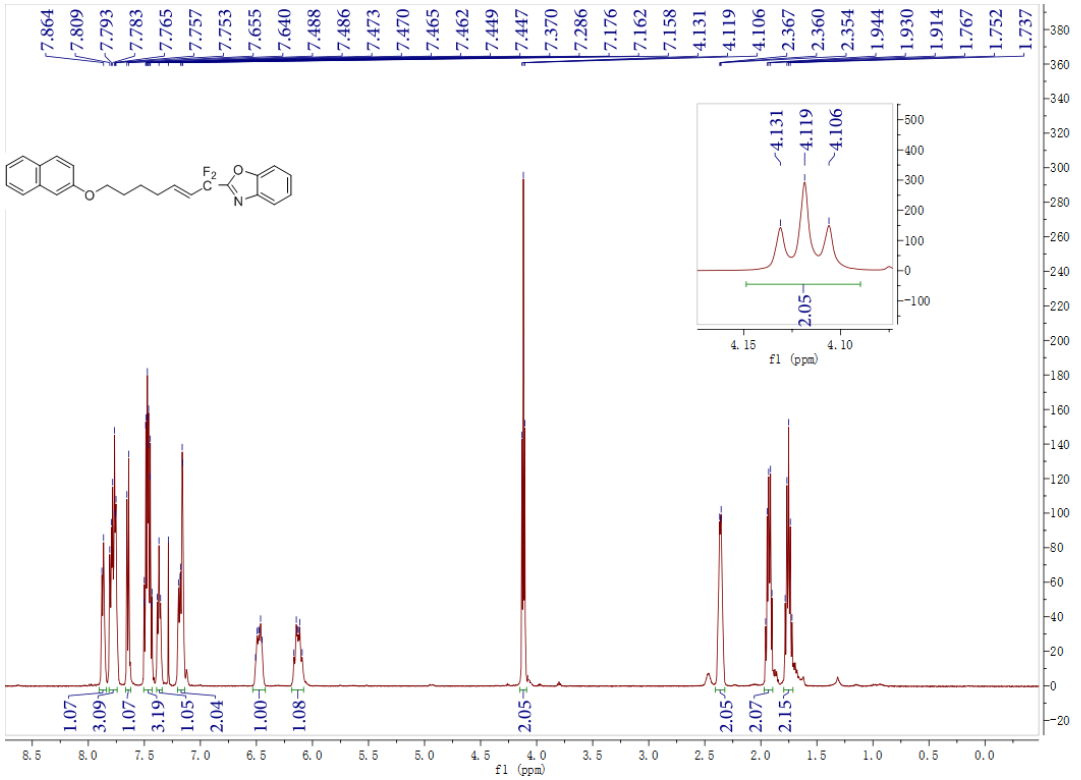
2-(1,1-difluoro-2-(4-phenylcyclohexylidene)ethyl)benzo[*d*]oxazole (3n)

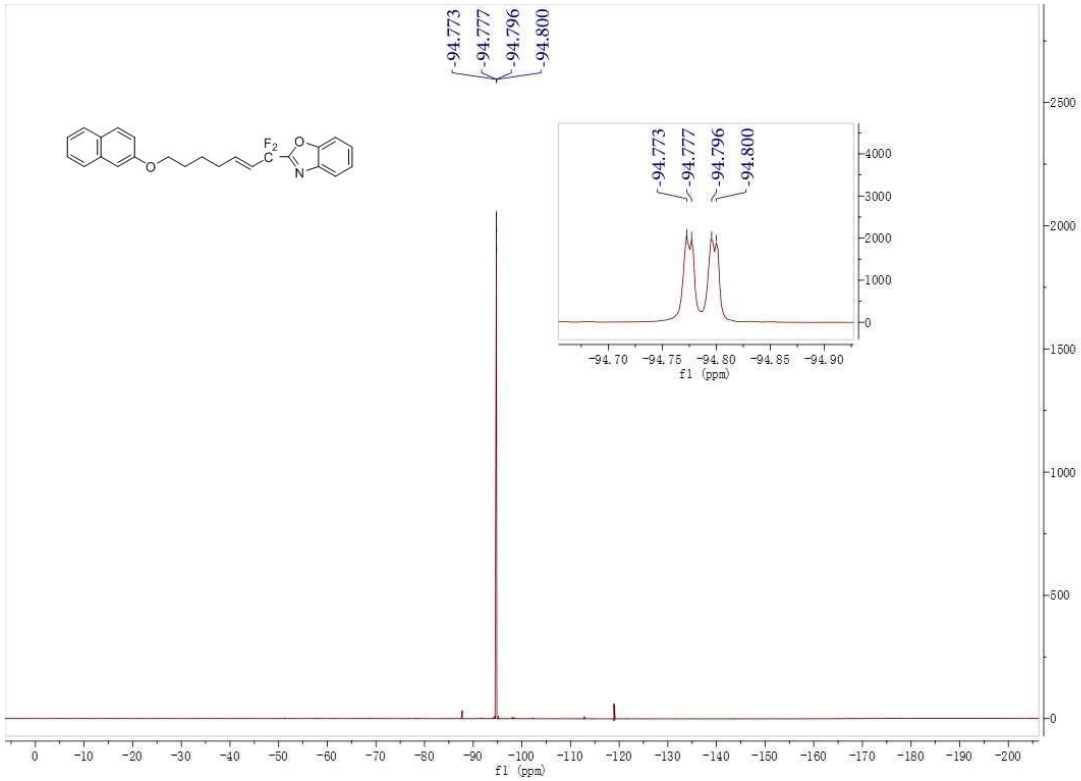

7.881
7.867
7.673
7.659
7.517
7.515
7.502
7.500
7.487
7.483
7.479
7.476
7.463
7.461
7.448
7.322
7.306
7.291
7.286
7.285
7.227
7.217
7.214
7.201
5.767
3.210
3.176
3.142
2.313
2.287
2.279
2.214
2.179
0.039
F2C
O
N
3.210
3.176
3.142
2.06
f1 (ppm)
1.00
1.02
1.06
1.04
2.22
3.15
1.03
2.06
1.06
2.10
2.14
1.05
1.07
f1 (ppm)

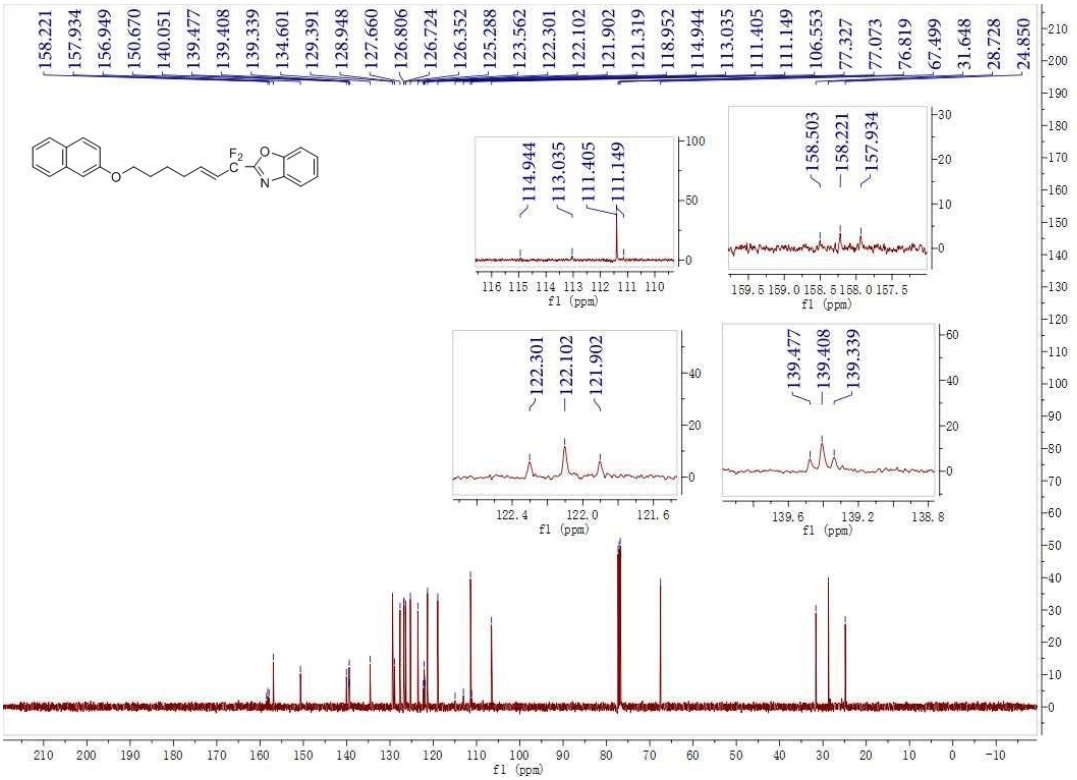

-96.710
-96.717
-96.746
-96.753
-96.782
-96.789
F2C
O
N
-96.710
-96.717
-96.746
-96.753
-96.782
-96.789
f1 (ppm)
f1 (ppm)



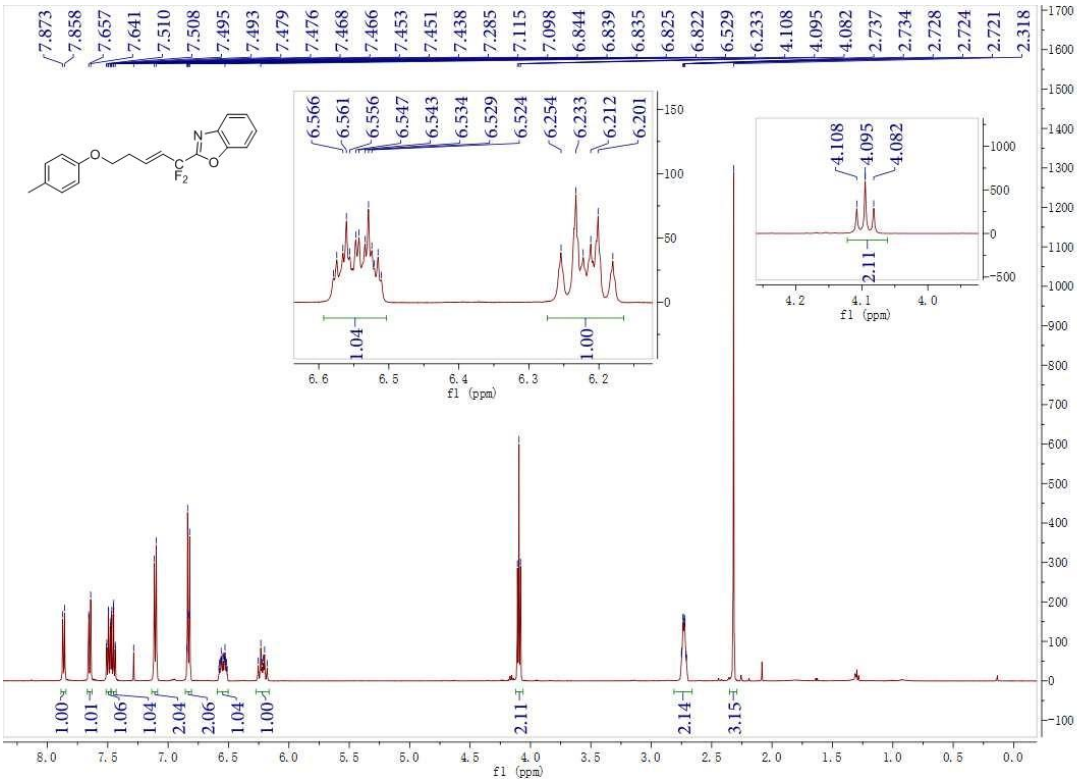
(*E*)-2-(1,1-difluoro-7-(naphthalen-2-yloxy)hept-2-en-1-yl)benzo[*d*]oxazole (3o)

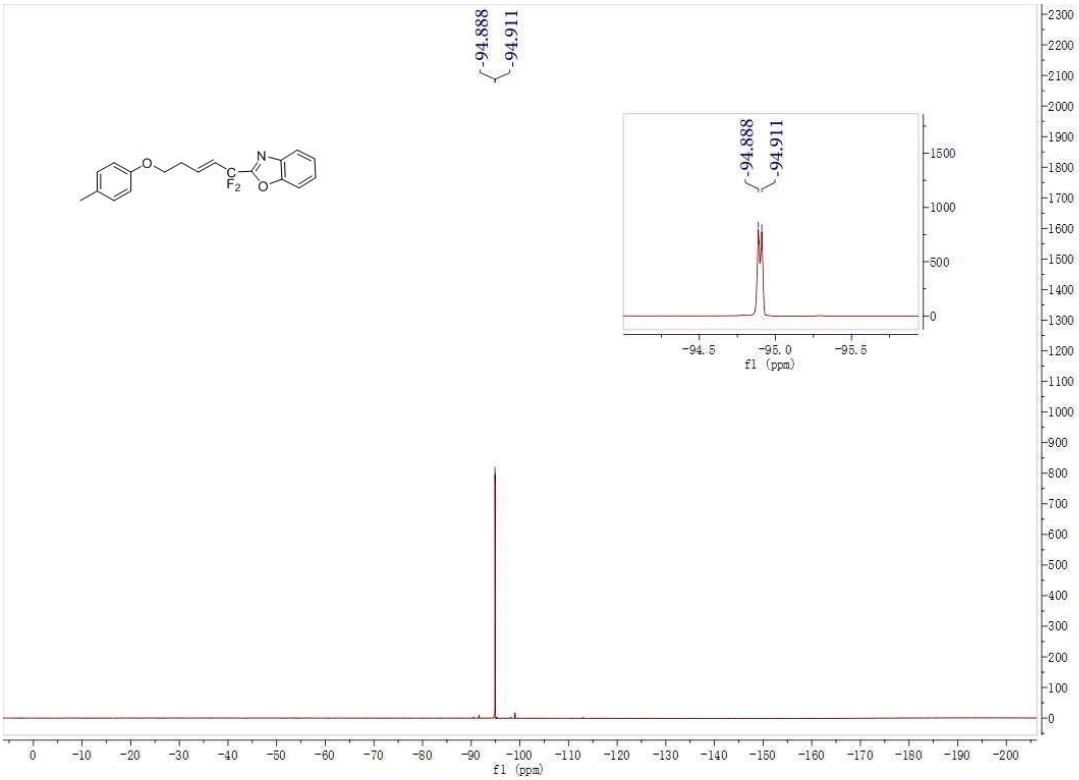

7.864
7.809
7.793
7.783
7.765
7.757
7.753
7.655
7.640
7.488
7.486
7.473
7.470
7.465
7.462
7.449
7.447
7.370
7.286
7.176
7.162
7.158
4.131
4.119
4.106
2.367
2.360
2.354
1.944
1.930
1.914
1.767
1.752
1.737
F2
O
N
4.131
4.119
4.106
2.05
4.15
4.10
f1 (ppm)
1.07
3.09
1.07
3.19
1.05
2.04
1.00
1.08
2.05
2.05
2.07
2.15
f1 (ppm)

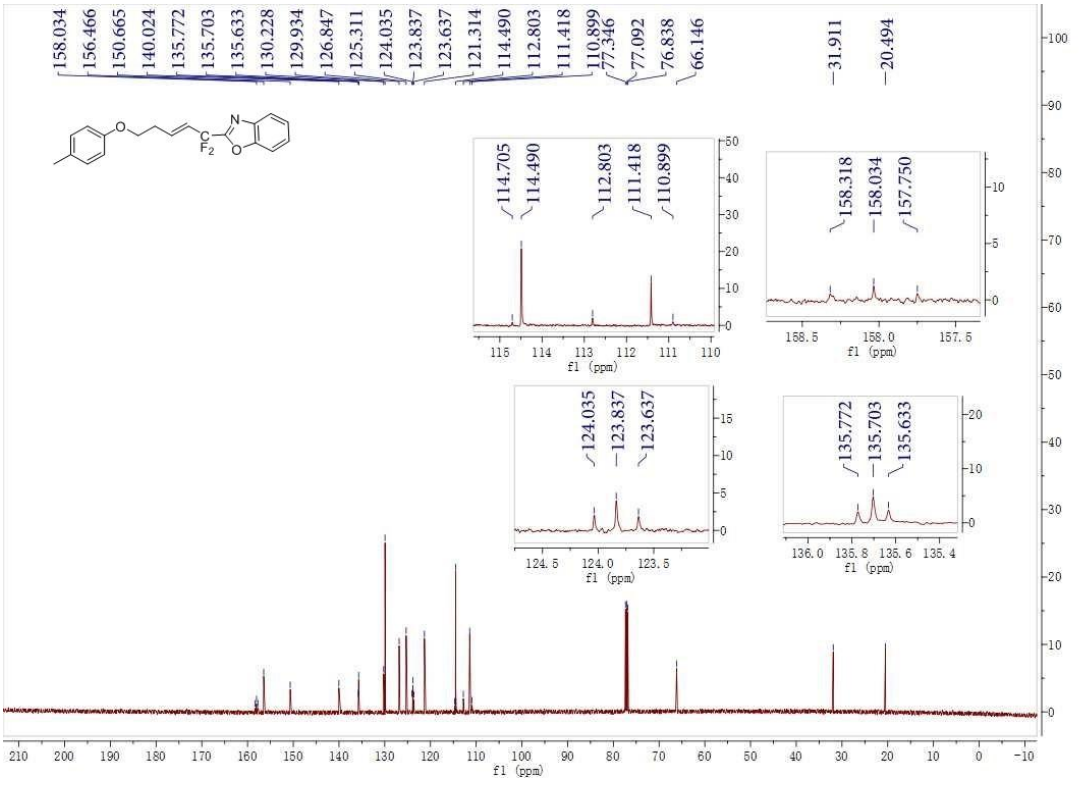

-94.773
-94.777
-94.796
-94.800
F2
O
N
-94.773
-94.777
-94.796
-94.800
-94.70
-94.75
-94.80
-94.85
-94.90
f1 (ppm)
f1 (ppm)



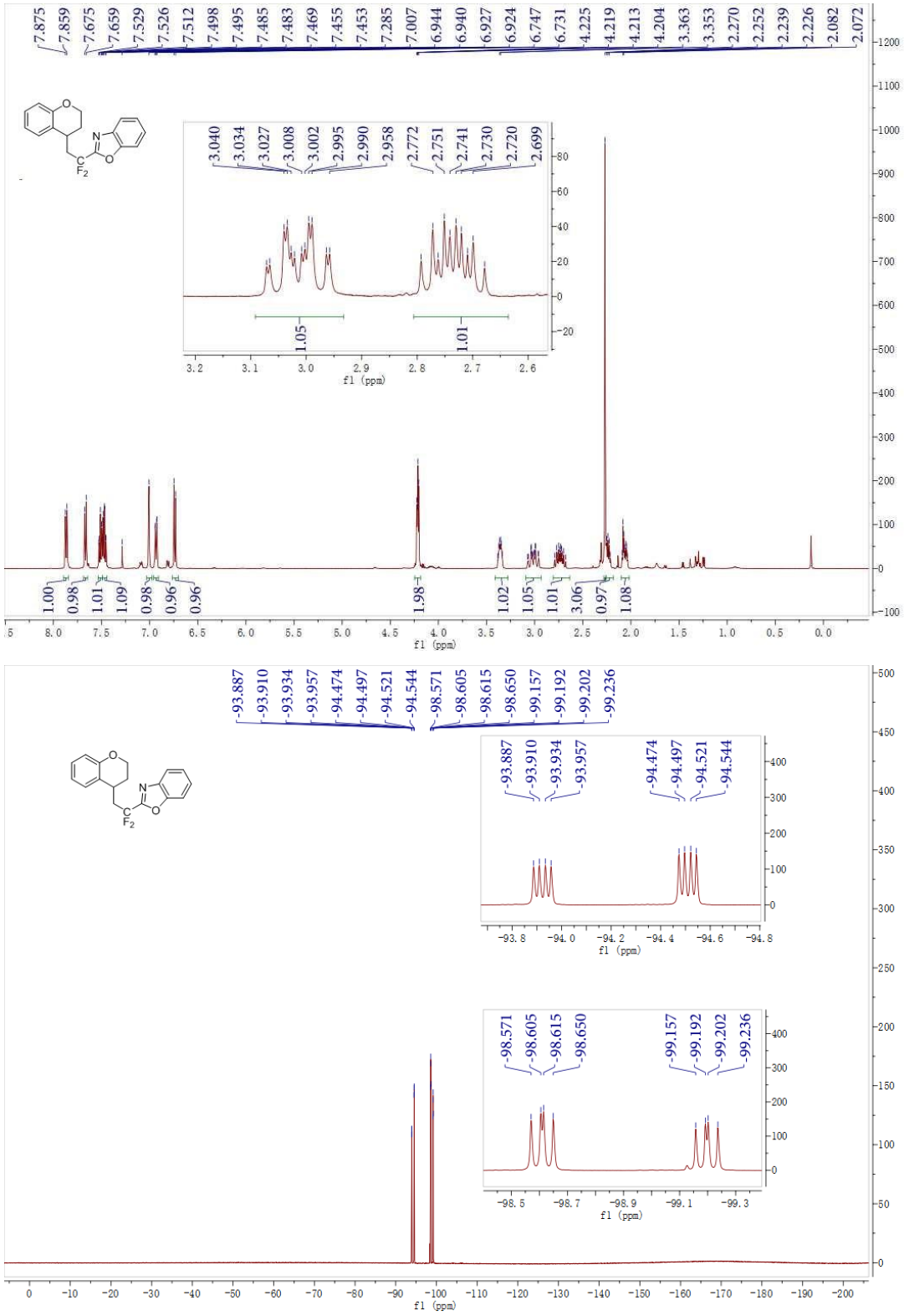
(*E*)-2-(1,1-difluoro-5-(*p*-tolyloxy)pent-2-en-1-yl)benzo[*d*]oxazole (3p)

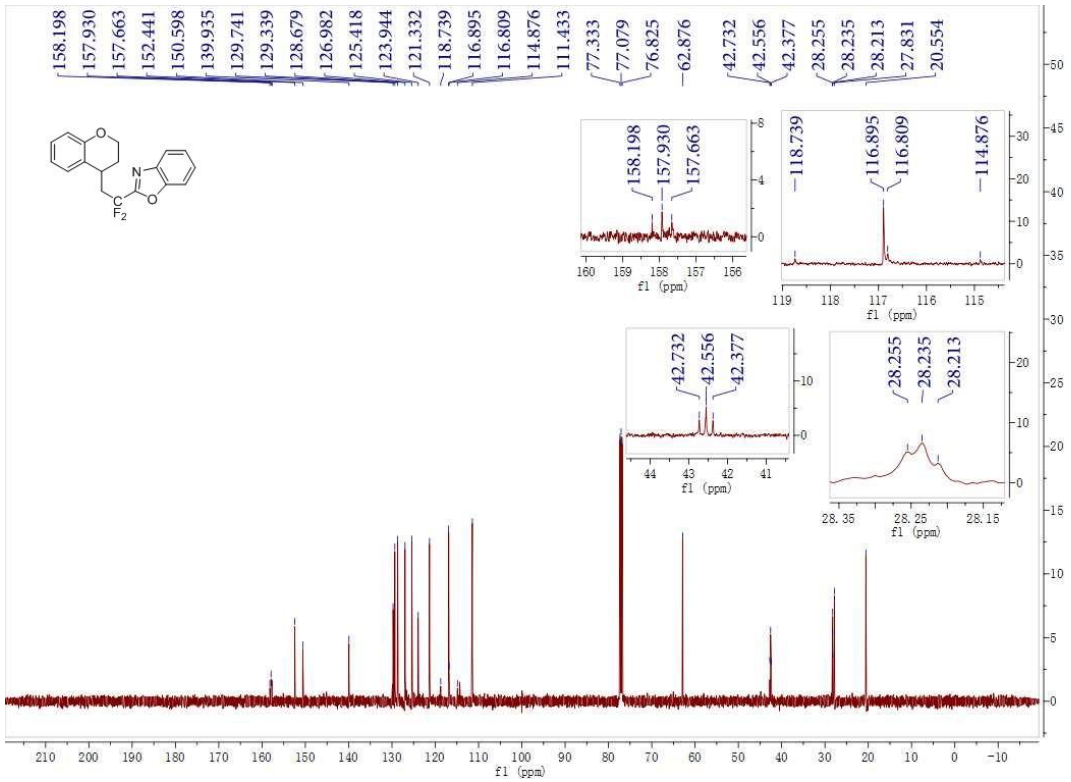



-94.888
-94.911
f1 (ppm)

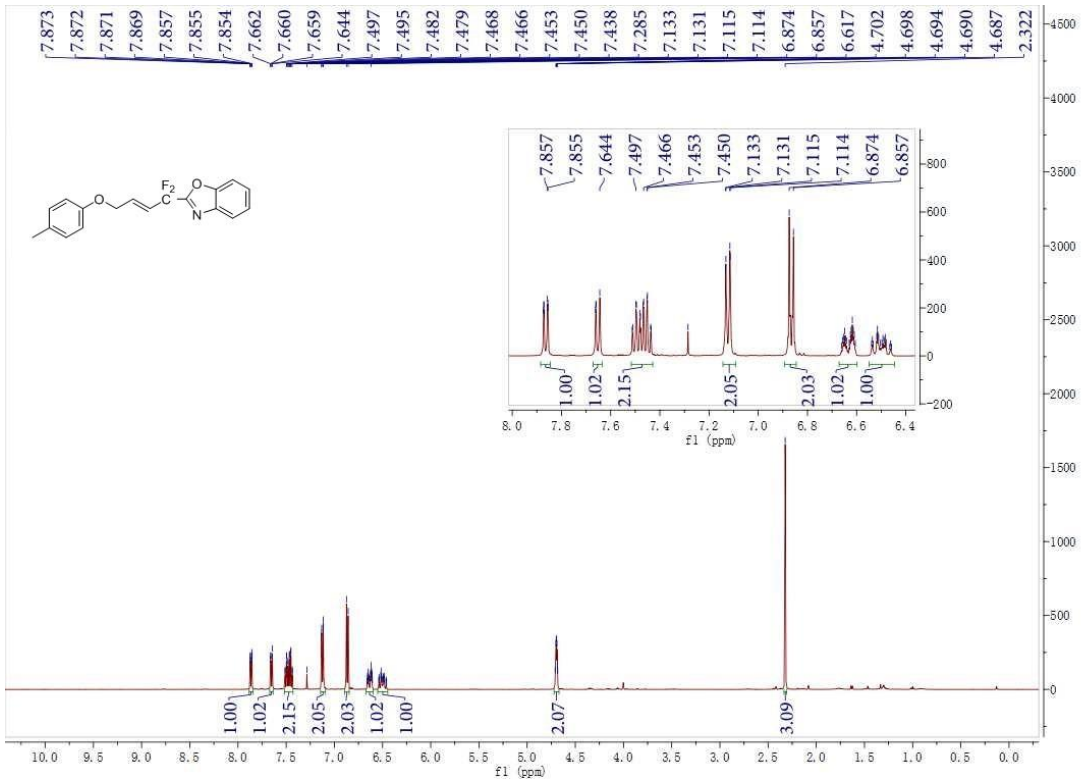

158.034
156.466
150.665
140.024
135.772
135.703
135.633
130.228
129.934
126.847
125.311
124.035
123.837
123.637
121.314
114.490
112.803
111.418
110.899
77.346
77.092
76.838
66.146
31.911
20.494
f1 (ppm)

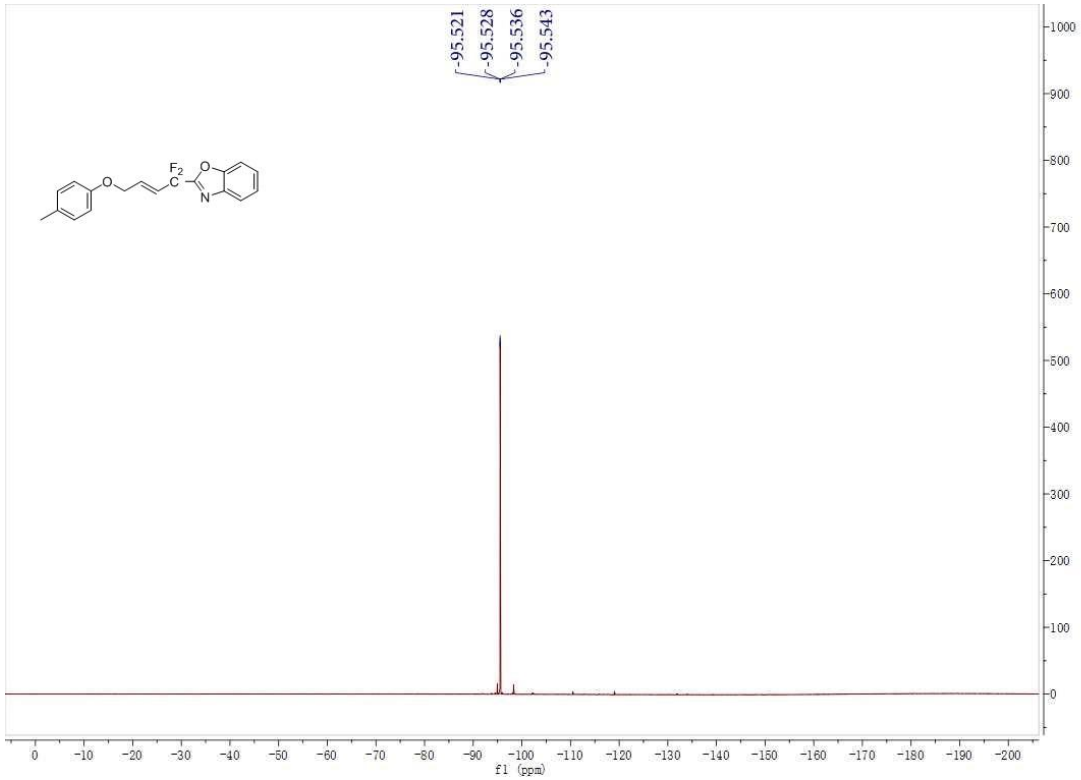
2-(2-(chroman-4-yl)-1,1-difluoroethyl)benzo[*d*]oxazole (4p)

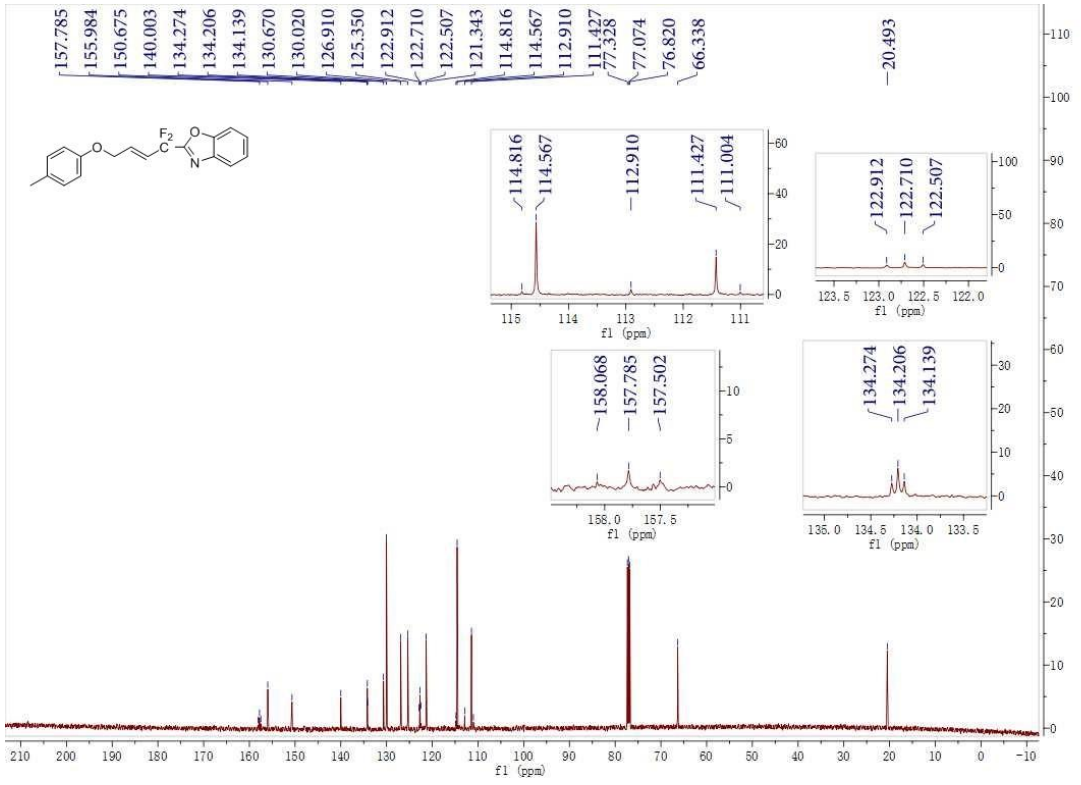




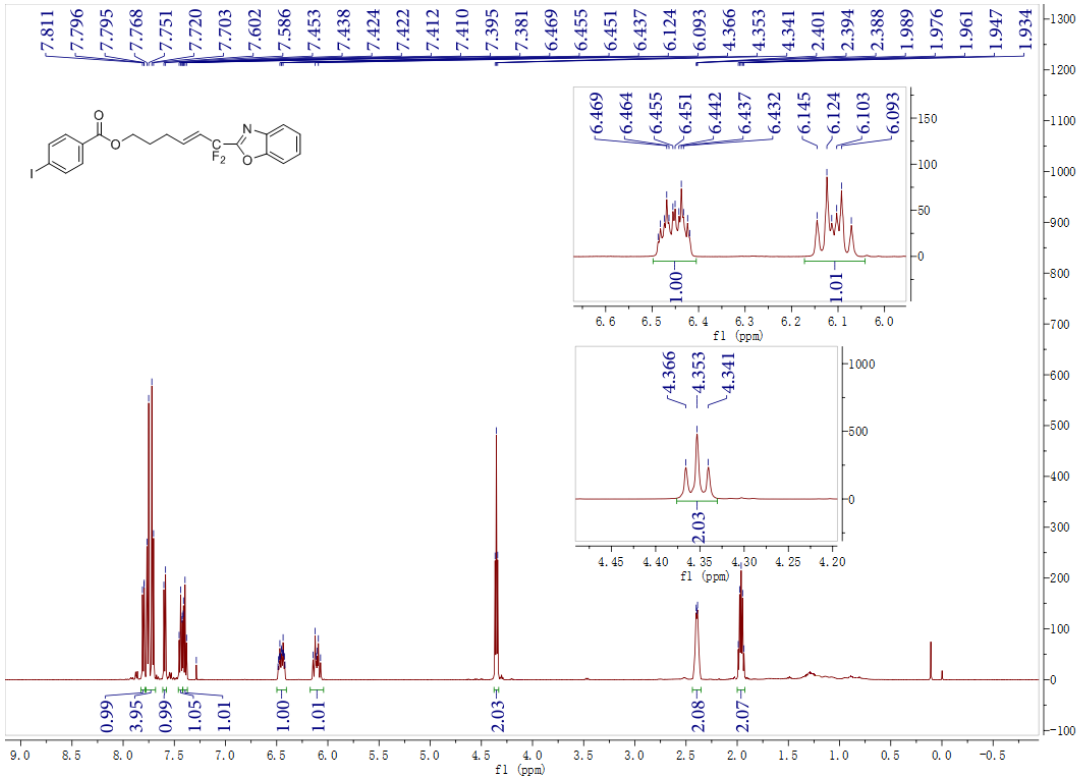
(*E*)-2-(1,1-difluoro-4-(p-tolyloxy)but-2-en-1-yl)benzo[*d*]oxazole (3q)

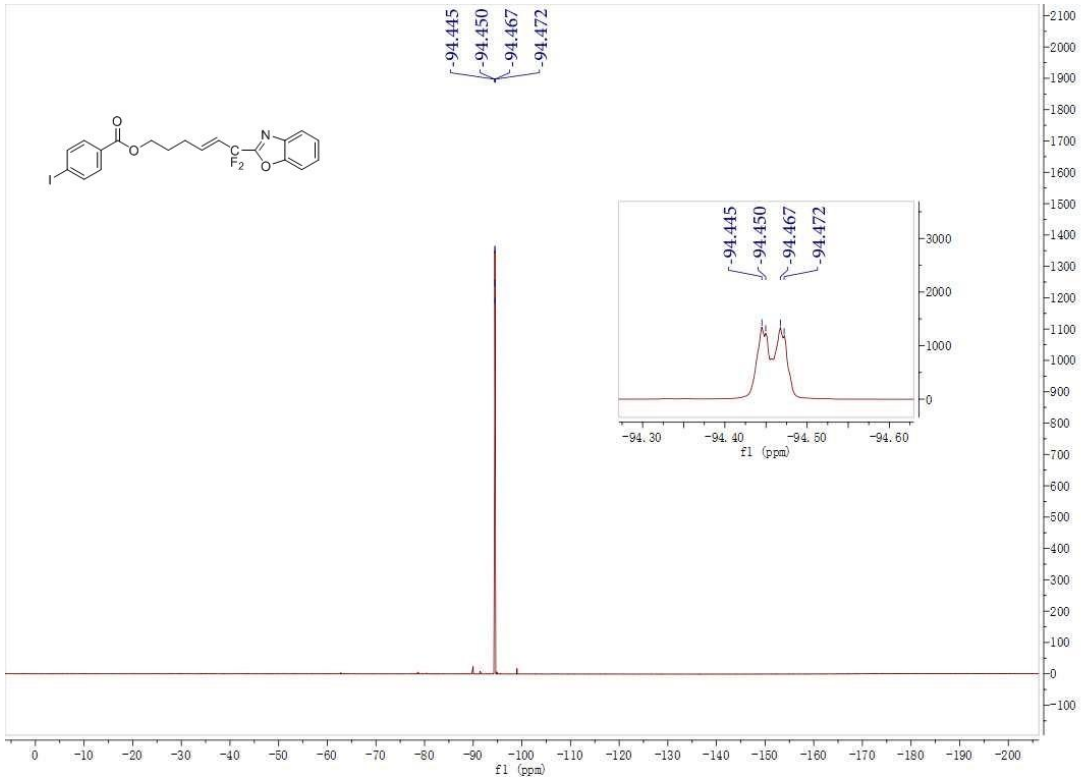


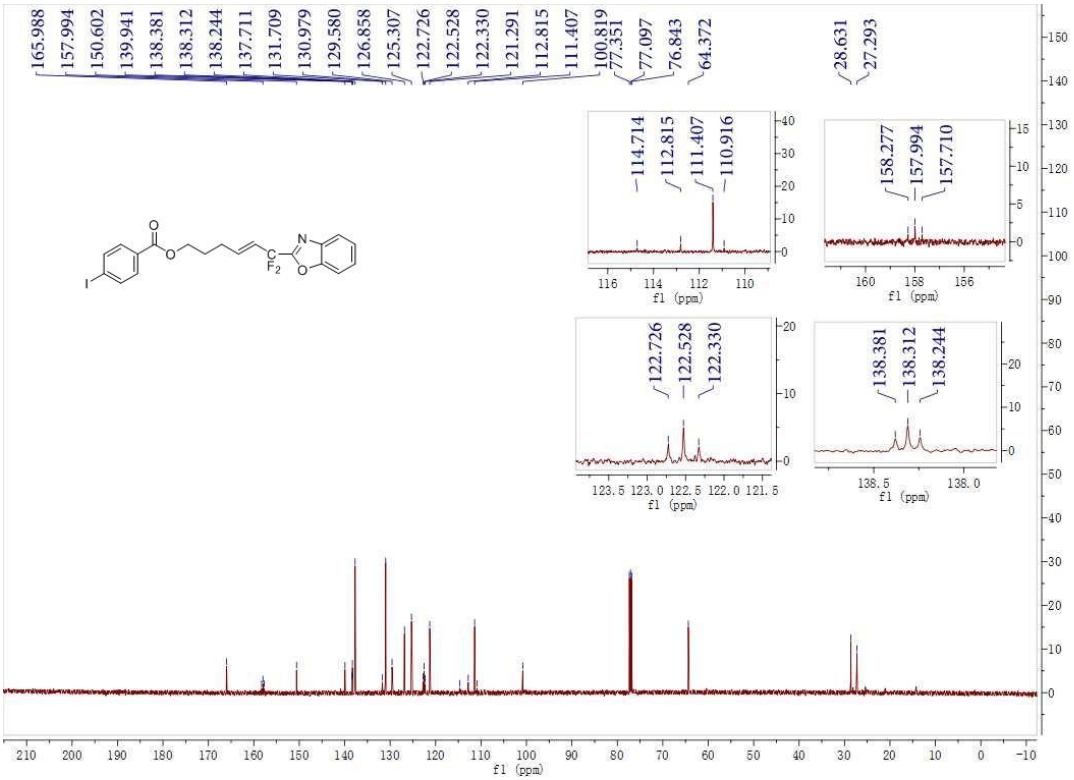

-95.521
-95.528
-95.536
-95.543
f1 (ppm)


157.785
155.984
150.675
140.003
134.274
134.206
134.139
130.670
130.020
126.910
125.350
122.912
122.710
122.507
121.343
114.816
114.567
112.910
111.427
77.328
77.074
76.820
66.338
20.493
f1 (ppm)

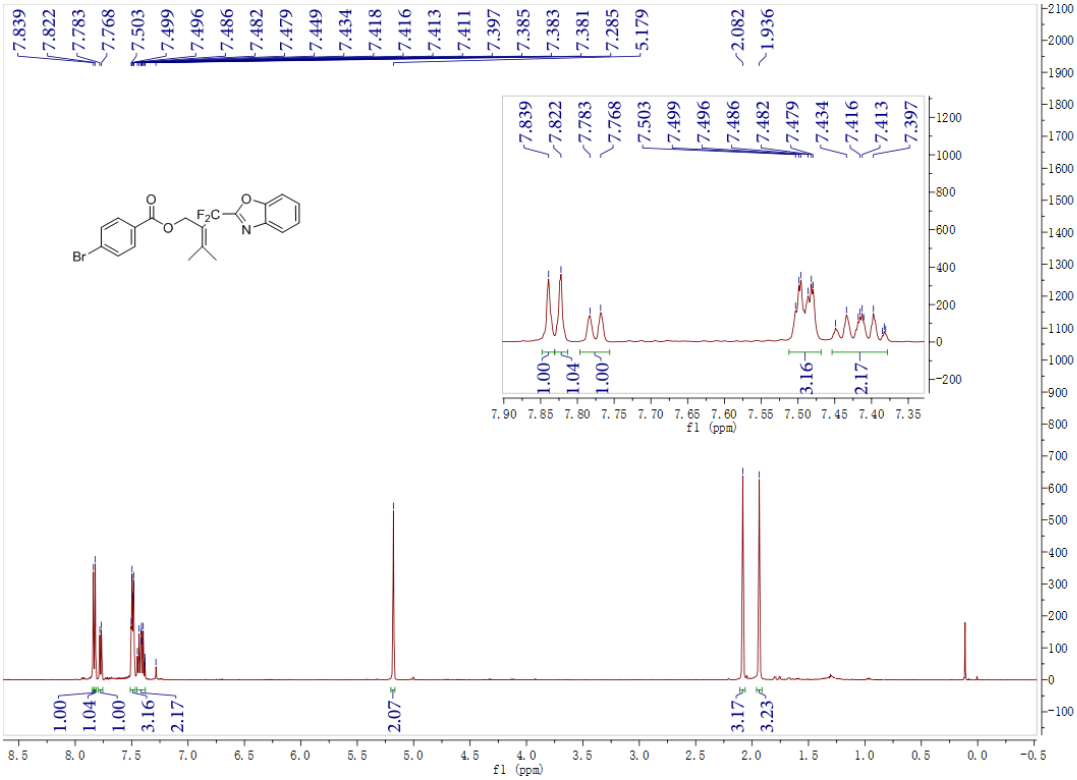
(*E*)-6-(benzo[*d*]oxazol-2-yl)-6,6-difluorohex-4-en-1-yl 4-iodobenzoate (3r)

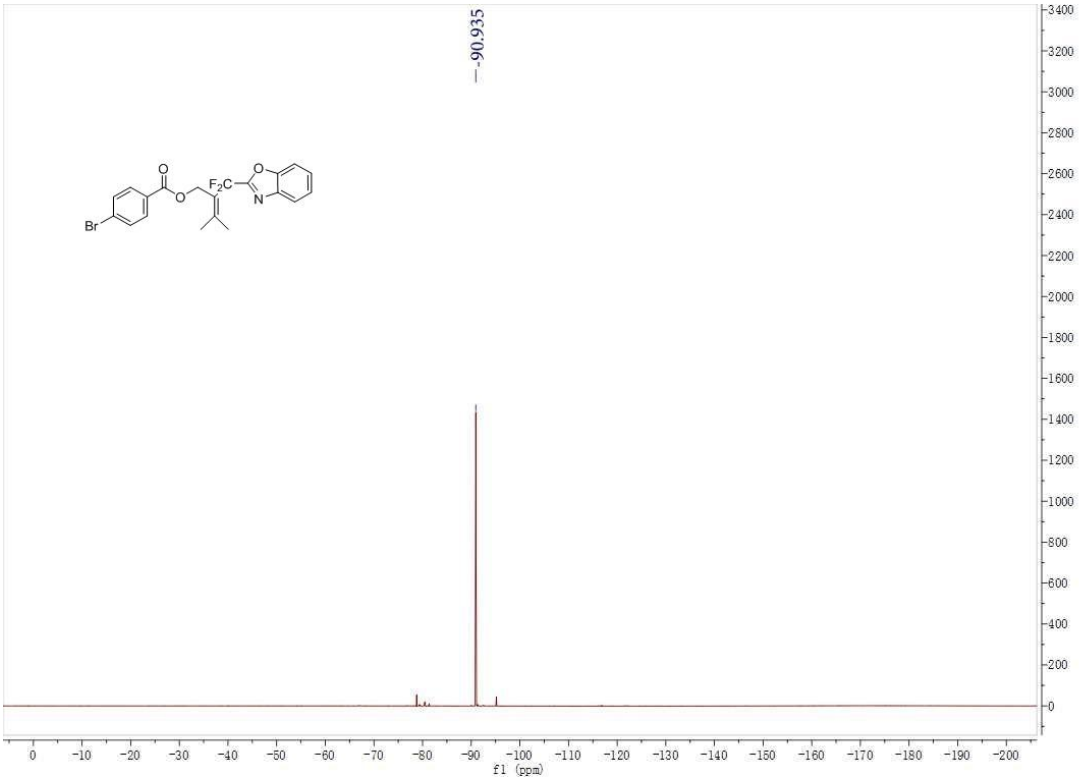


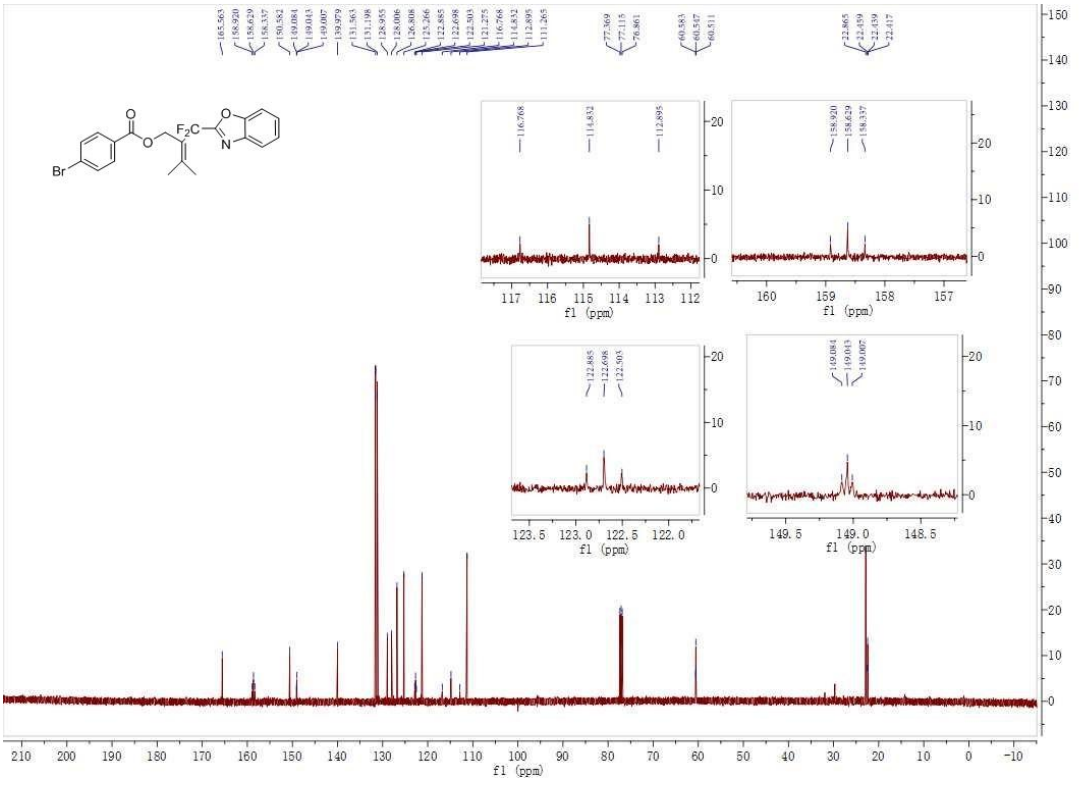




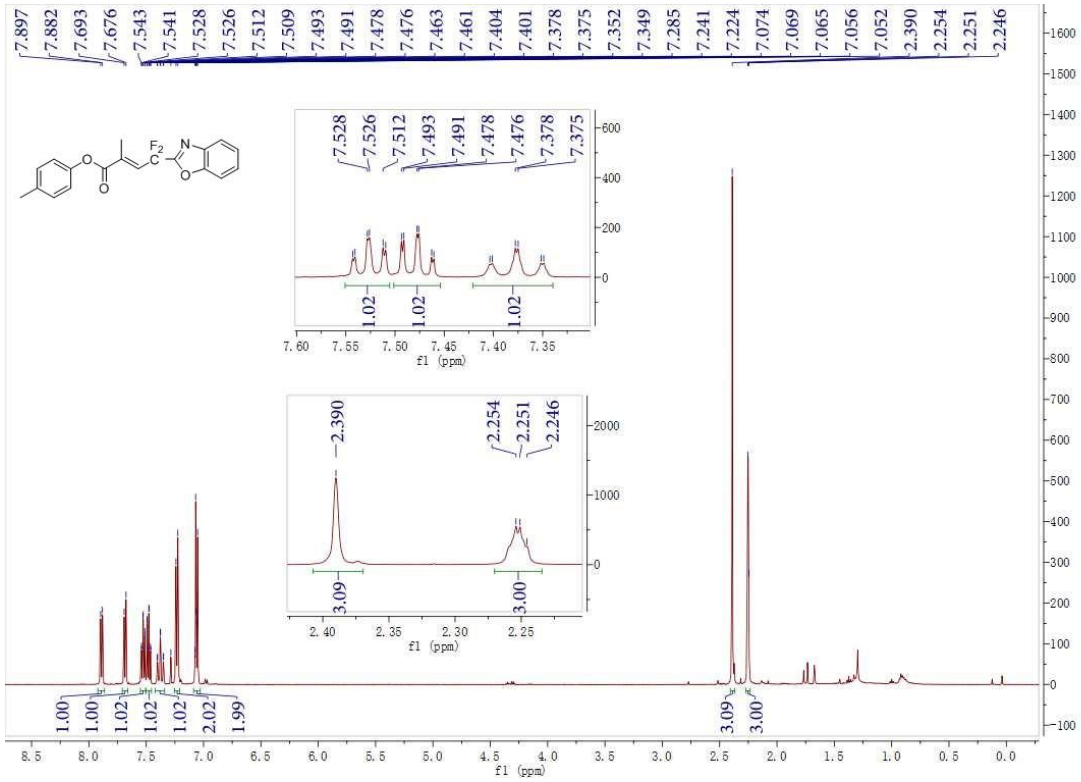
2-(benzo[*d*]oxazol-2-yldifluoromethyl)-3-methylbut-2-en-1-yl 4-bromobenzoate (3s)

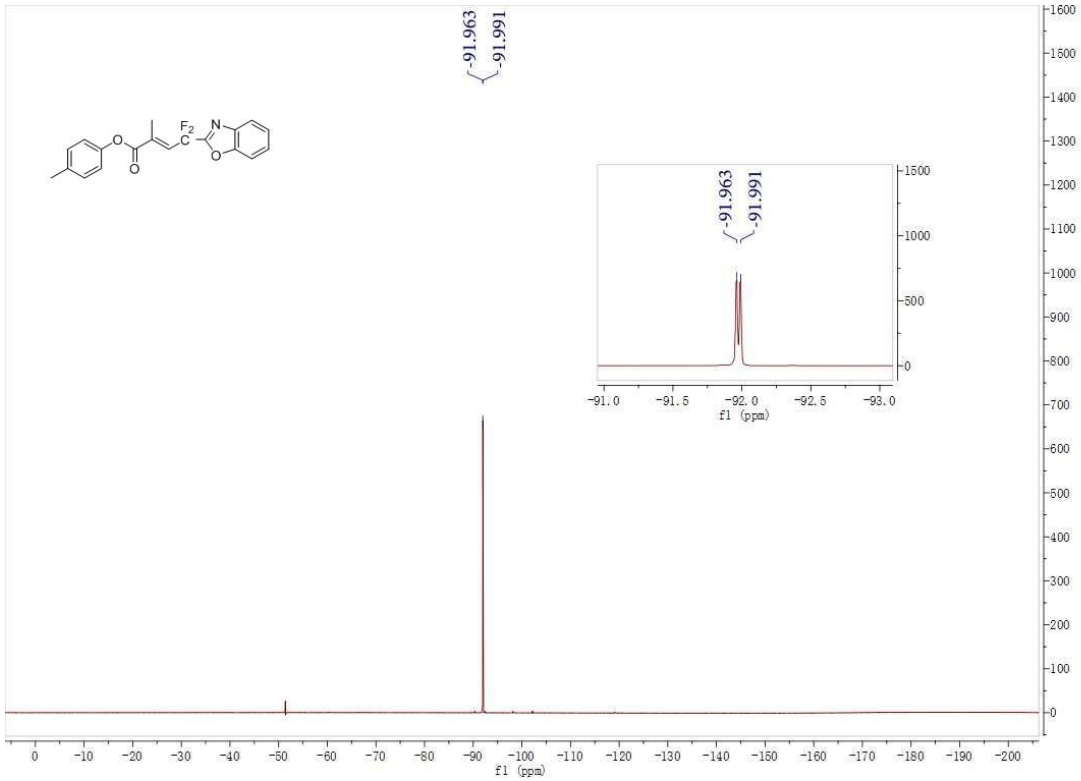


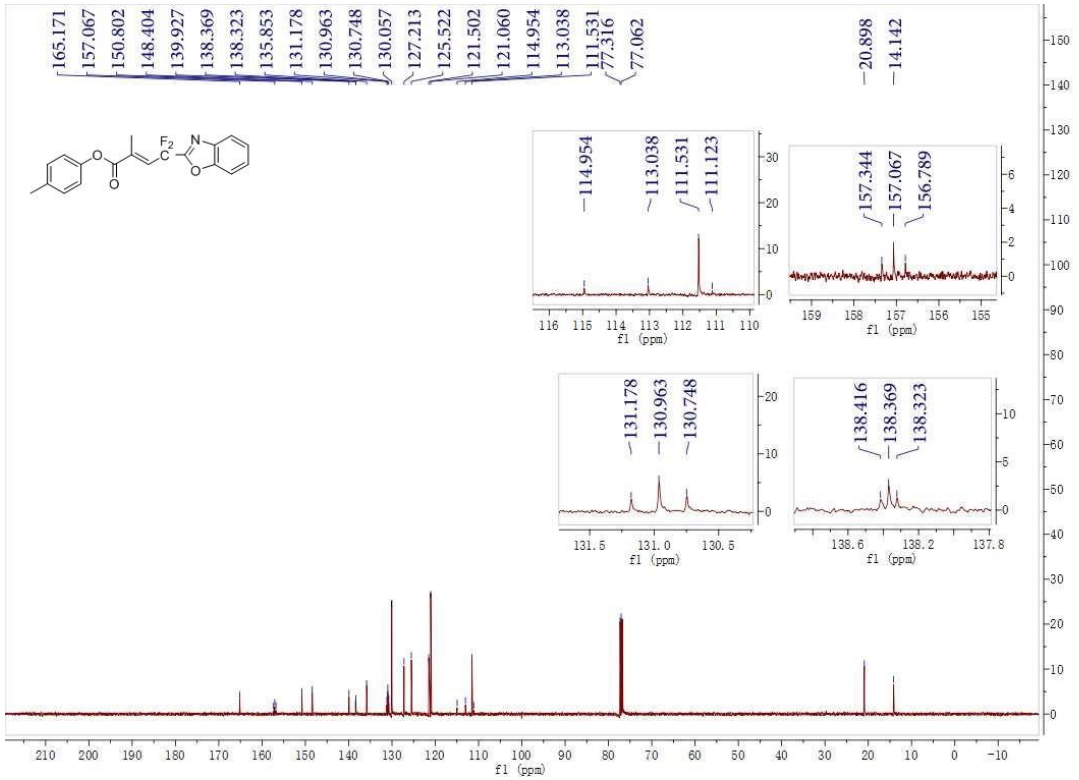

-90.935
f1 (ppm)


f1 (ppm)

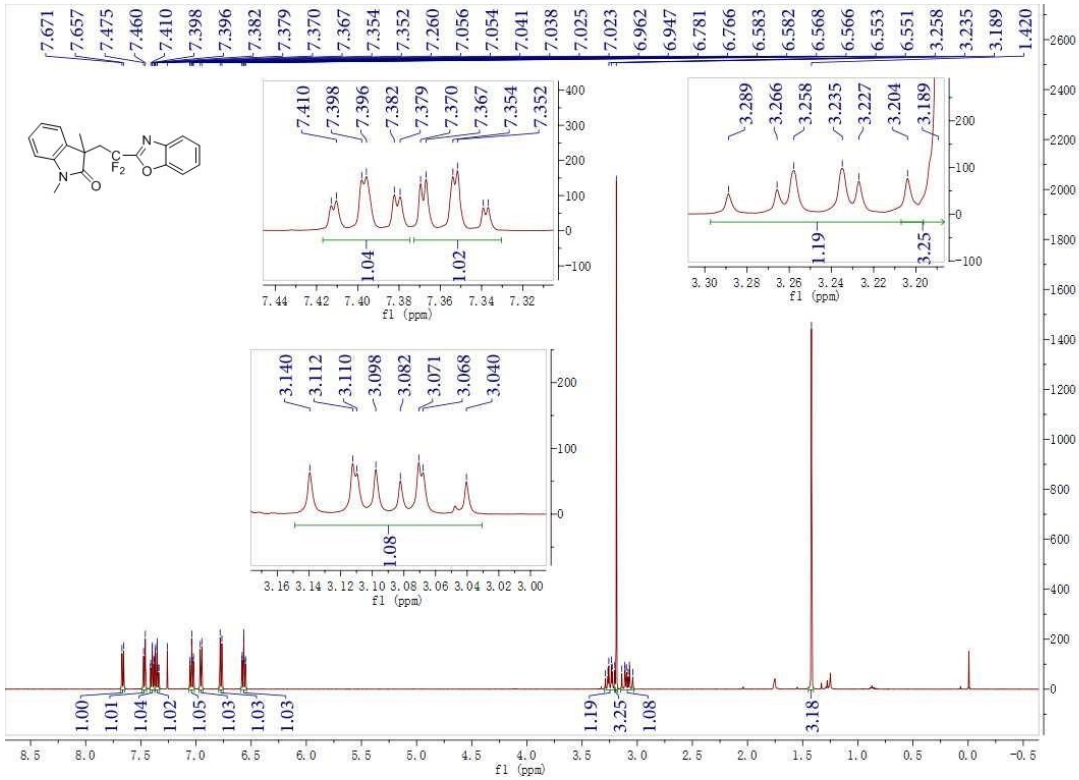
***p*-tolyl (*E*)-4-(benzo[*d*]oxazol-2-yl)-4,4-difluoro-2-methylbut-2-enoate (3t)**

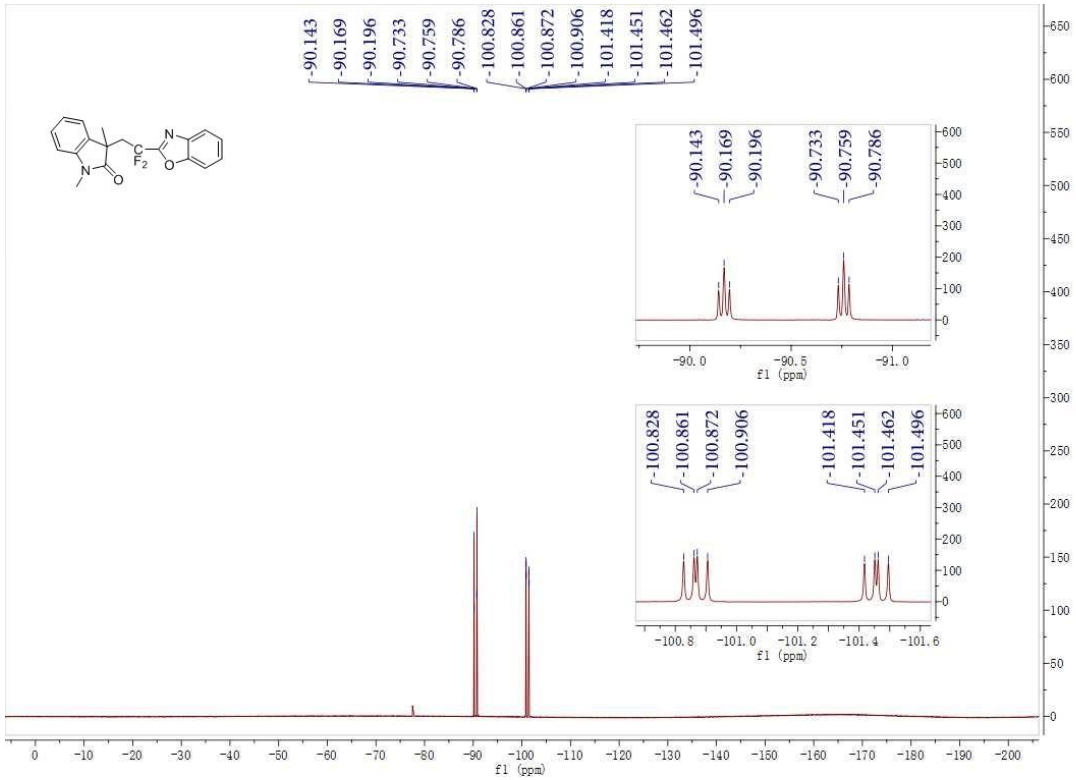


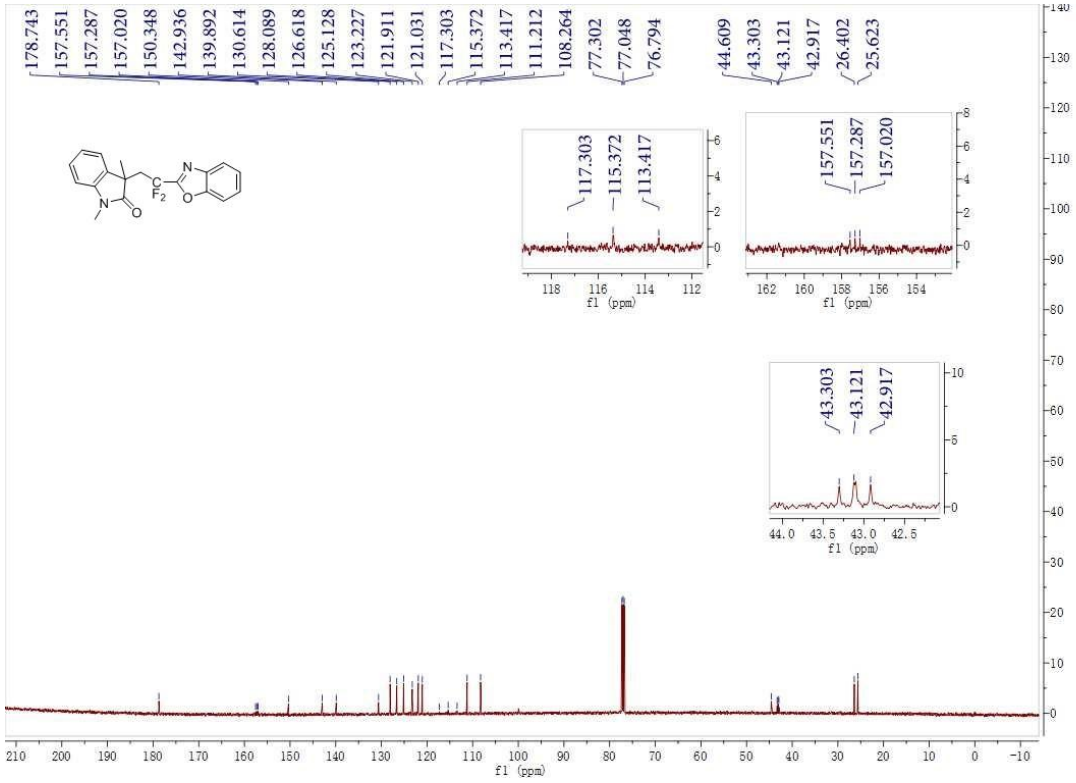




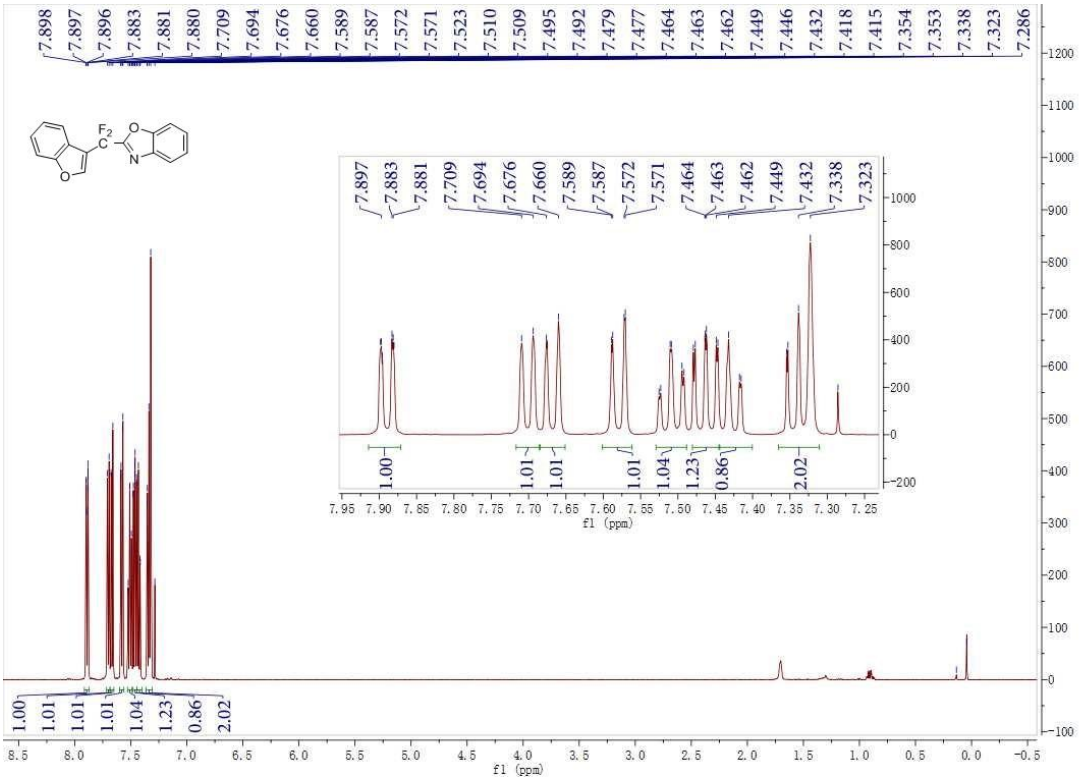
3-(2-(benzo[*d*]oxazol-2-yl)-2,2-difluoroethyl)-1,3-dimethylindolin-2-one (4u)

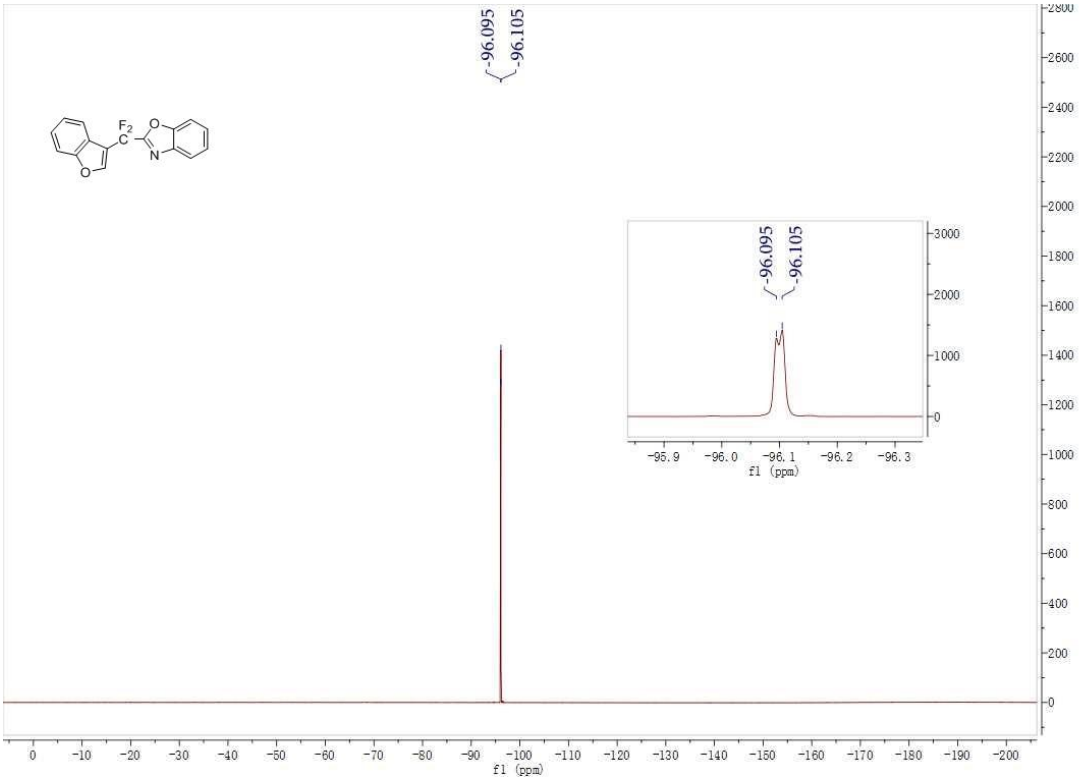


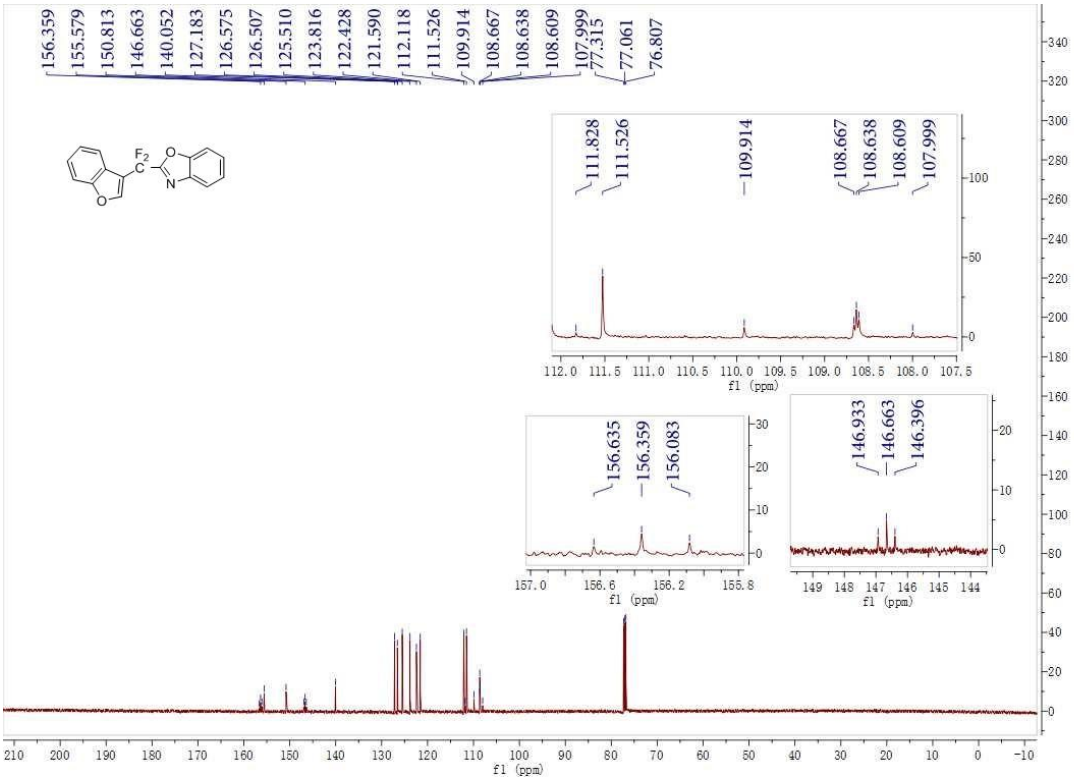

-90.143
-90.169
-90.196
-90.733
-90.759
-90.786
-100.828
-100.861
-100.872
-100.906
-101.418
-101.451
-101.462
-101.496
f1 (ppm)


178.743
157.551
157.287
157.020
150.348
142.936
139.892
130.614
128.089
126.618
125.128
123.227
121.911
121.031
117.303
115.372
113.417
111.212
108.264
77.302
77.048
76.794
44.609
43.303
43.121
42.917
26.402
25.623
f1 (ppm)

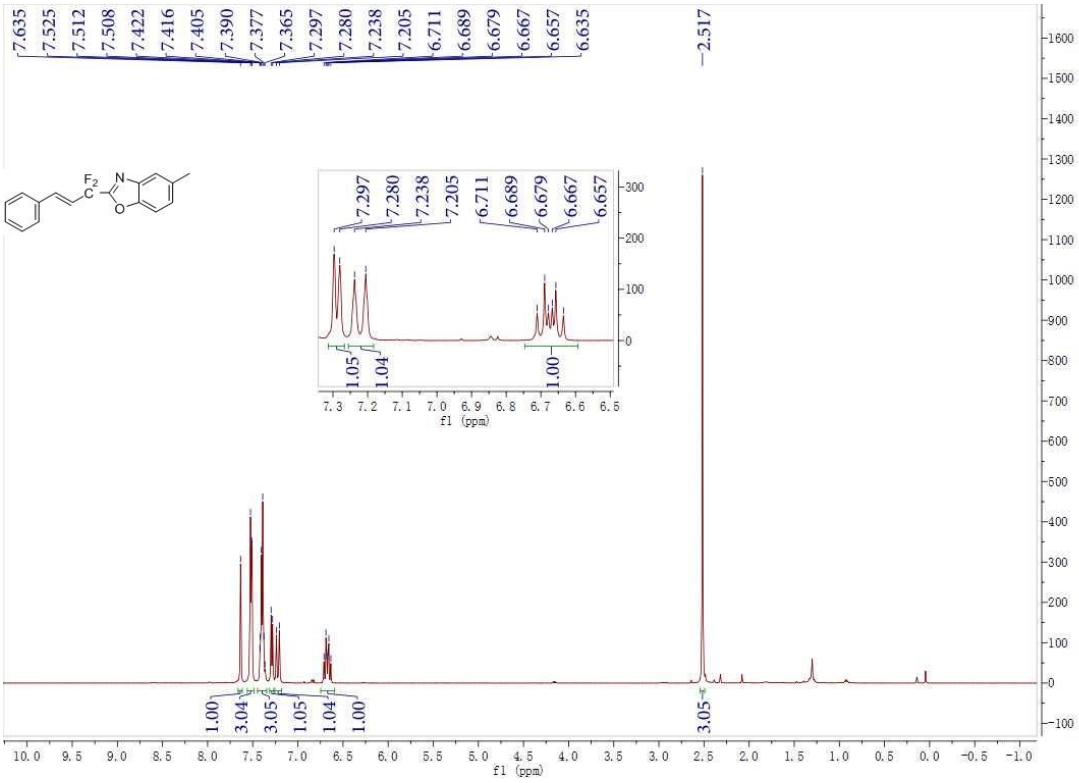
2-(benzofuran-3-yldifluoromethyl)benzo[*d*]oxazole (3v)

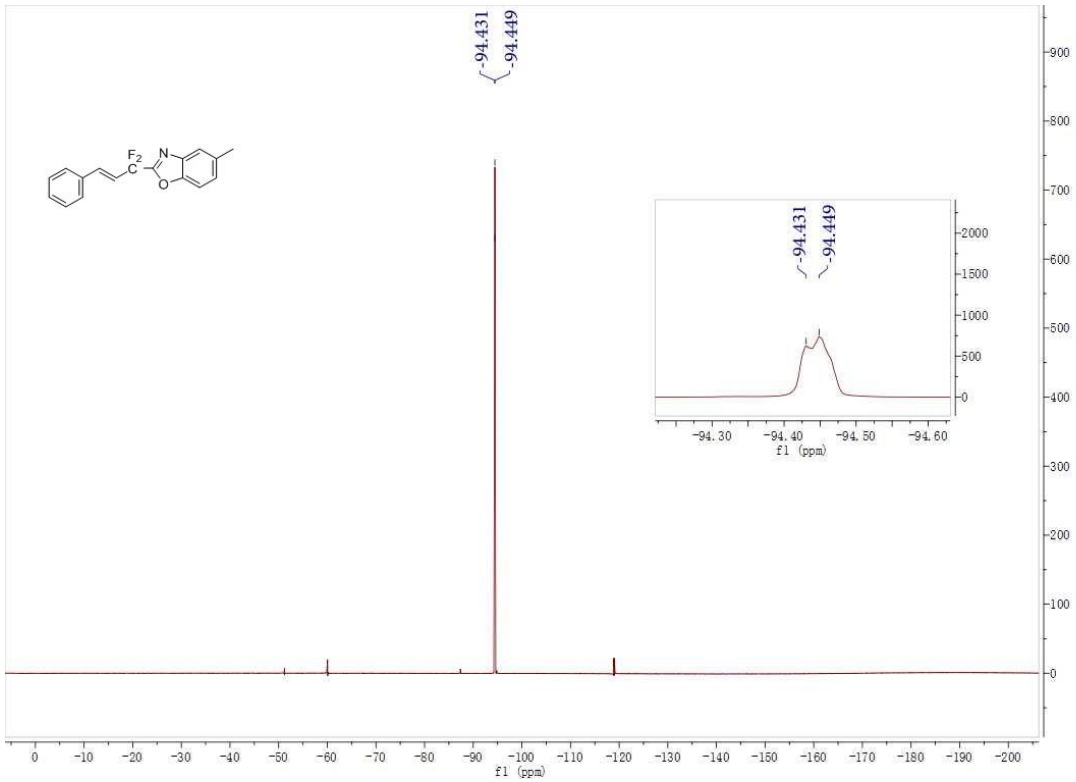


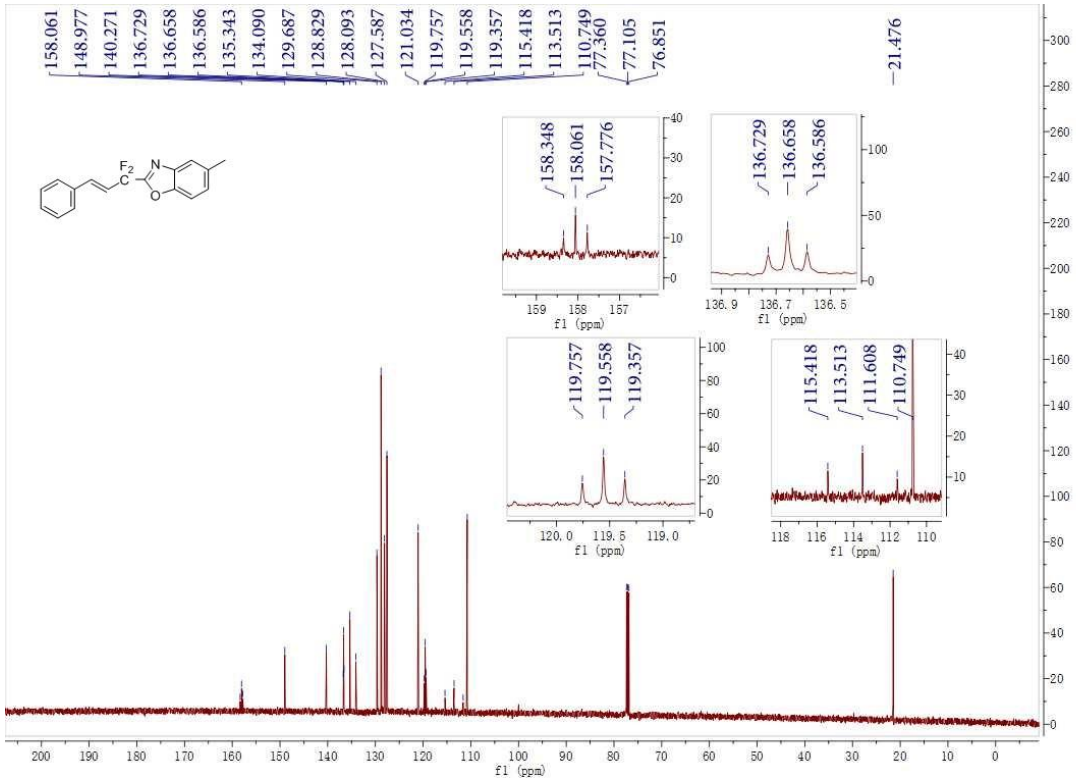




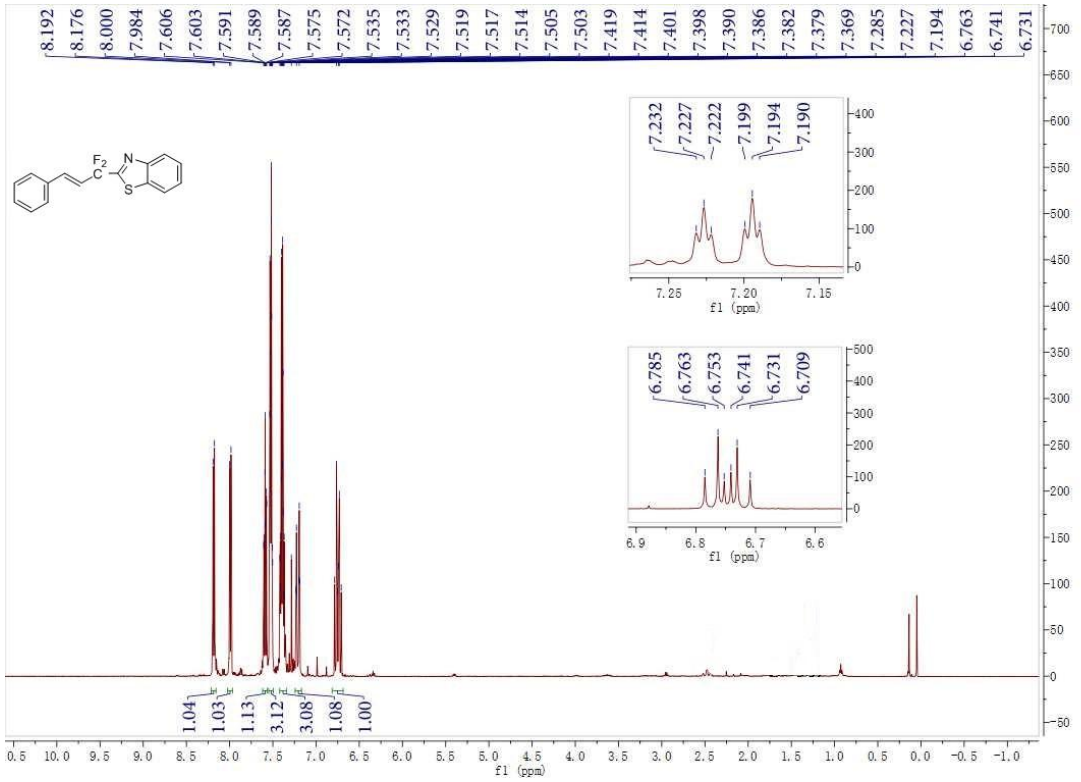
(E)-2-(1,1-difluoro-3-phenylallyl)-5-methylbenzo[d]oxazole (3w)

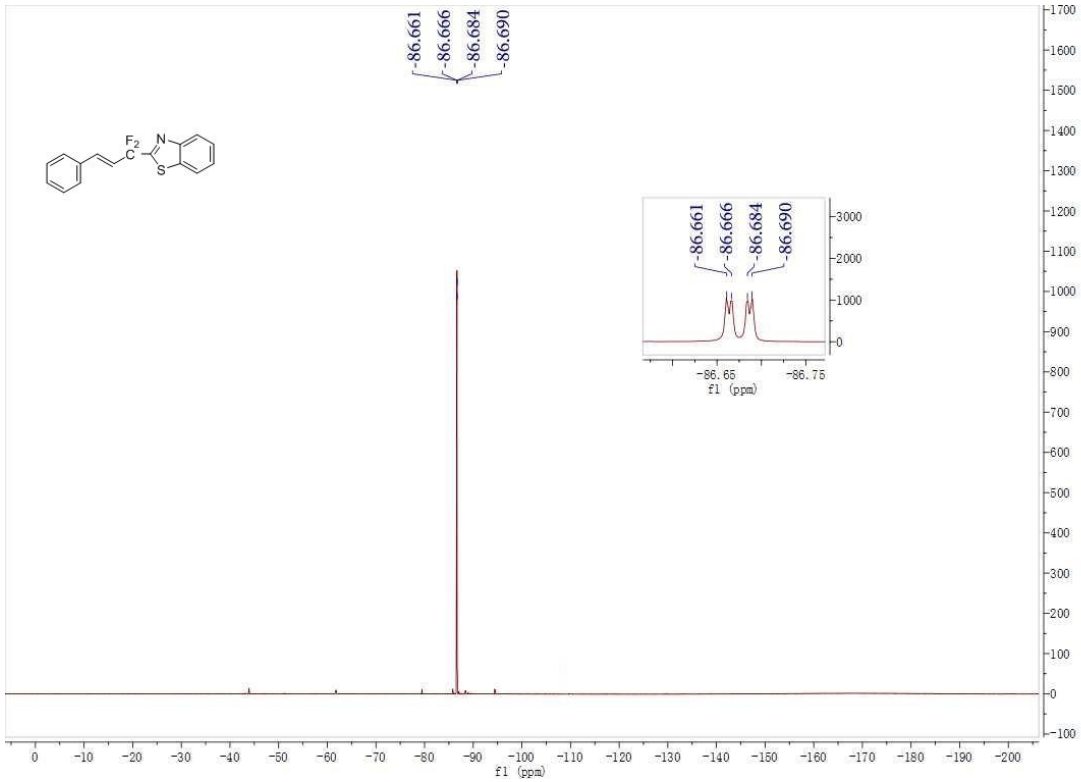


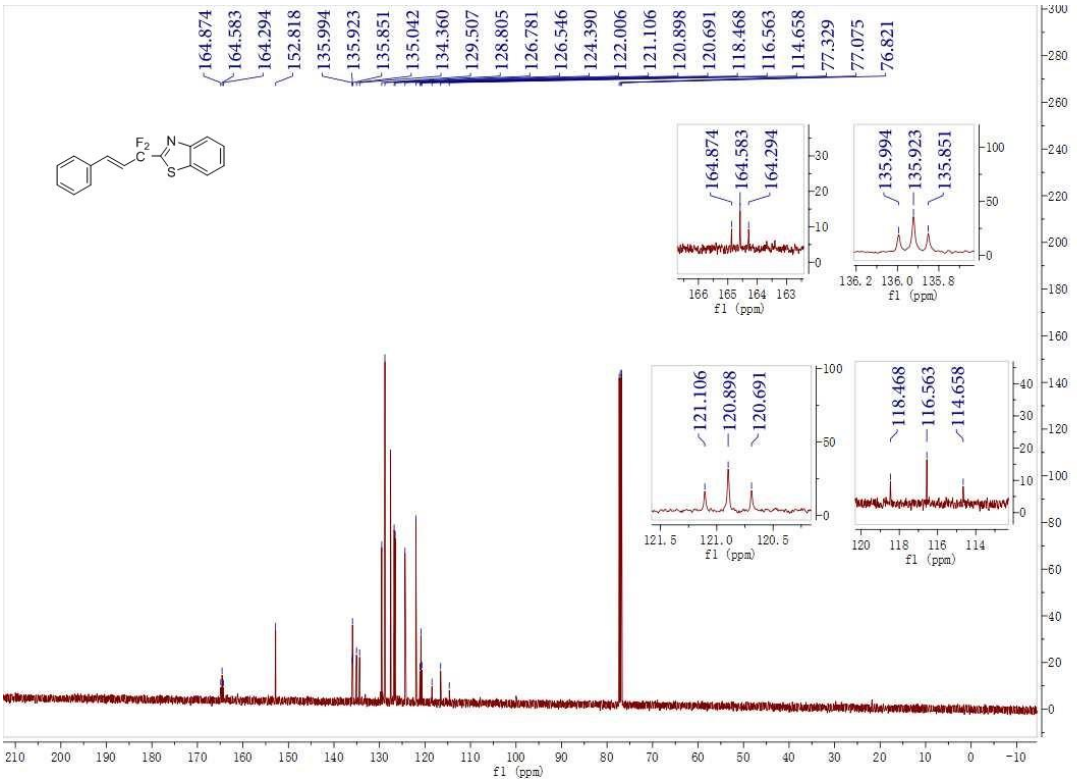

-94.431
-94.449
f1 (ppm)


158.061
148.977
140.271
136.729
136.658
136.586
135.343
134.090
129.687
128.829
128.093
127.587
121.034
119.757
119.558
119.357
115.418
113.513
110.749
77.360
77.105
76.851
21.476
f1 (ppm)

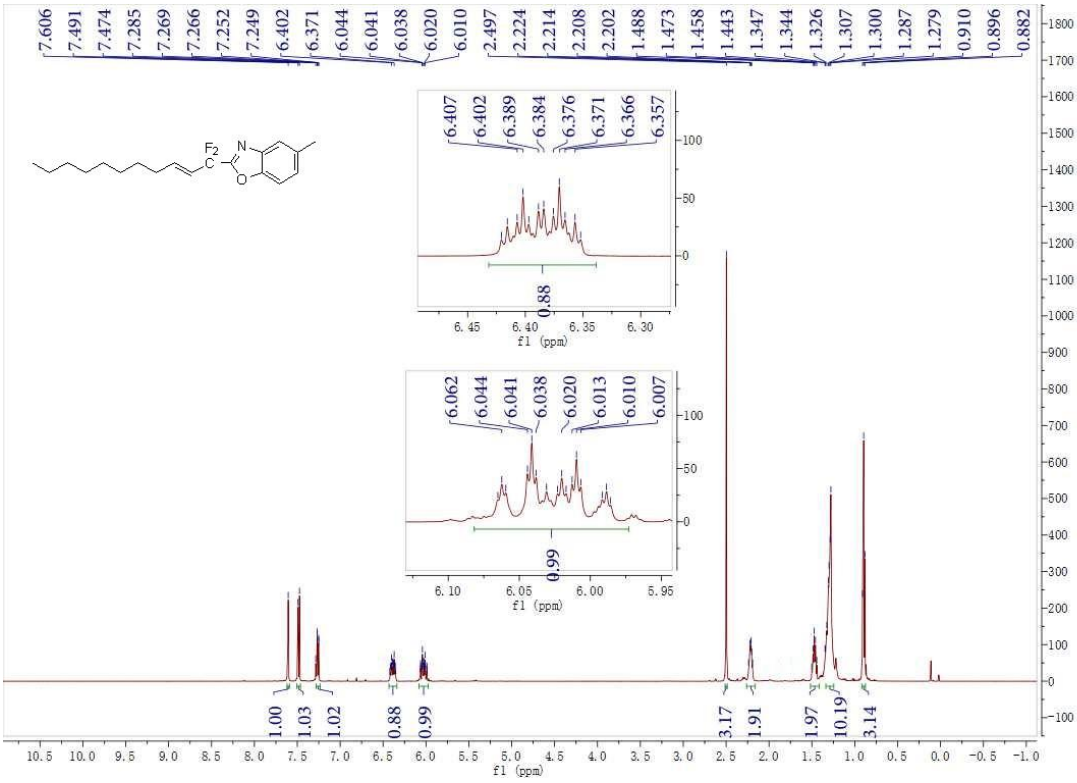
(*E*)-2-(1,1-difluoro-3-phenylallyl)benzo[d]thiazole (3x)

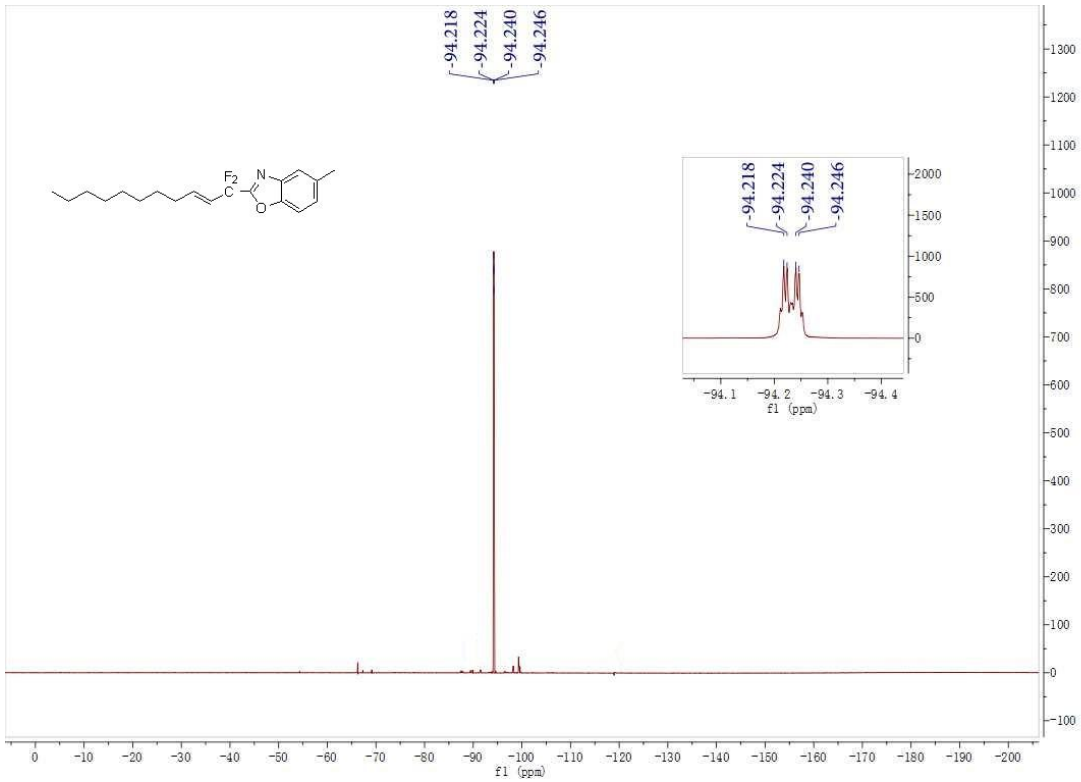


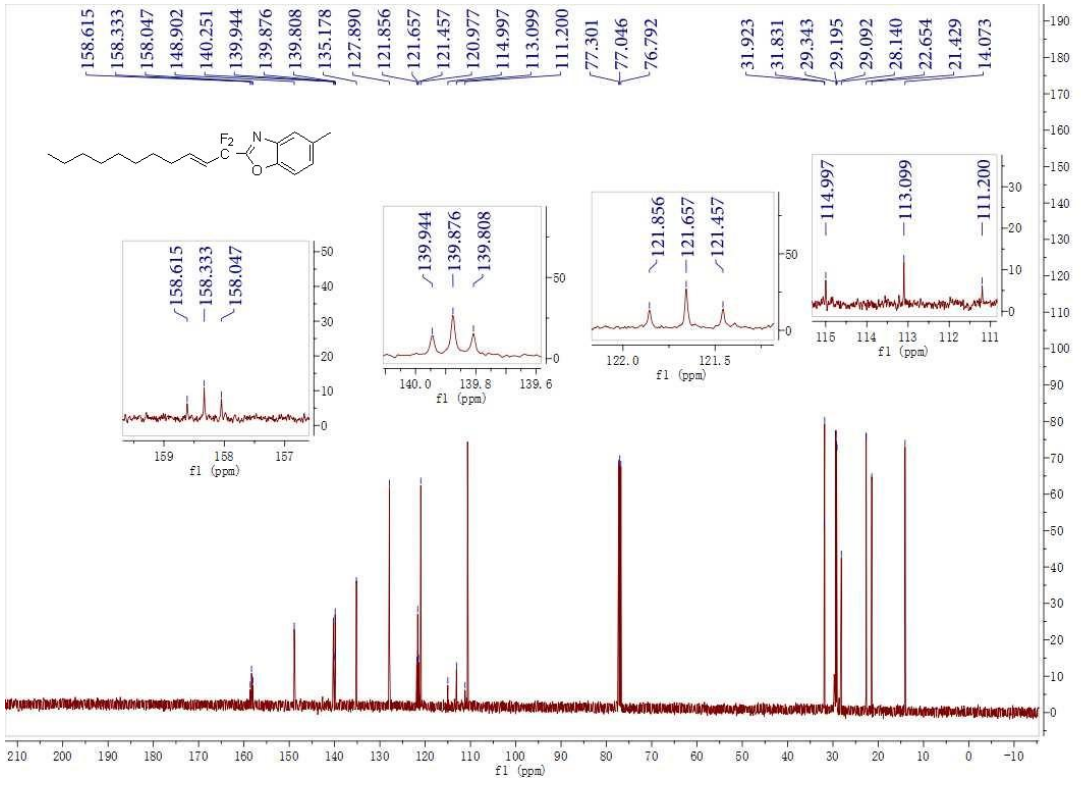




(*E*)-2-(1,1-difluoroundec-2-en-1-yl)-5-methylbenzo[*d*]oxazole (3y)




-94.218
-94.224
-94.240
-94.246
F2
N
C
O
f1 (ppm)


158.615
158.333
158.047
148.902
140.251
139.944
139.876
139.808
135.178
127.890
121.856
121.657
121.457
120.977
114.997
113.099
111.200
77.301
77.046
76.792
31.923
31.831
29.343
29.195
29.092
28.140
22.654
21.429
14.073
F2
N
C
O
f1 (ppm)