

Supporting Information

Trifluoromethyl benzoate (TFBz): A Versatile Trifluoromethoxylation Reagent

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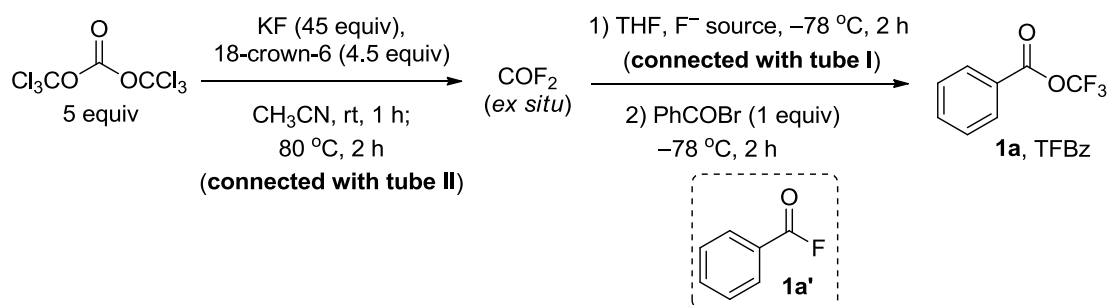
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1. General Information

Unless otherwise mentioned, reagents were purchased from commercial sources and used without further purification. *cis*-Dicyclohexano-18-crown-6 (*cis*-DCy-18-C-6) was purchased from TCI as a mixture of *cis-syn-cis*- and *cis-anti-cis*-isomers (Ref.: Pedersen C. J.; Feng E.; House, H. O. *Org. Synth.* **1972**, 52, 66). Anhydrous ethyl acetate (EtOAc) was purchased from J&K. Spray-dried KF was dried at >180 °C for 12 h under vacuum prior to use and stored in the N₂ glove-box. Benzoyl bromide (PhCOBr) was purchased from TCI and purified *via* distillation. Phenylethynyl bromide and phenylethynyl iodide were prepared according to reported procedures¹. Acetonitrile (CH₃CN) was distilled over CaH₂, and stored over activated molecular sieves. Tetrahydrofuran (THF) was freshly distilled over sodium with the use of benzophenone as an indicator. NMR spectra were obtained on a Bruker AV400 or Agilent MR400 (400 MHz for ¹H; 376 MHz for ¹⁹F; 101 MHz for ¹³C), or an Agilent MR500 (500 MHz for ¹H; 126 MHz for ¹³C) spectrometer. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.00 ppm or to the signal of a residual protonated solvent: CDCl₃ δ 7.26 ppm or (CD₃)₂CO δ 2.05 ppm. ¹³C NMR chemical shifts were determined relative to internal CDCl₃ at δ 77.0 ppm. ¹H, ¹³C and ¹⁹F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), septet (sept), doublet of doublets (dd), triplet of quartets (tq), triplet of triplets (tt), triplet of multiplets (tm), quartet of triplets (qt), multiplet (m), and broad resonance (br). Flash chromatography was performed using 230-400 mesh SiliaFlash® P60 (Silicycle Inc.). All the melting points were uncorrected. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. All reactions were monitored by TLC, ¹⁹F NMR spectroscopy, or GC-MS.

2. Optimization on the Reaction Conditions for Preparing TFBz (1a)

Table S1: Screening of Fluoride Sources^a



Entry	F^- source (1.5 equiv)	1a (%)	1a' (%)
1	TMAF	0	10
2	TBAF·4 ^t BuOH	0	39
3	CsF + 15-crown-5	0	0
4	CsF + Ph ₂ IOTf	4	18
5	TBAF in THF	0	95
6	TBAT	22	11
7	TBAT^{b,c}	94 (55)^d	0
8 ^e	TBAT ^c	quant (70) ^d	0

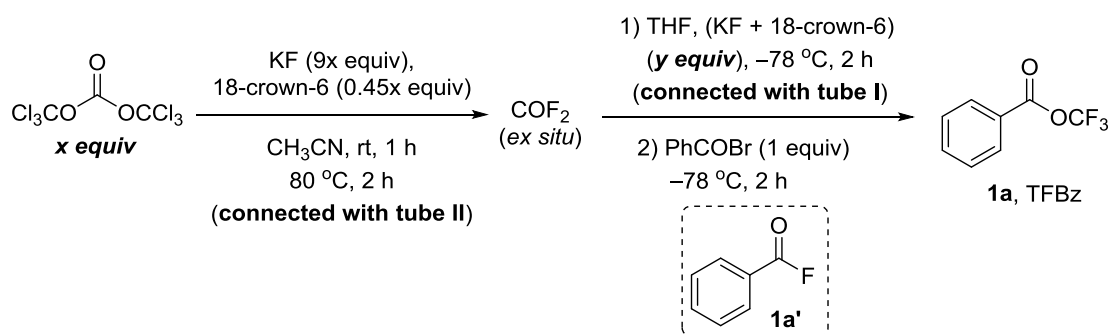
^aThe reaction was conducted on a 0.2 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard. ^bPhCOBr was fresh distilled. ^cTBAT was dried. ^dThe yield in the parenthesis was quenched by Ca(OTf)₂. ^e2-Iodobenzoyl bromide was used instead of PhCOBr. TMAF = tetramethylammonium fluoride; TBAF = tetrabutylammonium fluoride.

Typical Experimental Procedures (Taking Table S1, entry 1 as an example):

To a 10-mL oven-dried sealed tube (I) equipped with a robust stir bar were added KF (523 mg, 9 mmol, 45 equiv), 18-crown-6 (238 mg, 0.9 mmol, 4.5 equiv) and 5 mL dry CH₃CN, then triphosgene (297 mg, 1 mmol, 5.0 equiv) in the glove box. To another 10-mL oven-dried sealed tube (II) equipped with a robust stir bar were added TMAF (0.3 mmol, 1.5 equiv) and 1 mL dry THF in the glove box. The tubes were removed out of glove box. Tube (I) was stirred at room temperature for 1 h. Tube (I) and tube (II) was then connected with a gas-tube and tube (I) was heated to 80 °C while tube (II) was cooled to -78 °C. The COF₂ was transferred from tube (I) to tube

(II) for 2 h. Then benzoyl bromide (37 mg, 0.2 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N₂ and stirred for 2 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR at low temperature.

Table S2: Using KF/18-Crown-6 as the Fluoride Source for Preparing TFBz (1a)^a



Entry	x	y	1a (%)	1a' (%)
1	4	1.5	34	6
2	5	1.5	51	6
3	6	1.5	42	5
4	5	1.2	44	6
5	5	1.8	47	8
6 ^b	5	1.5	50	7
7 ^c	5	1.5	30	2
8 ^d	5	1.5	73	0

^aThe reaction was conducted on a 0.5 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard after it was quenched by Ca(OTf)₂. ^bWith 4A molecular sieves. ^cIt was kept at -78 °C for 5 h after PhCOBr was added. ^d18-crown-6 in tube II was dried. It was kept at -30 °C for 1 h after PhCOBr was added. It was quenched by NaOTf.

Typical Experimental Procedures (Take Table S2, entry 2 as an example):

To a 10-mL oven-dried sealed tube (I) equipped with a robust stir bar were added KF (1.3 g, 22.5 mmol, 45 equiv), 18-crown-6 (298 mg, 1.13 mmol, 2.25 equiv) and 5 mL dry CH₃CN, then triphosgene in the glove box. To another 10-mL oven-dried sealed tube (II) equipped with a robust stir bar were added KF (43.6 mg, 0.75 mmol, 1.5 equiv) and 18-crown-6 (198 mg, 0.75 mmol, 1.5 equiv) and 1 mL dry THF in the glove box. The tubes were removed out of glove box. Tube (I) was stirred at room

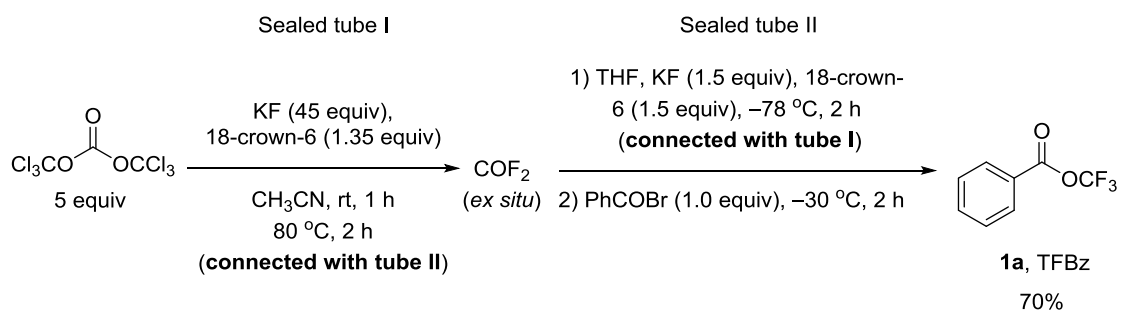
temperature for 1 h. Tube (I) and tube (II) was then connected with a gas-tube and tube (I) was heated to 80 °C while tube (II) was cooled to -78 °C. The COF₂ was transferred from tube (I) to tube (II) for 2 h. Then benzoyl bromide (93 mg, 0.5 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N₂ and stirred for 2 h. Ca(OTf)₂ was added and kept for another 30 min. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

3. Preparation of TFBz (1a)

3.1 Pre-treatment of 18-crown-6

To a 100-mL one-neck flask equipped with a stir bar were added 18-crown-6 and 50 mL ethyl acetate. The solution was azeotropic distillation for 5 h to remove trace amount of water under N₂. Then the solution was cooled down with stirring and the solvent was removed by vacuum pump. The solid was dried under vacuum pump to give white powder solid.

3.2 Preparation of TFBz (1a)





Experimental Procedures:

To a 350-mL oven-dried sealed tube (I) equipped with a robust stir bar were added KF (65.4 g, 1125 mmol, 45 equiv) and 18-crown-6 (8.9 g, 33.75 mmol, 1.35 equiv) in the glove box. Tube (I) was removed out of glove box and 230 mL dry CH_3CN was added under N_2 . To another 350-mL oven-dried sealed tube (II) equipped with a robust stir bar were added dried KF (2.18 g, 37.5 mmol, 1.5 equiv) and dried 18-crown-6 (9.91 g, 37.5 mmol, 1.5 equiv) in the glove box. Tube (II) was removed out of glove box and 100 mL dry THF was added under N_2 . Tube (I) was placed into dry-ice/acetone, and triphosgene (37.1 g, 125 mmol, 5 equiv) was added until the solution was frozen. Tube (I) was sealed. The mixture was warmed to room temperature and stirred for 1 h. Tube (II) was evacuated for 1-2 seconds before it was connected with tube (I) through a gas-tube and tube (I) was heated to 80 °C while tube (II) was cooled to -78 °C. The COF_2 was transferred from tube (I) to tube (II) for 2 h. Then benzoyl bromide (4.63 g, 25 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N_2 , then the solution was warmed to -30 °C and stirred for 2 h while the solution became very stick. Then sodium trifluoromethanesulfonate (8.6 g) was added at -78 °C under N_2 and stirred for another 30 min at -30 °C. Tube (II) was warmed to room temperature and over-excess COF_2 was absorbed by 10% NaOH (aq) carefully. The difluorophosgene dissolved in the reaction mixture in tube (II) was also completely removed by flowing N_2 gas to the reaction mixture and absorbed by 10% NaOH (aq). The solvent was evaporated under vacuum. Et_2O was added and the

mixture was filtered through a pad of celite. The solvent was evaporated under vacuum and product was further purified by flash column chromatography using petroleum ether (30-60 °C) as eluent to give product **1a** 3.31g as a colorless liquid.

(Caution! COF₂ was a toxic gas, so it should be handled in a well ventilated hood!)

TFBz has been stored in the air at room temperature for 5 months without detectable decomposition. Moreover, a mixture of TFBz and water (1:2, v/v) can be stored at room temperature for at least 5 days without detectable decomposition.

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.71 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 159.0, 135.1, 130.5, 128.9, 126.6 (q, *J* = 1.6 Hz), 119.9 (q, *J* = 265.4 Hz). MS (EI, *m/z*, %): 190 (M⁺, 22), 105 (100), 77 (58); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₈H₅F₃O₂, 190.0242; found, 190.0247.

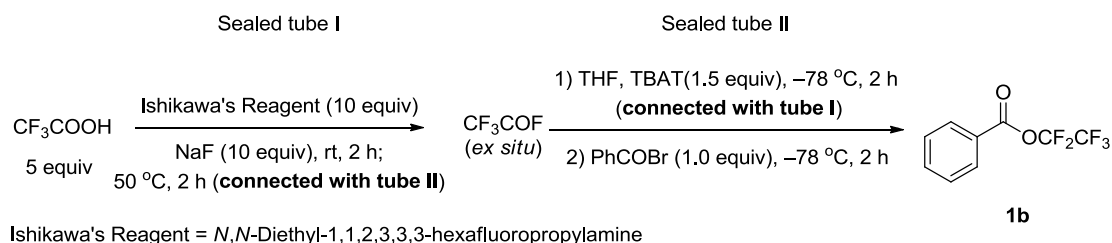
4. Preparation of Perfluoroalkyl Benzoates **1b-1e**

4.1 Preparation of TBAT²

Experimental Procedures:

To a 500-mL three-neck flask equipped with a stir bar were added PhSiF (29 g, 104 mmol, 1.02 equiv) and 4 g MgSO₄. The flask was evacuated and backfilled with N₂ for 3 times. Then 100 mL CH₂Cl₂ was added and 1M TBAF in THF (102 mL, 102 mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 10 min. After the solution was filtered and the solvent was evaporated under vacuum, the resulting white paste was dissolved in 700 mL of ethyl acetate. Approximately 250 mL of the ethyl acetate was distilled off under N₂ to remove water azeotropically. Additional ethyl acetate (250 mL) was then added and distilled off, resulting in a solution of TBAT in approximately 450 mL of ethyl acetate. The solution was allowed to cool to room temperature with stirring and white precipitate formed. Then the mixture was filtered under N₂ and washed with dry ethyl acetate. The solid was dried under vacuum pump to give white solid 45 g (82% yield).

4.2 Preparation of 1b



Experimental Procedures:

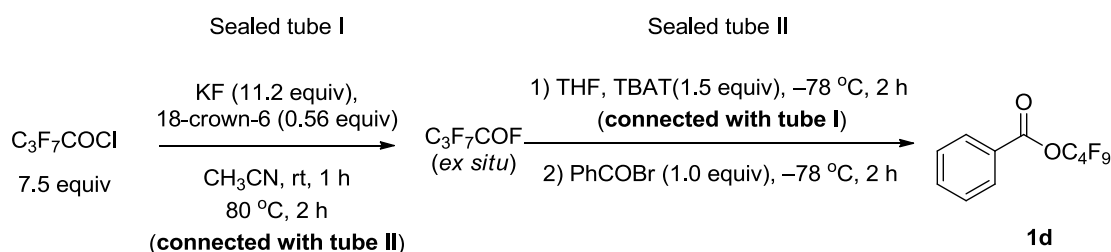
To a 10-mL oven-dried sealed tube (I) equipped with a robust stir bar was added NaF (1.26 g, 30 mmol, 10 equiv) in the glove box. Tube (I) was removed out of glove box and Ishikawa's Reagent (6.69 g, 30 mmol, 10 equiv) was added under N₂. To another 10-mL oven-dried sealed tube (II) equipped with a robust stir bar were added TBAT (2.43 g, 4.5 mmol, 1.5 equiv) in the glove box. Tube (II) was removed out of glove box and 6 mL dry THF was added under N₂. Tube (I) was placed into dry-ice/acetone, and trifluoroacetic acid (1.71 g, 15 mmol, 5 equiv) was added until the solution was frozen. Tube (I) was sealed. The mixture was warmed to room temperature and stirred for 2 h. Tube (II) was evacuated for 1-2 seconds before it was connected with tube (I) through a gas-tube and tube (I) was heated to 50 °C while tube (II) was cooled to -78 °C. The CF₃COF was transferred from tube (I) to tube (II) for 2 h. Then benzoyl bromide (555 mg, 3 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N₂ and stirred for 2 h. Then calcium trifluoromethanesulfonate (660 mg) was added under N₂ and stirred for another 30 min at -78 °C. Tube (II) was warmed to room temperature and over-excess CF₃COF was released carefully. Water was added and the mixture was extracted with Et₂O for 3 times. The combined solvent was dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the product was trapped using liquid nitrogen trap system under vacuum while mixture was heated at 100 °C for 1h. The product was further purified by flash column chromatography using petroleum ether (30-60 °C) as eluent to give product **1b** (372 mg, 52% yield) as a colorless liquid.

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -86.51 (s, 3F),

column chromatography using petroleum ether (30-60 °C) as eluent to give product **1c** (499 mg, 57% yield) as a colorless liquid.

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -81.16 (t, *J* = 7.1 Hz, 3F), -87.15 (m, 2F), -129.97 (m, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 135.2, 130.5, 128.9, 126.6, 117.4 (qt, *J* = 286.2, 33.3 Hz), 115.2 (tt, *J* = 283.9, 33.3 Hz), 106.6 (tm, *J* = 267.4 Hz). MS (EI, *m/z*, %): 290 (M⁺, 20), 105 (100), 77 (55); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₁₀H₅F₇O₂, 290.0178; found, 290.0175.

4.4 Preparation of **1d**



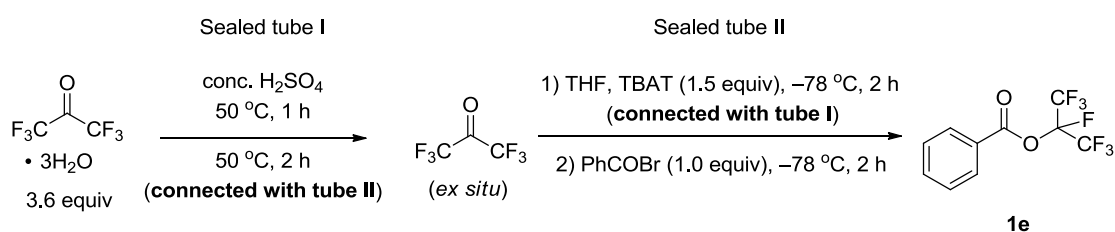
Experimental Procedures:

To a 50-mL oven-dried sealed tube (I) equipped with a robust stir bar was added KF (1.96 g, 33.75 mmol, 11.2 equiv) and 18-crown-6 (446 mg, 1.7 mmol, 0.56 equiv) in the glove box. Tube (I) was removed out of glove box and 12 mL dry CH₃CN was added under N₂. To another 10-mL oven-dried sealed tube (II) equipped with a robust stir bar were added TBAT (2.43 g, 4.5 mmol, 1.5 equiv) in the glove box. Tube (II) was removed out of glove box and 6 mL dry THF was added under N₂. Tube (I) was placed into dry-ice/acetone, and heptafluorobutyryl chloride (5.23 g, 22.5 mmol, 7.5 equiv) was added until the solution was frozen. Tube (I) was sealed. The mixture was warmed to room temperature and stirred for 1 h. Tube (II) was evacuated for 1-2 seconds before it was connected with tube (I) through a gas-tube and tube (I) was heated to 80 °C while tube (II) was cooled to -78 °C. The C₃F₇COF was transferred from tube (I) to tube (II) for 2 h. Then benzoyl bromide (555 mg, 3 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N₂ and stirred for 2 h. Then calcium

trifluoromethanesulfonate (660 mg) was added under N₂ and stirred for another 30 min at -78 °C. Tube (II) was warmed to room temperature and over-excess C₃F₇COF was released carefully. Water was added and the mixture was extracted with Et₂O for 3 times. The combined solvent was dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the product was trapped using liquid nitrogen trap system under vacuum while mixture was heated at 100 °C for 1 h. The product was further purified by flash column chromatography using petroleum ether (30-60 °C) as eluent to give product **1d** (547 mg, 54% yield) as a colorless liquid.

Colorless liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -80.98 (t, *J* = 9.5 Hz, 3F), -86.06 (td, *J* = 8.8, 1.9 Hz, 2F), -126.46 (m, 2F), -126.63 (m, 2F). **¹³C NMR** (126 MHz, CDCl₃) δ 158.6, 135.1, 130.4, 128.9, 126.7, 117.3 (qt, *J* = 287.8, 32.7 Hz), 115.4 (tt, *J* = 285.3, 30.2 Hz), 111.3 – 105.4 (m, 2C). **MS (EI, *m/z*, %)**: 340 (M⁺, 11), 122 (37), 105 (100), 77 (55); **HRMS (EI) (*m/z*)**: [M]⁺ Calcd for C₁₁H₅F₉O₂, 340.0146; found, 340.0148.

4.5 Preparation of **1e**



Experimental Procedures:

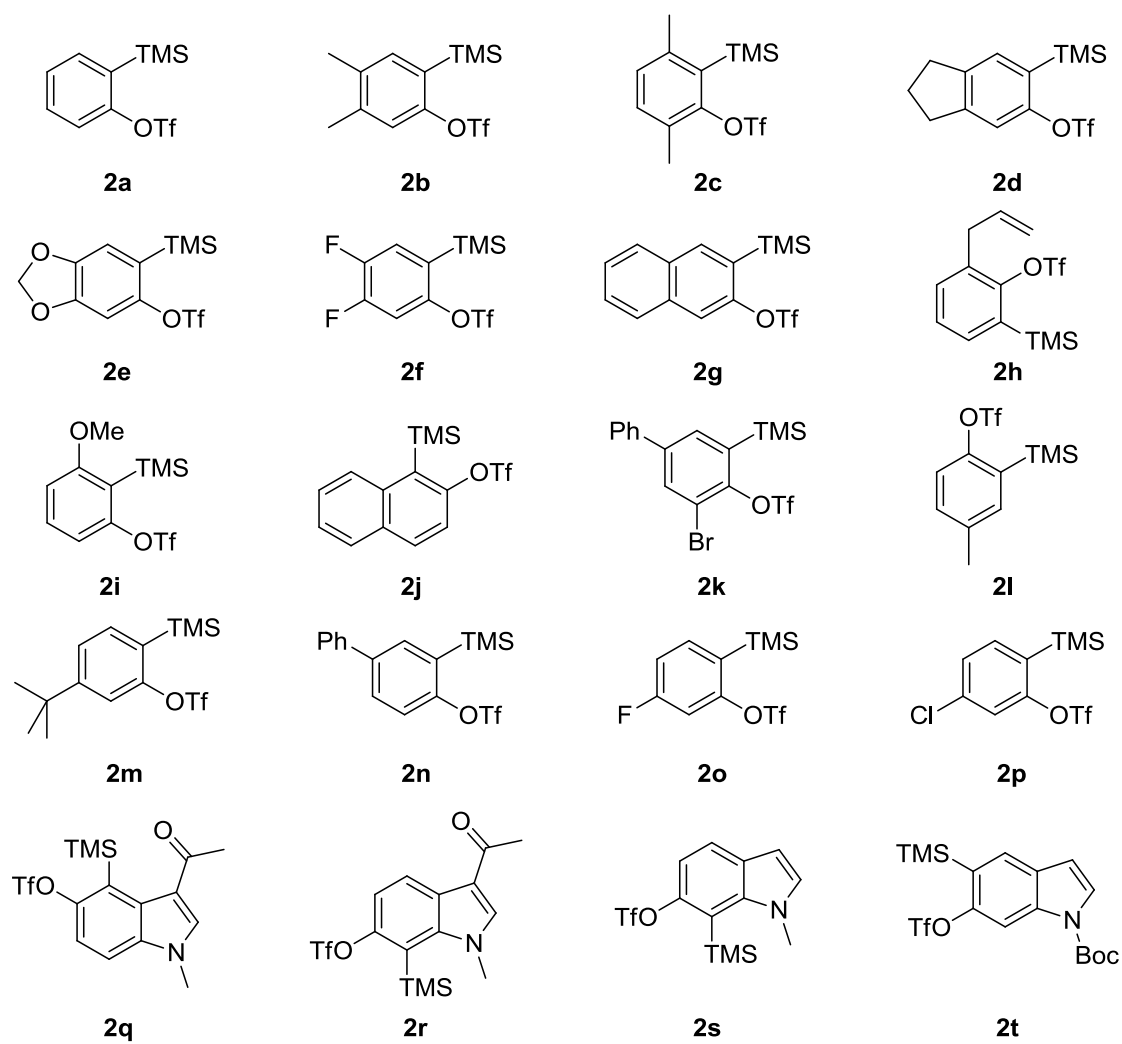
To a 100-mL oven-dried sealed tube (I) equipped with a robust stir bar was added 30 mL conc.H₂SO₄ under N₂. To another 10-mL oven-dried sealed tube (II) equipped with a robust stir bar were added TBAT (2.43 g, 4.5 mmol, 1.5 equiv) in the glove box. Tube (II) was removed out of the glove box and 6 mL dry THF was added under N₂. Tube (I) was placed into dry-ice/acetone, and hexafluoroacetone trihydrate (2.38 g, 10.8 mmol, 3.6 equiv) was added until the solution was frozen. Tube (I) was sealed. The mixture was warmed to 50 °C and stirred for 1 h. Tube (II) was evacuated for 1-2

seconds before it was connected with tube (I) through a gas-tube and tube (I) was heated to 50 °C while tube (II) was cooled to -78 °C. The perfluoroketone CF₃COCF₃ was transferred from tube (I) to tube (II) for 2 h. Then benzoyl bromide (555 mg, 3 mmol, 1.0 equiv) was added to tube (II) at -78 °C under N₂ and stirred for 2 h. Then calcium trifluoromethanesulfonate (660 mg) was added under N₂ and stirred for another 30 min at -78 °C. Tube (II) was warmed to room temperature and over-excess CF₃COCF₃ was released carefully. Water was added and the mixture was extracted with Et₂O for 3 times. The combined solvent was dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the product was trapped using liquid nitrogen trap system under vacuum while mixture was heated at 100 °C for 1h. The product was further purified by flash column chromatography using petroleum ether (30-60 °C) as eluent to give product **1e** (702 mg, 81% yield) as a colorless liquid.

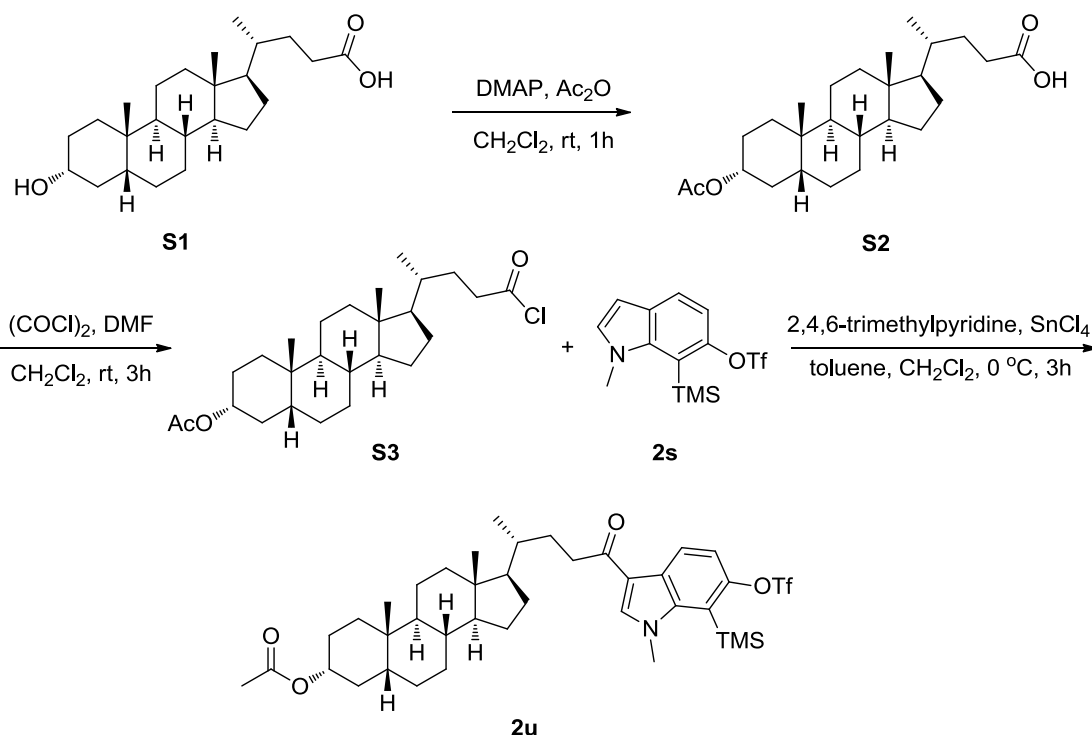
Colorless liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J = 7.4 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -77.87 (d, J = 1.9 Hz, 6F), -140.74 (m, 1F). **¹³C NMR** (101 MHz, CDCl₃) δ 159.6, 135.1, 130.6, 129.0, 126.8, 118.50 (qd, J = 288.3, 33.1 Hz), 101.7 (d(sept), J = 263.5, 37.7 Hz). **MS (EI, m/z , %)**: 290 (M⁺, 20), 105 (100), 77 (50); **HRMS (EI) (m/z): [M]⁺** Calcd for C₁₀H₅F₇O₂, 290.0178; found, 290.0174.

5. Preparation of Aryne Precursors 2a-2u

5.1 Aryne precursors **2a-2t** were prepared according to the literature procedures.³



5.2 Steroid-derived indolyne precursor **2u** was prepared as follows:



Experimental Procedures:

To a 50-mL oven-dried Schlenk tube equipped with a stir bar were added **S1** (921 mg, 2.45 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP, 60 mg, *cat.*) and CH₂Cl₂ (10 mL) under N₂. Then Ac₂O (0.83 mL, 8.82 mmol, 3.6 equiv) was added dropwise at room temperature and stirred for 1 h. The mixture was diluted with CH₂Cl₂, washed with 1N HCl (aq.) for 3 times, washed with 5% NaHCO₃ (aq.) for 3 times, washed by saturated brines and H₂O. Then the mixture was dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum to give the product (**S2**) without further purification.

To a 50-mL round-bottom flask equipped with a stir bar and **S2** was evacuated and backfilled with N₂ for 3 times. The flask was equipped with a N₂ balloon and added CH₂Cl₂ (5 mL), 10 drops DMF. Then (COCl)₂ (0.25 mL, 2.94 mmol, 1.2 equiv) was added dropwise at room temperature and stirred for 3 h. The solvent was evaporated under vacuum to give the product (**S3**) without further purification.

To a 50-mL round-bottom flask equipped with a stir bar, **S3**, and **2s** (351 mg, 1.0 mmol, 1.0 equiv) was evacuated and backfilled with N₂ for 3 times. The flask was equipped with a N₂ balloon and added toluene (20 mL) and 2, 4, 6-trimethylpyridine (133 mg, 1.1 mmol, 1.1 equiv), and tin tetrachloride (638 mg, 2.45 mmol, 2.45 equiv)

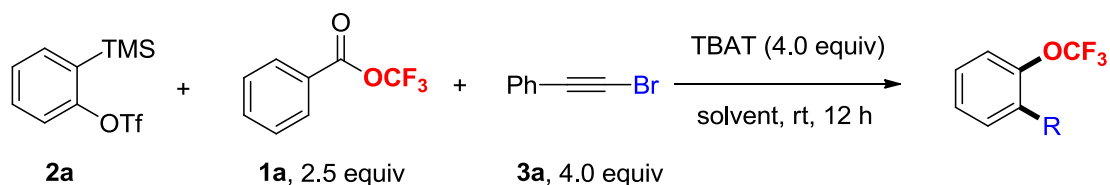
in CH₂Cl₂ (5.0 mL) was added dropwise at 0 °C and stirred at the same temperature for 3 h. The mixture was poured into a solution of saturated aqueous NaHCO₃, and further diluted with brine. The layers were separated, and the aqueous layer was extracted with EtOAc for 3 times. The combined organic layers were dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography using petroleum ether and ethyl acetate (5:1) as eluent to give product **2u** (598 mg, 80% yield) as a white solid.

2u: White solid. m.p. 169-170 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 8.7 Hz, 1H), 7.75 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 4.74 – 4.62 (m, 1H), 3.91 (s, 3H), 2.81 (ddd, *J* = 14.8, 10.3, 4.6 Hz, 1H), 2.70 (ddd, *J* = 15.2, 9.4, 5.9 Hz, 1H), 1.99 (s, 3H), 1.95 (d, *J* = 10.9 Hz, 1H), 1.91 – 1.75 (m, 5H), 1.65 (d, *J* = 10.0 Hz, 1H), 1.58 – 1.46 (m, 2H), 1.46 – 1.32 (m, 8H), 1.28 (d, *J* = 12.4 Hz, 1H), 1.25 – 1.16 (m, 3H), 1.15 – 0.97 (m, 5H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.89 (s, 3H), 0.62 (s, 3H), 0.49 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃) δ -72.74 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 196.1, 170.6, 151.8, 143.4, 138.9, 126.5, 125.6, 118.7(q, *J* = 320.7), 117.0, 116.5, 116.1, 74.3, 56.5, 56.2, 42.7, 41.9, 40.4, 40.2, 38.3, 36.7, 35.8, 35.7, 35.0, 34.5, 32.2, 31.0, 28.3, 27.0, 26.6, 26.3, 24.2, 23.3, 21.4, 20.8, 18.6, 12.1, 2.8. MS (ESI, m/z): 752.3 ([M+H]⁺). HRMS (ESI): Calcd for C₃₉H₅₇F₃NO₆SSi ([M+H]⁺) 752.3628; found, 752.3617.

6. Optimization on the Reaction Conditions of the Trifluoromethoxylation–Bromination of Benzyne

6.1 Preliminary Screening of Solvents

Table S3: Preliminary Screening of Solvents^a



Entry	Solvent	R = H	R = Br
1 ^b	CH ₃ CN	4	0
2	CH ₃ CN	0	9
3	toluene	21	7
4	CH ₂ Cl ₂	7	2
5	1,4-dioxane	0	31
6	DMSO	0	0
7	NMP	0	0
8	PhCF ₃	0	15
9	THF	0	39

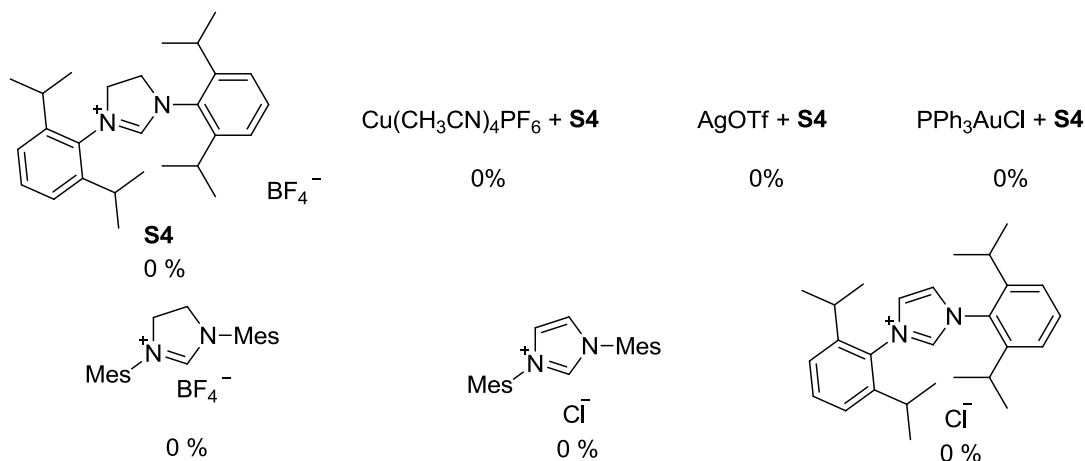
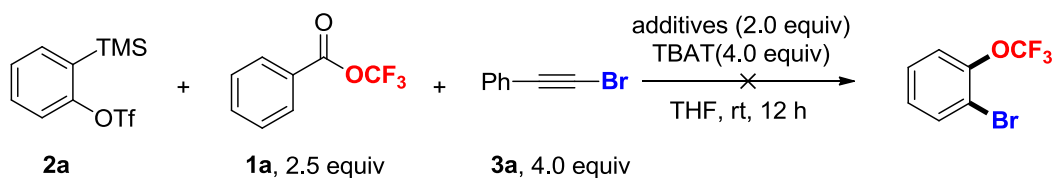
^aThe reaction was conducted on a 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard. ^bCF₃OAg *in situ* generated from TFBz (2.5 equiv) and AgF (4.0 equiv) was used.

Typical Experimental Procedures (Taking Table S3, entry 2 as an example):

To a 10-mL Polyethylene (PE) tube equipped with a stir bar were added TBAT (108 mg, 0.2 mmol, 4.0 equiv) and CH₃CN (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), **3a** (36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (23.8 mg, 0.125 mmol, 2.5 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.2 Screening of Additives and Metals

Table S4: Screening of Additives and Metals^a



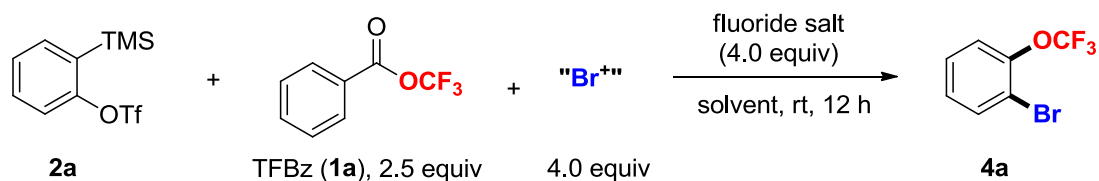
^aThe reaction was conducted on 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard.

Typical Experimental Procedures (Taking Table S4, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added TBAT (108 mg, 0.2 mmol, 4.0 equiv), **S4** (47.8 mg, 0.1 mmol, 2.0 equiv) and THF (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), **3a** (36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (23.8 mg, 0.125 mmol, 2.5 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.3 Further Screening of Fluoride Salt, 'Br⁺' and Solvents

Table S5: Further Screening of Fluoride Salt, 'Br⁺' and Solvents^a



Entry	"Br ⁺ "	Fluoride salt	Solvent	Yield (%)
1	Ph—C≡C—Br (3a)	TBAT	THF	39
2	C ₆ F ₁₃ Br (3b)	TBAT	THF	35
3	C ₈ F ₁₇ Br	TBAT	THF	21
4	C ₆ F ₅ Br (3c)	TBAT	THF	40
5	<i>p</i> -MeO-C ₆ H ₄ —C≡C—Br	TBAT	THF	33
6	<i>p</i> -NO ₂ -C ₆ H ₄ —C≡C—Br	TBAT	THF	35
7	Ph—C≡C—Br (3a)	KF + 18-crown-6	THF	49
8	Ph—C≡C—Br (3a)	CsF + 15-crown-5	THF	0
9	Ph—C≡C—Br (3a)	TBAF in THF	THF	0
10	Ph—C≡C—Br (3a)	KF + dibenzo-18-crown-6	THF	0
11	Ph—C≡C—Br (3a)	TASF	THF	0
12	Ph—C≡C—Br (3a)	CsF + Ph ₂ IOTf	THF	0
13	Ph—C≡C—Br (3a)	KF + 18-crown-6	DME	51
14	Ph—C≡C—Br (3a)	KF + 18-crown-6	Diglyme	64
15	Ph—C≡C—Br (3a)	KF + 18-crown-6	1,4-dioxane	34
16	Ph—C≡C—Br (3a)	KF + 18-crown-6	EtOAc	67

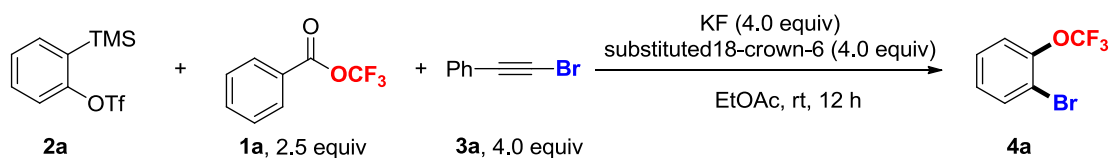
^aThe reaction was conducted on 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard.

Typical Experimental Procedures (Taking Table S5, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added TBAT (108 mg, 0.2 mmol, 4.0 equiv), and THF (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (23.8 mg, 0.125 mmol, 2.5 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.4 Further Screening of Crown ethers

Table S6: Further Screening of Crown Ethers^a



Entry	Substituted 18-crown-6	Yield (%)
1	4,13-diaza-18-crown-6	0
2	benzo-18-crown-6	11
3	<i>N,N'</i> -dibenzyl-4,13-diaza-18-crown-6	0
4	dibenzo-18-crown-6	0
5	<i>cis</i>-dicyclohexano-18-crown-6	76

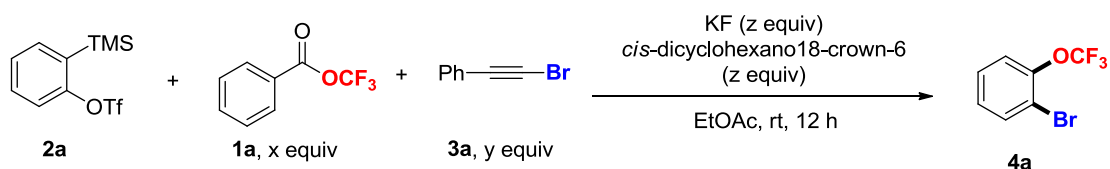
^aThe reaction was conducted on a 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard.

Typical Experimental Procedures (Taking Table S6, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added KF (11.6 mg, 0.2 mmol, 4.0 equiv), 4, 13-diaza-18-crown-6 (52.5 mg, 0.2 mmol, 4.0 equiv) and EtOAc (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (23.8 mg, 0.125 mmol, 2.5 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.5 Screening of the Ratio of 1a/3a/KF

Table S7: Screening of the Ratio of 1a/3a/KF^a



Entry	1a/3a/KF (molar ratio)	Yield (%)
1	3.0/4.0/4.5	82
2	3.5/4.0/5.0	82
3	4.0/4.0/5.5	82
4	3.0/1.2/4.5	74
5	3.0/1.5/4.5	76
6	3.0/2.0/4.5	77
7	3.0/3.0/4.5	81
8	3.0/4.0/3.5	77
9	3.0/4.0/4.0	79
10	3.0/4.0/5.0	82
11	3.0/4.0/5.5	79
12 ^b	3.0/4.0/4.5	75

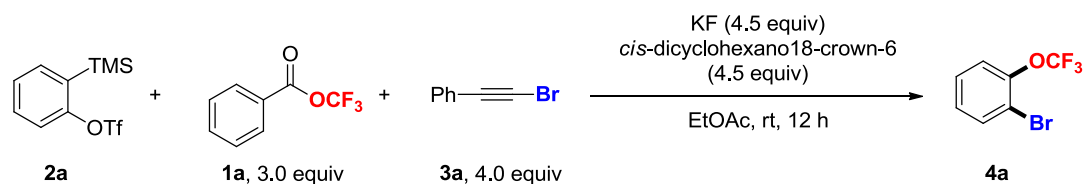
^aThe reaction was conducted on a 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard. ^bCF₃SO₂OCF₃ (TFMT) was used instead of **2a** (TFBz).

Typical Experimental Procedures (Taking Table S7, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 4.5 equiv) and EtOAc (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (28.5 mg, 0.15 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.6 Influence of the Reactors

Table S8: Influence of the Reactors



Entry	Reactor	Yield (%)
1	10-mL PE tube in glove box	83
2	25-mL Schlenk tube under N ₂ flow	0
3	10-mL sealed glass tube	81
4	10-mL glass vial in glove box	69
5	5-mL FEP vial in glove box	84
6	10-mL PE tube in glove box without a cap	64
7	10-mL PE tube in glove box containing 90 ppm H ₂ O	70
8	10-mL PE tube in glove box with H ₂ O (2 equiv)	0

^aThe reaction was conducted on a 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard. PE = polyethylene; FEP = fluorinated ethylene propylene, a copolymer of hexafluoropropylene and tetrafluoroethylene.

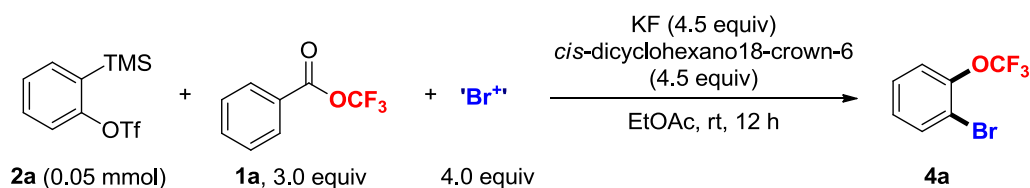
Typical Experimental Procedures (Taking Table S8, entry 4 as an example):

To a 10-mL oven-dried glass vial equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 4.5 equiv), cis-dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 4.5 equiv) and EtOAc (2 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (28.5 mg, 0.15 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

Summary: It is worth mentioning that water and flowing inert gas would lower the yield due to accelerating the collapse of trifluoromethoxide anion.

6.7 Effects of Concentration and Other Bromination Reagents

Table S9: Effects of Concentration and Other Bromination Reagents



Entry	'Br'+	EtOAc (mL)	Yield (%)
1	PhCCBr (3a)	1	81
2	PhCCBr (3a)	2	82
3	PhCCBr (3a)	0.5	75
4	PhCCBr (3a)	2.5	69
5	C ₆ F ₅ Br (3c)	1	79
6	C ₆ F ₁₃ Br (3b)	1	81

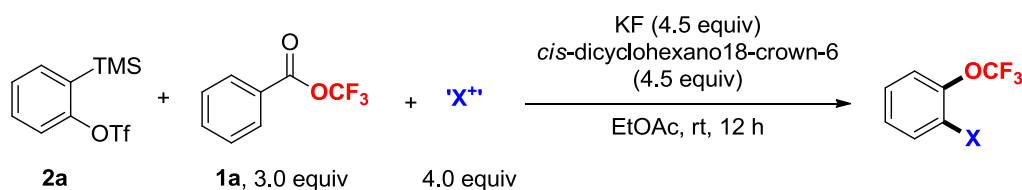
^aThe reaction was conducted on 0.05 mmol scale. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard.

Typical Experimental Procedures (Taking Table S9, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 4.5 equiv), dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 4.5 equiv) and EtOAc (1 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (28.5 mg, 0.15 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

6.8 Optimization on the Reaction Conditions of the Trifluoromethoxylation–Iodination and -Chlorination of Benzyne

Table S10: Optimization on the Reaction Conditions of the Trifluoromethoxylation–Iodination and -Chlorination of Benzyne^a



Entry	X^+	Yield (%)
1	Ph—C≡C—I	77
2	C ₄ F ₉ I	69
3	C ₆ F ₅ I (3d)	78
<hr/>		
4	CCl ₄ (3e)	50
5	C ₂ Cl ₆	32
6	TsCl	0
7	NCS	0
8	TCCA	0
9	C ₆ F ₅ Cl	29
10	Ph—C≡C—Cl	5
<hr/>		
11	CCl ₄ (10 equiv)	43
12	CCl ₄ (20 equiv)	47
13	CCl ₄ (100 equiv)	29
14	CCl ₄ (1 equiv)	51
15	CCl ₄ (2 equiv)	52

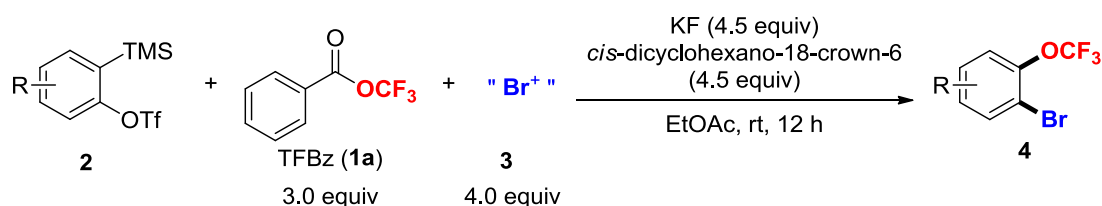
^aThe reaction was conducted on 0.05 mmol scale. 1.0 ml EA. Yield was determined by ¹⁹F NMR with PhCF₃ as an internal standard.

Typical experimental procedures (Take Table S10, entry 1 as an example):

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 4.5 equiv), cis-dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 4.5 equiv) and EtOAc (1 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl iodide (36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (28.5 mg, 0.15 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR.

7. Trifluoromethoxylation–Halogenation of Arynes

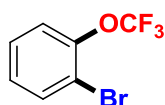
7.1 Trifluoromethoxylation–Bromination of Arynes



General Procedures:

To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (78.4 mg, 1.35 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (503 mg, 1.35 mmol, 4.5 equiv) and ethyl acetate (6 mL) in the glove box. Then **2** (0.3 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 218 mg, 1.2 mmol, 4.0 equiv) or perfluorohexyl bromide (**3b**, 479 mg, 1.2 mmol, 4.0 equiv) or pentafluorobromobenzene (**3c**, 296 mg, 1.2 mmol, 4.0 equiv), and **1a** (171 mg, 0.9 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. [When **2i** and **2e** were used as the substrates, 10 mL 2N NaOH (aq.) was added to the mixture and stirred at room temperature for 6 h to destroy the byproduct benzoyl fluoride (**1a'**). The reaction mixture was extracted with Et₂O for 3 times and the combined organic phase was washed with saturated NaCl (aq) and dried over MgSO₄.] After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **4**.

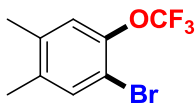
2-Bromo-1-(trifluoromethoxy)benzene (**4a**)



The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**) in 77% ¹⁹F NMR yield.

¹⁹F NMR (376 MHz, ethyl acetate) δ -57.86 (s), with PhCF₃ δ -62.84 (s) as internal standard. GC-MS (EI): 239.9 (M⁺).

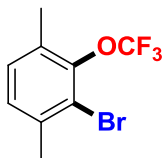
1-Bromo-4,5-dimethyl-2-(trifluoromethoxy)benzene (**4b**)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**), KF (6 equiv) and *cis*-dicyclohexano-18-crown-6 (6 equiv) for 48 h; (68 mg, 84% yield).

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (s, 1H), 7.08 (s, 1H), 2.23 (s, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.65 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 137.6, 137.2, 134.3, 123.3, 120.5 (q, J = 258.3 Hz), 112.4, 19.6, 19.0. MS (EI, m/z , %): 268 (M^+ , 100), 270 (98), 189 (80); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_8\text{BrF}_3\text{O}$; 267.9711, found, 267.9714.

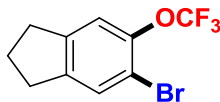
1-Bromo-3,6-dimethyl-2-(trifluoromethoxy)benzene (4c)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (69 mg, 85% yield).

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.09 (m, apparently s, 2H), 2.42 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -55.29 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 145.4, 137.9, 130.9, 129.8, 128.8, 120.9 (q, J = 259.1 Hz), 120.3, 23.1, 16.8. MS (EI, m/z , %): 268 (M^+ , 100), 270 (98), 189 (68); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_8\text{BrF}_3\text{O}$, 267.9711; found, 267.9707.

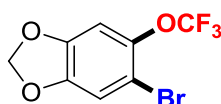
5-Bromo-6-(trifluoromethoxy)-2,3-dihydro-1H-indene (4d)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**), KF (6 equiv) and *cis*-dicyclohexano-18-crown-6 (6 equiv) for 48 h; (73 mg, 86% yield).

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (s, 1H), 7.16 (s, 1H), 2.92 – 2.87 (m, 4H), 2.12 (quint, $J = 7.5$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.62 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 145.4, 144.7, 129.2, 120.6 (q, $J = 258.3$ Hz), 118.4, 113.3, 32.7, 32.3, 25.8. MS (EI, m/z , %): 280 (M^+ , 82), 282 (82), 201 (77), 115 (100); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{BrF}_3\text{O}$, 279.9711; found, 279.9714.

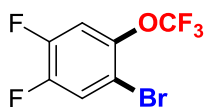
5-Bromo-6-(trifluoromethoxy)benzo[d][1,3]dioxole (4e)



The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**); (74 mg, 87% yield; 1.0-mmol scale, 233 mg, 82% yield).

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.03 (s, 1H), 6.83 (d, $J = 1.2$ Hz, 1H), 6.04 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -58.09 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 146.9, 140.4, 120.5 (q, $J = 258.9$ Hz), 112.4, 107.2, 104.1, 102.6. MS (EI, m/z , %): 284 (M^+ , 100), 286 (93), 69 (50); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_8\text{H}_4\text{BrF}_3\text{O}_3$, 283.9296; found, 283.9288.

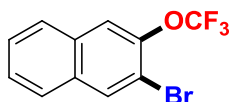
2-Bromo-4,5-difluoro-1-(trifluoromethoxy)benzene (4f)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**) in 56% NMR yield.

^{19}F NMR (376 MHz, ethyl acetate) δ -55.46 (s, 3F), -134.50 (dt, $J = 18.6, 9.2$ Hz, 1F), -136.33 (dt, $J = 20.6, 8.3$ Hz, 1F) with PhCF_3 -62.84 (s). GC-MS (EI): 275.9 (M^+).

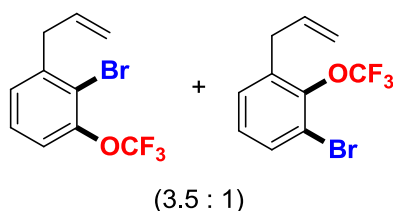
2-Bromo-3-(trifluoromethoxy)naphthalene (4g)



The title compound was prepared following the general procedures with pentafluorobromobenzene (**3c**); (59 mg, 67% yield).

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.86 – 7.77 (m, 2H), 7.77 (d, J = 1.4 Hz, 1H), 7.64 – 7.47 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.66 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 143.7, 133.1, 132.5, 132.4, 127.7, 127.4, 127.3, 126.8, 120.6 (q, J = 259.1 Hz), 119.6, 114.3. MS (EI, m/z , %): 290 (M^+ , 100), 292 (99), 193 (52), 195 (50); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_6\text{BrF}_3\text{O}$, 289.9554; found, 289.9556.

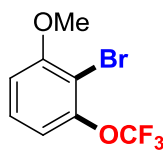
1-Allyl-2-bromo-3-(trifluoromethoxy)benzene and 1-allyl-3-bromo-2-(trifluoromethoxy)benzene (4h, 3.5:1)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (65 mg, 77% yield).

Colorless liquid. *For major isomer:* ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.28 (m, **1H**), 7.19 (d, J = 7.3 Hz, **2H**), 6.08 – 5.92 (m, **1H**), 5.92 – 5.81 (m, **2H**), 3.57 (d, J = 6.5 Hz, **2H**). ^{19}F NMR (376 MHz, CDCl_3) δ -57.47 (s, **3F**). ^{13}C NMR (101 MHz, CDCl_3) δ 146.8 (d, J = 1.3 Hz), 142.4, 134.8, 132.1, 128.4, 127.9, 120.5 (q, J = 258.9 Hz), 119.9, 117.2, 40.4. *For minor isomer:* ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, J = 7.9, 1.3 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.14 (d, J = 7.9 Hz, 1H), 5.92 – 5.81 (m, 2H), 5.19 – 5.05 (m, 1H), 3.50 (d, J = 6.6 Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -55.44 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9 (d, J = 1.6 Hz), 136.3, 135.0, 131.7, 130.0, 128.3, 120.7 (q, J = 259.7 Hz), 118.5, 117.4, 34.4. MS (EI, m/z , %): 280 (M^+ , 100), 282 (98); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{BrF}_3\text{O}$, 279.9711; found, 279.9718 and 279.9720.

2-Bromo-1-methoxy-3-(trifluoromethoxy)benzene (4i)



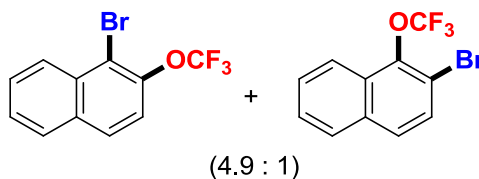
The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (69 mg, 85% yield).

Colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (t, $J = 8.4$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 3.93 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.45 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.5, 147.6, 128.3, 120.4 (q, $J = 259.0$ Hz), 113.9, 109.8, 106.3, 56.6. **MS (EI, m/z , %)**: 270 (M^+ , 100), 272 (95), 69 (43); **HRMS (EI) (m/z):** $[\text{M}]^+$ Calcd for $\text{C}_8\text{H}_6\text{BrF}_3\text{O}_2$, 269.9503; found, 269.9506.

1-Bromo-2-(trifluoromethoxy)naphthalene

and

2-bromo-1-(trifluoromethoxy)naphthalene (4j, 4.9:1)

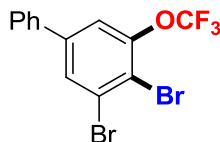


The title compound was prepared following the general procedures with pentafluorobromobenzene (**3c**); (70 mg, 80% yield).

Colorless liquid. *For major isomer:* $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.6$ Hz, **1H**), 7.87 (dd, $J = 8.3, 5.7$ Hz, **2H**), 7.72 – 7.52 (m, **2H**), 7.45 (dd, $J = 9.0, 1.3$ Hz, **1H**). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.98 (s, **3F**). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.5 (d, $J = 1.6$ Hz), 132.8, 132.6, 129.2, 128.3, 128.2, 127.5, 127.0, 120.7 (q, $J = 259.3$ Hz), 120.1 (d, $J = 1.2$ Hz), 115.9. *For minor isomer:* $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.7$ Hz, 1H), 7.87 (dd, $J = 8.3, 5.7$ Hz, 1H), 7.72 – 7.52 (m, 4H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -55.27 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.7 (d, $J = 1.1$ Hz), 133.6, 129.9, 128.9, 128.5, 127.9, 127.8, 127.1, 121.8 (d, $J = 1.6$ Hz), 121.1 (q, $J = 260.7$ Hz), 114.8. **MS (EI, m/z , %)**: 290 (M^+ , 100), 292 (96), 193 (60), 195 (58); **HRMS (EI) (m/z):** $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_6\text{BrF}_3\text{O}$,

289.9554; found, 289.9560 and 289.9543.

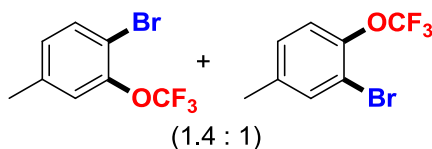
4,4-Dibromo -3-(trifluoromethoxy)-1,1'-biphenyl (4k)



The title compound was prepared following the general procedures with pentafluorobromobenzene (**3c**); (46 mg, 39% yield).

Colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 2.0$ Hz, 1H), 7.56 – 7.52 (m, 2H), 7.51 – 7.40 (m, 4H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.36 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.7, 142.7, 137.6, 130.3, 129.2, 128.8, 127.0, 126.9, 120.4 (q, $J = 260.2$ Hz), 119.5, 118.5. **MS (EI, m/z , %)**: 394 (M^+ , 54), 396 (100), 398 (51), 139 (82); **HRMS (EI)** (m/z): [M] $^+$ Calcd for $\text{C}_{13}\text{H}_7\text{Br}_2\text{F}_3\text{O}$, 393.8816; found: 393.8818.

1-Bromo-4-methyl-2-(trifluoromethoxy)benzene and 2-bromo-4-methyl-1-(trifluoromethoxy)benzene (4l, 1.4:1)

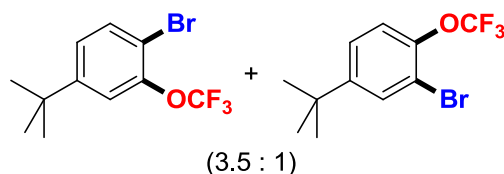


The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (55 mg, 72% yield).

Colorless liquid. *For major isomer:* $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.2$ Hz, 1H), 7.13 (s, 1H), 6.99 (d, $J = 8.2$ Hz, 1H), 2.34 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.49 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.2 (d, $J = 1.7$ Hz), 139.3, 133.5, 128.9, 123.0 (d, $J = 0.9$ Hz), 120.47 (q, $J = 258.8$ Hz), 112.6, 21.0. *For minor isomer:* $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (s, 1H), 7.19 (dd, $J = 8.4, 1.0$ Hz, 1H), 7.12 (d, $J = 6.4$ Hz, 1H), 2.34 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.77 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.3 (d, $J = 1.6$ Hz), 138.5, 134.3, 129.2, 122.1 (d, $J = 1.1$ Hz), 120.52 (q, $J = 258.6$ Hz), 115.8, 20.5. **MS (EI, m/z , %)**: 254 (M^+ , 100), 256

(98); **HRMS (EI)** (m/z): $[M]^+$ Calcd for $C_8H_6BrF_3O$, 253.9554; found, 253.9558 and 253.9559.

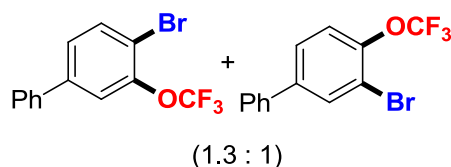
1-Bromo-4-*tert*-butyl-2-(trifluoromethoxy)benzene and 2-bromo -4-*tert*-butyl-1-(trifluoromethoxy)benzene (4m, 3.5:1)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (65 mg, 77% yield).

Colorless liquid. *For major isomer*: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.5$ Hz, **1H**), 7.30 (s, **1H**), 7.20 (dd, $J = 8.5, 2.0$ Hz, **1H**), 1.31 (s, **9H**). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.47 (s, **3F**). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.9, 146.2 (d, $J = 1.3$ Hz), 133.3, 125.7, 120.5 (q, $J = 258.5$ Hz), 119.9, 112.7, 34.8, 31.0. *For minor isomer*: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (d, $J = 1.9$ Hz, **1H**), 7.33 (dd, $J = 8.8, 2.1$ Hz, **1H**), 7.24 – 7.21 (m, **1H**), 1.31 (s, **9H**). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.66 (s, **3F**). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.7, 144.1 (d, $J = 1.3$ Hz), 131.1, 125.4, 121.8, 120.5 (q, $J = 258.5$ Hz), 115.7, 34.7, 31.1. **MS (EI, m/z , %)**: 296 (M^+ , 23), 298 (23), 281 (100), 283 (98); **HRMS (EI)** (m/z): $[M]^+$ Calcd for $C_{11}H_{12}BrF_3O$, 296.0024; found, 296.0020 and 296.0033.

3-Bromo-4-(trifluoromethoxy)-1,1'-biphenyl and 4-bromo-3-(trifluoromethoxy)-1,1'-biphenyl (4n, 1.3:1)

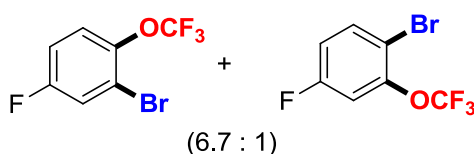


The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**); (79 mg, 83% yield).

Colorless liquid. *For major isomer:* ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.3 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.50 – 7.44 (m, 2H), 7.44 – 7.35 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.40 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 142.4, 138.7, 134.2, 129.1, 128.3, 126.9, 126.7, 121.0, 120.5 (q, J = 259.2 Hz), 114.9. *For minor isomer:* ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 2.2 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.50 – 7.44 (m, 2H), 7.44 – 7.35 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.56 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 145.7, 141.5, 138.5, 132.5, 129.0, 128.2, 127.2, 127.1, 122.4, 120.5 (q, J = 259.2 Hz), 116.4. MS (EI, m/z , %): 316 (M^+ , 100), 318 (98), 139 (58); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_8\text{BrF}_3\text{O}$, 315.9711; found, 315.9718 and 315.9721.

2-Bromo-4-fluoro-1-(trifluoromethoxy)benzene and

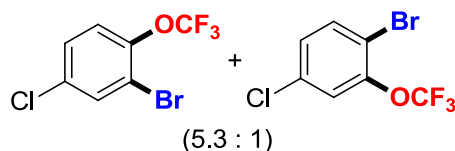
2-Bromo-5-fluoro-1-(trifluoromethoxy)benzene (4o, 6.7:1)



The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**) in 71% ^{19}F NMR yield with the ratio (6.7 : 1) of isomers. ^{19}F NMR (376 MHz, ethyl acetate) *minor isomer:* δ -58.08 (s, 3F), -111.17 (m, 1F) and *major isomer:* -58.31 (s, 3F), -112.66 (m, 1F), with PhCF_3 δ -62.84 (s) as internal standard. GC-MS (EI): 257.9 (M^+).

2-Bromo-4-chloro-1-(trifluoromethoxy)benzene and

2-bromo-5-chloro-1-(trifluoromethoxy)benzene (4p, 5.3:1)

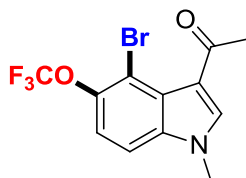


The title compound was prepared following the general procedures with perfluorohexyl bromide (**3b**); (55 mg, 66% yield).

Colorless liquid. *For major isomer:* ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J =

2.4 Hz, **1H**), 7.33 (dd, $J = 8.7, 2.4$ Hz, **1H**), 7.25 (d, $J = 8.8$ Hz, **1H**). **^{19}F NMR** (376 MHz, CDCl_3) δ -57.84 (s, **3F**). **^{13}C NMR** (101 MHz, CDCl_3) δ 145.2 (d, $J = 1.9$ Hz), 134.6, 133.7, 128.8, 123.1, 120.35 (q, $J = 259.7$ Hz), 117.0. *For minor isomer:* **^1H NMR** (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.6$ Hz, 1H), 7.32 (d, $J = 2.4$ Hz, 1H), 7.18 (dd, $J = 8.6, 2.2$ Hz, 1H). **^{19}F NMR** (376 MHz, CDCl_3) δ -57.68 (s, 3F). **^{13}C NMR** (101 MHz, CDCl_3) δ 146.8 (d, $J = 1.8$ Hz), 134.1, 133.2, 128.4, 122.8, 120.31 (q, $J = 260.4$ Hz), 114.3. **MS (EI, m/z , %):** 274 (M^+ , 80), 276 (100), 207 (74); **HRMS (EI) (m/z):** $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_3\text{BrClF}_3\text{O}$, 273.9008; found, 273.9010 and 273.9013.

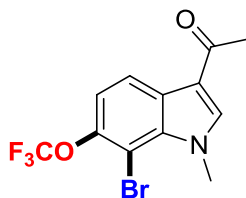
1-(4-Bromo -5-trifluoromethoxy-1-methyl-indole)ethanone (**4q**)



The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**); (80 mg, 83% yield).

Pale-yellow solid. m.p. 139-140 °C. **^1H NMR** (400 MHz, CDCl_3) δ 7.68 (s, 1H), 7.27 (s, 2H), 3.84 (s, 3H), 2.57 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -57.47 (s, 3F). **^{13}C NMR** (101 MHz, CDCl_3) δ 191.9, 142.3 (d, $J = 1.4$ Hz), 137.3, 136.7, 126.1, 120.8 (q, $J = 258.1$ Hz), 118.9, 117.5, 109.6, 33.8, 30.0. **MS (EI, m/z , %):** 335 (M^+ , 34), 337 (33), 320 (100), 322 (99); **HRMS (EI) (m/z):** $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_9\text{BrF}_3\text{NO}_2$, 334.9769; found, 334.9776.

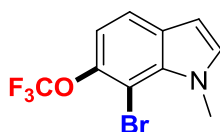
1-(7-Bromo -6-trifluoromethoxy-1-methyl-indole)ethanone (**4r**)



The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**); (77mg, 80% yield).

Pale-yellow solid. m.p. 133-134 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, J = 8.7 Hz, 1H), 7.68 (s, 1H), 7.24 (dd, J = 8.8, 1.3 Hz, 1H), 4.24 (s, 3H), 2.50 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.55 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 143.3, 139.4, 134.5, 127.4, 122.4, 120.7 (q, J = 258.6 Hz), 117.2, 115.9, 99.5, 38.3, 27.5. MS (EI, m/z , %): 335 (M^+ , 44), 337 (42), 320 (100), 322 (96); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_9\text{BrF}_3\text{NO}_2$, 334.9769; found, 334.9770.

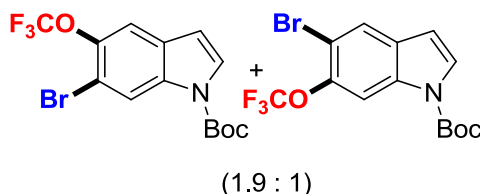
7-Bromo -6-trifluoromethoxy-1-methyl-indole (4s)



The title compound was prepared following the general procedures with pentafluorobromobenzene (**3c**); (67mg, 76% yield).

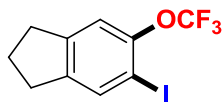
Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 8.6 Hz, 1H), 7.07 (dd, J = 8.6, 1.3 Hz, 1H), 7.05 (d, J = 3.1 Hz, 1H), 6.47 (d, J = 3.1 Hz, 1H), 4.19 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.56 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 142.0, 133.4, 133.3, 129.7, 120.8 (q, J = 257.7 Hz), 120.3, 114.3, 101.2, 99.2, 37.1. MS (EI, m/z , %): 293 (M^+ , 100), 295 (99), 224 (62), 226 (61); HRMS (EI) (m/z): $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_7\text{BrF}_3\text{NO}$, 292.9663; found, 292.9658.

6-Bromo -5-trifluoromethoxy-1-boc-indole and 5-bromo -6-trifluoromethoxy-1-boc-indole (4t, 1.9:1)



The title compound was prepared following the general procedures with phenylethynyl bromide (**3a**); (85 mg, 75% yield).

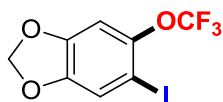
Pale-yellow sticky liquid. For major isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, br, **1H**), 7.63 (d, J = 3.2 Hz, **1H**), 7.50 (s, **1H**), 6.54 (d, J = 3.6 Hz, **1H**), 1.68 (s,



The title compound was prepared following the general procedures with KF (6 equiv) and *cis*-dicyclohexano-18-crown-6 (6 equiv) for 48 h; (68 mg, 69% yield).

Colorless liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.67 (s, 1H), 7.13 (s, 1H), 2.91 – 2.87 (m, 4H), 2.12 (p, *J* = 7.5 Hz, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.05 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 147.6, 146.7, 145.1, 135.3, 120.6 (q, *J* = 258.5 Hz), 117.3, 86.3, 32.7, 32.0, 25.8. **MS (EI, *m/z*, %)**: 328 (M⁺, 100), 243 (13), 201 (19), 115 (60); **HRMS (EI) (*m/z*): [M]⁺** Calcd for C₁₀H₈F₃IO, 327.9572; found, 327.9562.

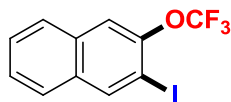
5- Iodo-6-(trifluoromethoxy)benzo[d][1,3]dioxole (5b)



The title compound was prepared following the general procedures; (74 mg, 74% yield).

Colorless liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.21 (s, 1H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.04 (s, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.50 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 148.9, 147.1, 143.6, 120.6 (q, *J* = 259.0 Hz), 117.7, 103.4, 102.7, 78.3. **MS (EI, *m/z*, %)**: 332 (M⁺, 100), 263 (23), 139 (33), 69 (18); **HRMS (EI) (*m/z*): [M]⁺** Calcd for C₈H₄F₃IO₃, 331.9157; found, 331.9161.

2- Iodo-3-(trifluoromethoxy)naphthalene (5c)

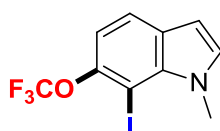


The title compound was prepared following the general procedures; (70 mg, 69% yield).

Pale-yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.40 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.71 (s, 1H), 7.61 – 7.49 (m, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.05 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 145.9, 140.0, 133.1,

133.0, 127.7, 127.5, 127.1, 126.6, 120.6 (q, $J = 259.1$ Hz), 118.0, 87.7. **MS (EI)**, m/z , %): 338 (M^+ , 100), 241 (20), 145 (70), 105 (63); **HRMS (EI)** (m/z): $[M]^+$ Calcd for $C_{11}H_6F_3IO$, 337.9415; found, 337.9409.

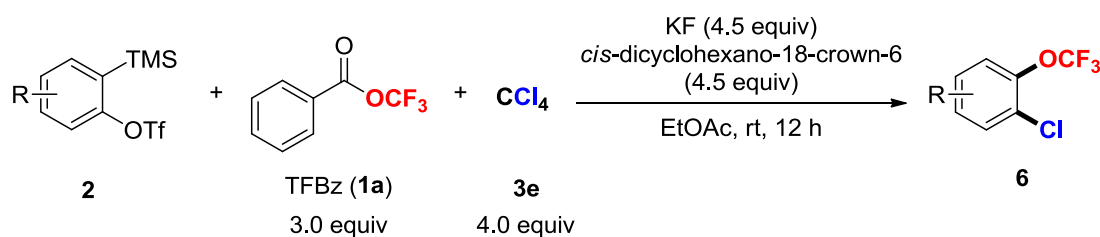
7- Iodo -6-trifluoromethoxy-1-methyl-indole (5d)



The title compound was prepared following the general procedures; (79 mg, 78% yield).

Colorless liquid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, $J = 8.5$ Hz, 1H), 7.09 – 7.05 (m, 2H), 6.45 (d, $J = 3.2$ Hz, 1H), 4.22 (s, 1H).. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.80 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 136.1, 133.7, 129.1, 121.8, 120.9 (q, $J = 257.8$ Hz), 113.4, 100.8, 71.1, 37.5. **MS (EI)**, m/z , %): 341 (M^+ , 100), 272 (37), 244 (12), 148 (34); **HRMS (EI)** (m/z): $[M]^+$ Calcd for $C_{10}H_7F_3INO$, 340.9524; found, 340.9528.

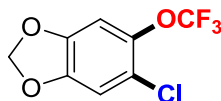
7.3 Trifluoromethoxylation–Chlorination of Arynes



General Procedures:

To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (78.4 mg, 1.35 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (*cis*-DCy-18-C-6, 503 mg, 1.35 mmol, 4.5 equiv) and EtOAc (6 mL) in the glove box. Then **2** (0.3 mmol, 1.0 equiv), carbon tetrachloride (**3e**, 92 mg, 0.6 mmol, 2.0 equiv) and **1a** (171 mg, 0.9 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF_3 was added as an internal standard, the reaction was monitored by ^{19}F NMR and GC-MS.

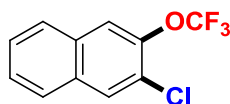
5- Chloro-6-(trifluoromethoxy)benzo[d][1,3]dioxole (6a)



The title compound was prepared following the general procedures in 55% ^{19}F NMR yield.

^{19}F NMR (376 MHz, ethyl acetate) δ -58.25 (s), with PhCF_3 δ -62.84 (s) as the internal standard. GC-MS (EI): 240.0 (M^+).

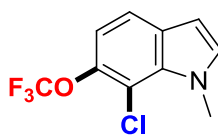
2- Chloro-3-(trifluoromethoxy)naphthalene (6b)



The title compound was prepared following the general procedures in 48% ^{19}F NMR yield.

^{19}F NMR (376 MHz, ethyl acetate) δ -58.22 (s), with PhCF_3 δ -62.84 (s) as the internal standard. GC-MS (EI): 246.0 (M^+).

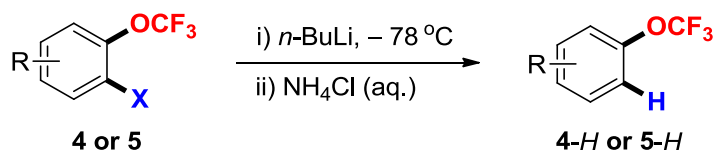
7- Chloro-6-trifluoromethoxy-1-methyl-indole (6c)



The title compound was prepared following the general procedures in 74% ^{19}F NMR yield.

^{19}F NMR (376 MHz, ethyl acetate) δ -58.74 (s), with PhCF_3 δ -62.84 (s) as the internal standard. GC-MS: 249.0 (M^+).

8. Identification of Regioisomers of 4 and 5



General Procedures:

To a 25-mL oven-dried sealed tube equipped with a stir bar were added **4** or **5** (0.1 mmol, 1.0 equiv) and THF (6 mL). Then *n*-BuLi (0.13 mmol, 1.3 equiv) was added slowly at $-78\text{ }^\circ\text{C}$ and kept 30 min. The reaction was quenched with saturated NH_4Cl (aq), diluted with Et_2O and dried over MgSO_4 . After the solution was filtered and the solvent was evaporated under vacuum, the crude product **4-H** or **5-H** was determined by ^1H NMR.

4h-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 8.0$ Hz, 1H), 7.25 – 7.22 (m, 1H), 7.12 (d, $J = 7.5$ Hz, 1H), 7.05 (s, 1H), 6.00 – 5.87 (m, 1H), 5.19 – 4.91 (m, 2H), 3.41 (d, $J = 6.6$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.78 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 8.1$ Hz, 3H), 6.00 – 5.87 (m, 1H), 5.19 – 4.91 (m, 2H), 3.46 – 3.43 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.15 (s). The characteristic peak of the major isomer of **4h-H** [δ 7.05 (s, 1H)] shows that it is 1-allyl-3-(trifluoromethoxy)benzene.

4i-H: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (t, $J = 8.3$ Hz, 1H), 6.84 (dd, $J = 8.3$, 2.2 Hz, 1H), 6.82 (d, $J = 8.5$ Hz, 1H), 6.76 (s, 1H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.81 (s). The only product **4i-H** is in consistency with 1-methoxy-3-trifluoromethoxy benzene.⁴

4j-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.84 (m, 2H), 7.84 (d, $J = 7.3$ Hz, 1H), 7.69 (s, 1H), 7.63 – 7.49 (m, 2H), 7.36 (dd, $J = 8.9$, 1.6 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.71 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 7.9$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.63 – 7.49 (m,

2H), 7.46 (t, $J = 7.9$ Hz, 1H), 7.42 – 7.38 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.47 (s). The major isomer of **4j-H** is in consistency with 2-trifluoromethoxy naphthalene.⁵

4l-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.27 (td, $J = 8.1$ 1.0 Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 7.7$ Hz, 2H), 2.38 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.77 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 2.35 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -58.05 (s). The major isomer **4l-H** is in consistency with 3-(trifluoromethoxy)toluene.⁶

4m-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.29 (m, 2H), 7.21 (s, 1H), 7.07 – 7.00 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.75 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.36 (m, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 1.33 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.95 (s). The minor isomer of **4m-H** is in consistency with 1-(*tert*-butyl)-4-(trifluoromethoxy)benzene.⁷

4n-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.56 (m, 2H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.50 – 7.44 (m, 4H), 7.40 (t, $J = 6.7$ Hz, 1H), 7.22 (ddd, $J = 8.1$, 2.2, 1.0 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.72 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.56 (m, 4H), 7.50 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 7.32 – 7.28 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.84 (s). The major isomer of **4n-H** is in consistency with 3-trifluoromethoxybiphenyl.⁷

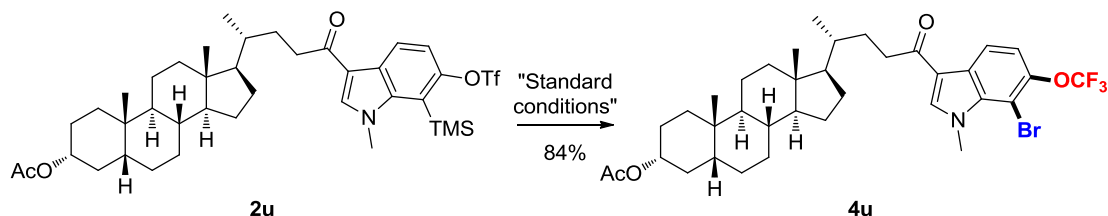
4p-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.34 (m, 2H), 7.16 (d, $J = 8.9$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -58.21 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.22 (s, 1H), other hydrogens cannot be determined. ^{19}F NMR (376 MHz, CDCl_3) δ -58.01 (s). The major isomer of **4p-H** is in consistency with 1-chloro-4-(trifluoromethoxy)benzene.⁸

4s-H: ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 8.6 Hz, 1H), 7.20 (s, 1H), 7.11 (d, J = 3.1 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 6.51 (d, J = 3.1 Hz, 1H), 3.78 (d, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.93 (s). The characteristic peak of **4s-H** [δ 7.20 (s, 1H)] shows that it is 1-methyl-6-trifluoromethoxyindole.

4t-H: Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 3.6 Hz, 1H), 7.42 (s, 1H), 7.18 (dd, J = 9.0, 1.5 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 1.68 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -58.11 (s). Minor isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.62 (d, J = 3.7 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.12 (dd, J = 8.5, 1.3 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 1.68 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.96 (s). The major isomer of **4t-H** is in consistency with 1-Boc-5-trifluoromethoxyindole.⁵

5d-H: ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 8.6 Hz, 1H), 7.20 (s, 1H), 7.11 (d, J = 3.1 Hz, 1H), 7.06 – 6.97 (m, 1H), 6.51 (d, J = 3.1 Hz, 1H), 3.78 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.93 (s). The characteristic peak of **5d-H** [δ 7.20 (s, 1H)] shows that it is 1-methyl-6-trifluoromethoxyindole.

9. Trifluoromethoxylation–Bromination of Steroid-Derived Indolyne Precursor **2u**



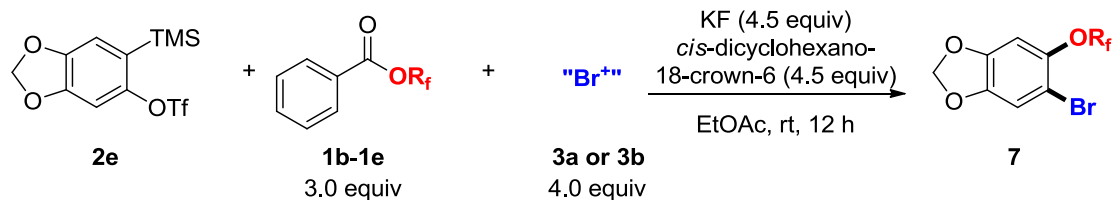
Experimental Procedures:

To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (52.3 mg, 0.9 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (335 mg, 0.9 mmol, 4.5

equiv) and EtOAc (4 mL) in the glove box. Then **2u** (150.4 mg, 0.2 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 145 mg, 0.8 mmol, 4.0 equiv) and **1a** (114 mg, 0.6 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, and the reaction was monitored by ¹⁹F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography to give product **4u** as a white solid (116 mg, 84% yield).

4u: White solid. m.p. 171-172 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 8.7 Hz, 1H), 7.68 (s, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 4.77 – 4.65 (m, 1H), 4.22 (s, 3H), 2.82 (ddd, *J* = 14.9, 10.3, 4.7 Hz, 1H), 2.70 (ddd, *J* = 15.2, 9.4, 5.9 Hz, 1H), 2.02 (s, 3H), 1.97 (d, *J* = 11.4 Hz, 1H), 1.94 – 1.74 (m, 5H), 1.67 (d, *J* = 10.2 Hz, 1H), 1.59 – 1.49 (m, 2H), 1.48 – 1.34 (m, 8H), 1.30 (d, *J* = 12.9 Hz, 1H), 1.27 – 1.00 (m, 8H), 0.97 (d, *J* = 6.1 Hz, 3H), 0.91 (s, 3H), 0.64 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.51 (s). ¹³C NMR (101 MHz, CDCl₃) δ 195.9, 170.7, 143.2, 138.8, 134.5, 127.6, 122.5, 120.69 (q, *J* = 258.5 Hz), 117.2, 115.6, 99.5, 74.4, 56.5, 56.2, 42.8, 41.9, 40.4, 40.2, 38.3, 36.8, 35.8, 35.7, 35.0, 34.6, 32.2, 31.1, 28.3, 27.0, 26.6, 26.3, 24.2, 23.3, 21.5, 20.9, 18.6, 12.1. MS (ESI, *m/z*): 694.2 ([M+H]⁺). HRMS (ESI): Calcd for C₃₆H₄₈BrF₃NO₄ ([M+H]⁺) 694.2719; found, 694.2712.

10. Perfluoroalkylation-Bromination of **2e**

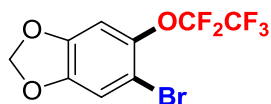


General Procedures:

To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (78.4 mg, 1.35 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (503 mg, 1.35 mmol, 4.5 equiv) and EtOAc (6 mL) in the glove box. Then **2e** (102.7 mg, 0.3 mmol, 1.0 equiv),

phenylethynyl bromide (**3a**, 218 mg, 1.2 mmol, 4.0 equiv) or perfluorohexyl bromide (**3c**, 479 mg, 1.2 mmol, 4.0 equiv), and perfluoroalkyl benzoates **1b-1e** (0.9 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. 10 mL 2N NaOH (aq) was added to the mixture and stirred at room temperature for 6 h to destroy the byproduct benzoyl fluoride (**1a'**). It was extracted with Et₂O for 3 times and the combined organic phase was washed with saturated NaCl (aq) and dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography to give product **7**.

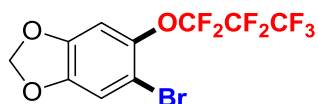
5-Bromo-6-(pentafluoroethoxy)benzo[*d*][1,3]dioxole (7a):



The title compound was prepared following the general procedures using **1b** and **3b**; (81 mg, 80% yield).

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 1H), 6.84 (s, 1H), 6.04 (s, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -85.60 (m, 3F), -87.63 (m, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 147.6, 147.0, 139.6, 116.6 (qt, *J* = 284.9, 43.6 Hz), 114.4 (tq, *J* = 276.1, 42.2 Hz), 112.5, 107.4, 104.7, 102.6. MS (EI, *m/z*, %): 334 (M⁺, 100), 336 (98), 215 (84), 217 (81); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₉H₄BrF₅O₃, 333.9264; found, 333.9260.

5-Bromo-6-(heptafluoropropoxy)benzo[*d*][1,3]dioxole (7b):

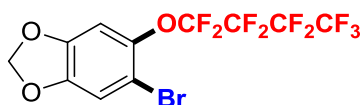


The title compound was prepared following the general procedures using **1c** and **3a**; (77 mg, 66% yield).

Pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 1H), 6.83 (s, 1H), 6.04

(s, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -81.06 (t, J = 6.8 Hz, 3F), -83.56 (m, 2F), -129.14 (m, 2F). **¹³C NMR** (101 MHz, CDCl₃) δ 147.6, 147.1, 139.5, 117.4 (qt, J = 287.0, 33.1 Hz), 115.8 (tt, J = 278.2, 30.3 Hz), 112.6, 107.4, 107.2 (tm, J = 267.1 Hz), 104.9, 102.7. **MS (EI, m/z , %)**: 384 (M^+ , 100), 386 (98), 217 (93), 215 (91); **HRMS (EI) (m/z):** [M]⁺ Calcd for C₁₀H₄BrF₇O₃, 383.9232; found, 383.9234.

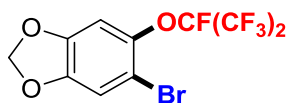
5-Bromo-6-(nonafluorobutoxy)benzo[d][1,3]dioxole (7c):



The title compound was prepared following the general procedures using **1d** and **3a**; (84 mg, 64% yield).

Pale-yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.04 (s, 1H), 6.83 (s, 1H), 6.04 (s, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -80.96 (t, J = 9.5 Hz, 3F), -82.50 (m, 2F), -125.74 (m, 2F), -126.29 (m, 2F). **¹³C NMR** (101 MHz, CDCl₃) δ 147.6, 147.1, 139.5, 117.4 (qt, J = 288.1, 33.1 Hz), 116.1 (tt, J = 278.5, 30.8 Hz), 112.6, 111.9 – 105.0 (m, 2C), 107.3, 104.8, 102.7. **MS (EI, m/z , %)**: 434 (M^+ , 74), 436 (70), 217 (99), 215 (100), 69 (71); **HRMS (EI) (m/z):** [M]⁺ Calcd for C₁₁H₄BrF₉O₃, 433.9200; found, 433.9192.

5-Bromo-6-(heptafluoroisopropoxy)benzo[d][1,3]dioxole (7d)



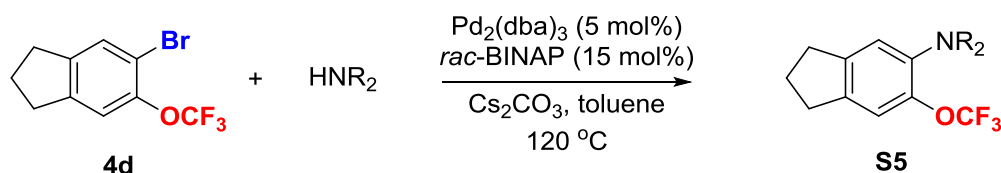
The title compound was prepared following the general procedures using **1e** and **3a**; (75 mg, 65% yield).

Pale-yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.01 (s, 1H), 6.83 (d, J = 1.7 Hz, 1H), 6.03 (s, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -78.07 (d, J = 3.0 Hz, 6F), -133.74 (m, 1F). **¹³C NMR** (101 MHz, CDCl₃) δ 147.5, 146.5, 142.2, 118.3 (qd, J = 289.5, 34.4 Hz), 106.3, 104.22, 104.19, 102.6, 102.2(d(sept), J = 254.0, 36.2 Hz). **MS (EI, m/z , %)**: 384 (M^+ , 71), 386 (70), 217 (97), 215 (100); **HRMS (EI) (m/z):** [M]⁺

Calcd for C₁₀H₄BrF₇O₃, 383.9232; found, 383.9230.

11. Synthetic Application of Compound 4

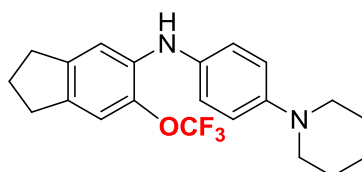
11.1 Pd-Catalyzed C–N Bond Formation to Afford S5



General Procedures:

To a 10-mL oven-dried sealed tube equipped with a stir bar were added Pd₂(dba)₃ (9.2 mg, 0.01 mmol, 5 mol%), *rac*-BINAP (18.6 mg, 0.03 mmol, 15 mol%) and Cs₂CO₃ (124 mg, 0.38 mmol, 1.9 equiv) in the glove box. The tube was removed out of glove box, and toluene (2 mL), **4d** (56 mg, 0.2 mmol, 1.0 equiv) and amine (0.3 mmol, 1.5 equiv) were added under N₂. The tube was sealed and stirred at 120 °C for hours. The mixture was cooled down to room temperature and the solution was filtered and the solvent was evaporated under vacuum. The crude product was purified by flash column chromatography to give product **S5**.

6-(Trifluoromethoxy)-*N*-(4-piperidinophenyl)-2,3-dihydro-1*H*-inden-5-amine (**S5a**)

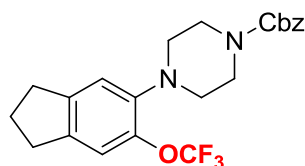


The title compound was prepared following the general procedures for 12 h with 4-piperidinoaniline; (67 mg, 89% yield).

Pale-yellow solid. m.p. 64-65 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.08 (s, 1H), 7.06 (s, 2H), 6.95 (br, s, 2H), 5.62 (s, 1H), 3.33 – 3.02 (m, 4H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.05 (quint, *J* = 7.4 Hz, 2H), 1.74 (br, s, 4H), 1.64 – 1.49

(m, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.76 (s, 3F). **¹³C NMR** (126 MHz, CDCl₃) δ 148.7, 143.3, 136.8, 135.8, 134.3, 133.8, 123.3, 121.0 (q, J = 257.6 Hz), 117.8, 117.2, 111.0, 51.4, 32.9, 32.3, 26.0, 25.8, 24.2. **MS (ESI, m/z)**: 377.4 ([M+H]⁺). **HRMS (ESI)**: Calcd for C₂₁H₂₄F₃N₂O ([M+H]⁺) 377.1841; found, 377.1840.

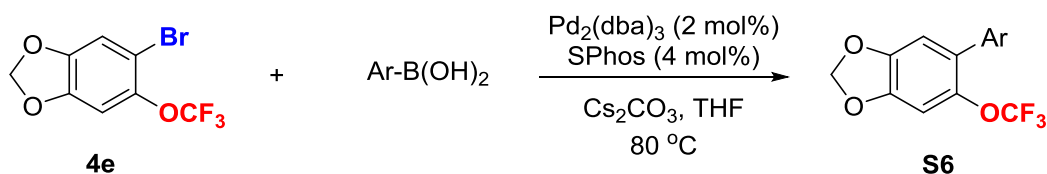
1-(6-Trifluoromethoxy-2,3-dihydro-1H-inden-5-yl)-4-cbz-piperazine (S5b)



The title compound was prepared following the general procedures for 15 h with 1-cbz-piperazine; (70 mg, 84% yield).

Orange liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.51 – 7.29 (m, 5H), 7.06 (s, 1H), 6.90 (s, 1H), 5.17 (s, 2H), 3.74 – 3.47 (m, 4H), 2.97 (br, s, 4H), 2.87 (t, J = 7.4 Hz, 4H), 2.09 (quint, J = 7.5 Hz, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.24 (s, 3F). **¹³C NMR** (126 MHz, CDCl₃) δ 155.3, 143.4, 143.2, 141.3 (q, J = 1.3 Hz), 139.3, 136.7, 128.5, 128.0, 127.9, 120.6 (q, J = 257.0 Hz), 118.0 (d, J = 0.8 Hz), 116.1, 67.2 51.2, 44.2, 32.8, 32.5, 25.8. **MS (ESI, m/z)**: 421.4 ([M+H]⁺). **HRMS (ESI)**: Calcd for C₂₂H₂₄F₃N₂O₃ ([M+H]⁺) 421.1739; found, 421.1730.

11.2 Pd-Catalyzed C–C Bond Formation to Afford S6



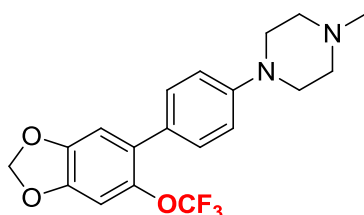
(SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl)

General Procedures:

To a 10-mL oven-dried sealed tube equipped with a stir bar were added Pd₂(dba)₃ (3.6 mg, 0.004 mmol, 2 mol%), SPhos (3.2 mg, 0.008 mmol, 4 mol%) and Cs₂CO₃ (130 mg, 0.4 mmol, 2.0 equiv) in the glove box. The tube was removed out of glove

box, and THF (2 mL), **4e** (57 mg, 0.2 mmol, 1.0 equiv) and aryl boronic acids (0.3 mmol, 1.5 equiv) were added under N₂. The tube was sealed and stirred at 80 °C for 24 h. The mixture was cooled down to room temperature and the solution was diluted with EtOAc, washed with water, saturated NaCl (aq) and dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography to give product **S6**.

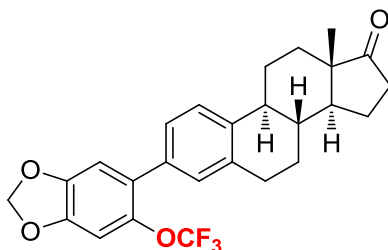
1-[4-(6-Trifluoromethoxy-1,3-benzodioxol-5-yl)phenyl]-4-methylpiperazine (S6a)



The title compound was prepared following the general procedures with [4-(4-methylpiperazin-1-yl)phenyl]boronic acid on 0.2 mmol scale; (72 mg, 95% yield).

Yellowish-brown solid. m.p. 126-127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.83 (s, 2H), 6.02 (s, 2H), 3.40 – 3.18 (m, 4H), 2.73 – 2.50 (m, 4H), 2.39 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.65 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 150.2, 146.7, 146.3, 139.9 (q, *J* = 1.7 Hz), 129.9, 128.9, 127.8, 120.5 (q, *J* = 257.4 Hz), 115.3, 109.8, 103.3 (q, *J* = 1.2 Hz), 102.0, 55.0, 48.5, 46.1. MS (ESI, *m/z*): 381.4 ([M+H]⁺). HRMS (ESI): Calcd for C₁₉H₂₀F₃N₂O₃ ([M+H]⁺) 381.1426; found, 381.1417.

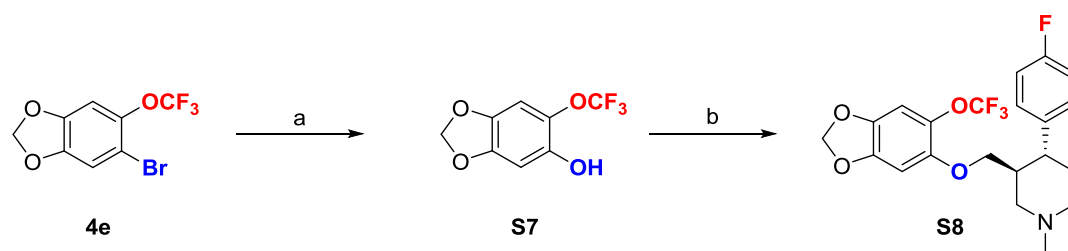
3-(6-Trifluoromethoxy-1,3-benzodioxol-5-yl)phenyl-estra-1,3,5(10)-triene-17-one (S6b)



The title compound was prepared following the general procedures with ((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)boronic acid on 0.1 mmol scale; (42 mg, 91% yield).

White solid. m.p. 69-70 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.1$ Hz, 1H), 7.20 (d, $J = 8.3$ Hz, 1H), 7.14 (s, 1H), 6.85 (s, 2H), 6.03 (s, 2H), 2.96 (dd, $J = 8.7$, 3.8 Hz, 2H), 2.58 – 2.41 (m, 2H), 2.40 – 2.30 (m, 1H), 2.24 – 1.92 (m, 4H), 1.79 – 1.40 (m, 6H), 0.94 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.42 (s, 3F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 220.8, 147.1, 146.3, 140.0 (q, $J = 1.7$ Hz), 139.0, 136.4, 134.3, 129.6, 128.7, 126.5, 125.2, 120.5 (q, $J = 257.4$ Hz), 110.0, 103.2 (q, $J = 1.2$ Hz), 102.1, 50.6, 48.0, 44.4, 38.1, 35.9, 31.6, 29.4, 26.5, 25.6, 21.6, 13.9. **MS (ESI, m/z)**: 459.4 ($[\text{M}+\text{H}]^+$). **HRMS (ESI)**: Calcd for $\text{C}_{26}\text{H}_{26}\text{F}_3\text{O}_4$ ($[\text{M}+\text{H}]^+$) 459.1783; found, 459.1774.

11.3. Synthesis of CF_3O -Paroxetine Analogue



Conditions: a) *n*-BuLi, THF, -78 °C, 30 min; then $\text{B}(\text{OMe})_3$, 3 h; then AcOH, H_2O_2 , 0 °C–rt, rt, overnight 80% yield. b) (3*S*,4*R*)-4-(4-Fluorophenyl)-3-hydroxymethyl-1-methylpiperidine, PPh_3 , DIAD, THF, 0 °C–50 °C, 50 °C 2 h, 93% yield. DIAD = Diisopropyl azodicarboxylate.

Experimental Procedures:

Step1: To a 50-mL oven-dried Schlenk tube equipped with a stir bar were added **4e** (285 mg, 1.0 mmol, 1.0 equiv) and THF (4 mL) under N_2 . *n*-BuLi (2.4 M) (0.54 mL, 1.3 mmol, 1.3 equiv) was added to mixture dropwise at -78 °C and stirred for 30

min. Then B(OMe)₃ (314 mg, 3.0 mmol, 3.0 equiv) was added and stirred at -78 °C for 3 h. The AcOH (300 mg, 5.0 mmol, 5.0 equiv) and H₂O₂ (30 w/w%) (170 mg, 5.0 mmol, 5.0 equiv) were added at 0 °C and stirred for 30 min. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched by water, extracted with Et₂O, washed with saturated Na₂SO₃ (aq), saturated NaCl (aq) and dried over MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum. The crude product was purified by flash column chromatography to give product **S7** (177 mg, 80% yield).

S7: White solid. m.p. 45-46 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.73 (s, 1H), 6.57 (s, 1H), 5.95 (s, 2H), 5.05 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -58.68 (s). ¹³C NMR (126 MHz, CDCl₃) δ 146.7, 143.0, 140.9, 129.1 (q, *J* = 1.8 Hz), 120.8 (q, *J* = 258.8 Hz), 102.7 (q, *J* = 1.0 Hz), 101.8, 98.6. MS (EI, *m/z*, %): 222 (M⁺, 100), 153 (94), 69 (64); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₈H₅F₃O₄, 222.0140; found, 222.0138.

Step2: To a 25-mL oven-dried Schlenk tube equipped with a stir bar were added (3*S*,4*R*)-4-(4-fluorophenyl)-3-hydroxymethyl-1-methylpiperidine (45 mg, 0.2 mmol, 1.0 equiv), PPh₃ (79 mg, 0.3 mmol, 1.5 equiv) and THF (2 mL) under N₂. DIAD (60.6 mg, 0.3 mmol, 1.5 equiv) was added to mixture at 0 °C and stirred for 10 min. A THF (0.8 mL) solution of **10** (89 mg, 0.4 mmol, 2equiv) was added to mixture at 0 °C and stirred for 10 min. Then the mixture was warmed to 50 °C and stirred for 2 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography to give product **S8** as a sticky liquid (80 mg, 93% yield).

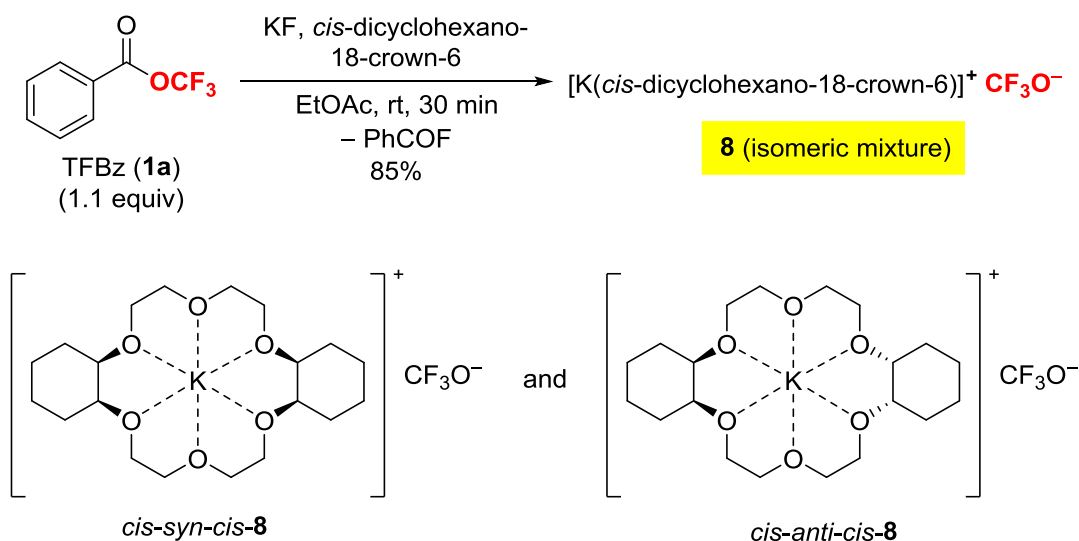
S8: Pale-yellow sticky liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (dd, *J* = 8.3, 5.4 Hz, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.71 (s, 1H), 6.28 (s, 1H), 5.90 (s, 2H), 3.59 (d, *J* = 9.1 Hz, 1H), 3.50 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.31 (d, *J* = 9.0 Hz, 1H), 3.18 (d, *J* = 11.0 Hz, 1H), 2.63 (t, *J* = 9.6 Hz, 1H), 2.52 (s, 3H), 2.48 – 2.36 (m, 2H), 2.30 (t, *J* = 11.4 Hz, 1H), 2.18 – 2.09 (m, 1H), 1.88 (d, *J* = 10.9 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃)

δ -58.72 (s, 3F), -116.41(m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 161.7 (d, $J = 244.9$ Hz), 146.4, 146.2, 141.0, 138.4, 131.5, 128.9 (d, $J = 7.8$ Hz), 120.7 (q, $J = 257.0$ Hz), 115.6 (d, $J = 21.2$ Hz), 104.5, 101.9, 97.0, 69.7, 58.4, 55.8, 45.6, 42.2, 41.3, 32.9. MS (ESI, m/z): 428.4 ($[\text{M}+\text{H}]^+$). HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{22}\text{F}_4\text{NO}_4$ ($[\text{M}+\text{H}]^+$) 428.1485; found, 428.1476.

12. Mechanism Investigations of

Trifluoromethoxylation-Halogenation of arynes

12.1 Preparation of **8**



Experimental Procedures:

To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (58.1 mg, 1.0 mmol, 1.0 equiv), *cis*-dicyclohexano-18-crown-6 (373 mg, 1.0 mmol, 1.0 equiv) and EtOAc (2.5 mL) in the glove box. Then **1a** (209 mg, 1.1 mmol, 1.1 equiv) was added and the solution was stirred at room temperature for 30 min. The solution was filtered and washed with minimum amount of EtOAc. 15 mL hexane was laid carefully and the mixture stood at $-20\text{ }^\circ\text{C}$ in the glove box for 48 h. The mixture was filtered and the solid was washed with hexane and dried to give $[\text{K}(\text{cis}\text{-dicyclohexano-18-crown-6})]\text{OCF}_3$ (**8**) as a white solid (423 mg, 85% yield). It can be stored at room temperature for 2 days without significant decomposition. It

can be kept for much longer time when storing in a glove box at -20 °C.

8: White solid. ^1H NMR (400 MHz, d^6 -acetone) δ 3.78 – 3.52 (m, 20H), 1.96 – 1.88 (m, 4H), 1.63 – 1.41 (m, 8H), 1.34 – 1.26 (m, 4H). ^{19}F NMR (376 MHz, d^6 -acetone) δ -21.93 (s, br, 3F).

12.2 Recrystallization to Prepare the Single Crystals of **8**

Experimental Procedures:

The single crystals for X-ray crystallography analysis were obtained as follows: To a 10-mL PE (polyethylene) tube equipped with a stir bar were added KF (9.9 mg, 0.17 mmol, 1.0 equiv), *cis*-dicyclohexano-18-crown-6 (63.4 mg, 0.17 mmol, 1.0 equiv) and EtOAc (1.0 mL) in the glove box. Then **1a** (35.6 mg, 0.187 mmol, 1.1 equiv) was added and the solution was stirred at room temperature for 30 min. The solution was filtered and 0.2 mL of the solution was placed in a small tube and 0.1 mL hexane was laid very slowly. Single crystals suitable for X-ray crystallography analysis were obtained after standing at -20 °C in the glove box for 5 days.

12.3 Decomposition of [K(*cis*-Dicyclohexano-18-Crown-6)]OCF₃ (**8**):

Experimental Procedures:

To a 10-mL PE (polyethylene) tube equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 1.5 equiv), *cis*-dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 1.5 equiv) and EtOAc (1 mL) in the glove box. Then **1a** (28.5 mg, 0.15 mmol, 1.0 equiv) was added and the solution was stirred at room temperature for 30 min. 1-fluoronaphthalene (4.3 mg) was added as an internal standard. Then 0.45 mL solution was taken up into an NMR tube and heated at 45 °C or 80 °C. It was monitored by ^{19}F NMR spectroscopy. [K(*cis*-Dicyclohexano-18-crown-6)]OCF₃ (**8**) was not completely decomposed to difluorophosgene (COF₂) even after 2 days at 45 °C (Figure S1), but almost completely decomposed within 2 h at 80 °C (Figure S3). The gradual decomposition of CF₃O⁻ was demonstrated by the change of **8** over time in Figure S2 and S4. [8]_t refers to the concentration of **8** at a given time; [8]₀ refers to the initial concentration of **8**. [8]_t/[8]₀ was calculated according to the ^{19}F NMR

integration of **8** and PhCOF.

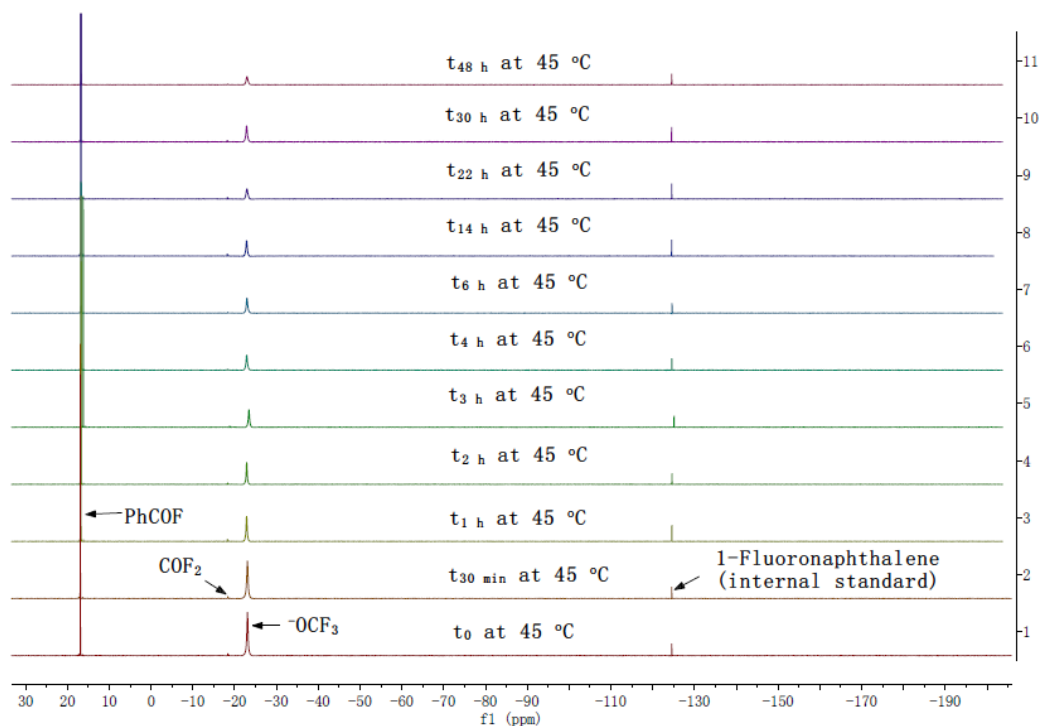


Figure S1. ^{19}F NMR Spectra of $[\text{K}(\text{cis-Dicyclohexano-18-Crown-6})]\text{OCF}_3$ (**8**) in EtOAc at 45 °C

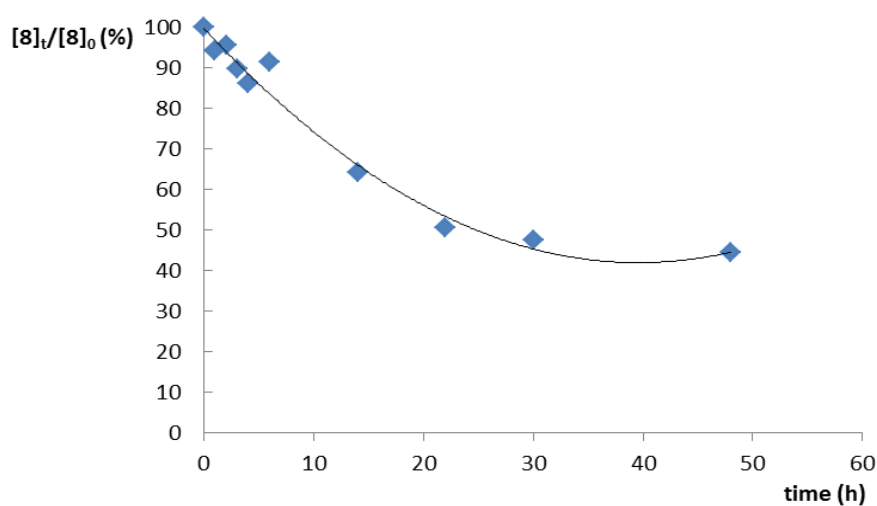


Figure S2. Decomposition of $[\text{K}(\text{cis-Dicyclohexano-18-Crown-6})]\text{OCF}_3$ (**8**) in EtOAc at 45 °C, $[\text{8}]_t$ refers to the concentration of **8** at a given time; $[\text{8}]_0$ refers to the initial concentration of **8**. $[\text{8}]_t/[\text{8}]_0$ was calculated according to the ^{19}F NMR integration of **8** and PhCOF.

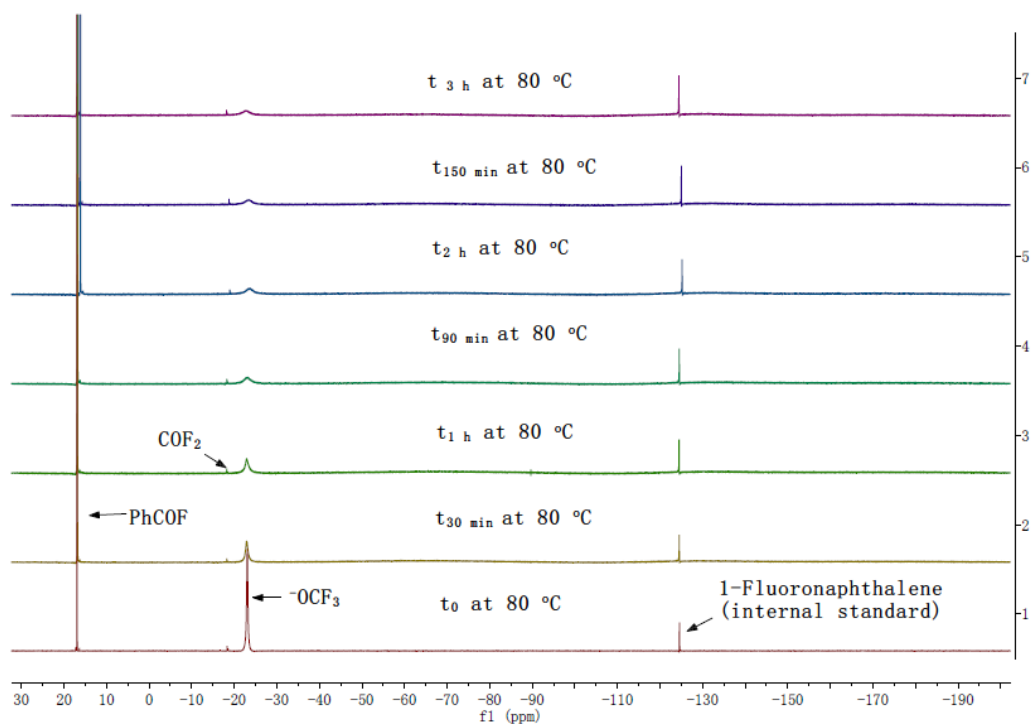


Figure S3. ^{19}F NMR Spectra of $[\text{K}(\text{cis}\text{-Dicyclohexano-18-Crown-6})]\text{OCF}_3$ (8**) in EtOAc at 80 °C**

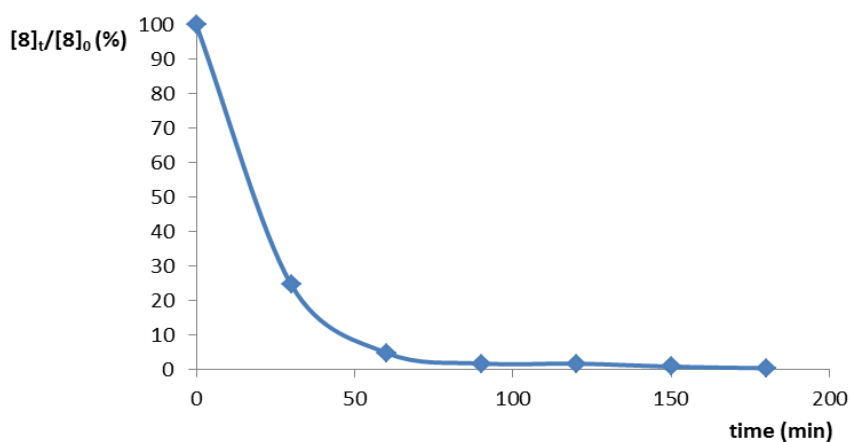
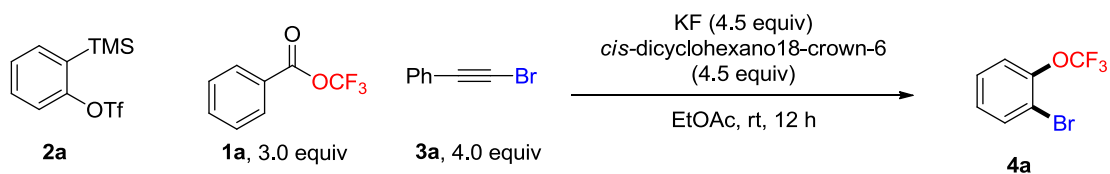


Figure S4. Decomposition of $[\text{K}(\text{cis}\text{-Dicyclohexano-18-Crown-6})]\text{OCF}_3$ (8**) in EtOAc at 80 °C, $[\mathbf{8}]_t$ refers to the concentration of **8** at a given time; $[\mathbf{8}]_0$ refers to the initial concentration of **8**. $[\mathbf{8}]_t/[\mathbf{8}]_0$ was calculated according to the ^{19}F NMR integration of **8** and PhCOF.**

12.4 ^{19}F NMR Monitoring of the Trifluoromethoxylation-Bromination Reaction

(Run Independently)



Experimental Procedures:

To a 10-mL polyethylene (PE) tube equipped with a stir bar were added KF (13.1 mg, 0.225 mmol, 1.5 equiv), *cis*-dicyclohexano-18-crown-6 (83.8 mg, 0.225 mmol, 1.5 equiv) and EtOAc (1 mL) in the glove box. Then **2a** (14.9 mg, 0.05 mmol, 1.0 equiv), phenylethynyl bromide (**3a**, 36.2 mg, 0.2 mmol, 4.0 equiv) and **1a** (28.5 mg, 0.15 mmol, 3 equiv) were added with stirring. The reaction was stirred at room temperature and monitored by ^{19}F NMR with PhCF_3 as an internal standard. The reaction process was shown in Figure S3.

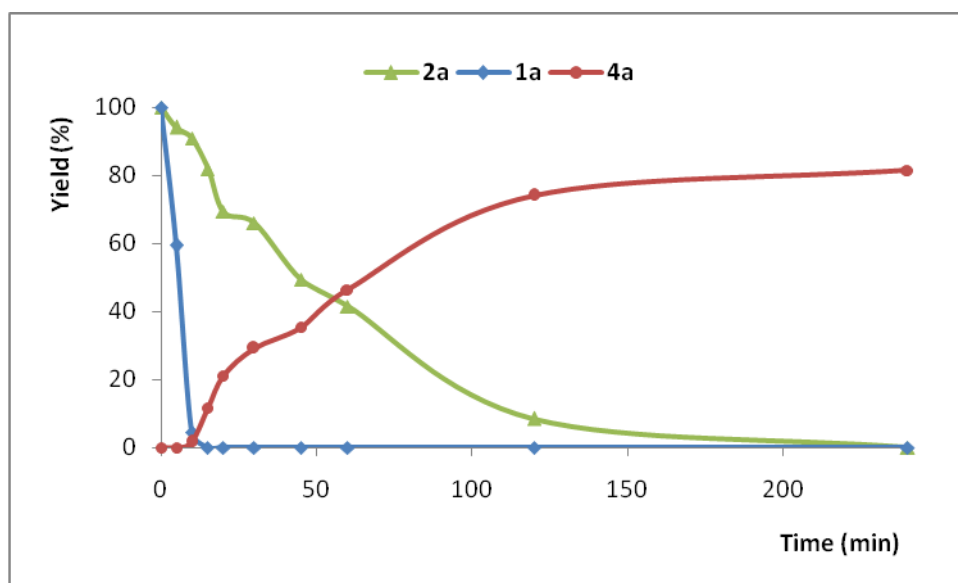
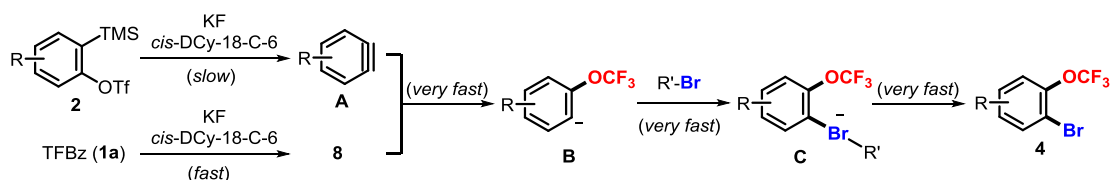


Figure S5. Trifluoromethoxylation-Bromination of **2a**

12.5 Proposed Mechanism

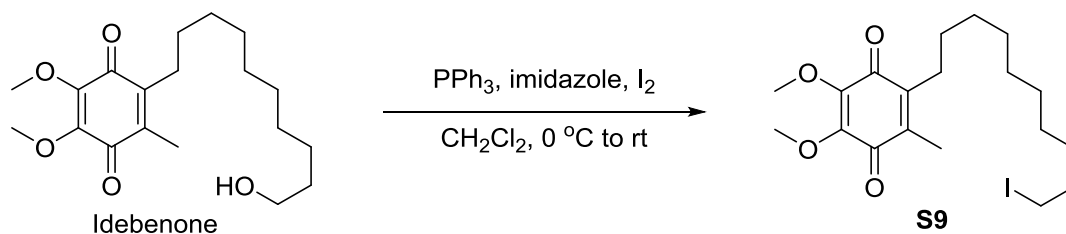
As shown in the following scheme, slowly *in situ* generated arynes intermediate **A** readily reacts with the rapidly generated, relatively stable intermediate **8** to afford an *o*-trifluoromethoxyaryl anion **B**, which is quickly *in-situ* captured by bromination reagents to give the desired products **4** through a bromine ate complex **C**.¹⁰ The

counteraction $[\text{K}(\text{cis-DCy-18-C-6})]^+$ not only enhances the stability and solubility of CF_3O^- , but also improves its reactivity, thus facilitating the trifluoromethoxylation-halogenation of arynes over competing reactions such as fluorination-halogenation and the collapses of CF_3O^- .



13. Versatile Trifluoromethoxylation with TFBz (1a)

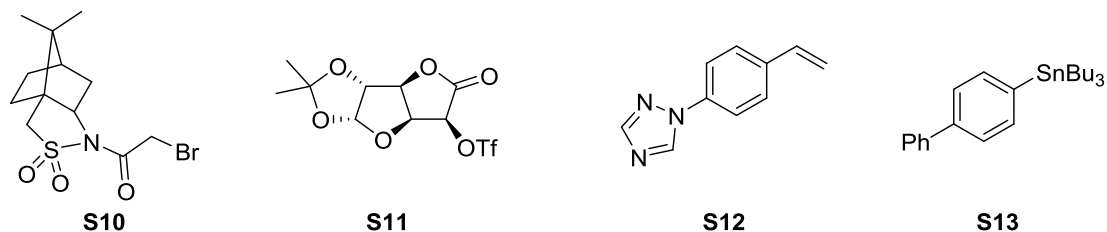
2-(10-iododecyl)-5,6-dimethoxy-3-methylcyclohexa-2,5-diene-1,4-dione (S9)



To a 50-mL oven-dried Schlenk tube equipped with a stir bar were added Triphenylphosphine (1.36 g, 5.2 mmol, 1.4 equiv), imidazole (364 mg, 5.35 mmol, 1.45 equiv) and CH_2Cl_2 (15 mL) under N_2 . I_2 (990 mg, 3.9 mmol, 1.3 equiv) was added to mixture at room temperature and stirred for 10 min. Idebeneone (1.02 g, 3.0 mmol, 1.0 equiv) was added to mixture at 0 °C. Then the mixture was warmed to room temperature and stirred for 4 h. The mixture was washed by water, saturated NaCl (aq) and dried over MgSO_4 . After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography to give product **S9** as an orange solid (1.29 g, 96% yield).

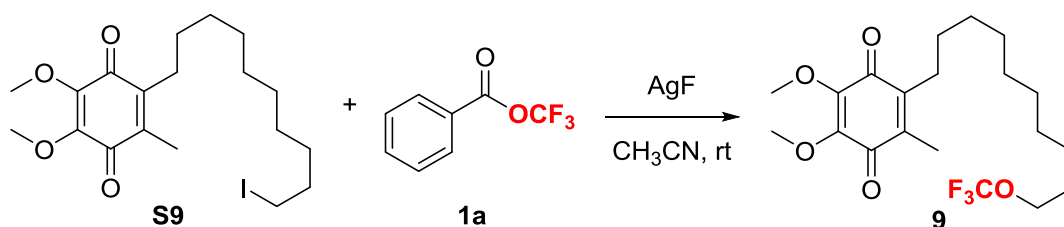
Orange solid. m.p. 35–36 °C. ^1H NMR (400 MHz, CDCl_3) δ 3.98 (s, 3H), 3.97 (s, 3H), 3.17 (t, $J = 7.0$ Hz, 2H), 2.49–2.26 (m, 2H), 2.00 (s, 3H), 1.90–1.70 (m, 2H), 1.44–1.18 (m, 14H). ^{13}C NMR (101 MHz, CDCl_3) δ 184.6, 184.1, 144.2, 143.0, 138.6, 61.1, 33.5, 30.4, 29.8, 29.3, 29.3, 28.7, 28.5, 26.3, 11.9, 7.3. MS (EI, m/z , %): 448

(M^+ , 13), 306 (18), 197 (100); **HRMS (EI)** (m/z): [M] $^+$ Calcd for $C_{19}H_{29}IO_4$, 448.1111; found, 448.1108.



S10^{9a}, **S11**^{9b}, **S12**^{9c}, **S13**^{9d} were synthesized according to the literature procedures.

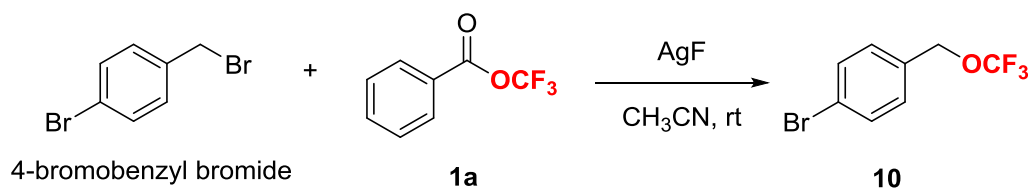
2,3-dimethoxy-5-methyl-6-(10-(trifluoromethoxy)decyl)cyclohexa-2,5-diene-1,4-dione (9)



To a 10-mL polyethylene (PE) tube equipped with a stir bar were added AgF (64.7 mg, 0.51 mmol, 1.7 equiv), **S9** (134.5 mg, 0.3 mmol, 1.0 equiv) and CH_3CN (3 mL) in the glove box. Then **1a** (114 mg, 0.6 mmol, 2.0 equiv) was added with stirring at room temperature. The solution was stirred at room temperature for 12 h. $PhCF_3$ was added as an internal standard, the reaction was monitored by ^{19}F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **9** as orange oil (105.6 mg, 87% yield).

Orange oil. 1H NMR (400 MHz, $CDCl_3$) δ 3.93 (m, 6H), 3.89 (t, J = 6.5 Hz, 2H), 2.42 – 2.34 (m, 2H), 1.95 (s, 3H), 1.66–1.57 (m, 2H), 1.36–1.16 (m, 14H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.75 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.6, 184.0, 144.2, 142.9, 138.6, 121.6 (q, J = 253.5 Hz), 67.4 (q, J = 3.0 Hz), 61.0, 29.7, 29.3, 29.3, 29.2, 28.9, 28.6, 26.3, 25.3, 11.8. **MS (ESI, m/z):** 407.1 ($[M+H]^+$). **HRMS (ESI):** Calcd for $C_{20}H_{30}F_3O_5$ ($[M+H]^+$) 407.2040; found, 407.2039.

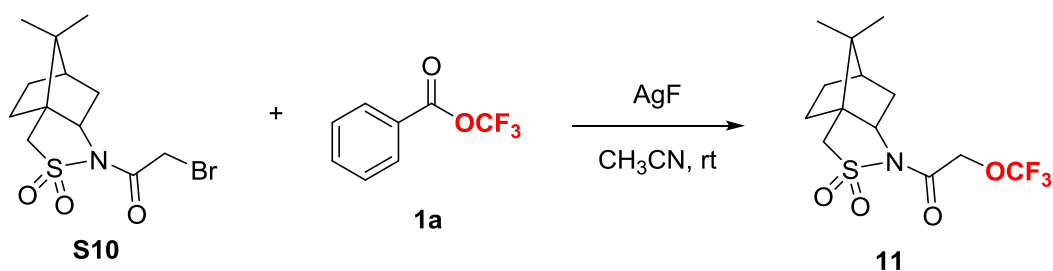
1-Bromo-4-((trifluoromethoxy)methyl)benzene (**10**)



To a 10-mL polyethylene (PE) tube equipped with a stir bar were added AgF (64.7 mg, 0.51 mmol, 1.7 equiv), 4-bromobenzyl bromide (75 mg, 0.3 mmol, 1.0 equiv) and CH₃CN (3 mL) in the glove box. Then **1a** (114 mg, 0.6 mmol, 2.0 equiv) was added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **10** as a colorless liquid (60 mg, 78% yield).

Colorless liquid ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 8.6, 2.1 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.92 (s, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -60.51 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 132.8, 131.9, 129.6, 123.0, 121.6 (q, *J* = 255.8 Hz), 68.2 (d, *J* = 3.5 Hz). MS (EI, *m/z*, %): 254 (M⁺, 65), 256 (M⁺+2, 65), 175 (100); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₈H₆BrF₃O, 253.9554; found, 253.9550.

1-((3aR,6R)-8,8-dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[*c*]isothiazol-1(4H)-yl)-2-(trifluoromethoxy)ethan-1-one (**11**)

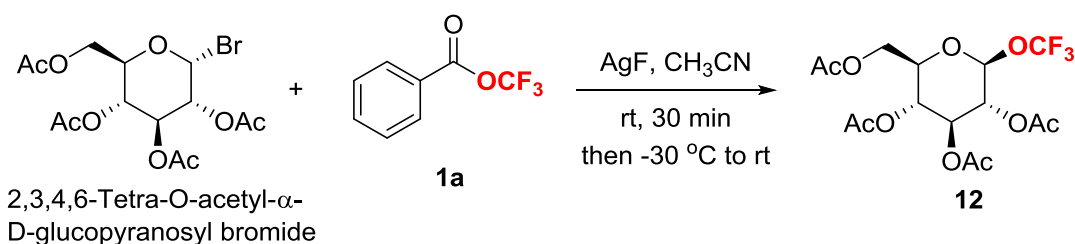


To a 10-mL polyethylene (PE) tube equipped with a stir bar were added AgF (76.2 mg, 0.6 mmol, 2.0 equiv) and CH₃CN (0.6 mL) in the glove box. Then **1a** (171 mg, 0.9 mmol, 3.0 equiv) was added and the solution was stirred at room temperature for 30 min. Then **S10** (100.8 mg, 0.3 mmol, 1.0 equiv) was added at room temperature

and stirred for 48 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **11** as a white solid (97.8 mg, 95% yield).

White solid. m.p. 82-83 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.87 (dd, *J* = 36.9, 15.9 Hz, 2H), 3.90 (dd, *J* = 7.7, 5.0 Hz, 1H), 3.48 (q, *J* = 13.9 Hz, 2H), 2.18 (ddd, *J* = 13.9, 7.8, 3.4 Hz, 1H), 2.09 (dd, *J* = 14.0, 7.8 Hz, 1H), 1.98 – 1.77 (m, 3H), 1.51 – 1.27 (m, 2H), 1.11 (s, 3H), 0.96 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -61.09 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 163.8, 121.4 (q, *J* = 257.0 Hz), 65.1, 64.1 (q, *J* = 3.1 Hz), 52.5, 49.6, 47.9, 44.5, 37.9, 32.7, 26.3, 20.6, 19.7. MS (ESI, *m/z*): 342.0 ([M+H]⁺). HRMS (ESI): Calcd for C₁₃H₁₉F₃NO₄S ([M+H]⁺) 342.0981; found, 342.0981.

2, 3, 4, 6-tetra-O-acetyl-1-(trifluoromethoxy)-β-D-glucopyranose (**12**)^{9e}

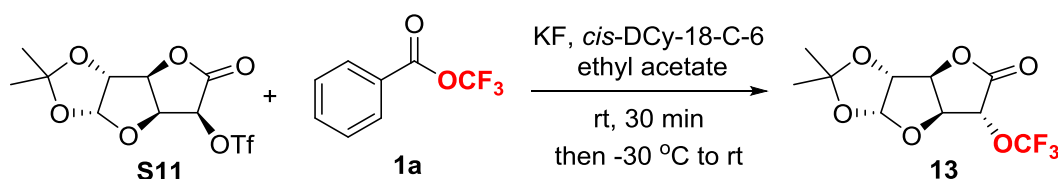


To a 10-mL oven-dried sealed tube equipped with a stir bar were added AgF (64.7 mg, 0.51 mmol, 1.7 equiv) and CH₃CN (3 mL) in the glove box. Then **1a** (114 mg, 0.6 mmol, 2.0 equiv) was added and the solution was stirred at room temperature for 30 min. Then 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (123.3 mg, 0.3 mmol, 1.0 equiv) was added with stirring at -30 °C. The solution was warmed to room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **12** as a white solid (105.3 mg, 84% yield).

White solid. m.p. 121-122 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.24 (t, *J* = 9.1 Hz, 1H), 5.17 – 5.05 (m, 3H), 4.30 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.13 (dd, *J* = 12.5, 2.2 Hz,

1H), 3.82 (ddd, $J = 9.9, 4.8, 2.3$ Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -59.19 (s, 3F). **^{13}C NMR** (101 MHz, CDCl_3) δ 170.4, 169.9, 169.2, 168.9, 121.0 (q, $J = 259.6$ Hz), 95.8 (q, $J = 2.8$ Hz), 72.7, 72.1, 70.1, 67.5, 61.3, 20.5, 20.4, 20.3. **MS (ESI, m/z):** 434.1 ($[\text{M} + \text{NH}_4]^+$). **HRMS (ESI):** Calcd for $\text{C}_{15}\text{H}_{23}\text{F}_3\text{NO}_{10}$ ($[\text{M} + \text{NH}_4]^+$) 434.1269; found, 434.1267.

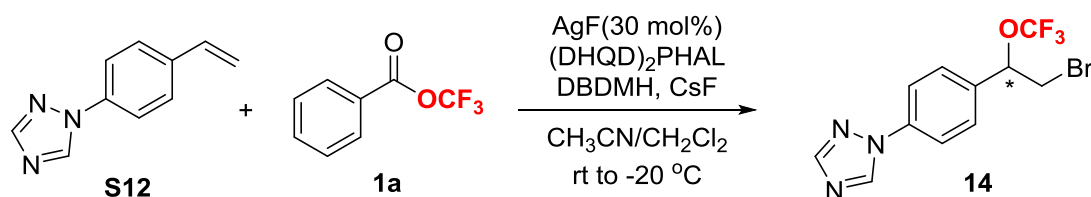
(3aR,3bS,6R,6aS,7aR)-2,2-dimethyl-6-(trifluoromethoxy)tetrahydrofuro[2',3':4,5]furo[2,3-d][1,3]dioxol-5(3bH)-one (13)



To a 10-mL oven-dried sealed tube equipped with a stir bar were KF (34.8 mg, 0.6 mmol, 2.0 equiv), *cis*-dicyclohexano-18-crown-6 (213 mg, 0.6 mmol, 2.0 equiv) and ethyl acetate (3.0 mL) in the glove box. Then **1a** (171 mg, 0.9 mmol, 3.0 equiv) was added and the solution was stirred at room temperature for 30 min. Then **S11** (104.7 mg, 0.3 mmol, 1.0 equiv) was added with stirring at -30 °C. The solution was warmed to room temperature gradually for 16h. PhCF_3 was added as an internal standard, the reaction was monitored by ^{19}F NMR. The solution was extracted with ethyl acetate and dried over MgSO_4 . After the solution filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **13** as a white solid (53.1 mg, 62% yield).

White solid. m.p. $46\text{--}47$ °C. **^1H NMR** (400 MHz, CDCl_3) δ 5.93 (d, $J = 3.6$ Hz, 1H), 5.05 (d, $J = 3.1$ Hz, 1H), 4.89 (d, $J = 3.1$ Hz, 1H), 4.85 (d, $J = 3.6$ Hz, 1H), 4.65 (s, 1H), 1.51 (s, 3H), 1.34 (s, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -60.03 (s, 3F). **^{13}C NMR** (126 MHz, CDCl_3) δ 168.1, 121.1 (q, $J = 259.9$ Hz), 113.6, 106.3, 84.7, 81.8, 80.1, 73.6 (q, $J = 2.8$ Hz), 26.9, 26.4. **MS (EI, m/z , %):** 269 ($[\text{M} - \text{CH}_3]^+$, 100), 227 ($\text{M}^+ - 57, 49$), 141 (36); **HRMS (EI) (m/z):** $[\text{M} - \text{CH}_3]^+$ Calcd for $\text{C}_9\text{H}_8\text{F}_3\text{O}_6$ ($[\text{M} - \text{CH}_3]^+$), 269.0267; found, 269.0273.

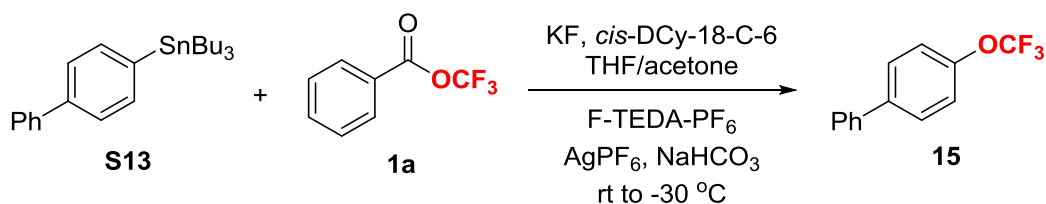
1-(4-(2-bromo-1-(trifluoromethoxy)ethyl)phenyl)-1H-1,2,4-triazole (14**)^{9c}**



To a 10-mL oven-dried sealed tube equipped with a stir bar were added CsF (91.1 mg, 0.6 mmol, 2.00 equiv) and CH₃CN (2.4 mL) in the glove box. Then **1a** (171 mg, 0.9 mmol, 3.0 equiv) was added and the solution was stirred at room temperature for 30 min. Then CH₂Cl₂ (1.2 mL), AgF (11.4 mg, 0.09 mmol, 30 mol%), (DHQD)₂PHAL (hydroquinidine 1,4-phthalazinediyl diether) (23.4 mg, 0.03 mmol, 10 mol%) and DBDMH (85.5 mg, 0.3 mmol, 1.00 equiv) were added at room temperature. Then the solution was cooled down to -20 °C and 1-(4-Vinylphenyl)-1H-1,2,4-triazole (**S12**) (51 mg, 0.3 mmol, 1.00 equiv) was added and the reaction mixture was stirred at -20 °C for another 24 h. The reaction was quenched with saturated aqueous solution of Na₂SO₃ (1.2 mL), then followed by saturated aqueous solution of NH₄Cl (2.4 mL) at -20 °C. The aqueous layers were extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄. After the solution filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **14** as a white solid (69.5 mg, 69% yield).

White solid, m.p. 62-63 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 8.13 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 5.40 – 5.30 (m, 1H), 3.69 (dd, *J* = 11.1, 7.3 Hz, 1H), 3.58 (dd, *J* = 11.1, 5.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -58.53 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 141.0, 137.6, 136.5, 127.9, 121.3 (q, *J* = 257.5 Hz), 120.3, 78.6 (q, *J* = 2.4 Hz), 33.1. MS (EI, *m/z*, %): 335 (M⁺, 9), 337 (M⁺+2, 9), 242 (100), 188(20); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₁₁H₉BrF₃N₃O, 334.9881; found, 334.9883. The characterization data are consistent with previous report.^{9c} [α]_D²⁴ = +26.1 (*c* 0.25, CHCl₃). 89.5 : 10.5 e.r. HPLC (IG, 1 μm, hexane/ isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 21.01 min (major minor) and 23.02 min (minor).

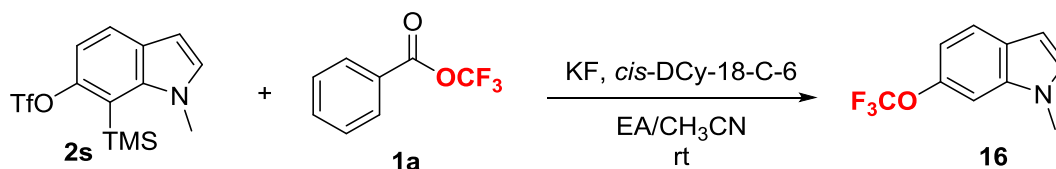
4-(trifluoromethoxy)-1,1'-biphenyl (**15**)^{9d}



To a 10-mL oven-dried sealed tube equipped with a stir bar were added KF (34.8 mg, 0.6 mmol, 2.0 equiv), *cis*-dicyclohexano-18-crown-6 (213 mg, 0.6 mmol, 2.0 equiv) and anhydrous THF (1.2 mL) in the glove box. Then **1a** (171 mg, 0.9 mmol, 3.0 equiv) was added and the solution was stirred at room temperature for 30 min. NaHCO₃ (50.4 mg, 0.6 mmol, 2.0 equiv) and **S13** (133 mg, 0.3 mmol, 1.0 equiv) were added to solution after it was cooled down to -30 °C. Then a solution of 1-chloromethyl-4-fluoro-1, 4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (169.5 mg, 0.36 mmol, 1.2 equiv) and silver hexafluorophosphate (91 mg, 0.36 mmol, 1.2 equiv) in anhydrous acetone (3.6 mL) was added. The reaction mixture was stirred for 4 hours in the dark, and warmed to room temperature. The reaction mixture was filtered through a pad of celite eluting with CH₂Cl₂ and the filtrate concentrated in vacuum. the crude product was purified by flash column chromatography on silica gel to give product **15** as a white solid (59 mg, 82% yield).

White solid. m.p. 53-54 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.53 (m, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.31 (d, *J* = 8.7 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.82 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 148.7 (q, *J* = 1.8 Hz), 140.0, 139.9, 128.9, 128.5, 127.7, 127.1, 121.2, 120.6 (q, *J* = 257.1 Hz). MS (EI, *m/z*, %): 238 (M⁺, 100), 169 (20), 141 (100); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₁₃H₉F₃O, 238.0605; found, 238.0602.

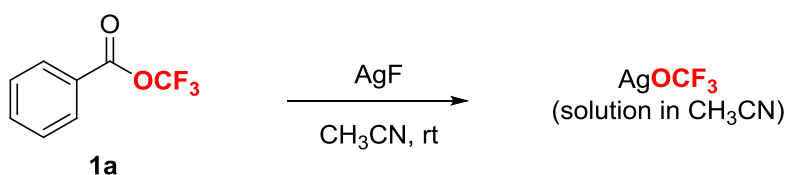
1-methyl-6-(trifluoromethoxy)-1H-indole (**16**)



To a 20-mL polyethylene (PE) tube equipped with a stir bar were added KF (78.4 mg, 1.35 mmol, 4.5 equiv), *cis*-dicyclohexano-18-crown-6 (503 mg, 1.35 mmol, 4.5 equiv), ethyl acetate (5.4 mL) and CH₃CN (0.6 mL) in the glove box. Then **2s** (105.4 mg, 0.3 mmol, 1.0 equiv) and **1a** (171 mg, 0.9 mmol, 3 equiv) were added with stirring at room temperature. The solution was stirred at room temperature for 12 h. PhCF₃ was added as an internal standard, the reaction was monitored by ¹⁹F NMR. The solvent was evaporated under vacuum, the crude product was purified by flash column chromatography on silica gel to give product **16** as a colorless liquid (44.2 mg, 69% yield).

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.6 Hz, 1H), 7.22 (s, 1H), 7.12 (dd, *J* = 3.0, 0.8 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.53 (d, *J* = 3.1 Hz, 1H), 3.78 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.90 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 136.3, 130.2, 127.1, 121.4, 120.8 (q, *J* = 255.6 Hz), 113.4, 102.3, 101.2, 32.9. MS (EI, *m/z*, %): 215 (M⁺, 100), 146 (55), 118 (27); HRMS (EI) (*m/z*): [M]⁺ Calcd for C₁₀H₈F₃NO, 215.0558; found, 215.0552.

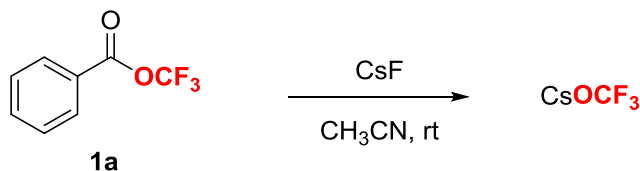
Preparation of CH₃CN-solvalated AgOCF₃



To a 10-mL polyethylene (PE) tube equipped with a stir bar were added AgF (127 mg, 1.0 mmol, 1.0 equiv) and dry CH₃CN (2.0 mL) in the glove box. Then **1a** (209 mg, 1.1 mmol, 1.1 equiv) was added and the solution was stirred at room temperature for 30 min. After the solution was filtered, the AgOCF₃ solution in CH₃CN (~0.5 mol/L, 2.0 mL) was obtained. PhCF₃ was added as an internal standard, the solution was determined by ¹⁹F NMR. ¹⁹F NMR (376 MHz, CH₃CN): δ -25.54 (s, br, 3F),

PhCF₃ (δ -62.47). The characterization data are consistent with previous report.^{9f}

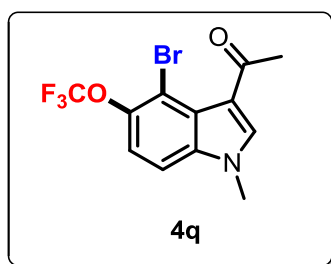
Preparation of CsOCF₃

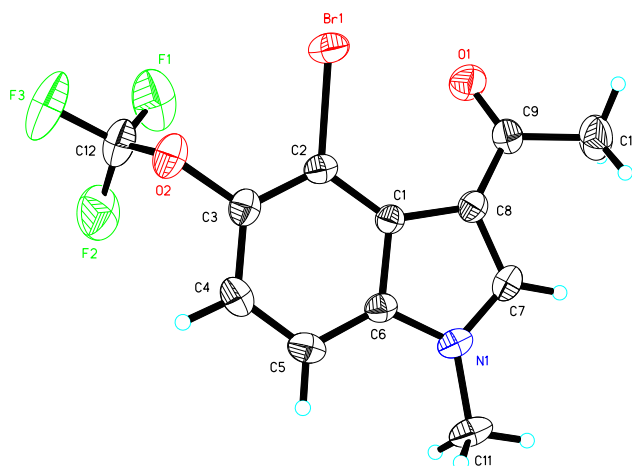


To a 10-mL polyethylene (PE) tube equipped with a stir bar were added CsF (152 mg, 1.0 mmol, 1.0 equiv) and dry CH₃CN (1.0 mL) in the glove box. Then **1a** (285 mg, 1.5 mmol, 1.5 equiv) was added and the solution was stirred at room temperature for 2 h. After the solution was filtered and washed by Et₂O in the glove box, the CsOCF₃ was obtained as a white solid (155.8 mg, 72% yield). PhCF₃ was added as an internal standard, the THF solution (low solubility at room temperature) of CsOCF₃ was determined by ¹⁹F NMR. ¹⁹F NMR (376 MHz, THF): δ -21.20 (s, 3F), PhCF₃ (δ -63.16). The characterization data are consistent with previous report.^{9f}

14. X-ray Structure of 4q, 8 and 12

14.1 X-ray Structure of 4q





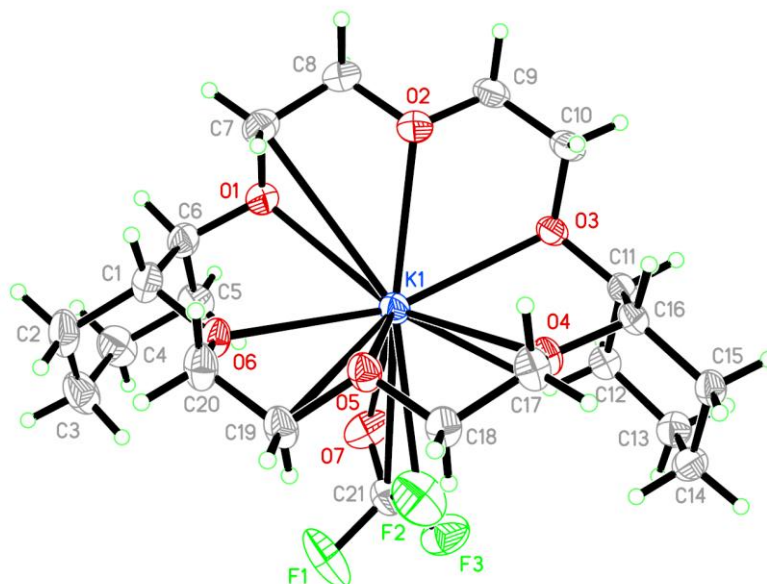
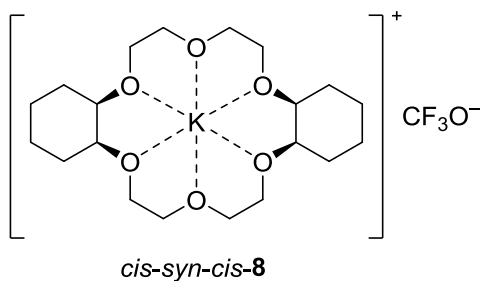
Crystal data and structure refinement for **4q**

Identification code	cd17190
Empirical formula	C ₁₂ H ₉ Br F ₃ N O ₂
Formula weight	336.11
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	$a = 7.6617(12)$ Å $\alpha = 90^\circ$ $b = 13.777(2)$ Å $\beta = 98.910(4)^\circ$ $c = 12.0151(19)$ Å $\gamma = 90^\circ$
Volume	$1253.0(3)$ Å ³
Z	4
Density (calculated)	1.782 Mg/m ³
Absorption coefficient	3.315 mm ⁻¹
F(000)	664
Crystal size	0.200 x 0.170 x 0.140 mm ³
Theta range for data collection	2.265 to 25.500 °
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 15, -14 ≤ l ≤ 13
Reflections collected	7086
Independent reflections	2334 [R(int) = 0.0493]
Completeness to theta = 25.242 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5190
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2334 / 0 / 174

Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0382$, $wR2 = 0.0984$
R indices (all data)	$R1 = 0.0578$, $wR2 = 0.1075$
Extinction coefficient	n/a
Largest diff. peak and hole	0.423 and $-0.263 \text{ e.}\text{\AA}^{-3}$

14.2 X-ray Structure of **8**

[K(*cis*-dicyclohexano-18-crown-6)]**OCF₃**
8 (the *cis-syn-cis*-isomer)



Crystal data

$\text{C}_{21}\text{H}_{36}\text{F}_3\text{KO}_7$	$Z = 2$
$M_r = 496.60$	$F(000) = 528$

Triclinic, $P\bar{1}$	$D_x = 1.365 \text{ Mg m}^{-3}$
$a = 9.0405 (12) \text{ \AA}$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
$b = 10.1068 (19) \text{ \AA}$	Cell parameters from 9333 reflections
$c = 14.4034 (15) \text{ \AA}$	$\theta = 3.2\text{--}68.2^\circ$
$\alpha = 77.981 (10)^\circ$	$\mu = 2.47 \text{ mm}^{-1}$
$\beta = 76.059 (11)^\circ$	$T = 173 \text{ K}$
$\gamma = 73.121 (10)^\circ$	Block, colorless
$V = 1208.6 (3) \text{ \AA}^3$	$0.20 \times 0.20 \times 0.20 \text{ mm}$

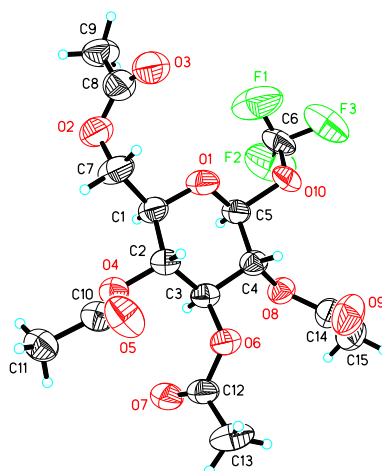
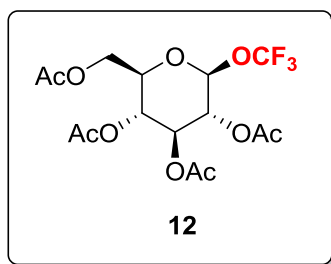
Data collection

Bruker D8 VENTURE CMOS photon 100 diffractometer	$R_{\text{int}} = 0.031$
ϕ and ω scans	$\theta_{\text{max}} = 68.7^\circ$, $\theta_{\text{min}} = 3.2^\circ$
25646 measured reflections	$h = -10 \rightarrow 10$
4406 independent reflections	$k = -12 \rightarrow 12$
4083 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.7922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4406 reflections	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
289 parameters	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

14.3 X-ray Structure of 12



Crystal data and structure refinement for **12**

Identification code	cu_d8v18207_0m	
Empirical formula	C ₁₅ H ₁₉ F ₃ O ₁₀	
Formula weight	416.30	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 18.8290(8) Å	α = 90 °
	b = 5.8347(3) Å	β = 98.902(2) °
	c = 18.4856(8) Å	γ = 90 °
Volume	2006.39(16) Å ³	
Z	4	
Density (calculated)	1.378 Mg/m ³	
Absorption coefficient	1.175 mm ⁻¹	
F(000)	864	
Crystal size	0.190 x 0.150 x 0.120 mm ³	
Theta range for data collection	4.754 to 66.997 °	
Index ranges	-22 ≤ h ≤ 21, -6 ≤ k ≤ 6, -22 ≤ l ≤ 21	
Reflections collected	23811	

Independent reflections	3507 [R(int) = 0.0578]
Completeness to theta = 67.679 °	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.4188
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3507 / 69 / 307
Goodness-of-fit on F ²	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0715, wR2 = 0.2193
R indices (all data)	R1 = 0.0779, wR2 = 0.2338
Absolute structure parameter	0.09(10)
Extinction coefficient	0.009(2)
Largest diff. peak and hole	0.516 and -0.218 e.Å ⁻³

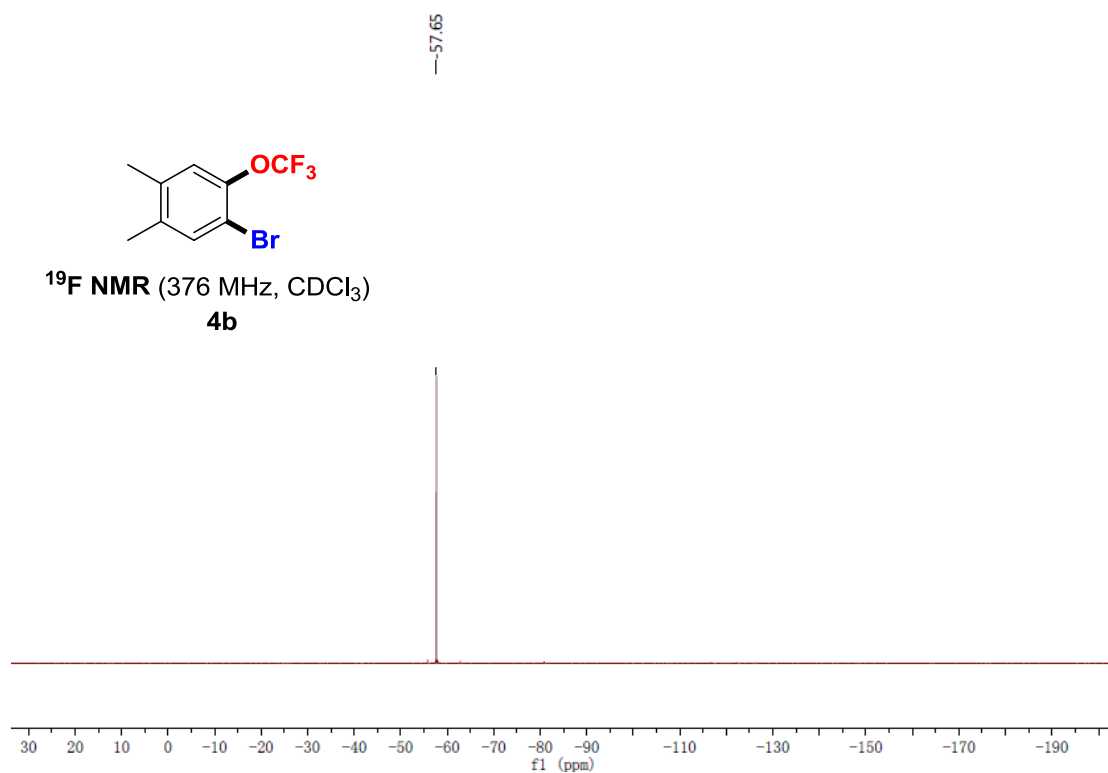
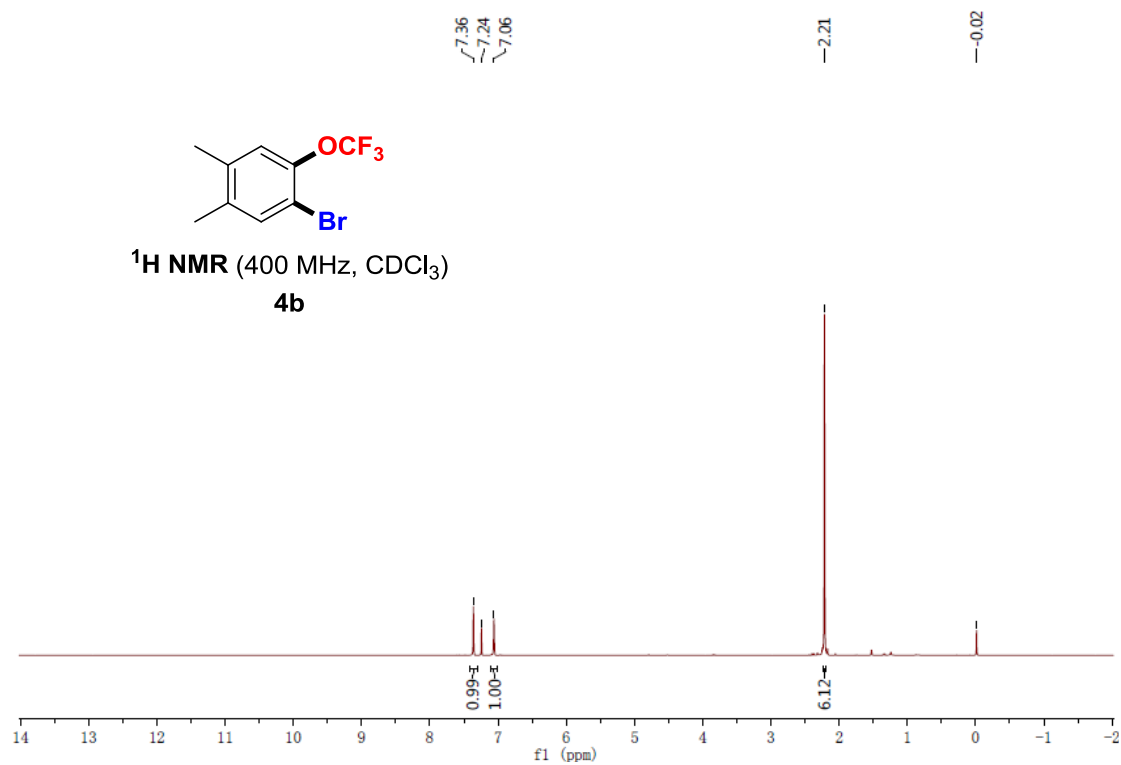
15. References

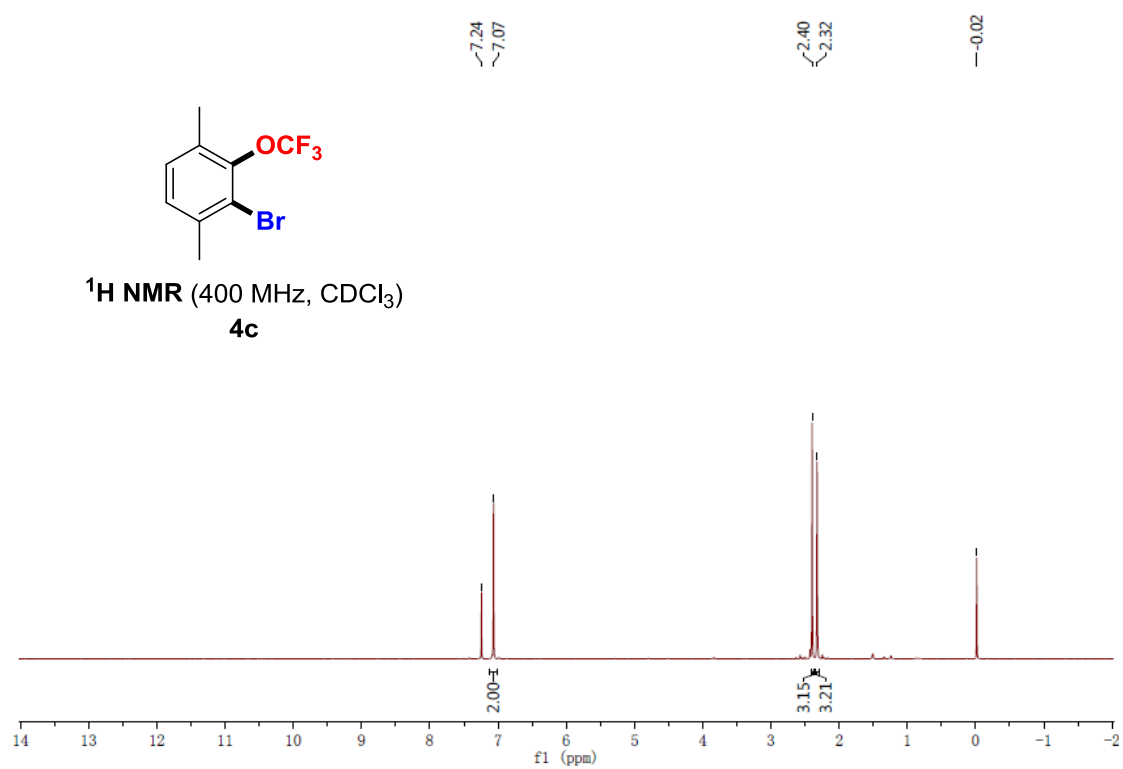
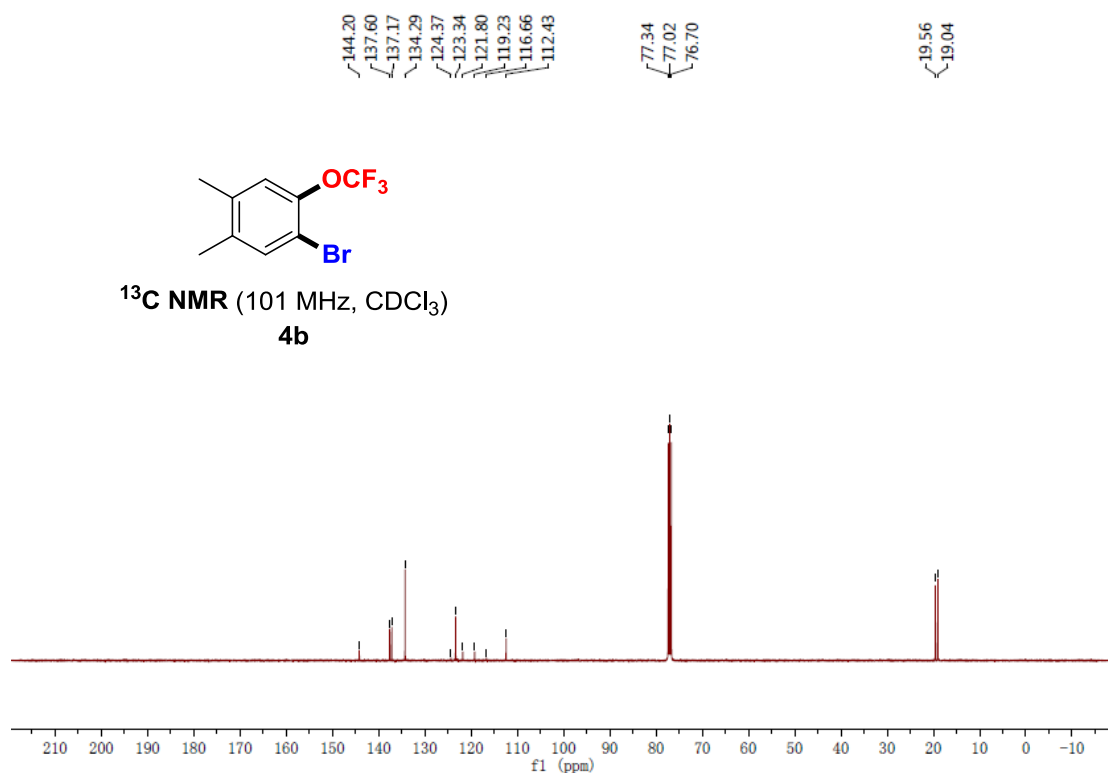
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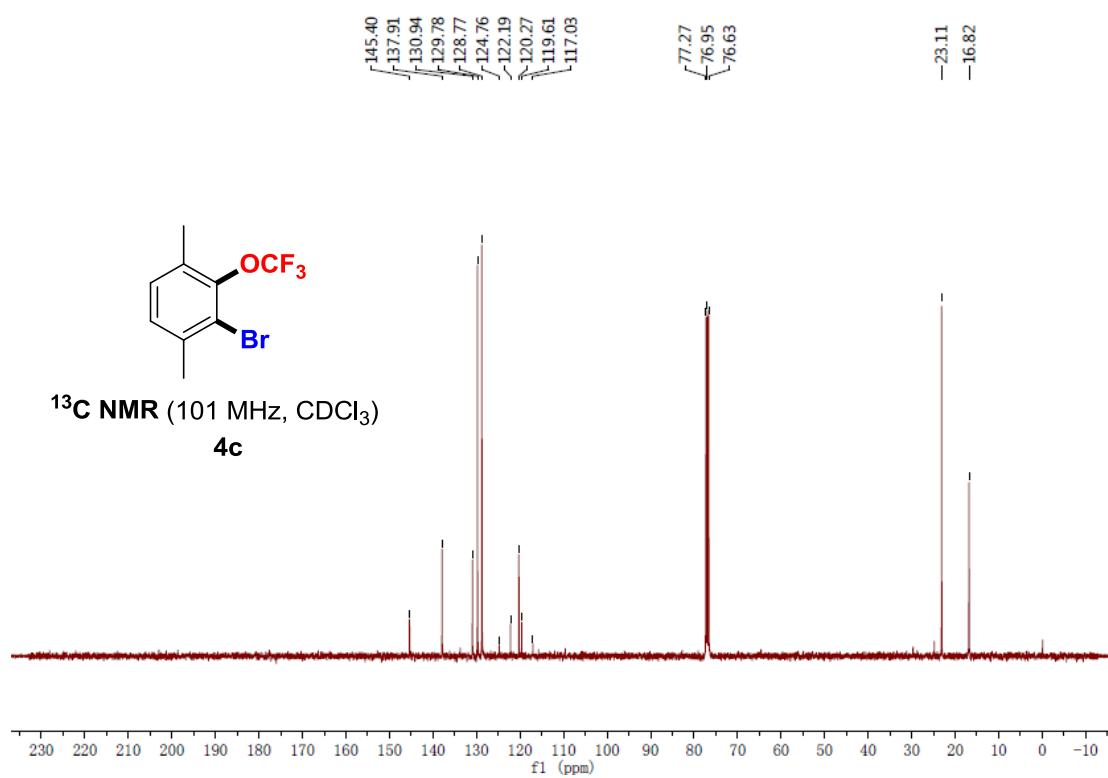
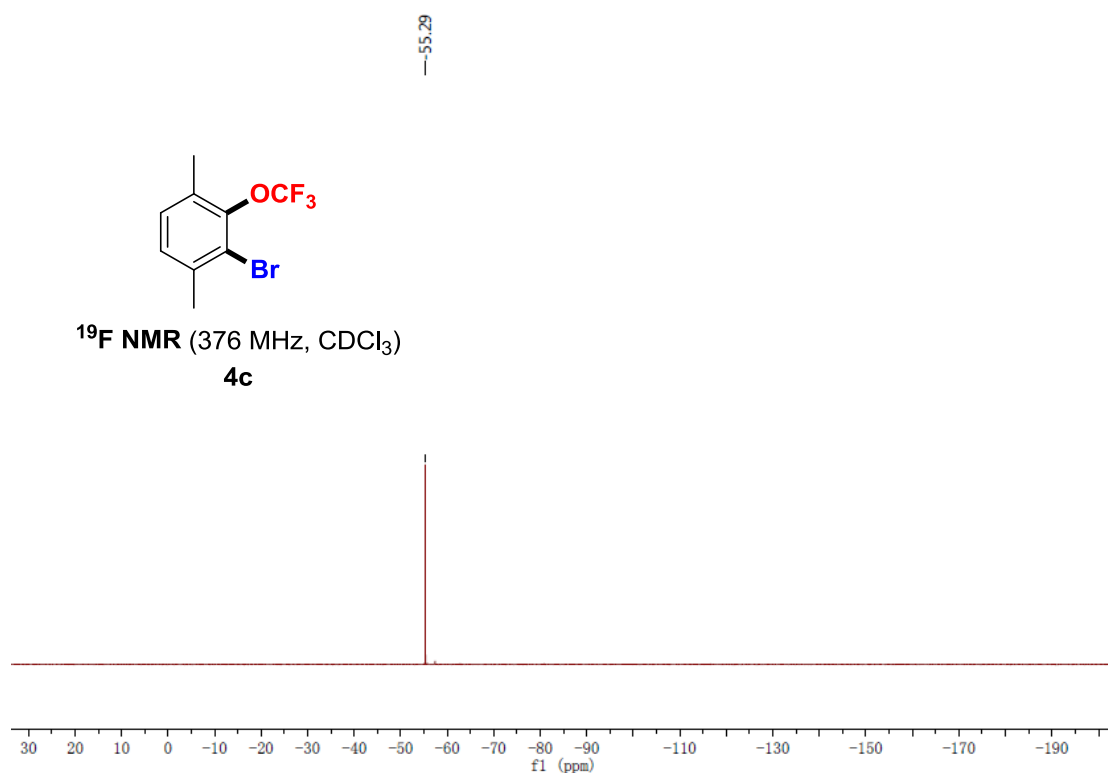
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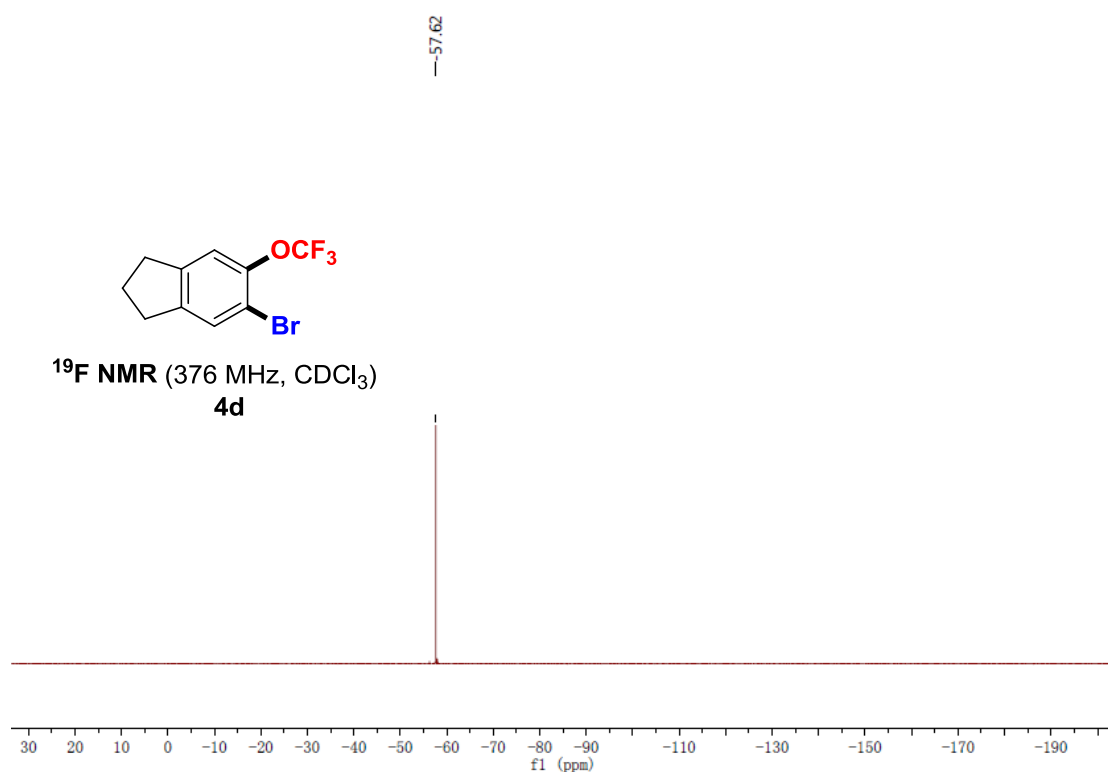
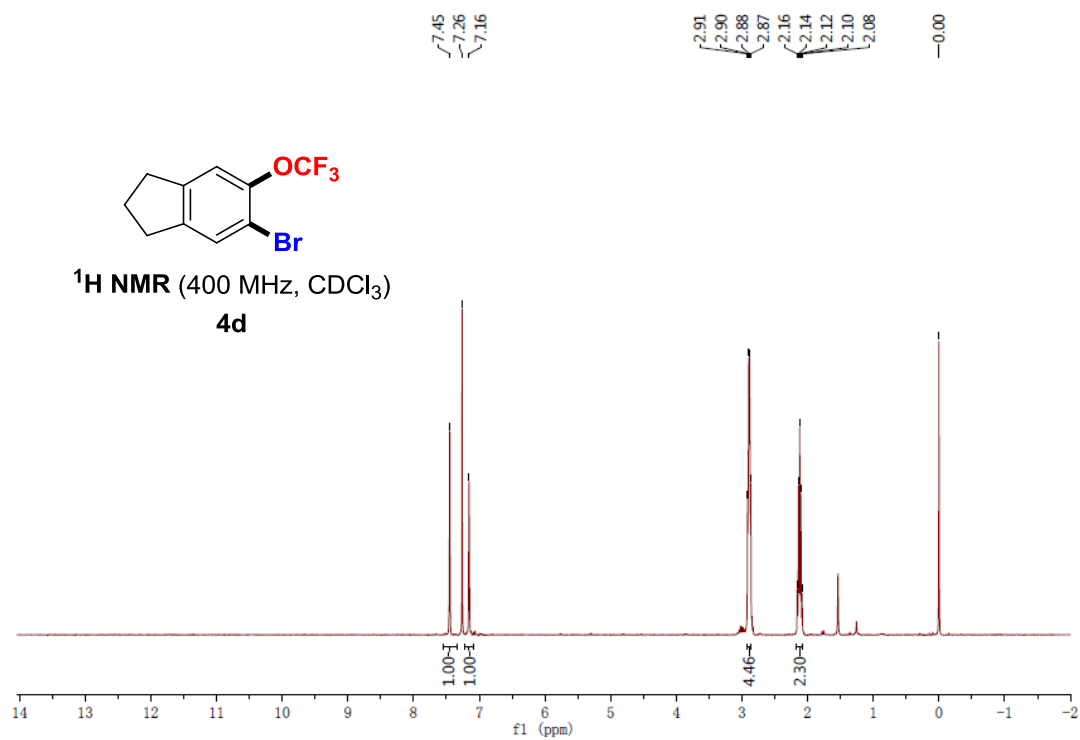
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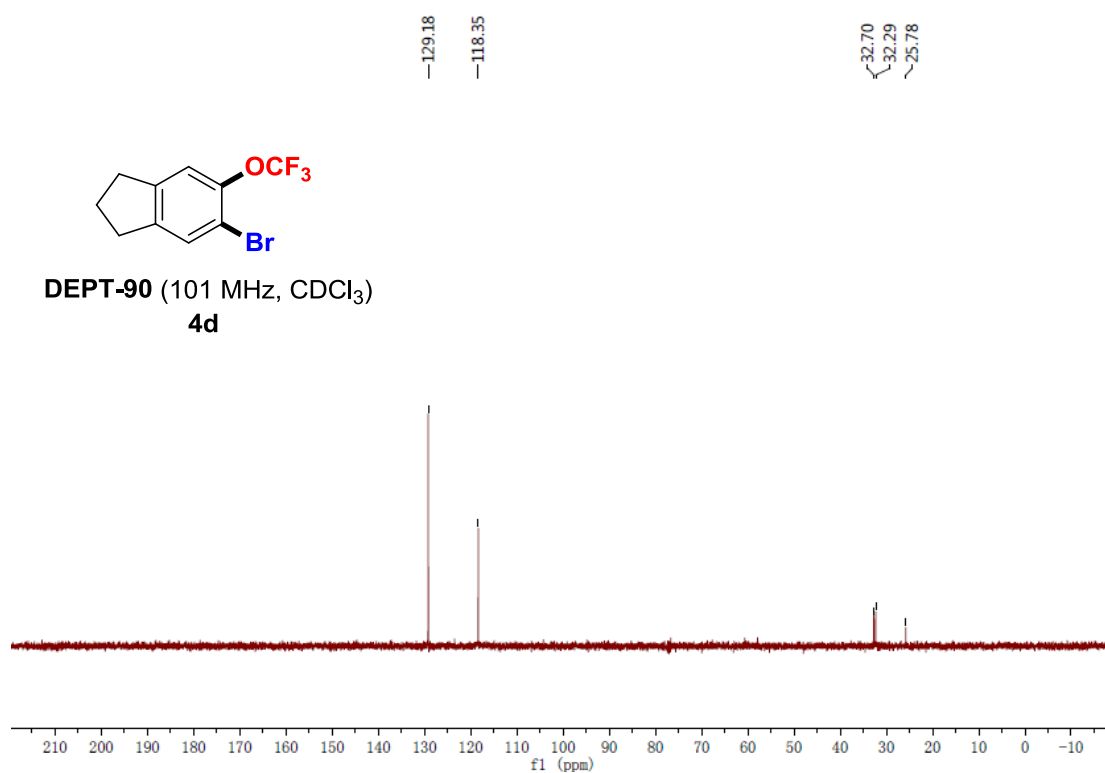
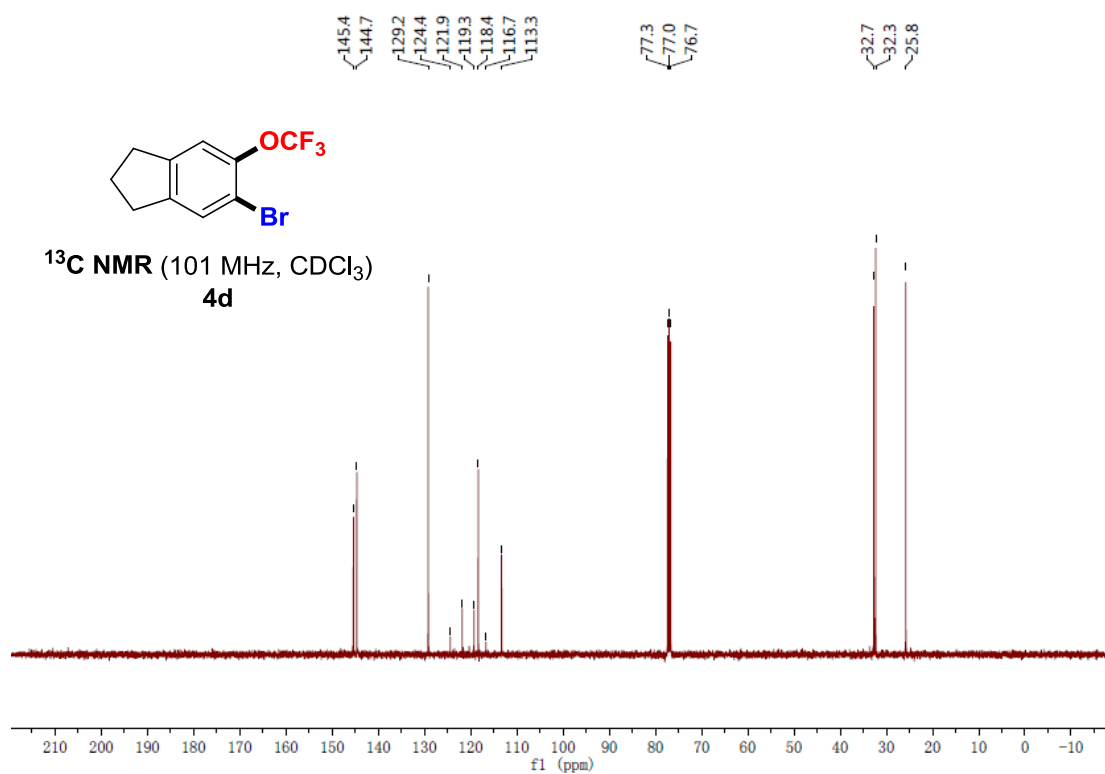
16. Spectra of Isolated Products

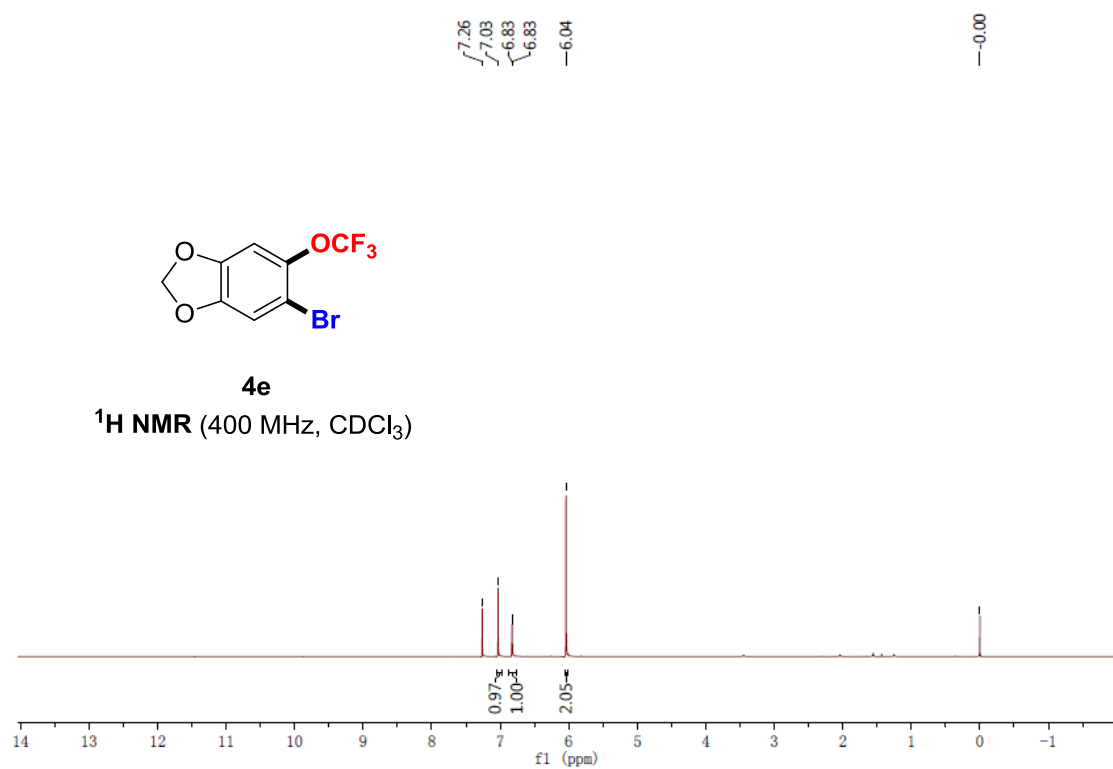
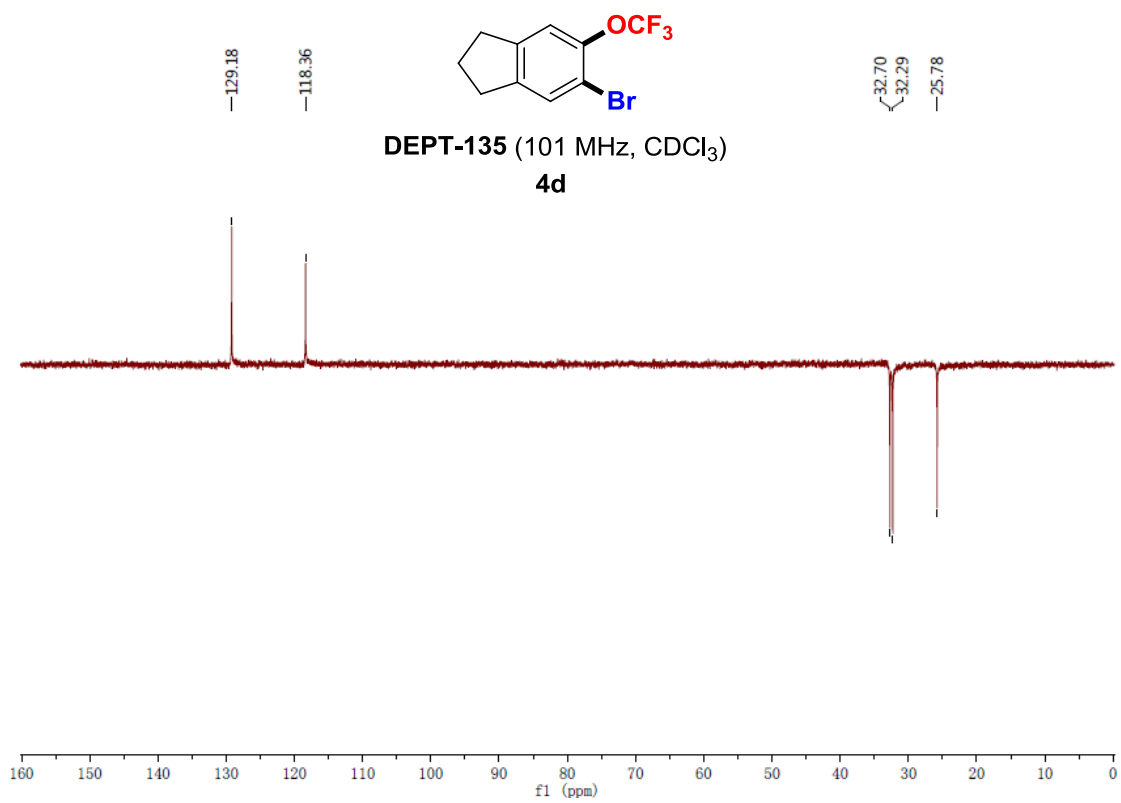


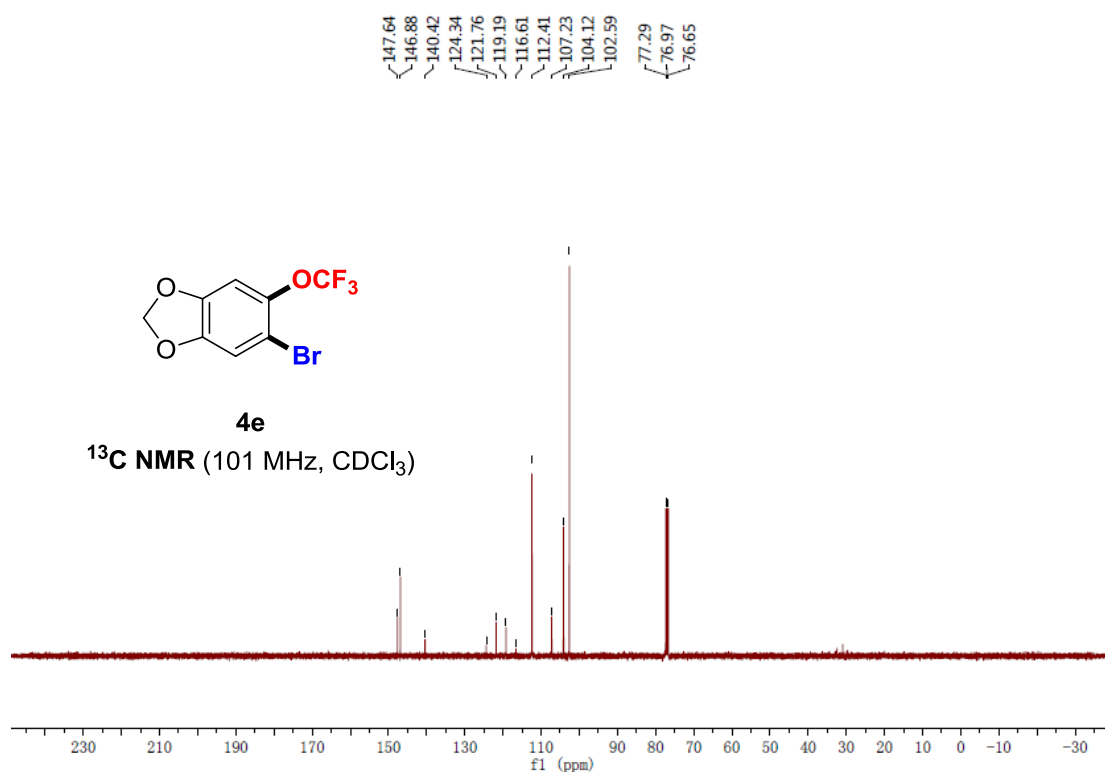
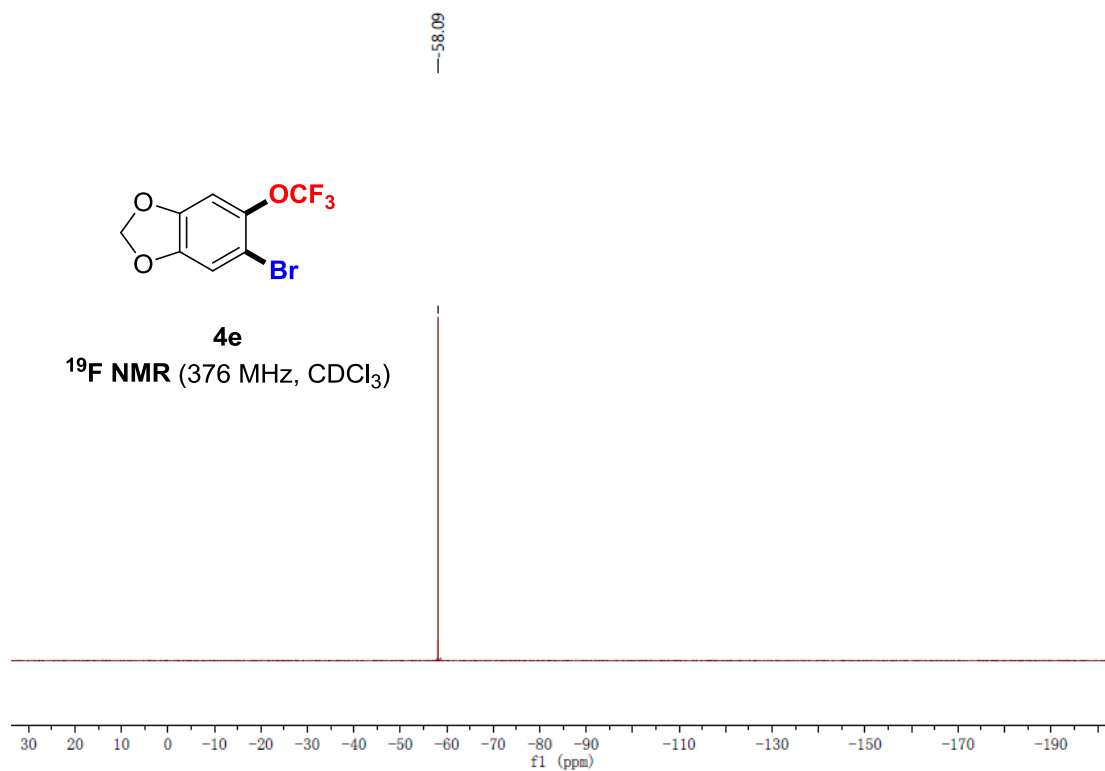


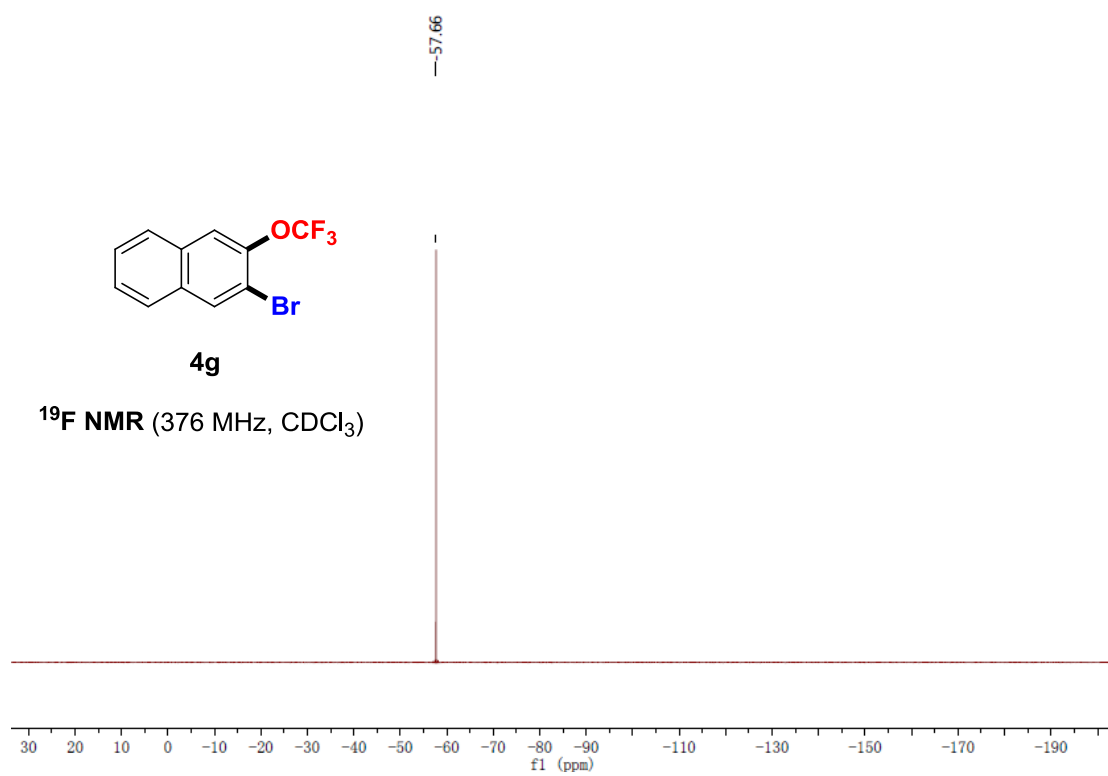
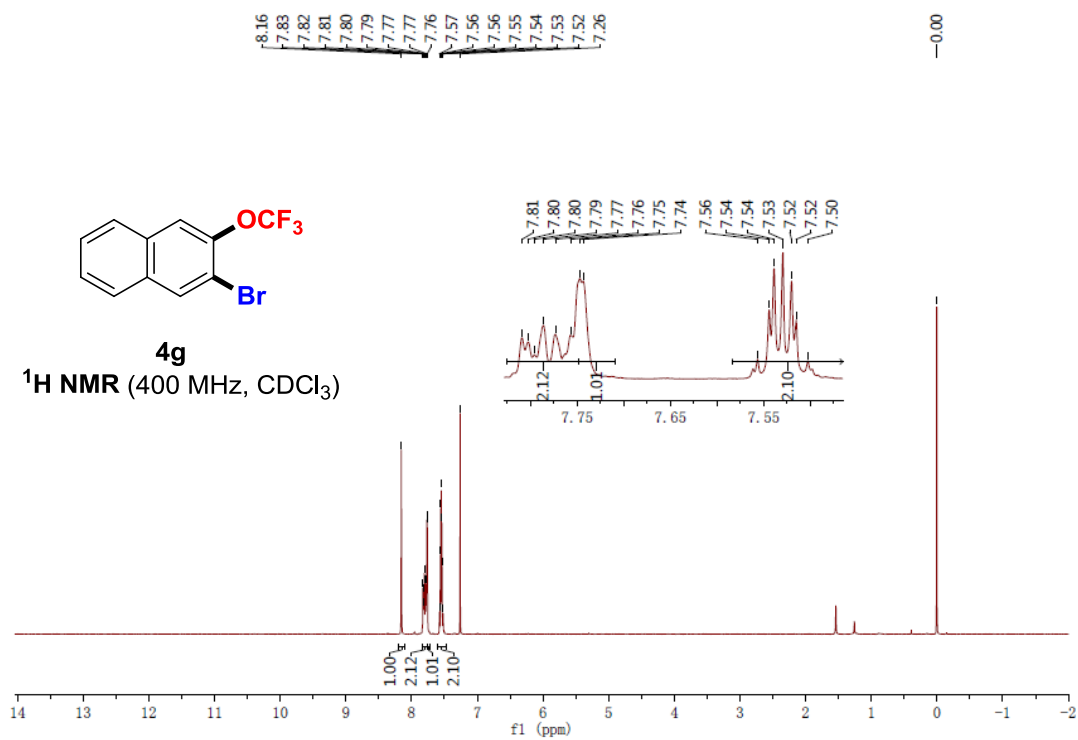


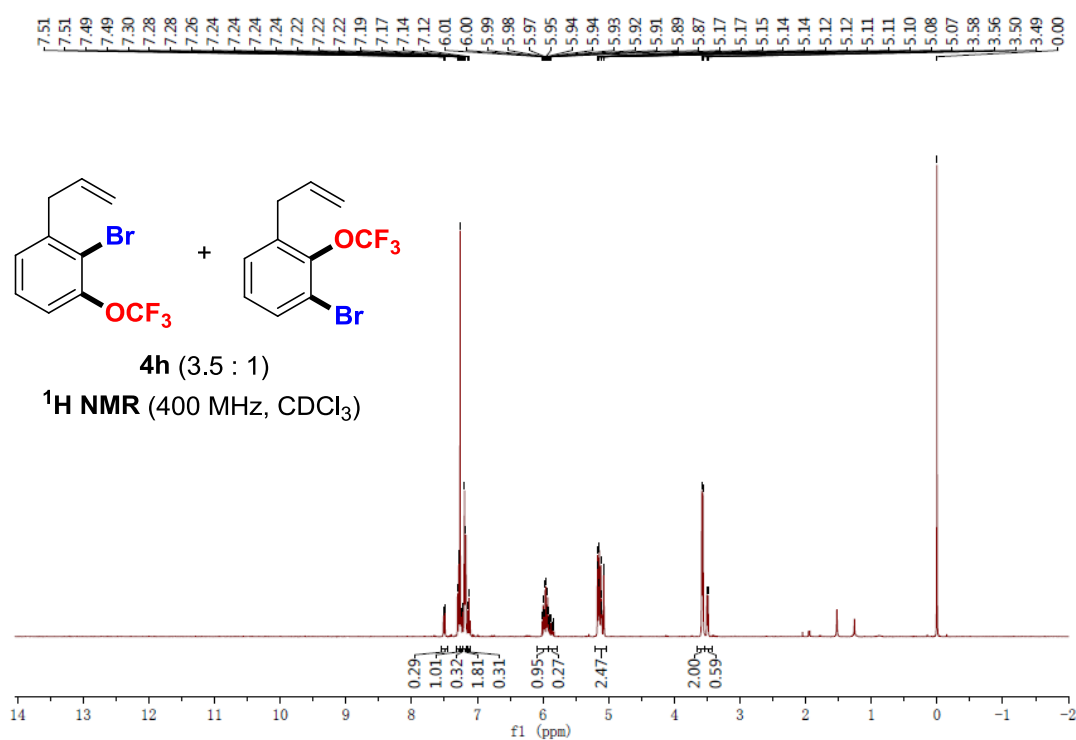
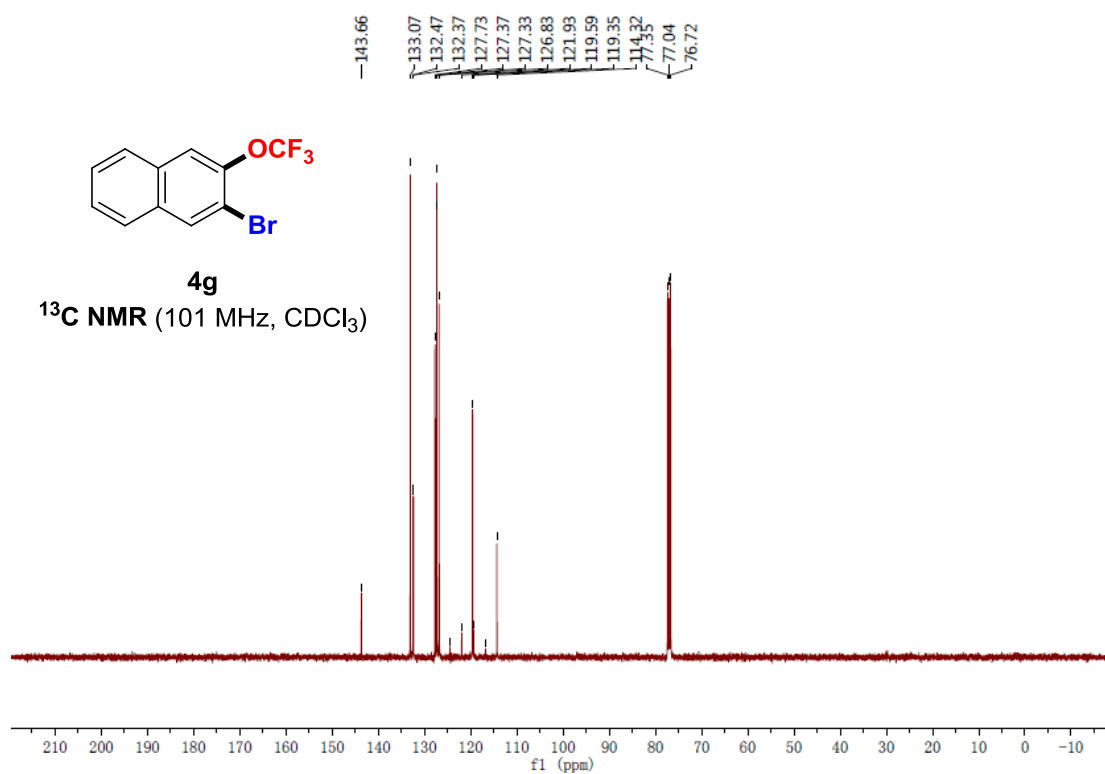


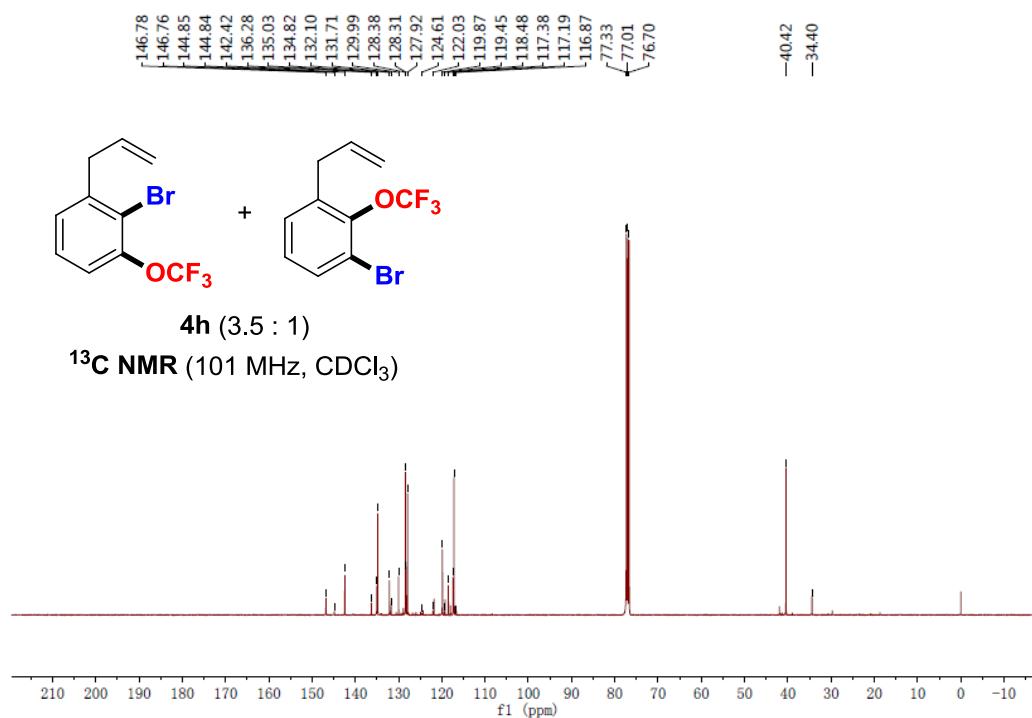
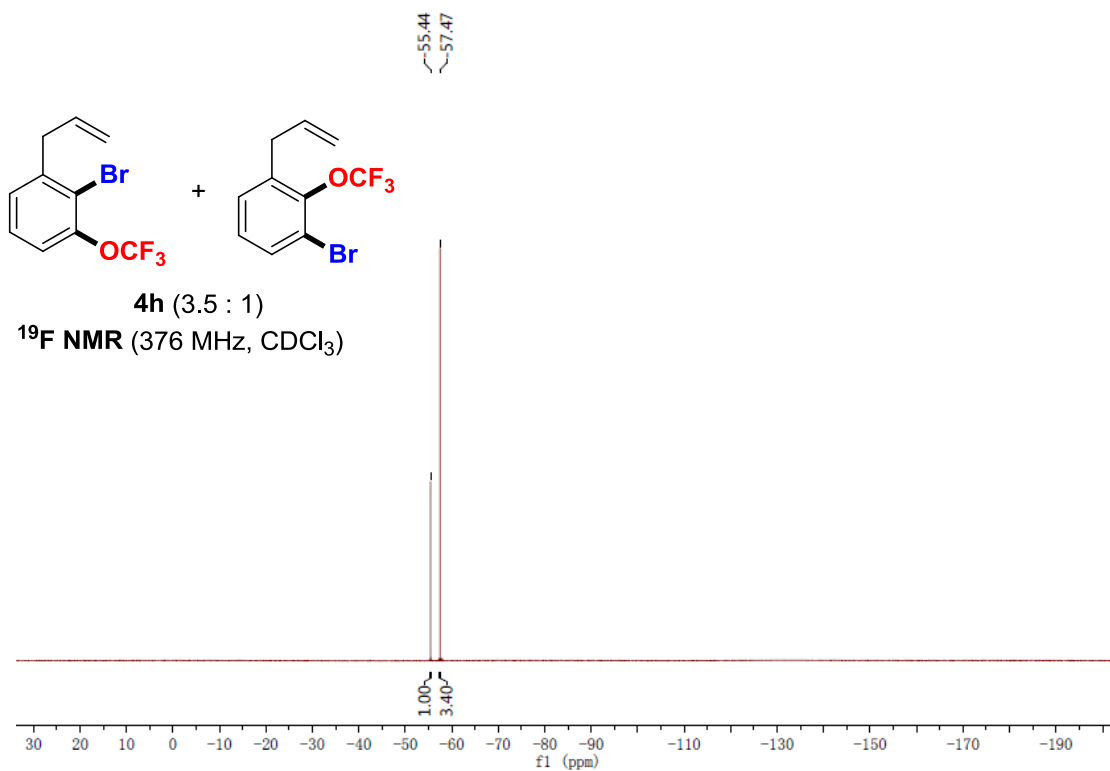


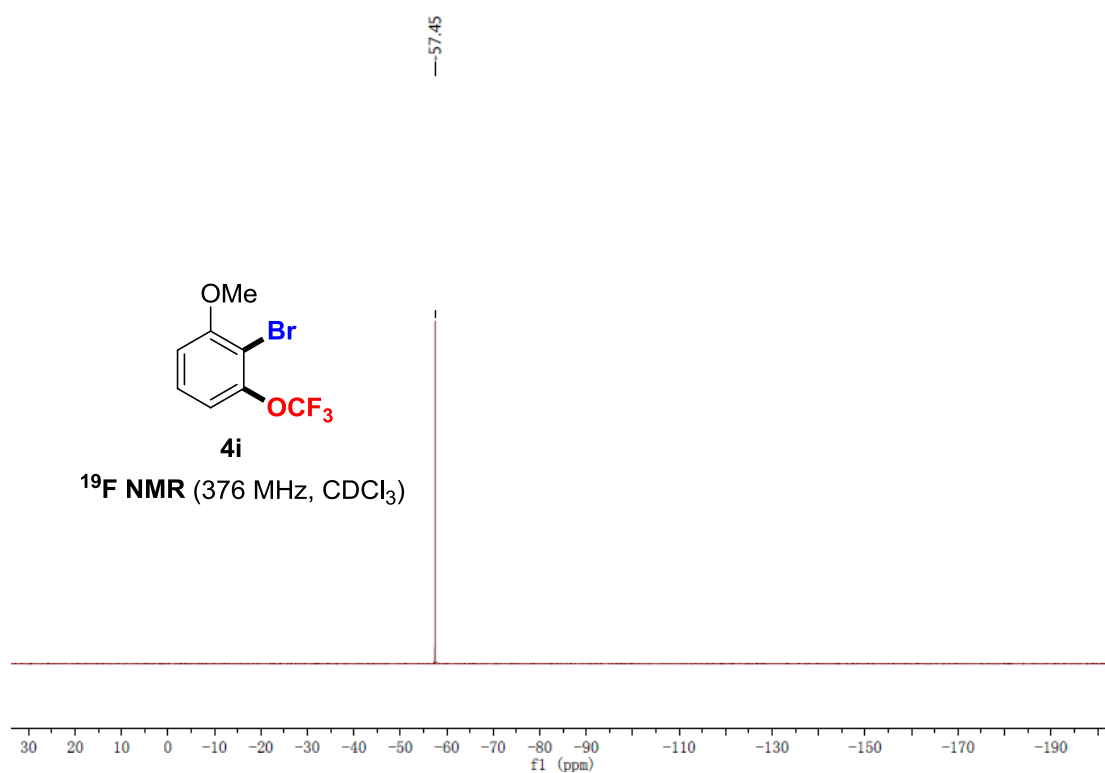
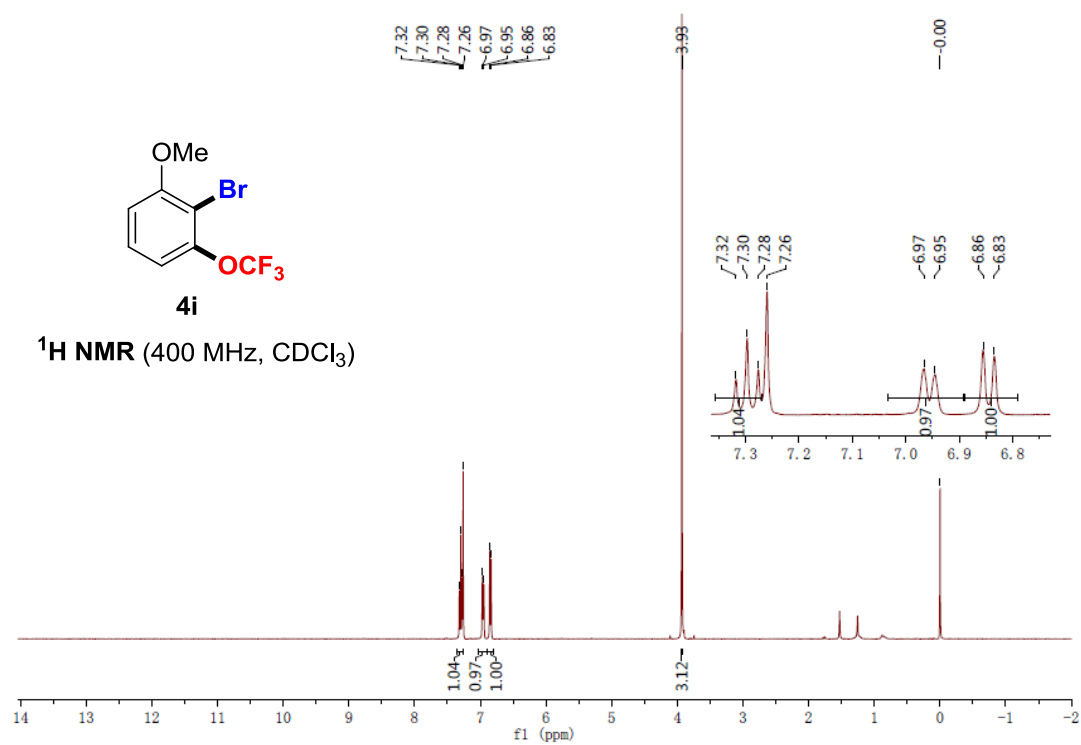


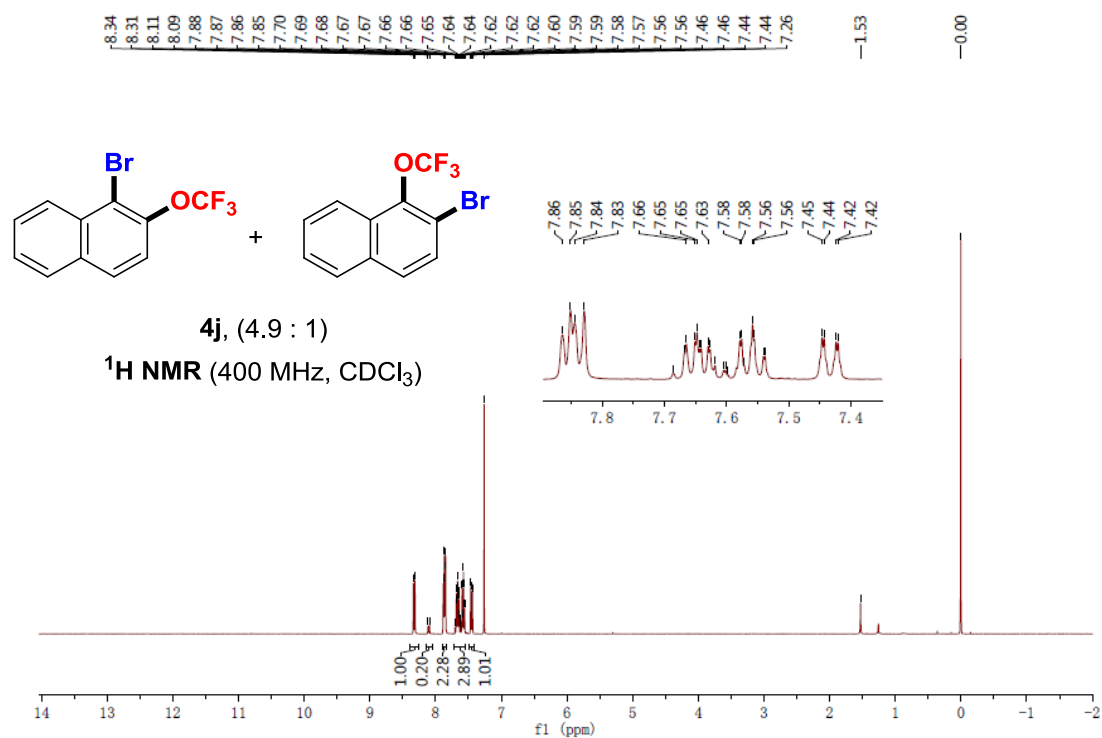
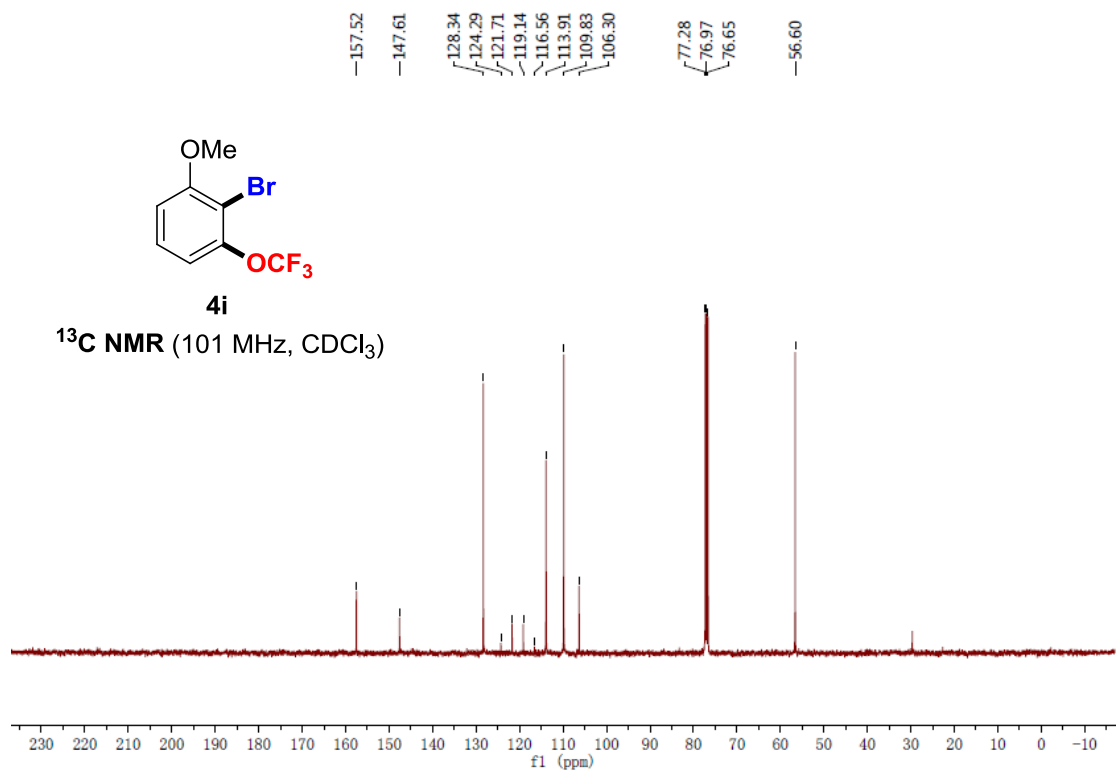


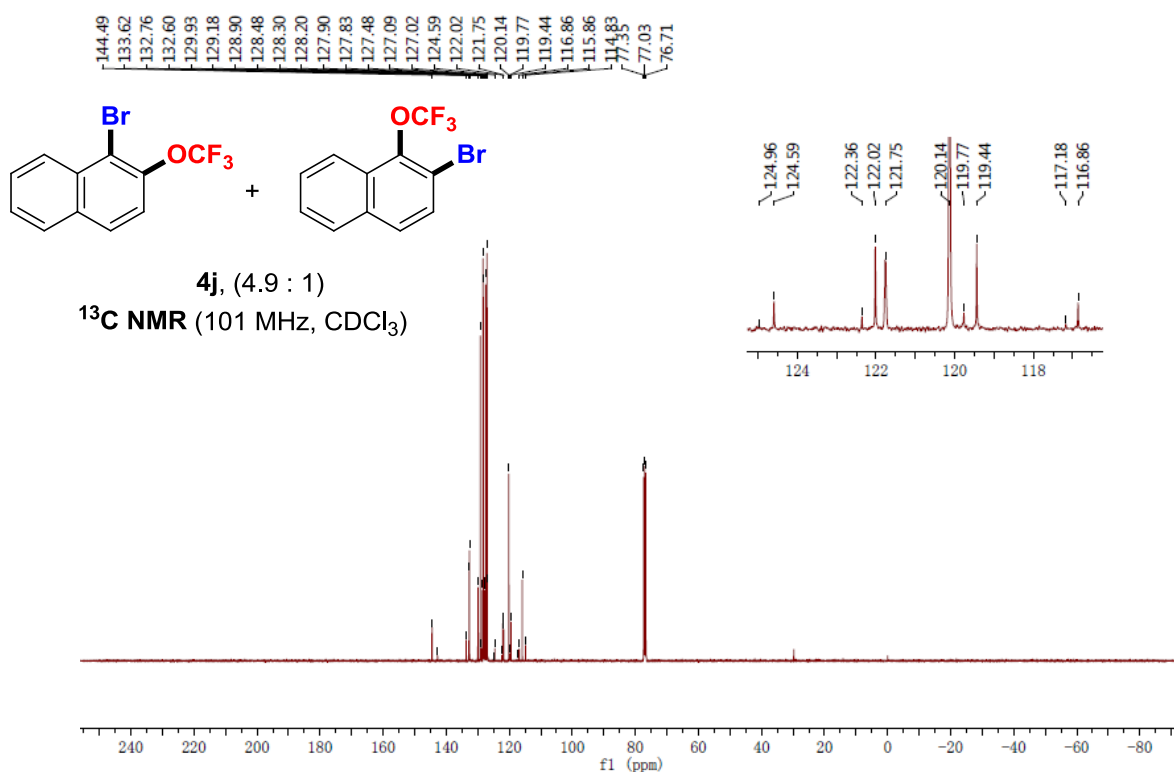
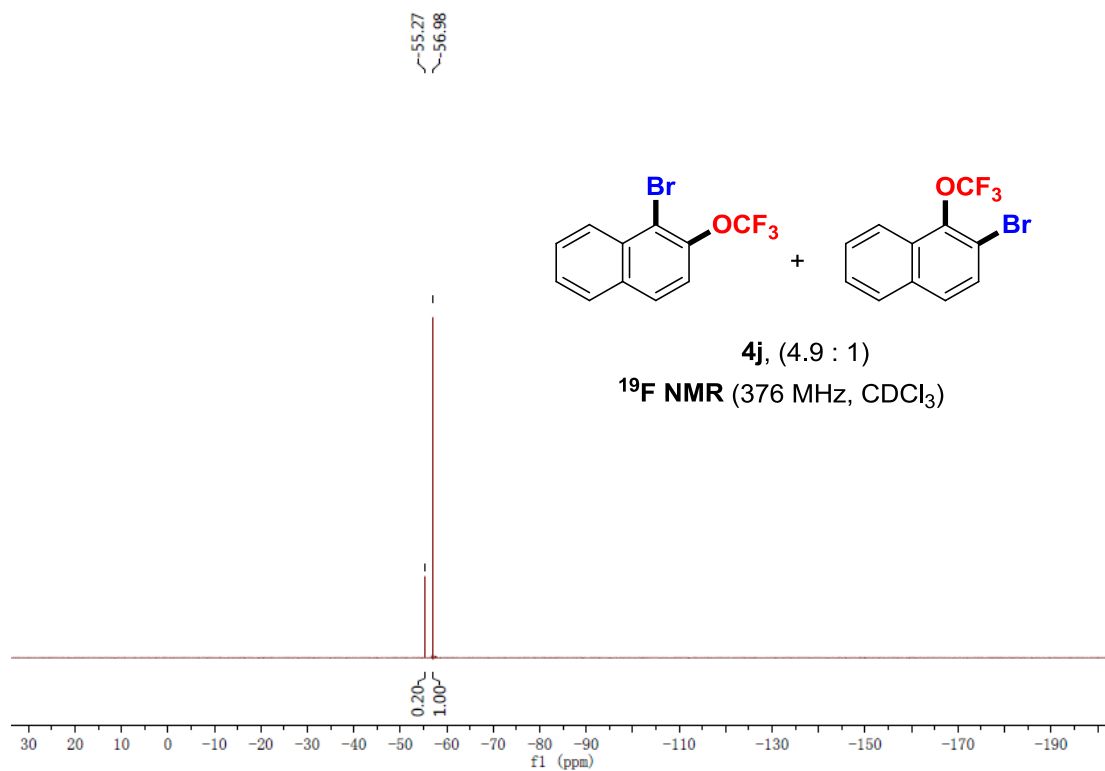


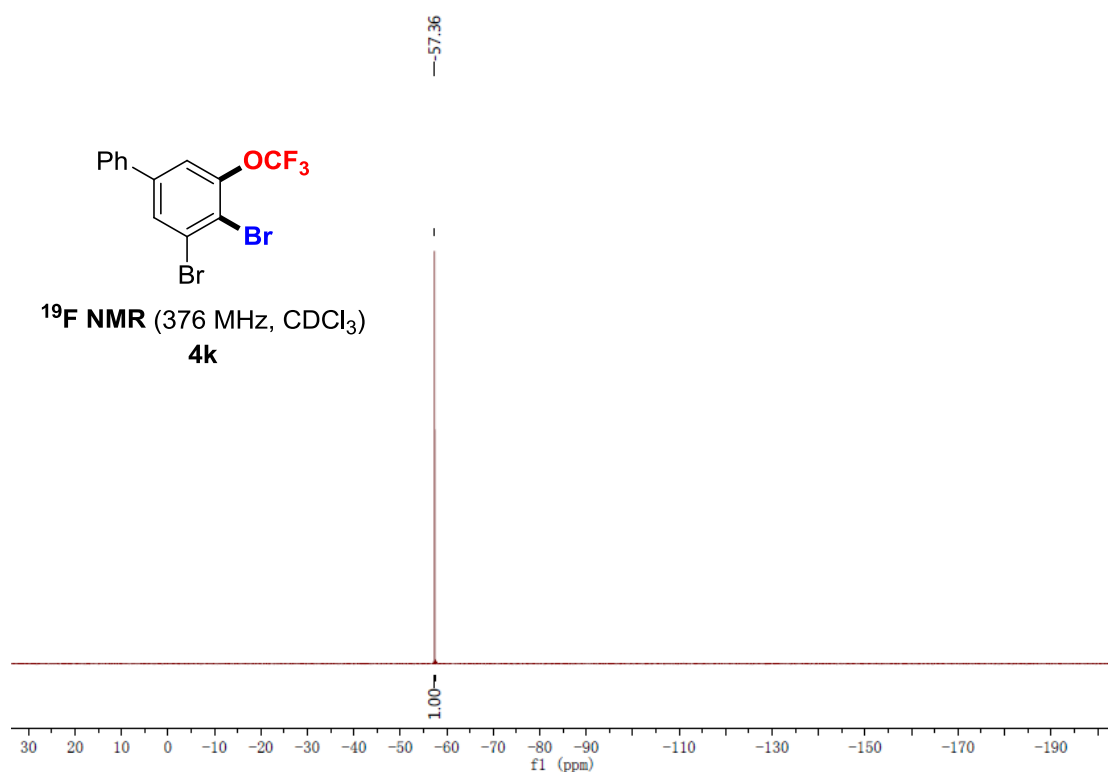
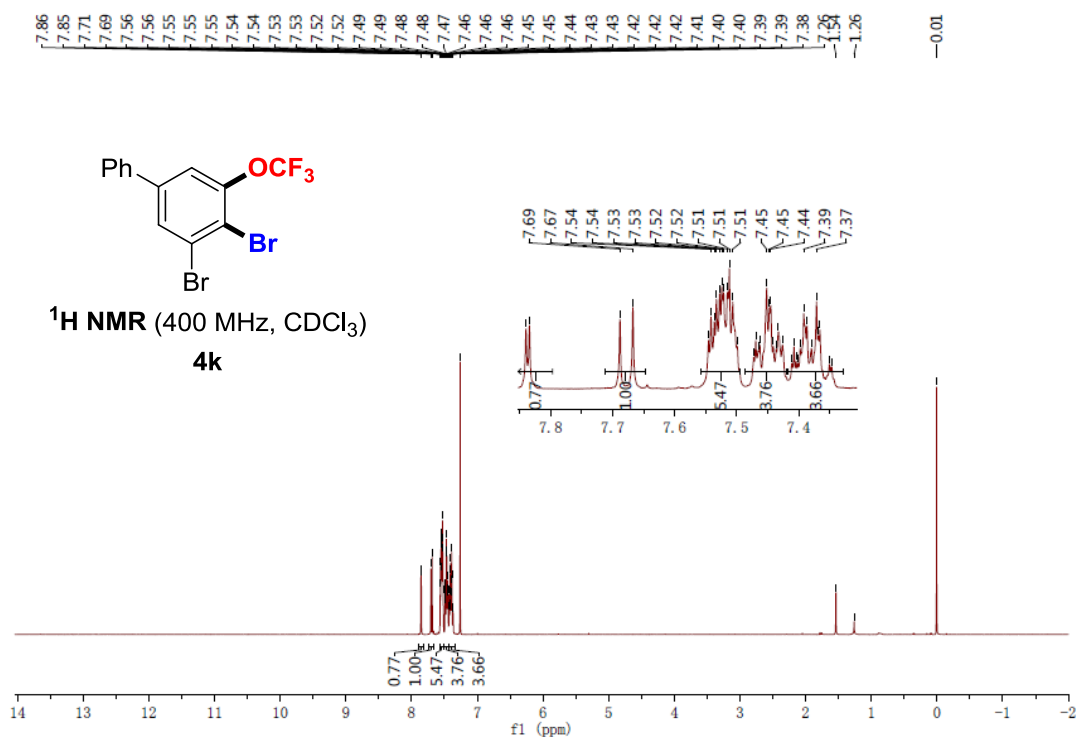


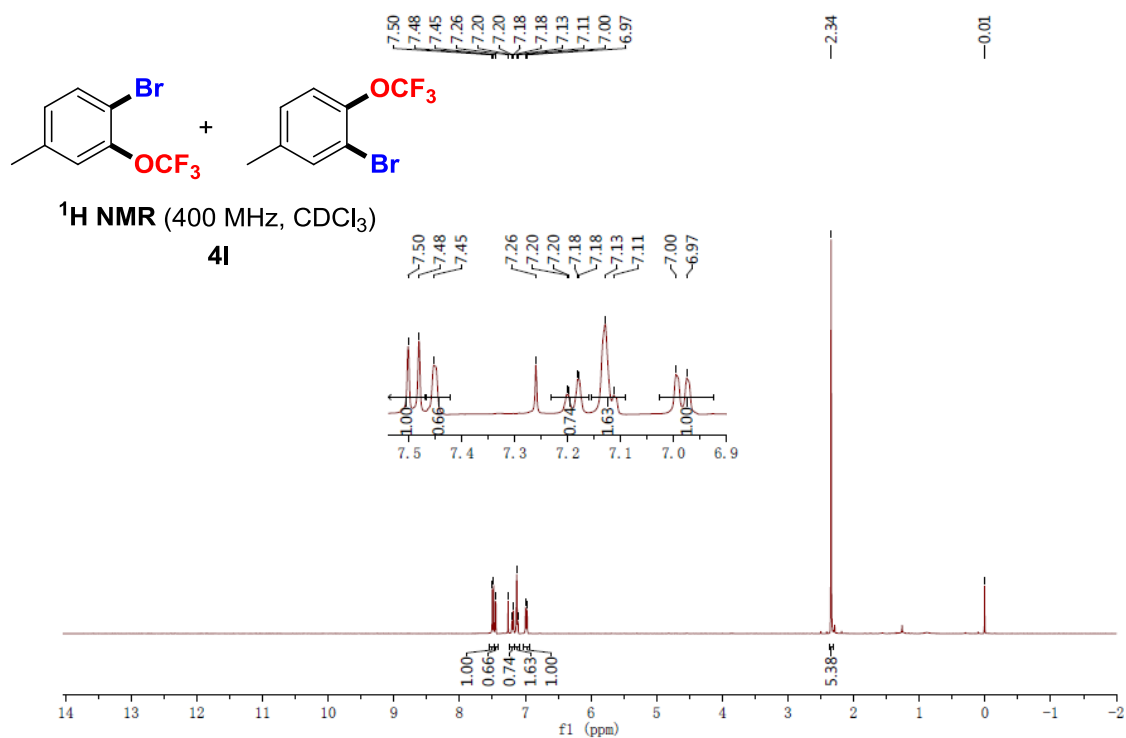
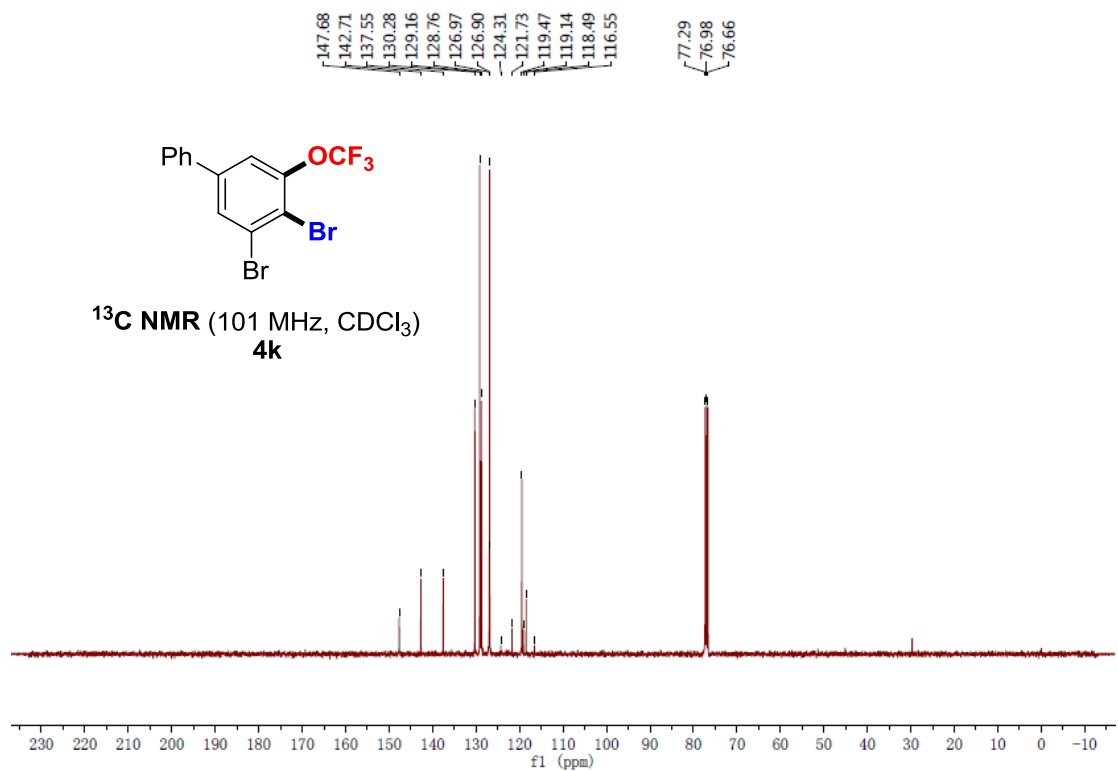


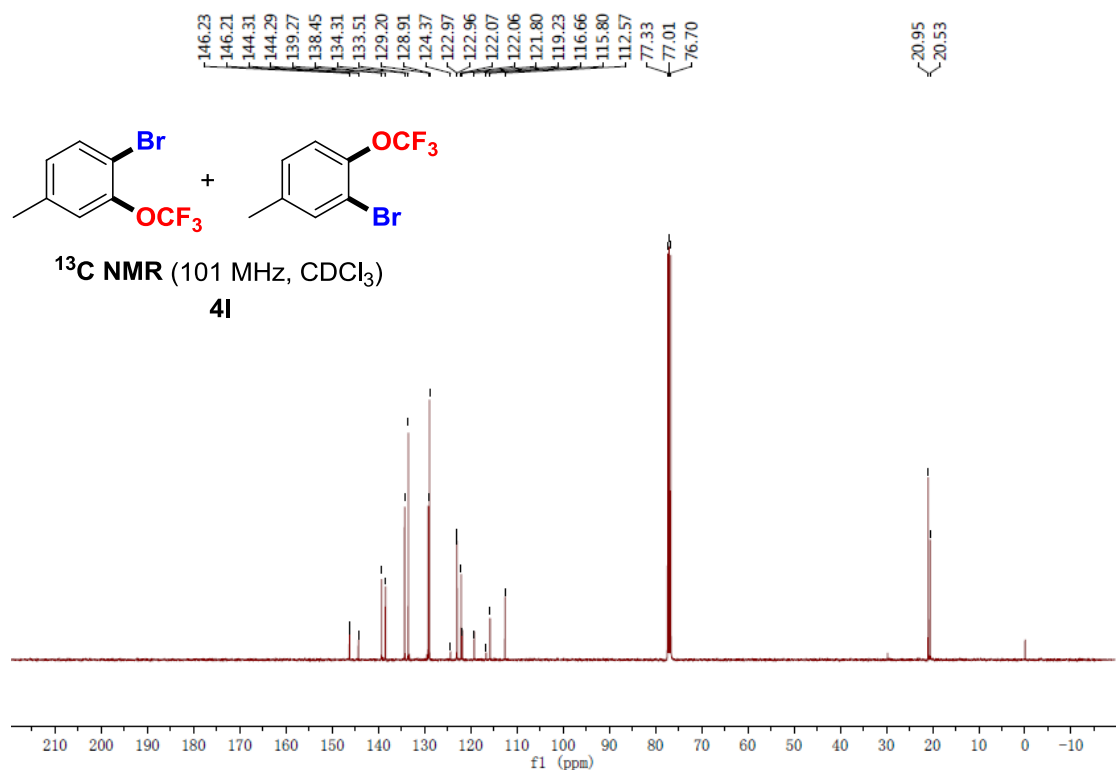
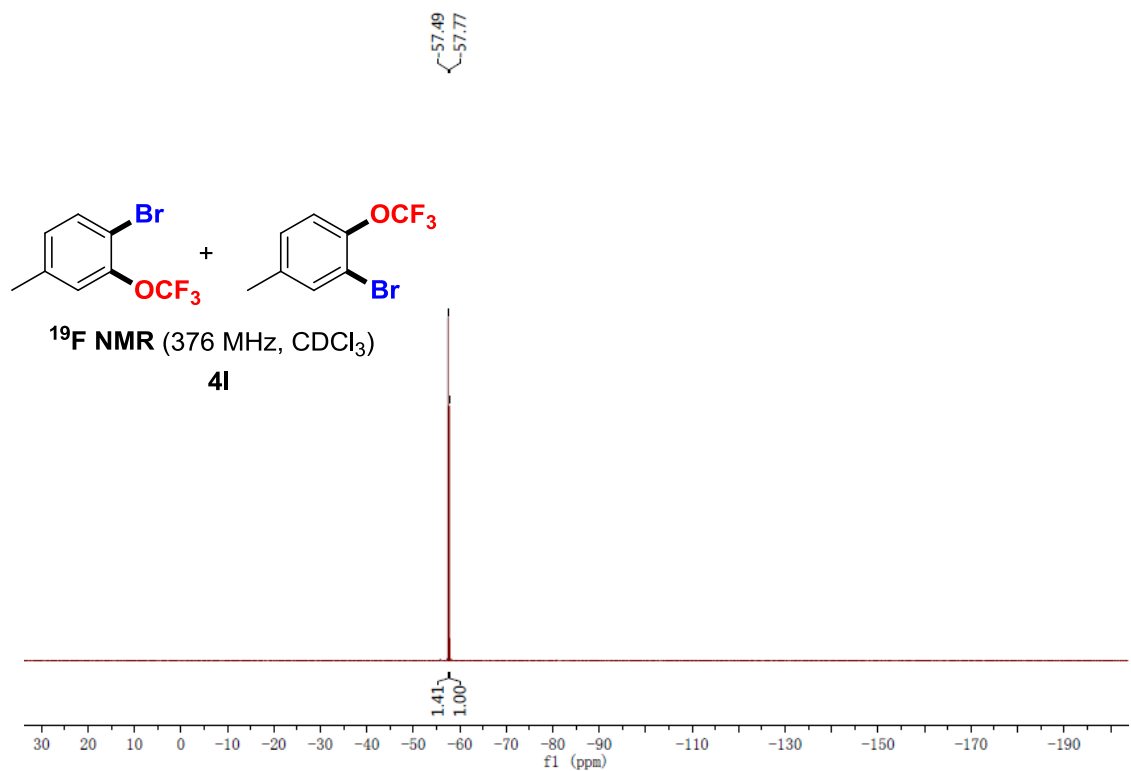


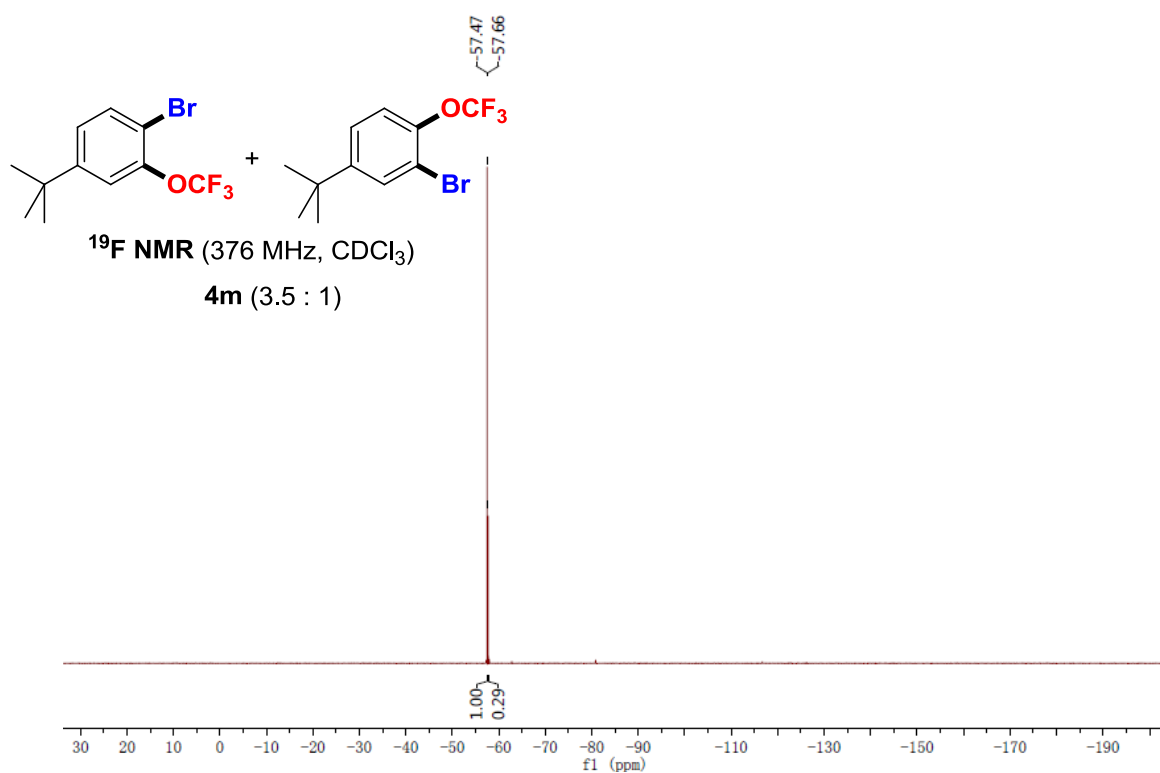
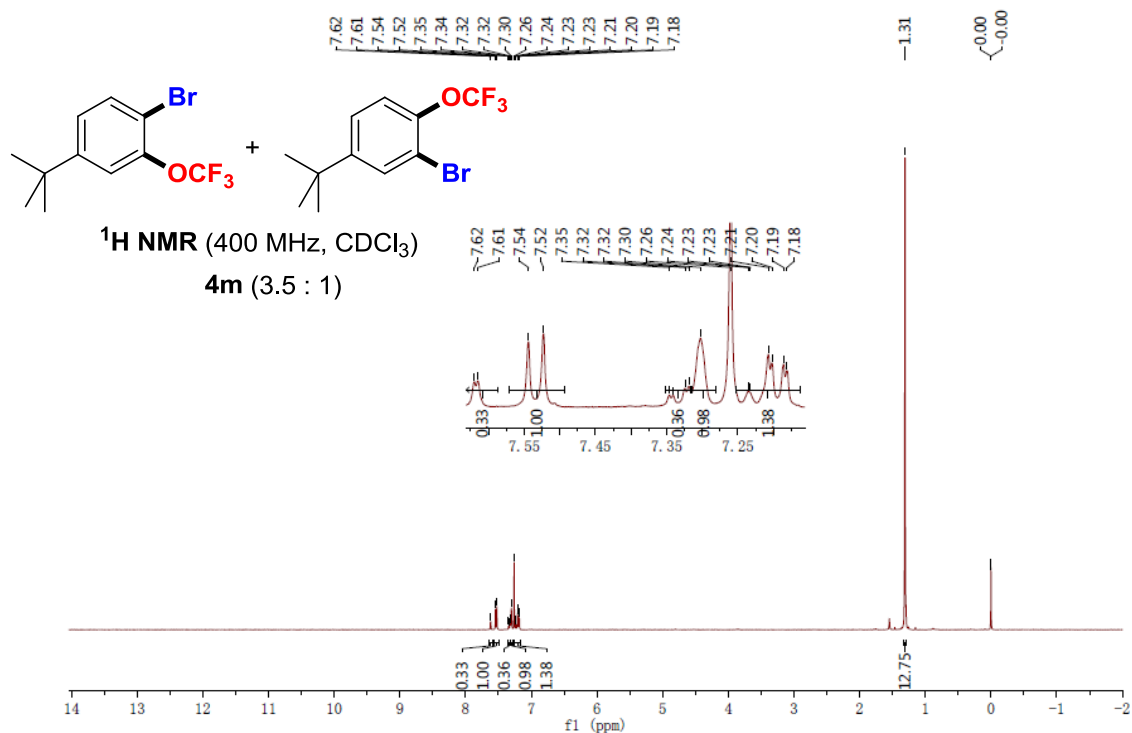


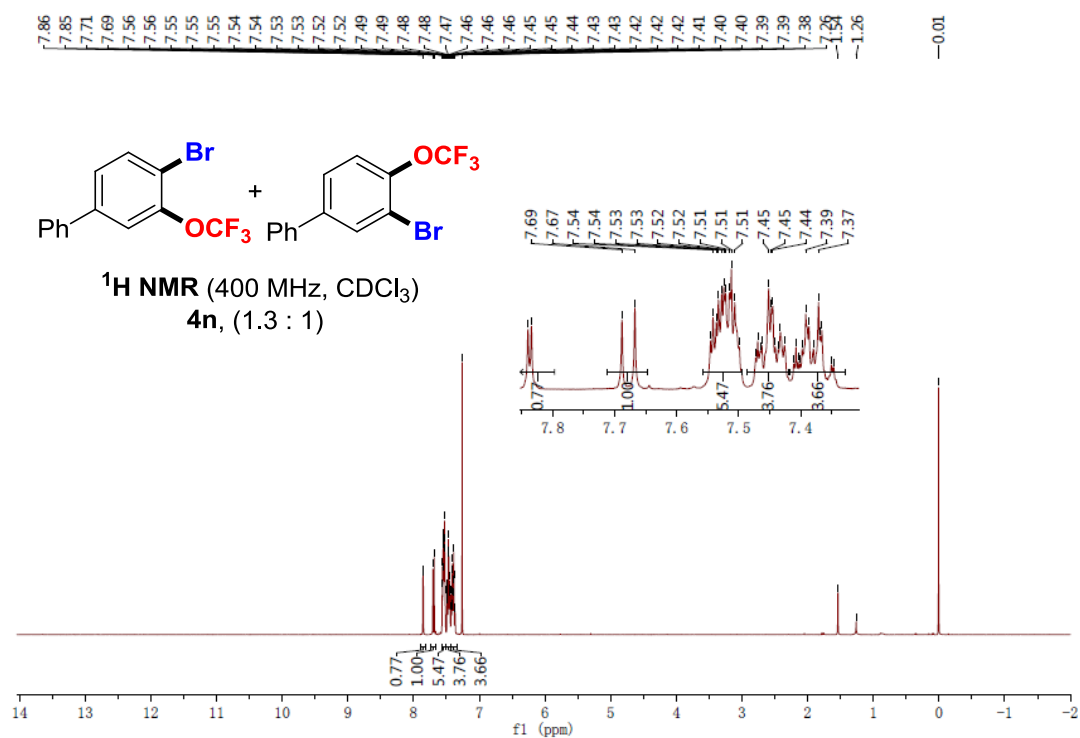
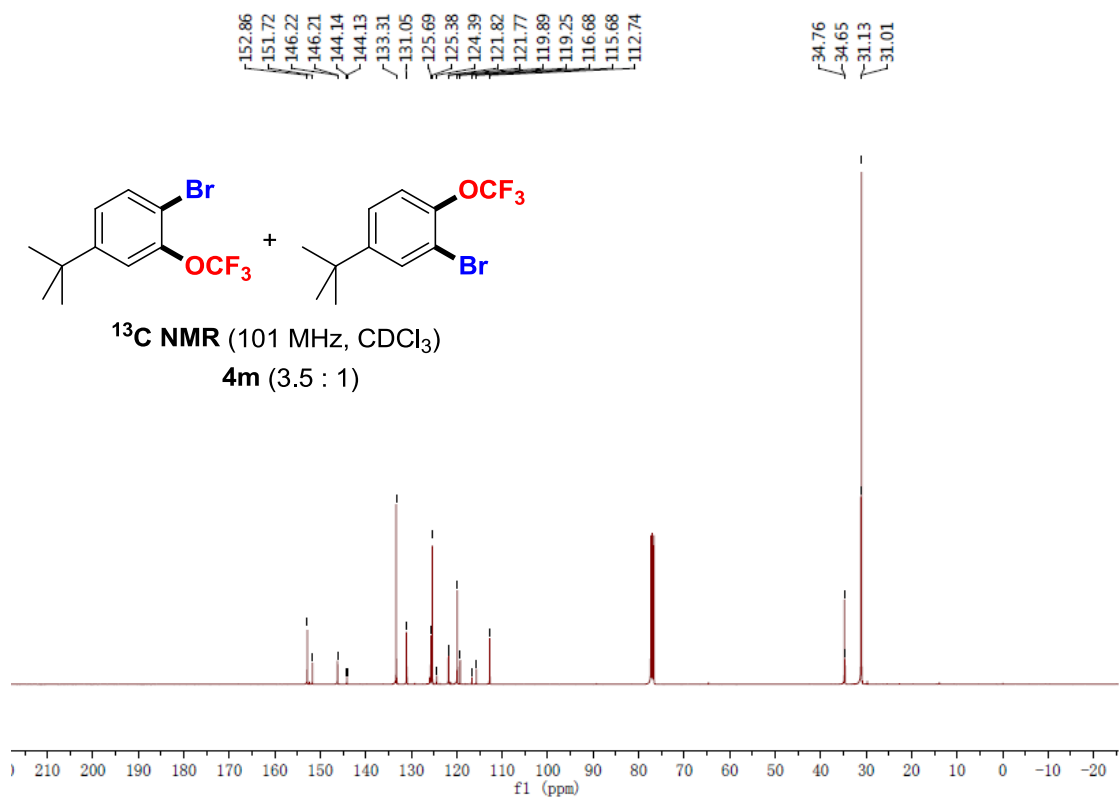


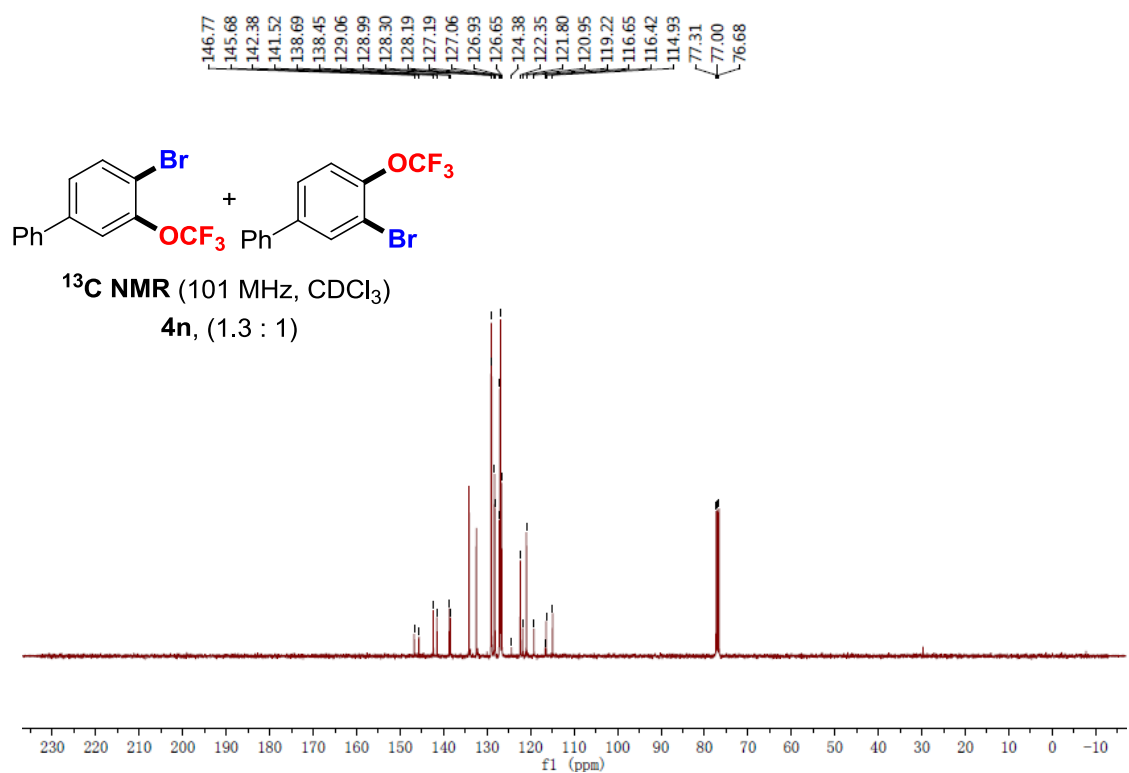
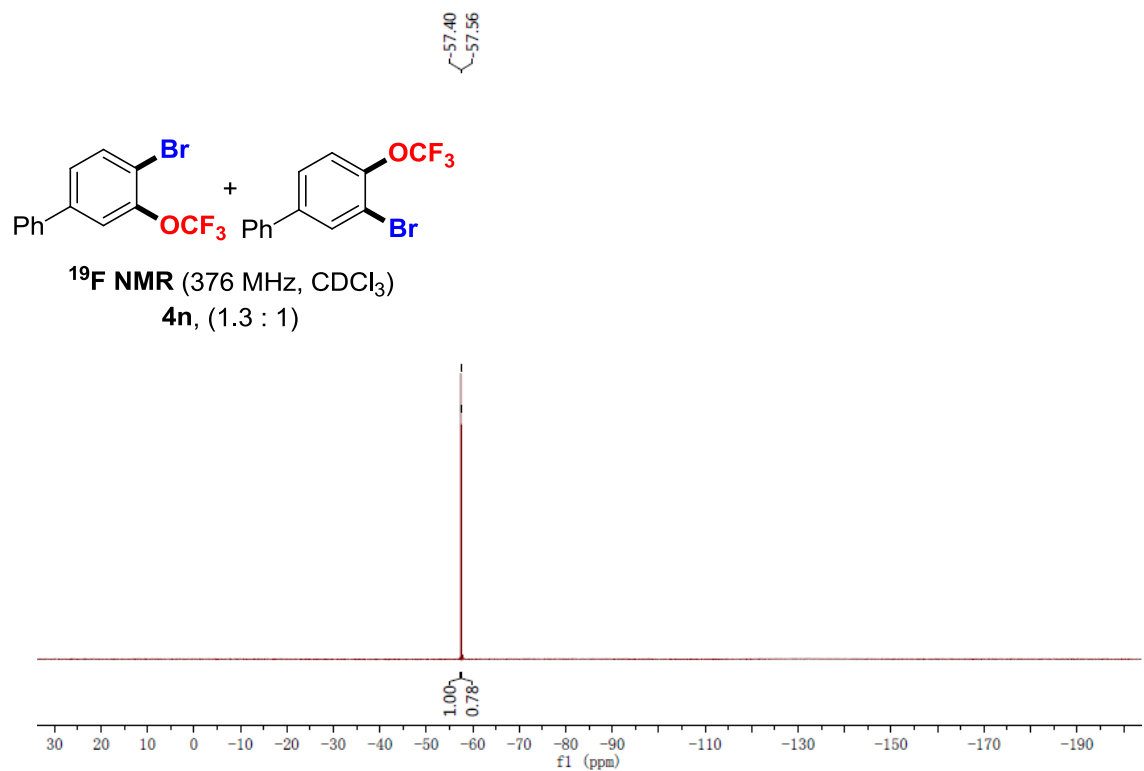


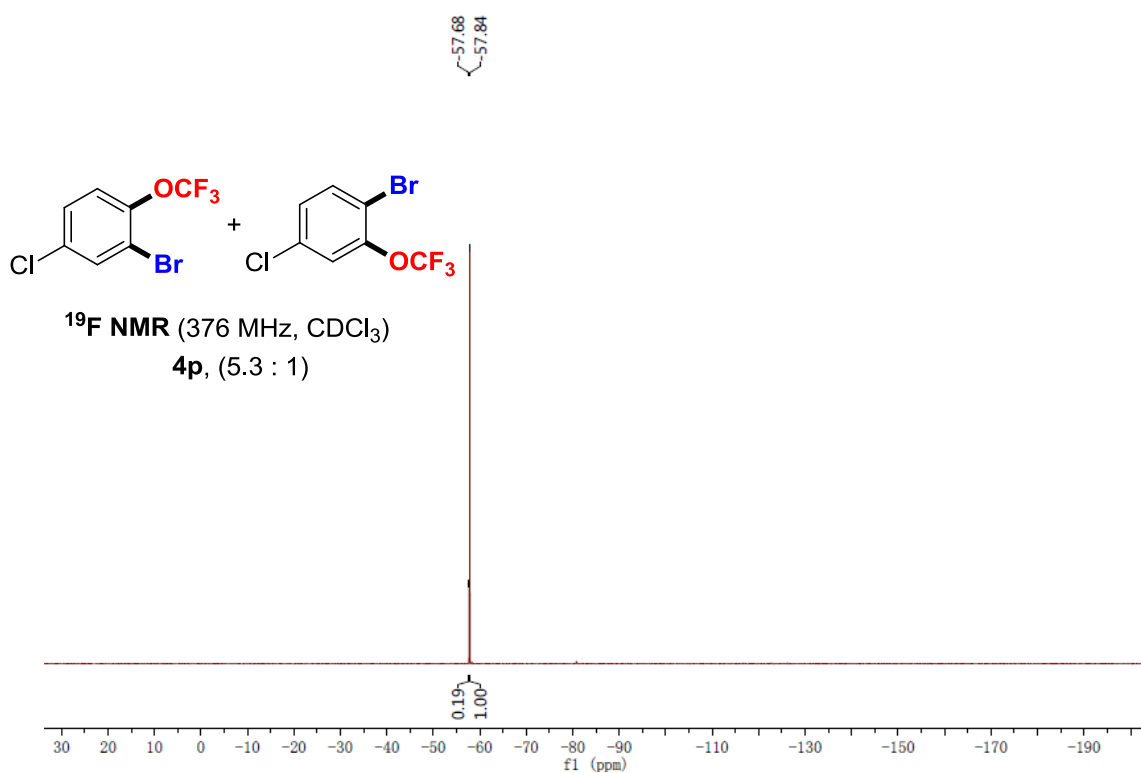
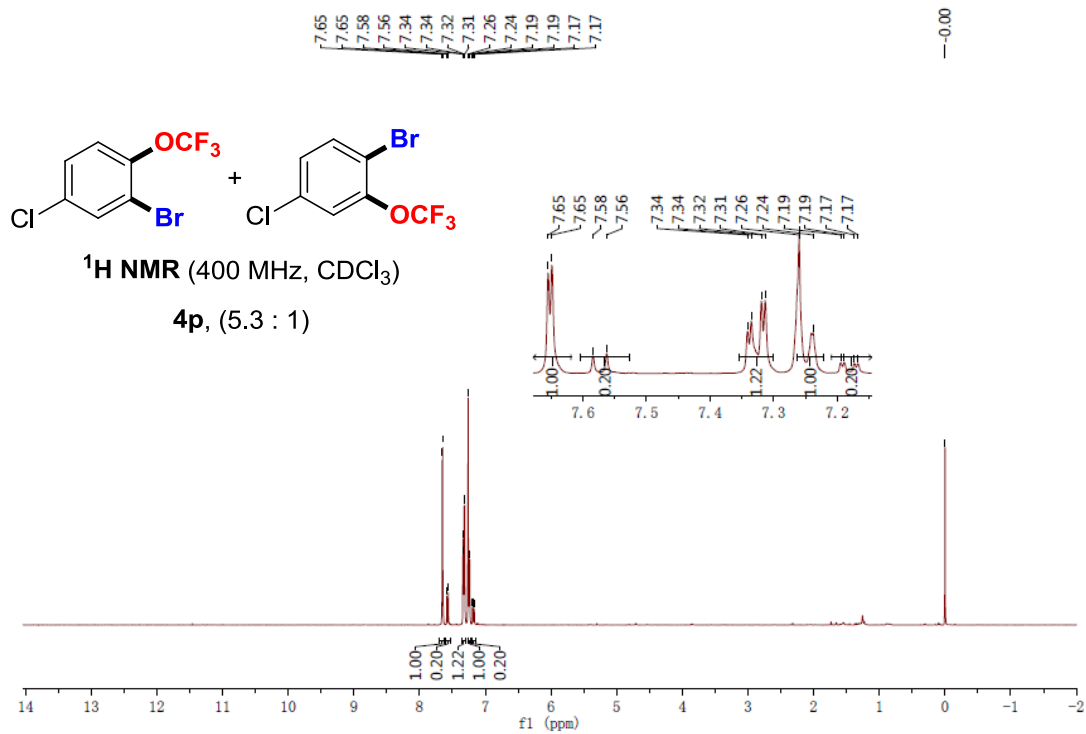


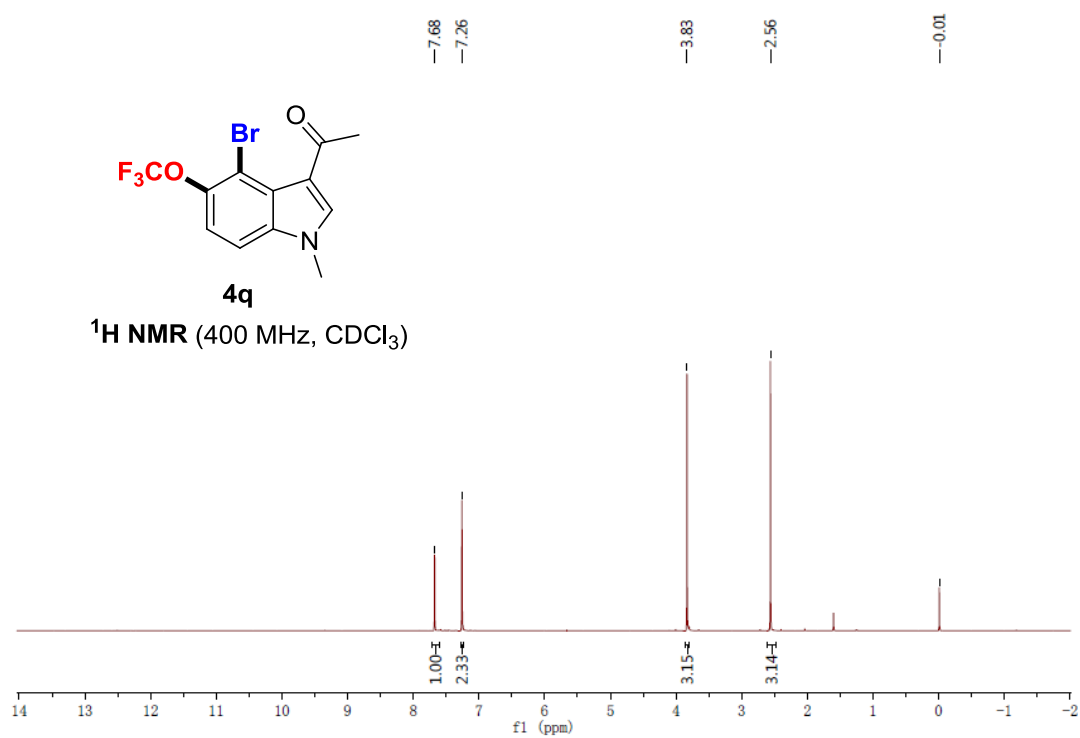
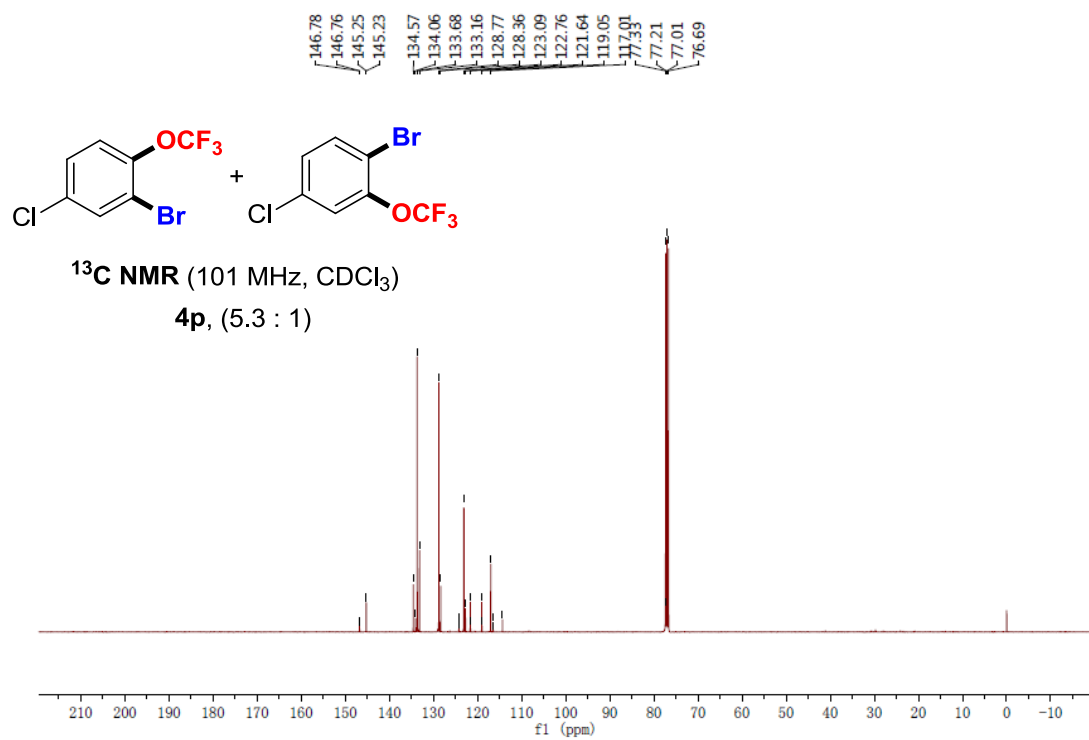


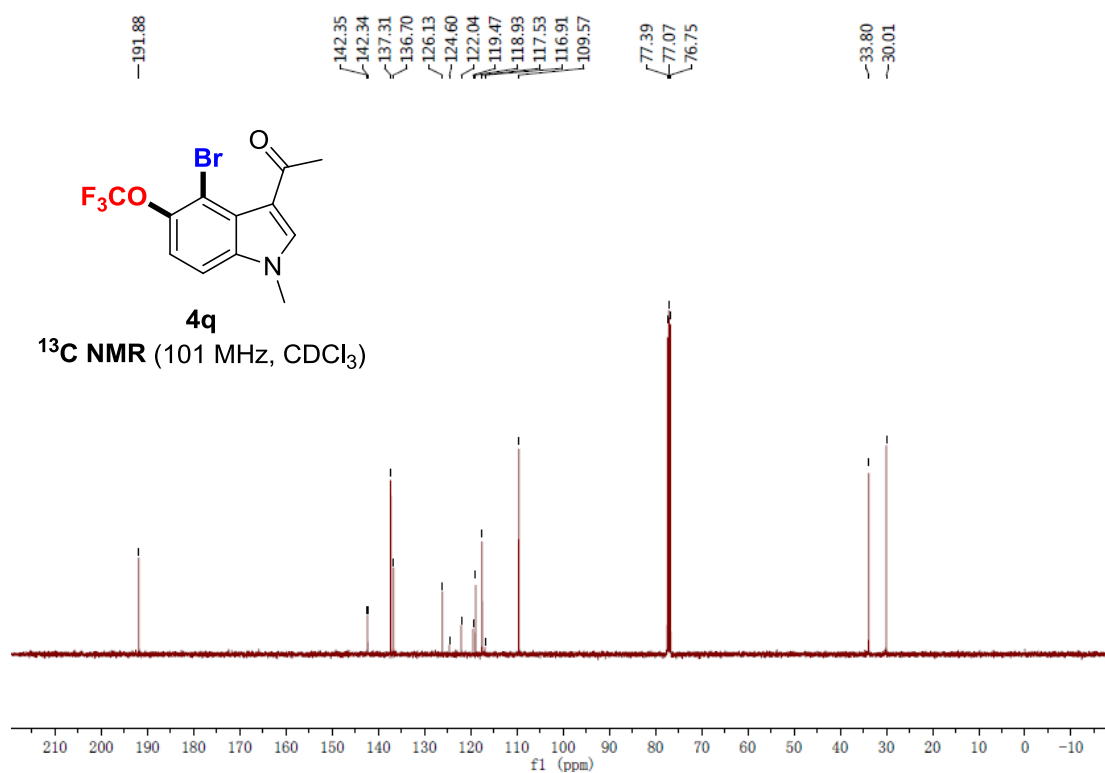
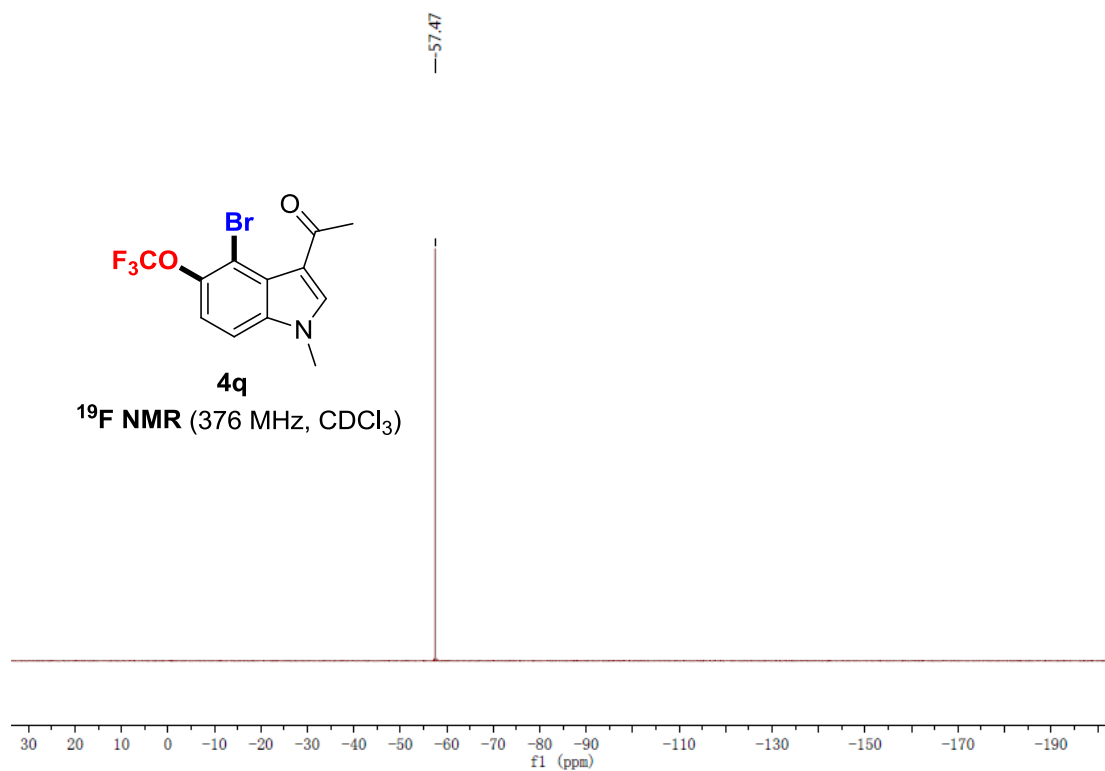


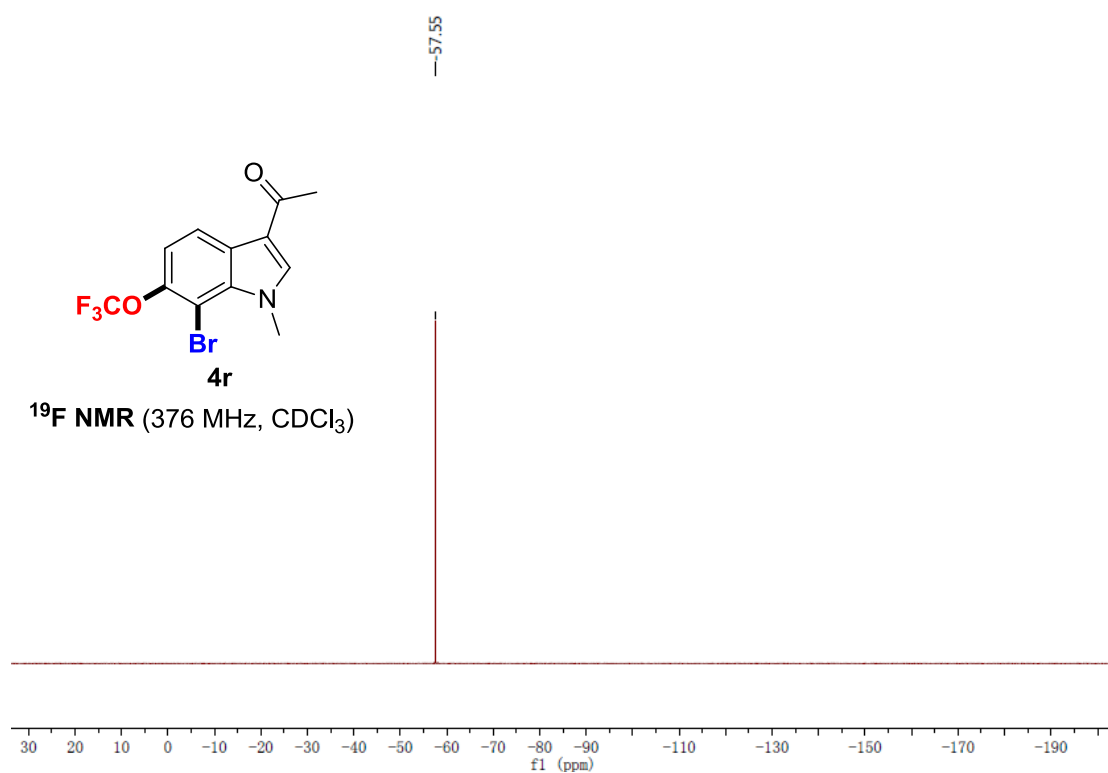
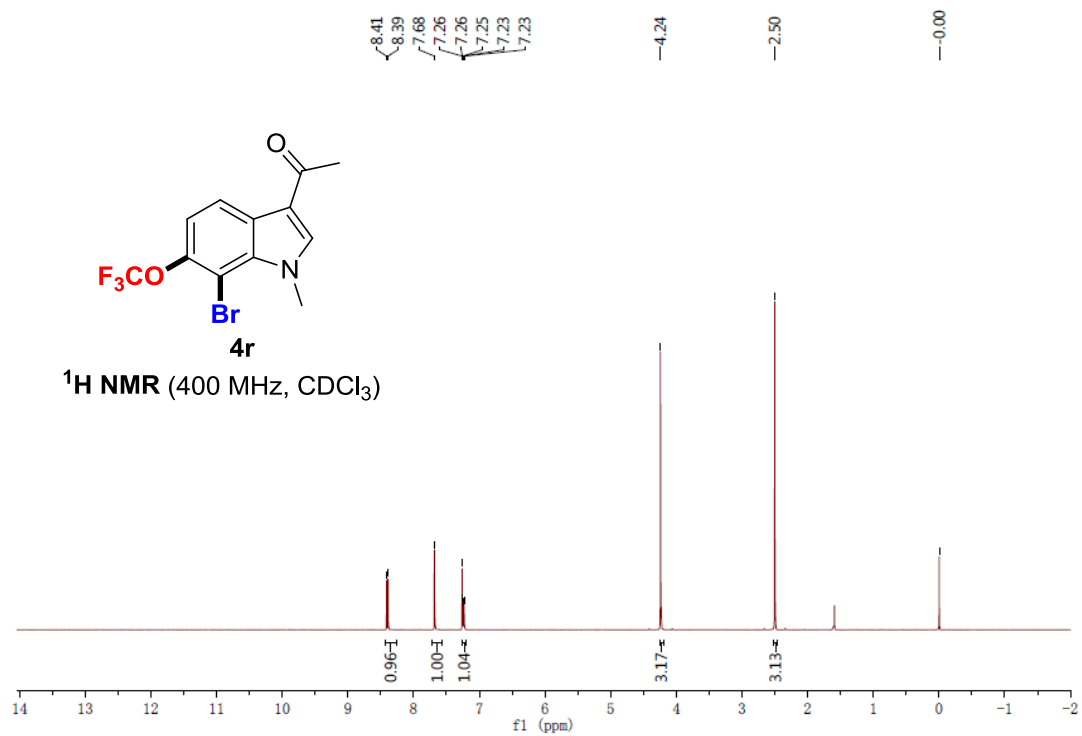


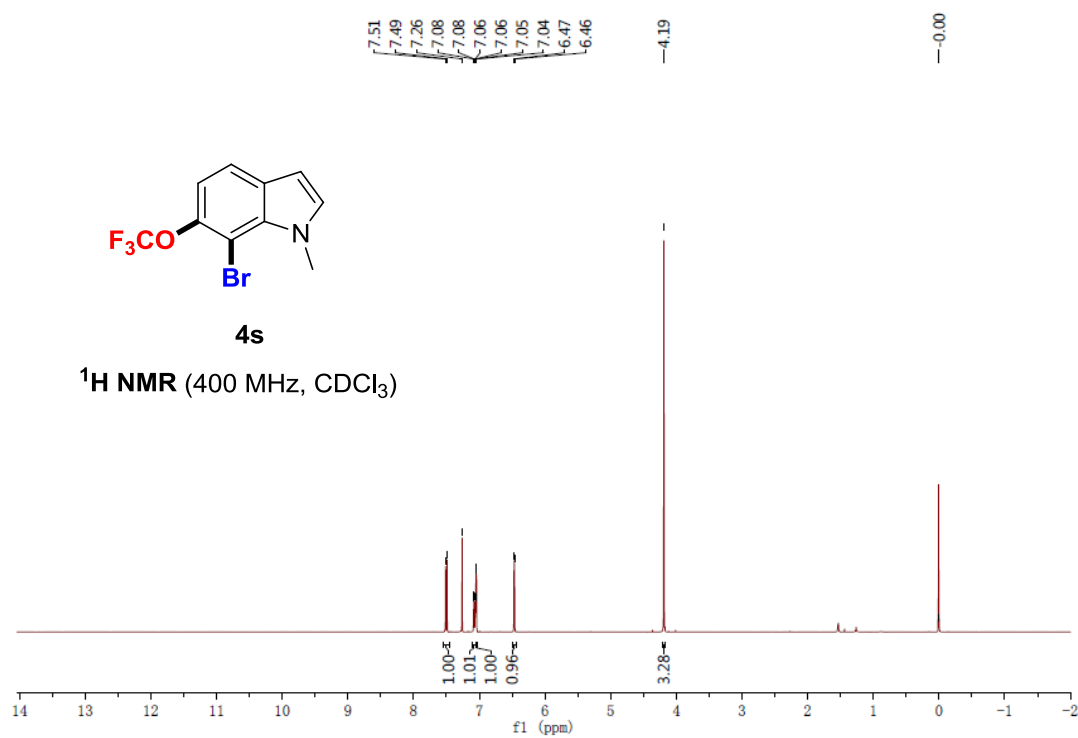
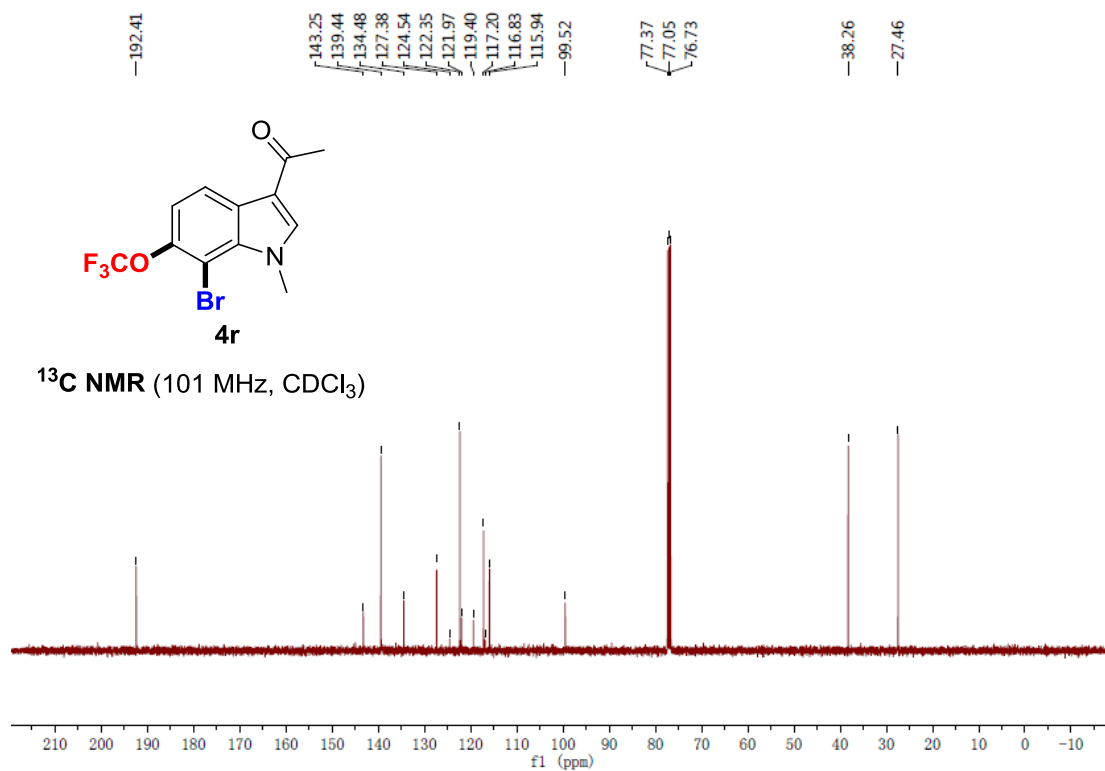


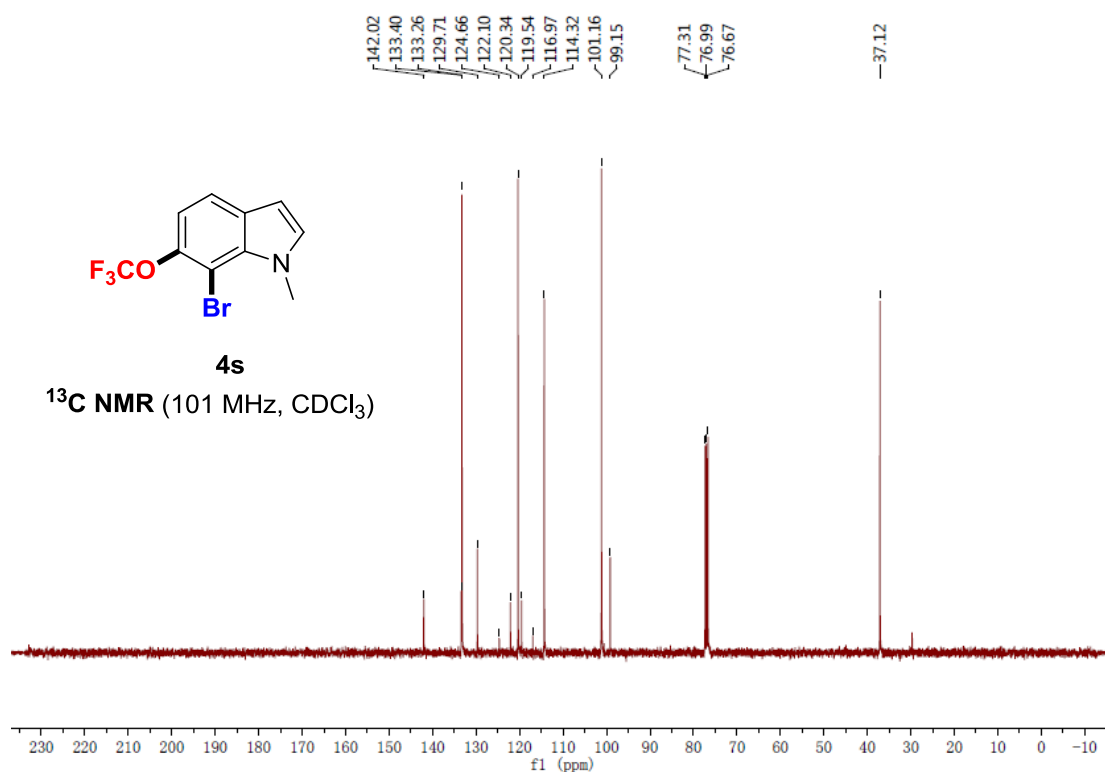
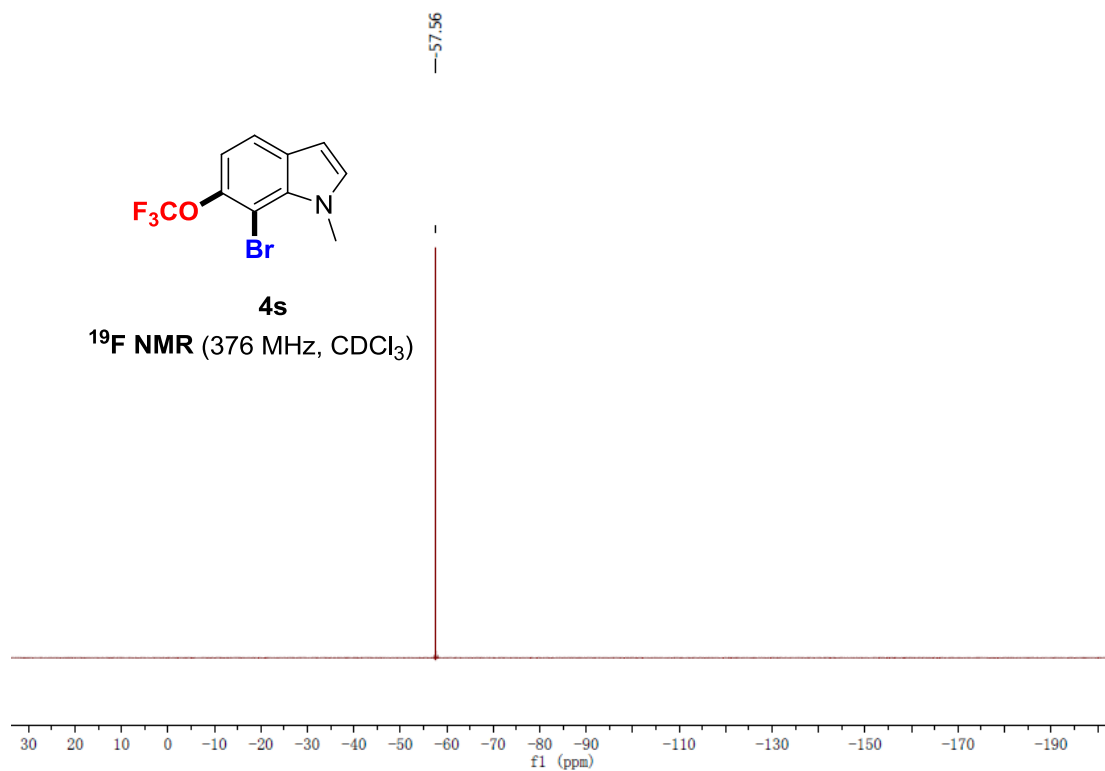


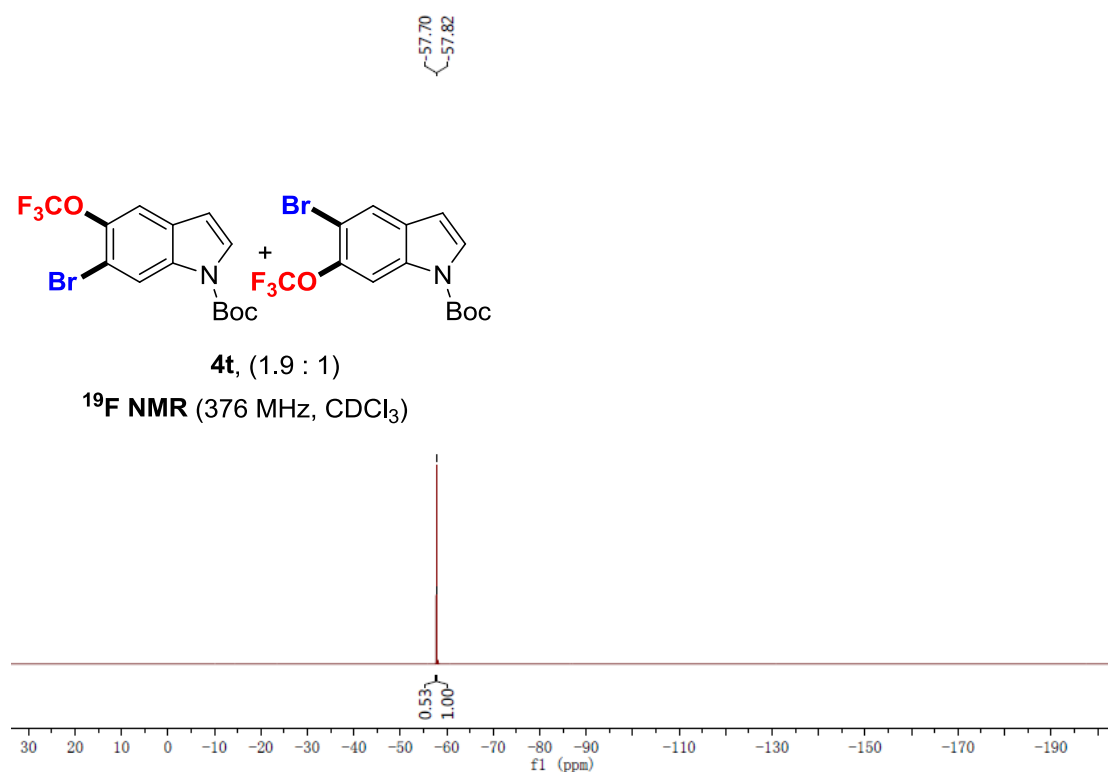
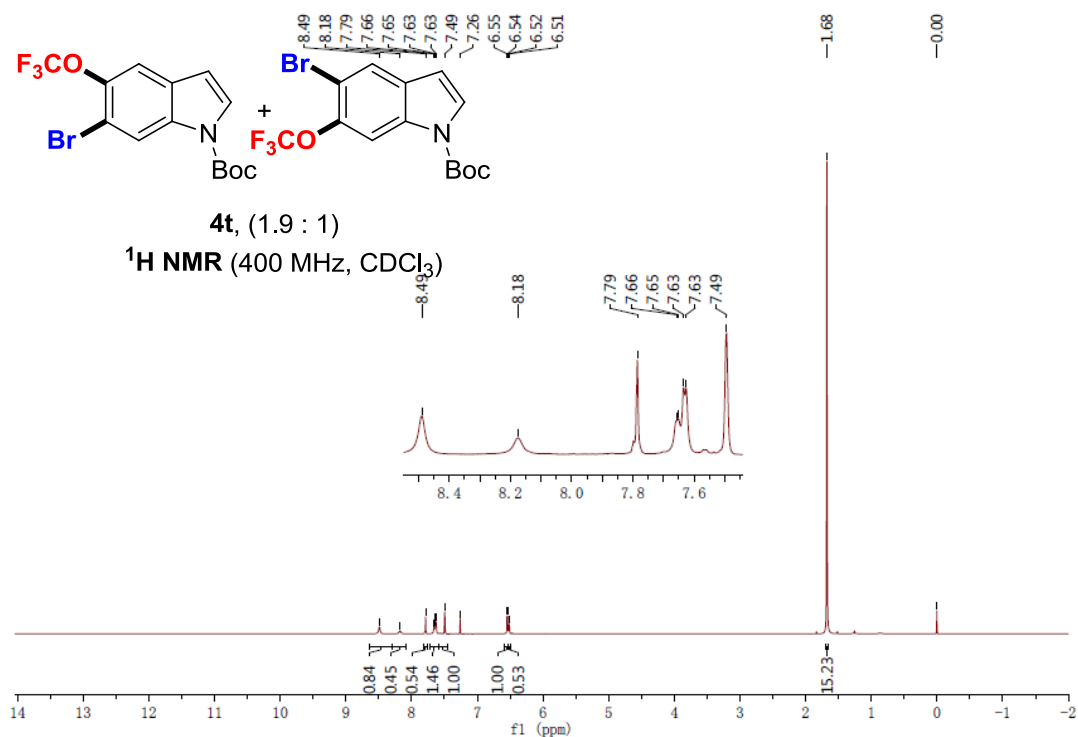


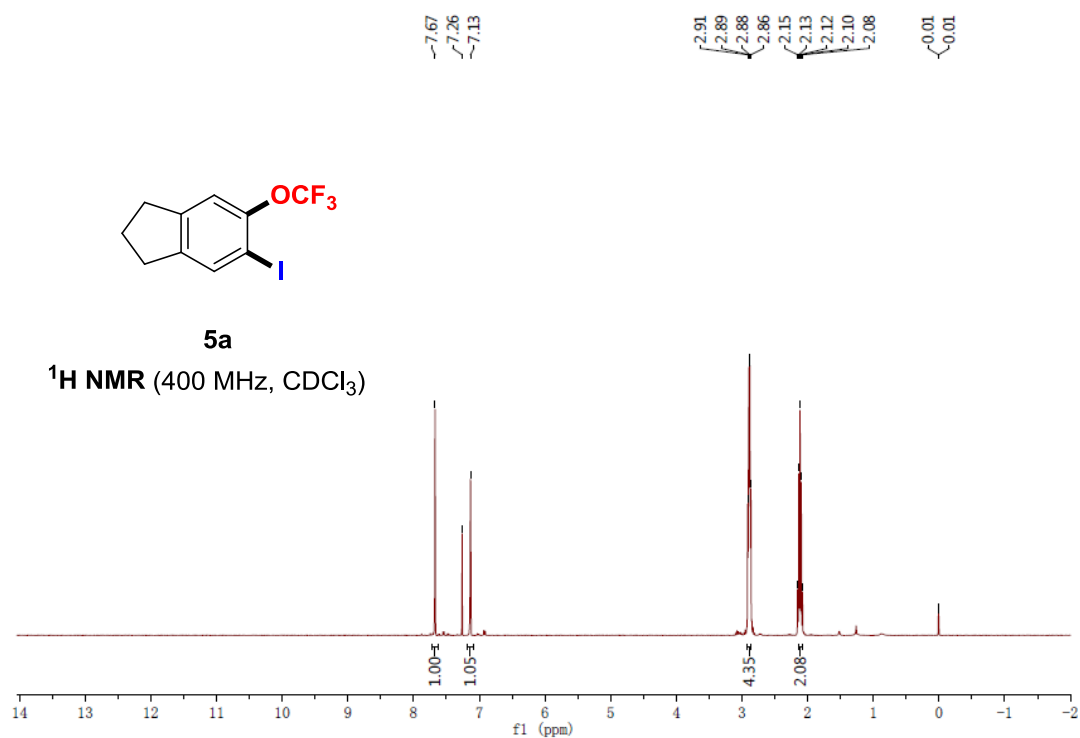
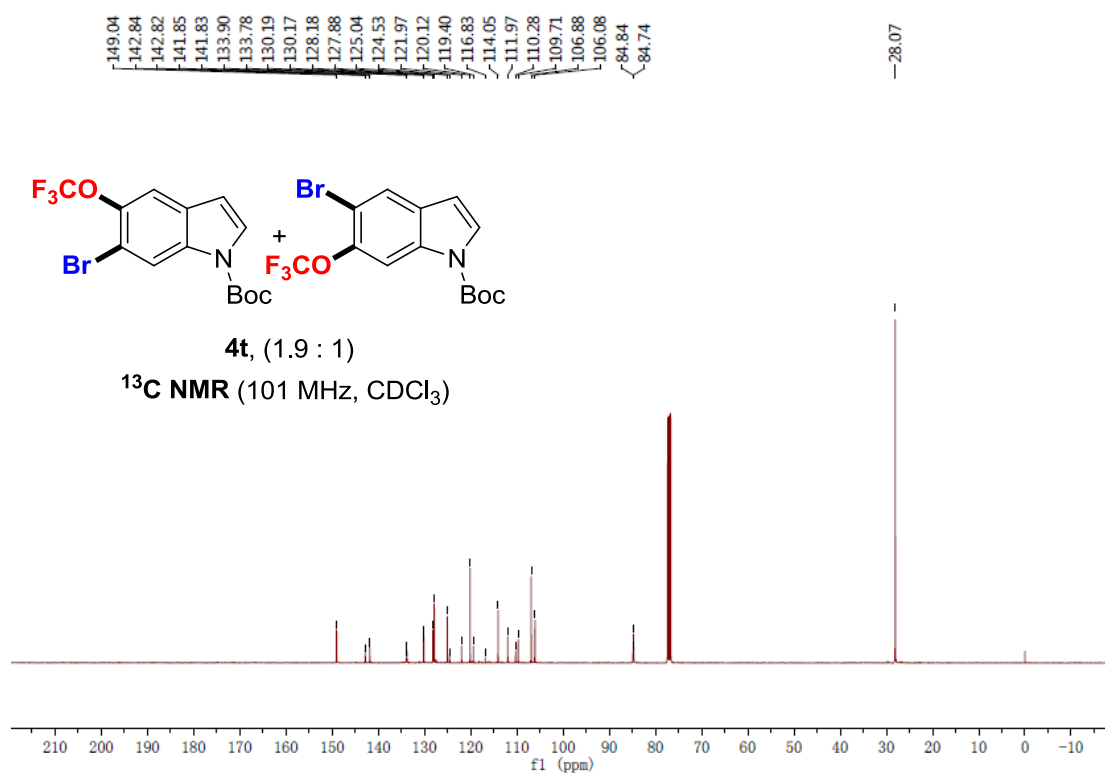


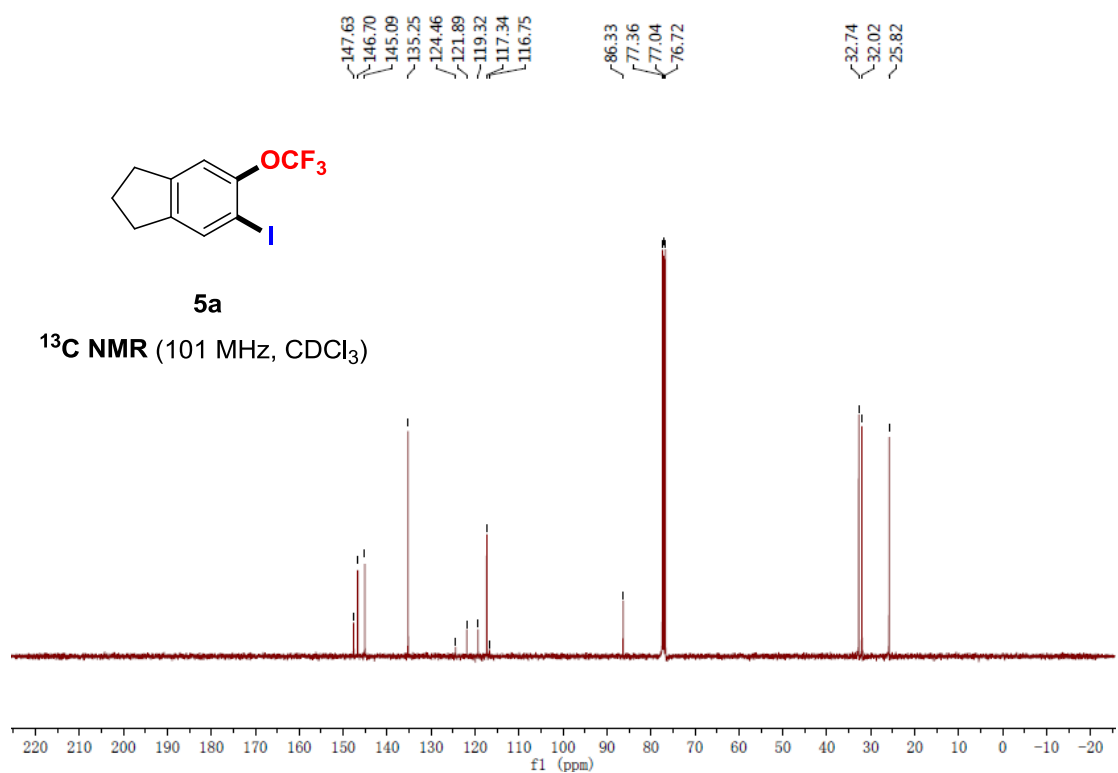
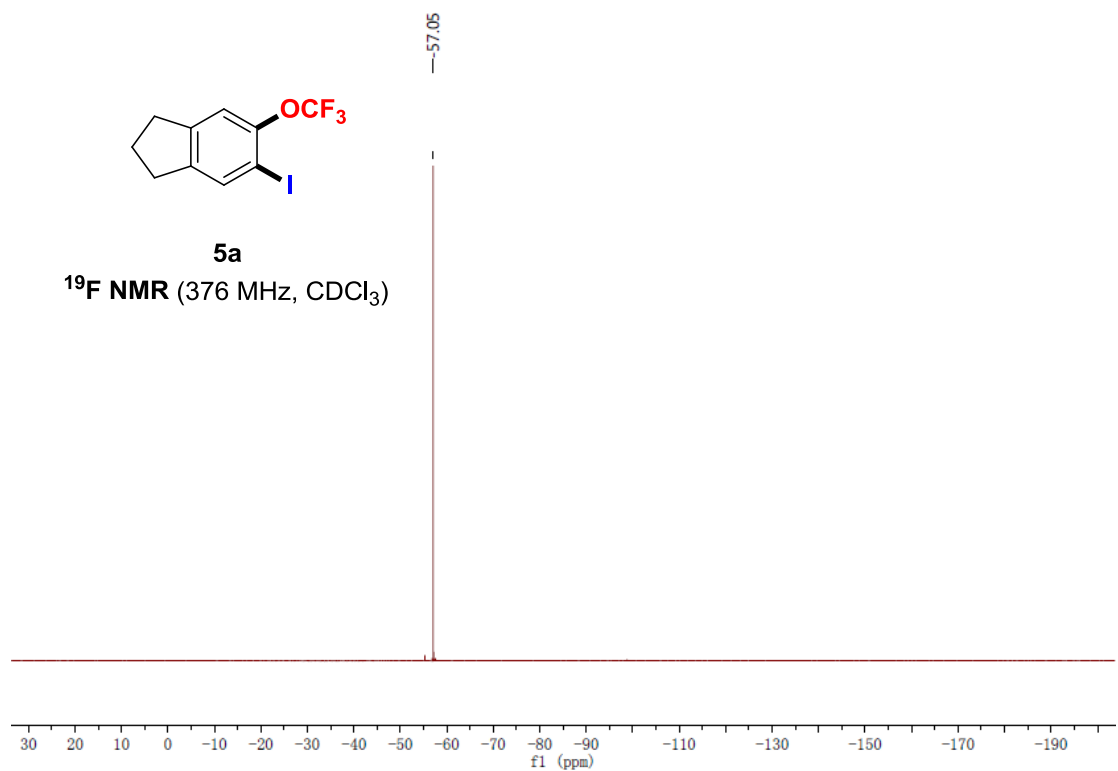


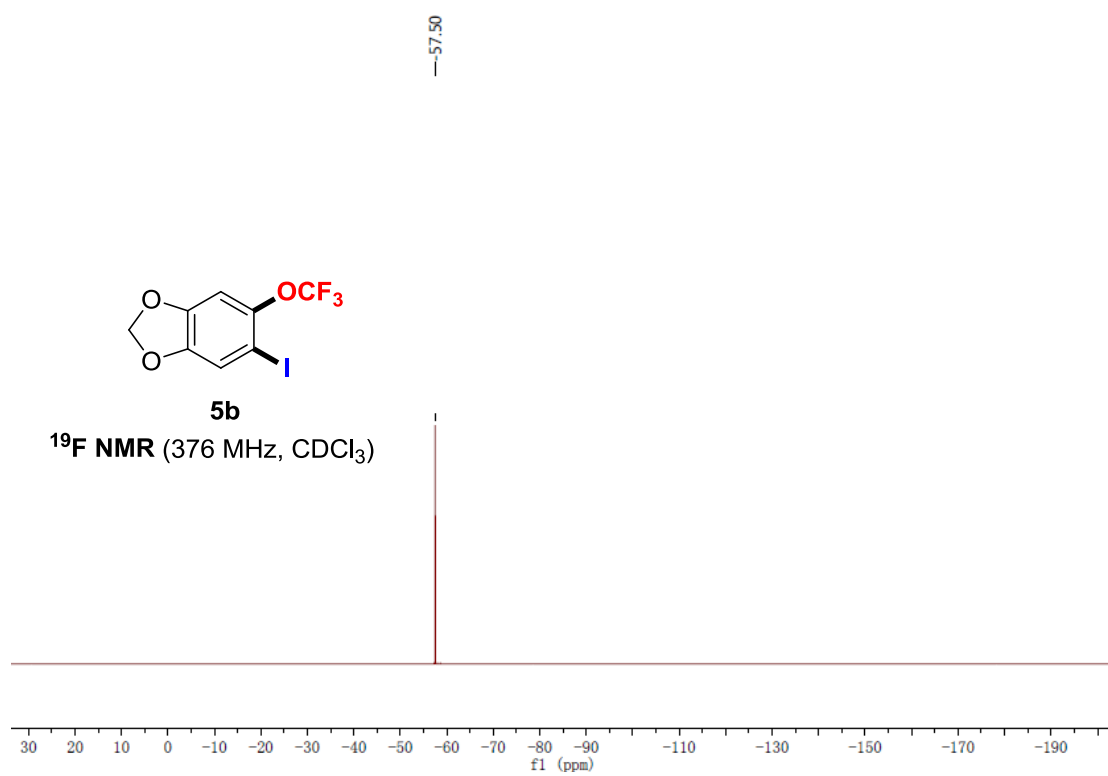
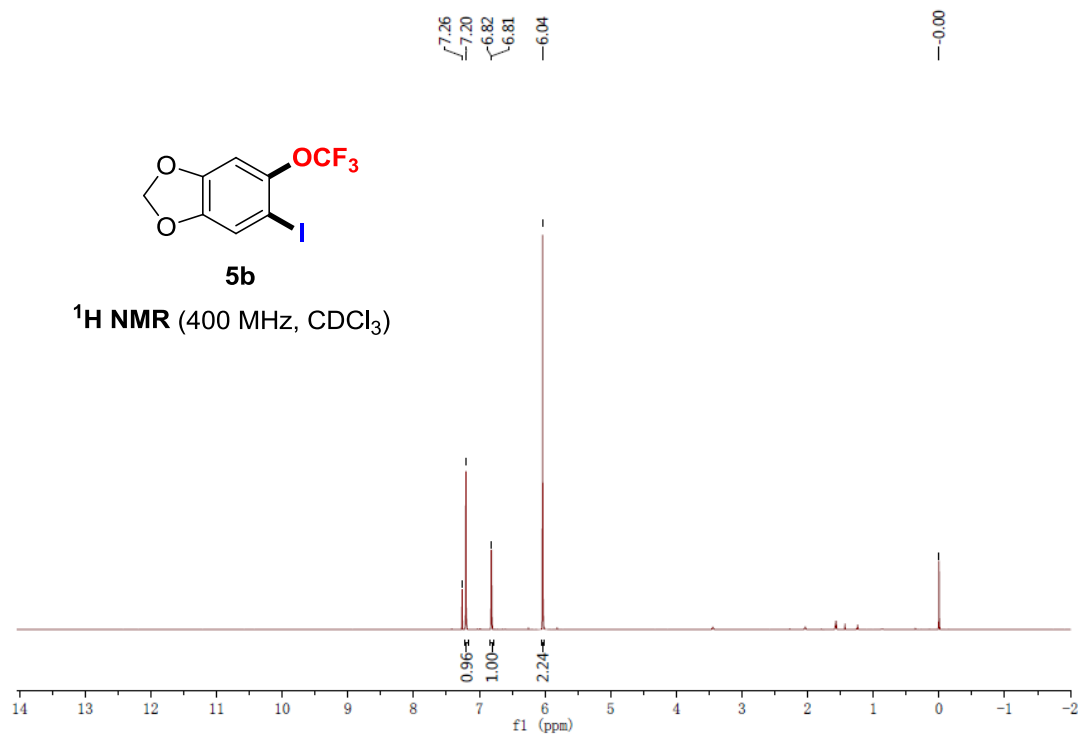


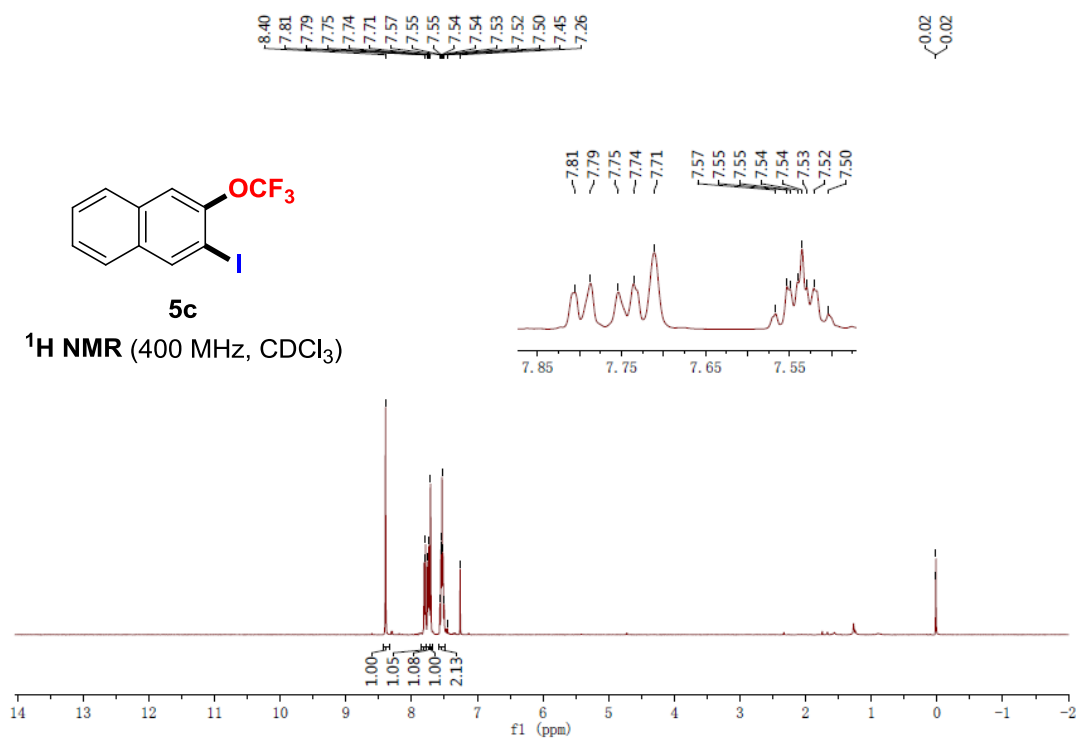
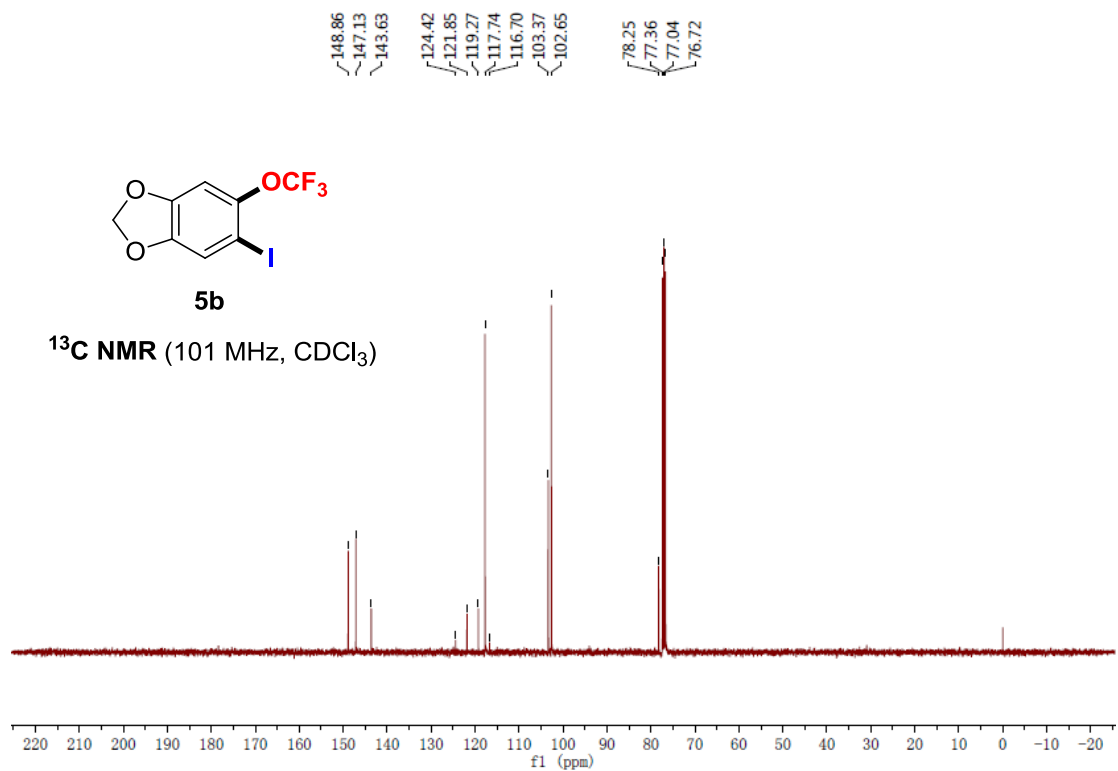


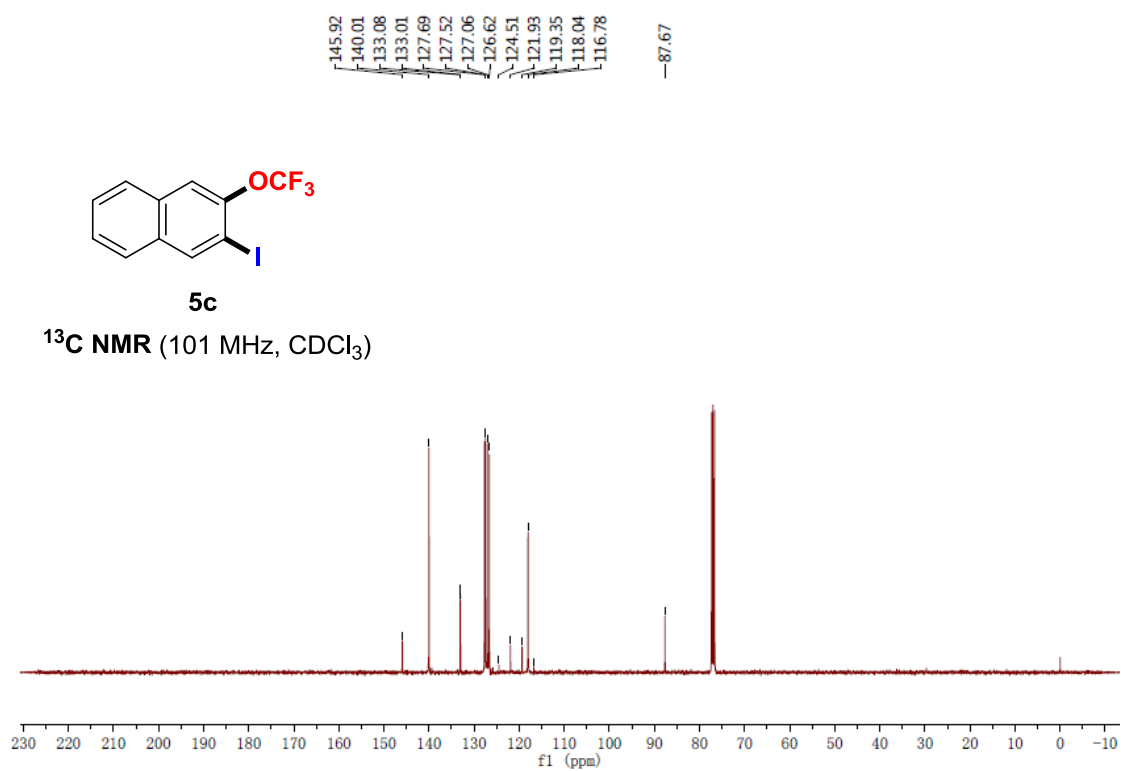
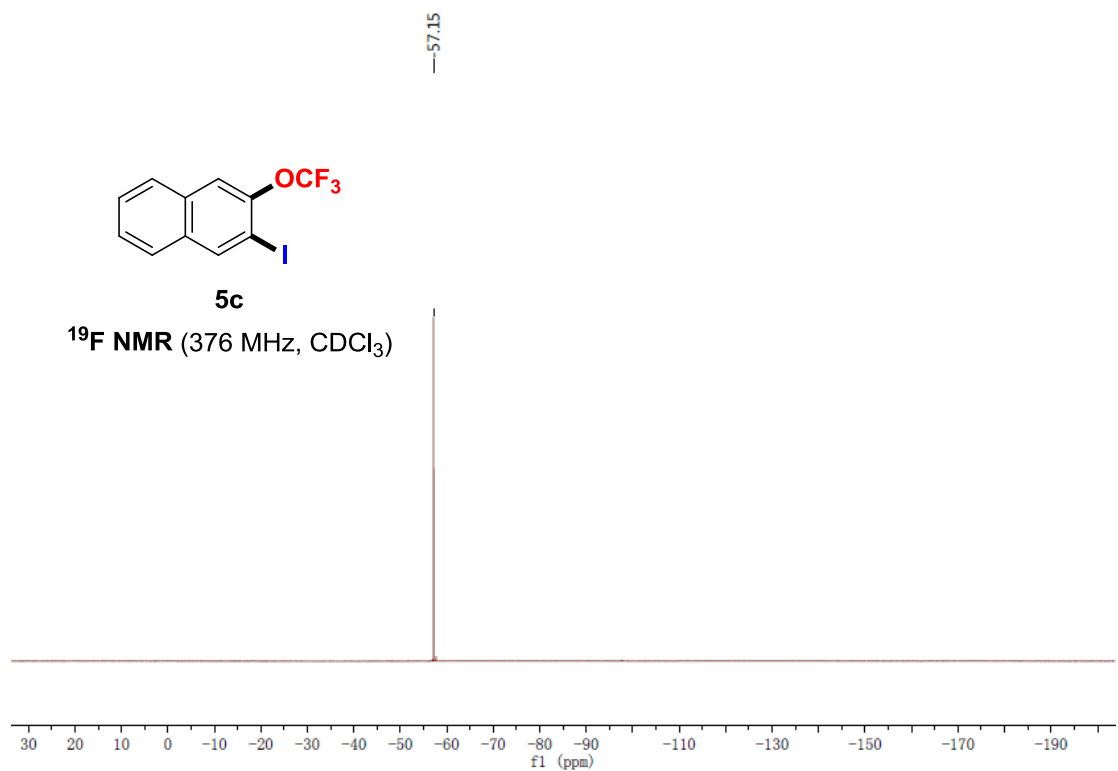


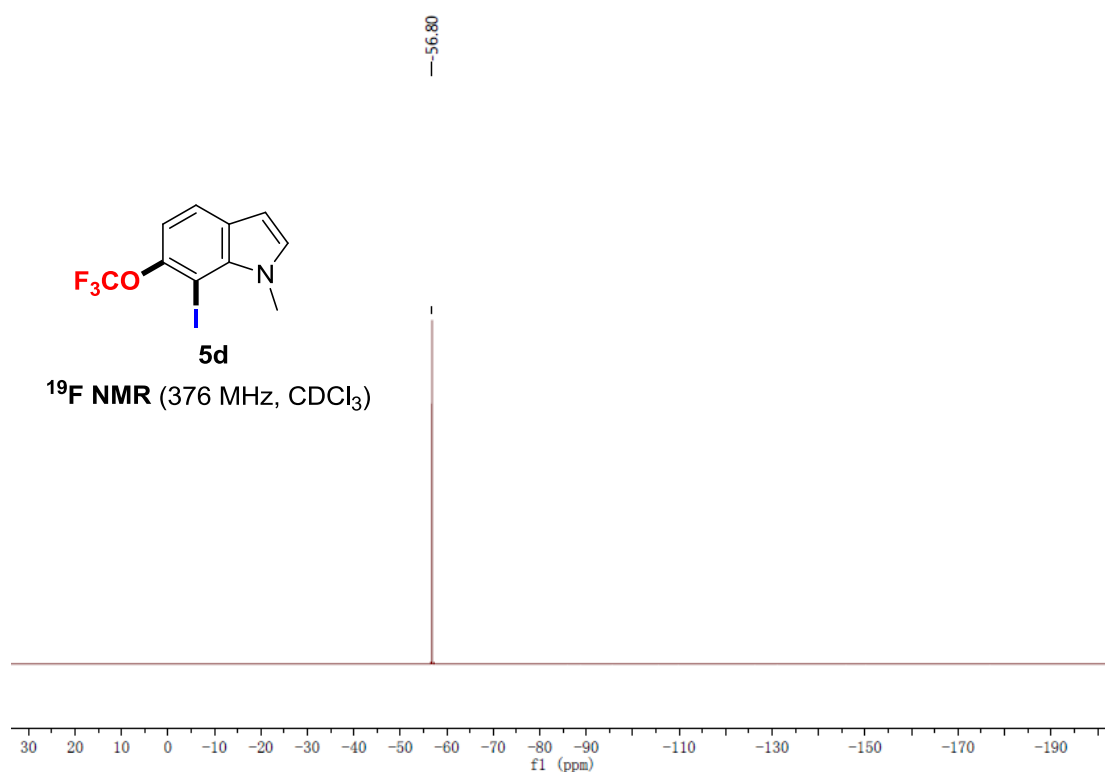
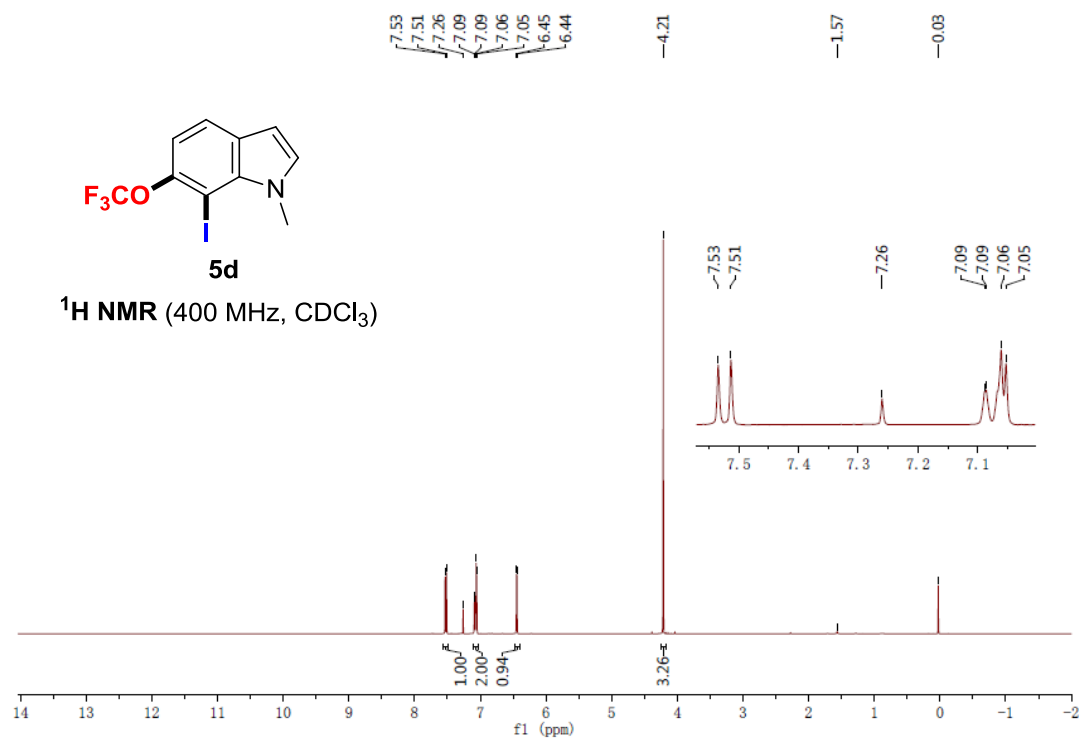


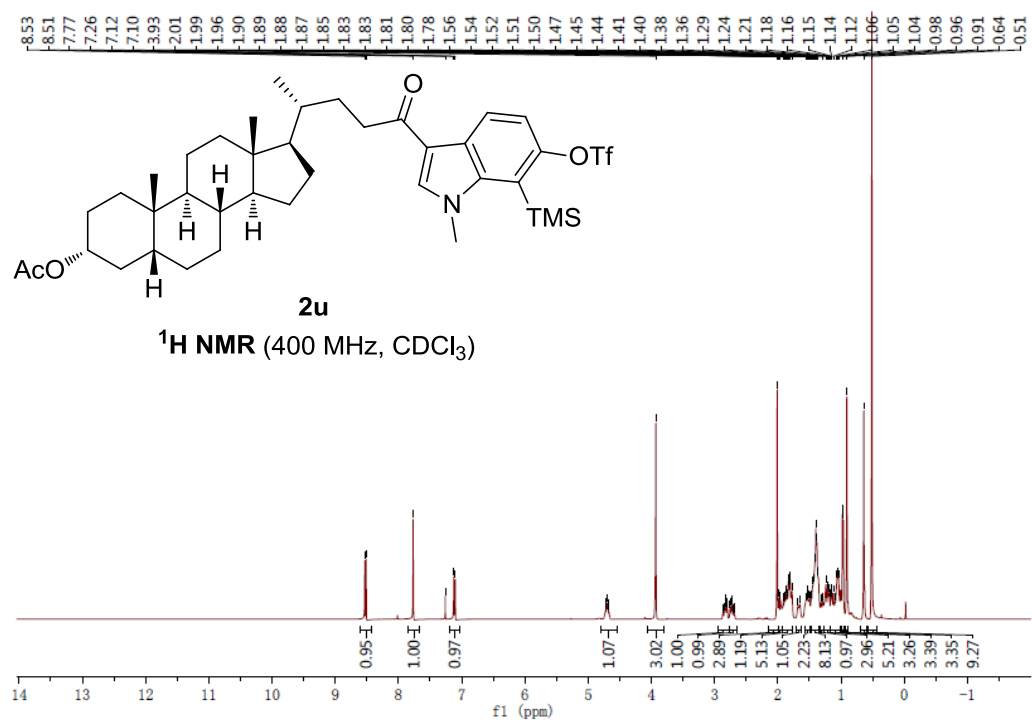
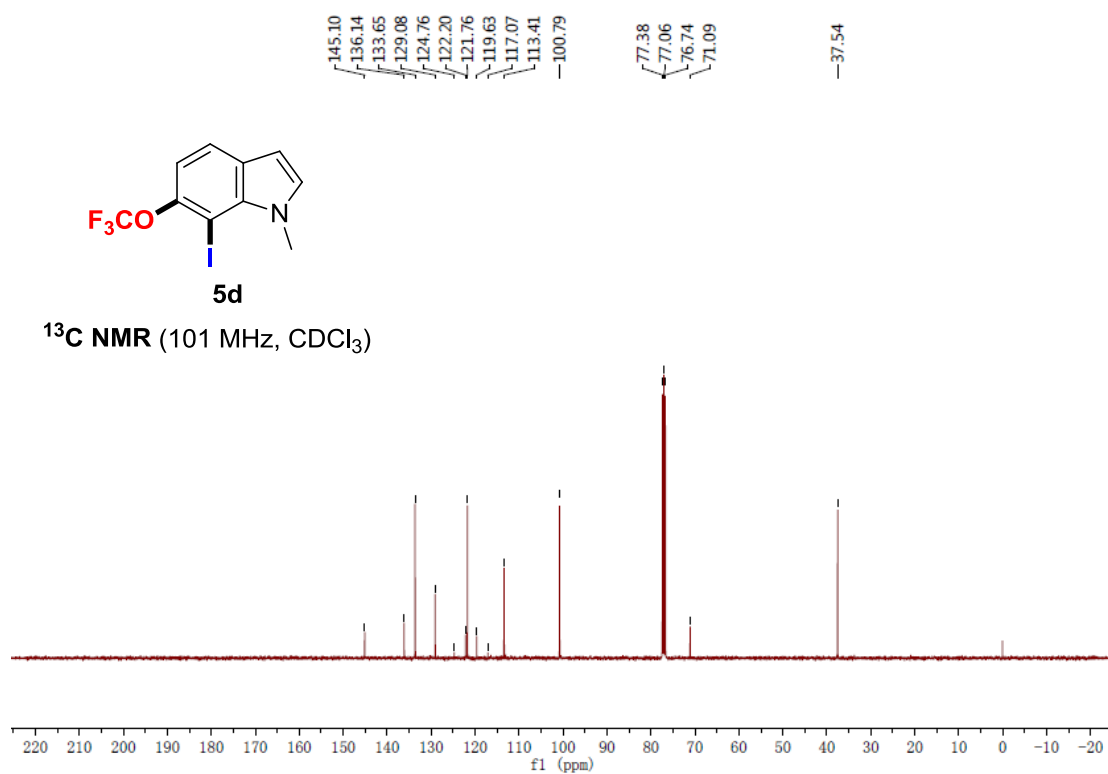


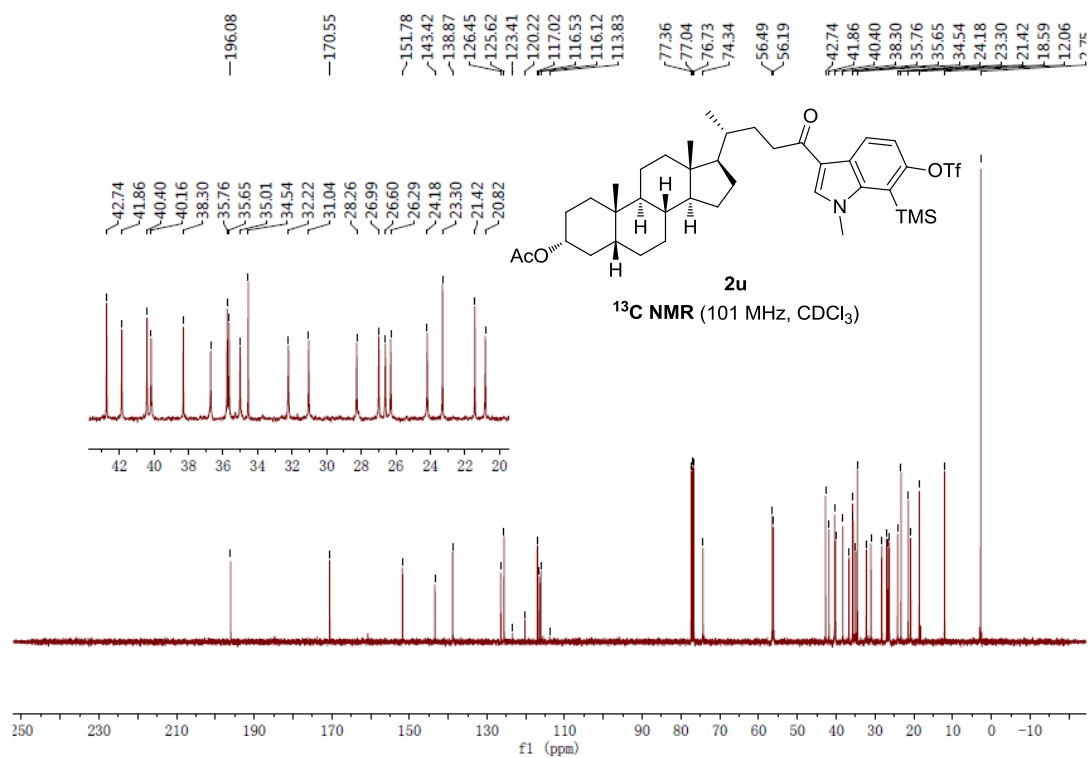
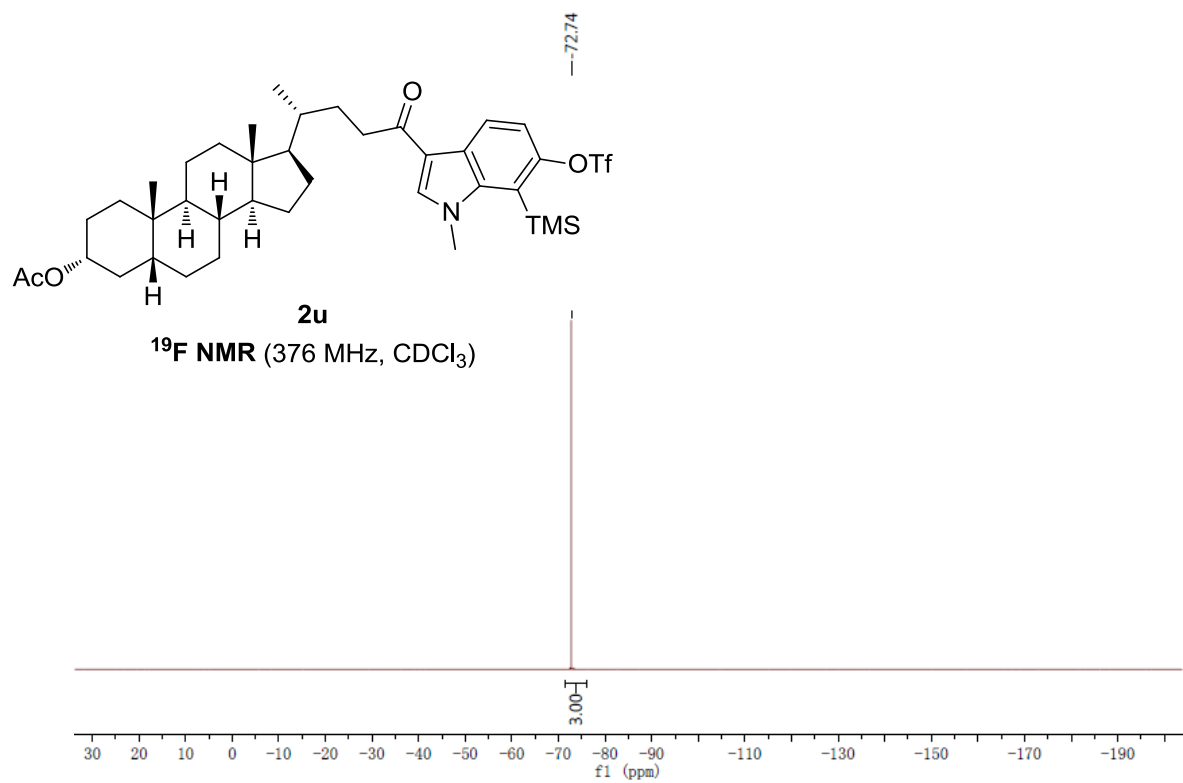


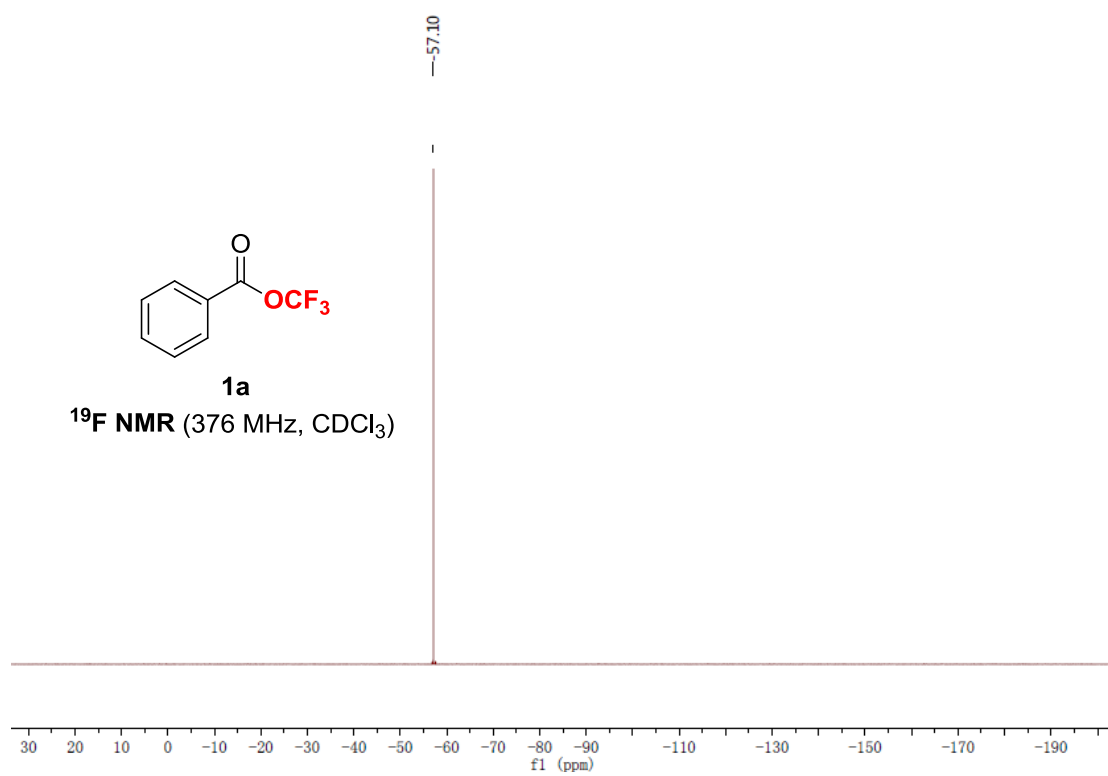
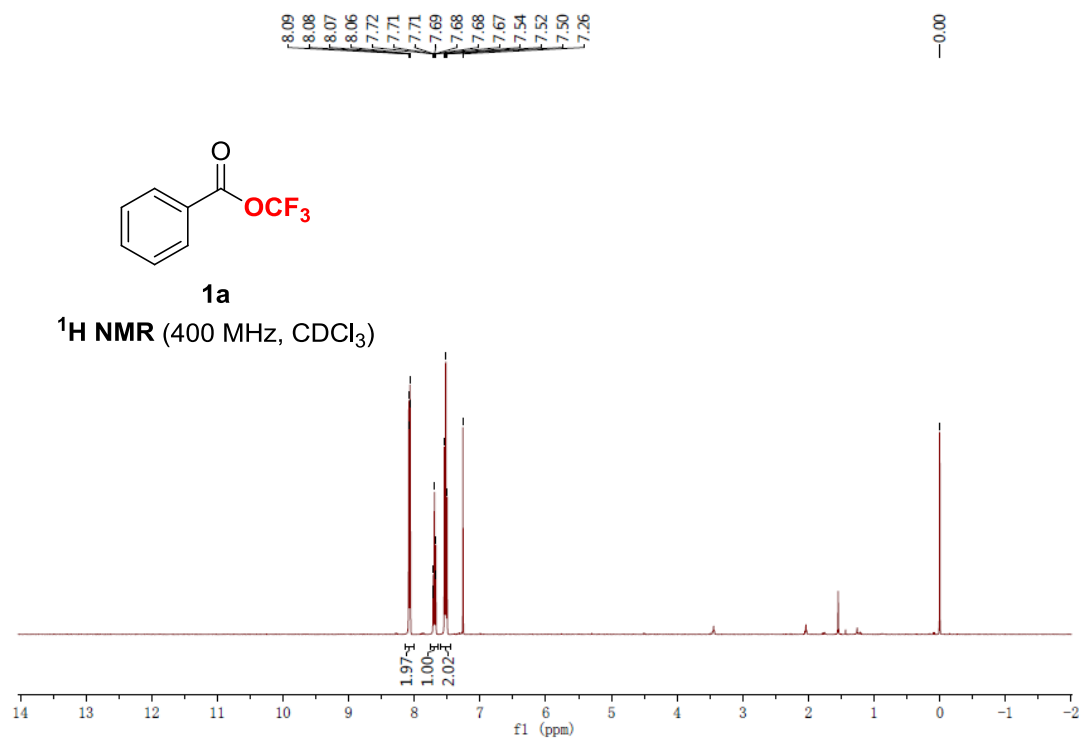


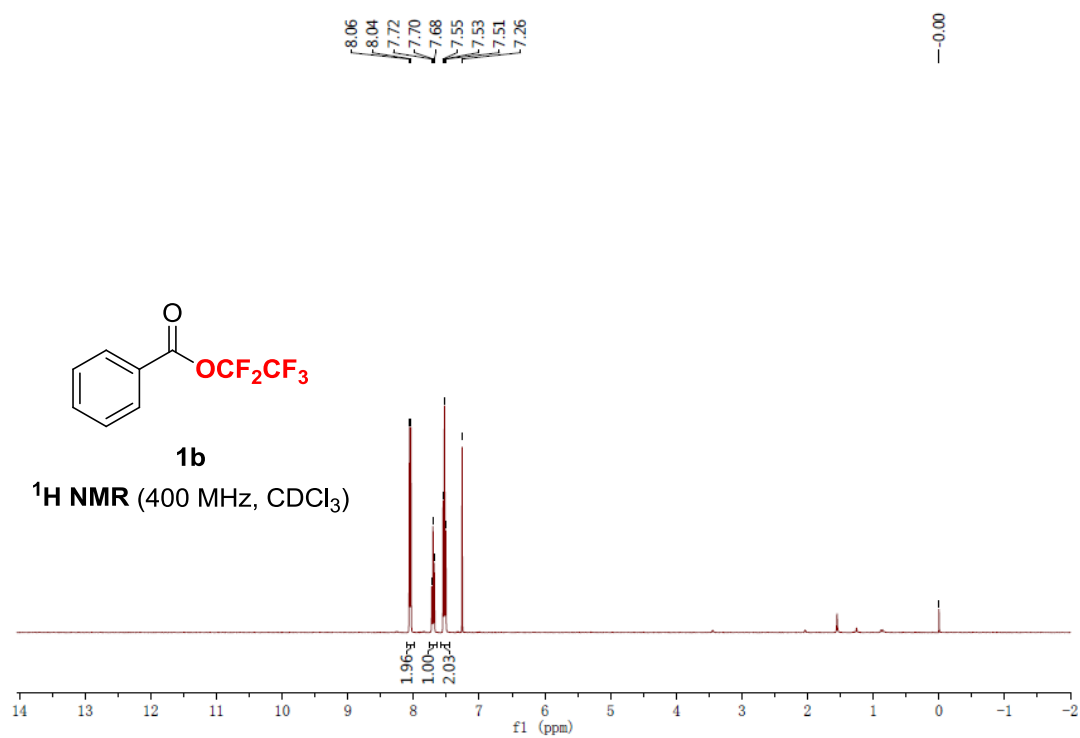
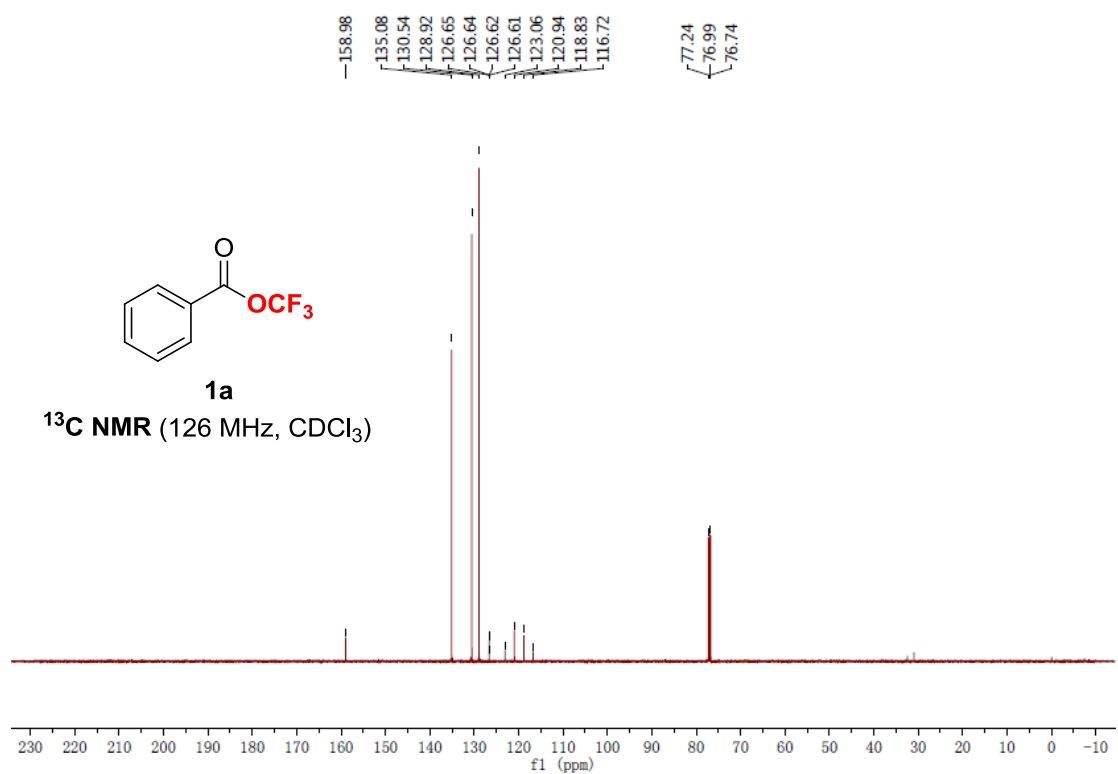


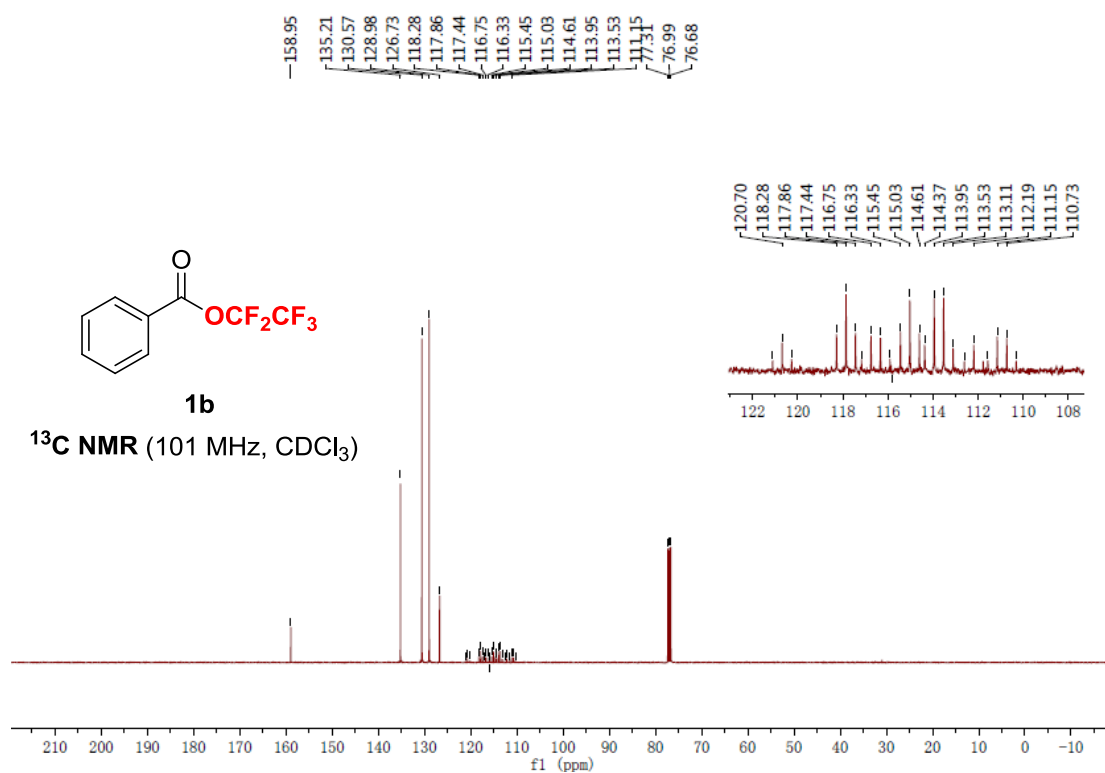
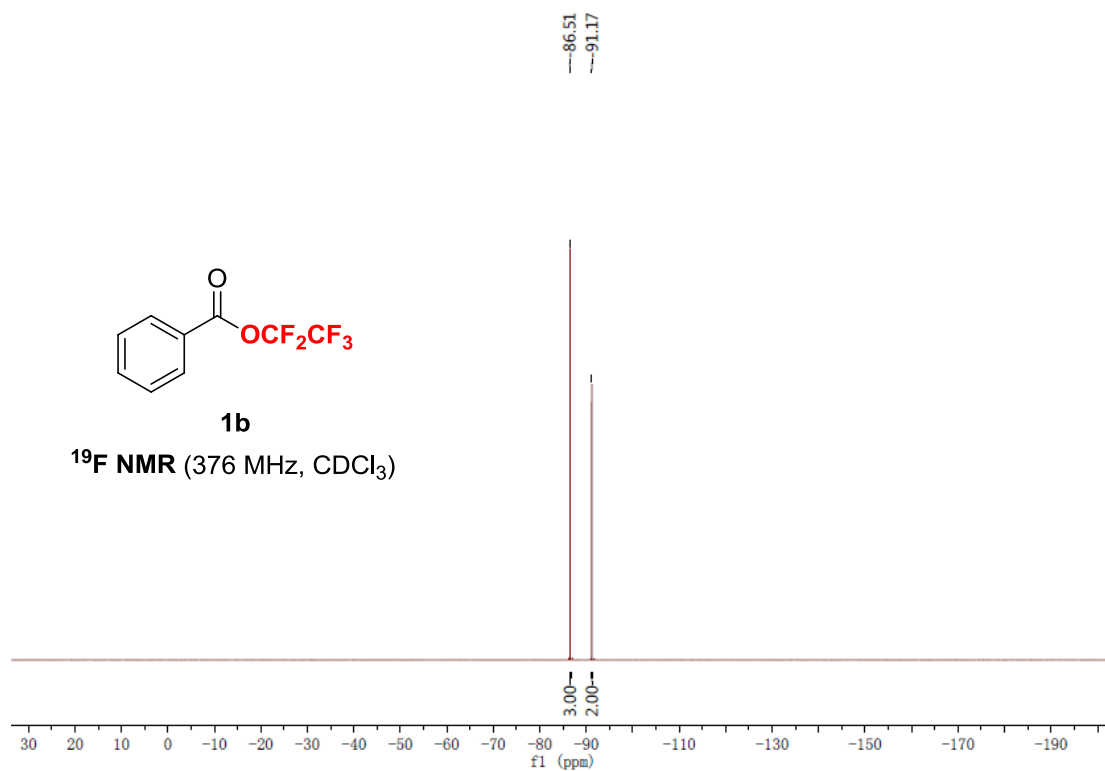


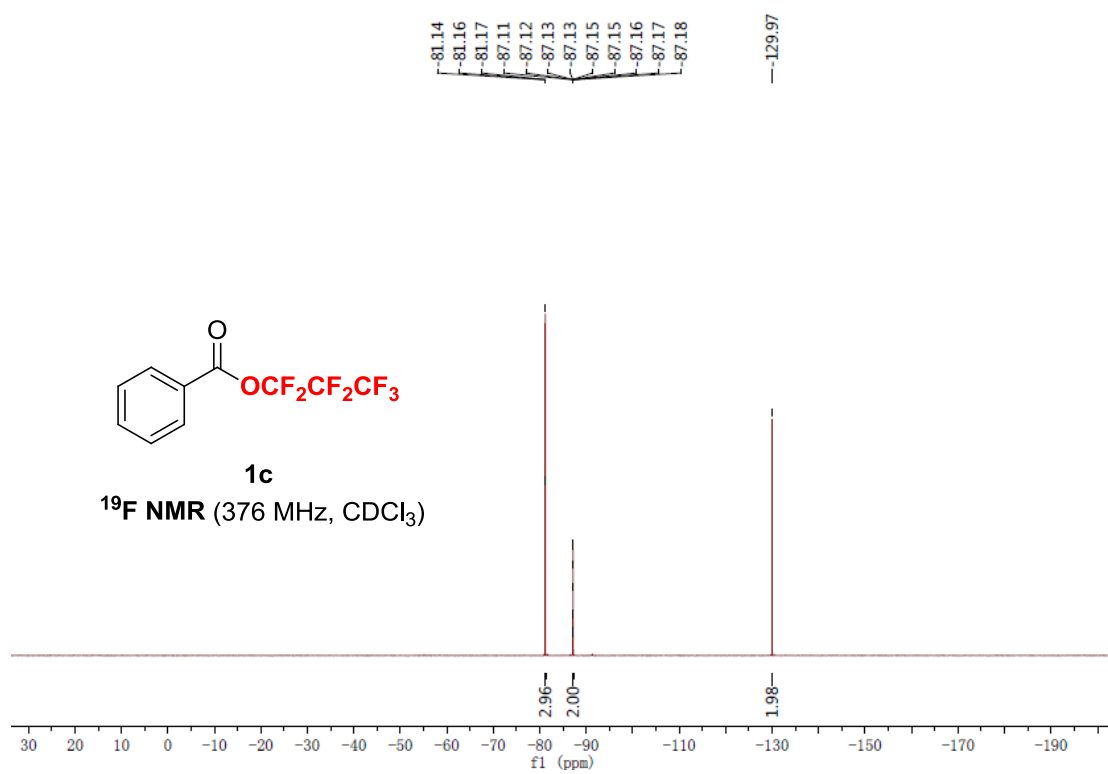
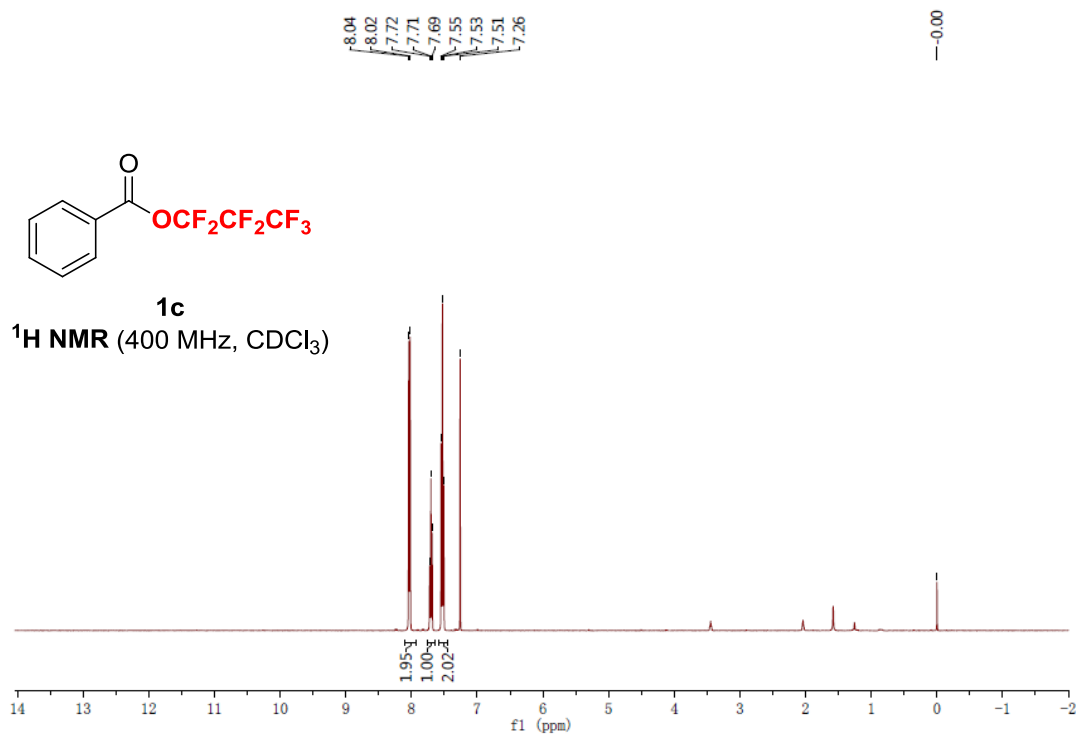


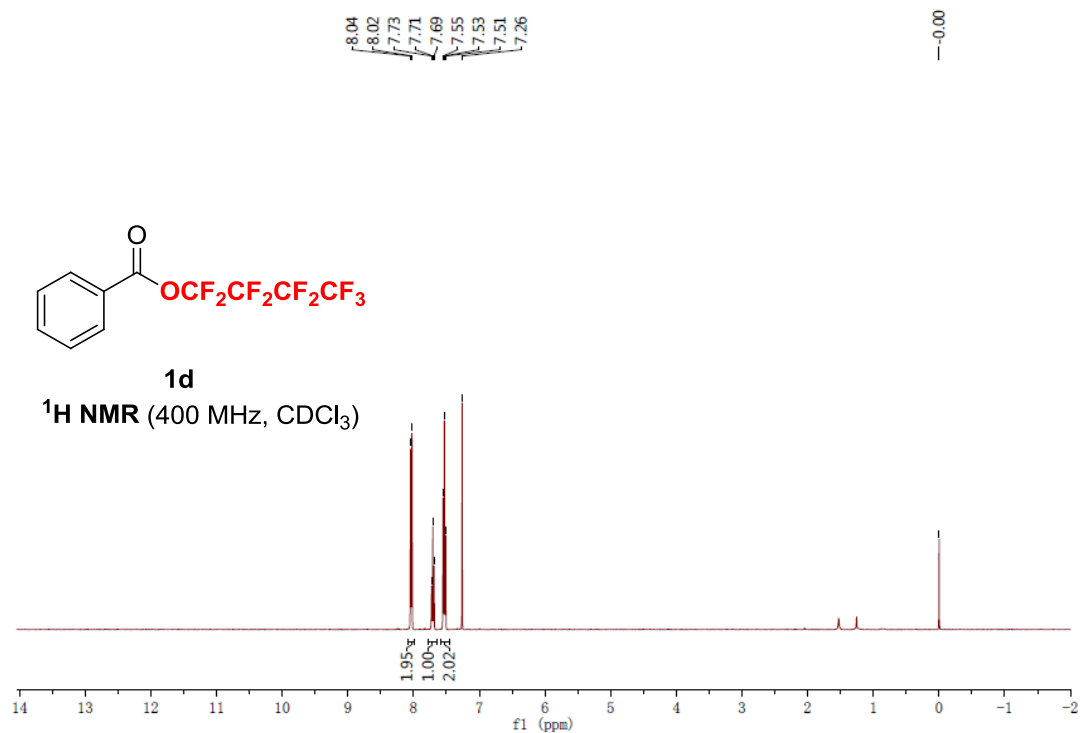
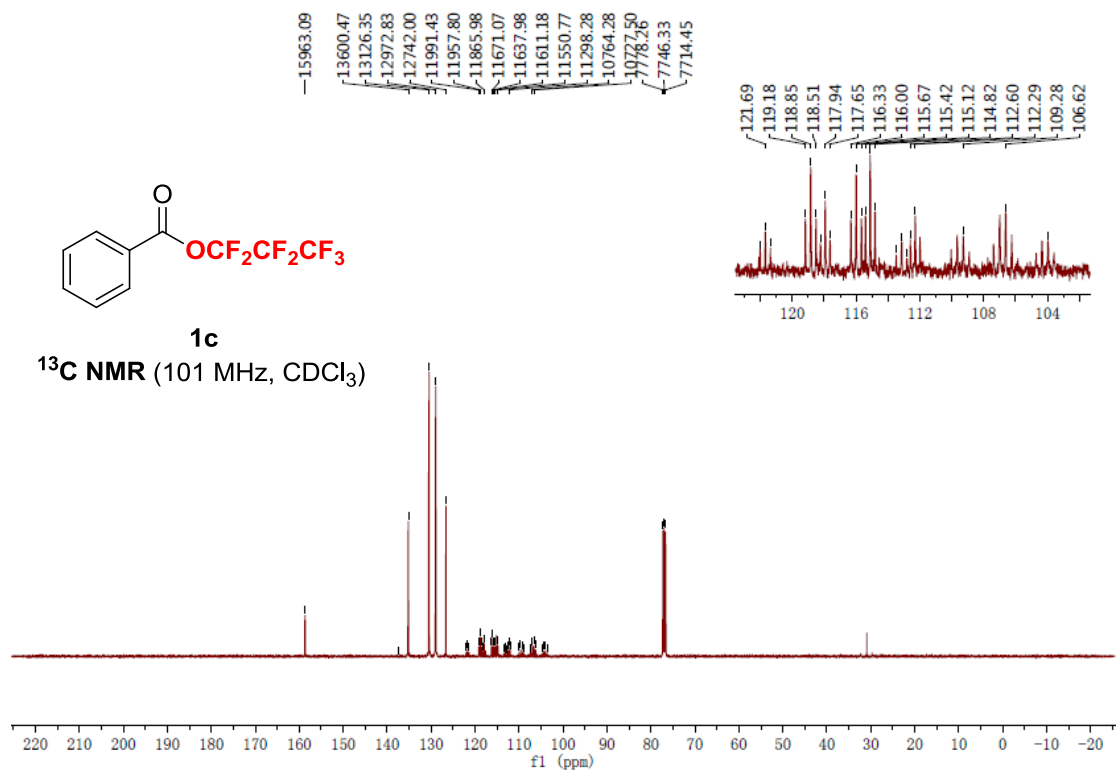


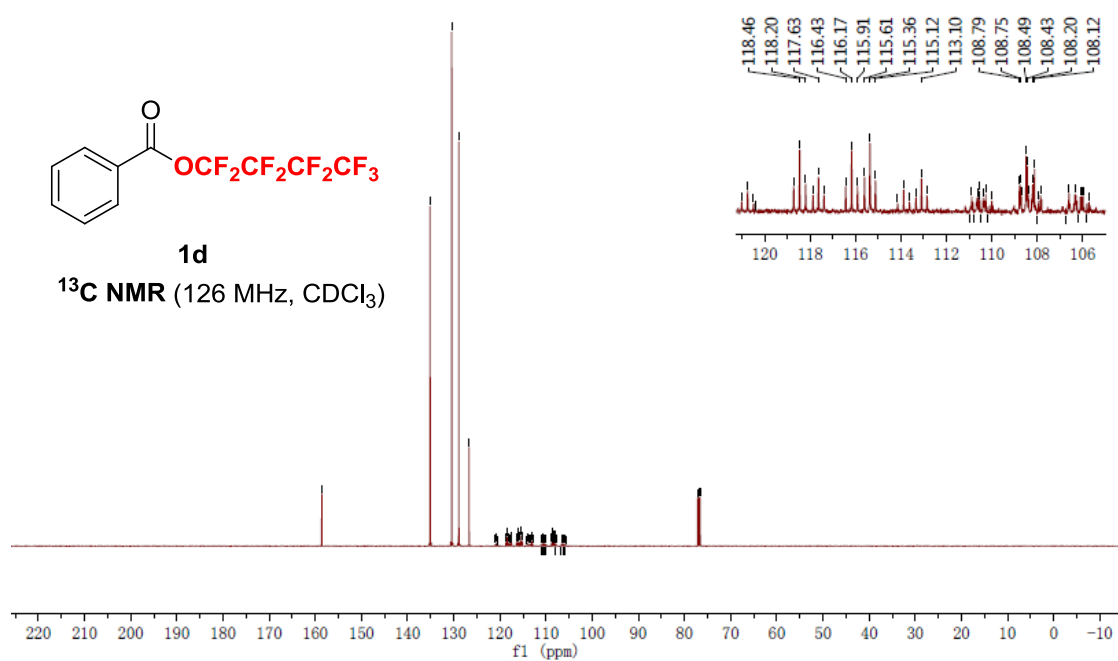
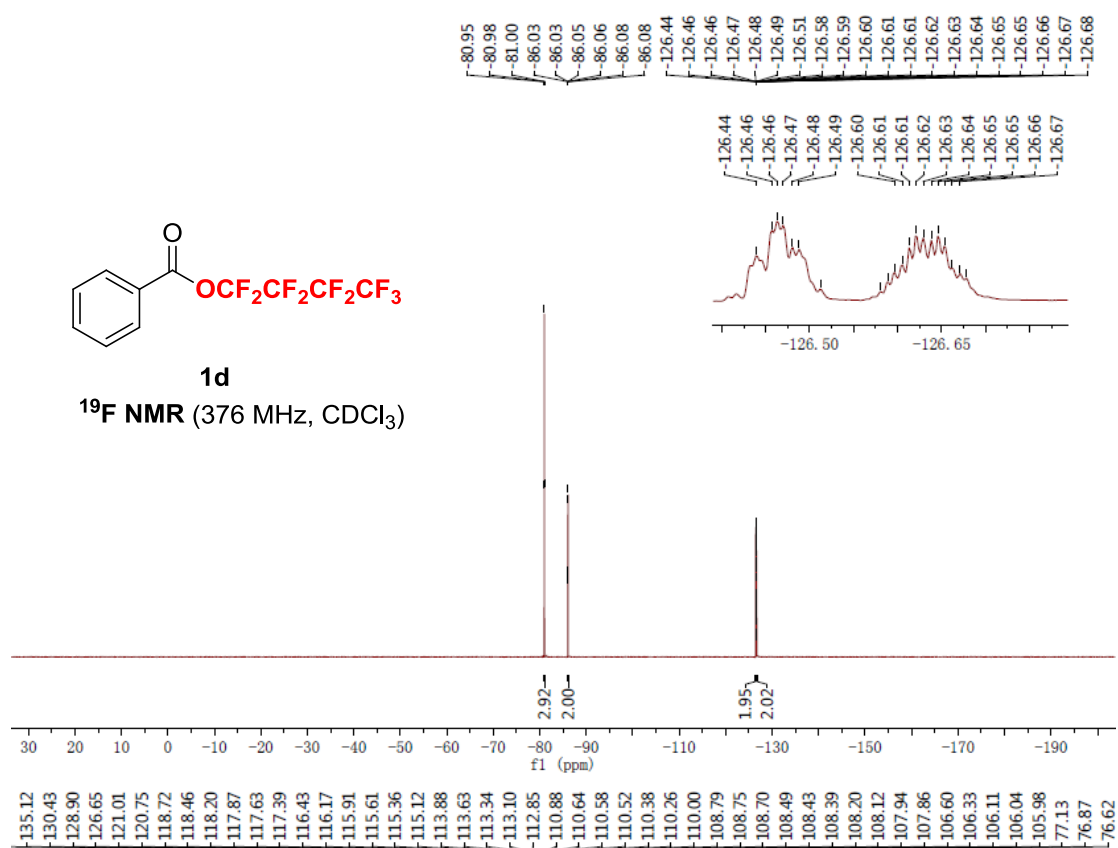


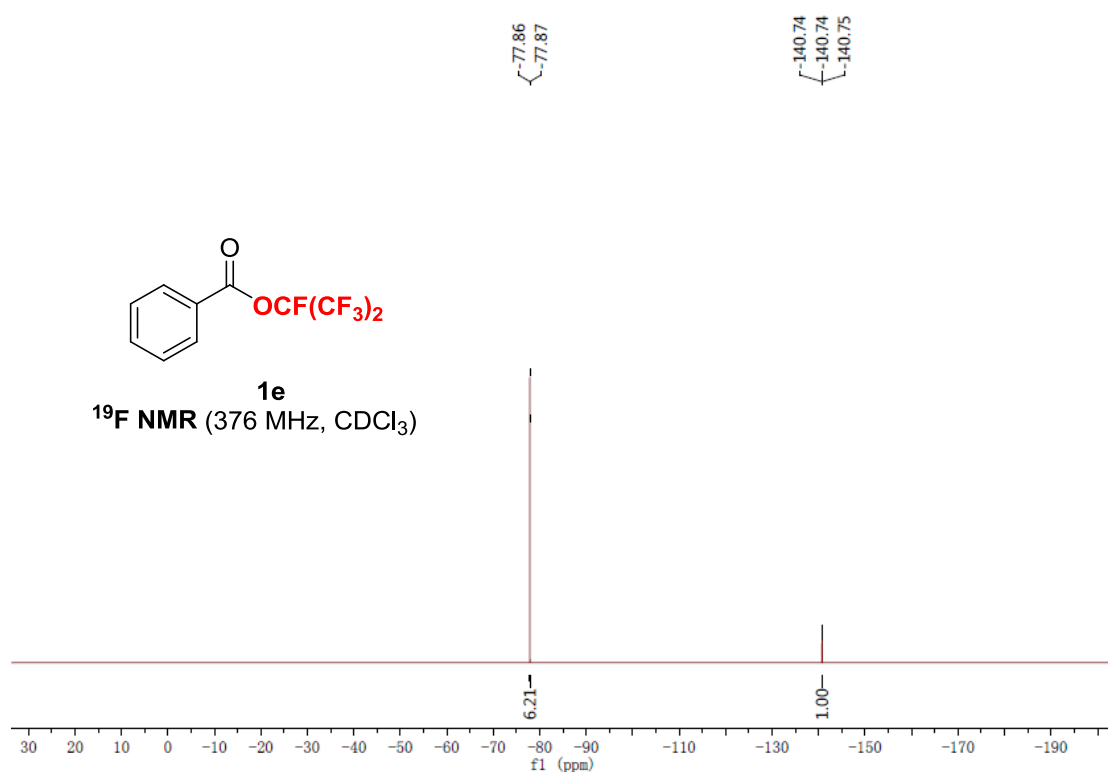
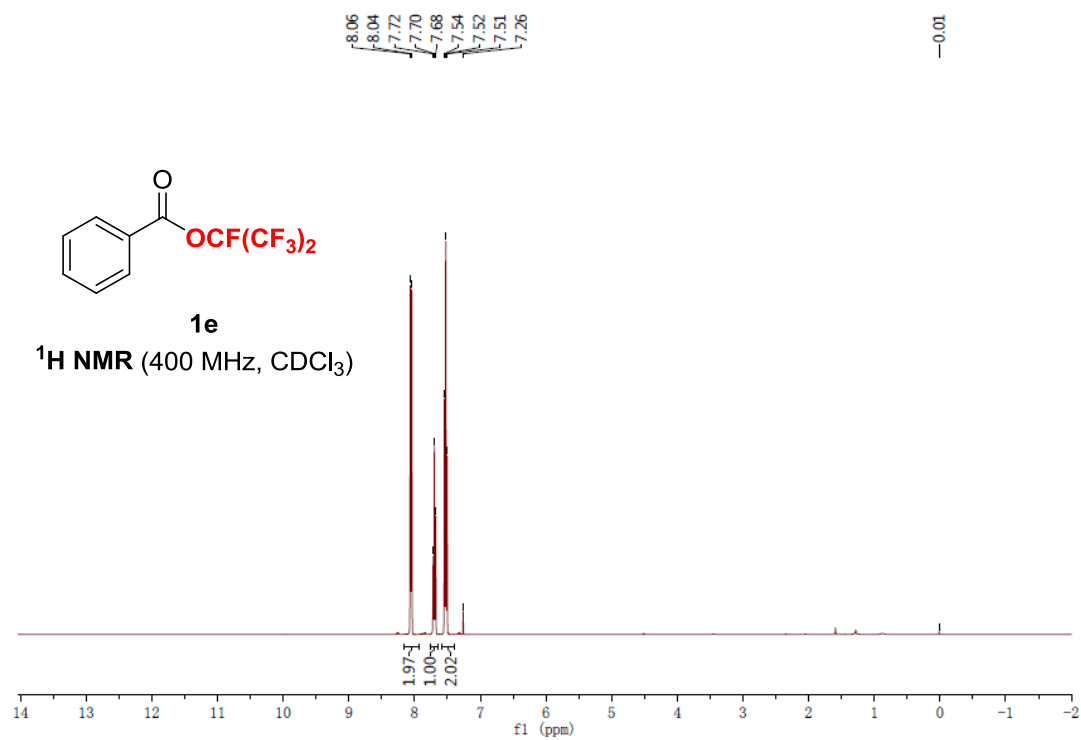


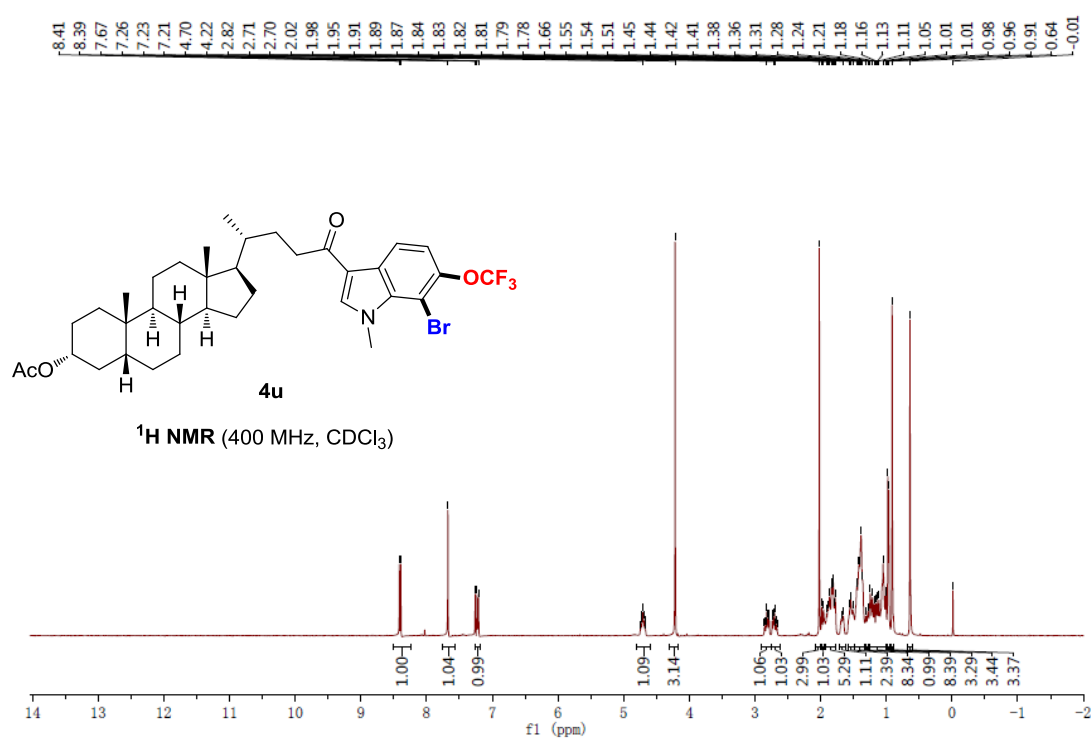
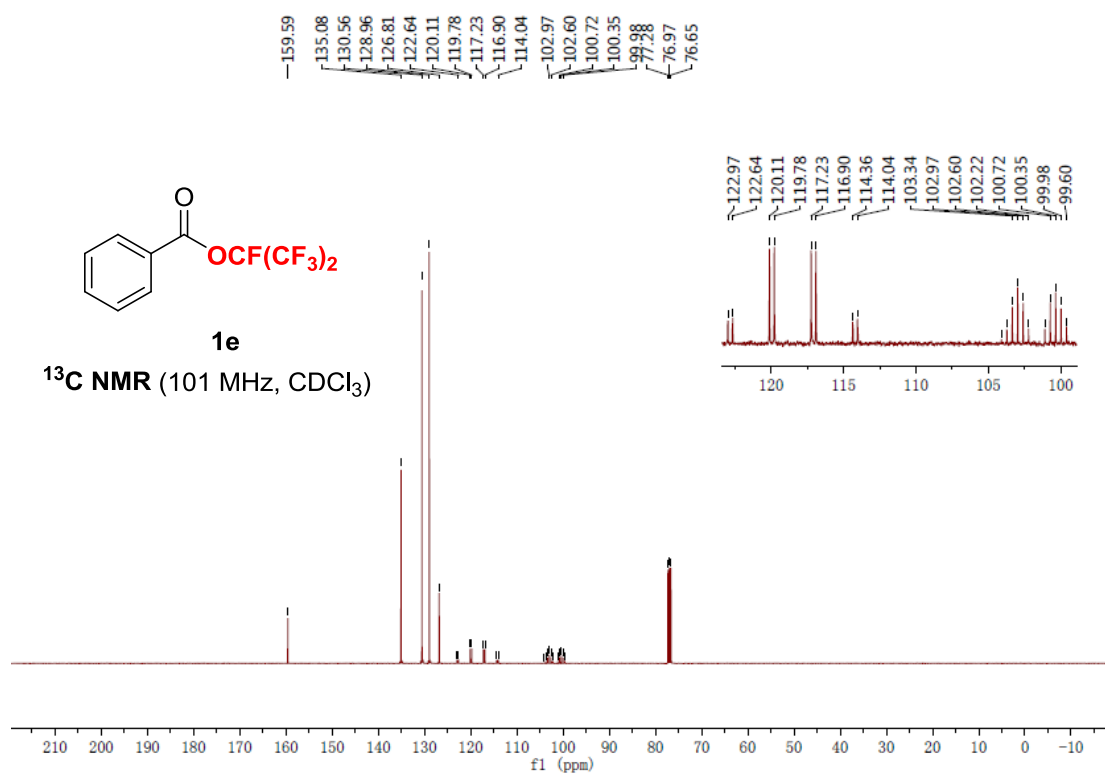


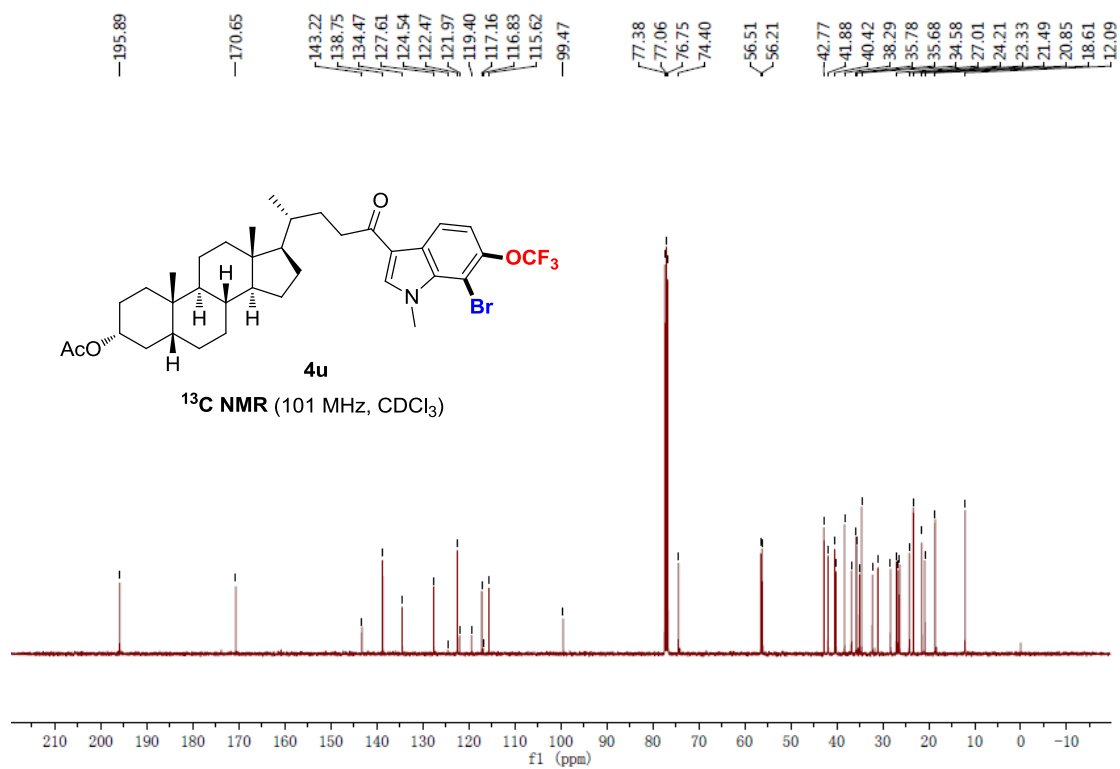
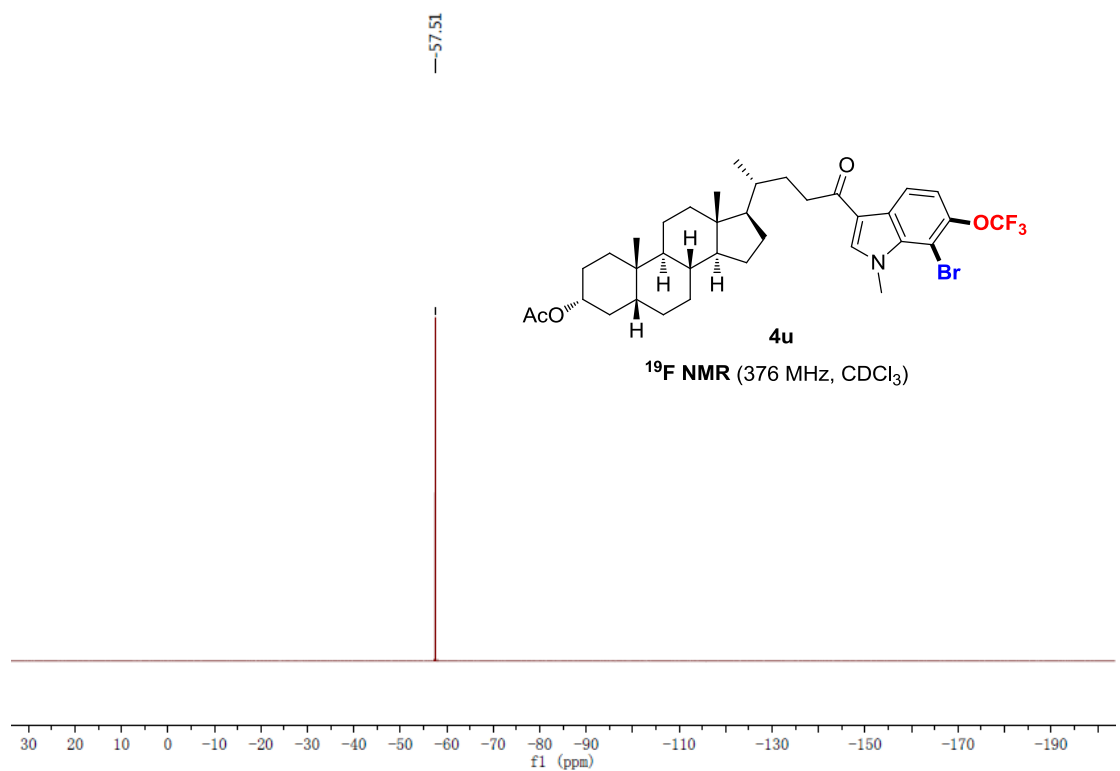


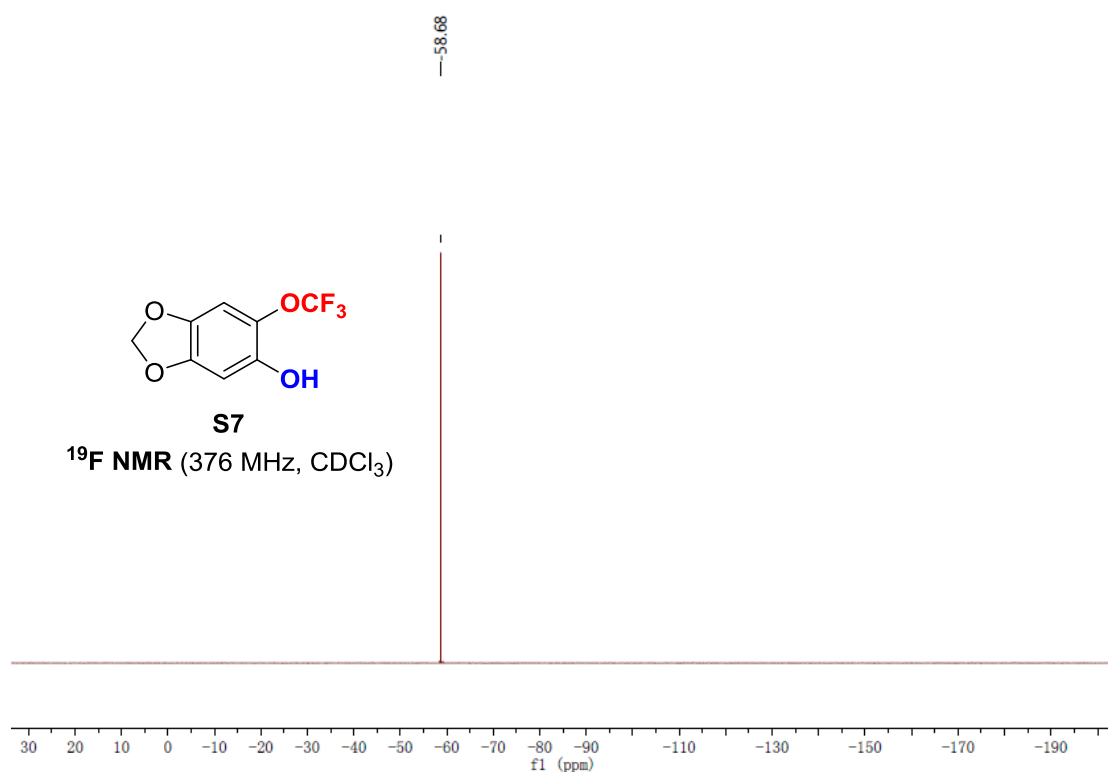
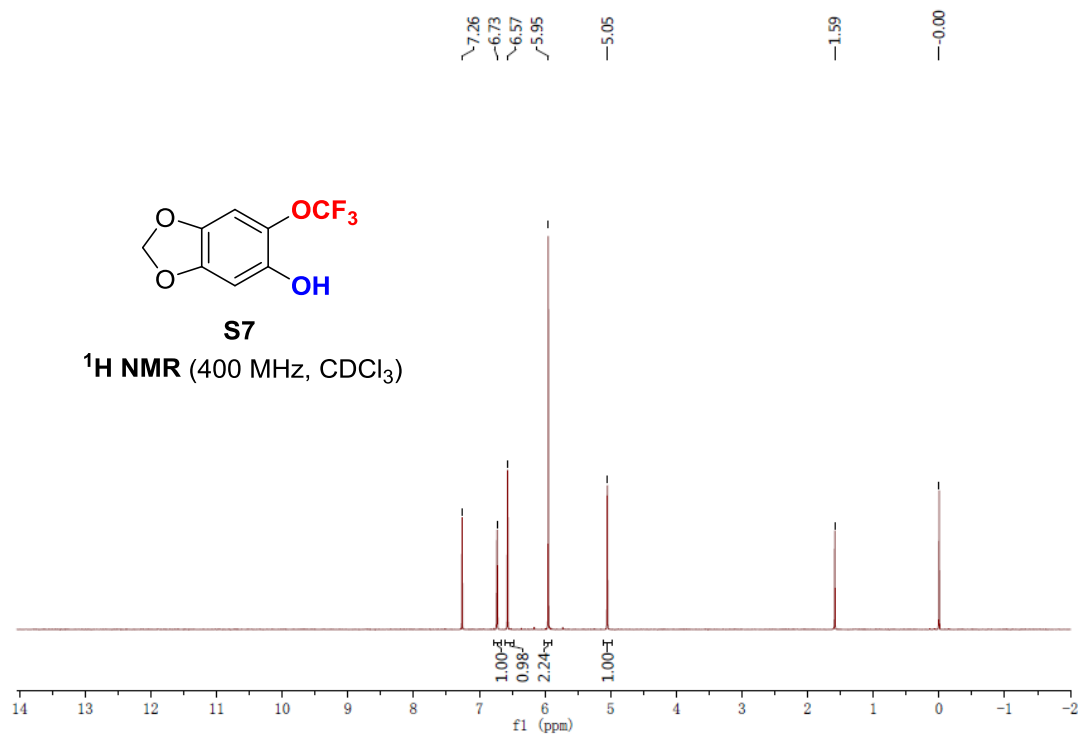


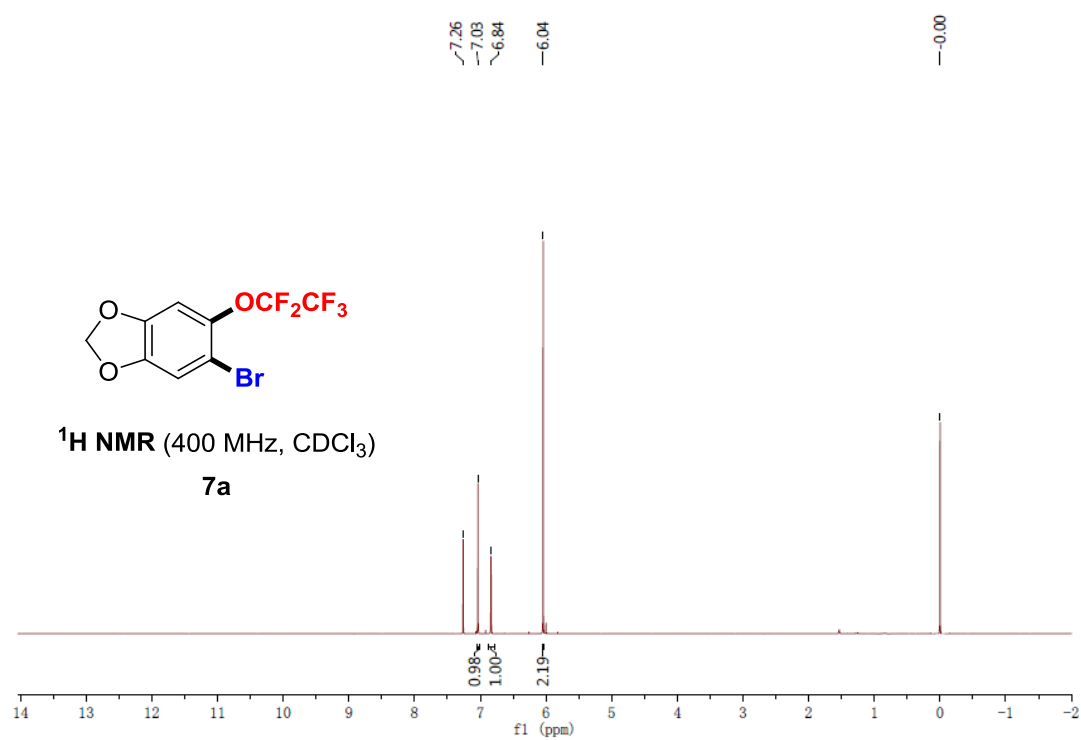
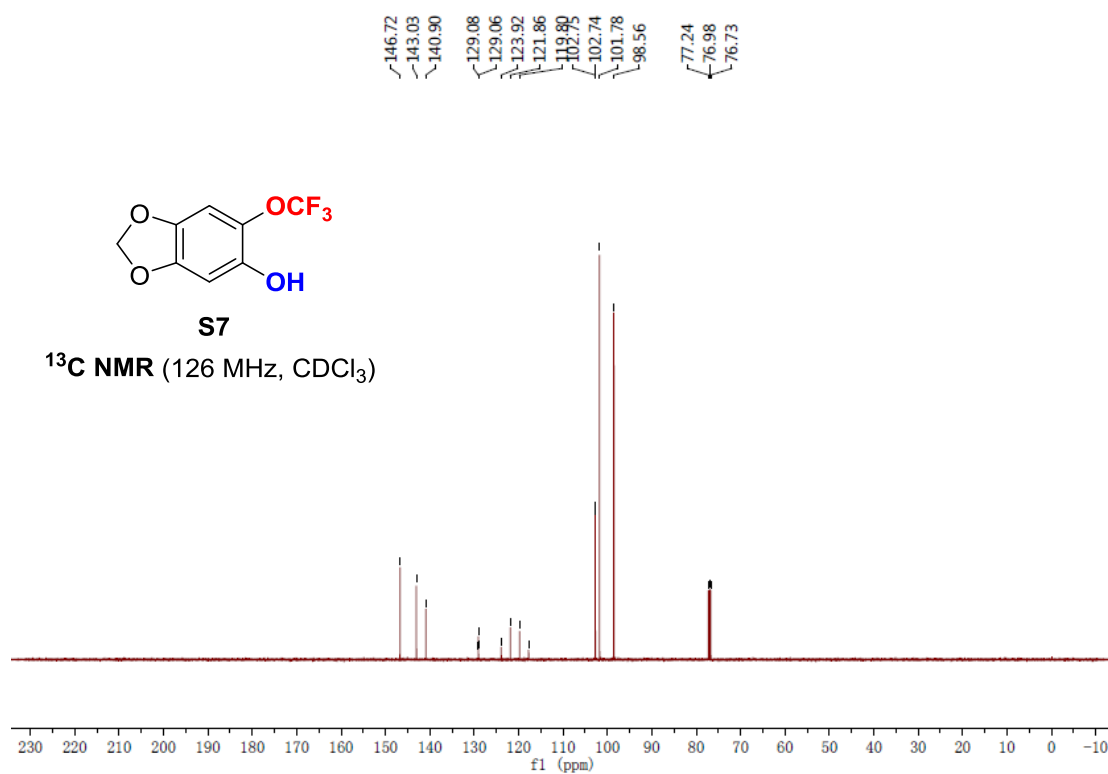


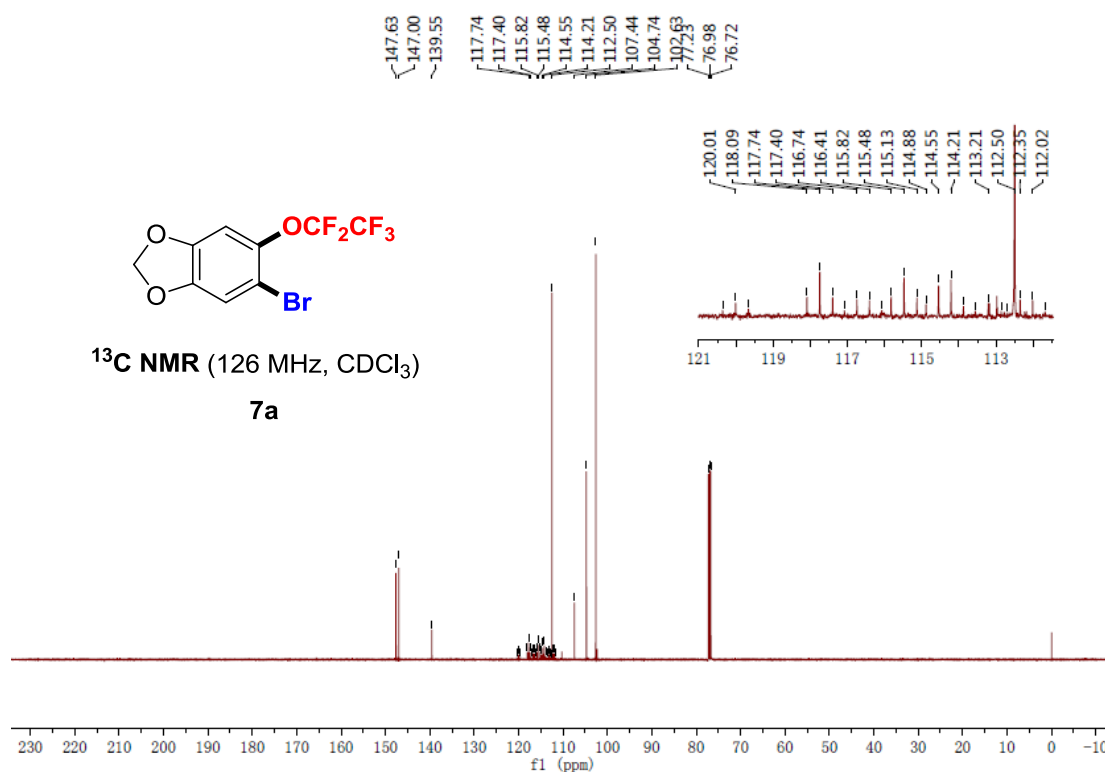
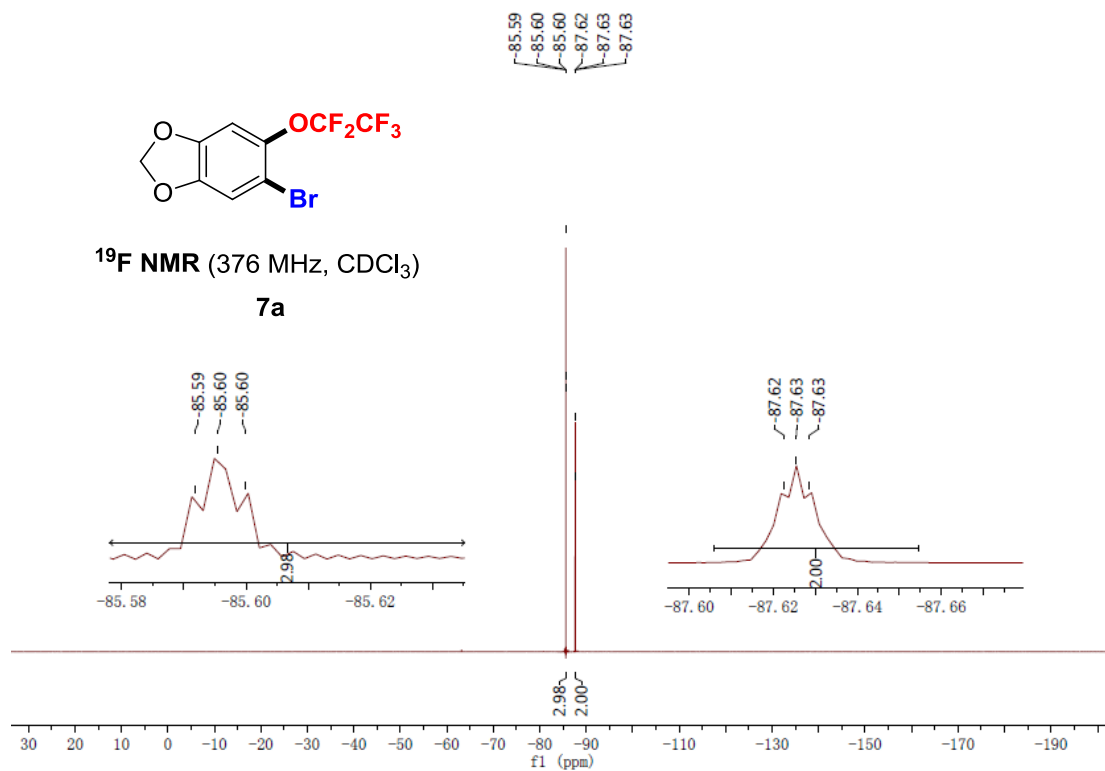


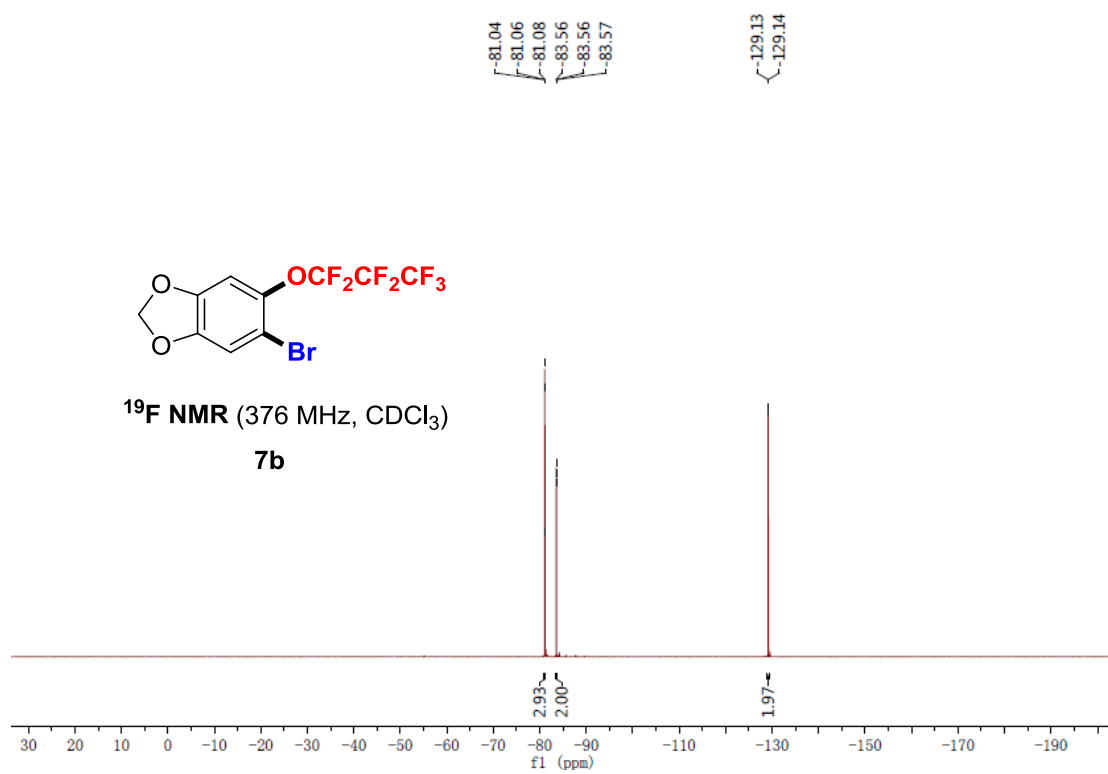
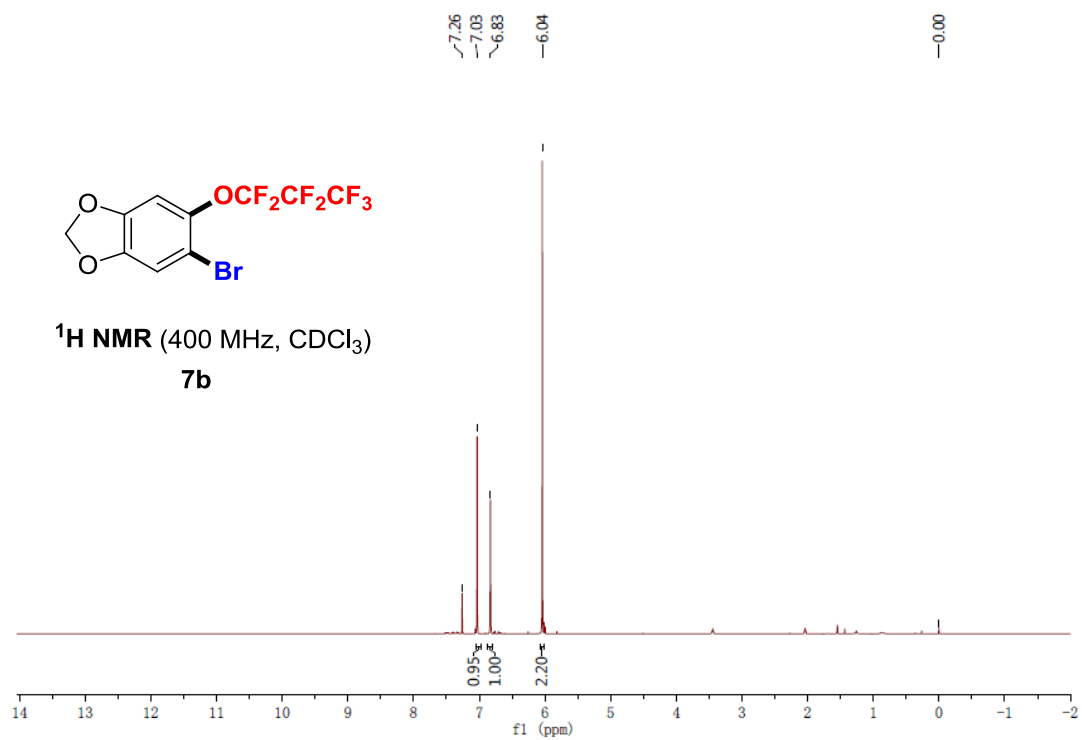


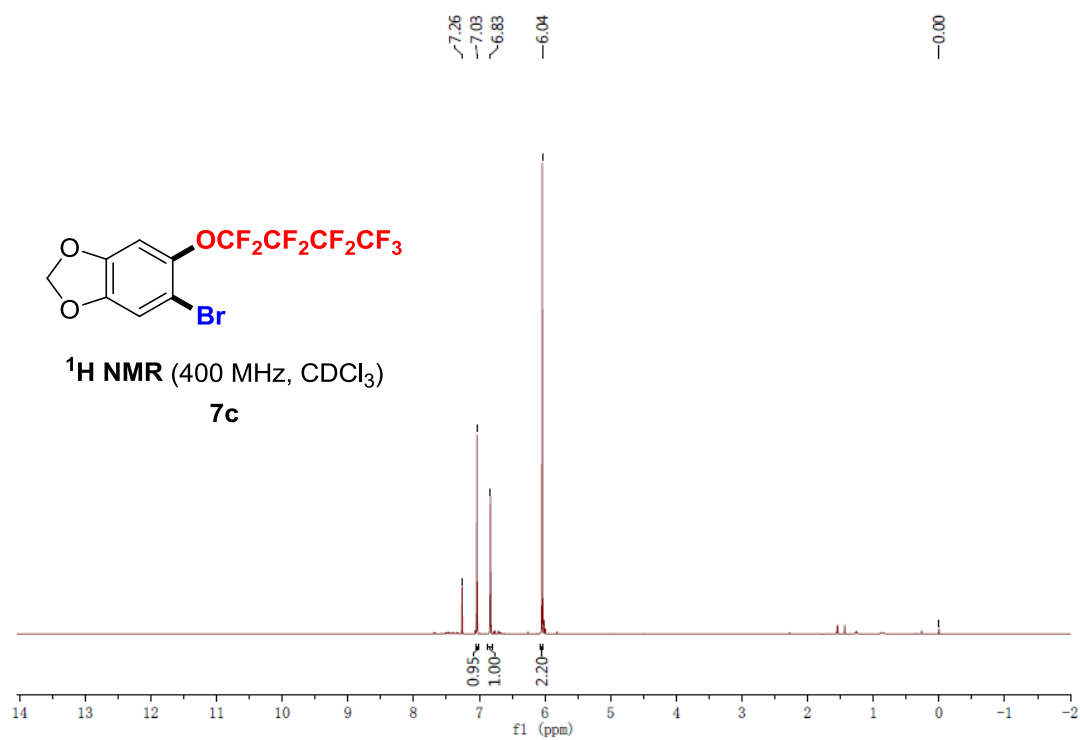
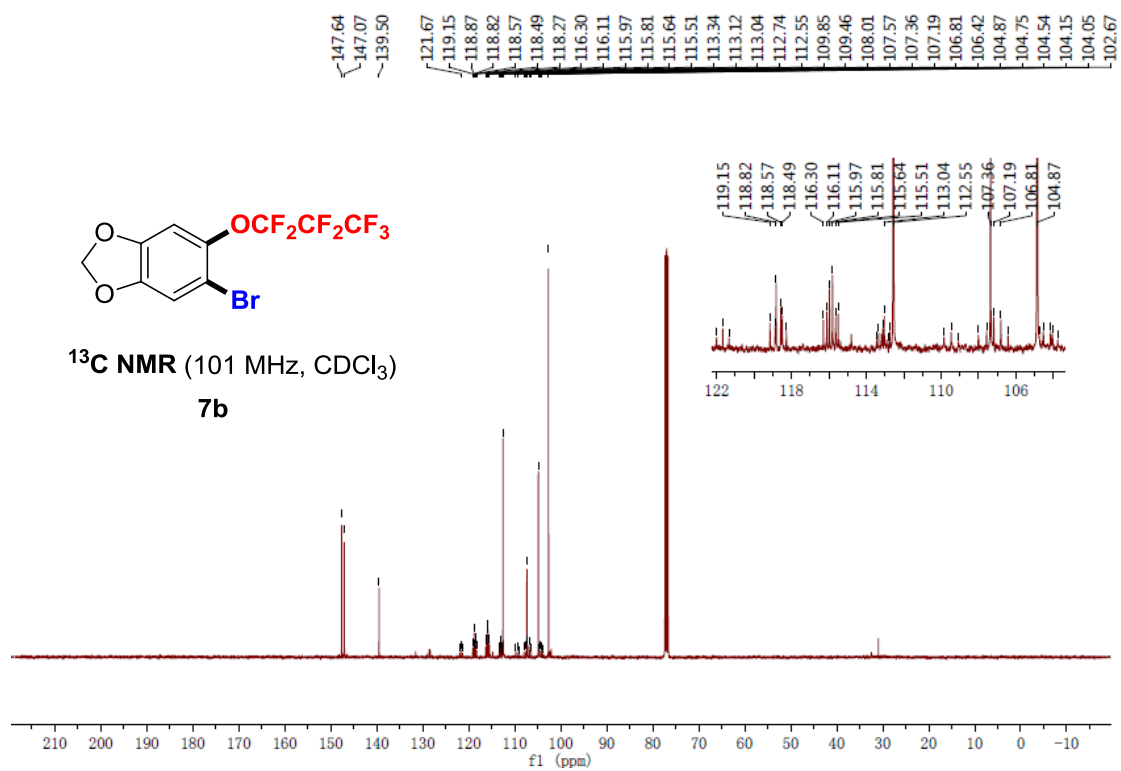


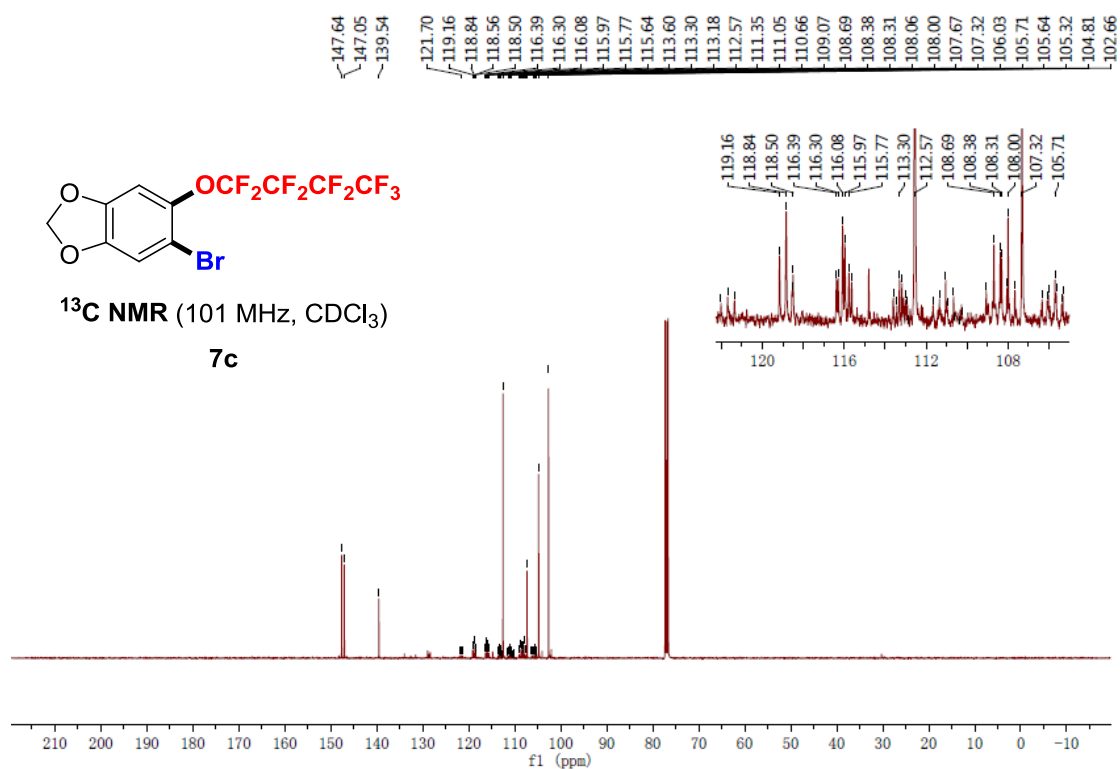
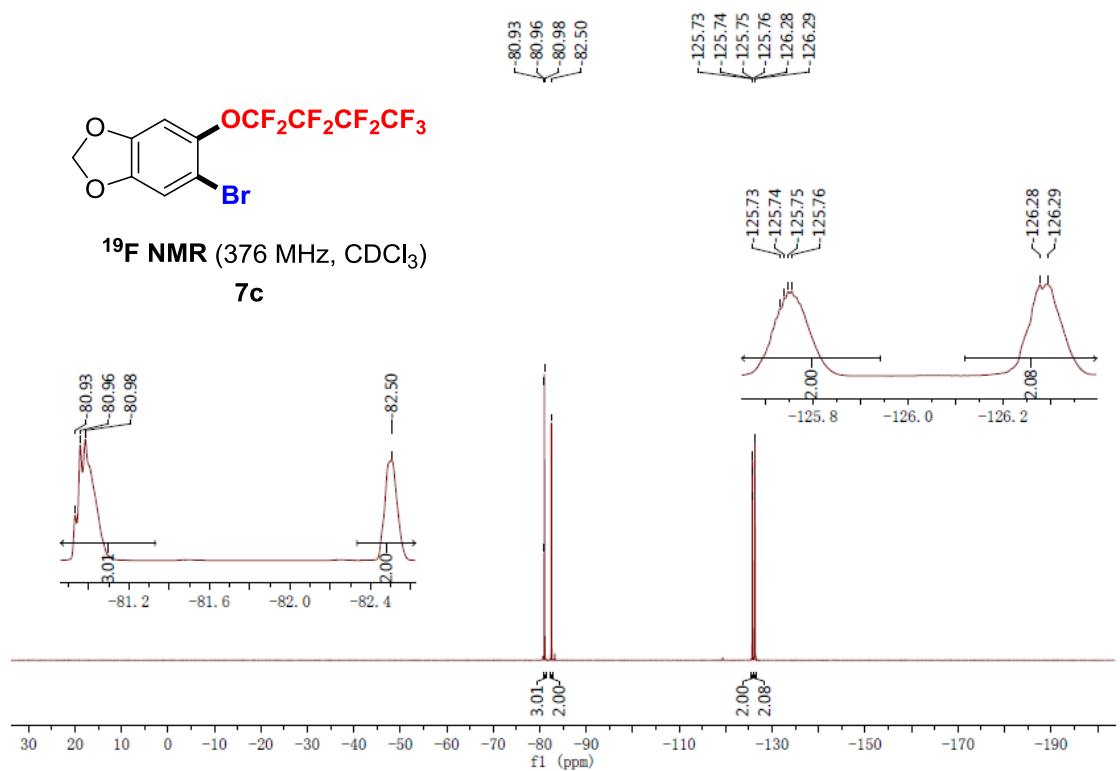


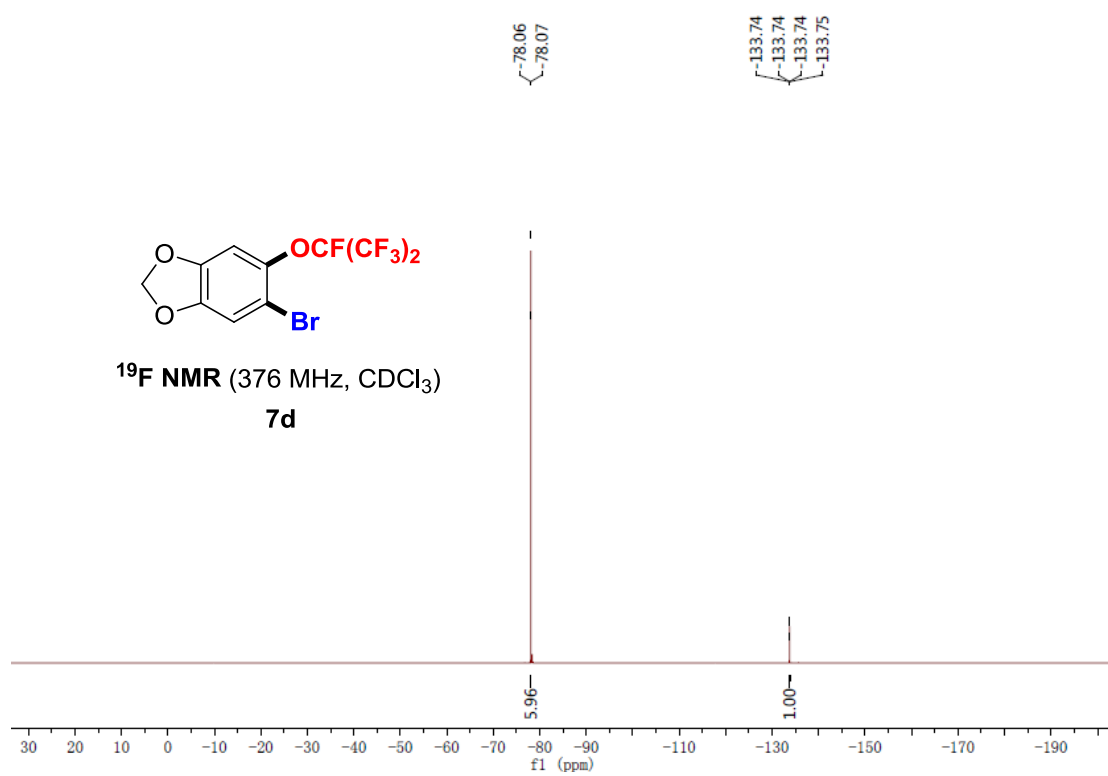
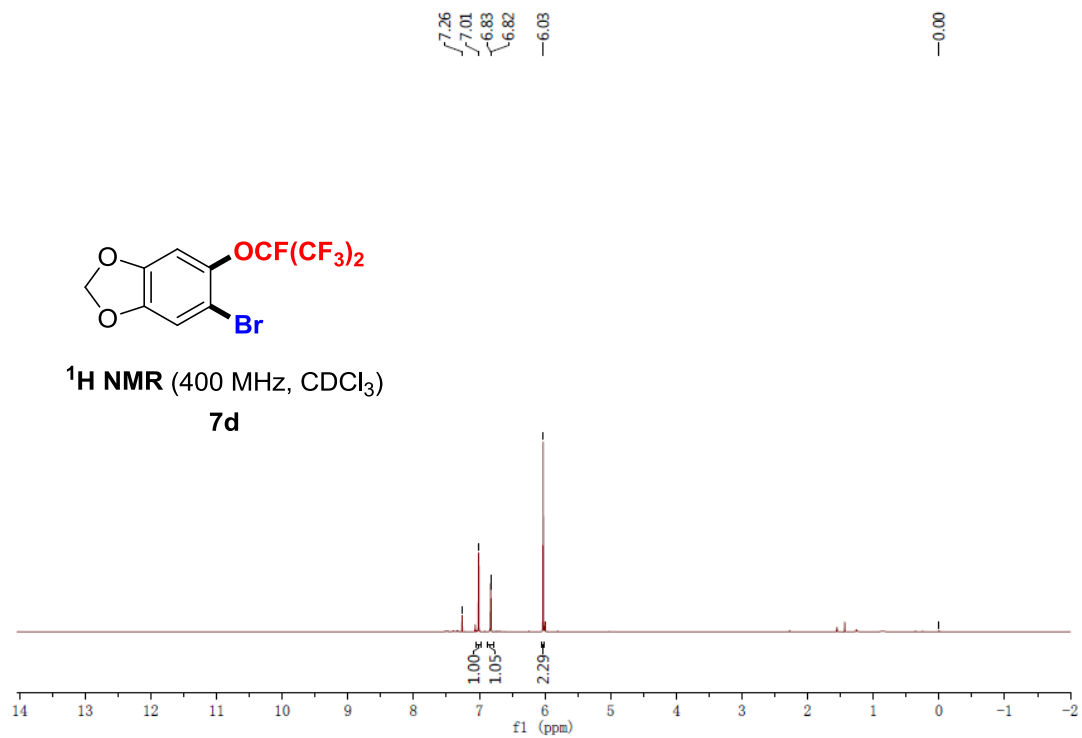


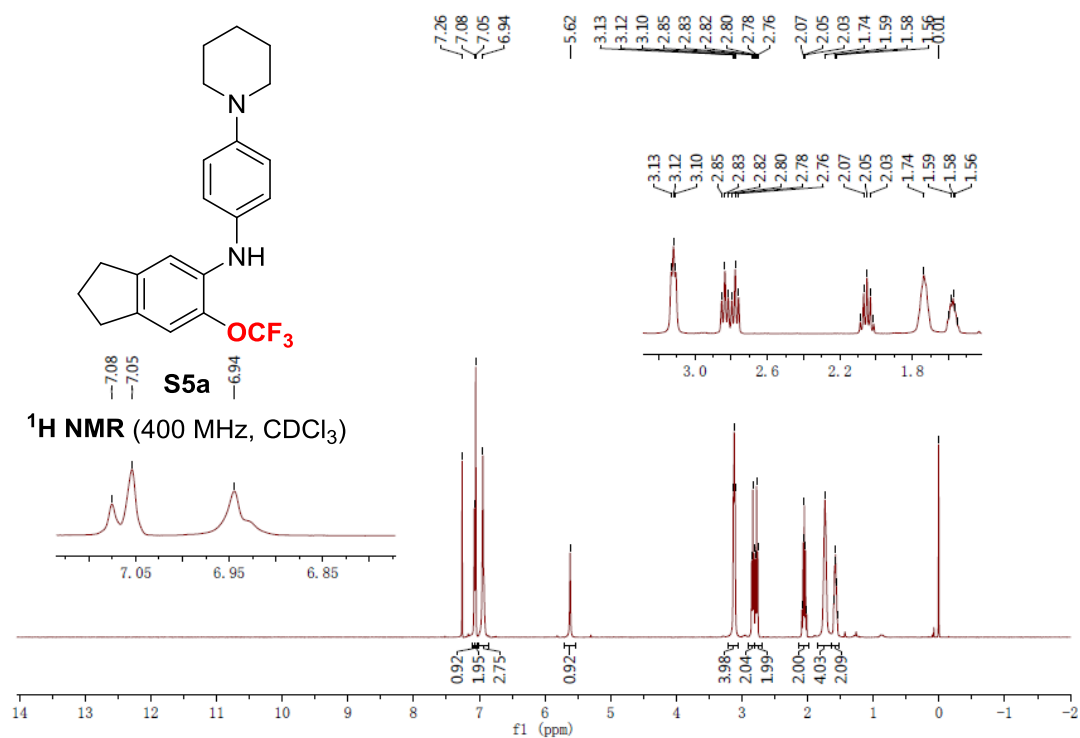
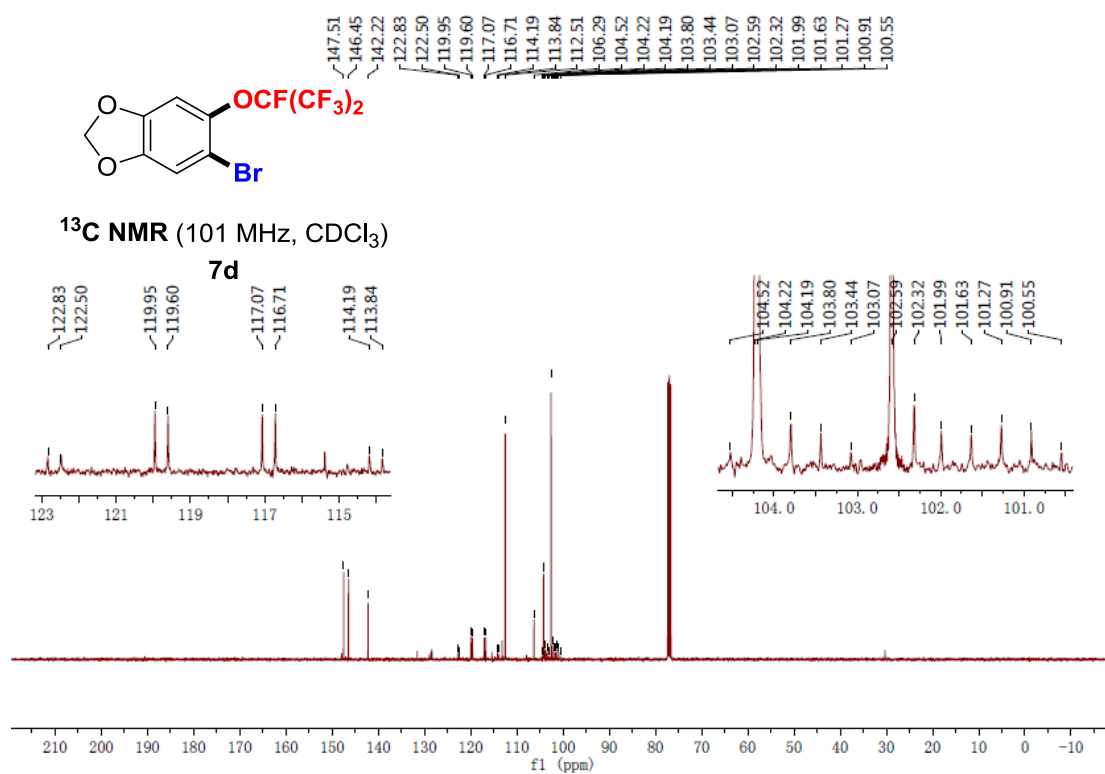


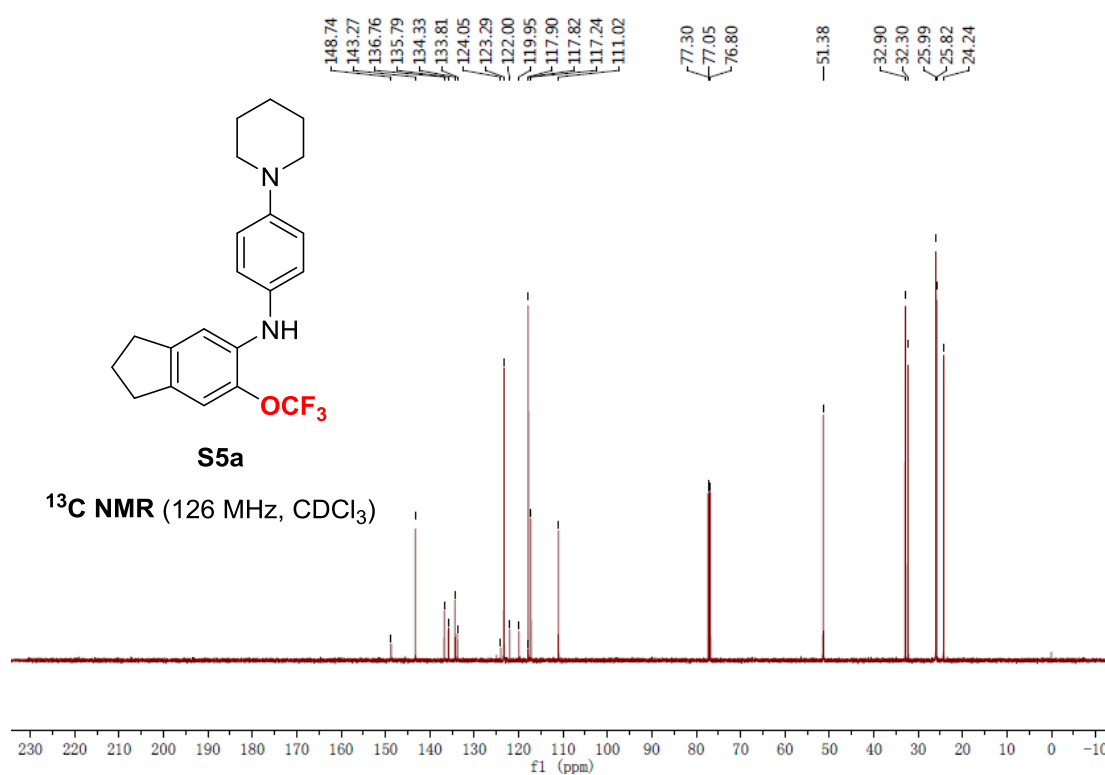
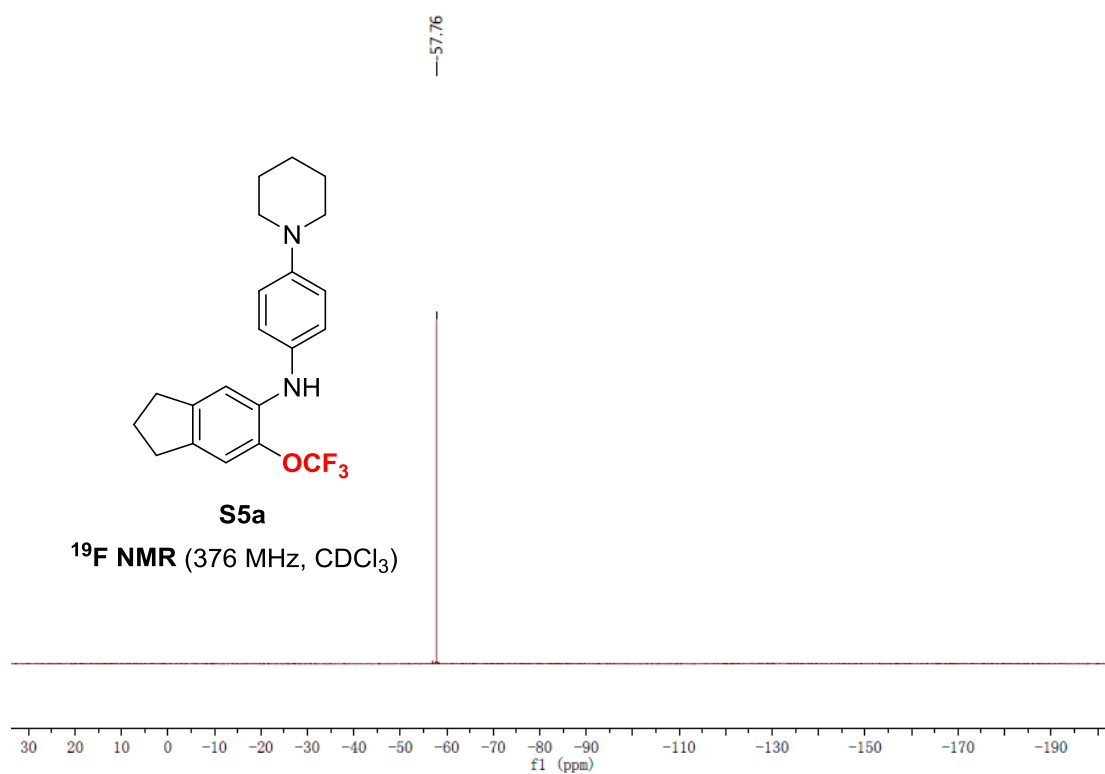


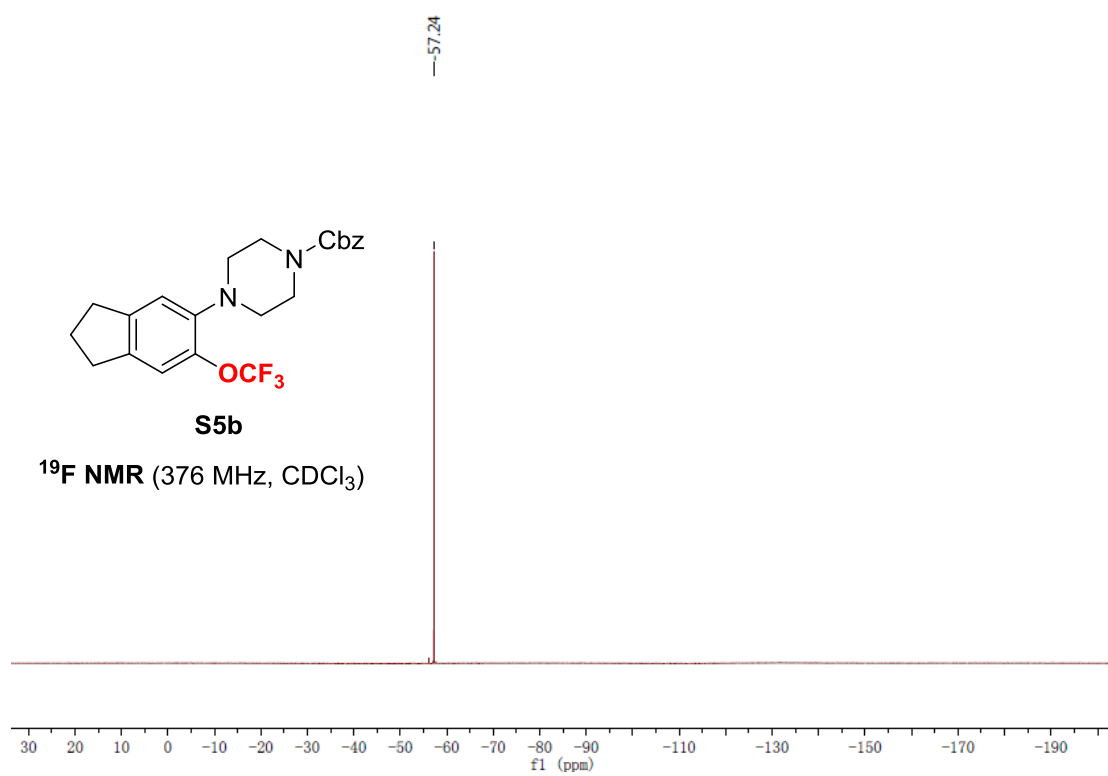
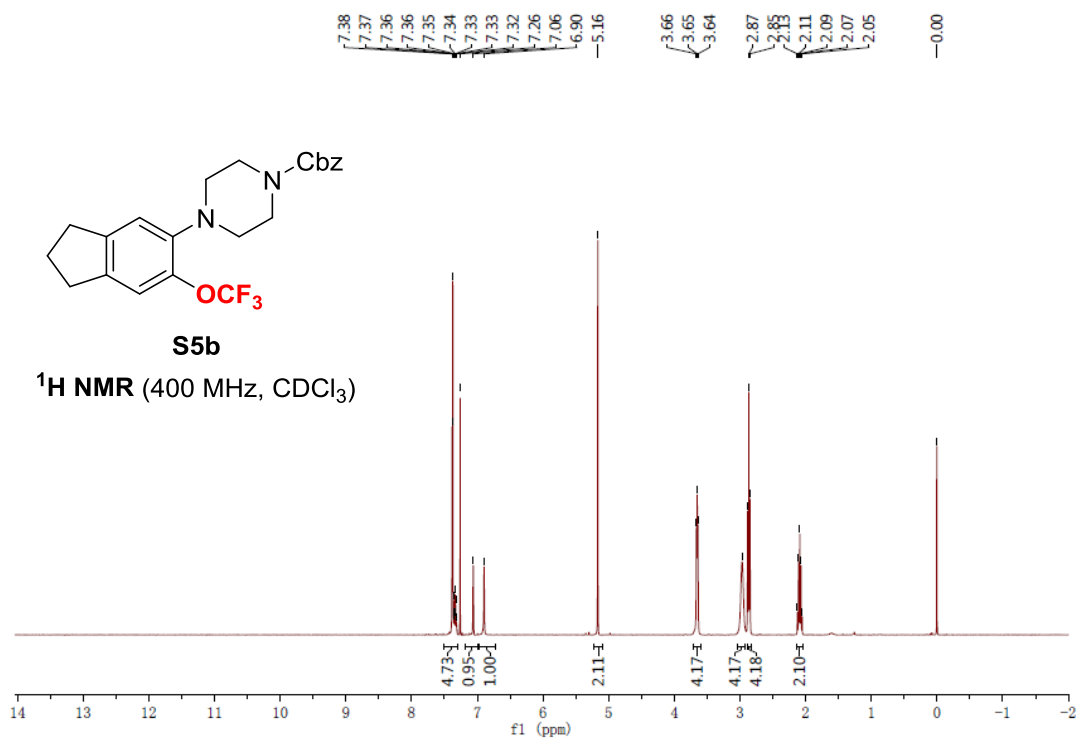


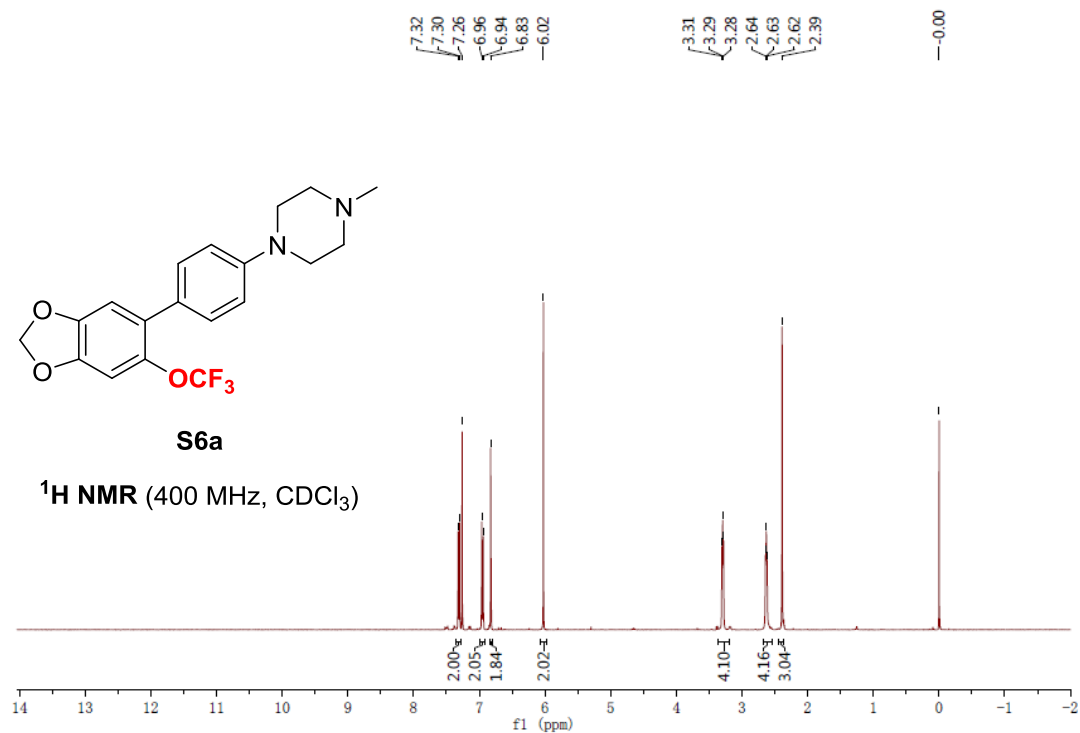
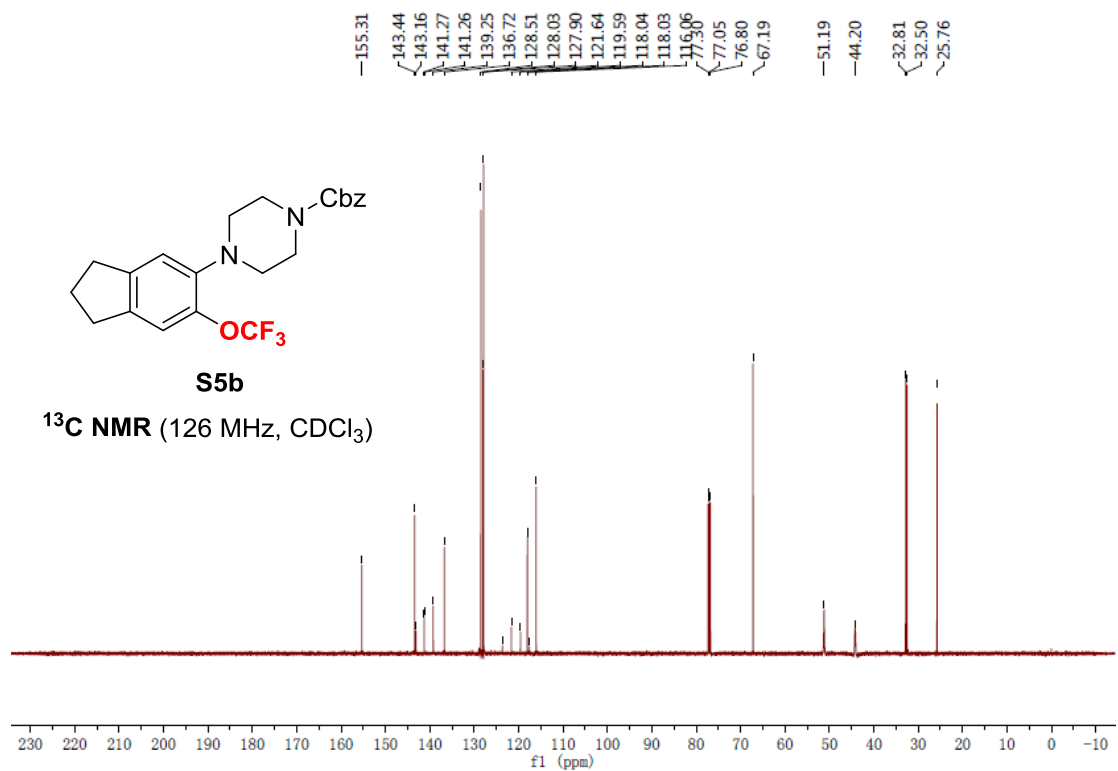


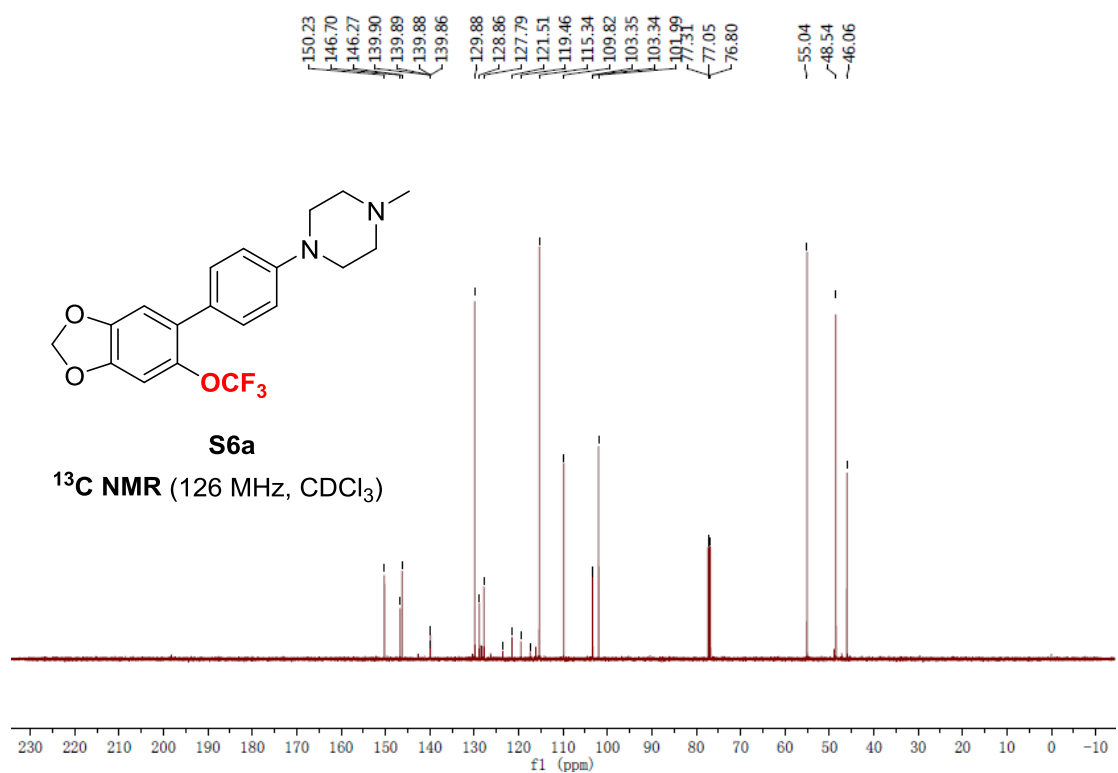
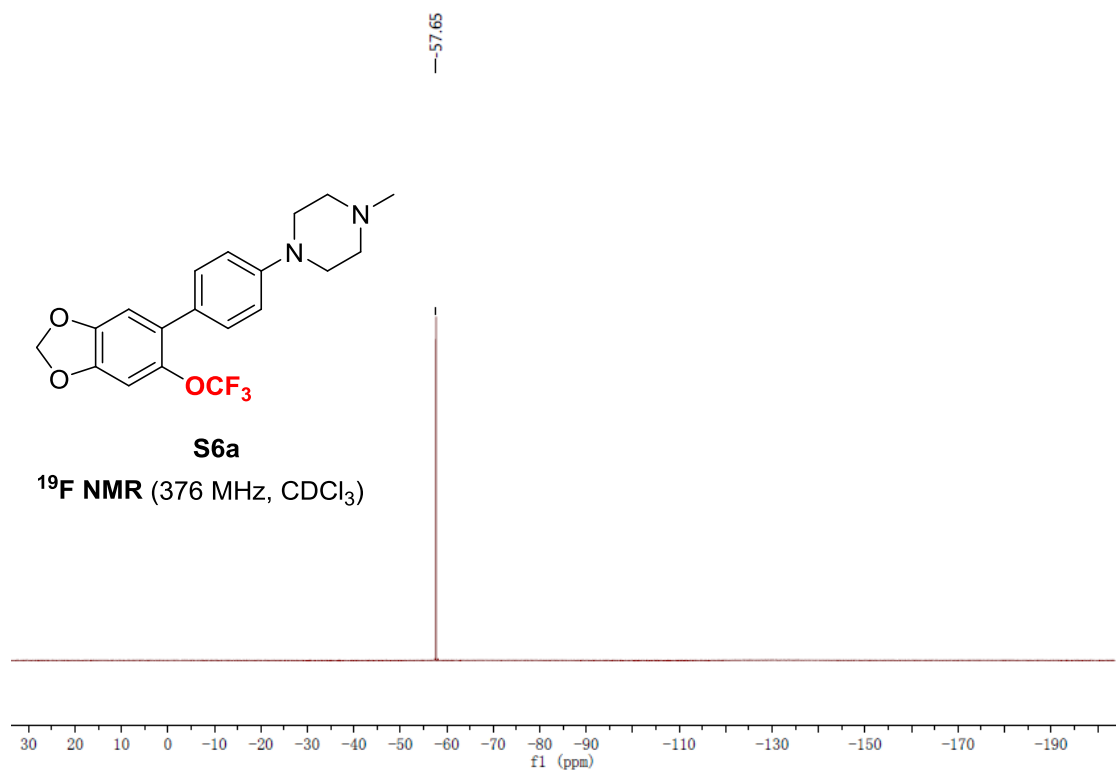


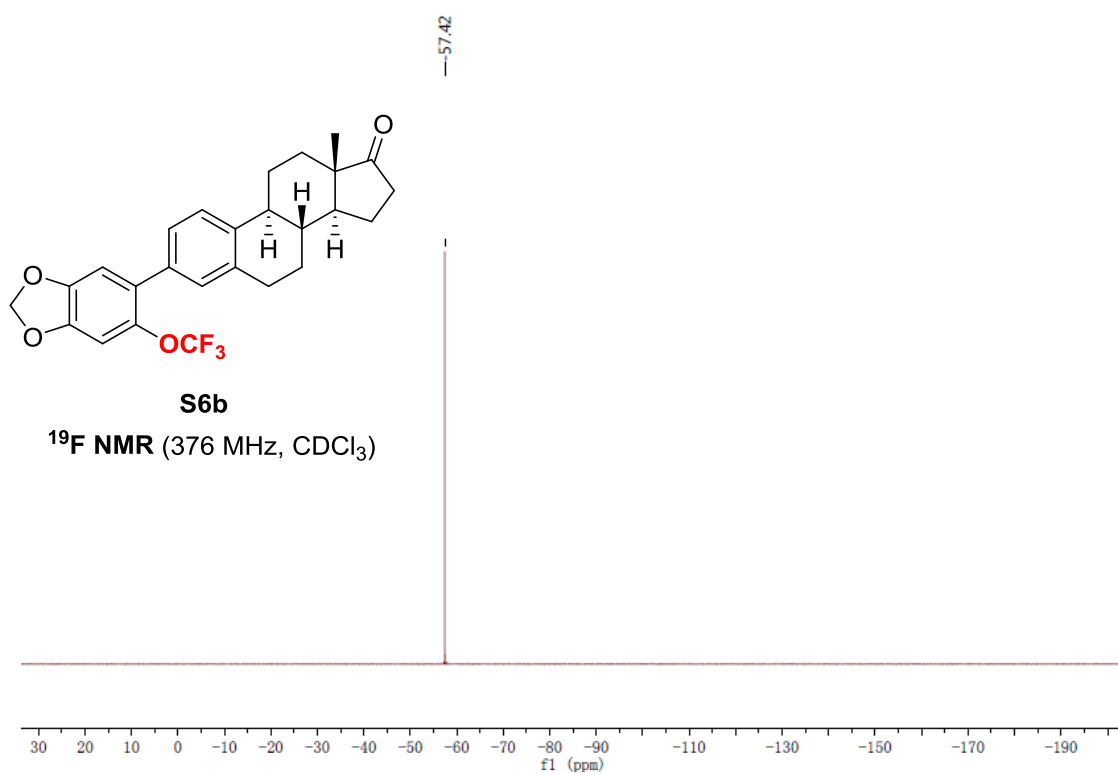
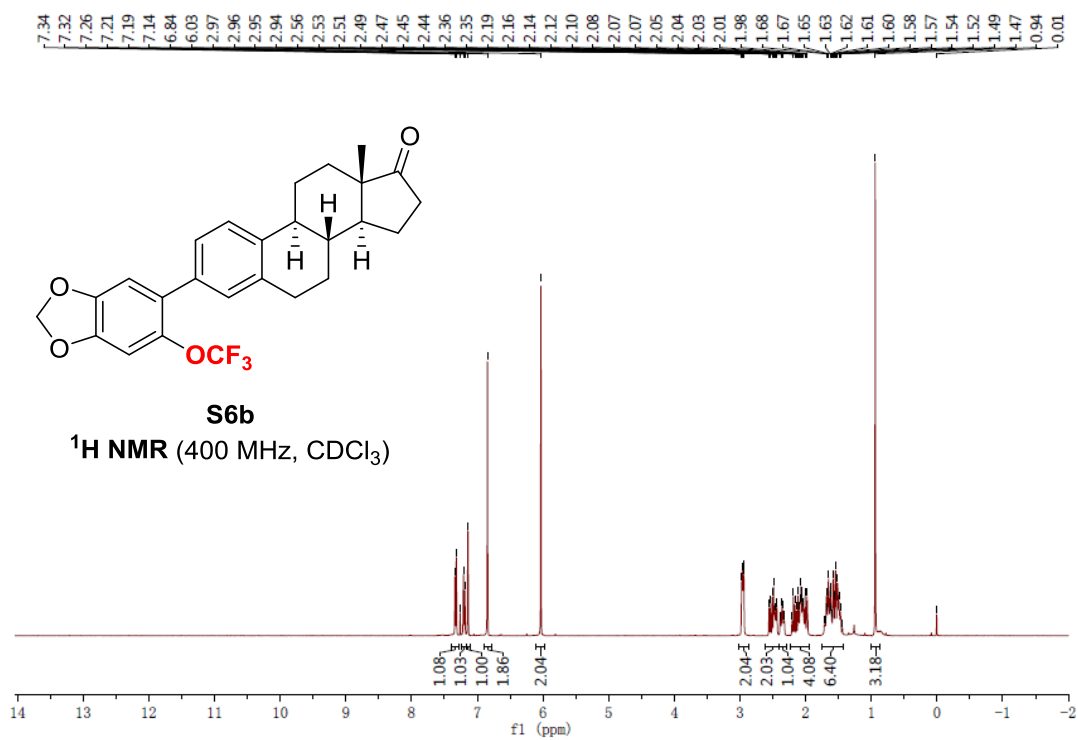


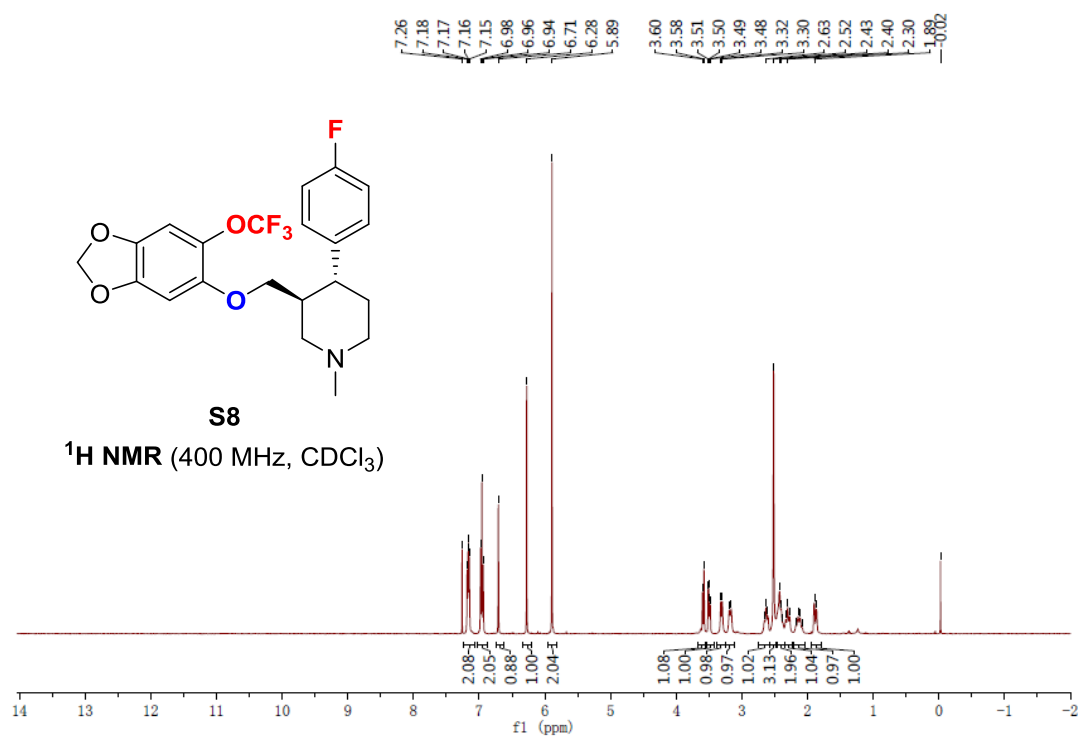
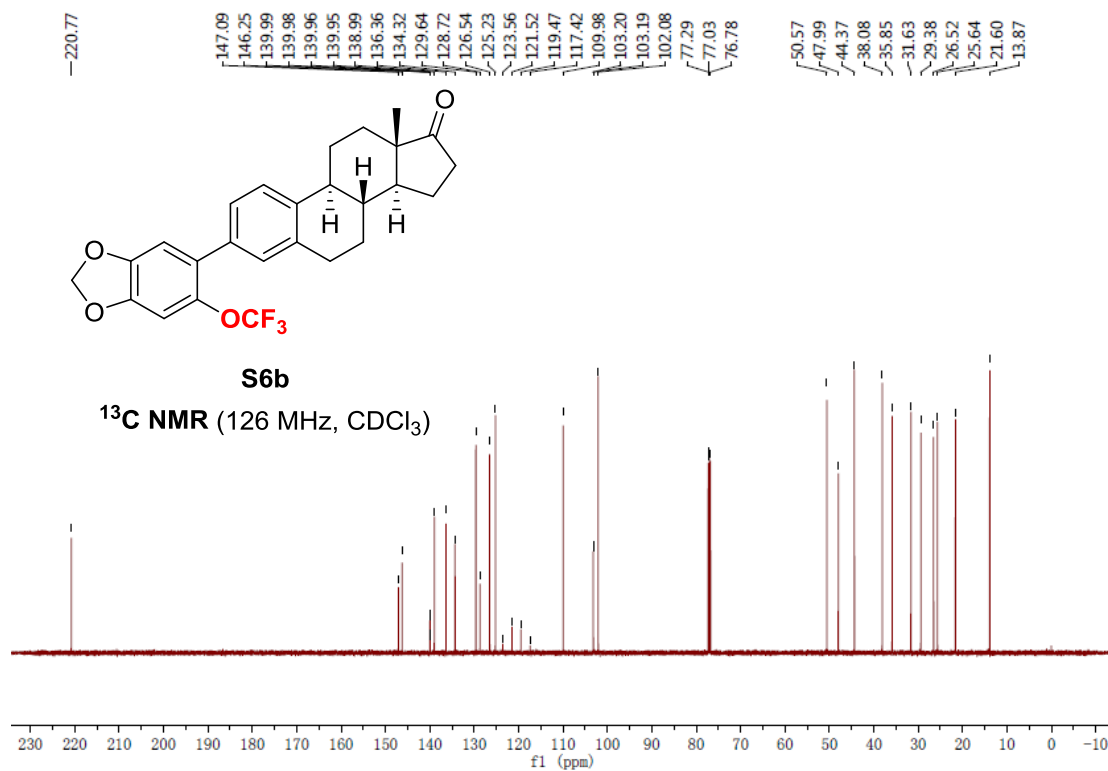


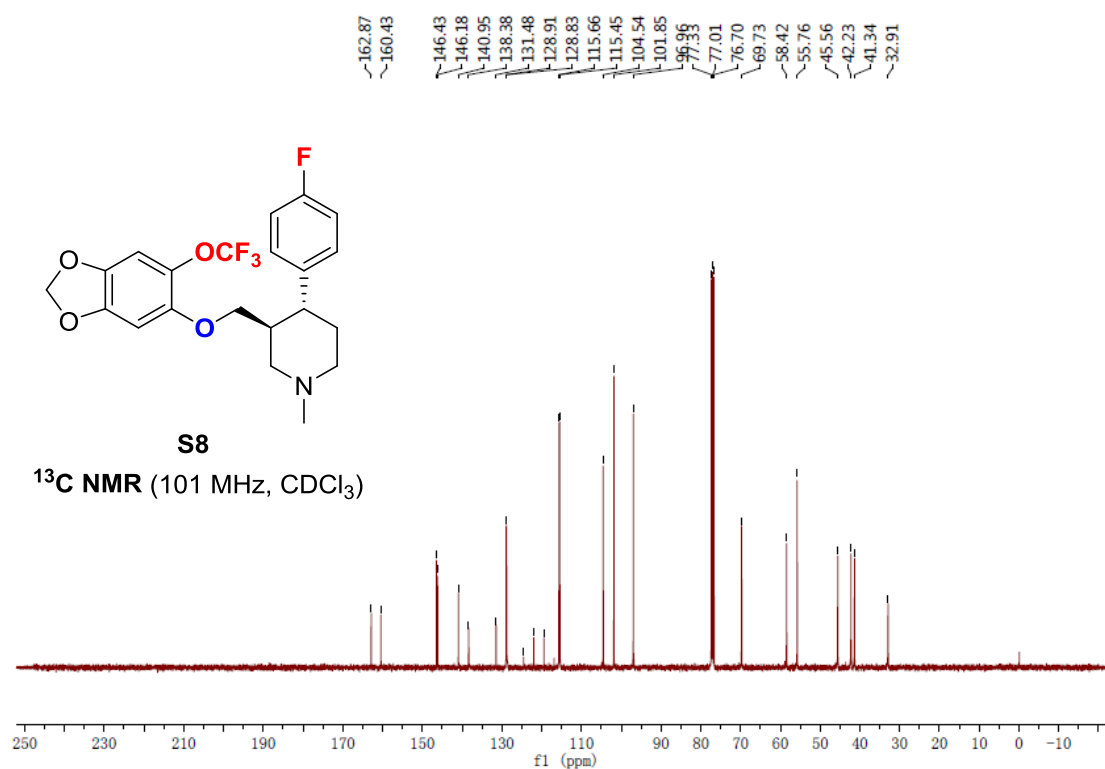
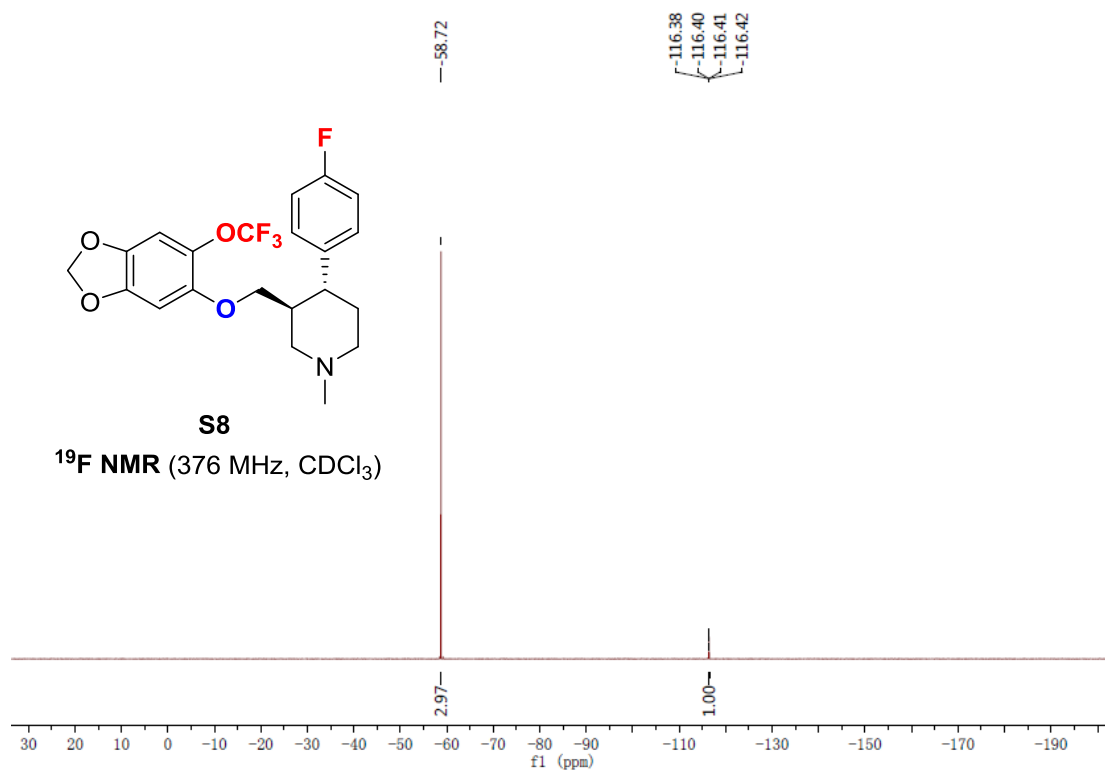


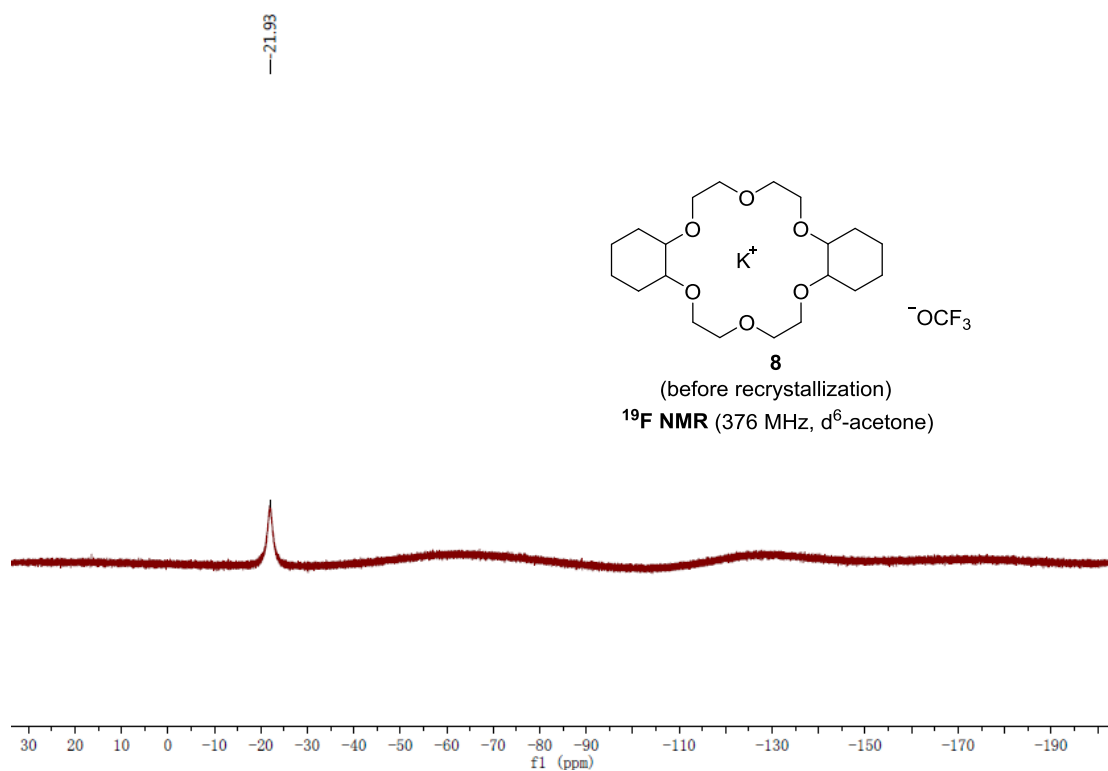
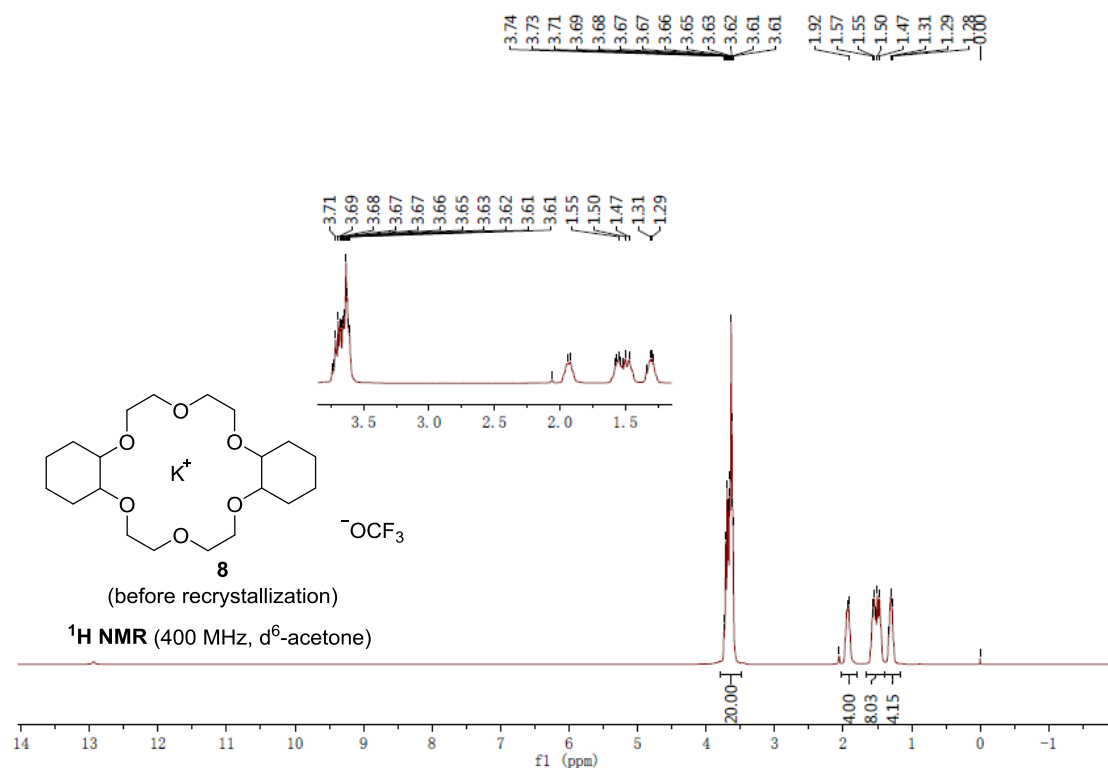


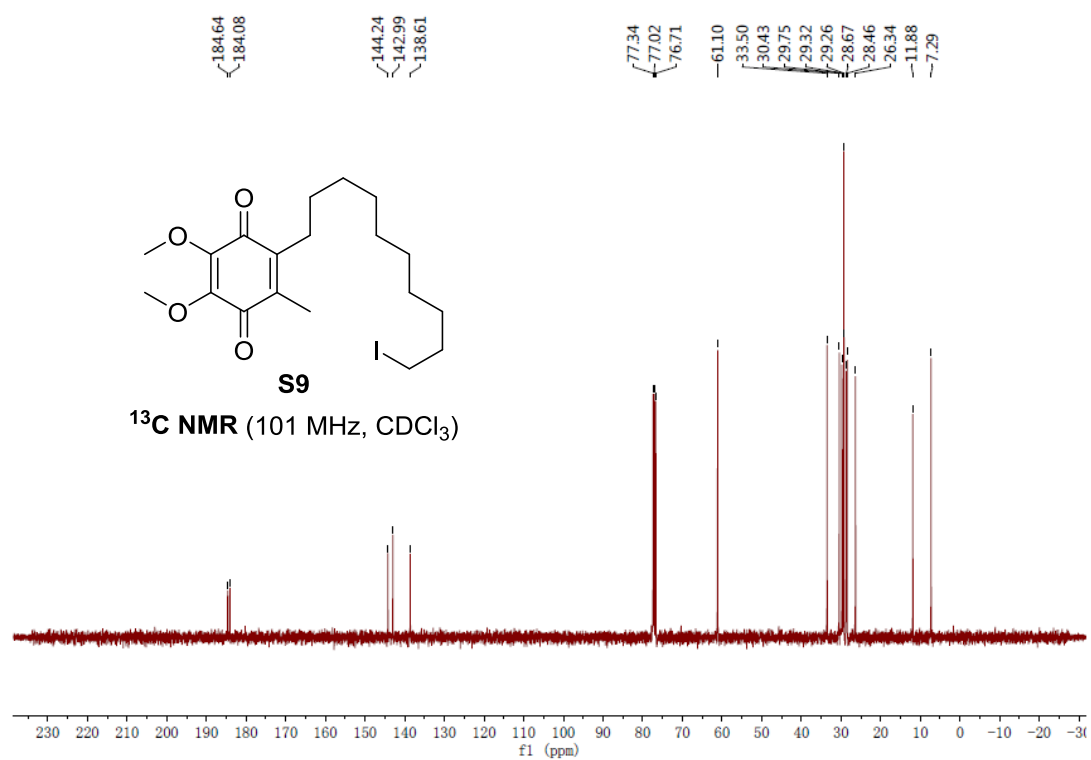
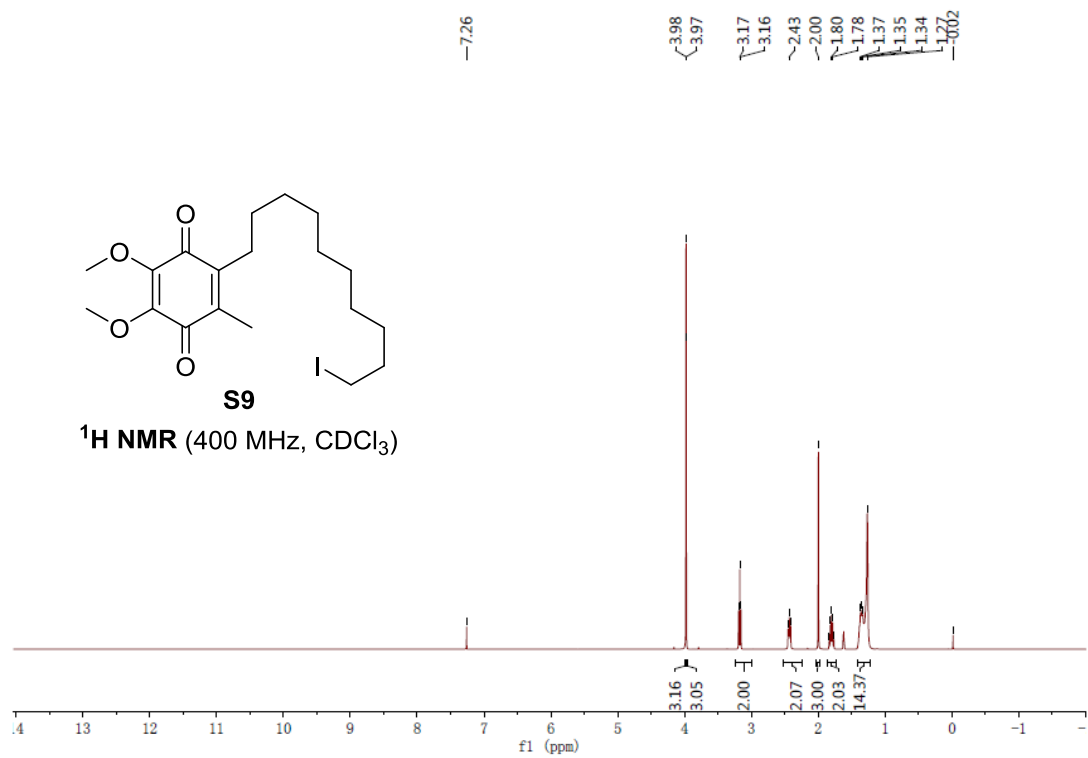


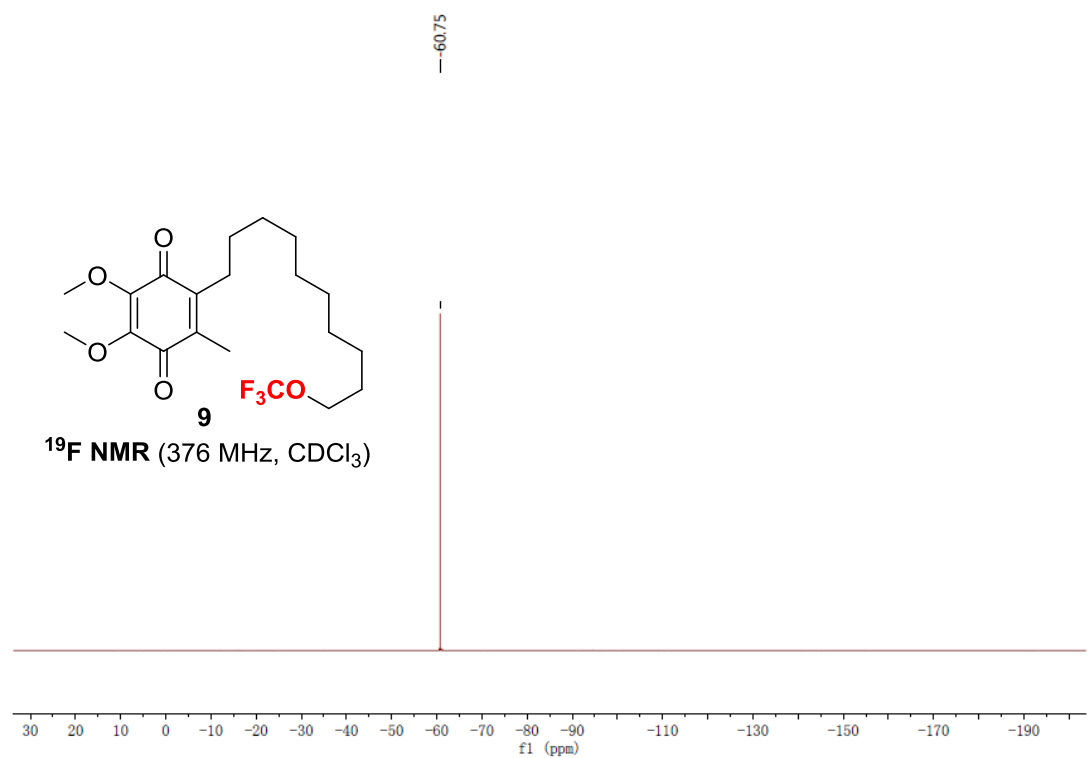
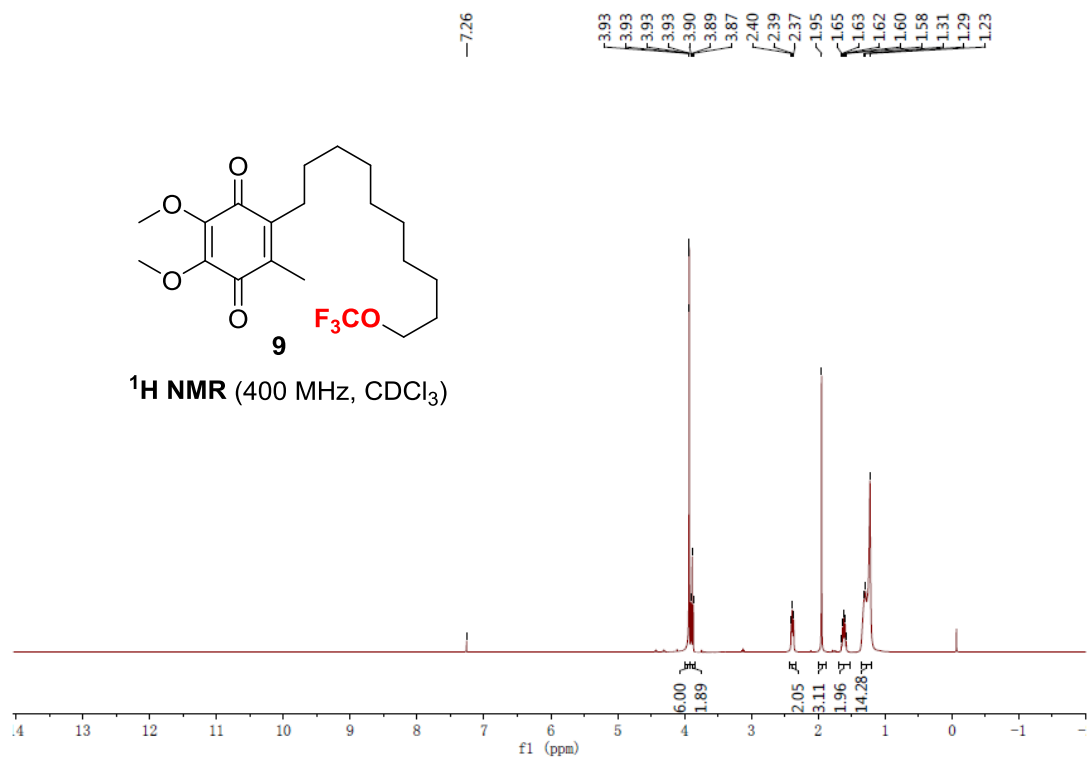


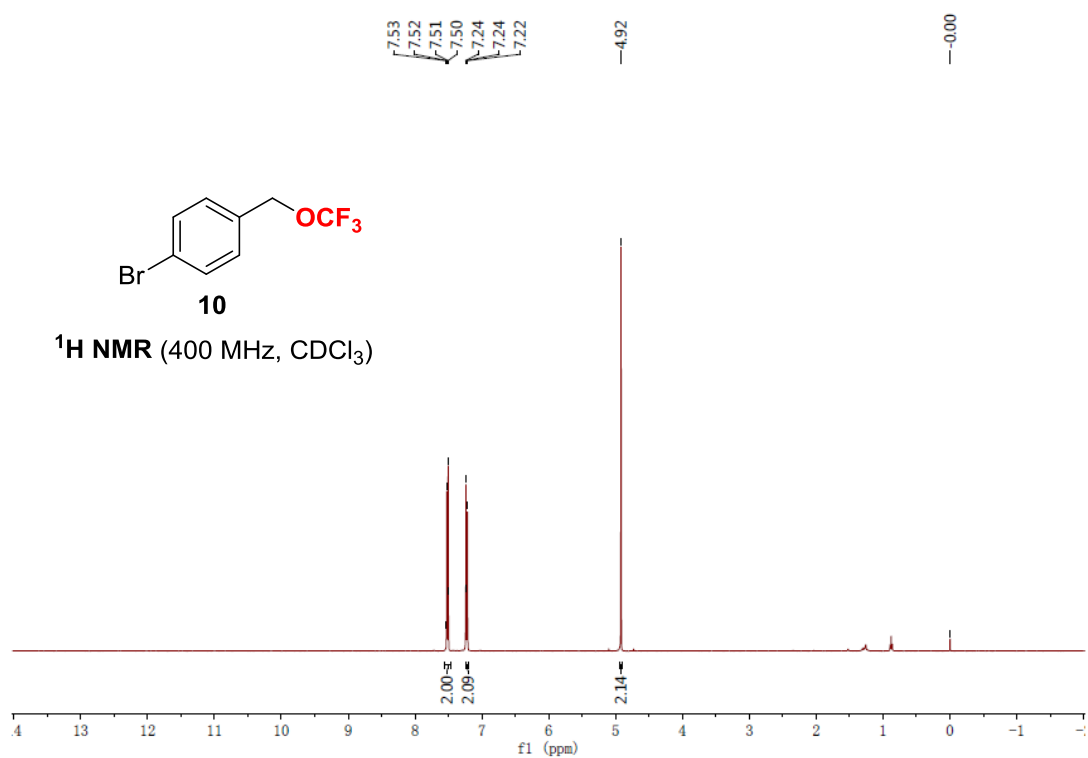
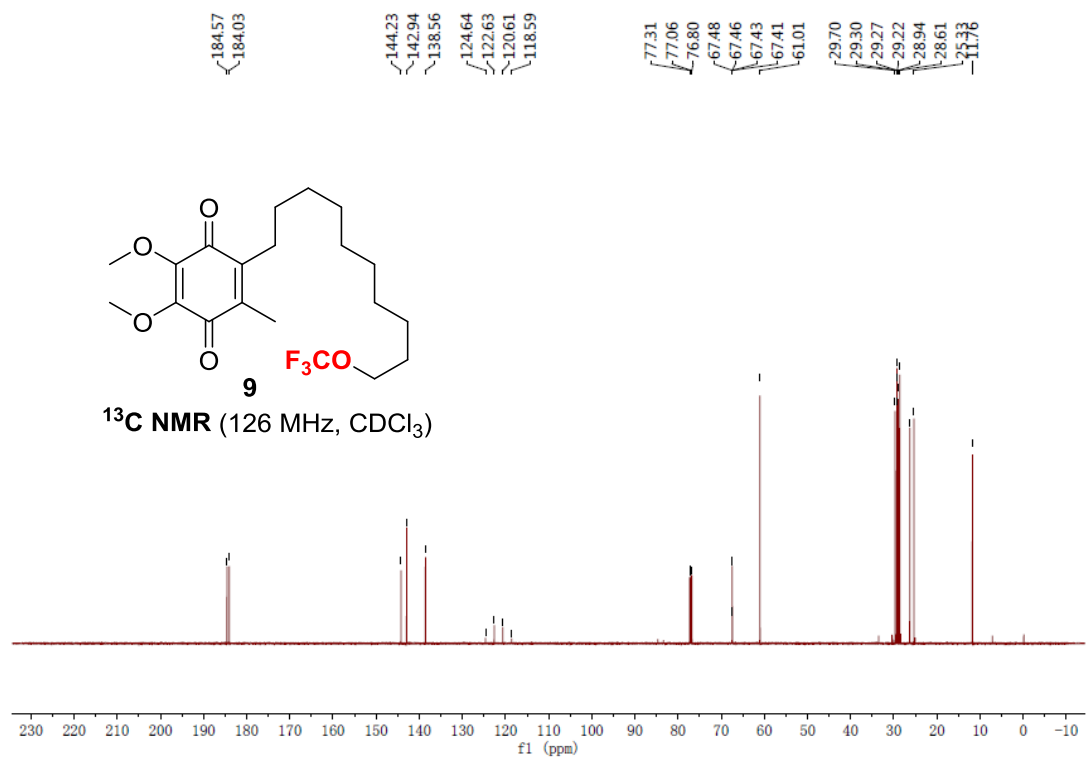


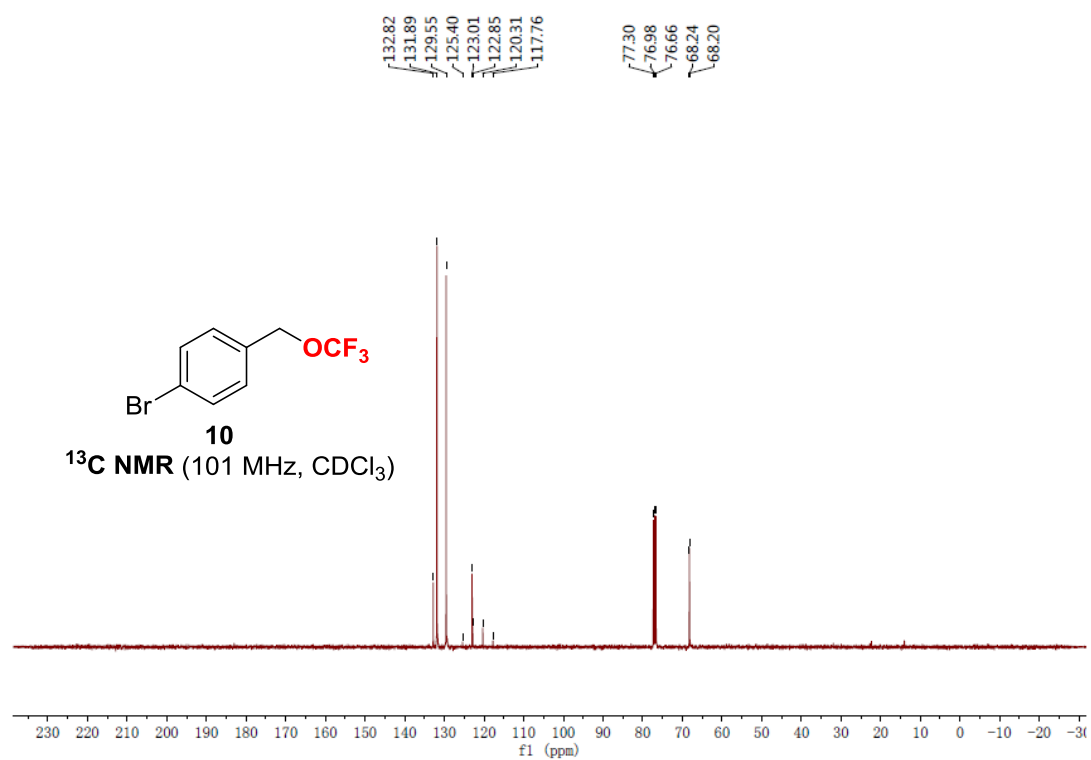
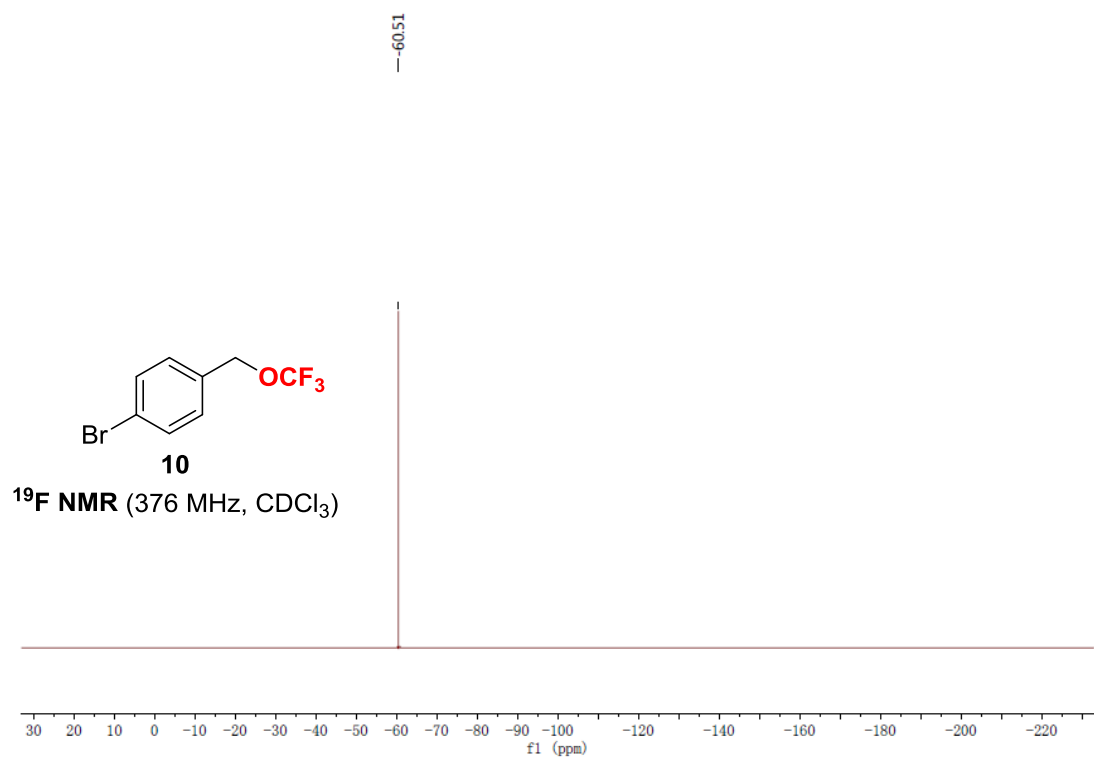


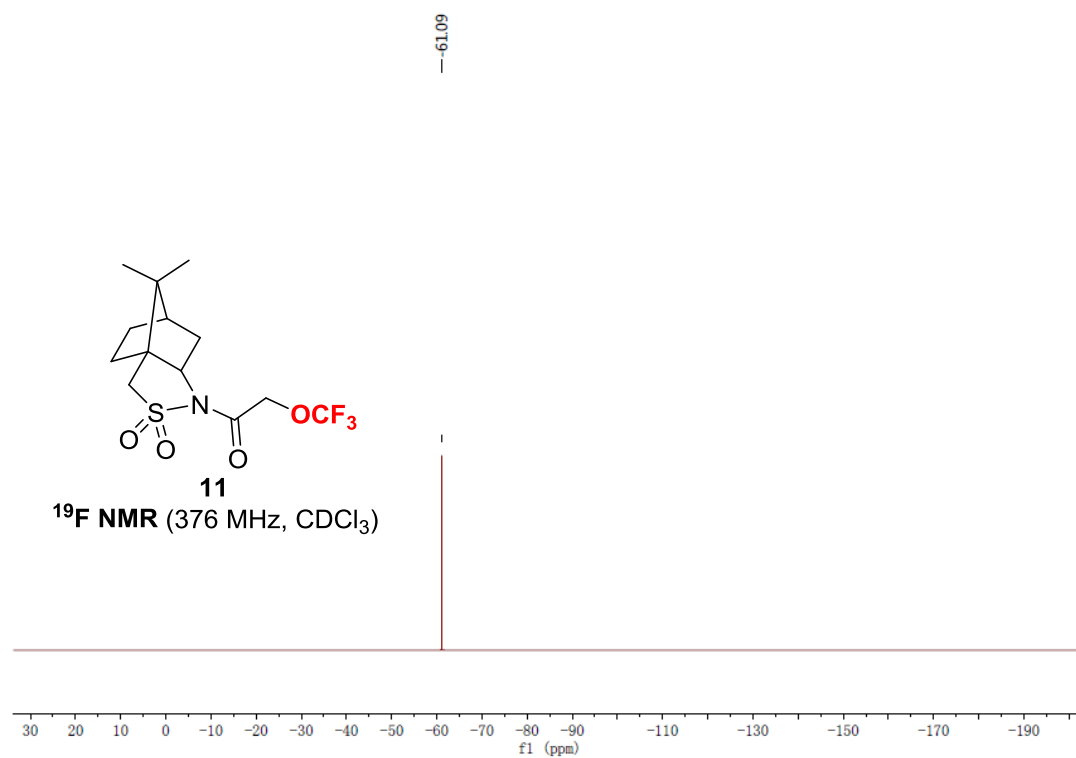
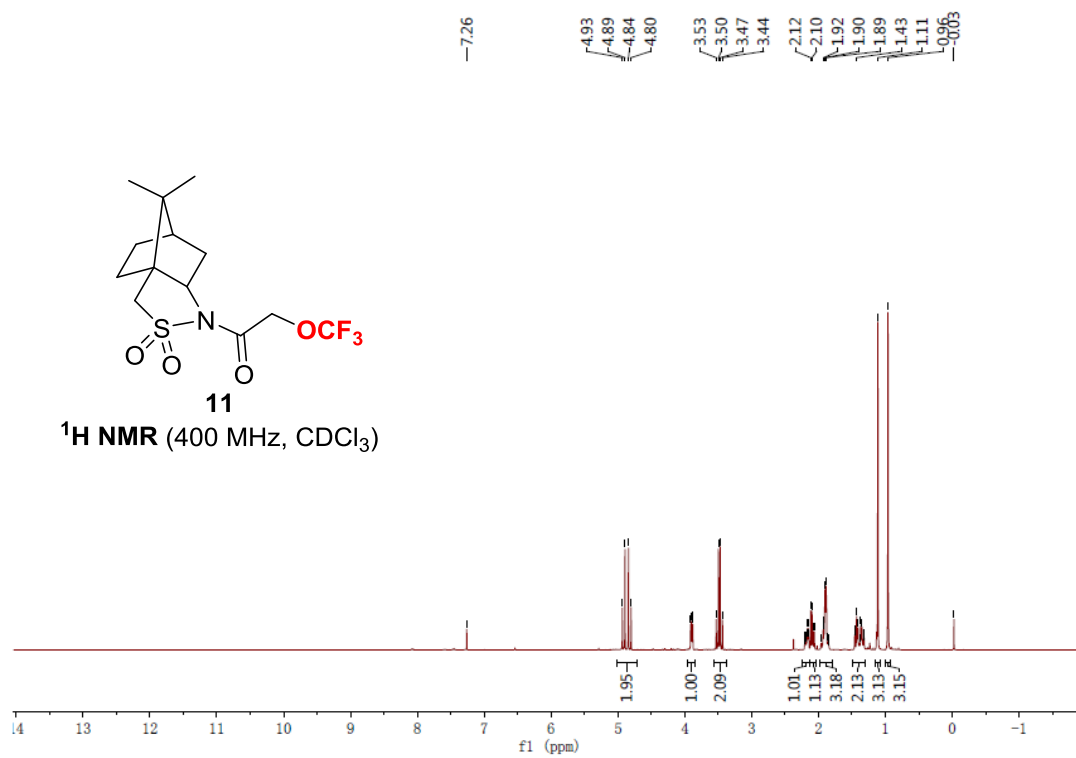


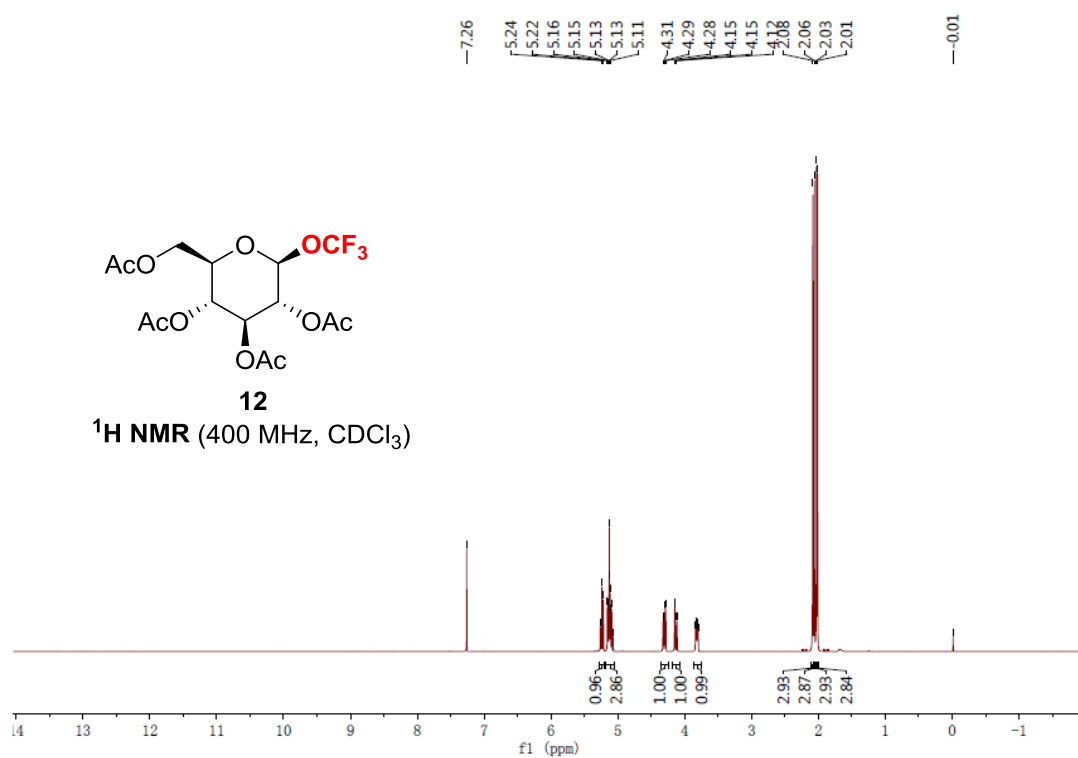
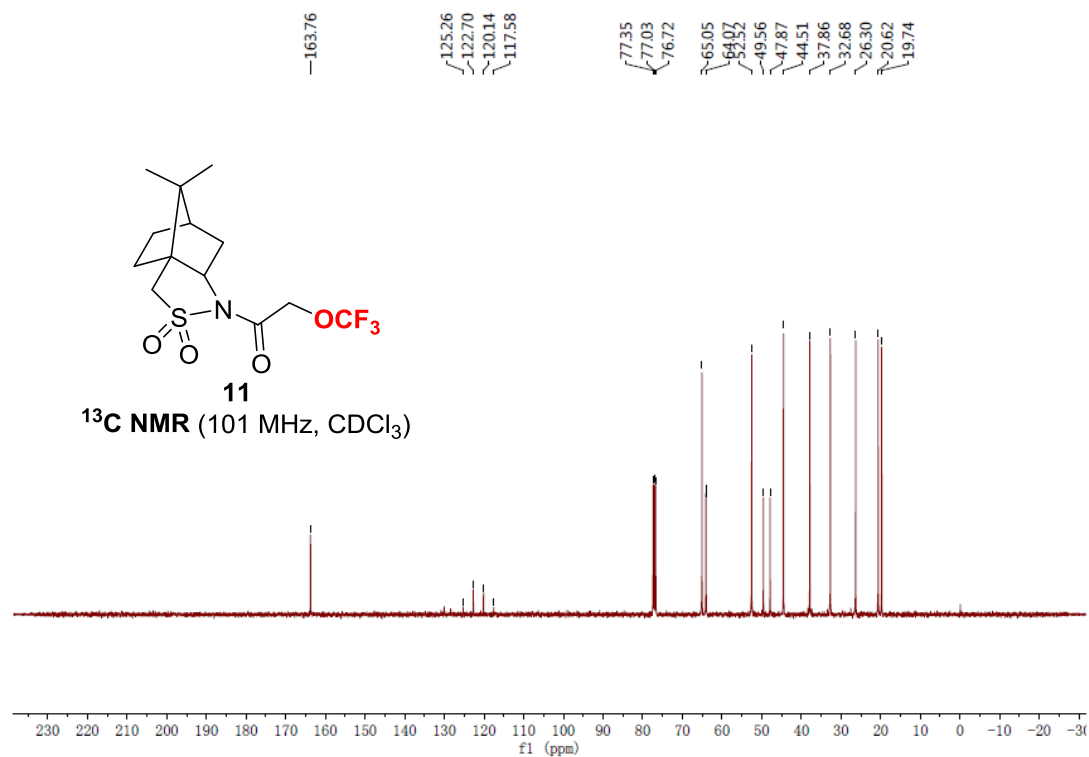


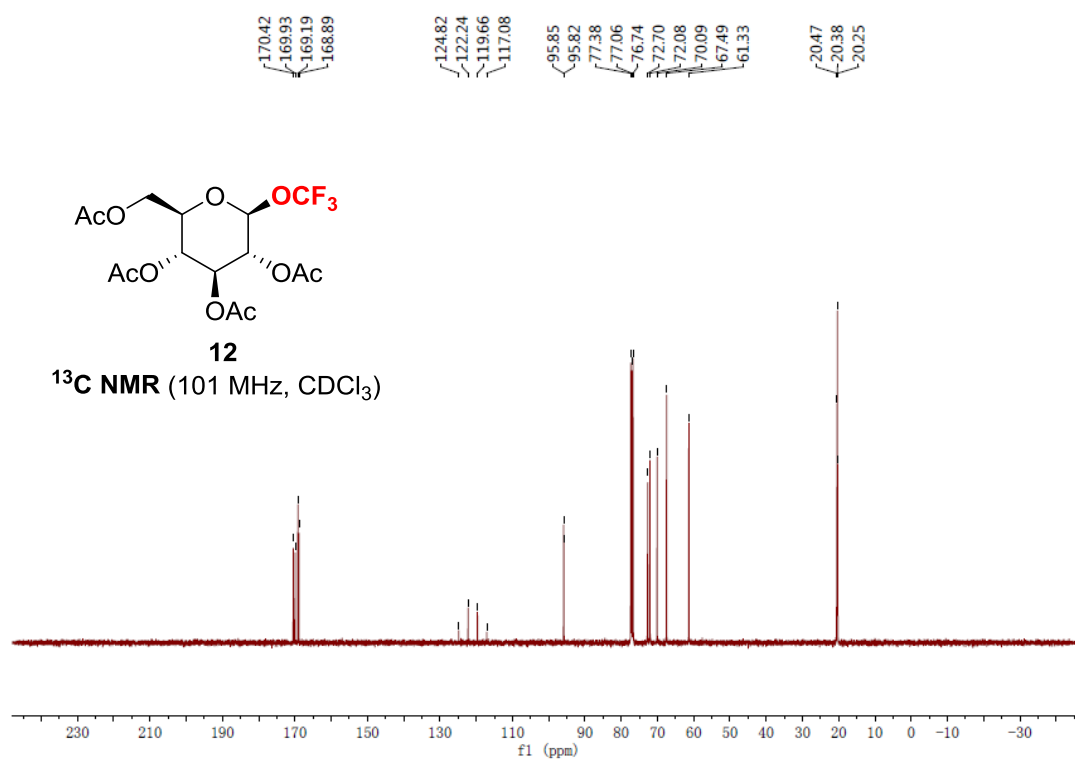
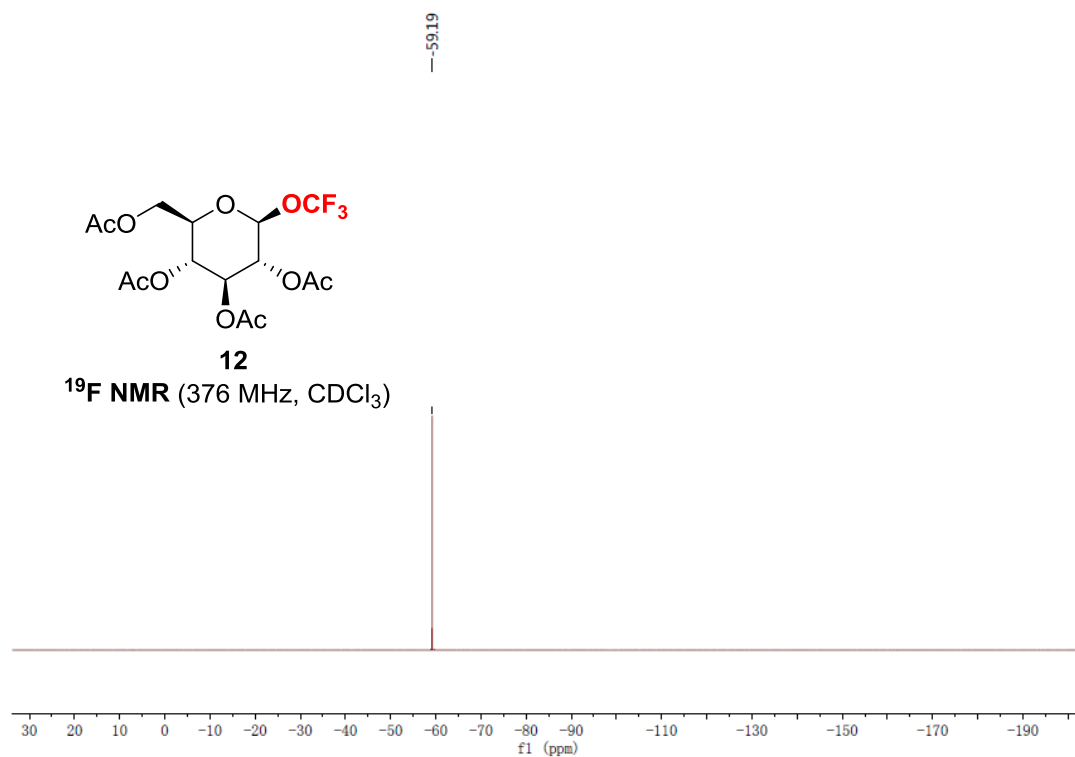


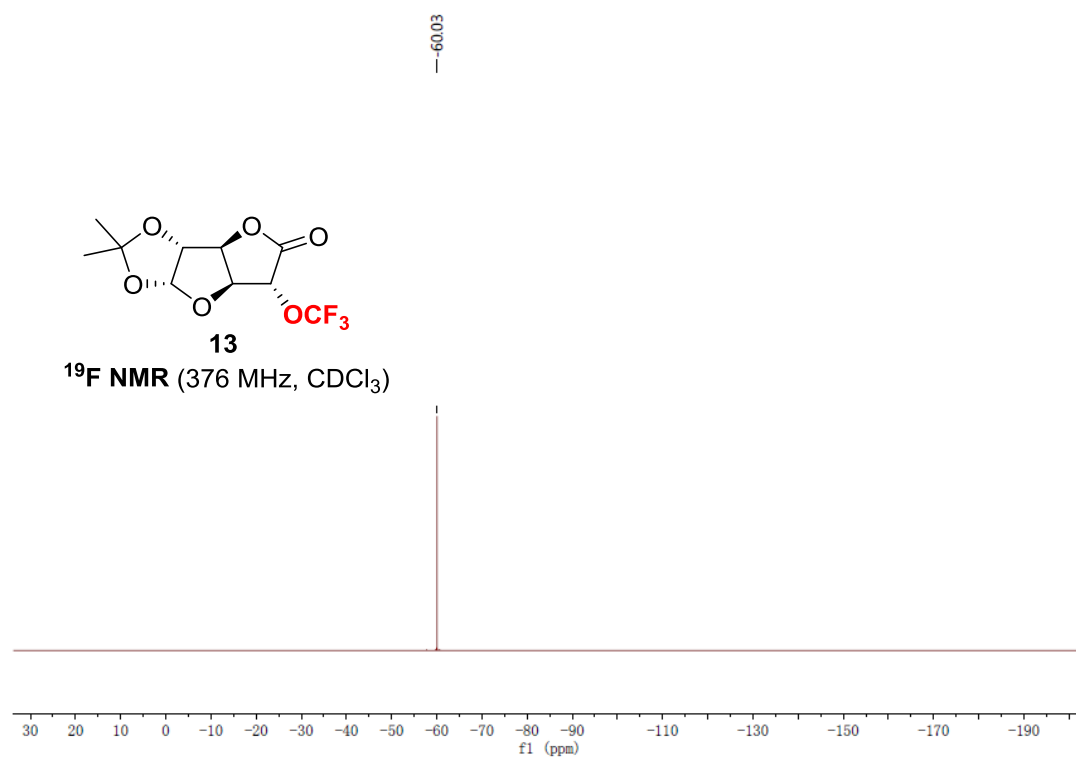
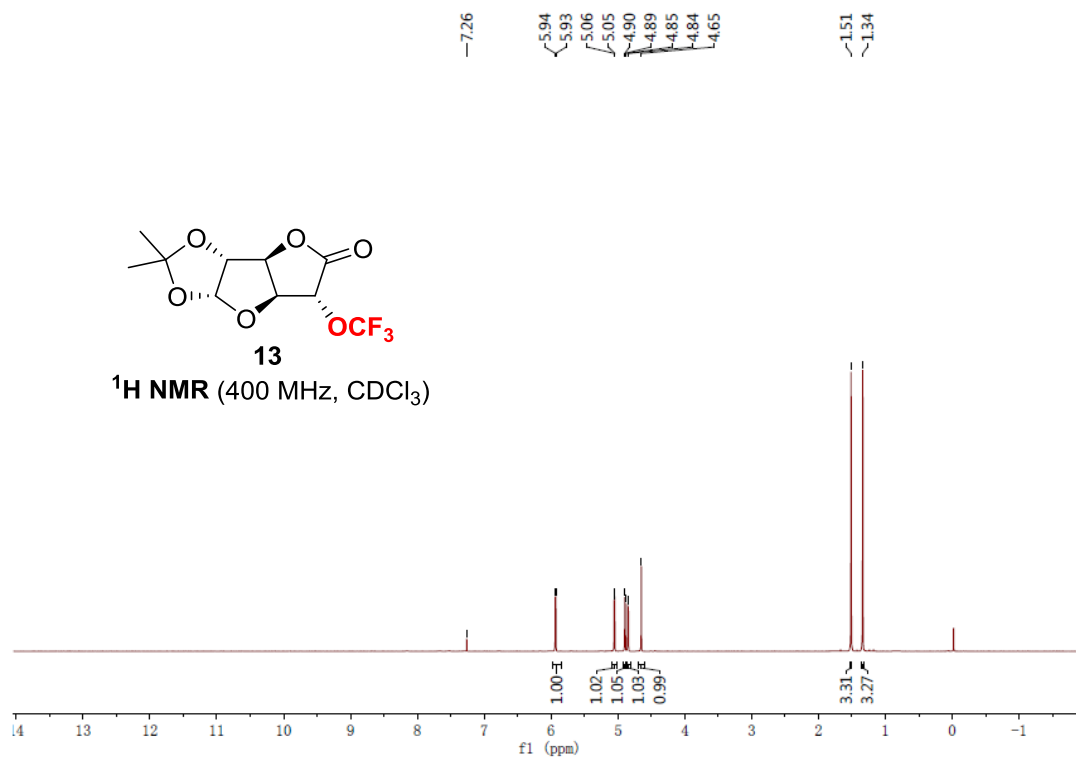


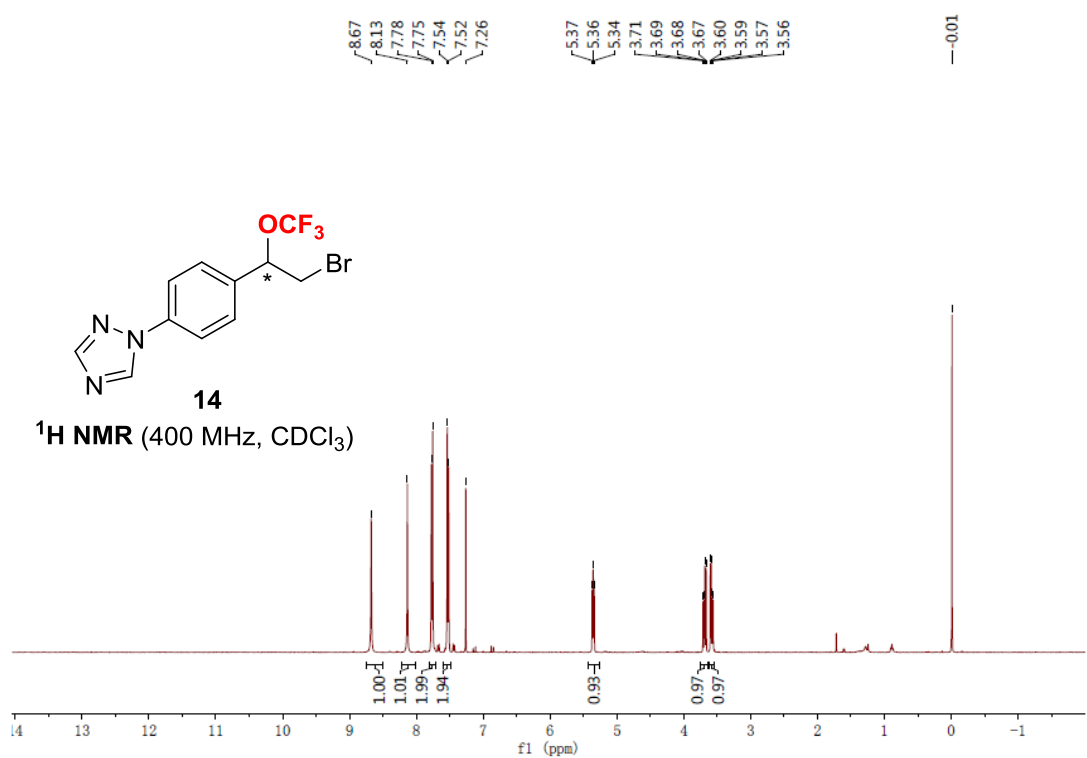
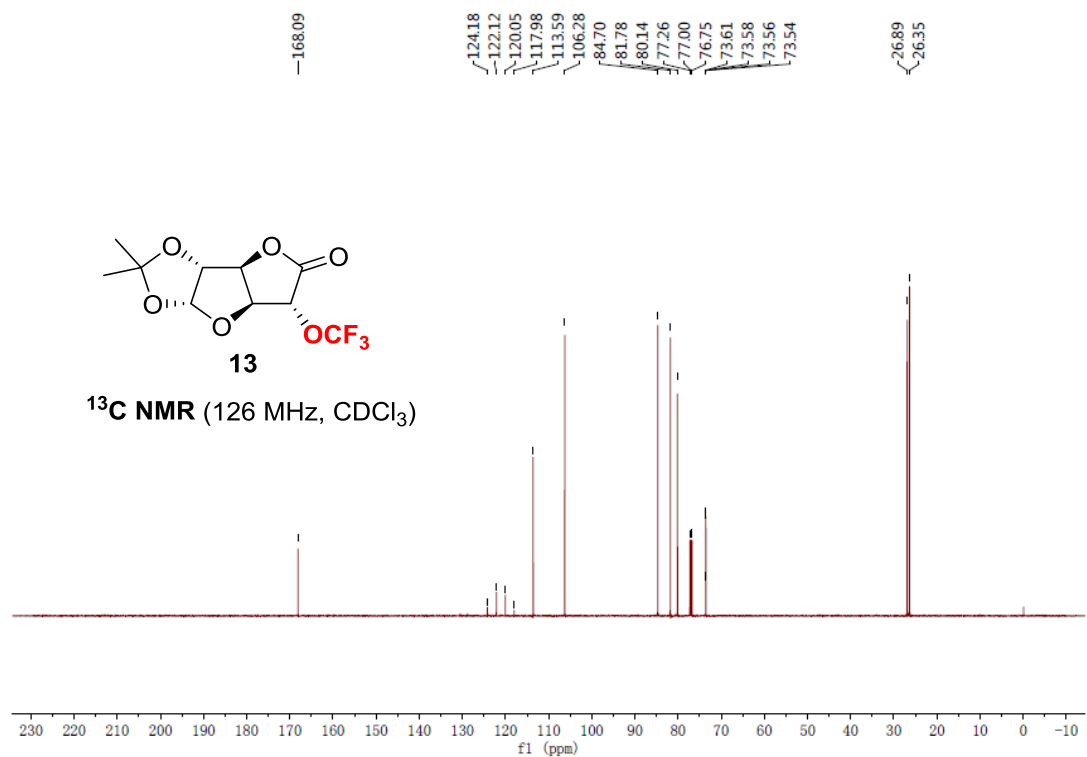


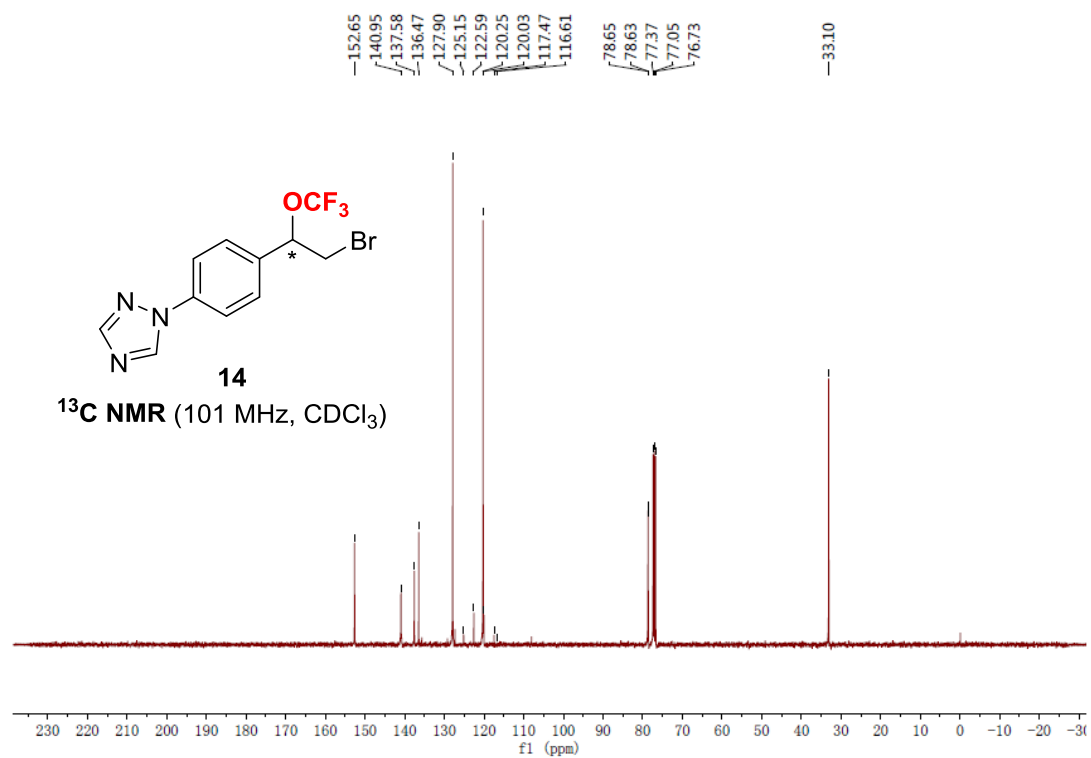
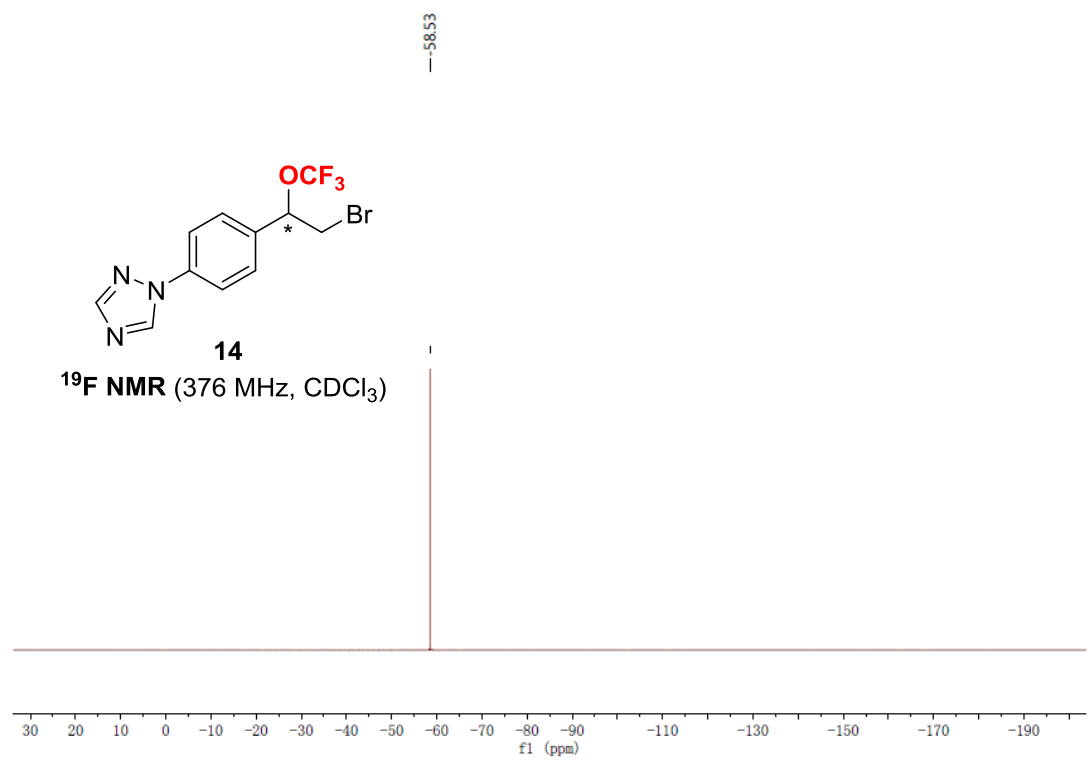


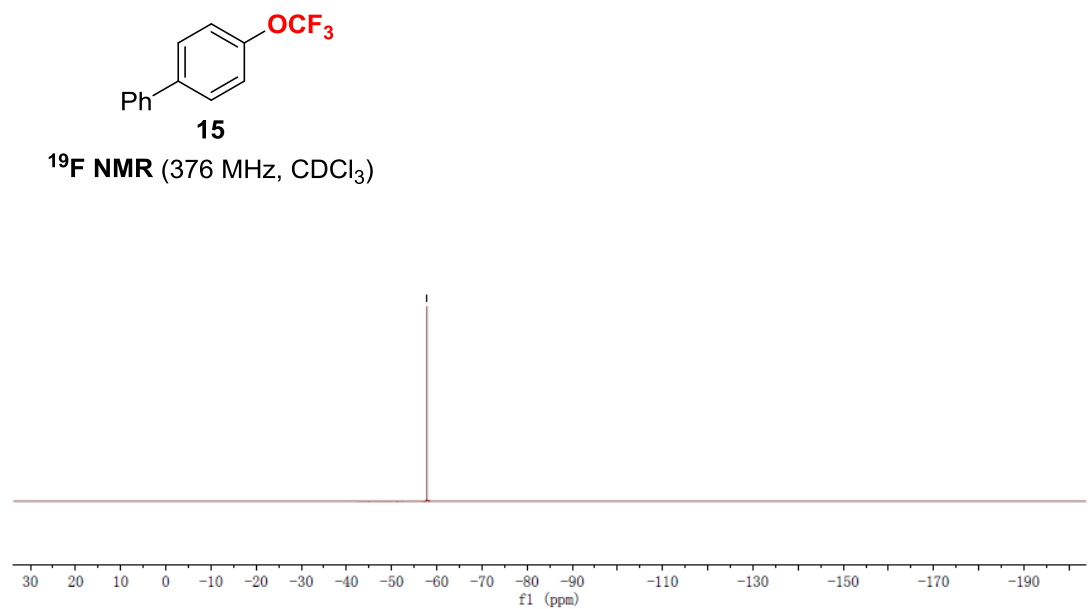
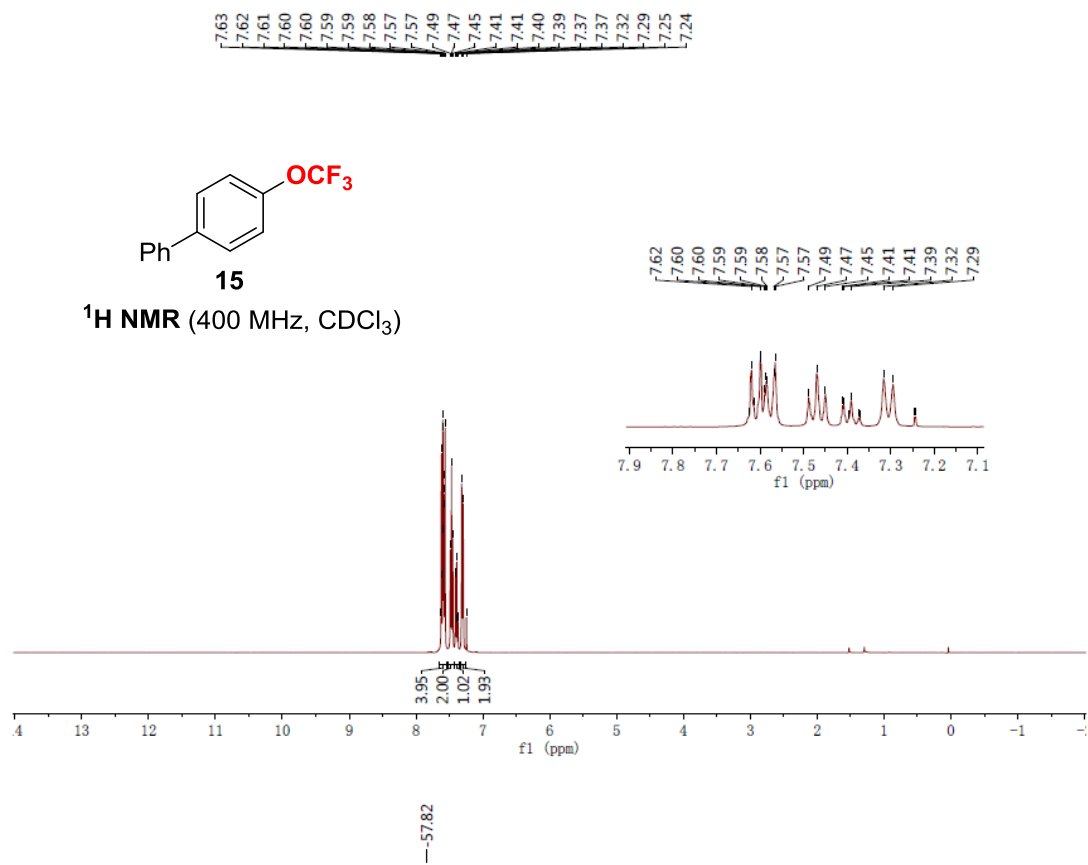


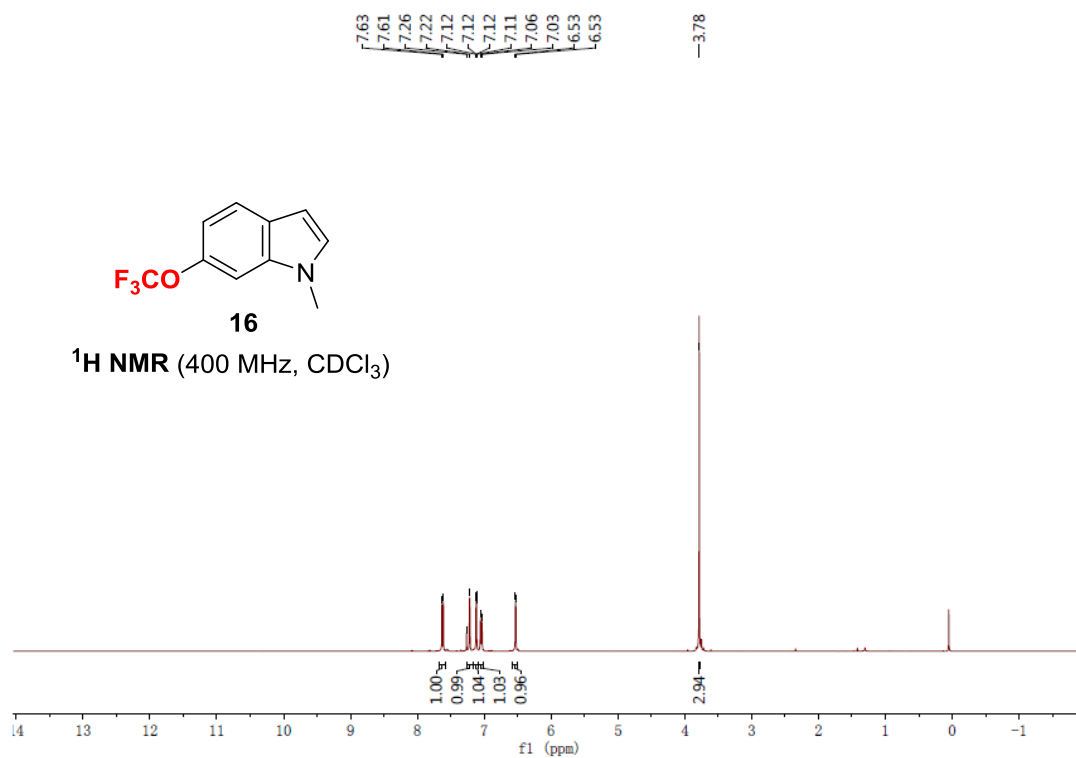
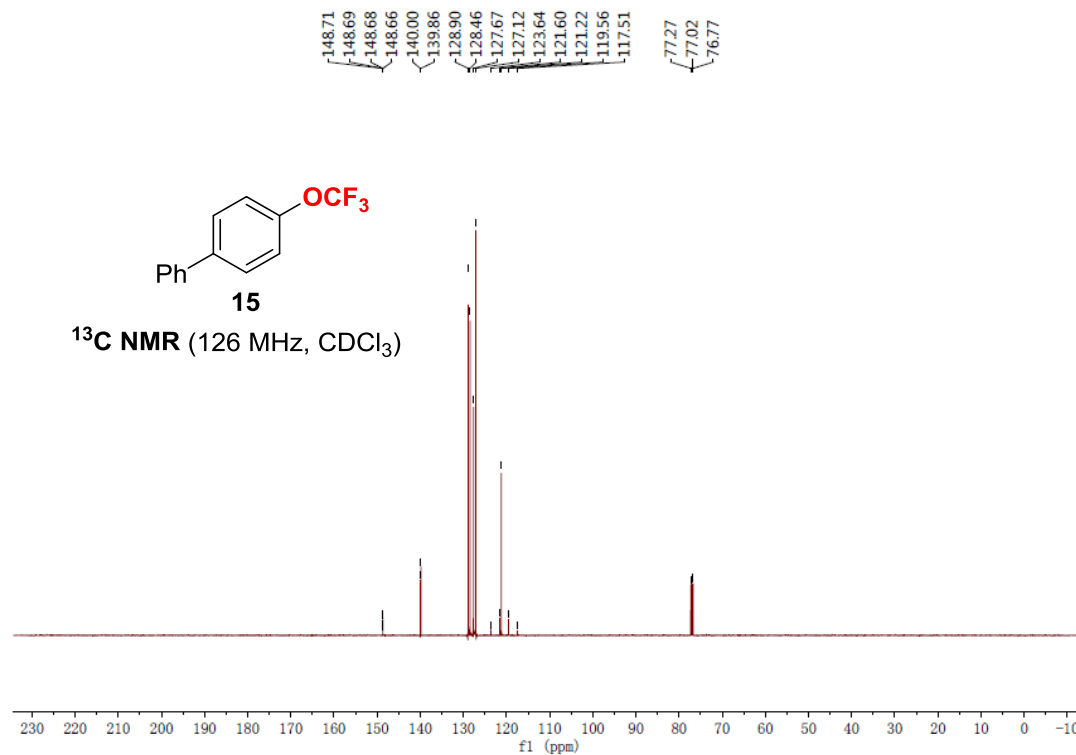


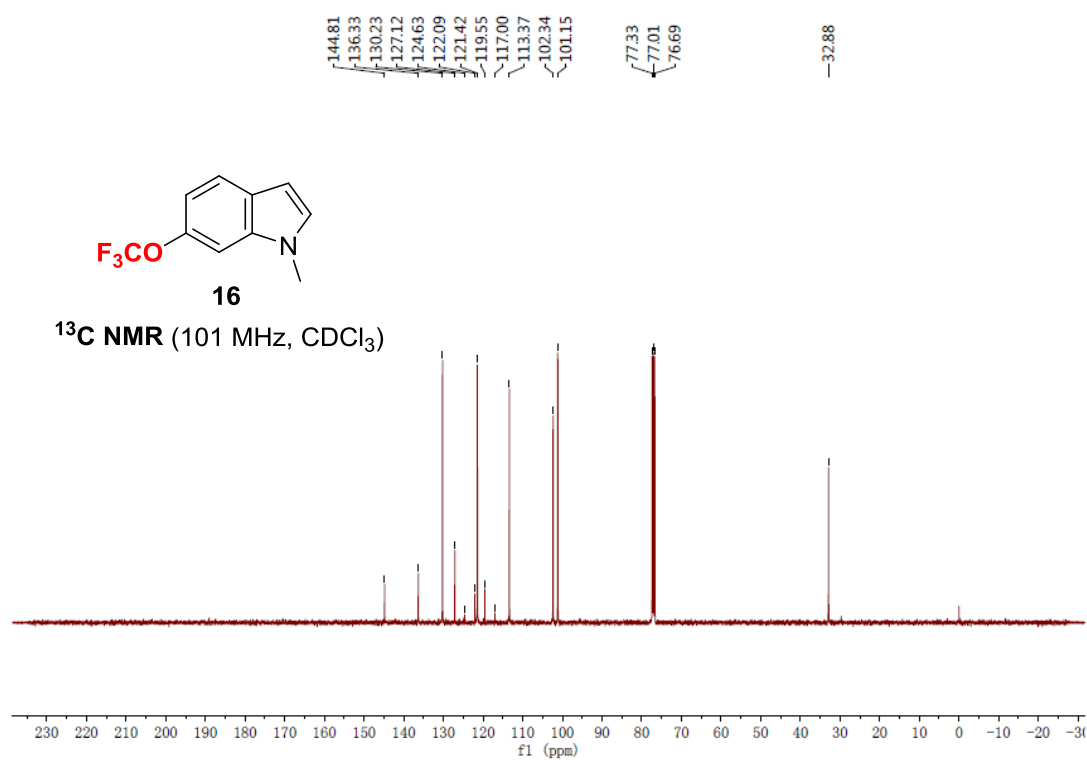
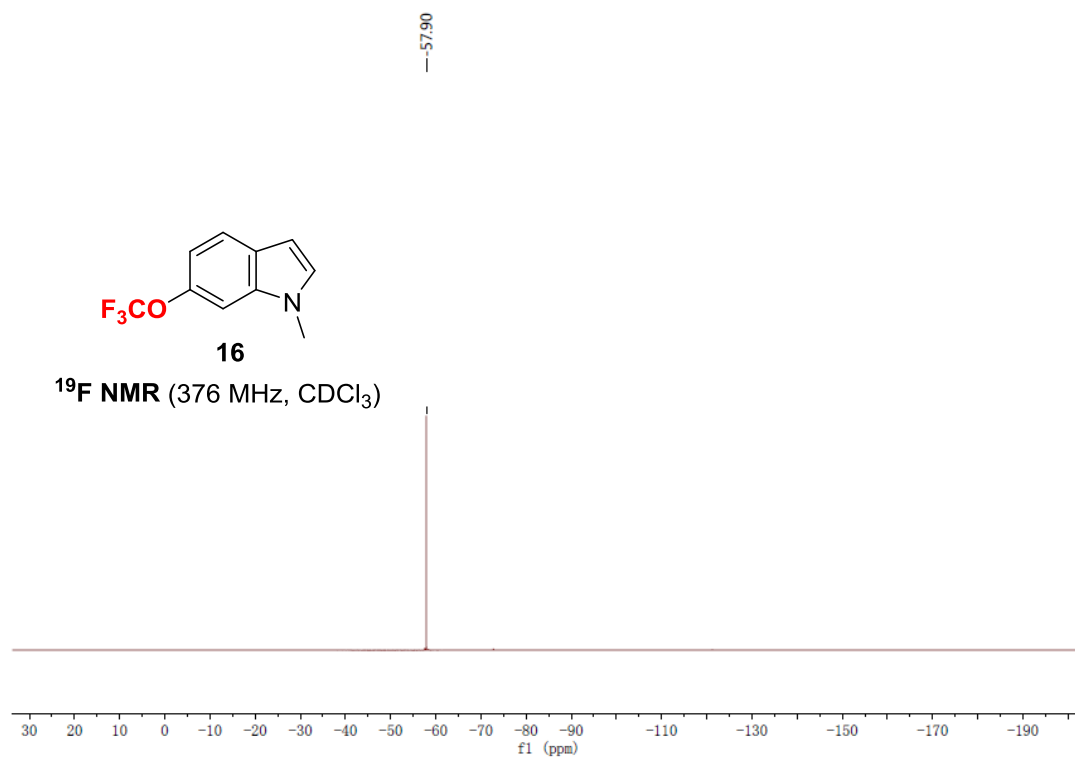


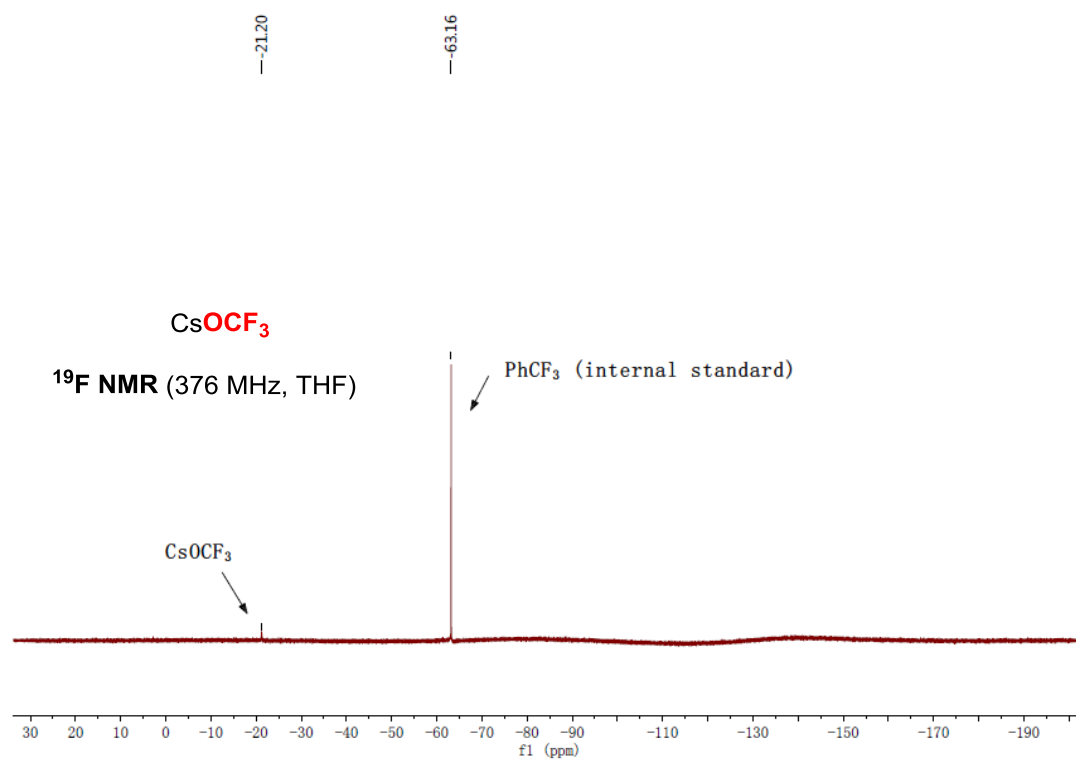
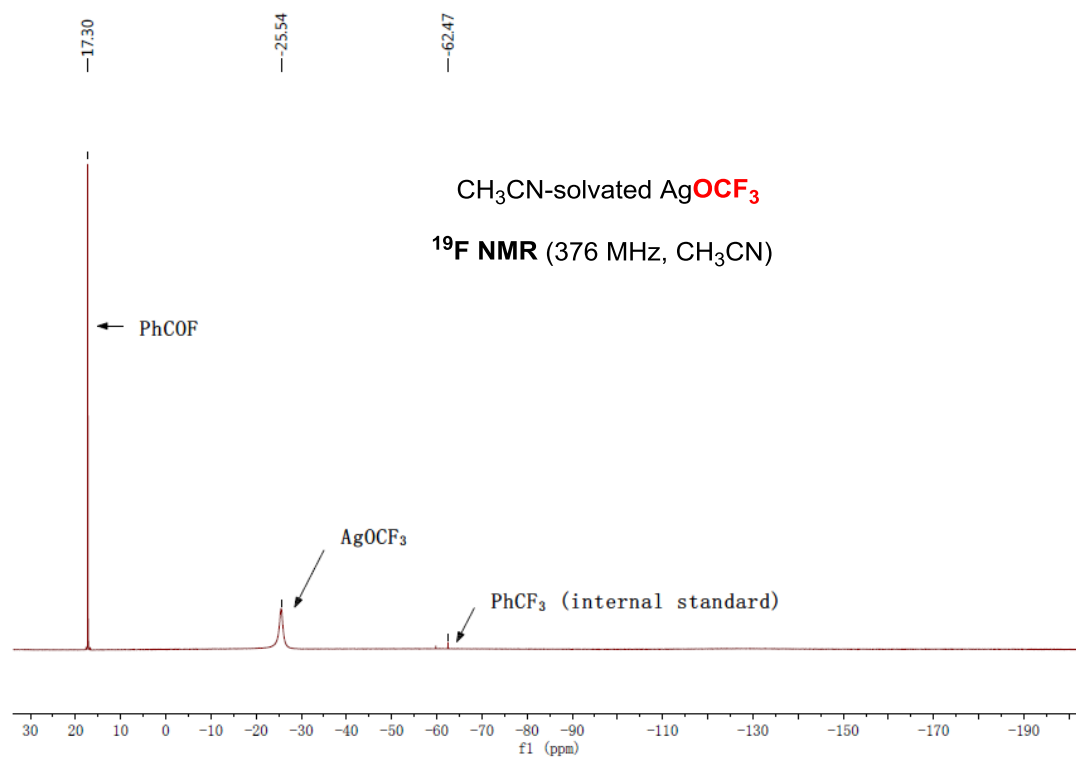


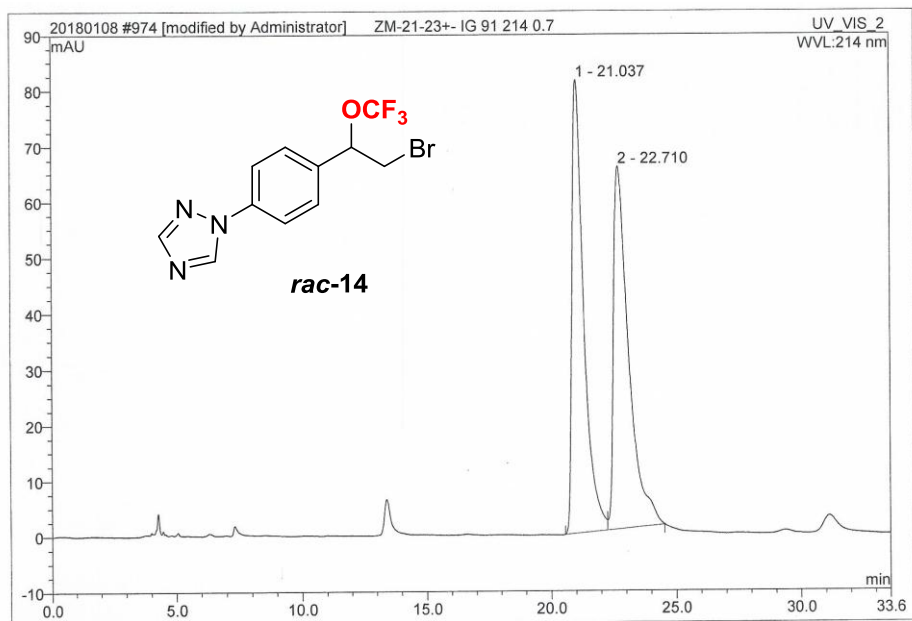




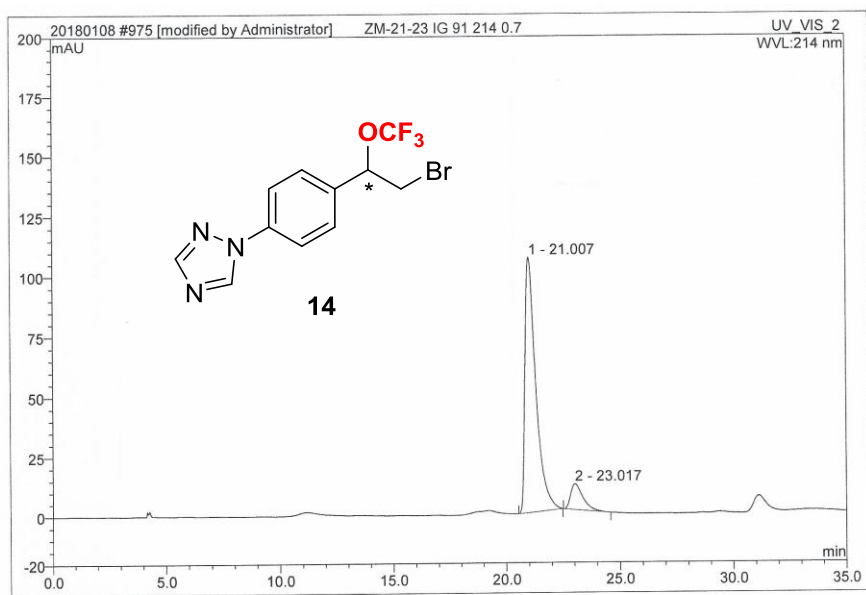








No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.04	n.a.	81.427	44.604	49.36	n.a.	BM
2	22.71	n.a.	65.192	45.758	50.64	n.a.	MB
Total:			146.620	90.362	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.01	n.a.	106.628	59.094	89.60	n.a.	BMB
2	23.02	n.a.	10.978	6.862	10.40	n.a.	BMB*
Total:			117.606	65.955	100.00	0.000	