Supporting Information for

A visible light photoredox catalyzed carbon radical-mediated generation of *o*-QMs for 2,3-dihydrobenzofuran synthesis

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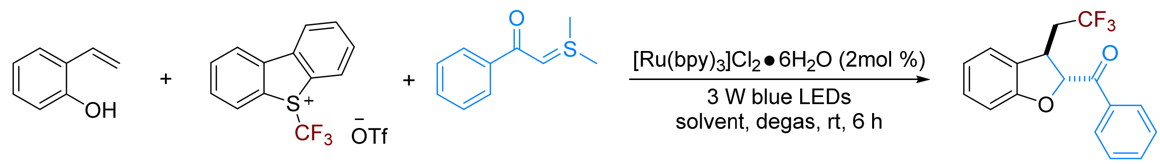
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. *fac*-Ir(4'-CF_3-ppy)$_3$ was prepared according to literature.[1] The solvents used were treated by distillation over the drying agents. Flash column chromatography was performed using 200-300 mesh silica gel. ^1H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Bruker ESI-O-TOF MS mass spectrometer. 2-Vinylphenols **1**,[2] sulfonium bromides **5** and sulfur ylides **2** were prepared according to previous reported procedures.[3]

2. Detailed Optimization of Reaction Conditions and Control Experiments

2.1 Optimization of Reaction Conditions

***Table S1*. Screen of the solvents**



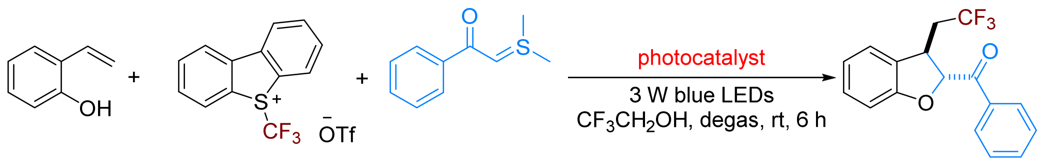
1a, 0.20 mmol **2**, 0.22 mmol **3a**, 0.30 mmol (±)-**4aa**

Entry[a]	solvent	Yield[b] [%]
1	CH_2Cl_2	36
2	Toluene	13
3	DMF	20
4	*CF_3CH_2OH*	*42*

[a] Unless otherwise noted, reactions were carried out with **1a** (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (54.0 mg, 0.30 mmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2 mol%) in solvent (2.0 mL) at rt under irradiation of 3 W blue LEDs. [b] Determined by ^{1}HNMR yield using 1,3,5-trimethoxybenzene as the internal standard.

As shown in *Table S1*, among all the solvents tested, CF_3CH_2OH gave the best results in terms of yield (42% yield), and was thus selected for further optimization studies.

***Table S2*. Screen of the photocatalysts**



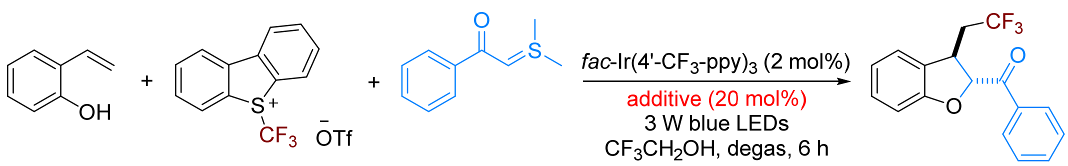
1a, 0.20 mmol **2**, 0.22 mmol **3a**, 0.30 mmol (±)-**4aa**

Entry[a]	photocatalyst	Yield[b] [%]
1	*fac*-Ir(ppy)$_3$	51
2	[Ru(bpz)$_3$]PF$_6$	49
3	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	57
4	[IrdF(CF$_3$ppy)$_2$(dtbpy)]PF$_6$	60
5	*fac-Ir(4'-CF$_3$-ppy)$_3$*	*73*
6	Ir(4-Fppy)$_3$	52
7	Eosin Y	53
8	No photocatalyst	45

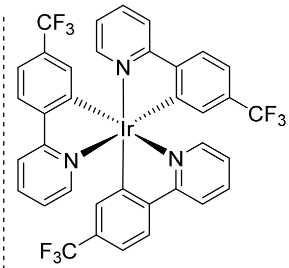
[a] Unless otherwise noted, reactions were carried out with **1a** (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (54.0 mg, 0.30 mmol), photocatalyst (2 mol%) in CF_3CH_2OH (2.0 mL) at rt under irradiation of 3 W blue LEDs. [b] Determined by ^{1}HNMR yield using 1,3,5-trimethoxybenzene as the internal standard.

As shown in *Table S2*, among all the photocatalysts tested, *fac*-Ir(4'-CF$_3$-ppy)$_3$ gave the best results in terms of yield (73% yield), and was thus selected for further optimization studies.

***Table S3*. Screen of the additives**



1a, 0.20 mmol **2**, 0.22 mmol **3a**, 0.30 mmol (±)-**4aa**



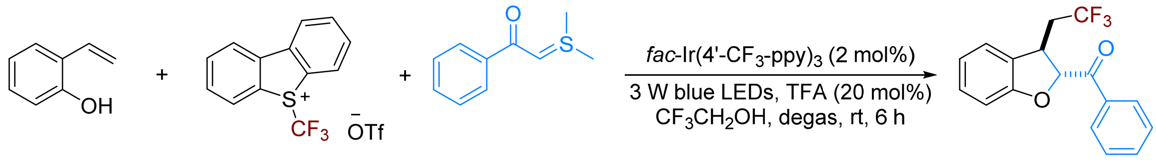
fac-Ir(4'-CF$_3$-ppy)$_3$

Entry[a]	additive	Yield[b] [%]
1	*TFA*	*77*
2	TsOH	47
3	Isobutyric acid	30
4	Pivalic acid	70
5	1-Adamantane carboxylic acid	55
6	-	73

[a] Unless otherwise noted, reactions were carried out with **1a** (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (54.0mg, 0.30 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (2 mol%), additive (20 mol%) in CF_3CH_2OH (2.0 mL) at rt under irradiation of 3 W blue LEDs. [b] Determined by ^{1}HNMR yield using 1,3,5-trimethoxybenzene as the internal standard.

As shown in *Table S3,* among all the additives tested, TFA gave the best result in terms of yield (77% yield), and was thus selected for further optimization studies.

***Table S4*. Screen of the ratio of the substrates**



1a, 0.20 mmol **2** **3a** (±)-**4aa**

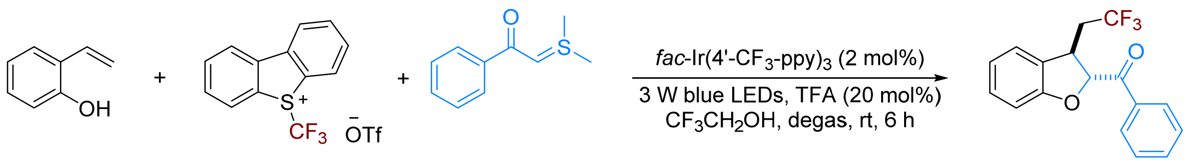
Entry[a]	Equivalent of **2**	Equivalent of **3a**	Yield[b] [%]
1	1.1	1.5	77
2	1.5	1.5	66
3	2.0	1.5	62
4	*1.1*	*2.0*	*81*
5	1.1	3.0	62

[a] Unless otherwise noted, reactions were carried out with **1a** (24.0 mg, 0.20 mmol), **2**, **3a**, *fac*-Ir(4'-CF_3-ppy)$_3$ (2 mol%), TFA (20 mol%) in CF_3CH_2OH (2.0 mL) at rt under irradiation of 3 W blue LEDs. [b] Determined by ^{1}HNMR yield using 1,3,5-trimethoxybenzene as the internal standard.

As shown in *Table S4*, among all the conditions tested, 1.1 equivalent of **2,** 2.0 equivalent of **3a** gave the best results in terms of yield (81% yield), and was thus selected for further optimization studies.

2.2 Control Experiments

***Table S5*. Control experiments**



1a, 0.20 mmol **2**, 0.22 mmol **3a**, 0.30 mmol (±)-**4aa**

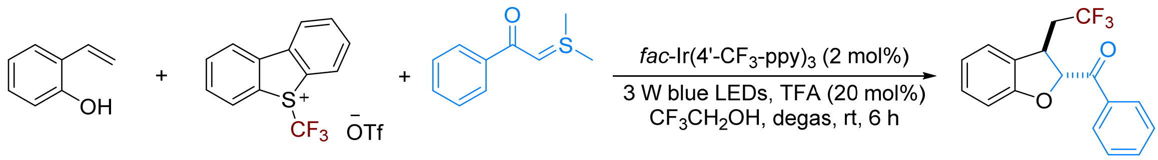
Entry[a]	hv	photocatalyst	Yield[b] (%)
1	+	+	75
2	-	+	Trace
3	+	-	40
4	-	-	No reaction

[a] Unless otherwise noted, reactions were carried out with **1a** (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (54.0 mg, 0.30 mmol) *fac*-Ir(4'-CF_3-ppy)$_3$ (2 mol%), TFA (20 mol%) in CF_3CH_2OH (2.0 mL) at rt under irradiation of 3 W blue LEDs. [b] Determined by isolated yield.

The results of *Table S5* revealed that synthesis of 4aa is indeed a photoredox catalysis process.

3. Experimental Procedure and Spectral Data of Products

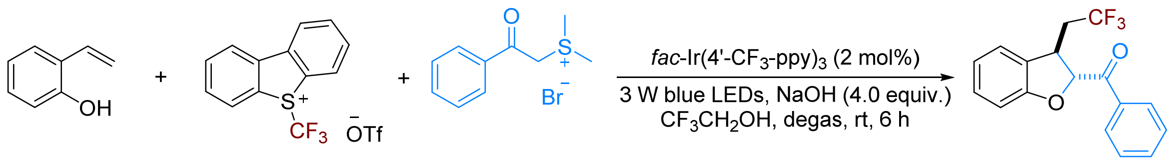
3.1 General Process



1a, 0.20 mmol **2**, 0.22 mmol **3a**, 0.40 mmol (±)-**4aa**

1a (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (72.0 mg, 0.40 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), TFA (4.5 mg, 20 mol%) were dissolved in CF_3CH_2OH (2.0 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4aa** in 81% isolated yield as a white solid. Other products were prepared according to the above procedure.

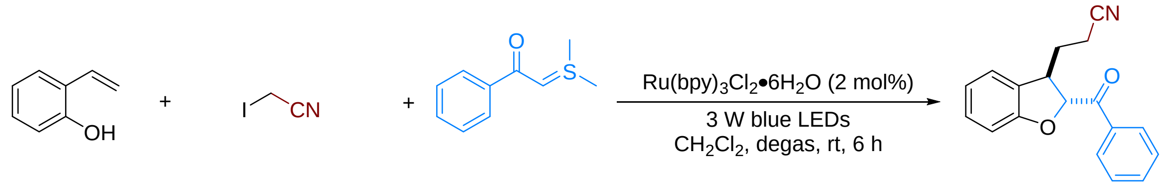
3.2 Experimental Procedure of Reaction Using Sulfonium Bromide



1a, 0.20 mmol **2**, 0.22 mmol **5**, 0.40 mmol (±)-**4aa**

1a (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **5** (104.0 mg, 0.40 mmol), NaOH (32.0 mg, 0.80 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), were dissolved in CF_3CH_2OH (2.0 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4aa** in 50% isolated yield as a white solid.

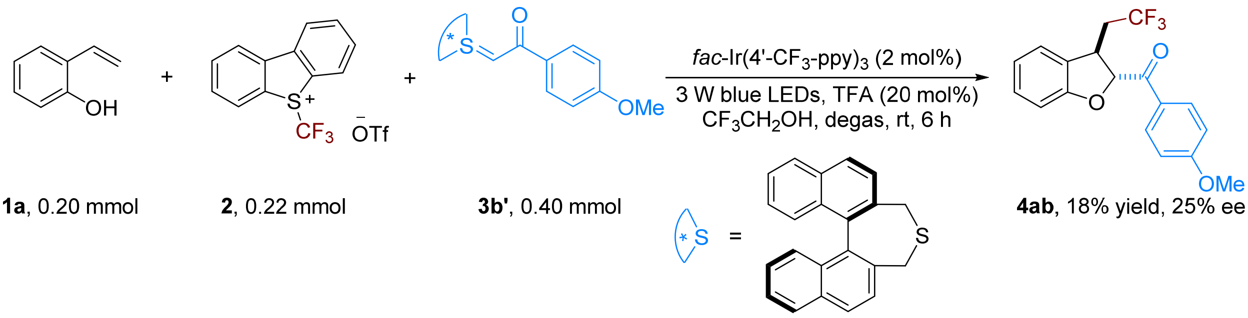
3.3 Experimental Procedure of Reaction Using Iodoacetonitrile as Radical Source



1a, 0.20 mmol **6**, 0.40 mmol **3a**, 0.40 mmol (±)-**7**

1a (24.0 mg, 0.20 mmol), **6** (66.8 mg, 0.40 mmol), **3a** (72.0 mg, 0.40 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$(3.0 mg, 2 mol%), were dissolved in CH_2Cl_2 (2.0 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **7** in 70% isolated yield as a yellow oil.

3.4 Experimental Procedure of Reaction Using (R)-BINOL-derived Chiral Sulfur Ylide

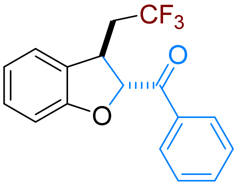


1a, 0.20 mmol **2**, 0.22 mmol **3b'**, 0.40 mmol **4ab**, 18% yield, 25% ee

1a (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3b'** (92.1 mg, 0.40 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), TFA (4.5 mg, 20 mol%) were dissolved in CF_3CH_2OH (2.0 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4ab** in 18% isolated yield as a white solid.

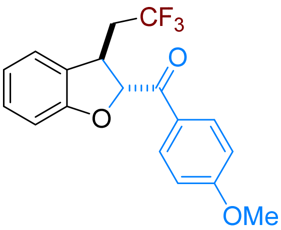
3.5 Spectral Data of Products

Product 4aa



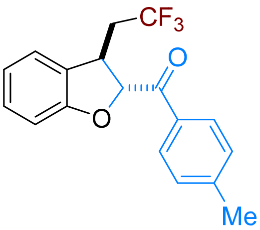
48 mg, white solid, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.70 (d, *J* = 5.2 Hz, 1H), 4.46 – 4.41 (m, 1H), 2.75 – 2.64 (m, 1H), 2.58 – 2.49 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 193.5, 158.0, 134.7, 133.9, 129.5, 129.3, 128.7, 127.0, 126.0 (q, *J* = 275.9 Hz), 124.5, 121.7, 110.1, 87.0, 38.9 (q, *J* = 27.7 Hz), 37.4 (q, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.14. HRMS (ESI) for: $C_{17}H_{13}F_3O_2$ $[M + H]^+$: calcd: 307.0940, found: 307.0950.

Product 4ab



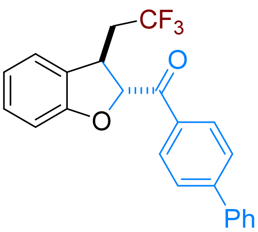
37 mg, white solid, yield: 55%. The ee was determined by chiral HPLC (Chiralpak AD-H, n-hexane/isopropanol 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retention times: Rt = 9.246 min (major), Rt = 12.158 min (minor). ee = 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 4.47 – 4.42 (m, 1H), 3.90 (s, 3H), 2.74 – 2.62 (m, 1H), 2.57 – 2.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.7, 164.1, 158.1, 131.9, 129.2, 127.6, 127.5 (q, *J* = 275.7 Hz), 127.2, 124.5, 122.2, 121.6, 114.0, 110.0, 87.0, 55.5, 38.7 (q, *J* = 27.2 Hz), 37.3 (q, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.12. HRMS (ESI) for: $C_{18}H_{15}F_3O_3$ $[M + K]^+$: calcd: 375.0605, found: 375.0602.

Product 4ac



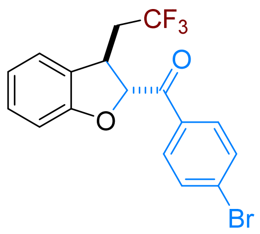
38 mg, white solid, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.68 (d, *J* = 5.2 Hz, 1H), 4.45 – 4.40 (m, 1H), 2.71 – 2.63 (m, 1H), 2.57 – 2.48 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.1, 158.1, 144.9, 132.1, 129.6, 129.4, 129.2, 127.4 (q, *J* = 275.7 Hz), 127.1, 124.5, 121.6, 110.1, 86.9, 39.0 (q, *J* = 27.7 Hz), 37.3 (d, *J* = 2.3 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.09. HRMS (ESI) for: $C_{18}H_{15}F_3O_2$ $[M + H]^+$: calcd: 321.1097, found: 321.1096.

Product 4ad



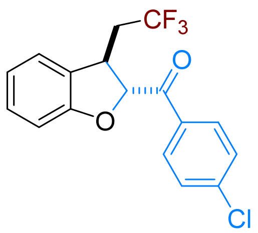
48 mg, white solid, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.72 (d, *J* = 4.8 Hz, 1H), 4.50 – 4.45 (m, 1H), 2.75 – 2.64 (m, 1H), 2.59 – 2.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.1, 158.1, 146.5, 139.7, 133.3, 130.1, 129.3, 129.0, 128.4, 127.4, 127.3, 127.1, 126.1 (q, *J* = 275.9 Hz) 124.5, 121.7, 110.1, 87.1, 38.9 (q, *J* = 27.7 Hz), 37.32 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.09. HRMS (ESI) for: $C_{23}H_{17}F_3O_2$ $[M + H]^+$: calcd: 383.1253, found: 383.1255.

Product 4ae



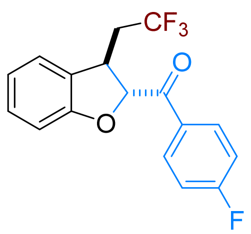
54 mg, white solid, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 – 7.87 (m, 2H), 7.60 – 7.56 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H) , 5.55 (d, J = 5.2 Hz, 1H), 4.37 (m, 1H), 2.67 – 2.53 (m, 1H), 2.51 – 2.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.7, 157.8, 133.4, 132.1, 131.0, 129.4, 129.2, 126.9, 126.0 (q, J = 275.8 Hz), 124.5, 121.9, 110.1, 87.1, 38.9 (q, J = 27.8 Hz), 37.2 (q, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.17. HRMS (ESI) for: $C_{17}H_{12}BrF_3O_2$ $[M + H]^+$: calcd: 385.0046, found: 385.0042.

Product 4af



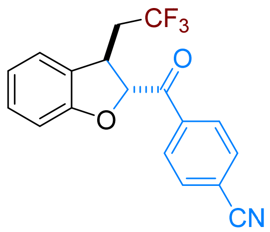
44 mg, white solid, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.63 (d, J = 5.2 Hz, 1H), 4.47 – 4.42 (m, 1H), 2.75 – 2.64 (m, 1H), 2.57 – 2.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.5, 157.8, 140.4, 132.9, 130.9, 129.3, 129.0, 127.4 (q, J = 276.1 Hz), 126.9, 124.5, 121.8, 110.1, 87.0, 38.7 (q, J = 27.7 Hz), 37.1 (q, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.20. HRMS (ESI) for: $C_{17}H_{12}ClF_3O_2$ $[M + H]^+$: calcd: 341.0551, found: 341.0558.

Product 4ag



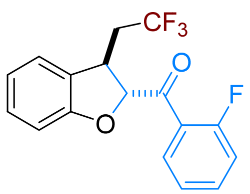
43 mg, white solid, yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 – 8.11 (m, 2H), 7.25 (d, J = 7.6 Hz, 1H), 7.21 – 7.16 (m, 3H), 6.97 – 6.93 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 5.64 (d, J = 5.2 Hz, 1H), 4.80 – 4.43 (m, 1H), 2.72 – 2.61 (m, 1H), 2.57 – 2.48 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 192.0, 166.2 (d, J = 254.8 Hz), 157.9, 132.3, 131.1, 129.3, 127.0, 126.0 (q, J = 275.8 Hz) 124.5, 121.8, 116.0, 110.1, 87.1, 38.9 (q, J = 27.7 Hz), 37.2 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.20, -103.48. HRMS (ESI) for: $C_{17}H_{12}F_4O_2$ $[M + H]^+$: calcd: 325.0846, found: 325.0851.

Product 4ah



35 mg, white solid, yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.65 (d, J = 5.2 Hz, 1H), 4.49 – 4.44 (m, 1H), 2.74 – 2.63 (m, 1H), 2.60 – 2.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.7, 157.5, 137.7, 132.4, 129.9, 129.4, 127.3 (q, J = 275.7 Hz), 126.6, 124.5, 122.0, 117.8, 116.9, 110.1, 87.1, 38.9 (q, J = 27.7 Hz), 37.1 (q, J = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.22. HRMS (ESI) for: $C_{18}H_{12}F_3NO_2$ $[M + Na]^+$: calcd: 354.0712, found: 354.0722.

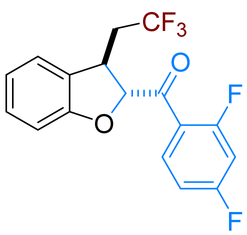
Product 4ai



40 mg, white solid, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 – 7.78 (m, 1H), 7.61 – 7.56 (m, 1H), 7.28 – 7.16 (m, 4H), 6.94 – 6.90 (m, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.63 – 5.62 (m, 1H), 4.21 (dd, J = 11.2, 5.6 Hz, 1H), 2.66 – 2.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.6, 162.9 (d, J = 252.7 Hz), 158.4, 135.3 (d, J = 9.1 Hz), 131.3 (d, J = 2.9 Hz), 129.4, 126.7, 126.0 (q, J = 275.7 Hz), 124.8 (m), 123.6 (d, J = 13.5 Hz), 121.6, 116.7 (d, J = 23.2 Hz), 110.1, 89.7 (d, J = 16 Hz), 39.4

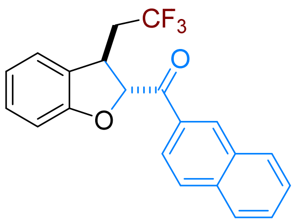
(q, J = 27.7 Hz), 38.0 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.06, -109.65. HRMS (ESI) for: $C_{17}H_{12}F_4O_2$ [M + H]$^+$: calcd: 325.0846, found: 325.0851.

Product 4aj



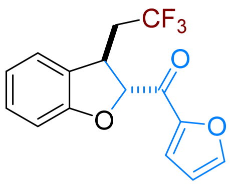
38 mg, white solid, yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.82 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.84 (d, J = 8.0 Hz, 1H), 5.58 (dd, J = 3.6, 2.4 Hz, 1H), 4.26 – 4.22 (m, 1H), 2.67 – 2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.1 (d, J = 4.2, Hz), 167.6 (dd, J = 256.6, 12.4 Hz), 163.9 (dd, J = 255.9, 12.6 Hz), 158.2, 133.3 (dd, J = 10.6, 4.5 Hz), 129.4, 127.4 (q, J = 275.8 Hz), 126.7, 124.8, 121.7, 120.2 (dd, J = 13.5, 3.5 Hz), 112.7 (dd, J = 21.5, 3.3 Hz), 110.1, 104.8 (dd, J = 27.0, 17.5 Hz), 89.5 (d, J = 5.9 Hz), 39.4 (q, J = 27.7 Hz), 37.8 (q, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.15, -100.32, -104.81. HRMS (ESI) for: $C_{17}H_{11}F_5O_2$ [M + Na]$^+$: calcd: 365.0571, found: 365.0589.

Product 4ak



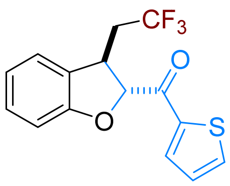
44 mg, white solid, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.66 (s, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H) 7.88 (d, J = 8.0 Hz, 1H), 7.65 – 7.53 (m, 2H), 7.25 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 5.86 (d, J = 4.8 Hz, 1H), 4.53 – 4.48 (m, 1H), 2.77 – 2.66 (m, 1H), 2.64 – 2.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.4, 158.1, 135.9, 132.4, 131.9, 131.7, 129.8, 129.2, 128.9, 128.5, 127.8, 127.1, 126.8, 126.0 (q, J = 275.9 Hz) 124.5, 124.4, 121.7, 110.1, 87.0, 38.9 (q, J = 27.7 Hz), 37.4 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.09. HRMS (ESI) for: $C_{21}H_{15}F_3O_2$ [M + H]$^+$: calcd: 357.1097, found: 357.1095.

Product 4al



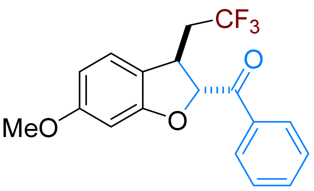
40 mg, white solid, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 – 7.68 (m, 1H), 7.47 (d, J = 3.6 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.97 – 6.93 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.60 (dd, J = 1.0, 0.8 Hz, 1H), 5.49 (d, J = 4.8 Hz, 1H), 4.25 – 4.20 (m, 1H), 2.68 – 2.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.3, 158.4, 150.5, 147.7, 129.4, 127.3 (q, J = 275.8 Hz), 126.7, 124.7, 121.8, 120.6, 112.6, 110.1, 87.1, 39.2 (q, J = 27.9 Hz), 38.6 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.01. HRMS (ESI) for: $C_{15}H_{11}F_3O_3$ [M + H]$^+$: calcd: 297.0733, found: 297.0731.

Product 4am



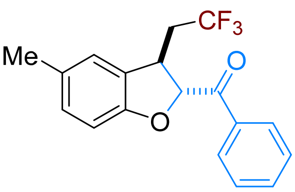
38 mg, corlorless oil, yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (dd, J = 4.0, 1.2 Hz, 1H), 7.73 (dd, J = 4.8, 0.8 Hz, 1H), 7.25 – 7.17 (m, 3H), 6.98 – 6.94 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.44 (d, J = 5.2 Hz, 1H), 4.35 – 4.30 (m, 1H), 2.68 – 2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.1, 158.1, 140.7, 135.4, 134.6, 129.4, 128.3, 126.8, 126.0 (q, J = 275.8 Hz), 124.7, 121.9, 110.2, 88.3, 39.0 (q, J = 27.8 Hz), 38.7 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.93. HRMS (ESI) for: $C_{15}H_{11}F_3O_2S$ [M + Na]$^+$: calcd: 335.0324, found: 335.0325.

Product 4ba



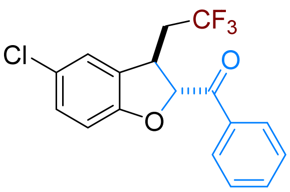
27 mg, yellow oil, yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (d, J = 7.6 Hz, 2H) 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.50 (dd, J = 8.4, 2.0 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 5.70 (d, J = 5.2 Hz, 1H), 4.34 – 4.29 (m, 1H), 3.75 (s, 1H), 2.66 – 2.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.7, 161.2, 159.4, 134.6, 133.9, 129.4, 128.7, 127.4 (q, J = 276.0 Hz) 124.7, 118.8, 107.6, 96.5, 87.9, 55.5, 39.3 (q, J = 27.4 Hz), 37.0 (q, J = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.09. HRMS (ESI) for: $C_{18}H_{15}F_3O_3$ $[M + H]^+$: calcd: 337.1046, found: 337.1042.

Product 4ca



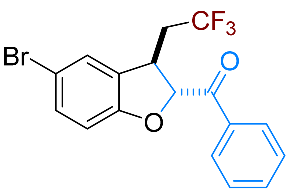
41 mg, white solid, yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 – 8.06 (m, 2H), 7.63 – 7.59 (m, 1H), 7.52 – 7.48 (m, 2H), 7.03 (s, 1H), 6.98 – 6.96 (d, J = 8.0 Hz，1H), 6.73 – 6.71 (d, J = 8.0 Hz， 1H), 5.67 – 5.66 (d, J = 5.6 Hz, 1H), 4.40 – 4.35 (m, 1H), 2.69 – 2.60 (m, 1H), 2.55 – 2.46 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.7, 156.0, 134.7, 133.8, 131.1, 129.7, 129.4, 128.7, 127.0, 126.1 (q, J = 275.8 Hz), 124.9, 109.6, 87.1, 38.9 (q, J = 27.6 Hz), 37.4 (q, J = 2.7 Hz), 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.2. HRMS (ESI) for: $C_{18}H_{15}F_3O_2$ $[M + Na]^+$: calcd: 343.0916, found: 343.0900.

Product 4da



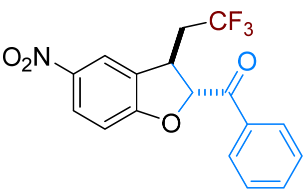
43 mg, white solid, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 – 7.99 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.13 (s, 1H), 7.08 (dd, J = 8.4, 2.0 Hz, 1H) , 6.70 – 6.68 (d, J = 8.4 Hz, 1H), 5.66 – 5.64 (d, J = 5.2 Hz, 1H), 4.37 – 4.33 (m, 1H), 2.64 – 2.54 (m, 1H), 2.52 – 2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.0, 156.7, 134.3, 134.0, 129.4, 129.2, 128.9, 128.7, 126.5, 125.8 (q, J = 275.9 Hz), 124.7, 111.1, 87.3, 38.6 (q, J = 27.9 Hz), 37.3 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.10. HRMS (ESI) for: $C_{17}H_{12}ClF_3O_2$ $[M + Na]^+$: calcd:363.0370, found: 363.0380.

Product 4ea



52 mg, white solid, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 – 7.98 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 7.27 (s, 1H), 7.20 (dd, J = 8.4, 2.0 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 5.65 (d, J = 5.6 Hz, 1H), 4.38 – 4.33 (m, 1H), 2.61 – 2.54 (m, 1H), 2.51 – 2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.9, 157.2, 134.4, 134.0, 132.2, 129.5, 129.4, 128.8, 127.6, 125.8 (q, J = 275.8 Hz) 113.5, 111.7, 87.3, 38.7 (q, J = 27.6 Hz), 37.3 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.12. HRMS (ESI) for: $C_{17}H_{12}BrF_3O_2$ $[M + Na]^+$: calcd: 406.9865, found: 406.9882.

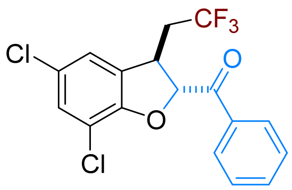
Product 4fa



14 mg, white solid, yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (m, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 6.87 – 6.84 (m, 1H), 5.86 (d, J = 5.2 Hz, 1H), 4.48 – 4.43 (m, 1H), 2.71 – 2.61 (m, 1H), 2.58 – 2.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.9, 163.1, 142.9, 134.4, 134.0, 129.5, 128.9, 128.7 (q, J = 276.0 Hz), 127.0, 126.7, 121.1, 110.2, 88.2, 38.7 (q, J = 28.2 Hz), 36.8 (q, J = 2.6 Hz). ^{19}F NMR (376

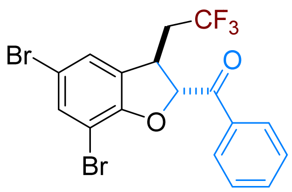
MHz, $CDCl_3$) δ (ppm) -63.97. HRMS (ESI) for: $C_{17}H_{12}F_3NO_4$ $[M + Na]^+$: calcd: 374.0611, found: 374.0617.

Product 4ga



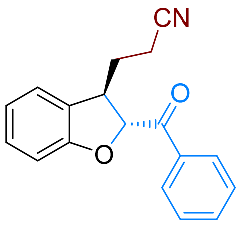
43 mg, white solid, yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 – 8.00 (m, 2H), 7.58 – 7.54 (m, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.12 (d, J = 2.0 Hz, 1H), 7.03 (s, 1H), 5.72 (d, J = 5.2 Hz, 1H), 4.43 – 4.38 (m, 1H), 2.60 – 2.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.5, 153.1, 134.2, 134.2, 130.1, 129.5, 129.3, 128.8, 127.1 (q, J = 275.8 Hz), 126.9, 123.2, 116.3, 87.7, 38.7 (q, J = 28.2 Hz), 38.3 (q, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.05. HRMS (ESI) for: $C_{17}H_{11}F_3O_3$ $[M + Na]^+$: calcd: 396.9980, found: 396.9976.

Product 4ha



46 mg, white solid, yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.47 (s, 1H), 7.28 (s, 1H), 5.78 (d, J = 7.2 Hz, 1H), 4.53 – 4.48 (m, 1H), 2.67 – 2.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.5, 155.0, 134.6, 134.2, 134.1, 130.1, 129.5, 128.8, 126.6, 125.7 (q, J = 275.8 Hz), 113.8, 103.9, 87.4, 38.6 (q, J = 28.2 Hz), 38.5 (q, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.04. HRMS (ESI) for: $C_{17}H_{11}Br_2F_3O_3$ $[M + K]^+$: calcd: 500.8709, found: 500.8704.

Product 7



39 mg, yellow oil, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H) , 7.22 – 7.17 (m, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.53 (d, J = 5.2 Hz, 1H), 4.04 (q, J = 6.0 Hz, 1H), 2.55 – 2.37 (m, 2H), 2.31 – 2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.4, 158.6, 134.3, 133.9, 129.3, 129.3, 128.8, 126.9, 124.4, 121.6, 119.0, 110.3, 88.0, 43.1, 30.5, 14.5. IR (in KBr): 1688, 1596, 1478, 1461, 1448, 1221, 751, 691 cm^{-1}. HRMS (ESI) for: $C_{18}H_{15}NO_2$ $[M + Na]^+$: calcd: 300.0995, found: 300.0998.

References:

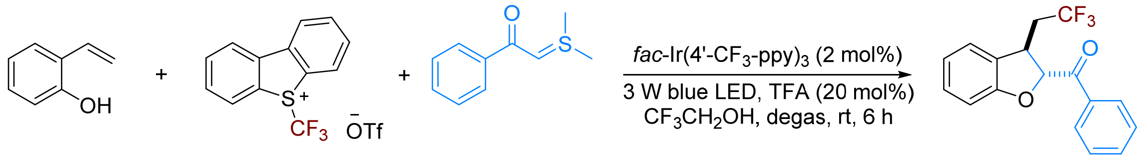
[1] A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* 2014, **776**, 51-59.

[2] a) V. Hirschbeck, P. H. Gehrtz and I. Fleischer, *Chem. - Eur. J.* 2018, **24**, 7092-7107.; b) P. Liu, S. Zou, B. Yu, L. Li and H. Huang, *Org. Lett.* 2018, **20**, 3601-3604. c) H. Konishi, T. Ueda, T. Muto, and K. Manabe, *Org. Lett.* 2012, **14**, 4722. d) F. Yang, K. Rauch, K. Kettelhoit and L. Ackermann, *Angew. Chem. Int. Ed*, 2014, **53**, 11285-11288.

[3] Y.-Y. Liu, X.-Y. Yu, J.-R. Chen, M.-M. Qiao, X. Qi, D.-Q. Shi and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2017, **56**, 9527-9531.

4. Synthetic Utility

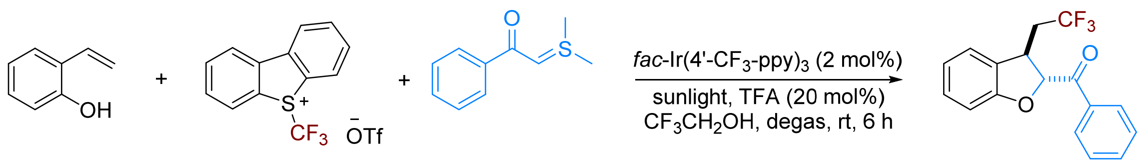
4.1 1.0 mmol Scale Reaction



1a, 1.0 mmol **2**, 1.1 mmol **3a**, 2.0 mmol **4aa**

1a (120.0 mg, 1.0 mmol), **2** (440.0 mg, 1.1 mmol), **3a** (360.0 mg, 2.0 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (17.2 mg, 2 mol%), TFA (22.8 mg, 20 mol%) were dissolved in CF_3CH_2OH (10 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the resulting mixture was stirred at 3 W blue LEDs at rt about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4aa** in 76% isolated yield as a white solid.

4.2 Sunlight-driven Reaction

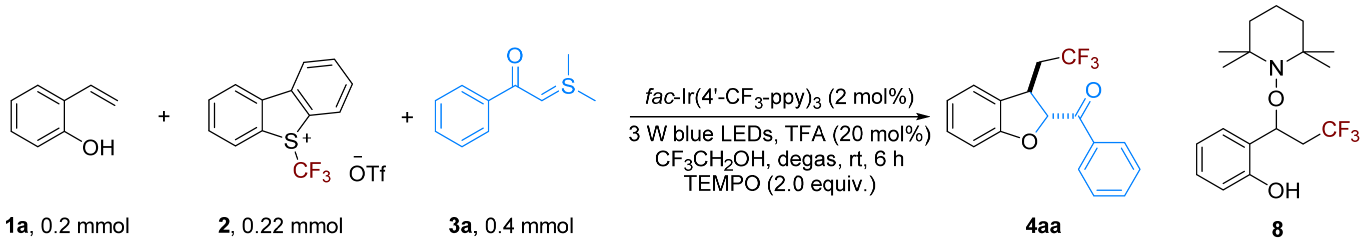


1a, 0.2 mmol **2**, 0.22 mmol **3a**, 0.4 mmol **4aa**

1a (24.0 mg, 0.2 mmol), **2** (88.0 mg, 0.22 mmol), **3a** (72.0 mg, 0.4 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), TFA (4.5 mg, 20 mol%) were dissolved in CF_3CH_2OH (2 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the resulting mixture was stirred at 3 W blue LEDs at rt about 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4aa** in 57% isolated yield as a white solid.

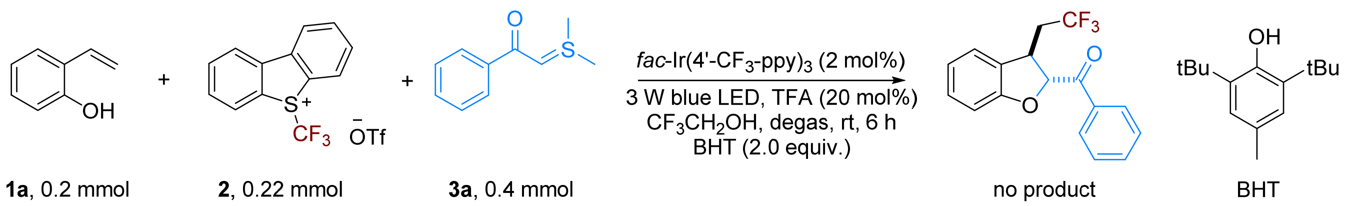
5. Mechanism Study

TEMPO Trapping Experiment



1a (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (72.0 mg, 0.4 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), TFA (4.5 mg, 20 mol%), TEMPO (62.4 mg, 2.0 equiv.) were dissolved in CF_3CH_2OH (2.0 mL). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1) directly to give the desired product **4aa** in 28% isolated yield as a white solid. The TEMPO trapped intermediate **8** was detected by HRMS. HRMS (ESI) for: ($C_{18}H_{26}F_3NO_2$) $[M + H]^+$ calcd: 346.1988, found: 346.1991.

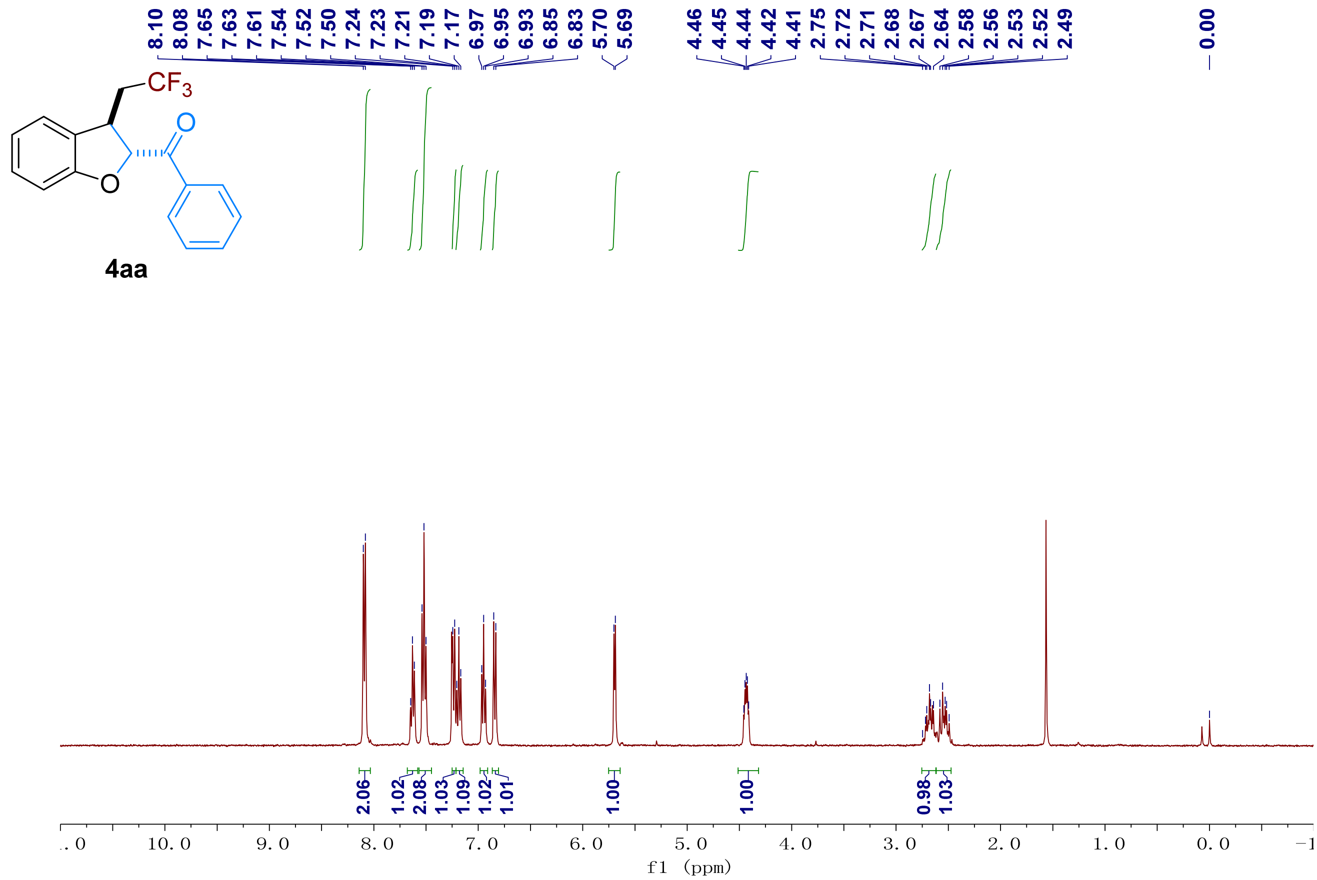
BHT Traping Experiment

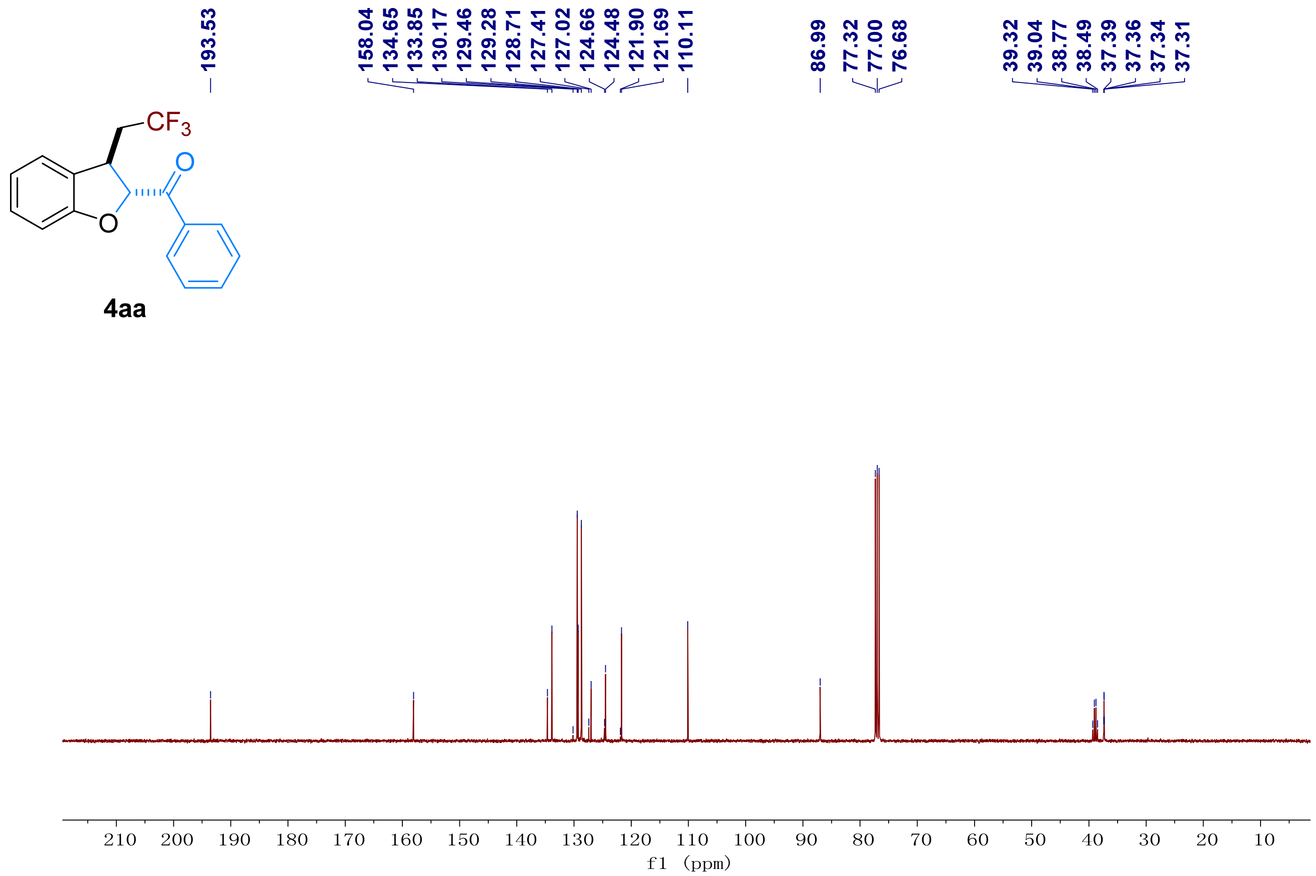


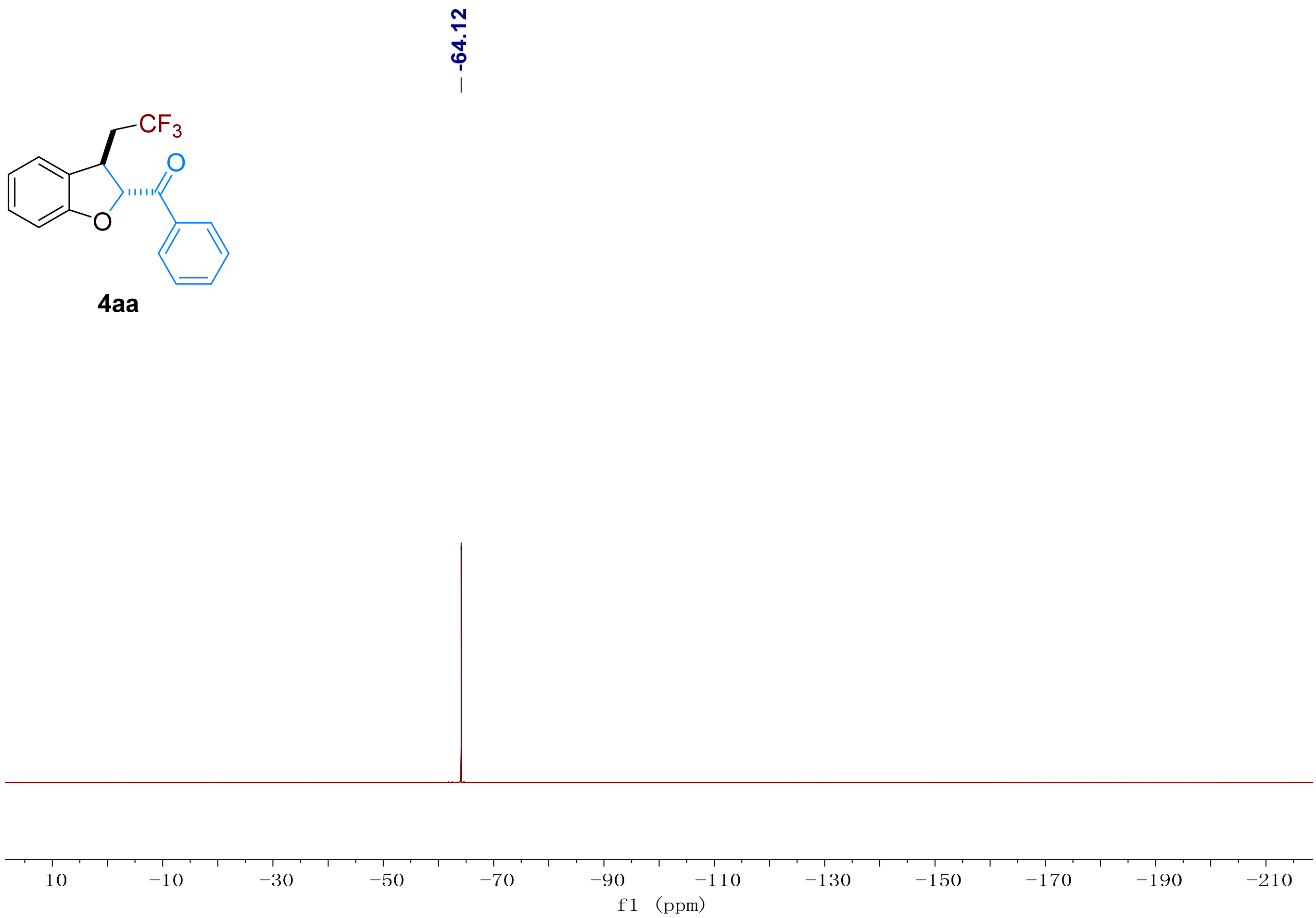
1a (24.0 mg, 0.20 mmol), **2** (88.4 mg, 0.22 mmol), **3a** (72.0 mg, 0.4 mmol), *fac*-Ir(4'-CF_3-ppy)$_3$ (3.4 mg, 2 mol%), TFA (4.5 mg, 20 mol%), BHT (88.1 mg, 2.0 equiv.) were dissolved in CF_3CH_2OH (2.0 ml). The resulting mixture was degased by a "freeze-pump-thaw" procedure (3 times). Then, the mixture was stirred at 3 W blue LEDs at room temperature about 6 h. No desired product **4aa** can be detected.

6. Spectra of Products

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4aa

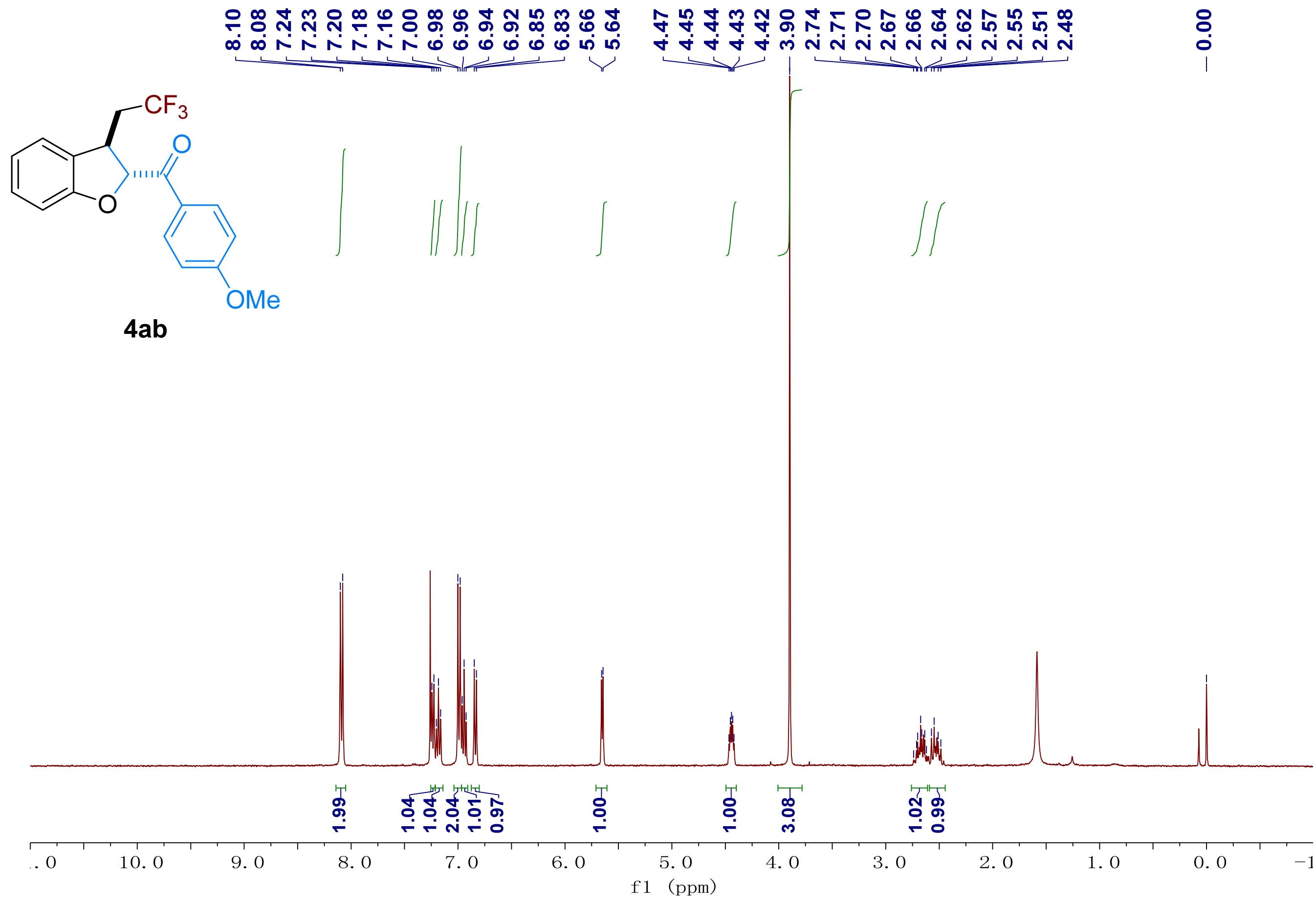


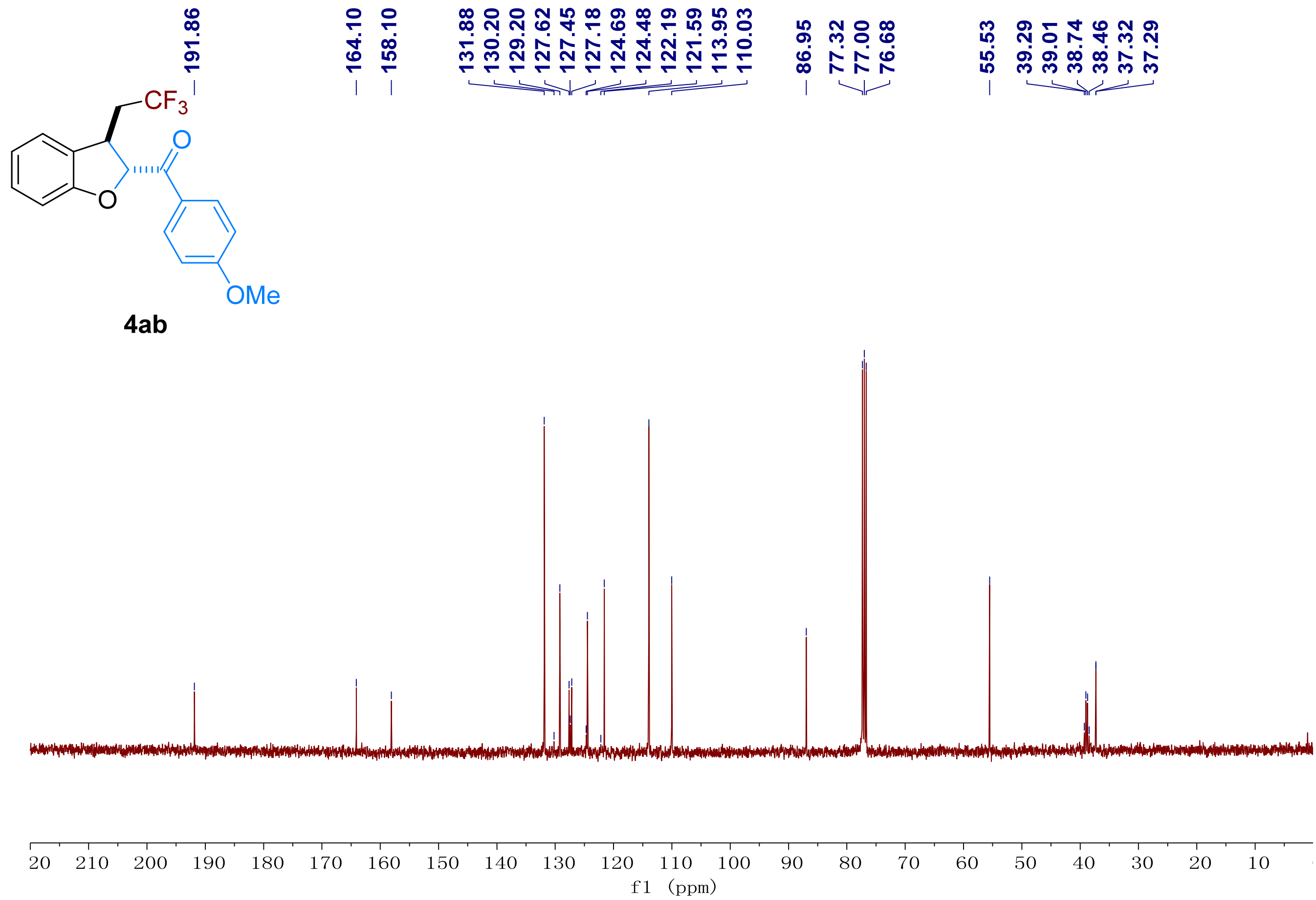


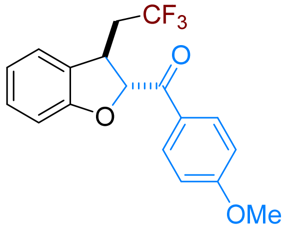


4aa

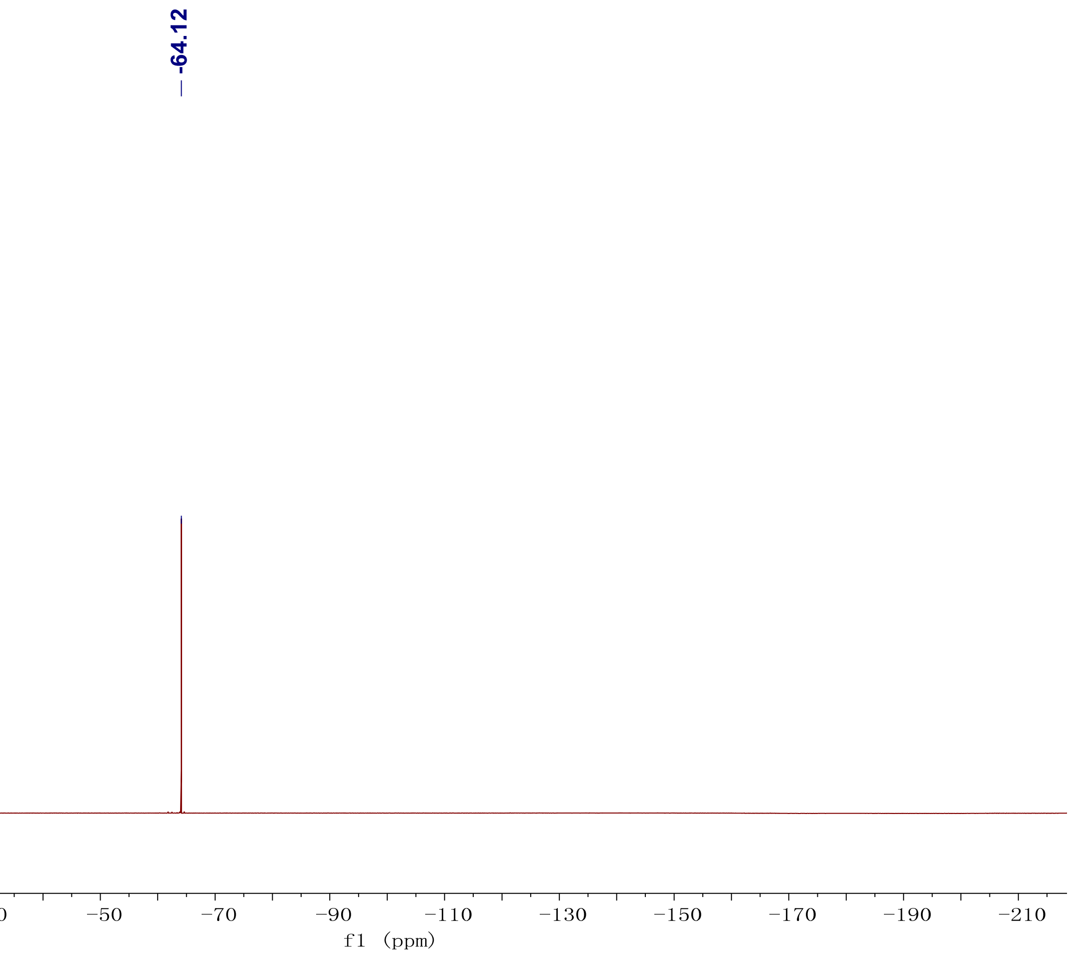
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, CDCl$_3$) spectra of product 4ab



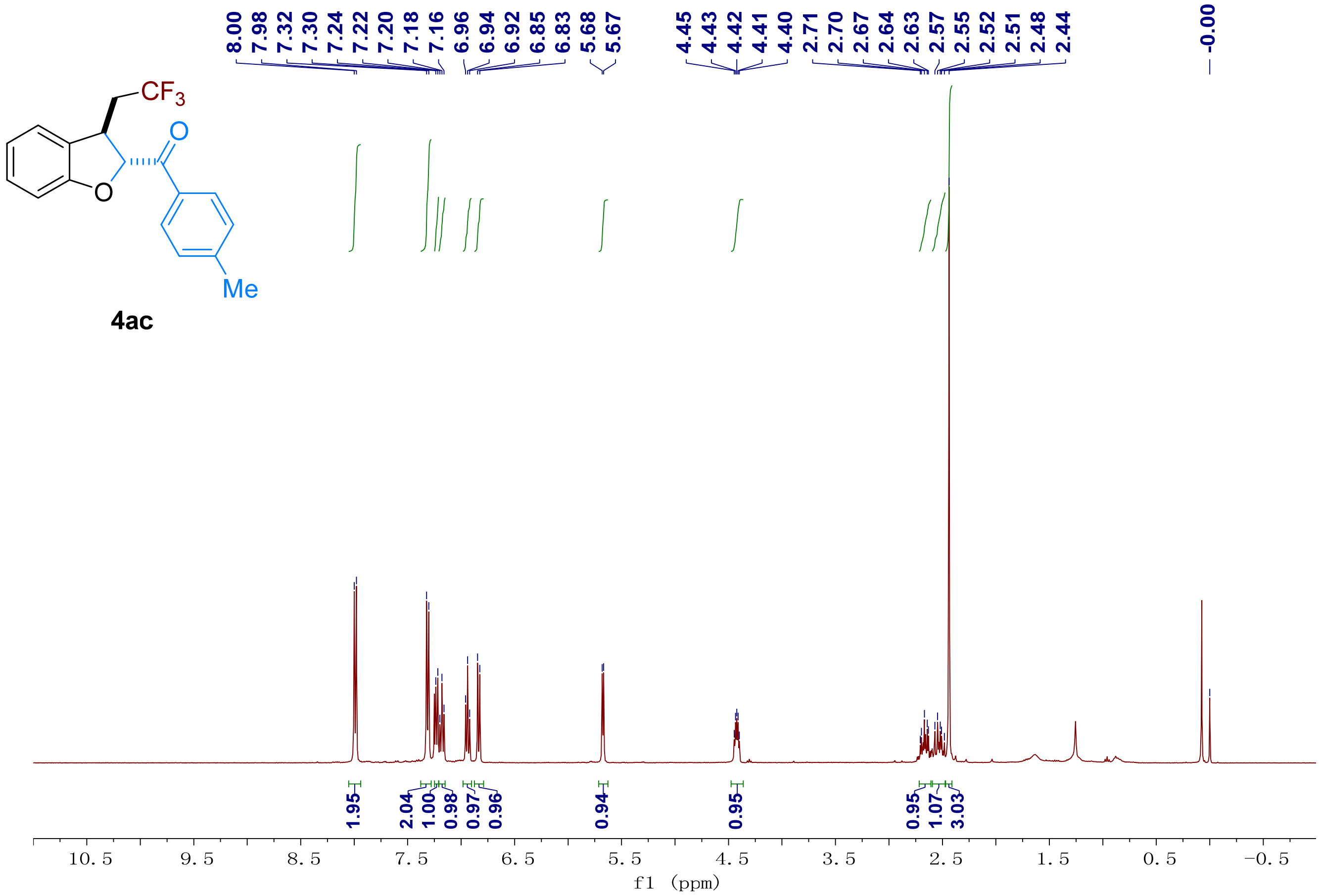


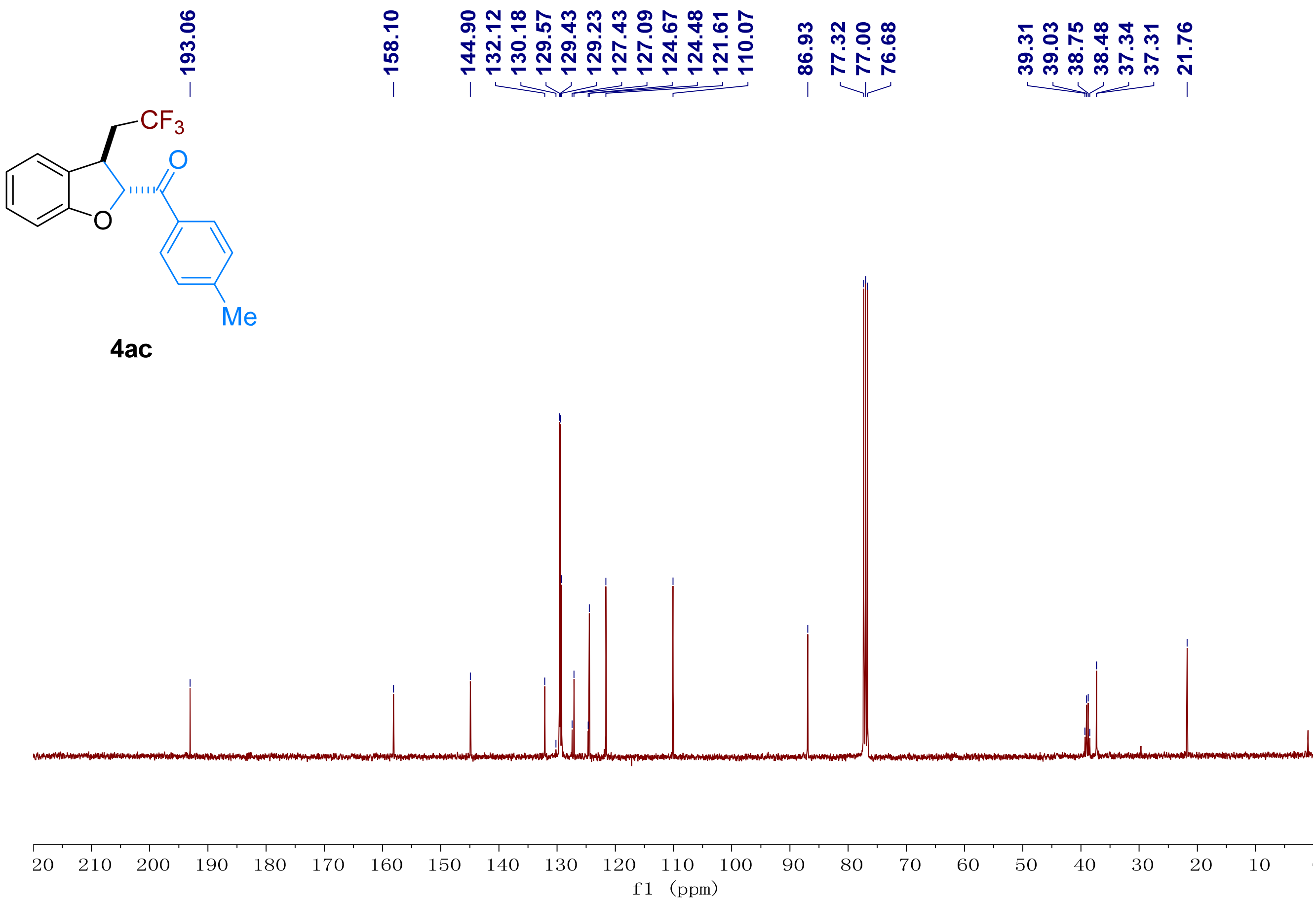


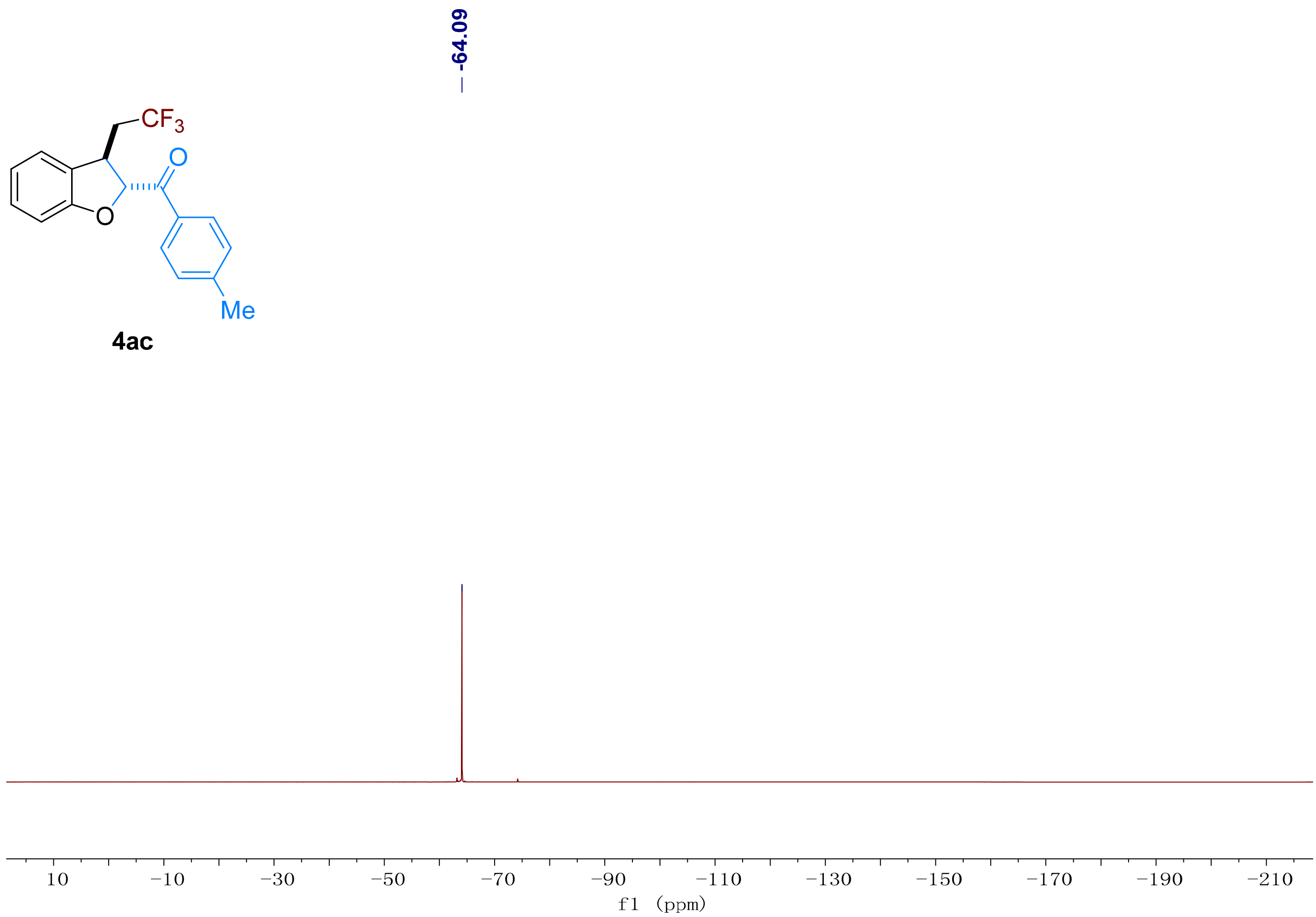
4ab



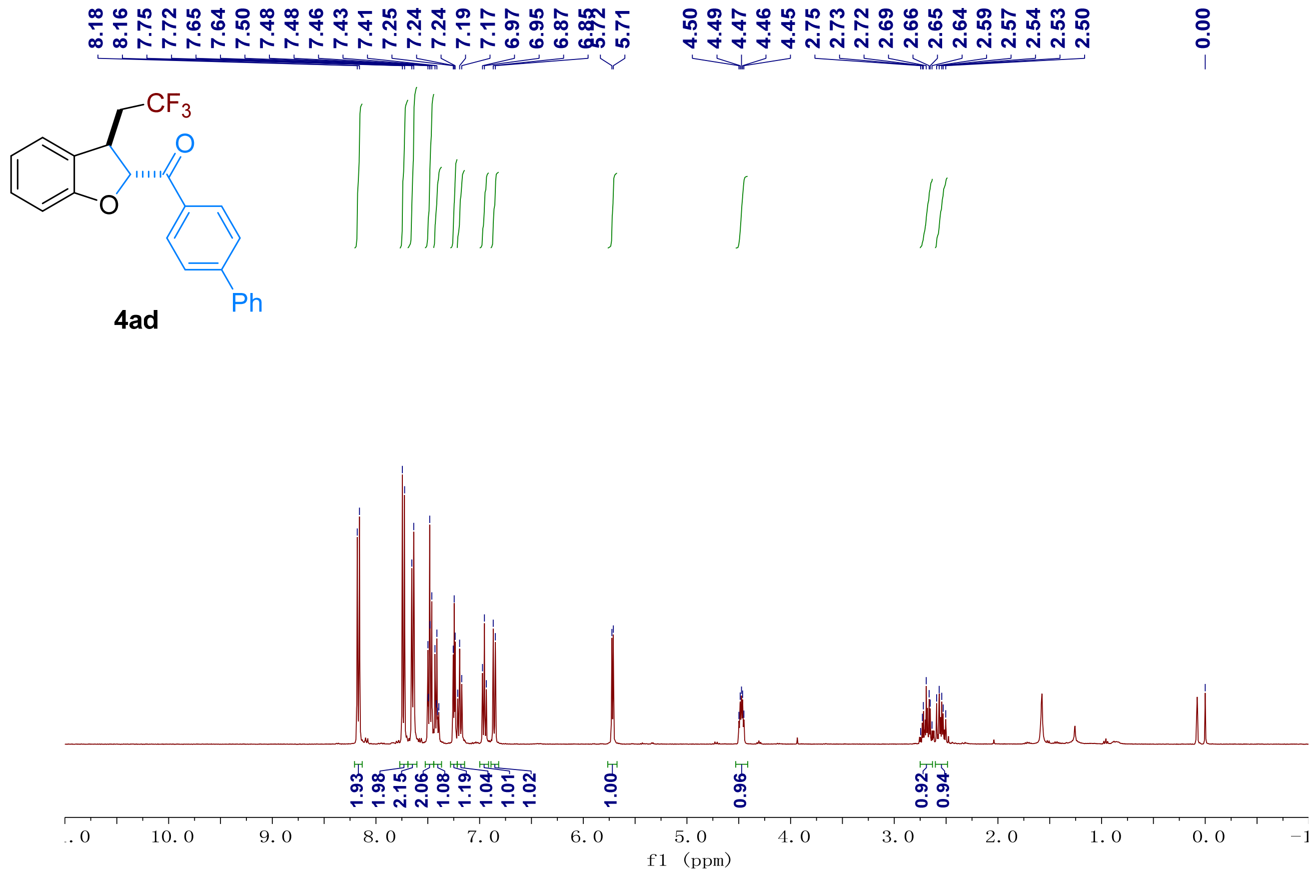
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ac

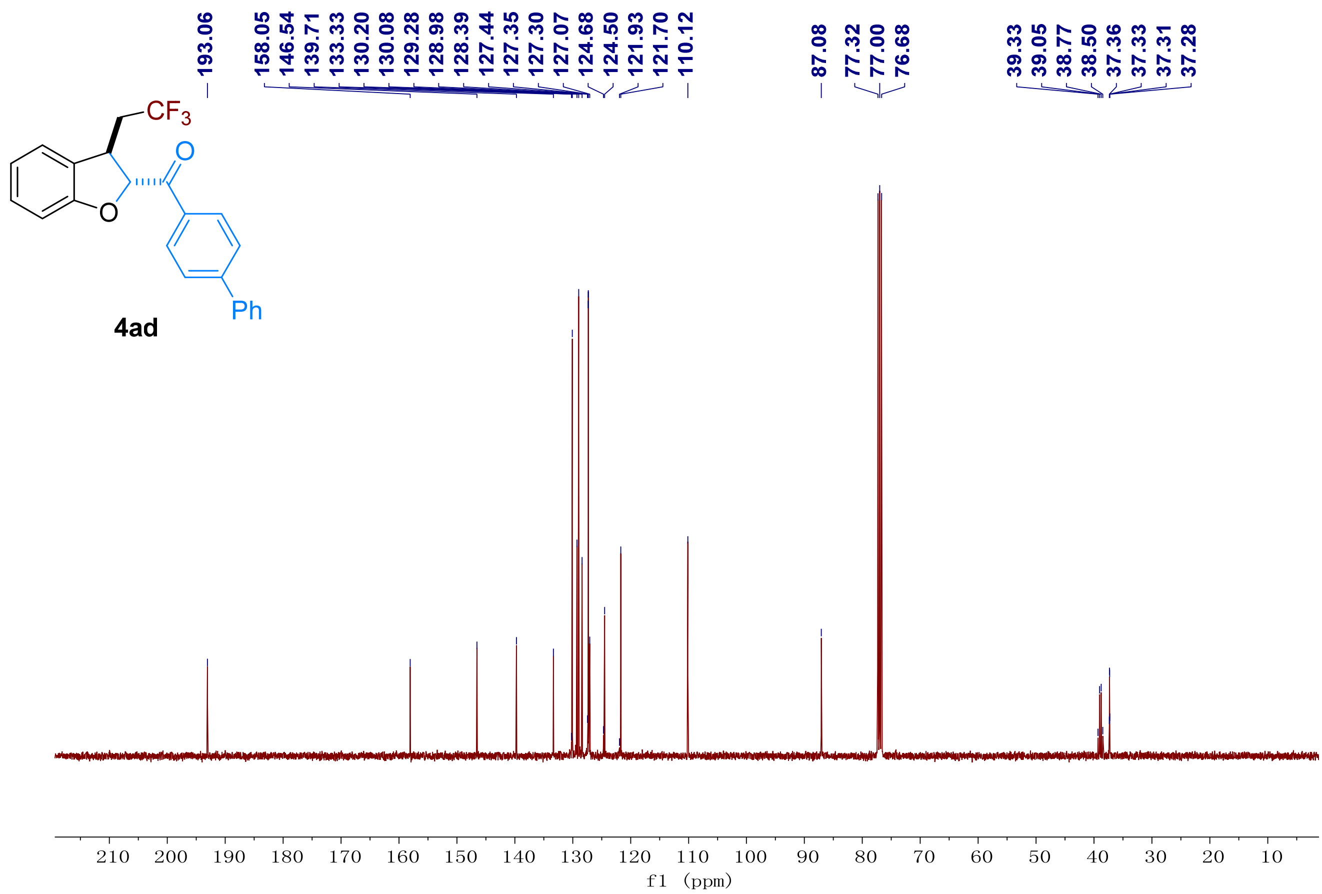


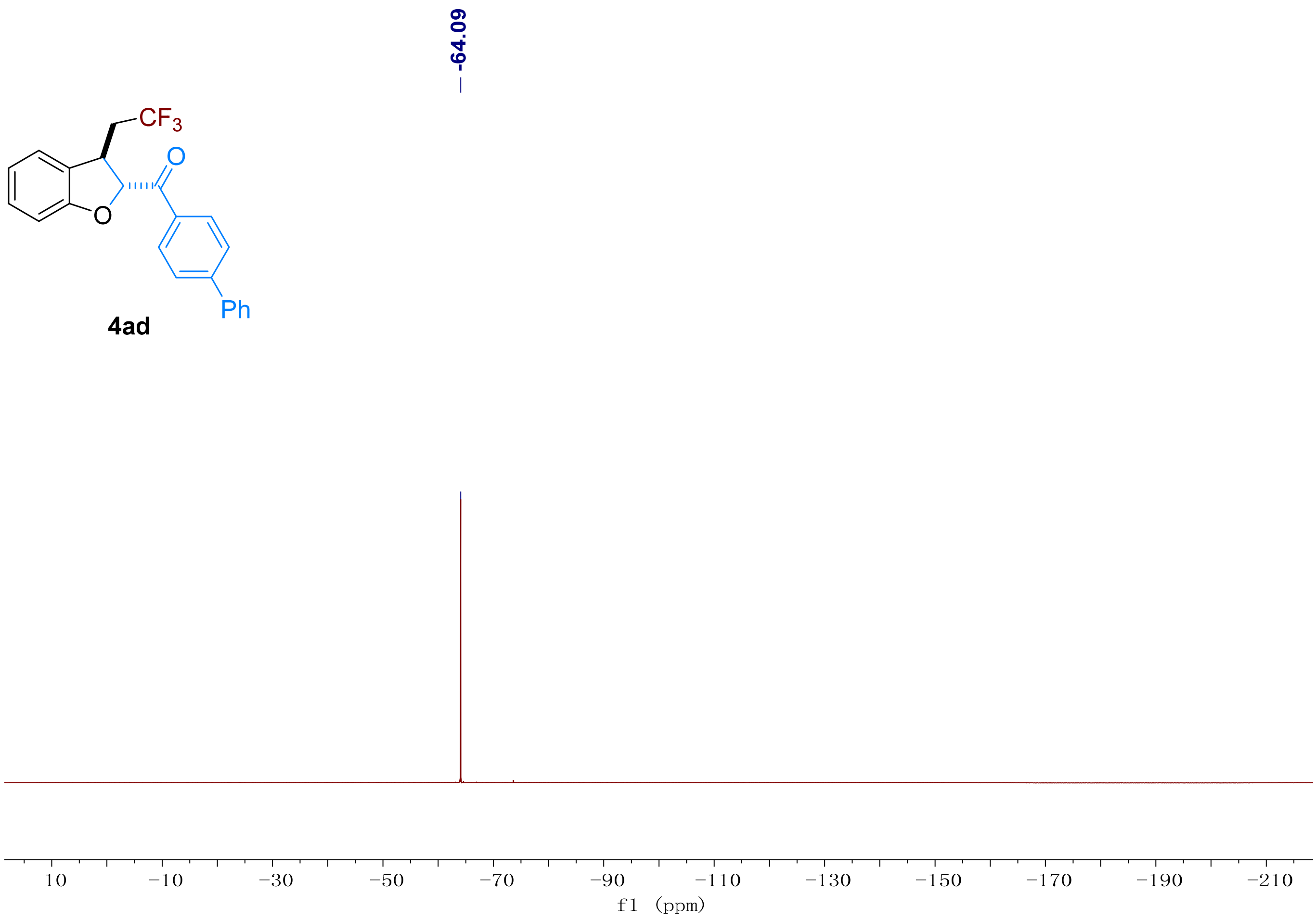



-64.09
CF3
O
O
Me
4ac
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

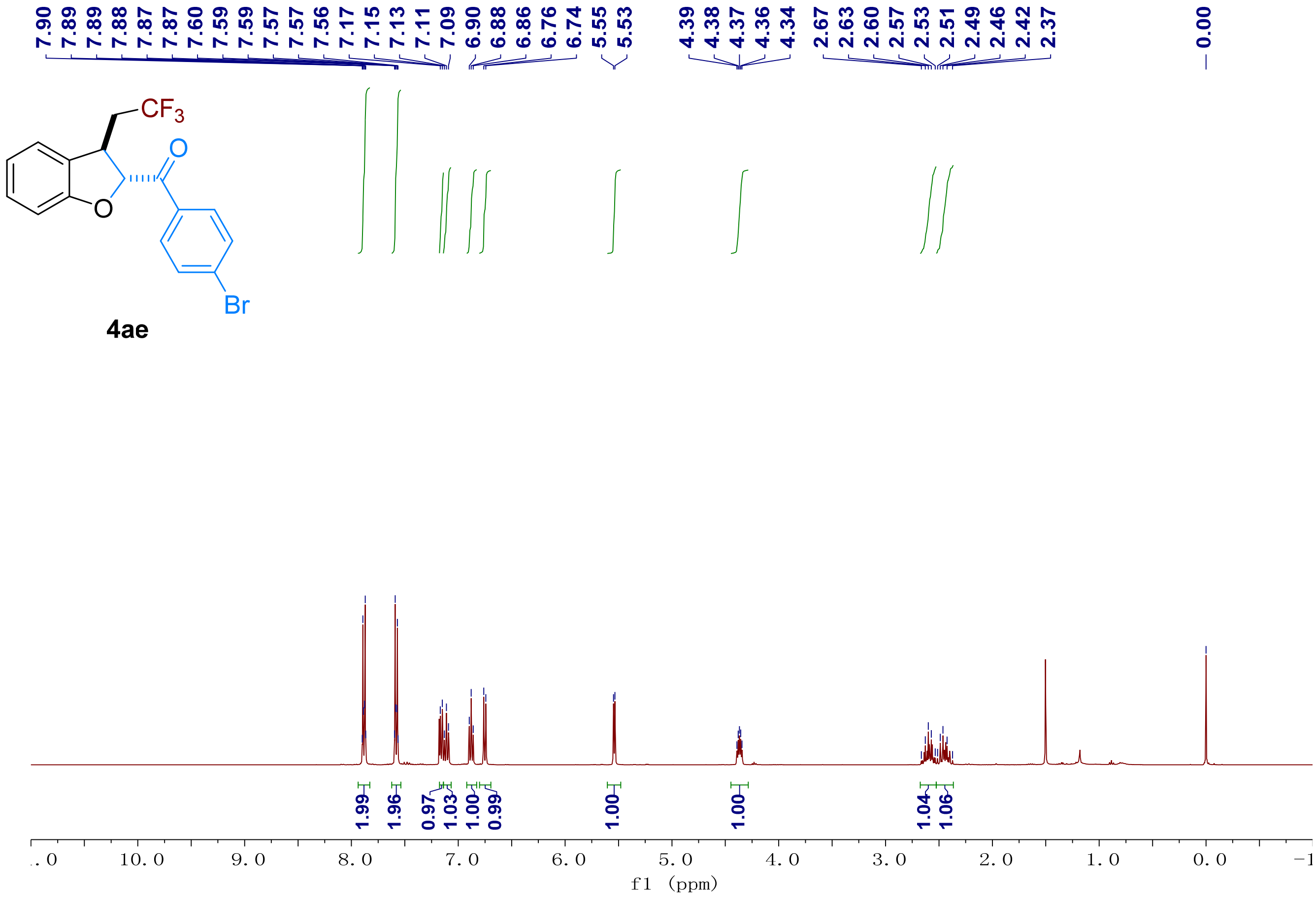
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4ad

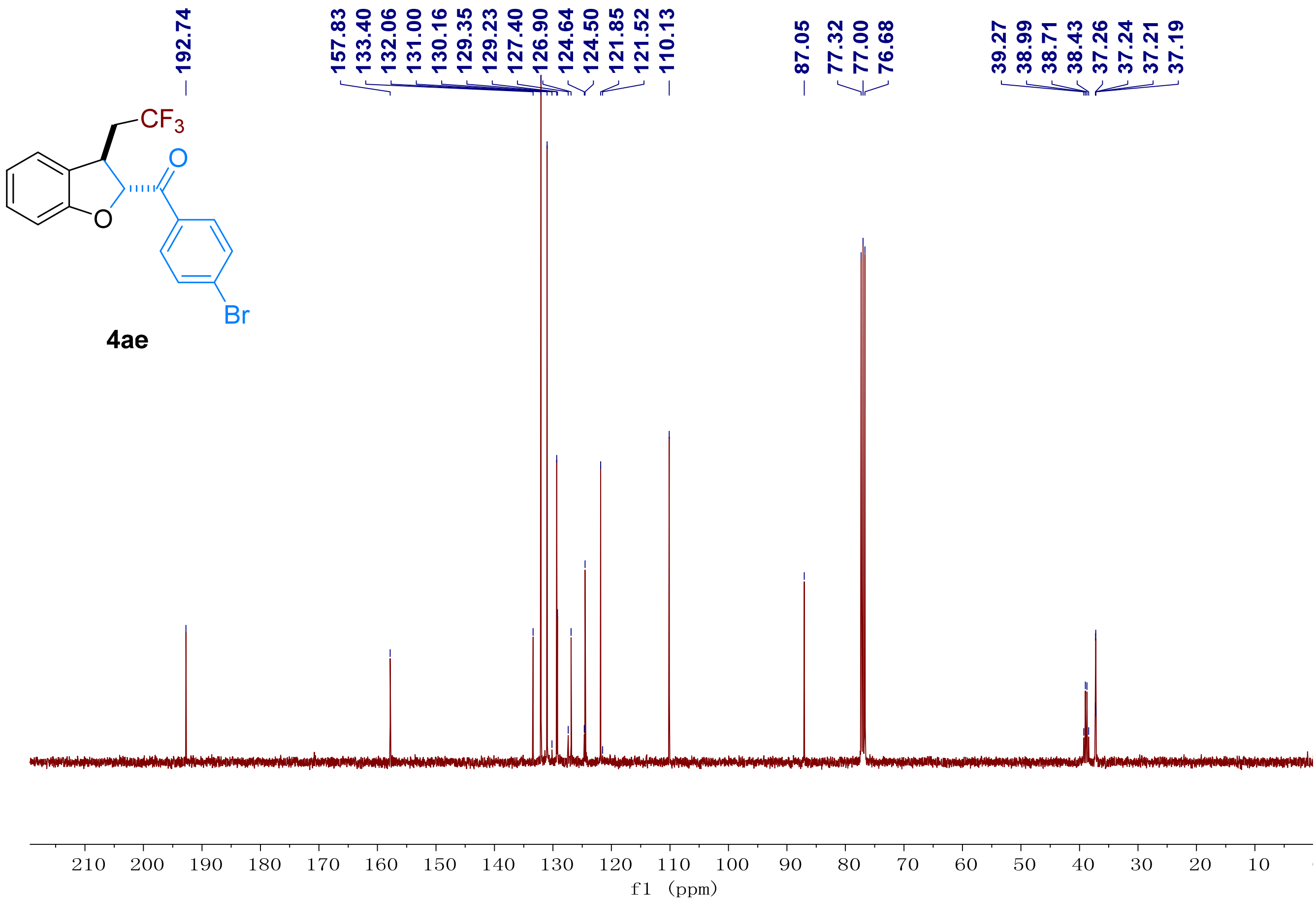


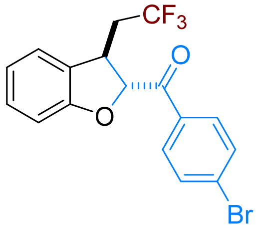



CF3
O
O
Ph
4ad
-64.09
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

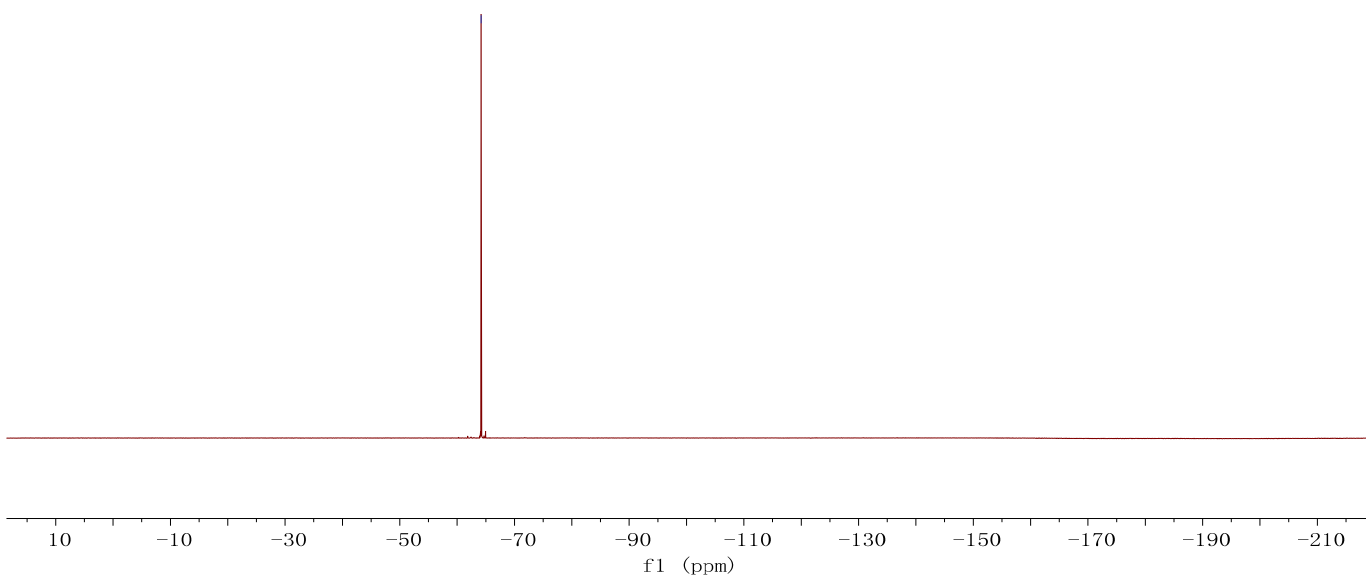
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4ae



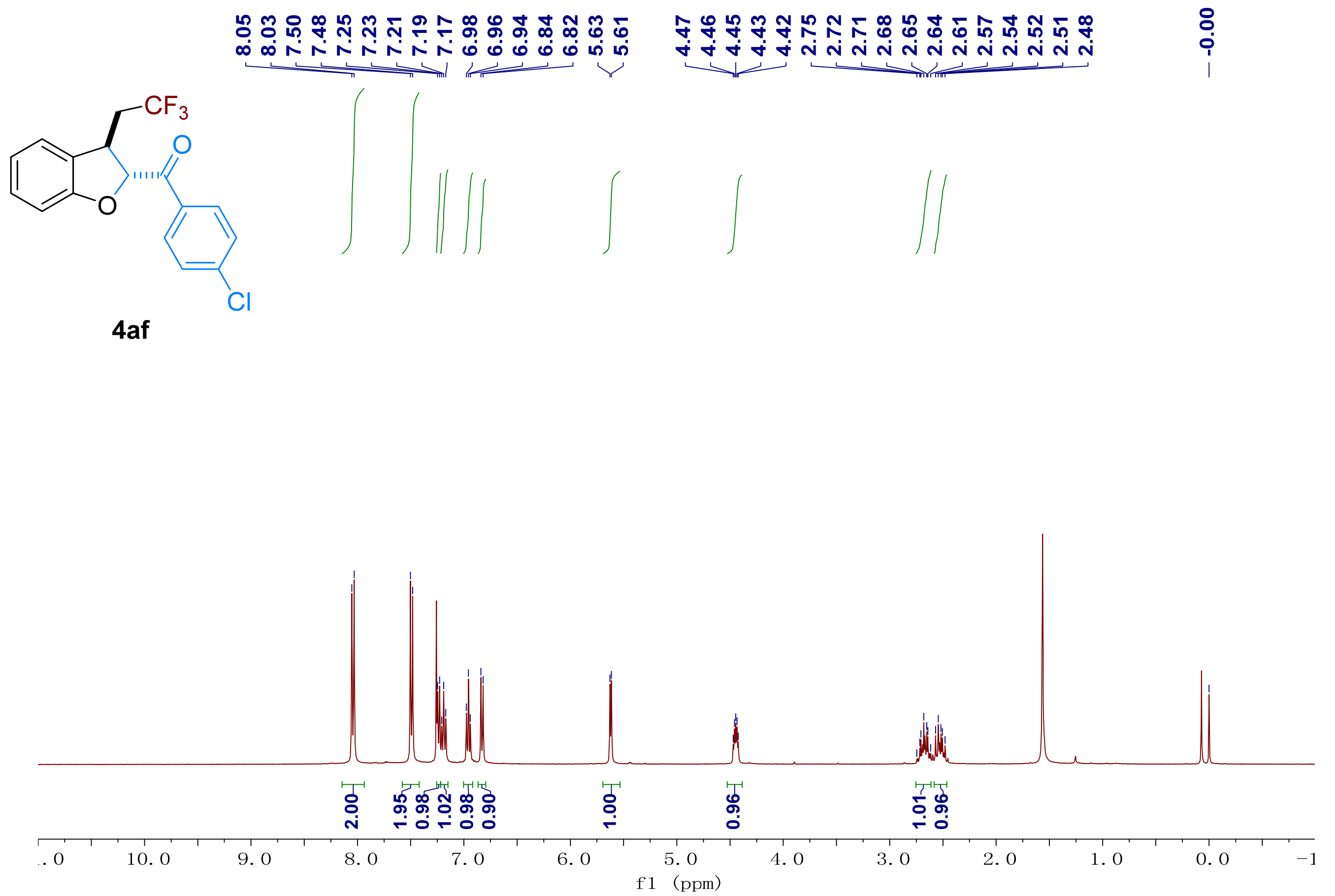


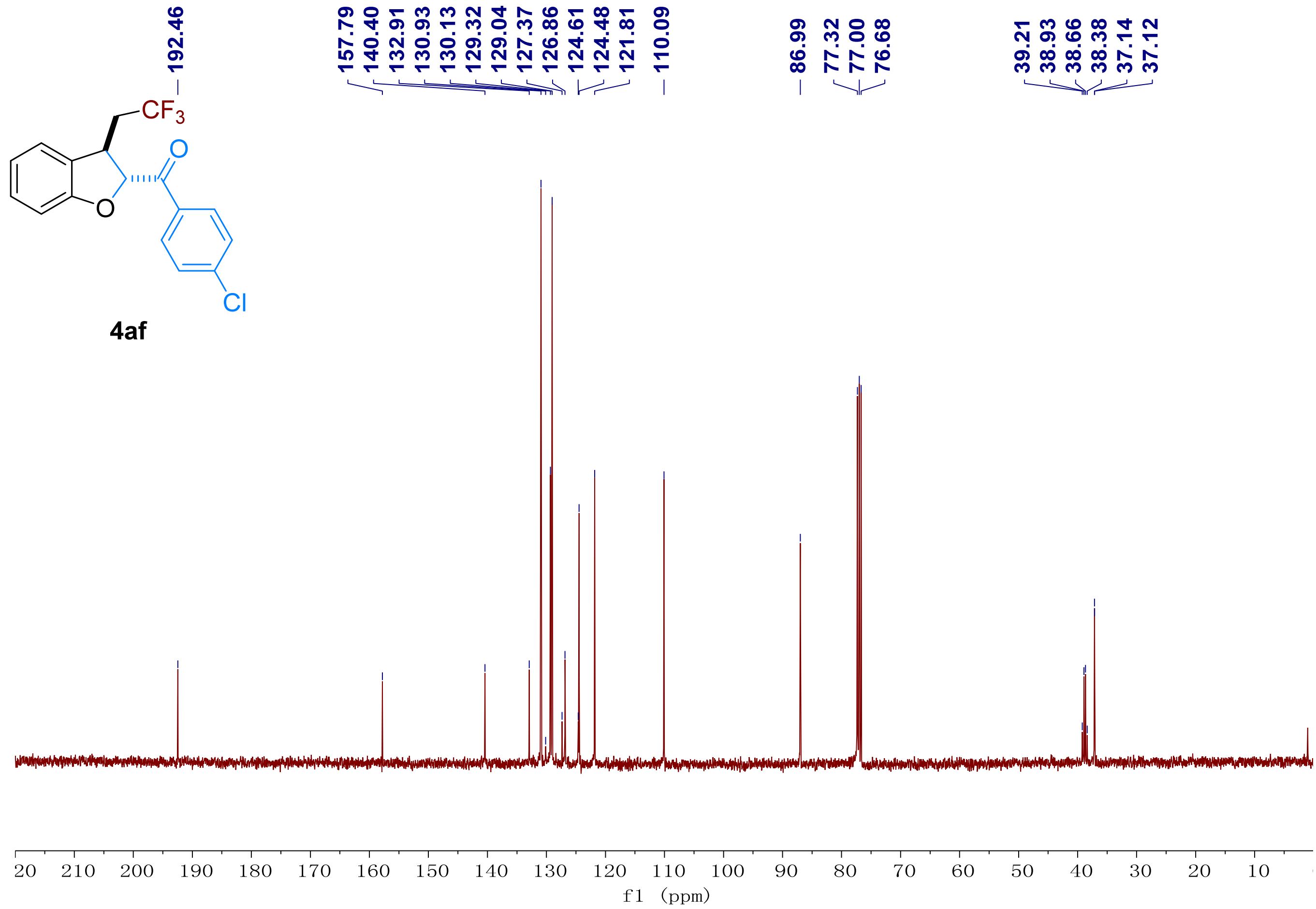


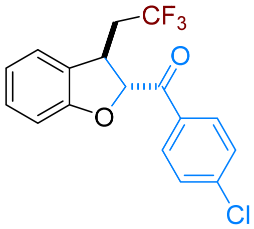
4ae



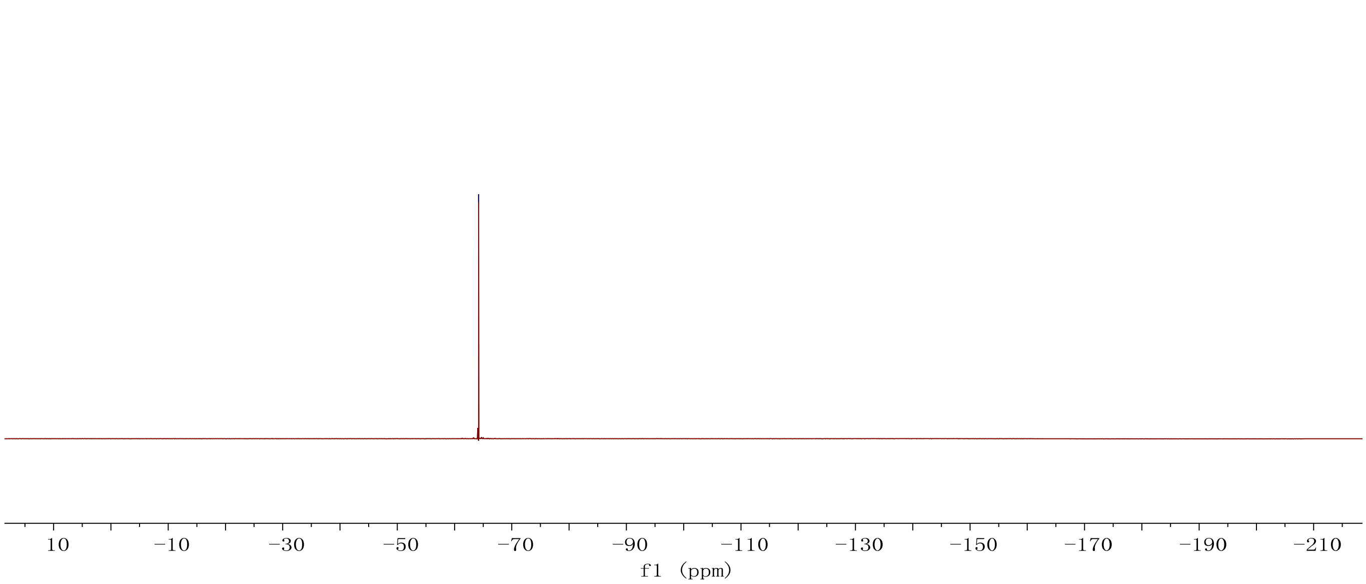
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4af



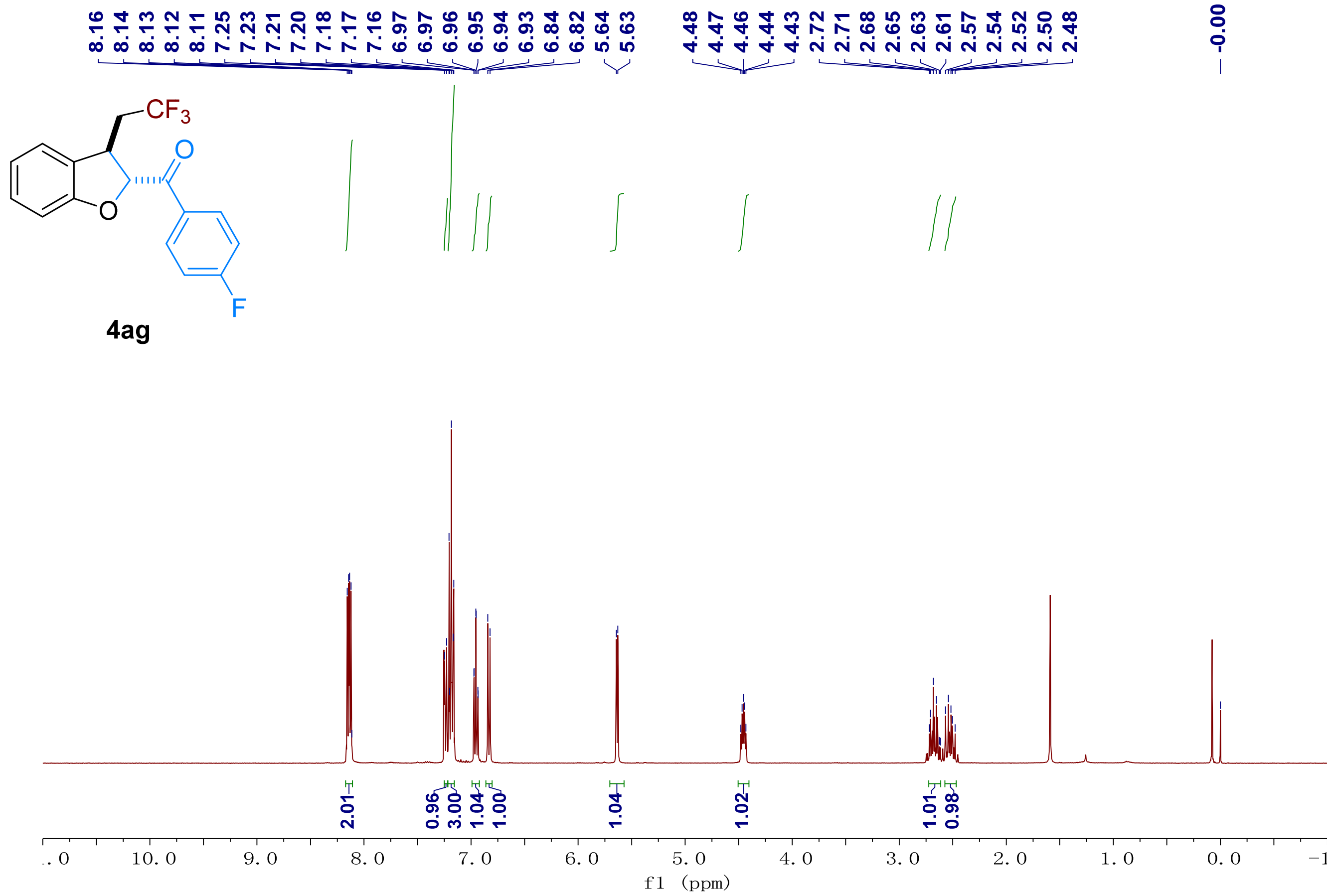


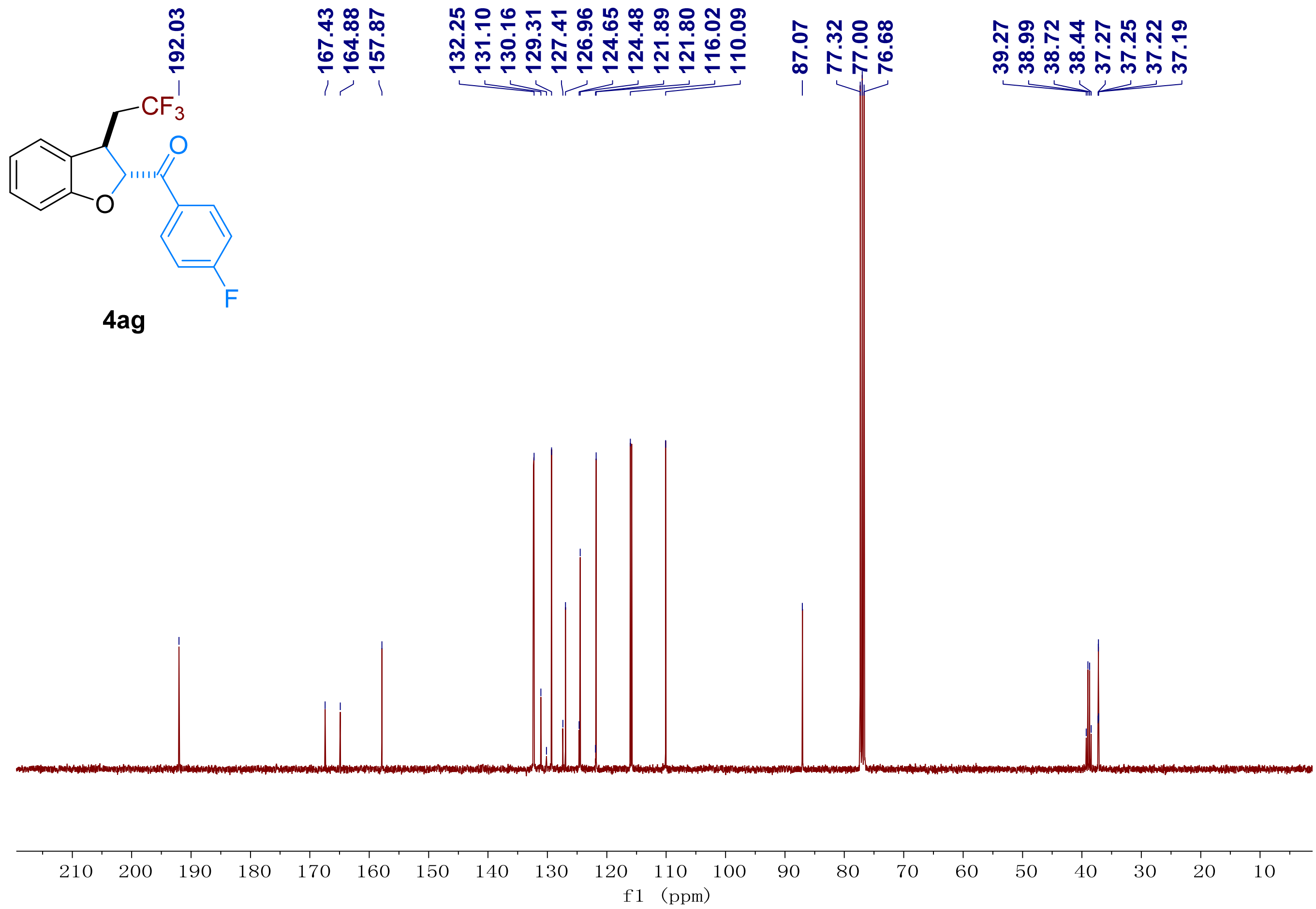


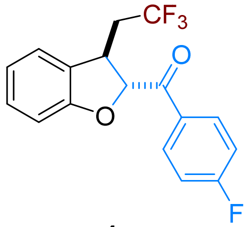
4af



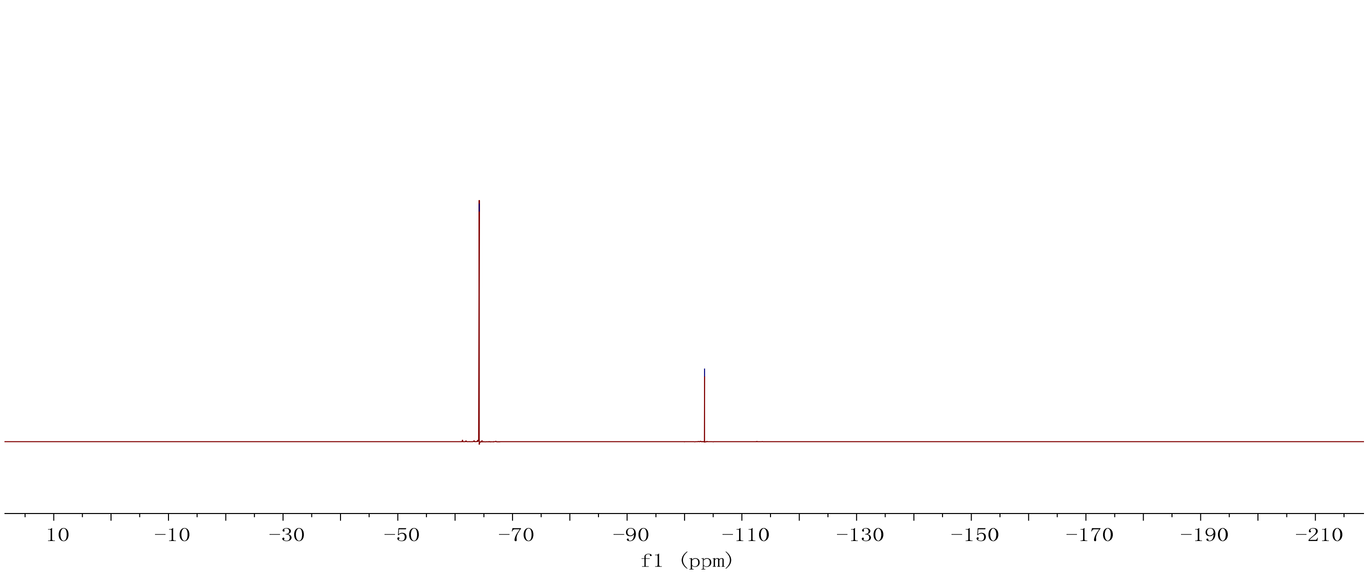
^{1}H NMR (400 MHz, CDCl$_3$), ^{13}C NMR (100 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 4ag



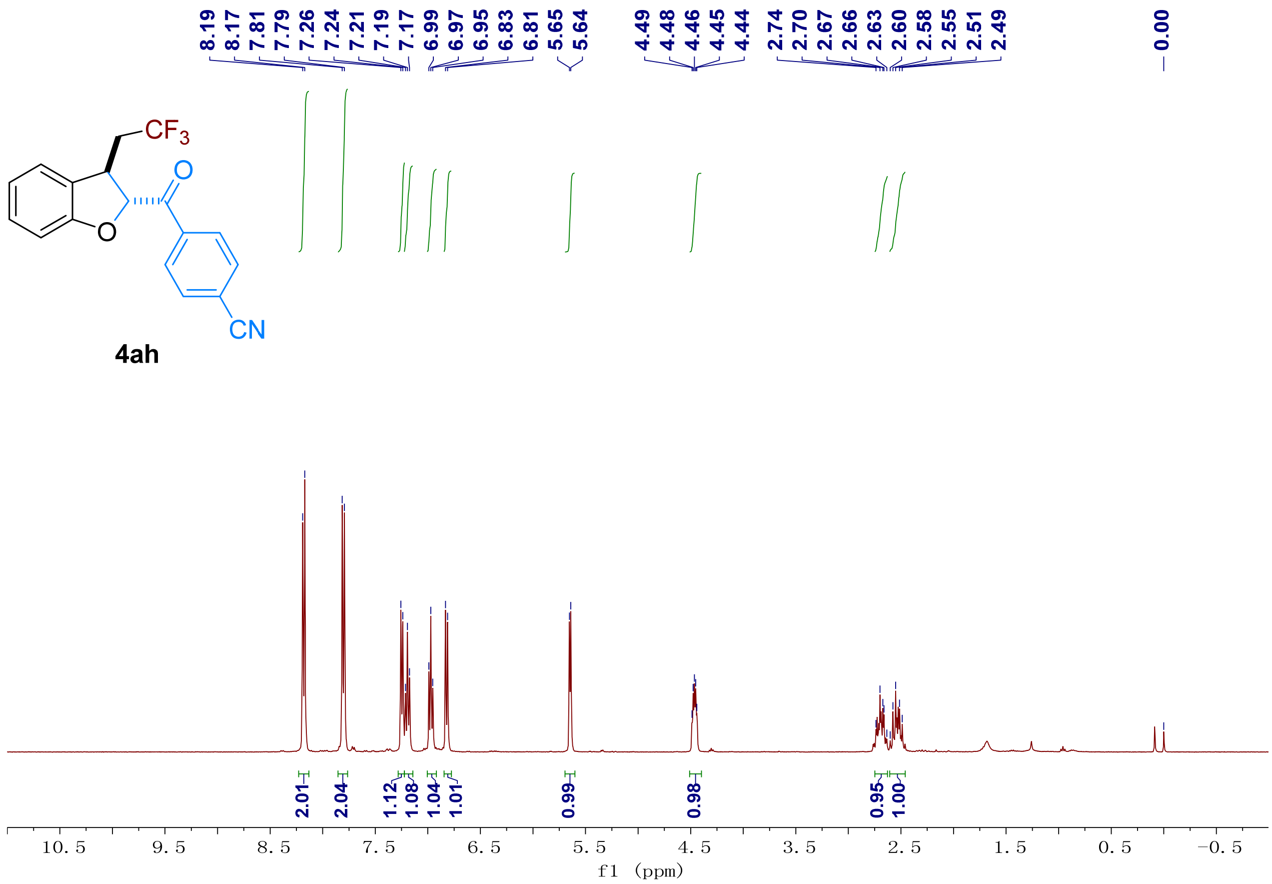


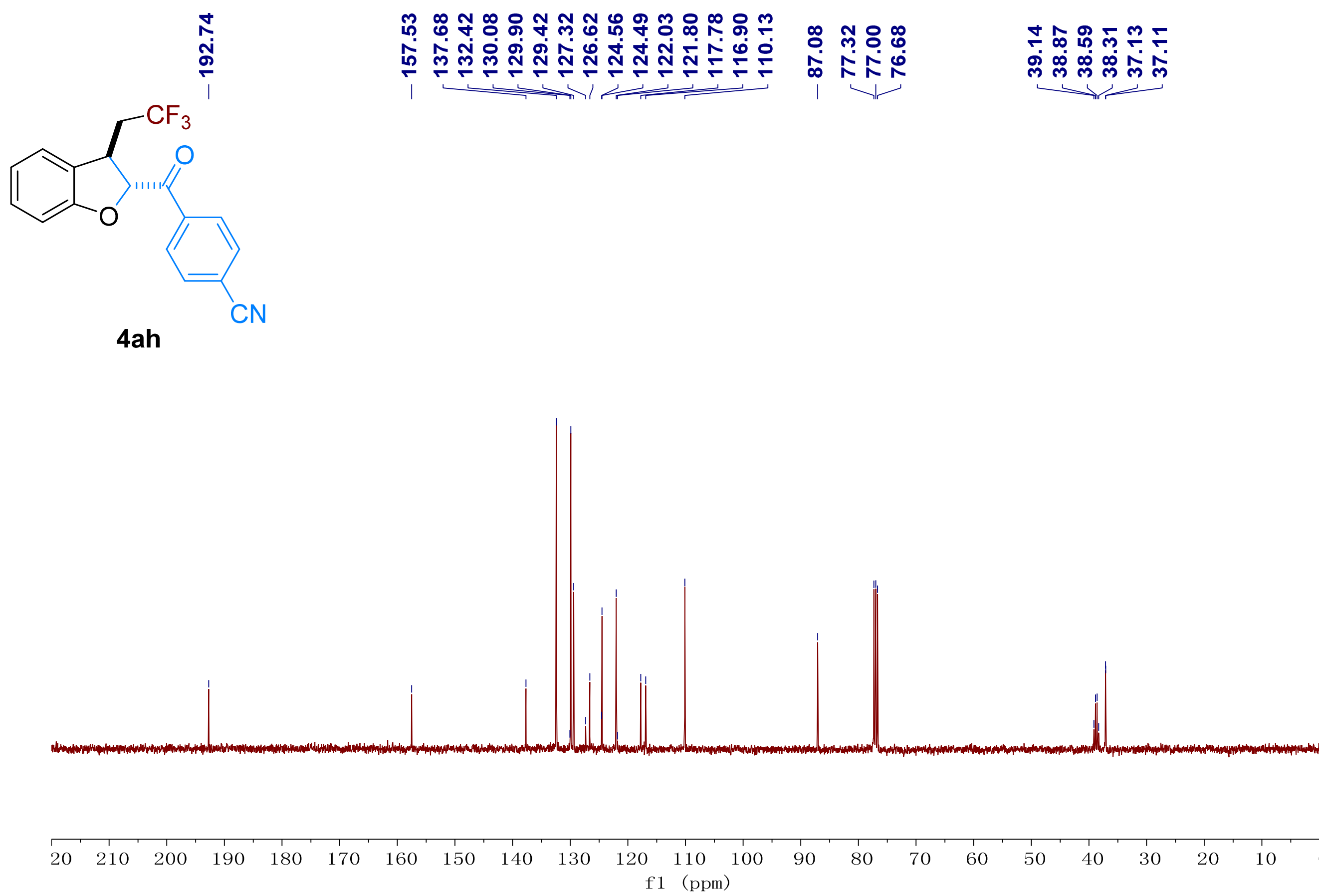

CF3
O
O
F

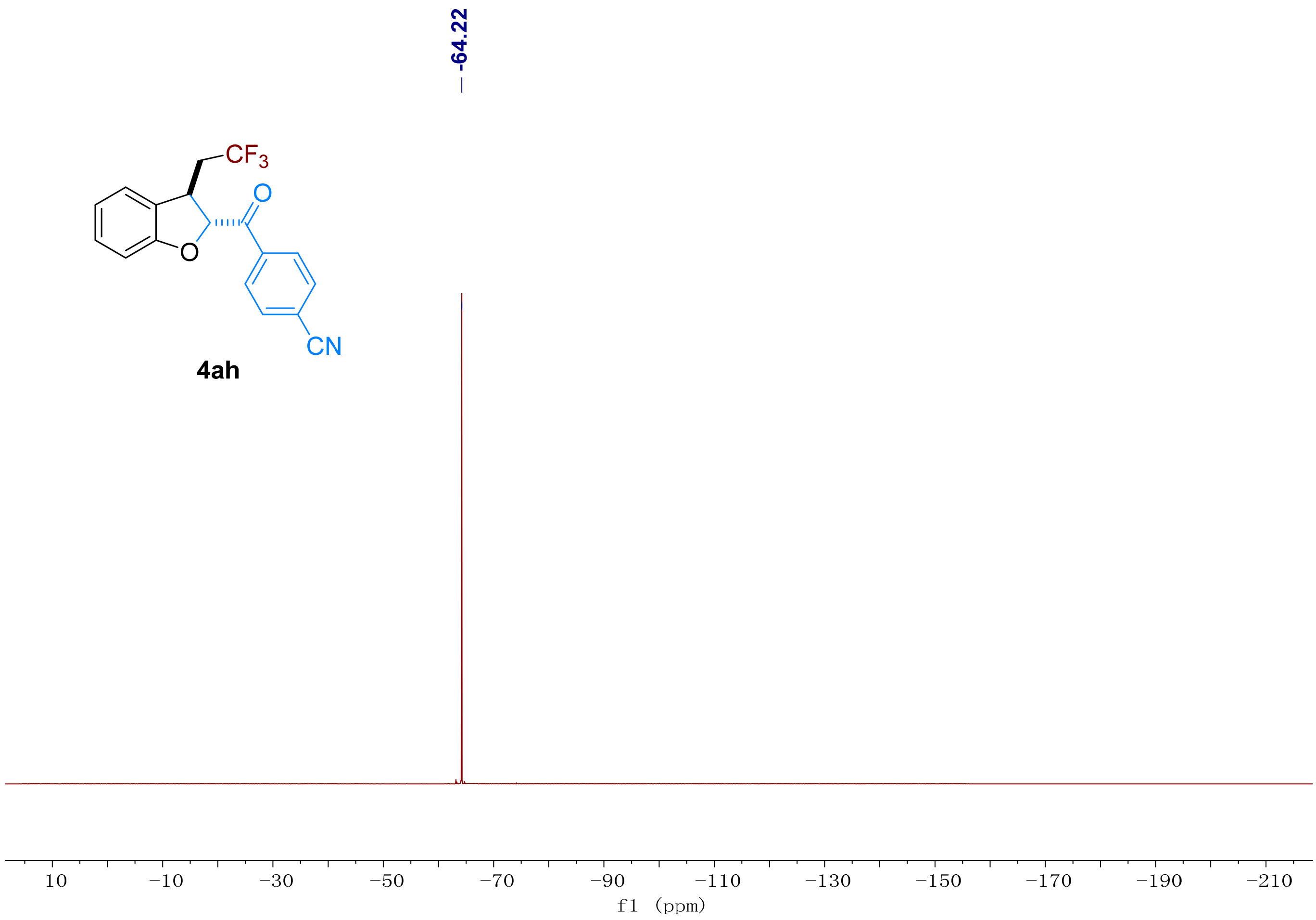
4ag


-64.20
-103.48
10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)

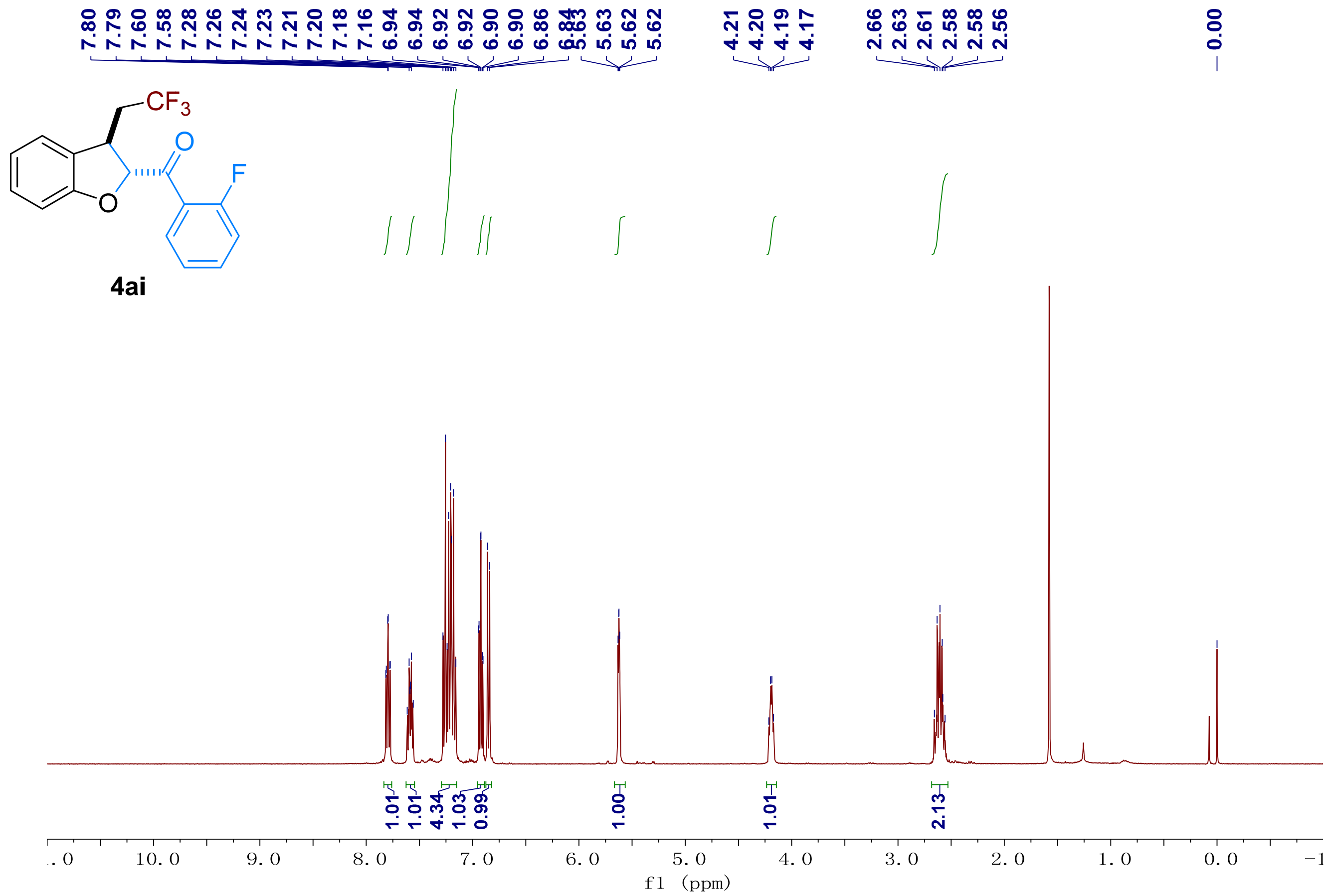
[1]H NMR (400 MHz, $CDCl_3$), [13]C NMR (100 MHz, $CDCl_3$) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ah

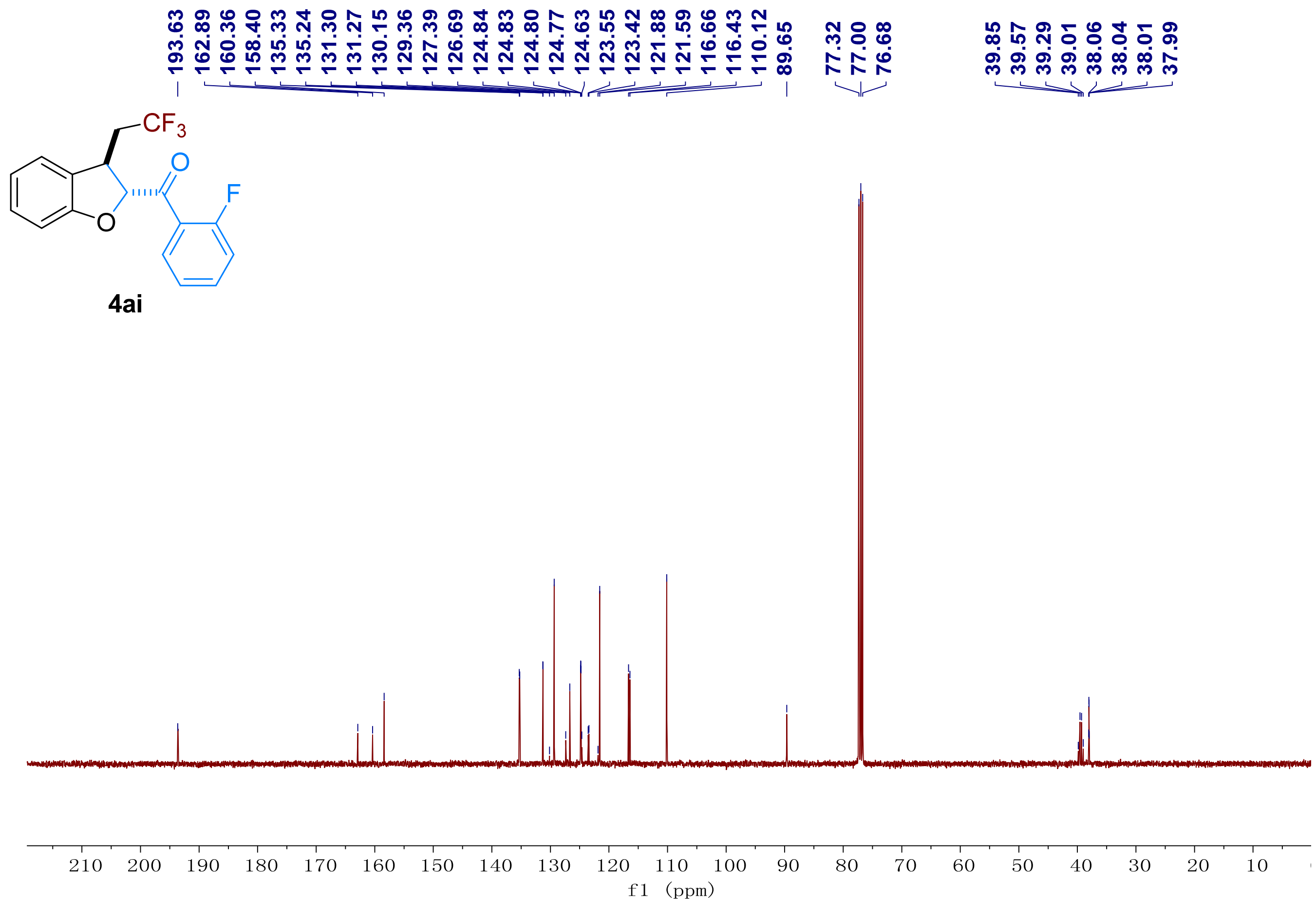


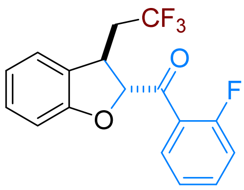



-64.22
CF3
O
CN
4ah
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

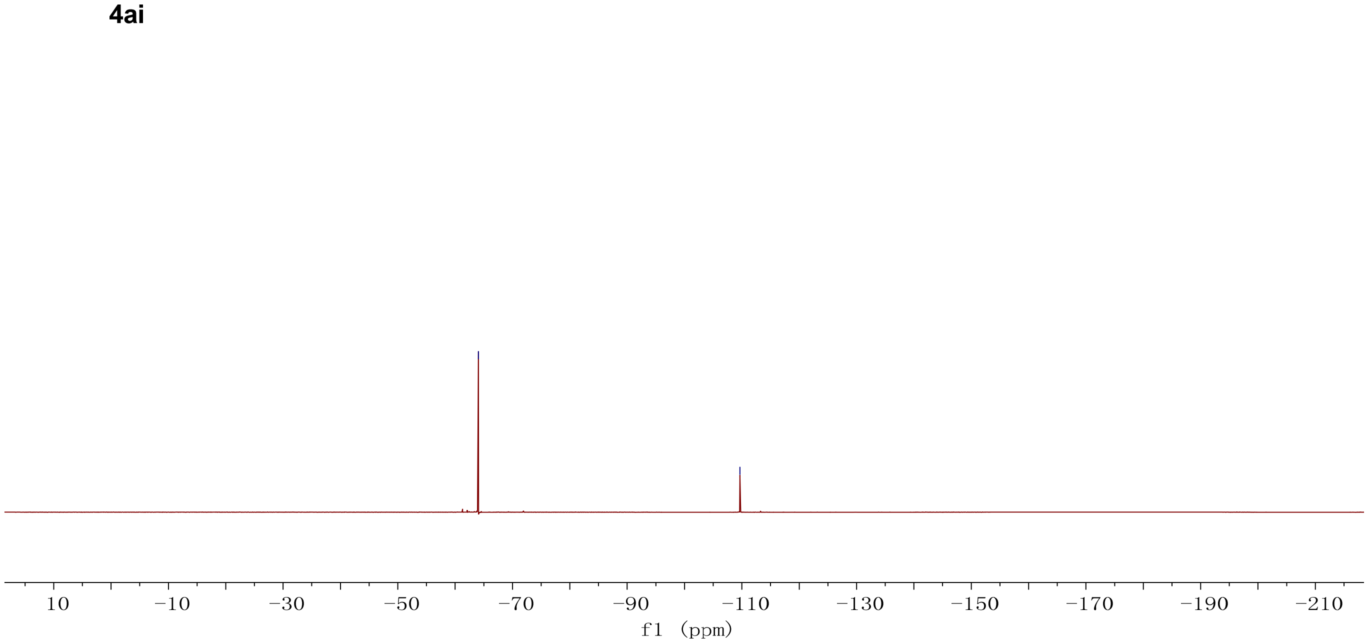
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ai



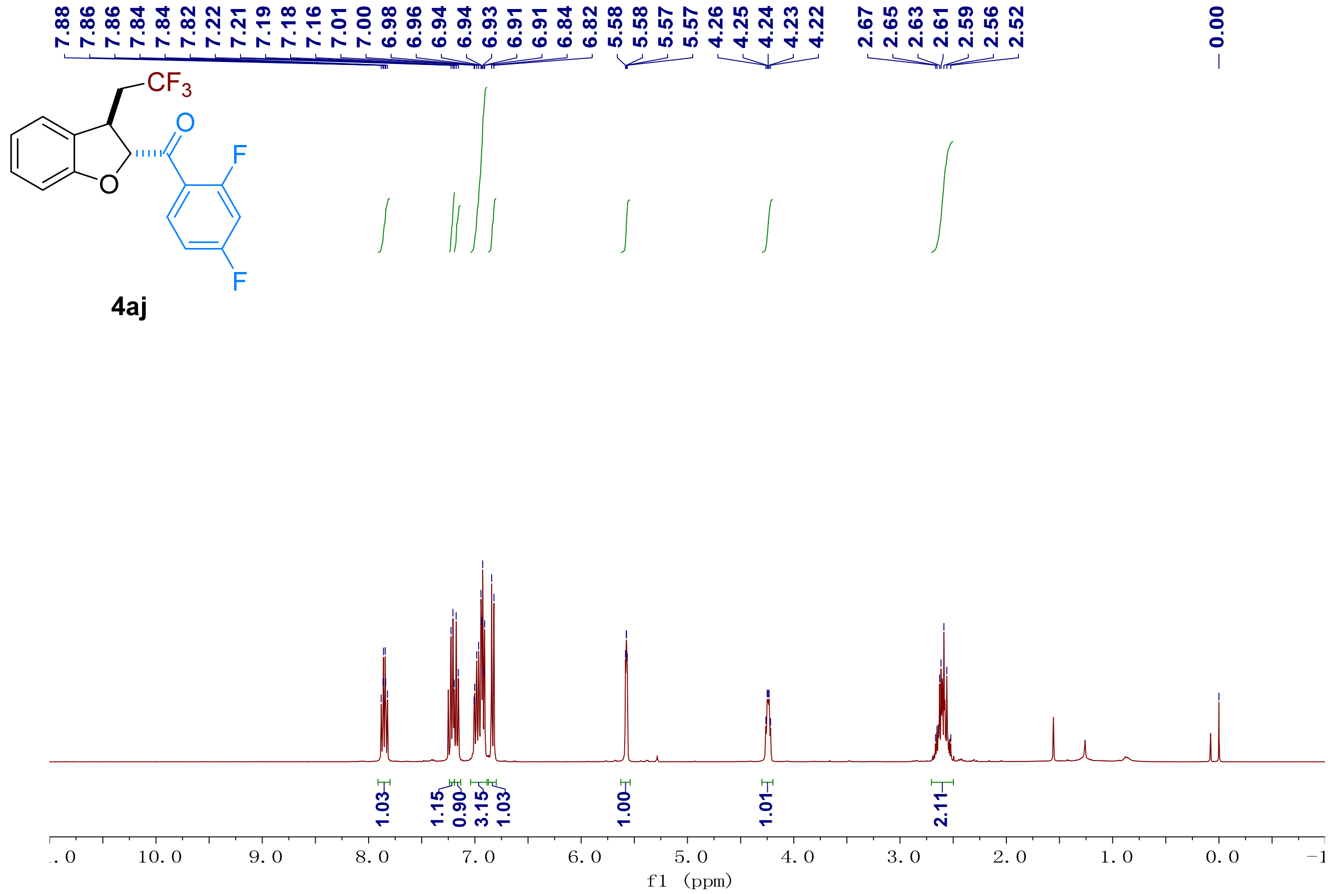


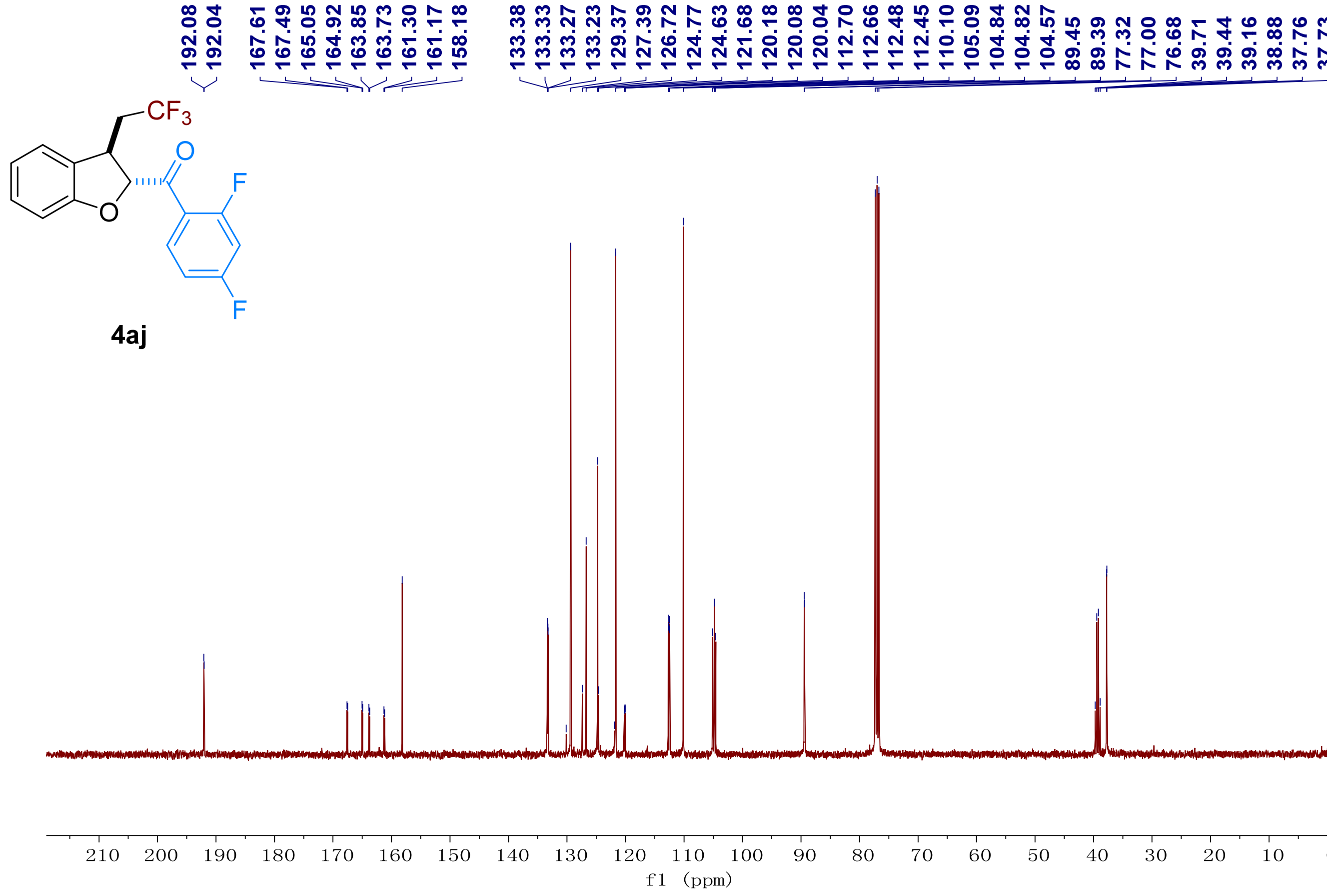

CF3
O
F
O

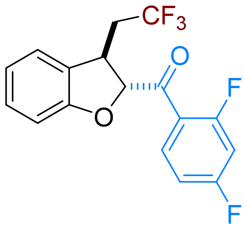
4ai


-64.06
-109.65
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

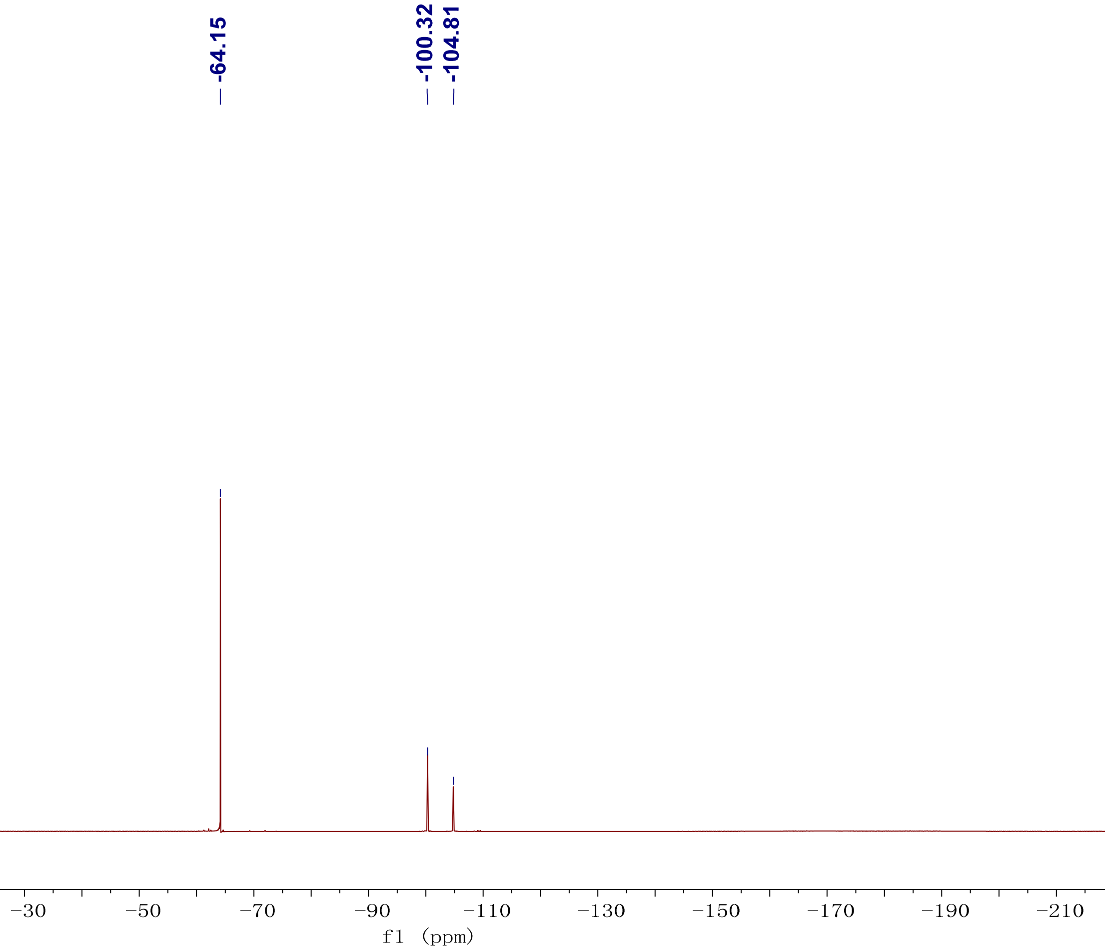
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4aj



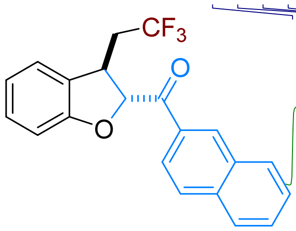



CF3
O
F
O
F

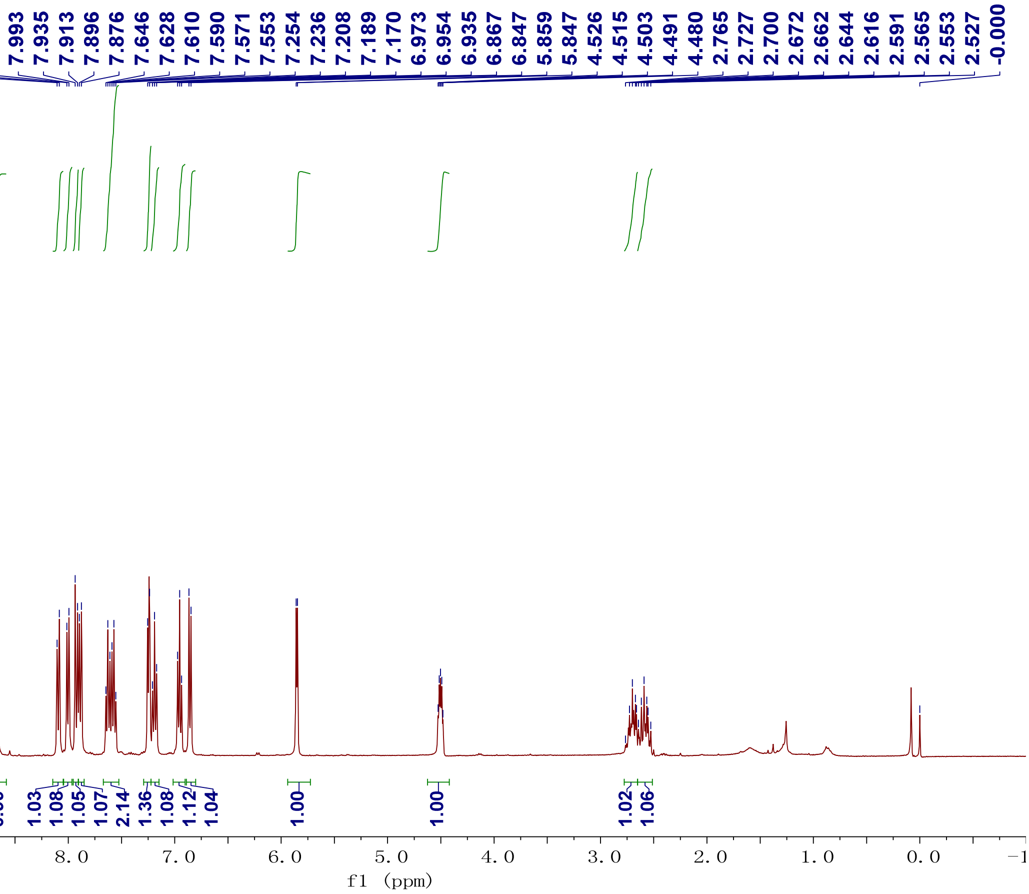
4aj

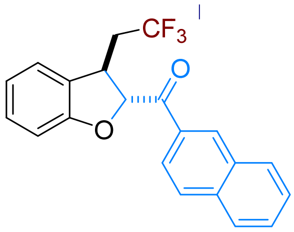

-64.15
-100.32
-104.81
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

[1]H NMR (400 MHz, $CDCl_3$), [13]C NMR (100 MHz, $CDCl_3$) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ak

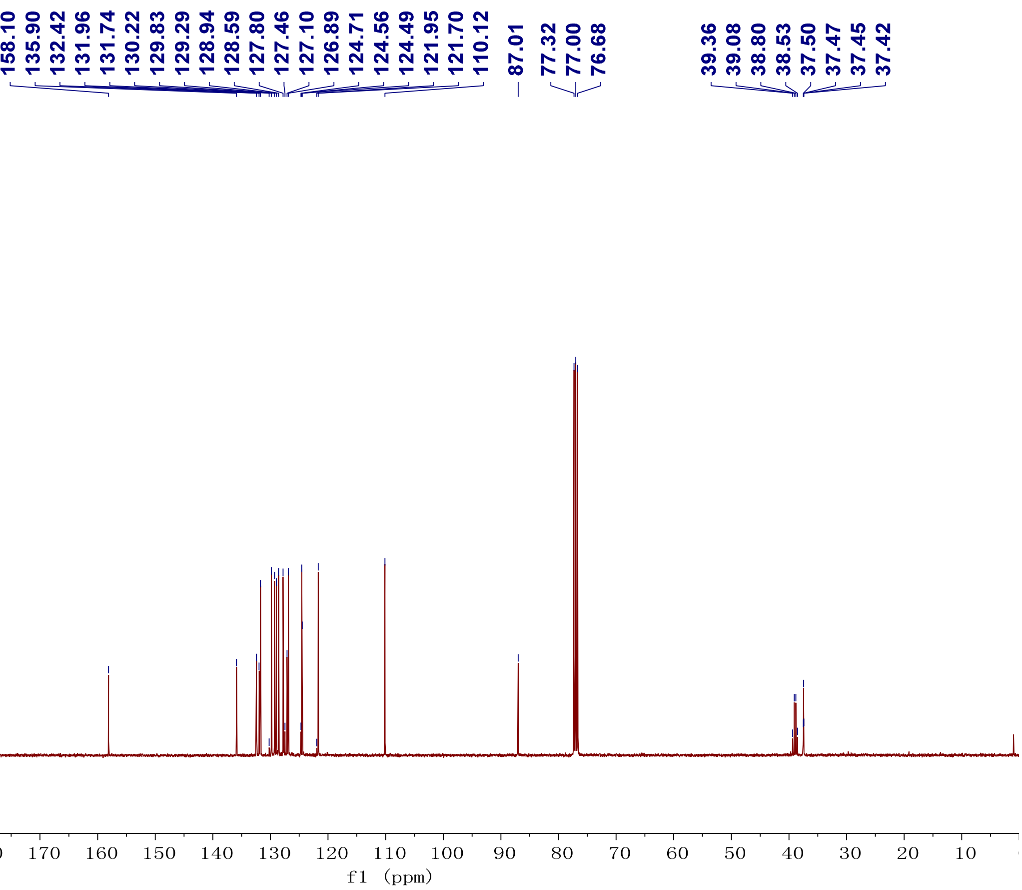


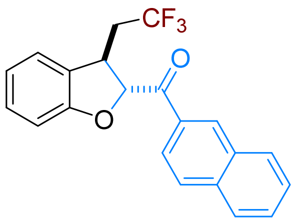
4ak



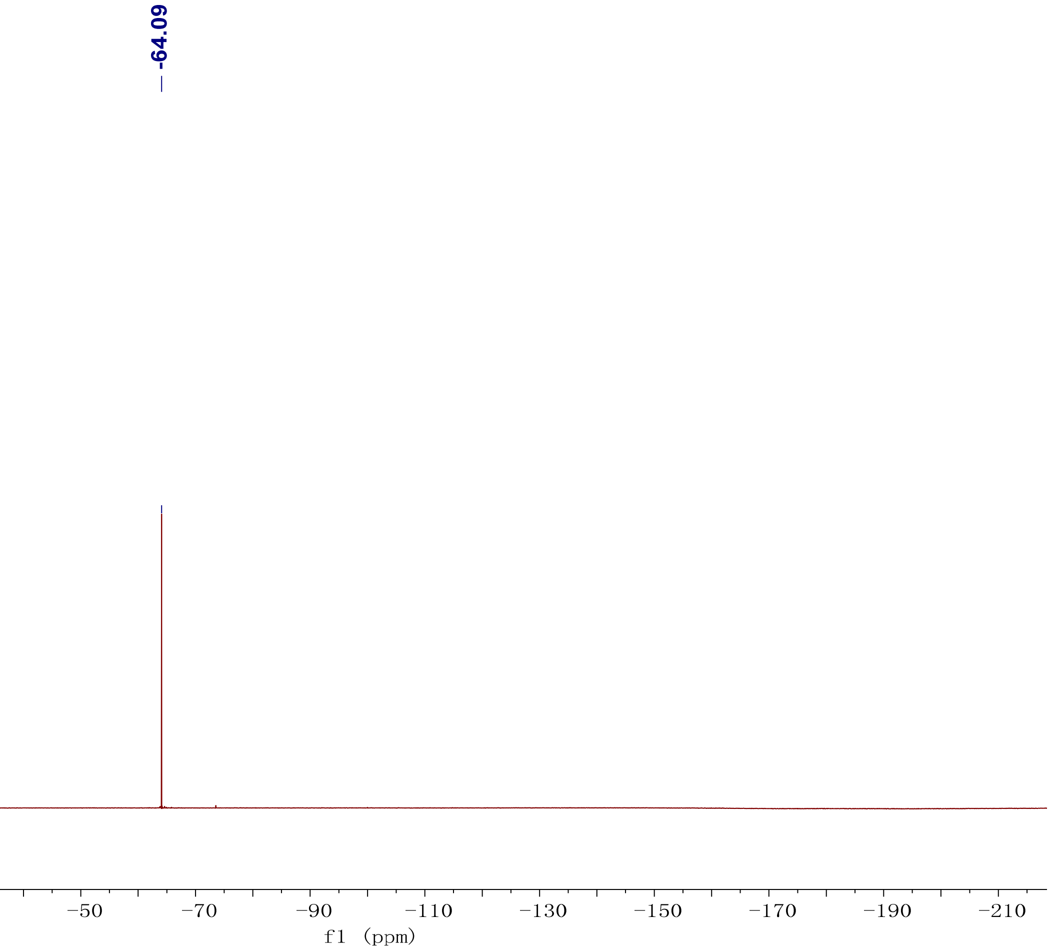


4ak

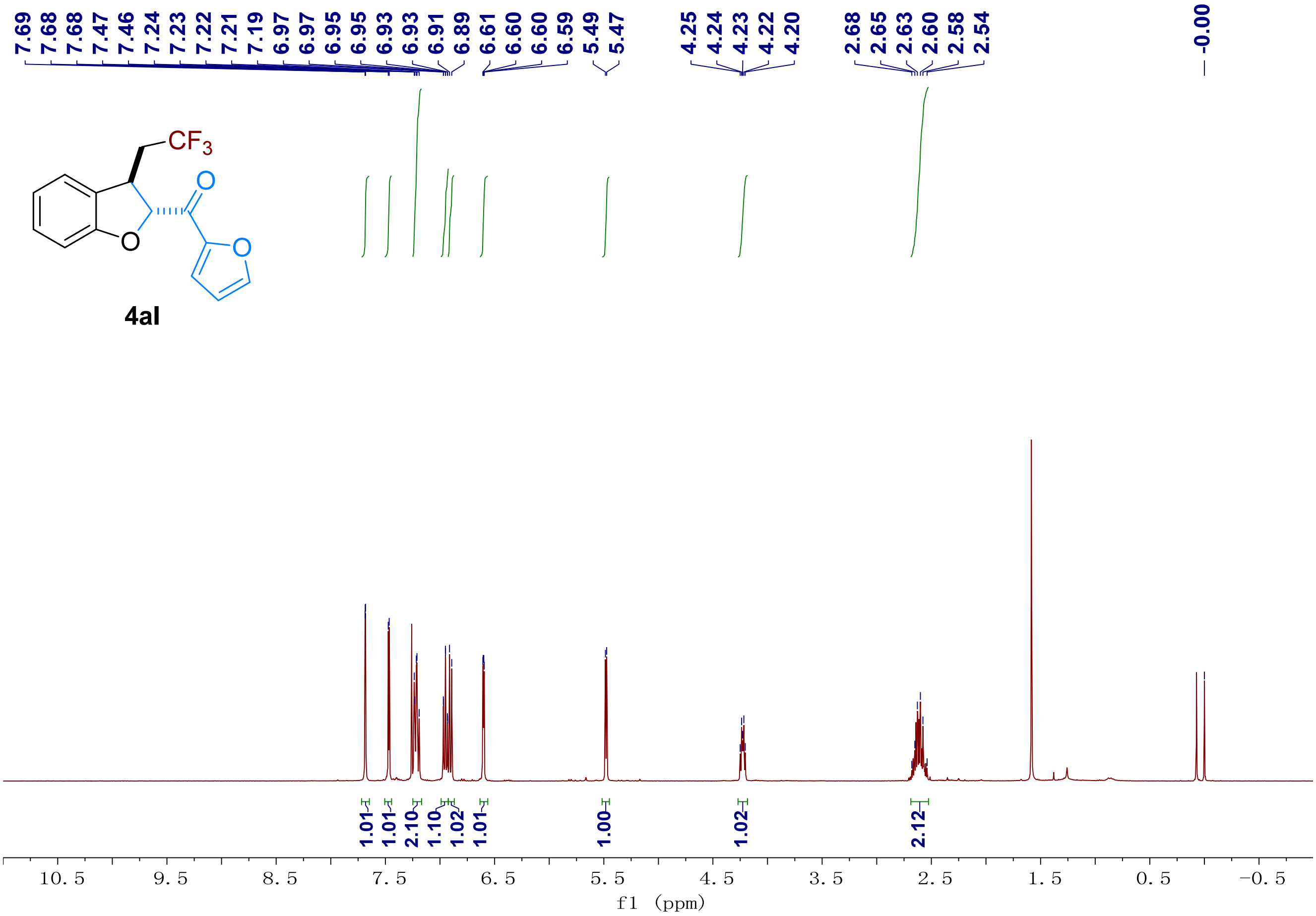


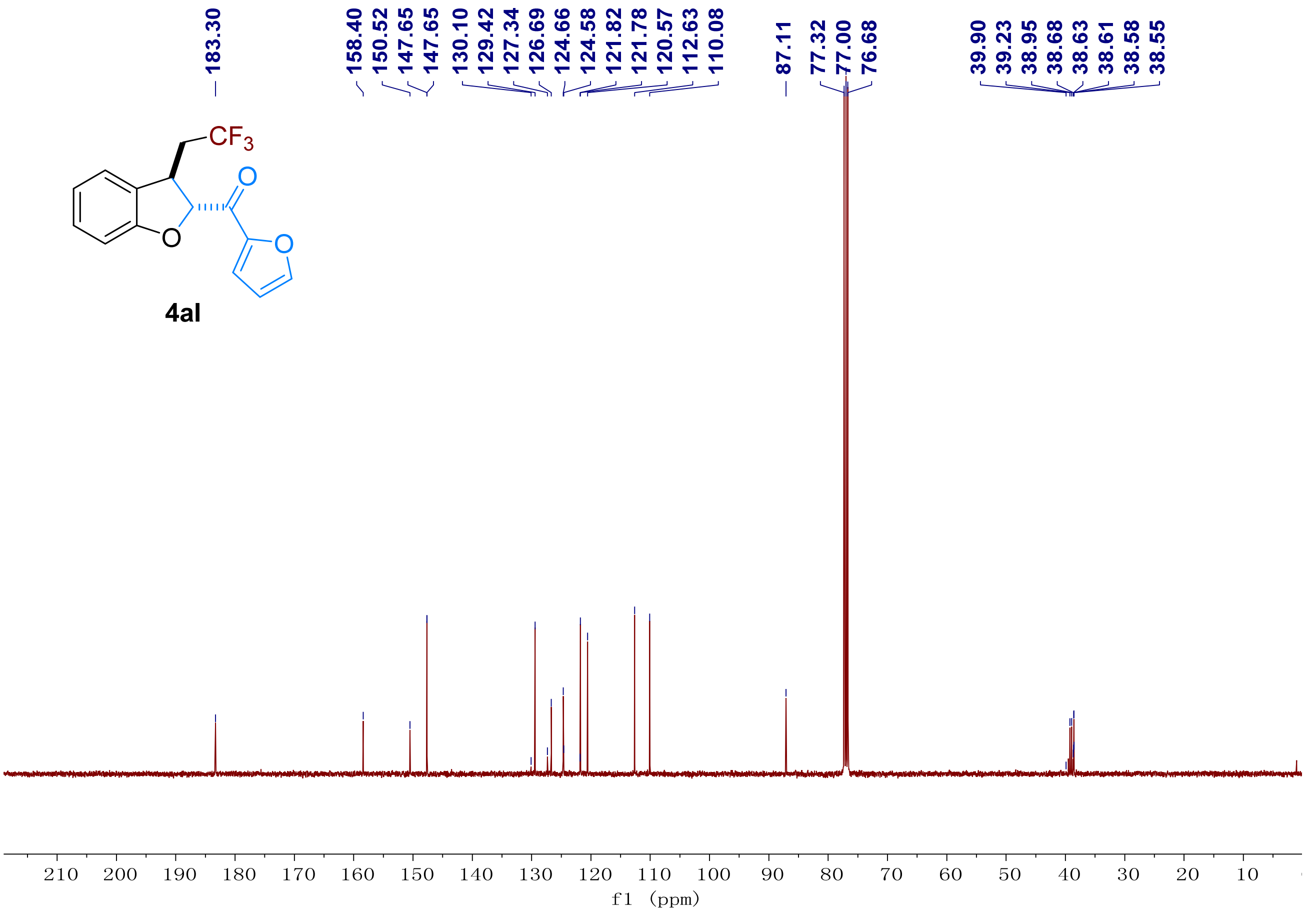


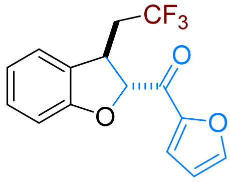
4ak



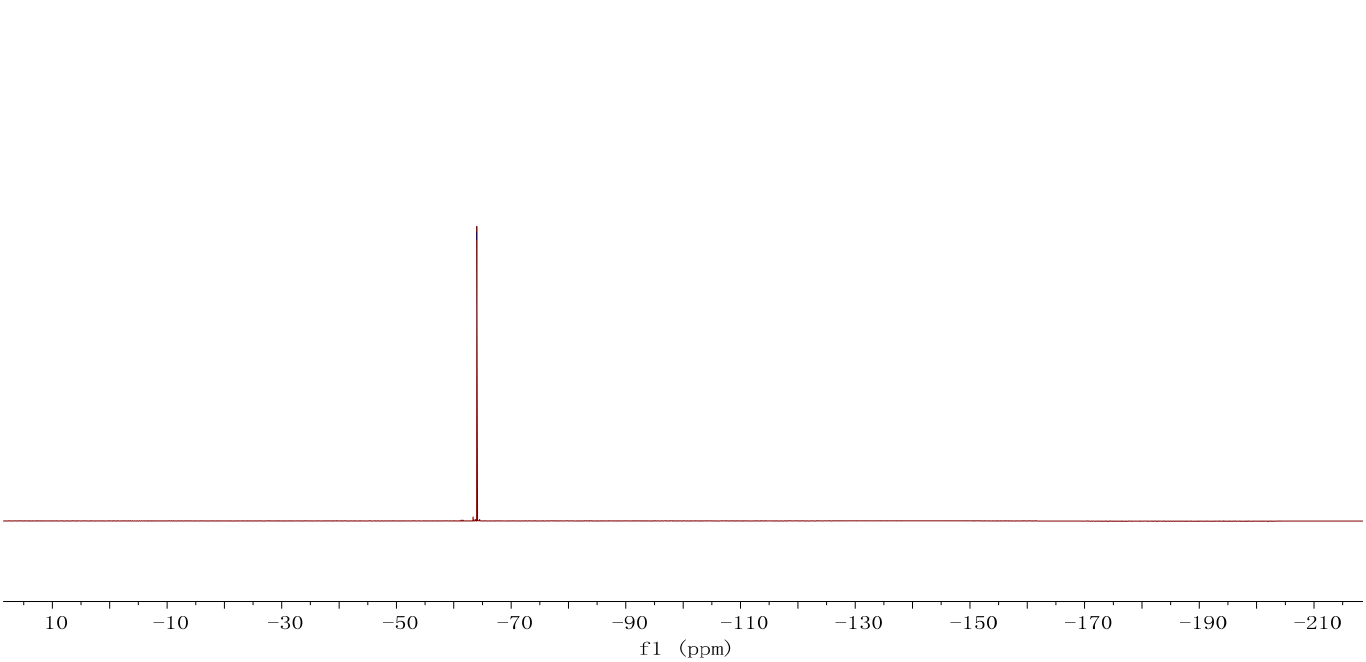
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4al



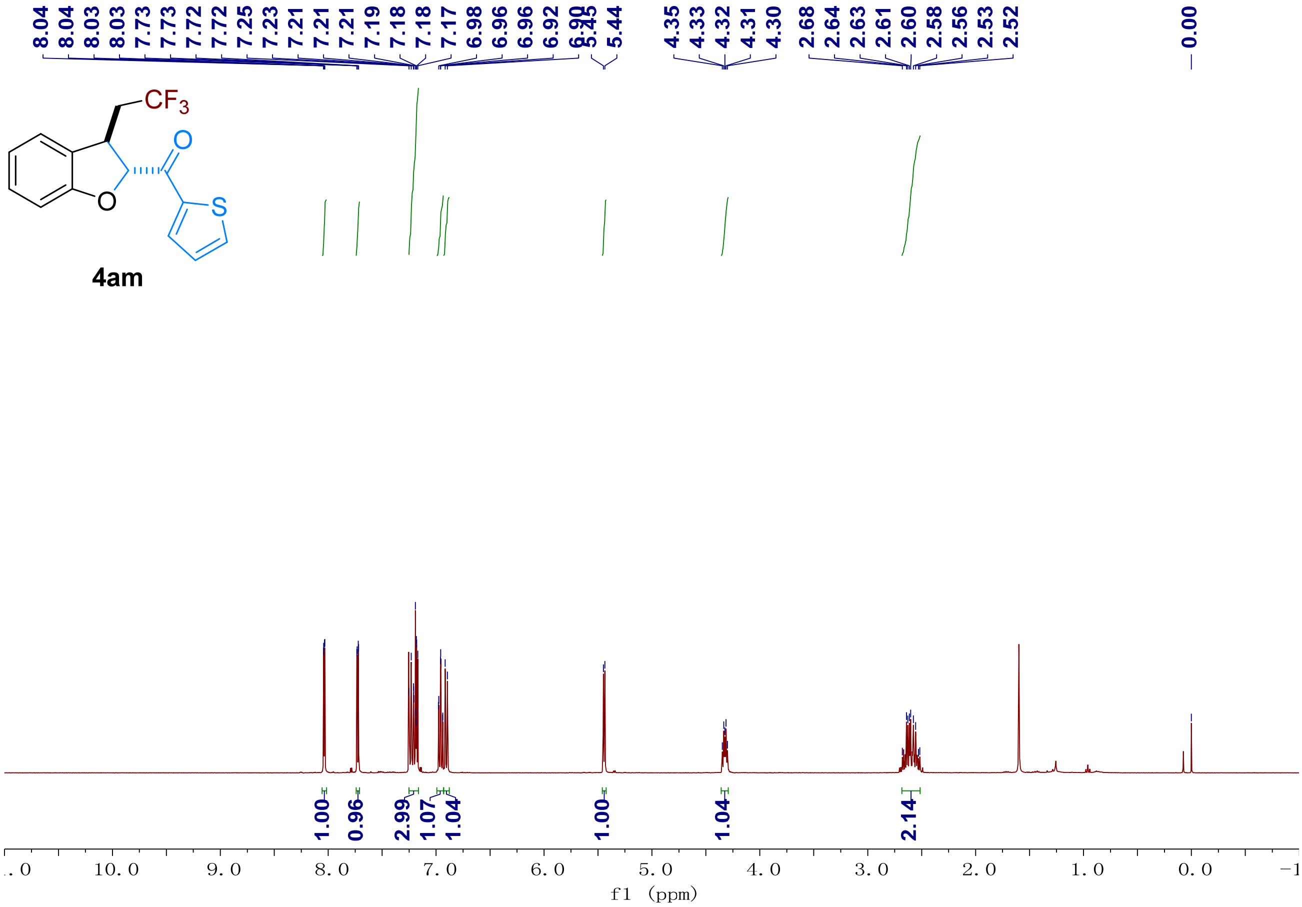


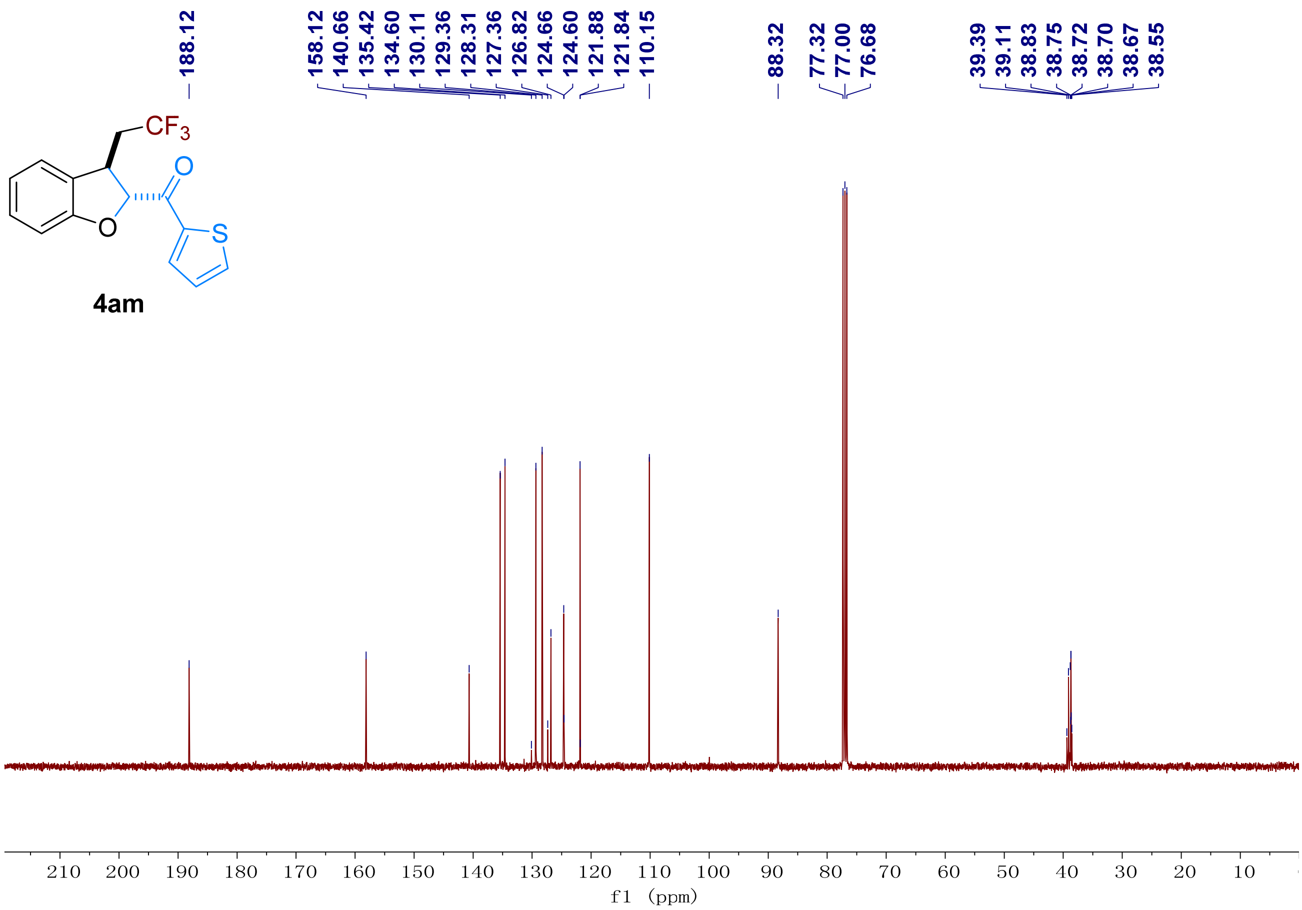


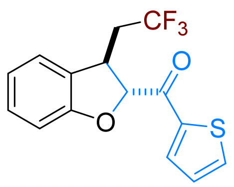
4al



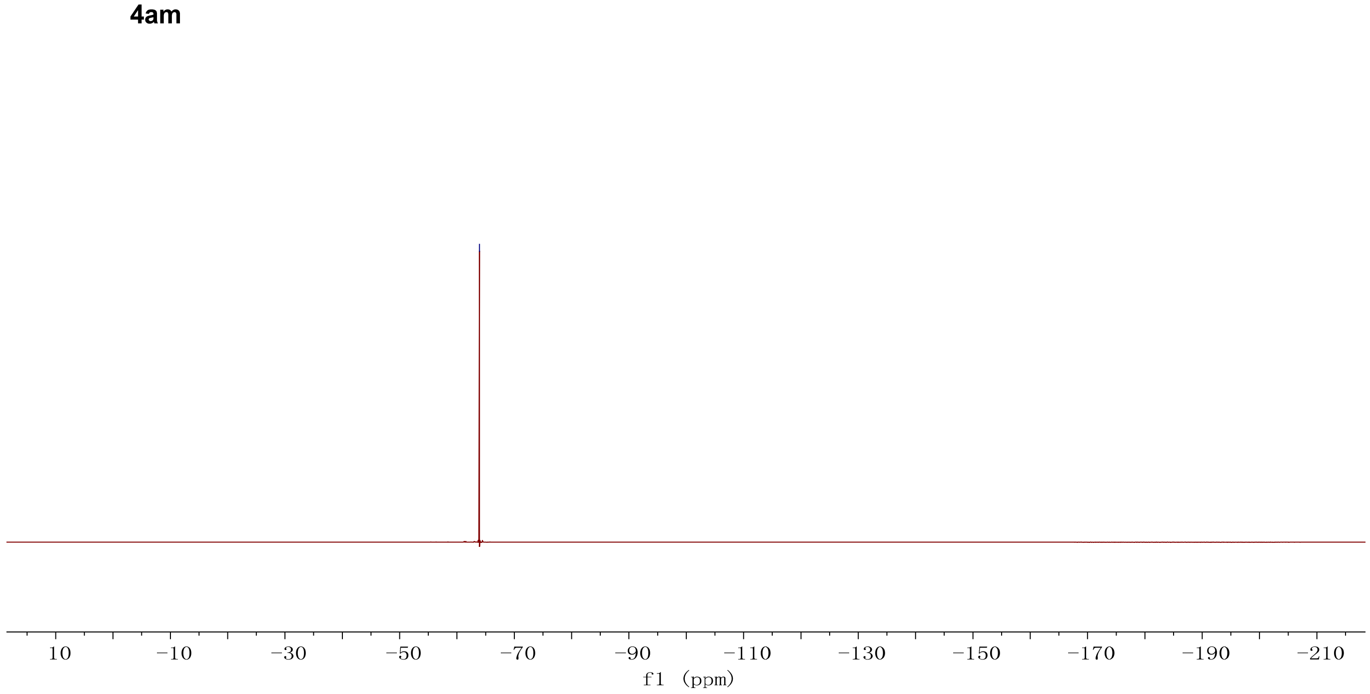
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 4am



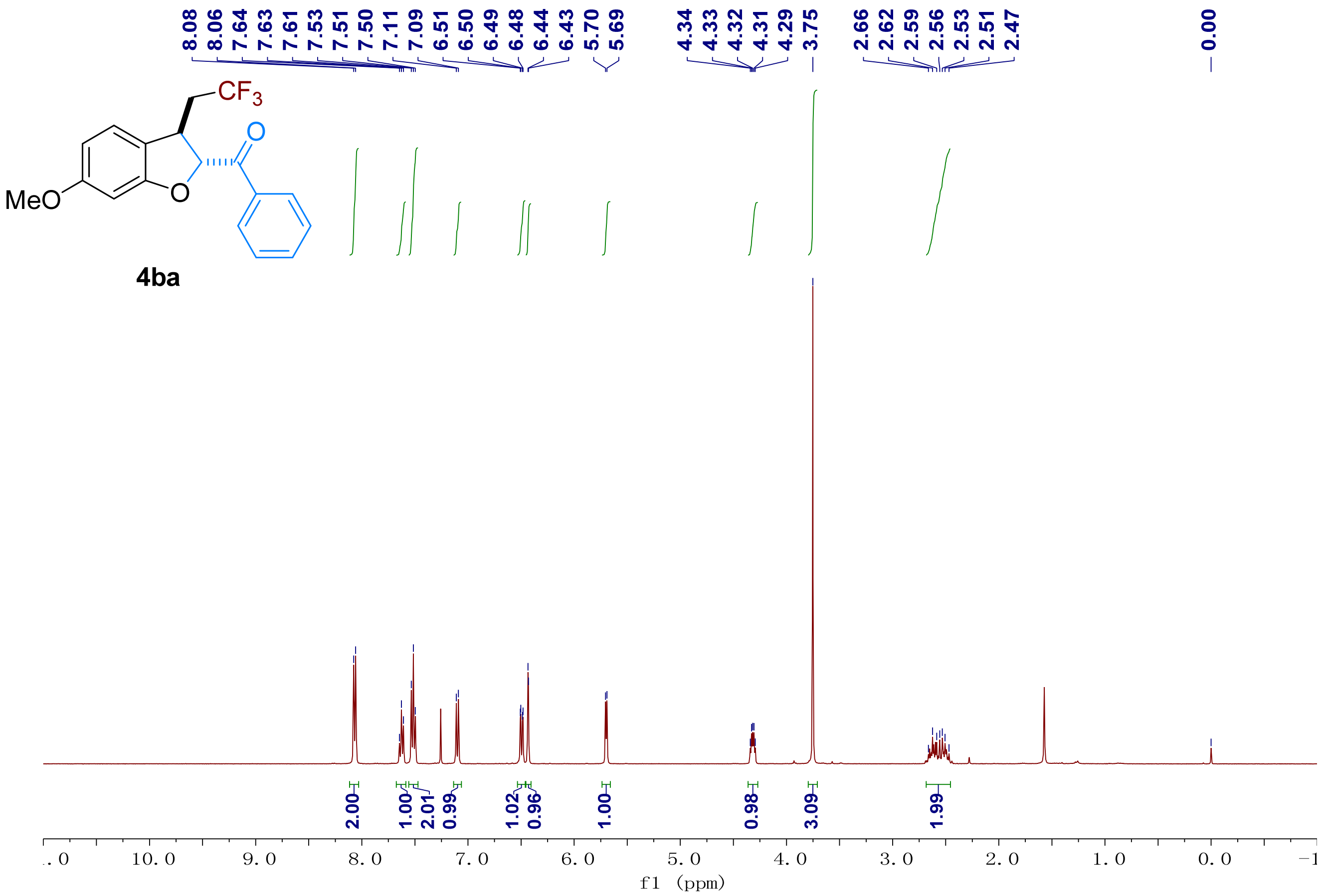


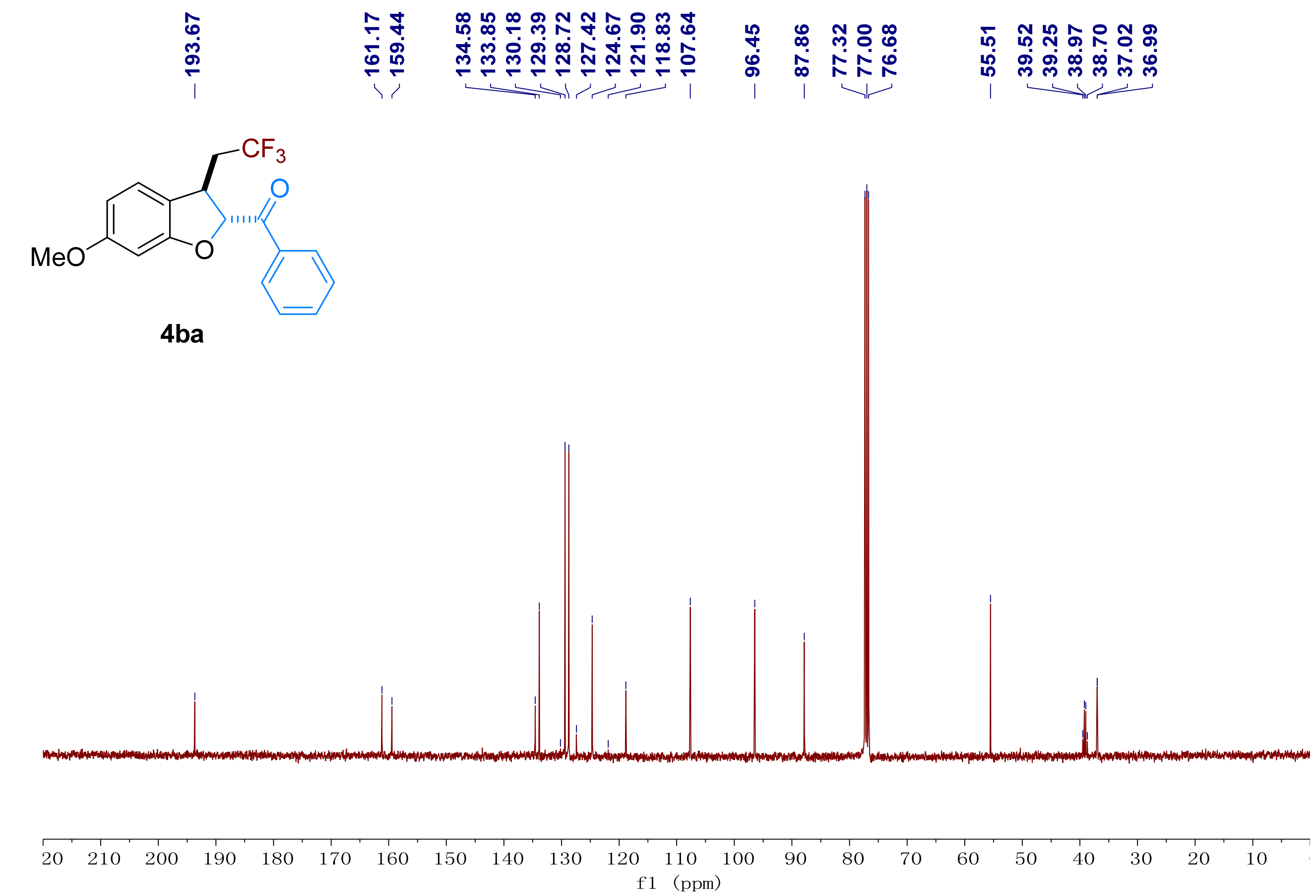


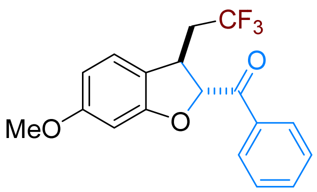
4am



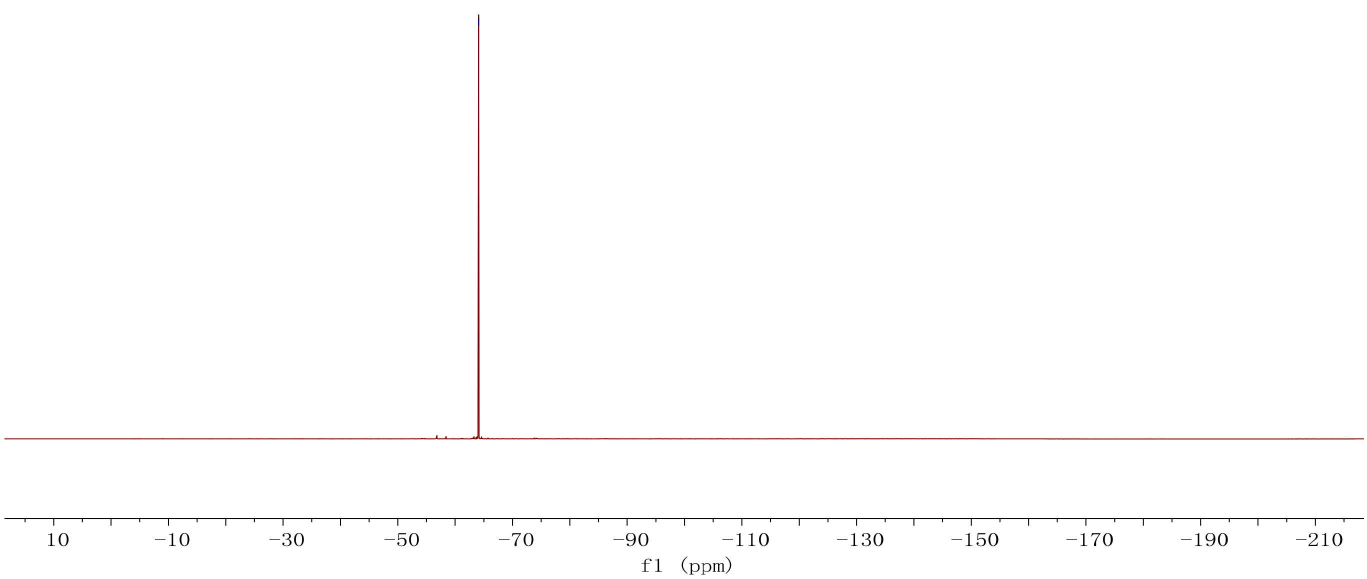
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ba



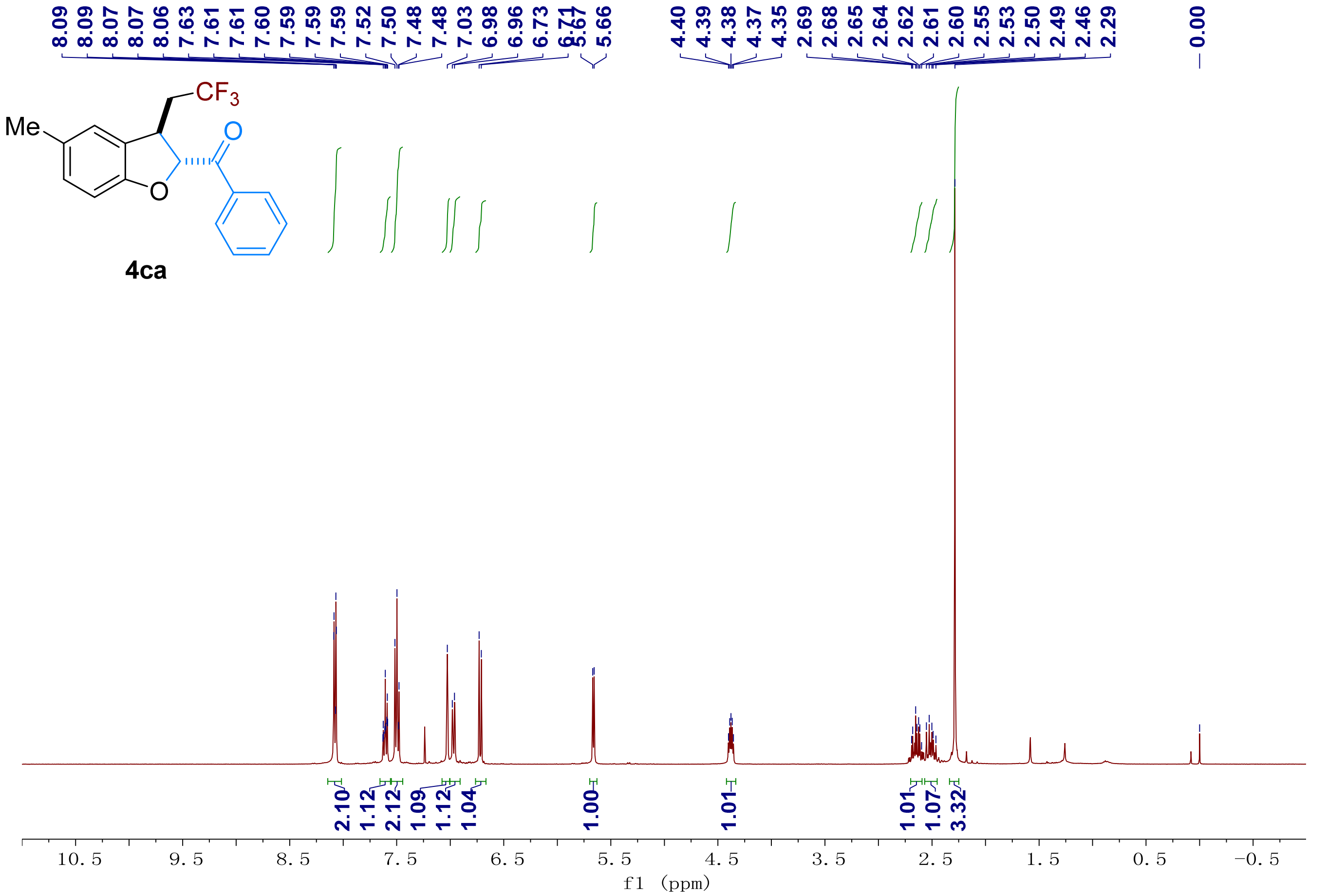


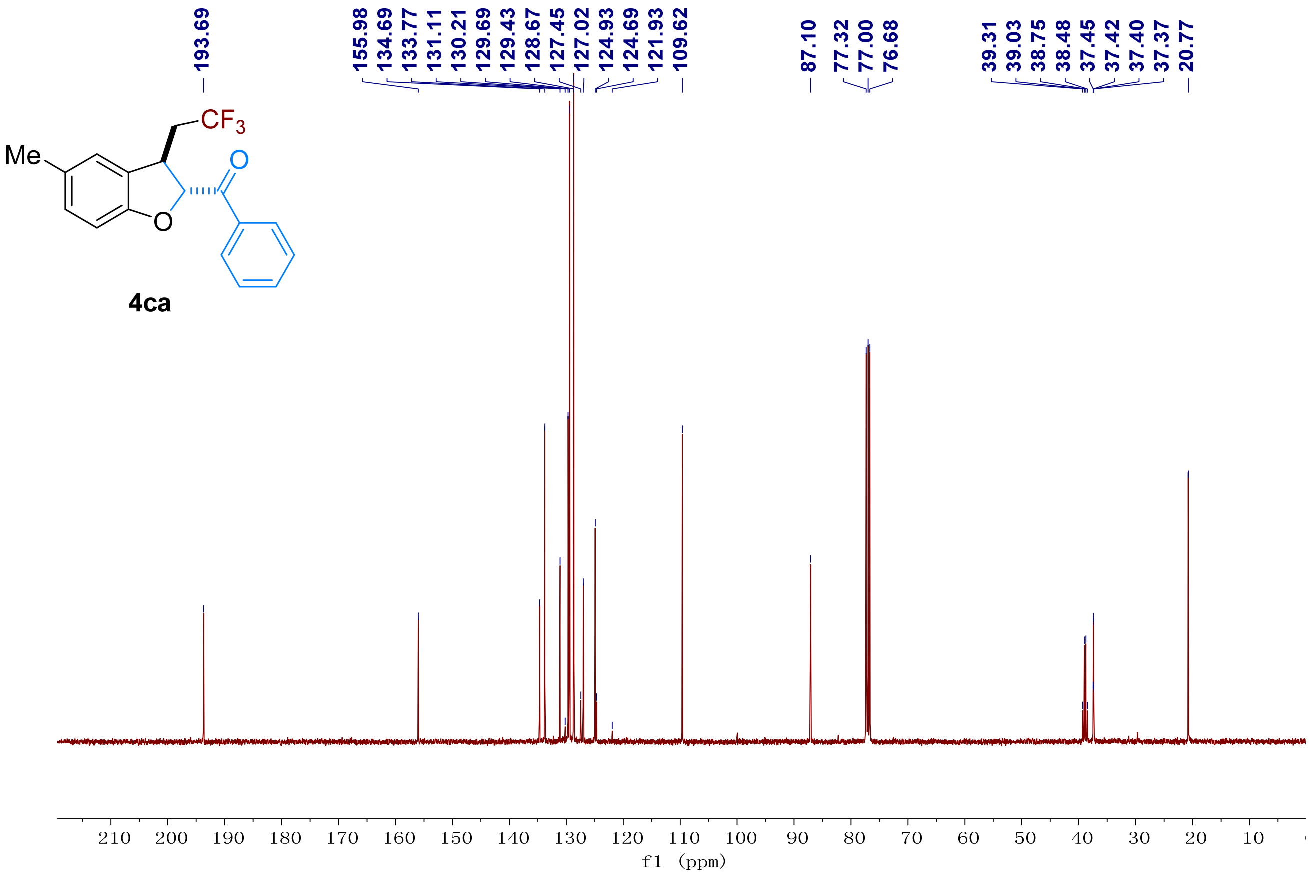


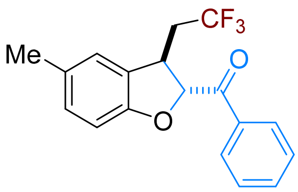
4ba



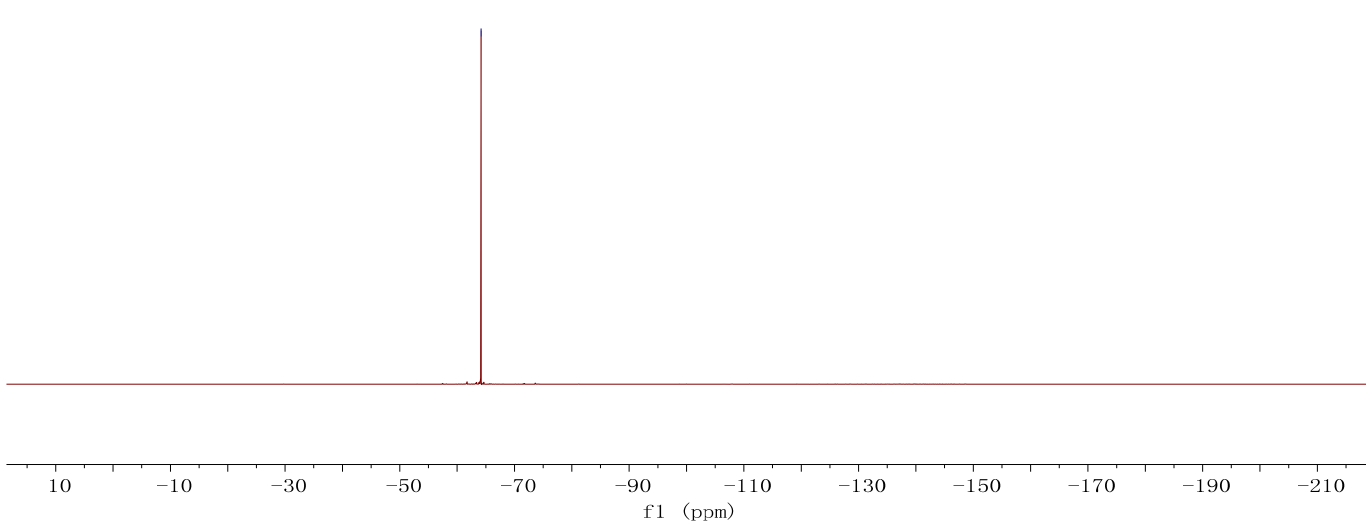
^{1}H NMR (400 MHz, CDCl$_3$), ^{13}C NMR (100 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 4ca



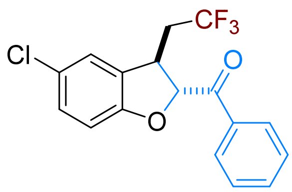




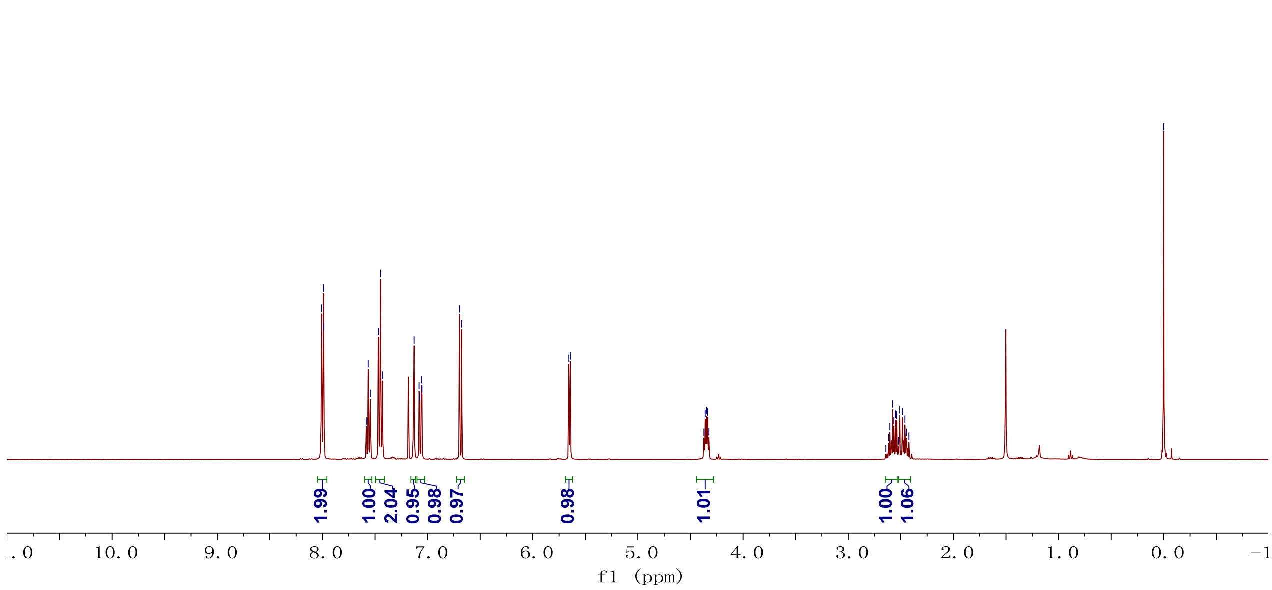
4ca

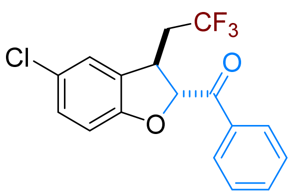


[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4da

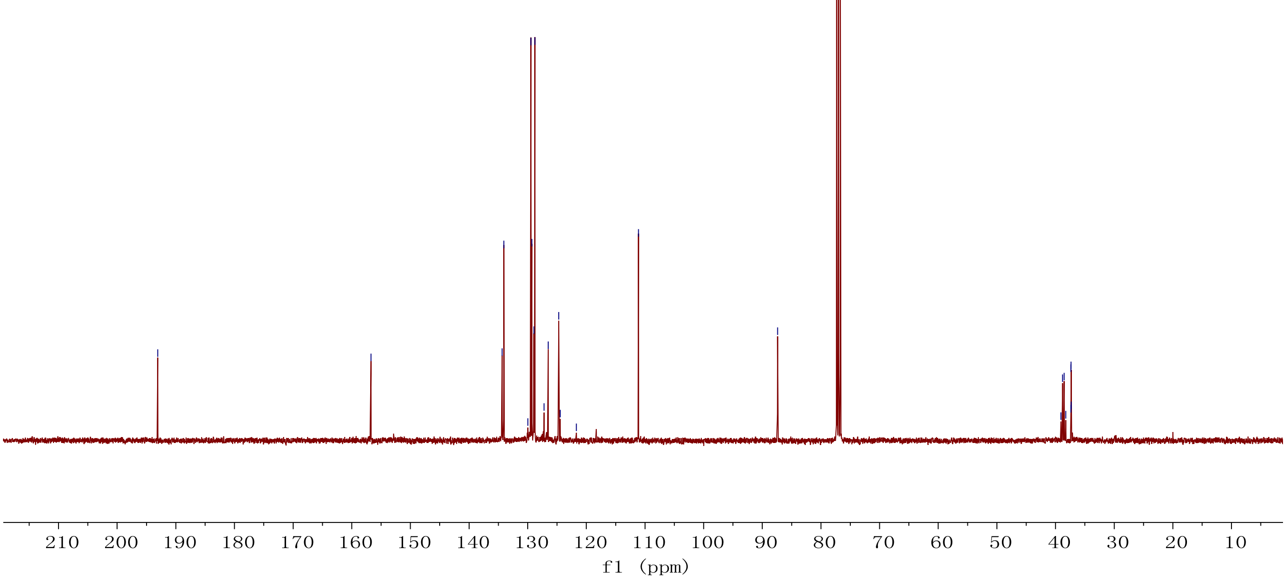


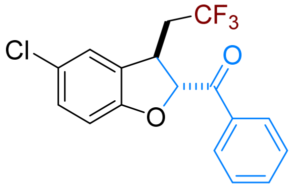
4da



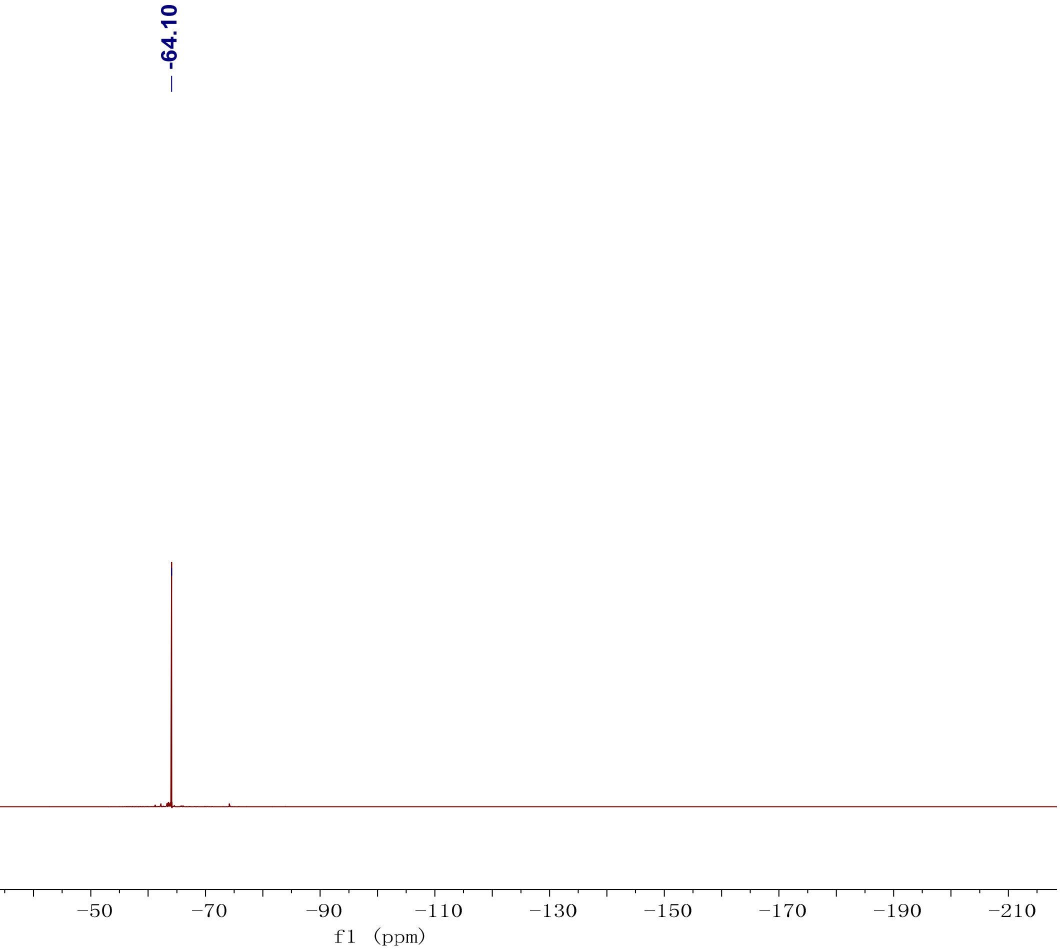


4da

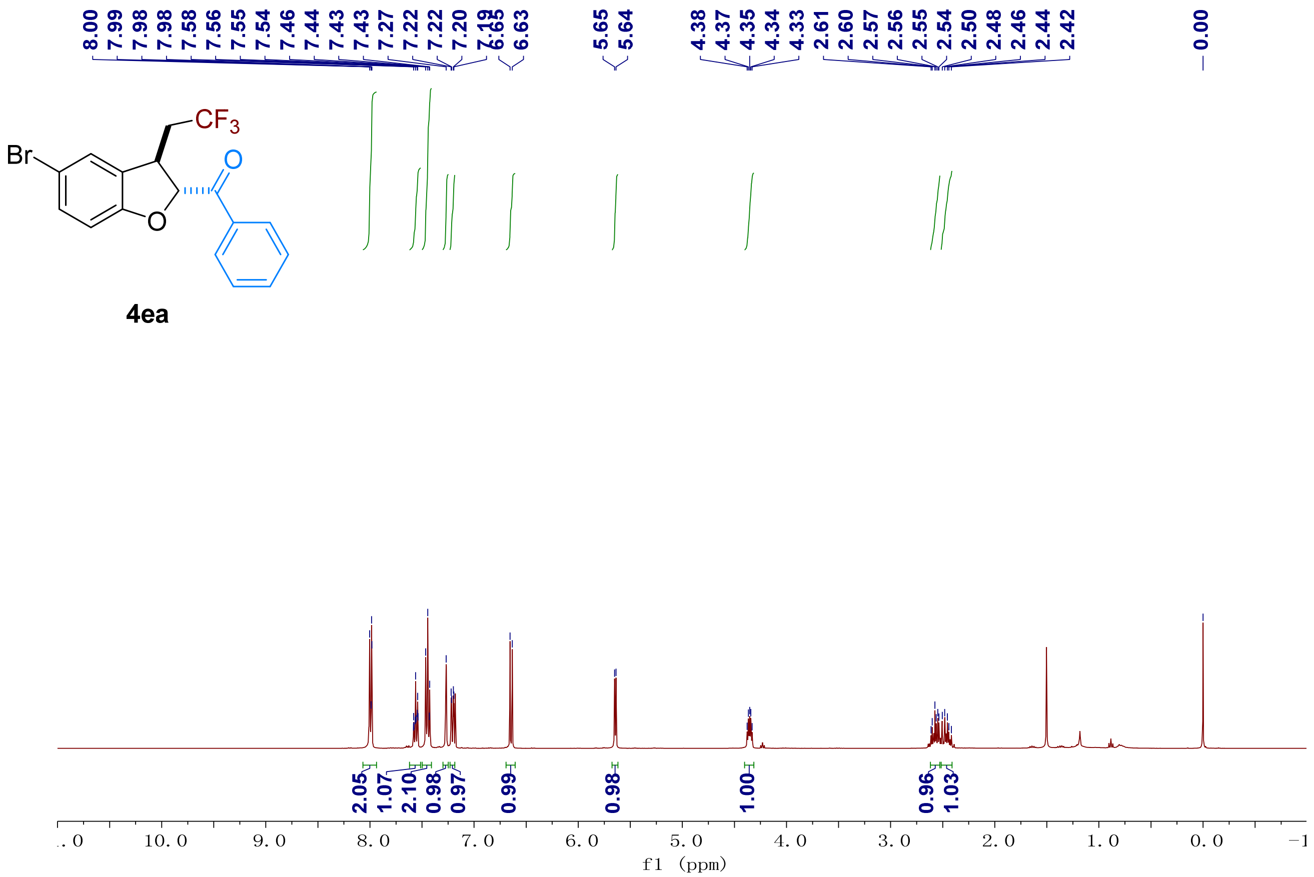


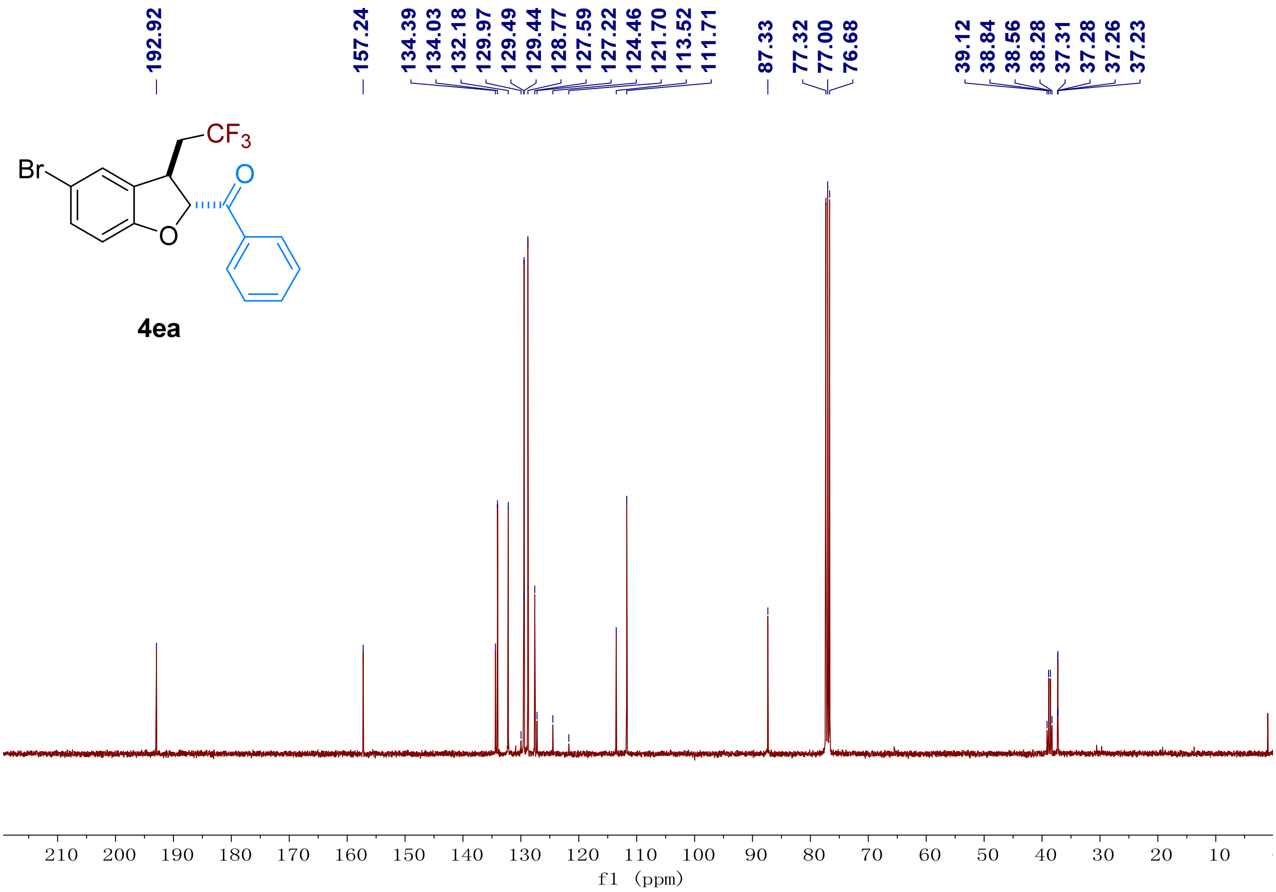


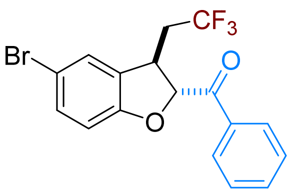
4da



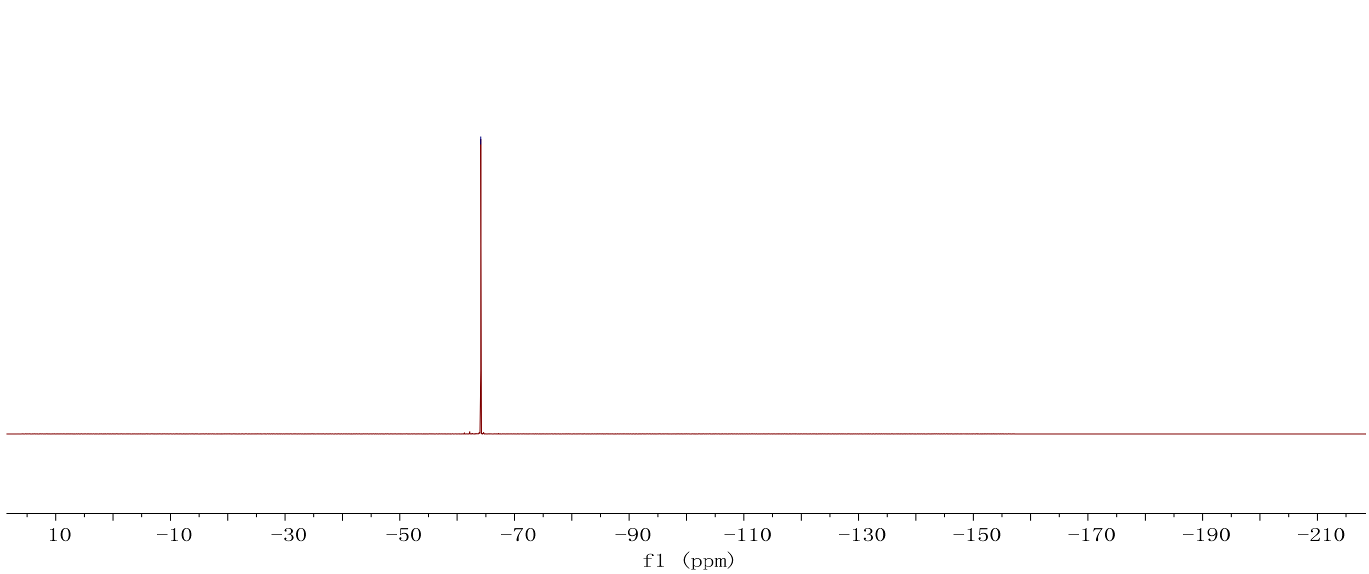
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ea



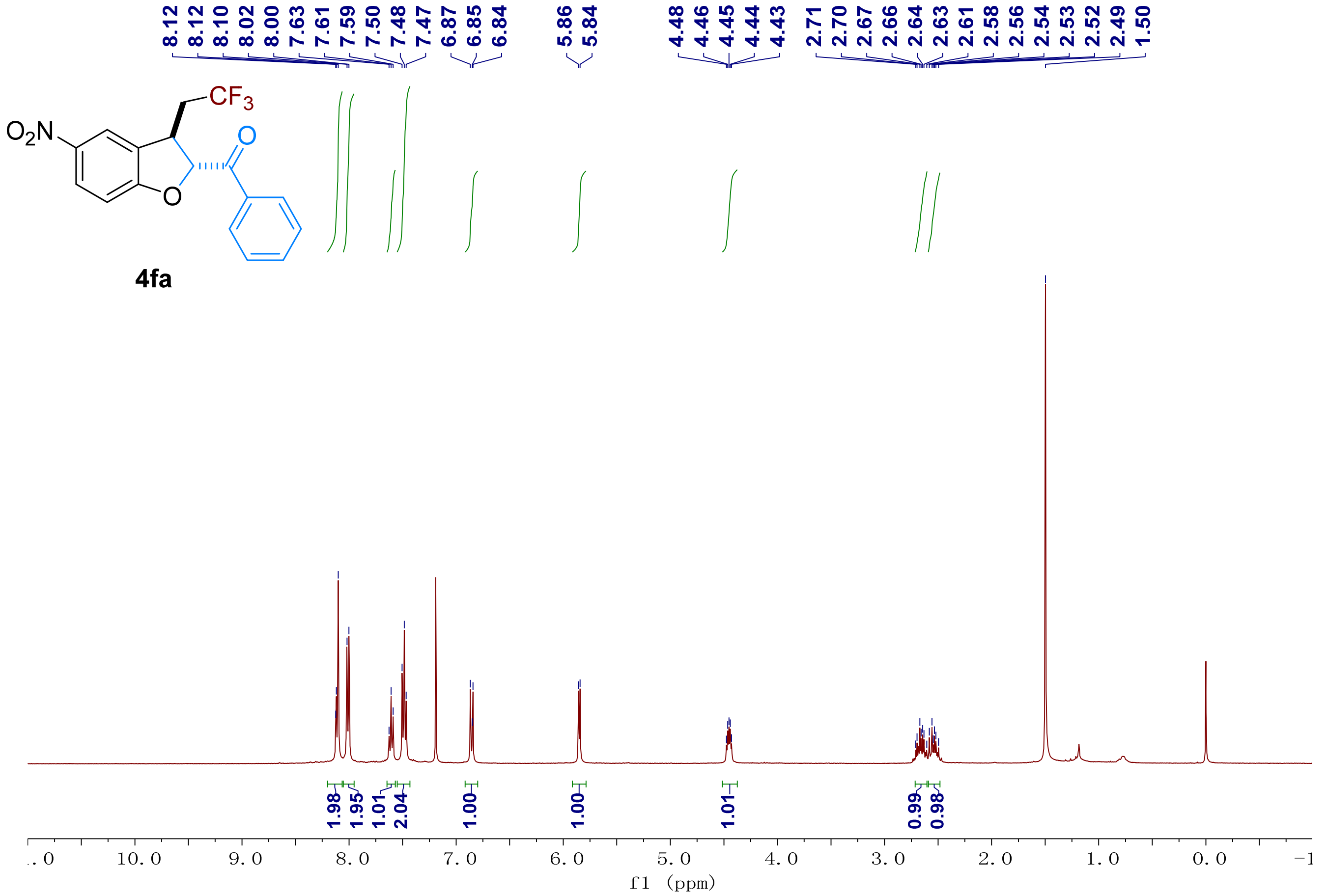


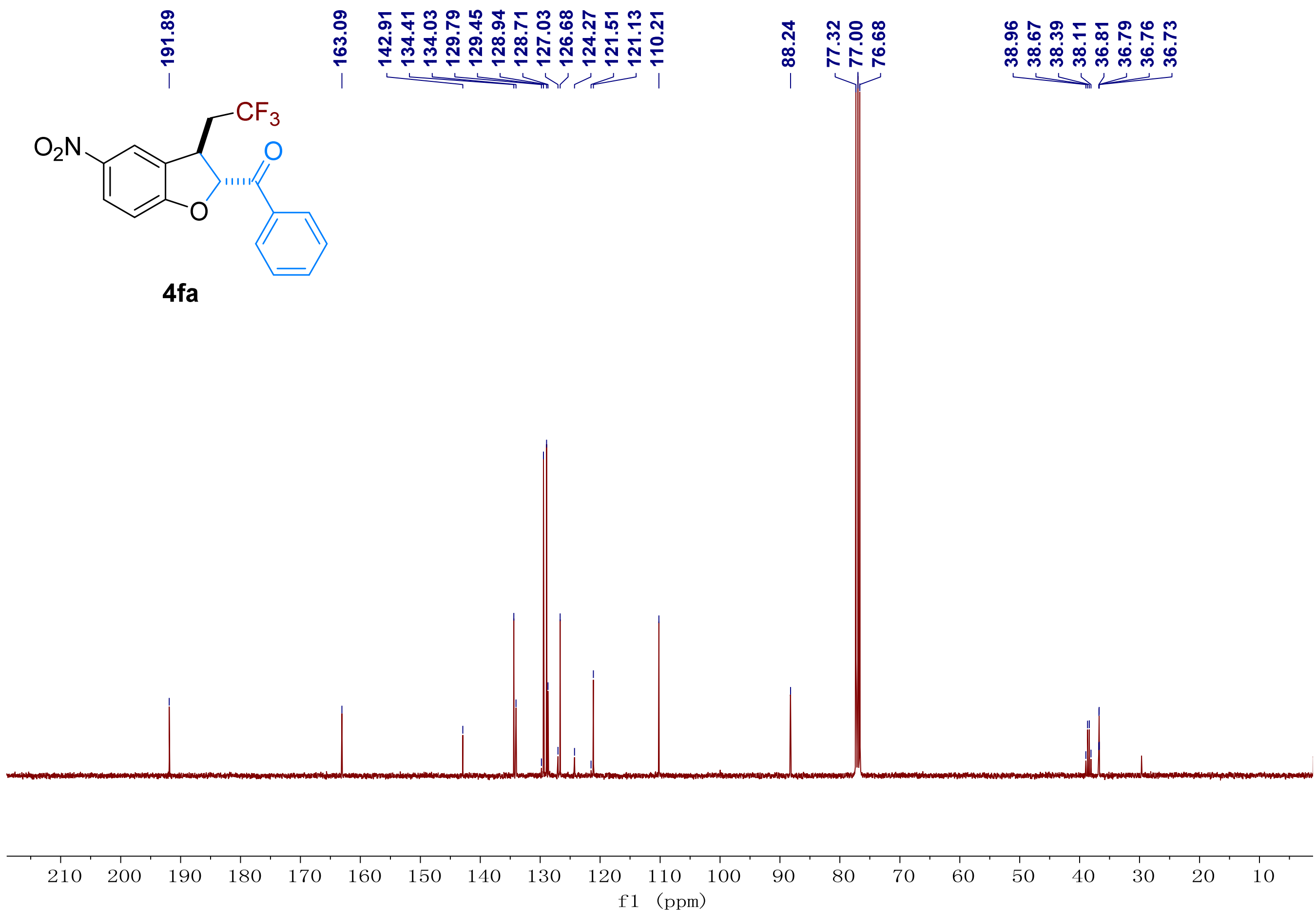


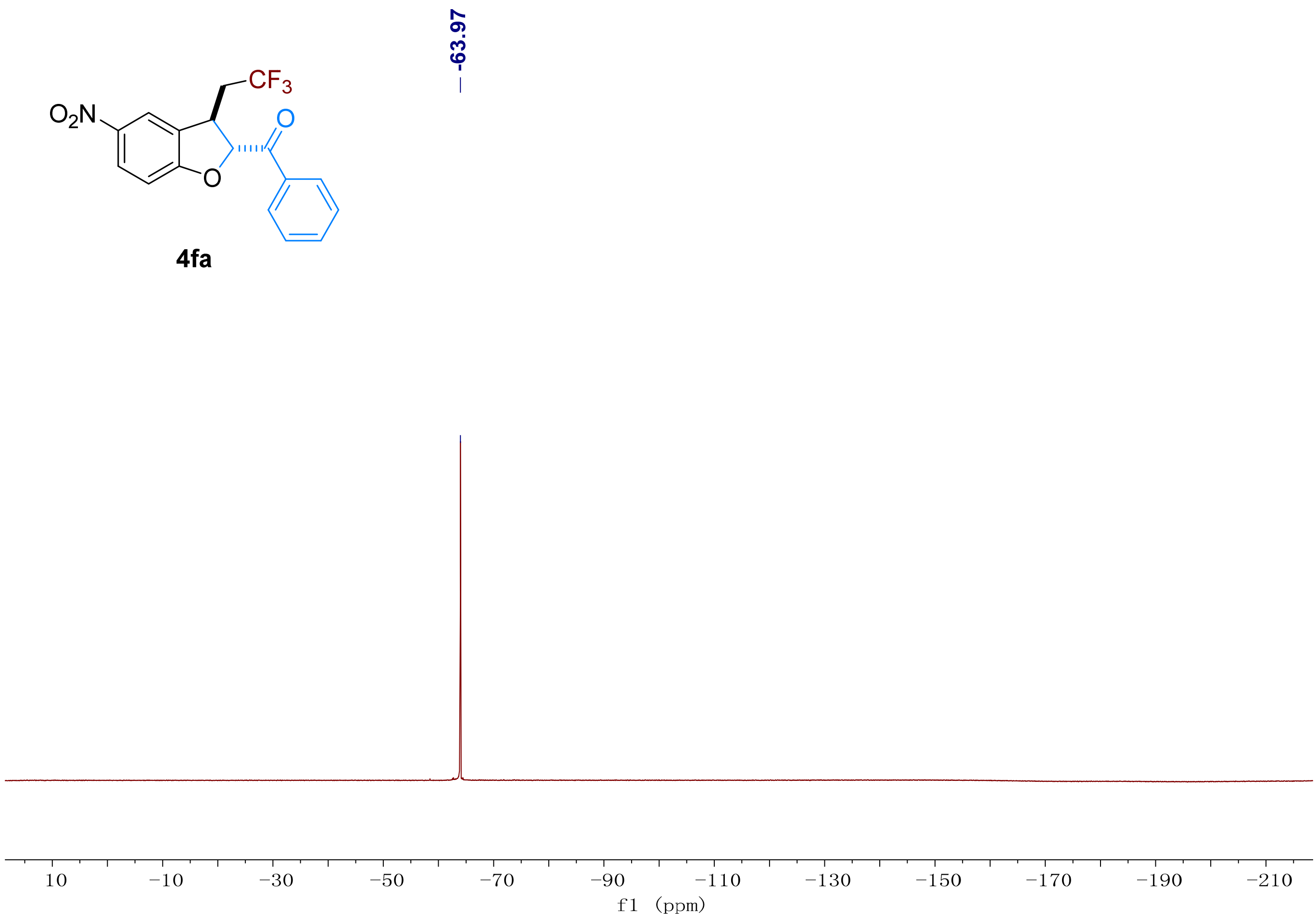
4ea



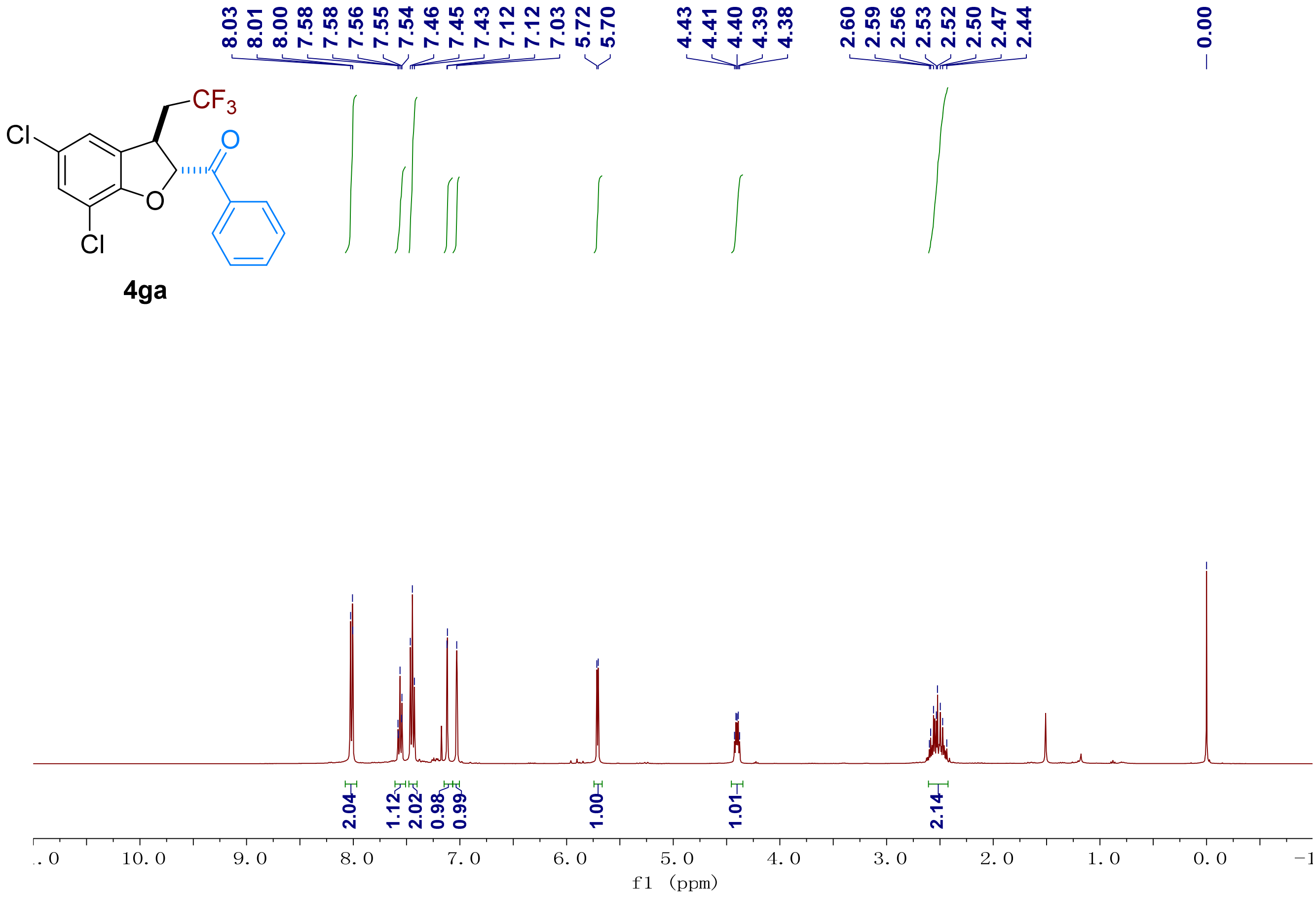
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4fa

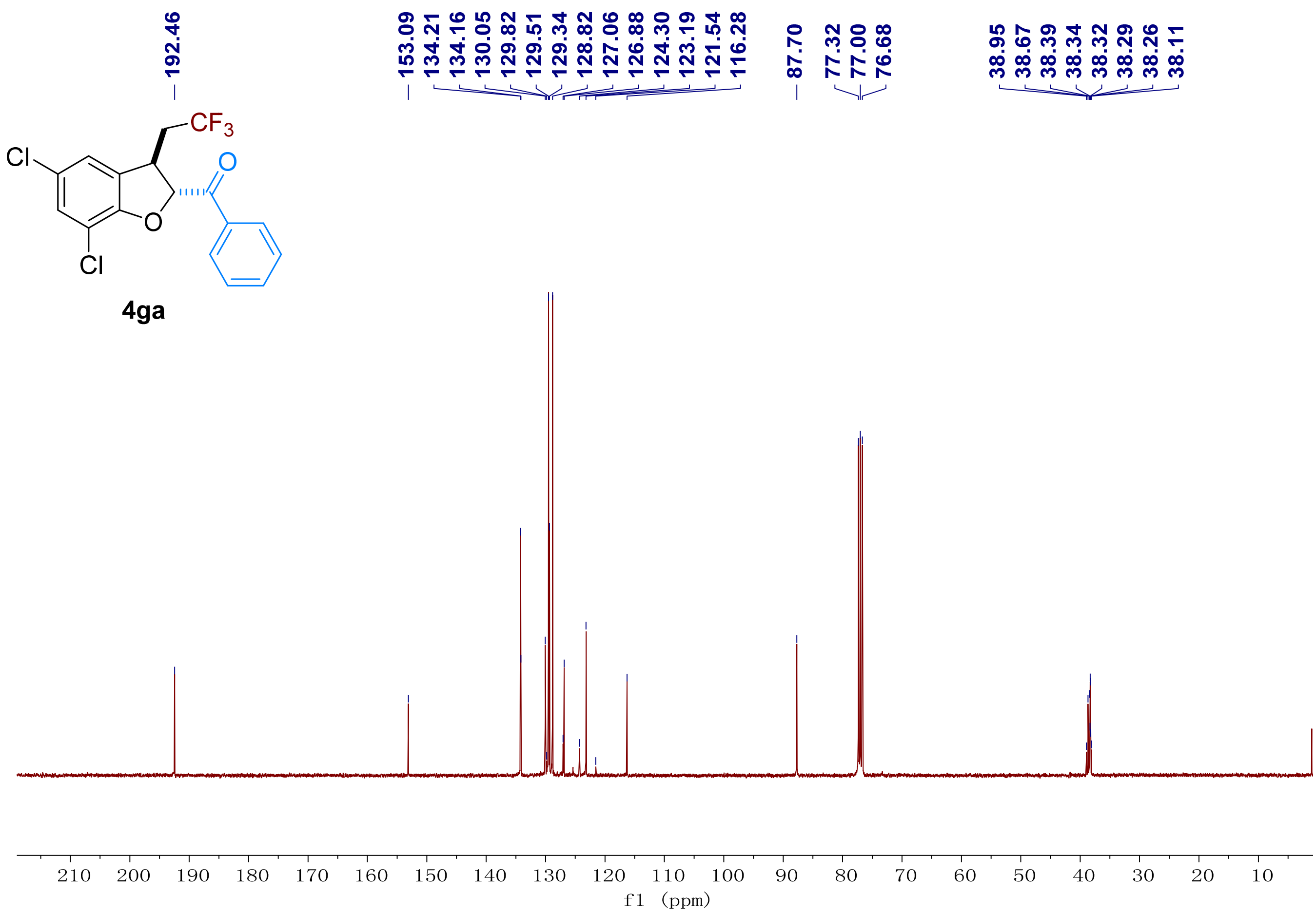


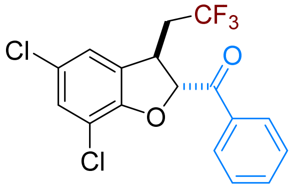



O2N
CF3
O
O
4fa
-63.97
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

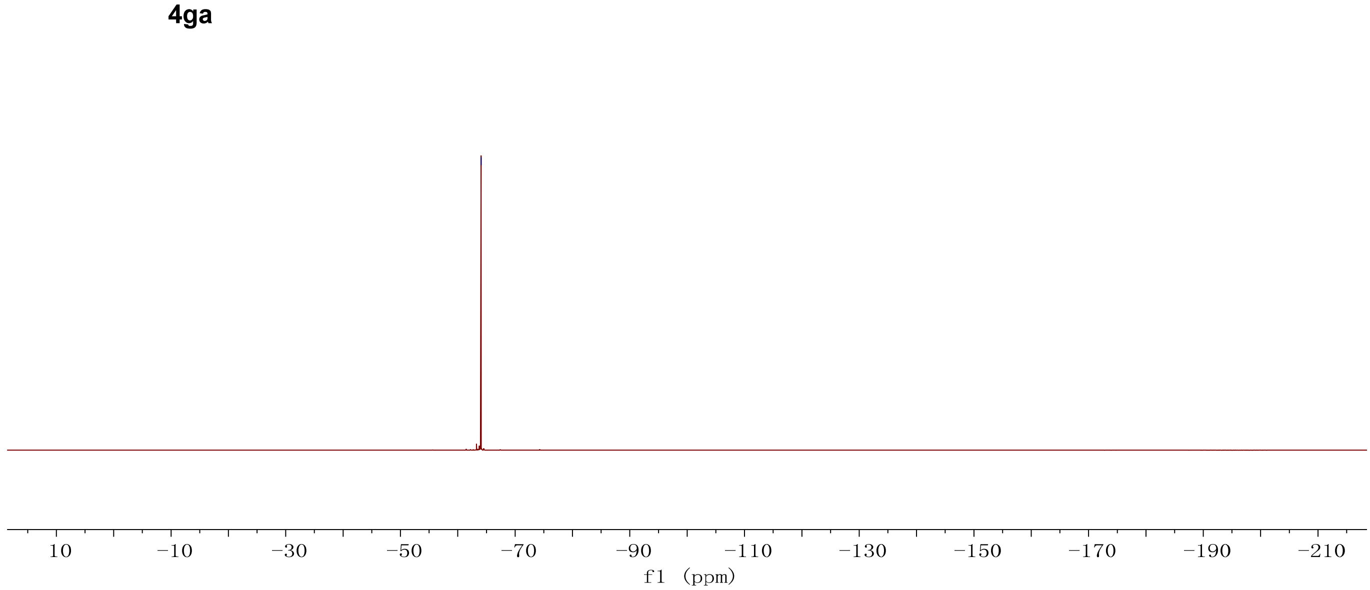
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ga



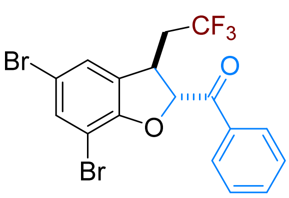




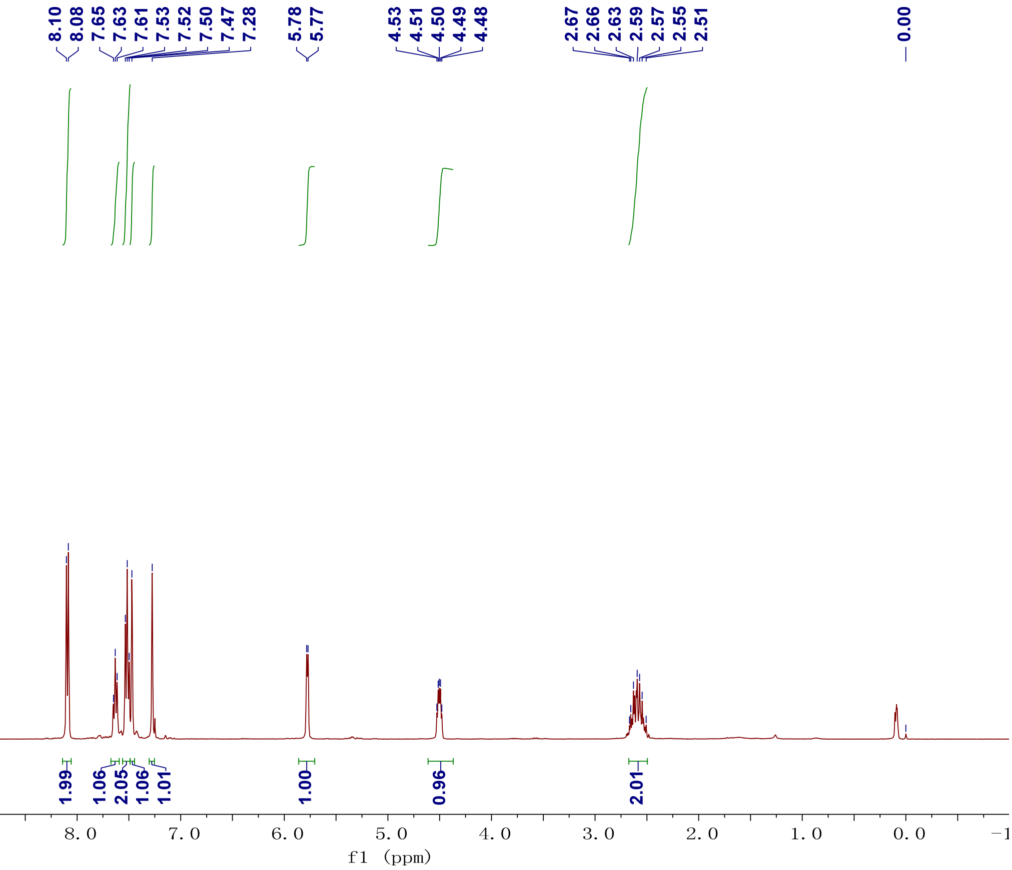
4ga

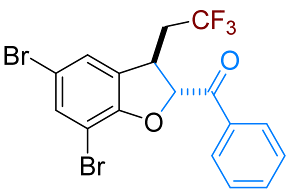


[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) and [19]F NMR (376 MHz, $CDCl_3$) spectra of product 4ha

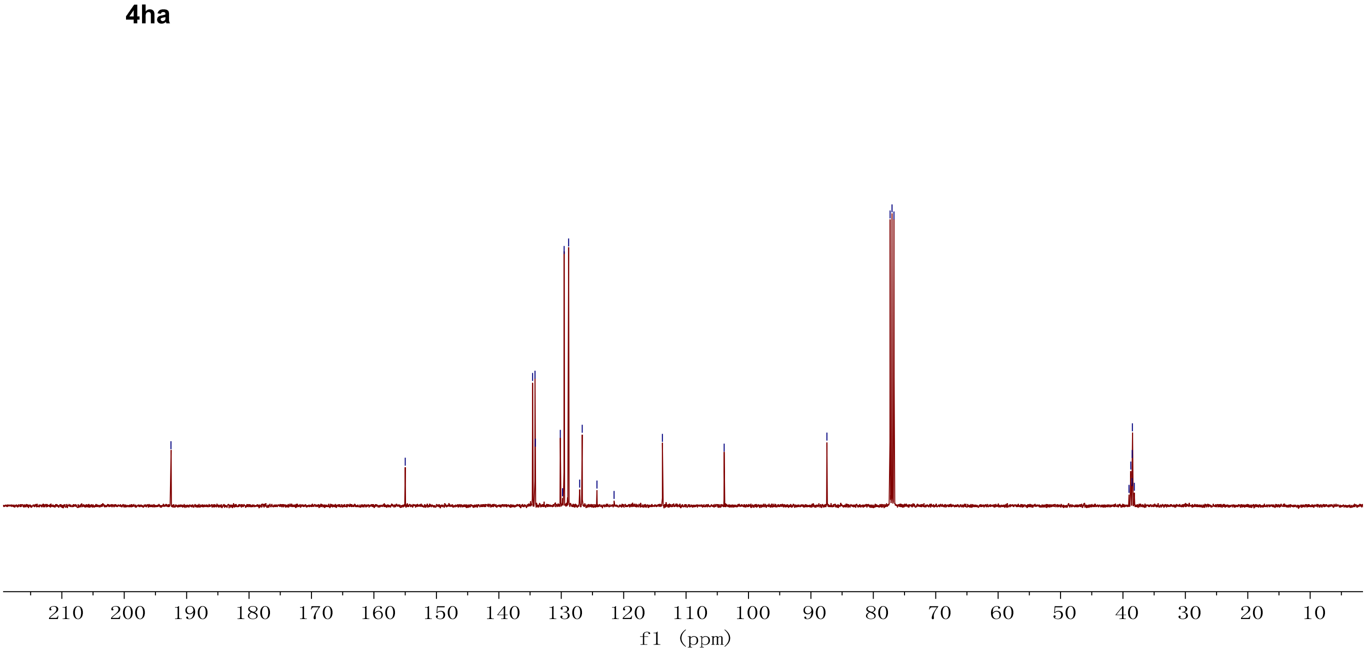


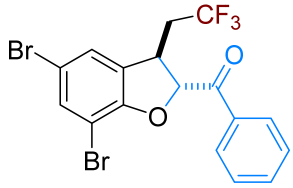
4ha



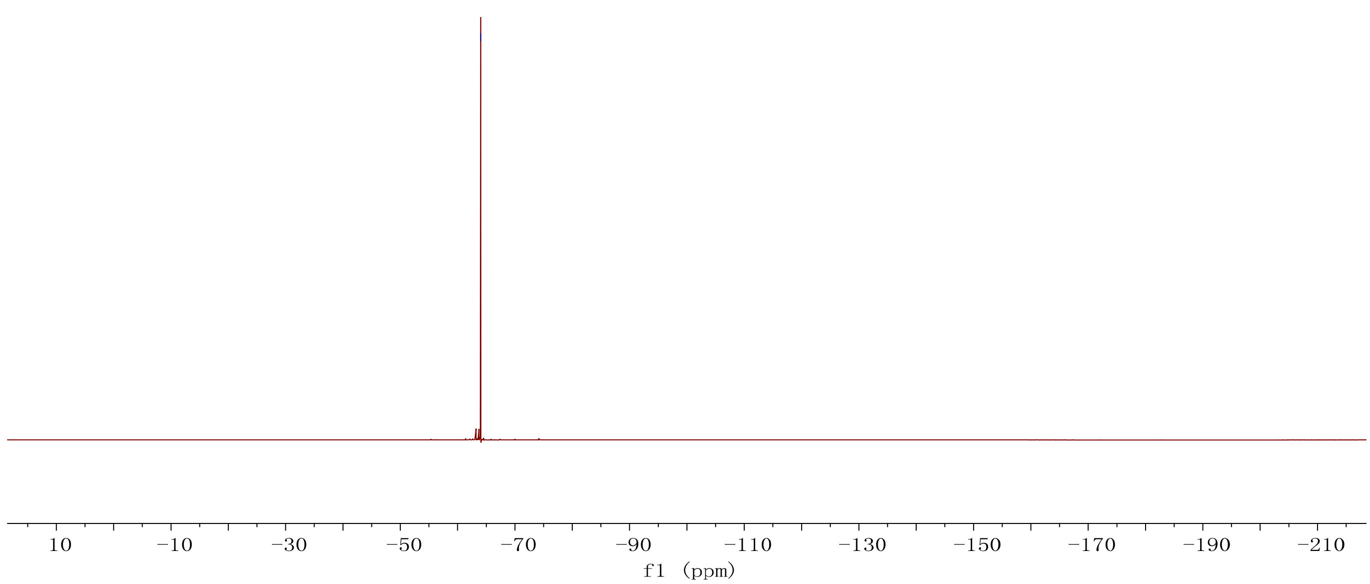


4ha

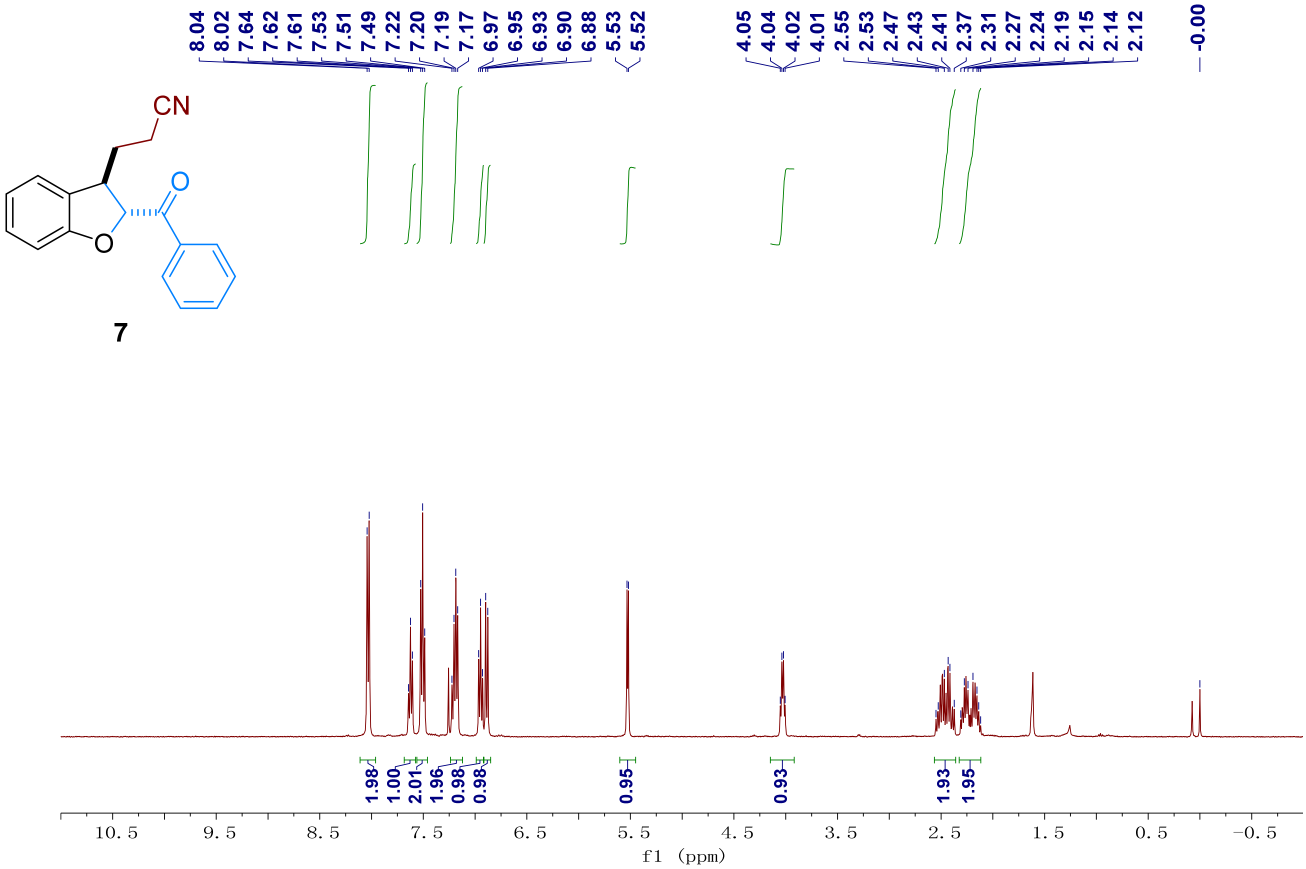


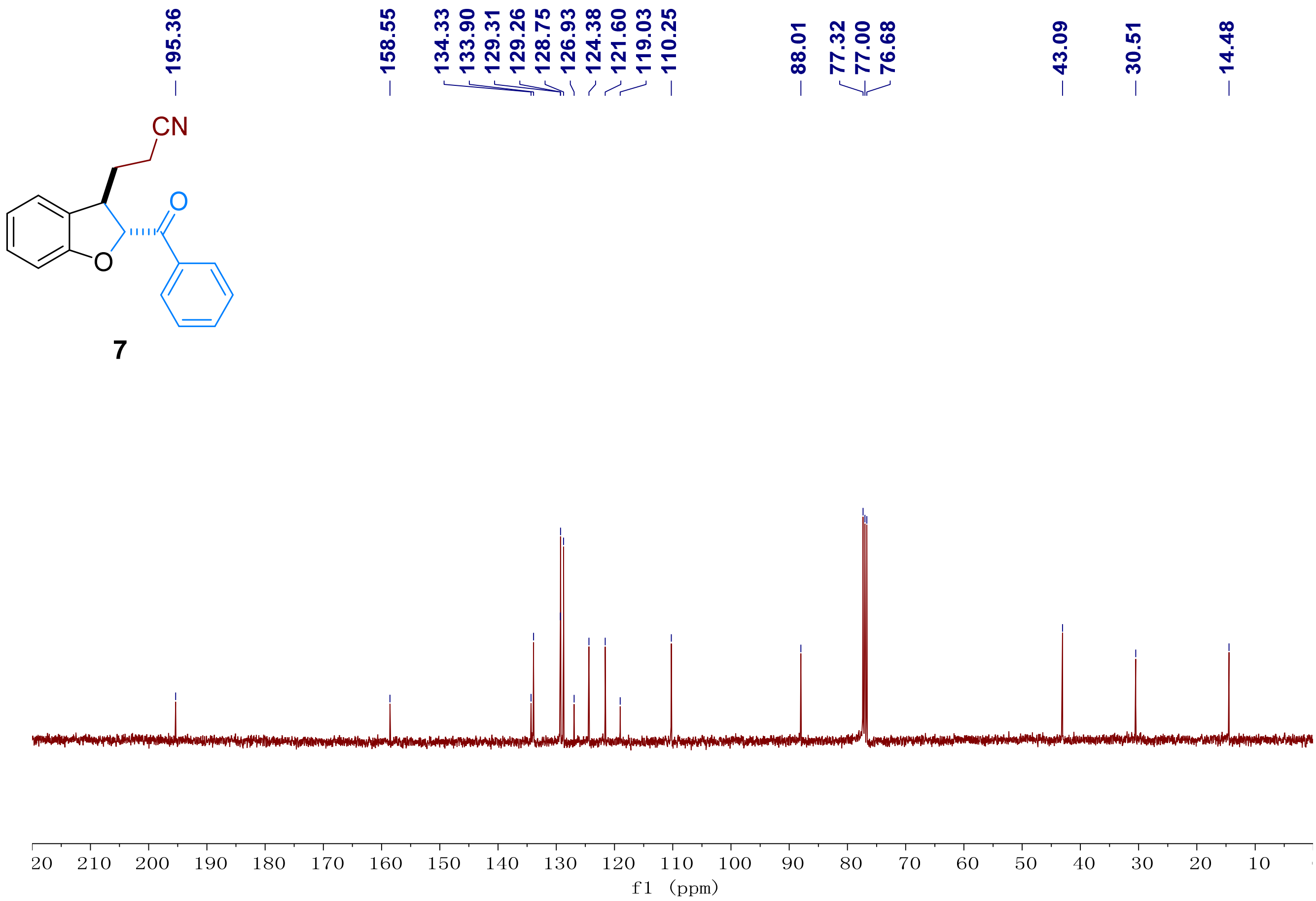


4ha

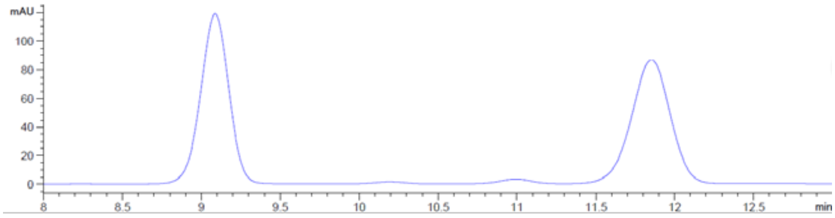


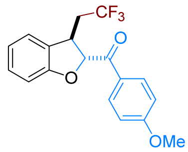
[1]H NMR (400 MHz, CDCl3), [13]C NMR (100 MHz, CDCl3) spectra of product 7





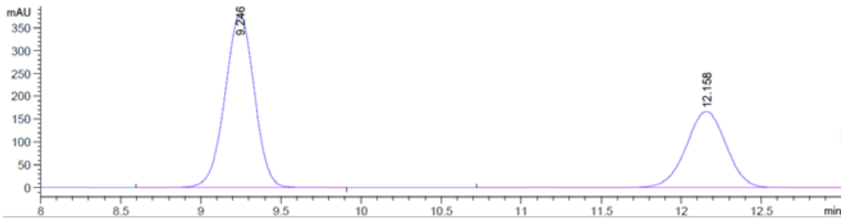
7. Copy of HPLC Chromatograms

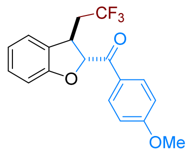




rac-4ab

#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.087	BV	0.1935	4014.92822	321.96268	49.8480
2	11.852	VB	0.2671	4039.41479	234.39531	50.1520





4ab

#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.246	BB	0.1990	4834.23828	378.52832	62.3220
2	12.158	VB R	0.2718	2922.63086	167.09079	37.6780