

SUPPORTING INFORMATION

Synthesis of Chiral Non-racemic α -Difluoromethylthio Compounds with Tetrasubstituted Stereogenic Centers via a Palladium-catalyzed Decarboxylative Asymmetric Allylic Alkylation

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Optimization of the reaction conditions for the DAAA of **8a^a**

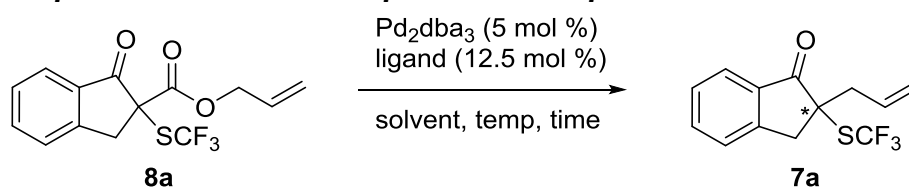
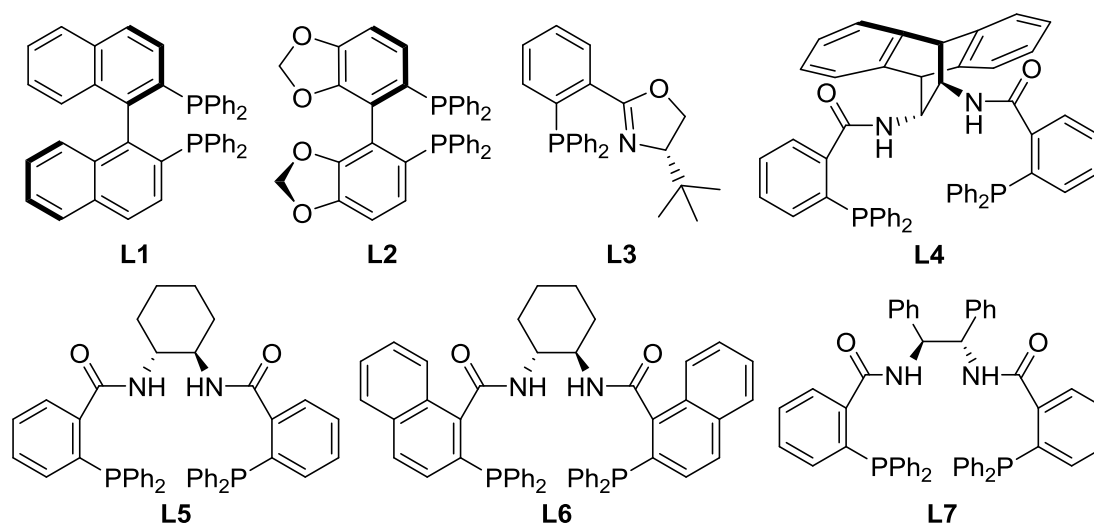


Table S1

run	ligand	solvent	temp (°C)	time	yield (%) ^b	ee (%) ^c
1	L1	THF	r.t.	2 h	56	6
2	L2	THF	r.t.	5 min	84	6
3	L3	THF	r.t.	10 min	97	5
4	L4	THF	r.t.	30 min	87	35
5	L5	THF	r.t.	5 min	85	33
6	L6	THF	r.t.	5 min	92	46
7	L7	THF	r.t.	5 min	98	78
8	L7	Toluene	r.t.	5 min	81	79
9	L7	DCM	r.t.	5 min	92	74
10	L7	1,4-Dioxane	r.t.	5 min	91	51
11	L7	Et ₂ O	r.t.	5 min	84	85
12	L7	TBME	r.t.	5 min	80	87
13	L7	TBME	-40	1 h	93	90
14	L7	TBME	-80	1 h	91	93

^aReaction condition: **8a** (0.05 mmol, 1.0 equiv), Pd₂dba₃ (5 mol %), ligand (12.5 mol %) in TBME (0.05 M) at prescribed temperature, unless otherwise noted. ^bIsolated yield. ^cEe was determined by HPLC.



General Information

All reactions were performed in dried glassware under a positive pressure of nitrogen. Solvents were transferred by syringe through a rubber septum. Commercially available chemicals were obtained from Aldrich Chemical Co., Nacalai tesque, TCI, Wako and used as received unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) performed with 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light (254 nm) and *p*-anisaldehyde in ethanol/heat. Column chromatography was performed on a column packed with silica gel 60M spherical neutral size 40-63 μm . ^1H (300 MHz and 500 MHz), ^{13}C (126 MHz) and ^{19}F (282 MHz) NMR spectra for solution in CDCl_3 were recorded on Varian Mercury 300, Avance 500US and ECZ700R. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane ($\delta\text{H} = 0.00$ ppm) or CHCl_3 ($\delta\text{C} = 77.0$ ppm) or hexafluorobenzene ($\delta\text{F} = -162.2$ ppm). The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublet, dt: doublet of triplet, ddd: doublet of doublet of doublet, ddt: doublet of doublet of triplet, td: triplet of doublet, m: multiplet. Optical rotations were measured with a Horiba SEPA-300 operating at 589 nm. High resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. The wave numbers ($\tilde{\nu}$) of recorded IR-signals are quoted in cm^{-1} on a JASCO FT/IR-4100 spectrometer. UV-vis spectra were recorded on a SHIMADU UV-3600 spectrometer. CD spectra were recorded on a JASCO J-820. HPLC analyses were performed on a JASCO LC-2000 Plus series using 4.6 x 250 mm CHIRALCEL[®] series or CHIRALPAK series. Melting points were recorded on a BUCHI M-565.

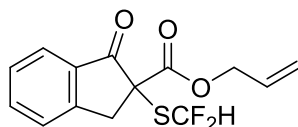
Preparation of α -SCF₂H- β -ketoallylesters 5

Difluoromethylthio- β -ketoallylesters were prepared following a reported procedure.¹

Procedure A: To a schlenk tube charged with β -ketoallylesters (1.0 equiv), K_2CO_3 (1.1 equiv) and *N*-(difluoromethylthio)phthalimide (1.2 equiv) were added CH_2Cl_2 (0.175 M) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography.

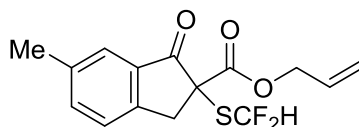
Procedure B: To a mixture of β -ketoallylesters (1.0 equiv), CuF_2 (20 mol %) and K_2CO_3 (20 mol %) in DMAc (0.08 M), 2-((difluoromethyl)sulfonyl)-2-(mesityl- λ^3 -iodaneylidene)-1-(4-nitrophenyl)ethan-1-one (2.0 equiv) were added at room temperature under nitrogen atmosphere. After stirring at room temperature for 24 h. The resulting mixture was then extracted with ethyl acetate, the organic layer was washed with water and brine once then dried over MgSO_4 . The solvent was removed by rotary evaporation and purified by flash silica gel column chromatography.

Allyl 2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5a)



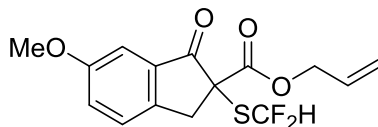
5a was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.22. Pale yellow oil; **procedure A**: 841 mg; 50% yield. **procedure B**: 82.5 mg; 93% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ = 7.85 (d, J = 7.6 Hz, 1 H), 7.75 - 7.68 (m, 1 H), 7.52 (t, J = 55.7 Hz, 1 H), 7.49 - 7.42 (m, 2 H), 5.97 - 5.80 (m, 1 H), 5.37 - 5.21 (m, 2 H), 4.71 (d, J = 5.9 Hz, 2 H), 4.05 (d, J = 18.2 Hz, 1 H), 3.27 (d, J = 17.9 Hz, 1 H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -91.8 (dd, J = 250.7, 55.5 Hz, 1F), -93.3 (dd, J = 250.7, 55.5 Hz, 1F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 196.7, 168.0, 150.5, 136.3, 133.0, 130.7, 128.6, 126.2, 125.8, 120.3 (t, J = 272.2 Hz), 119.5, 67.5, 58.4 - 58.4 (m), 39.4 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2951, 1720, 1606, 1466, 1273, 1184, 1063, 943, 779 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{F}_2\text{NaO}_3\text{S}$ 321.0373; Found 321.0374.

Allyl 2-((difluoromethyl)thio)-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5b)



5b was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.32. Pale yellow oil; **procedure A**: 33.3 mg; 53% yield. **procedure B**: 253.5 mg; 81% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.63 (s, 1H), 7.51 (t, J = 55.0 Hz, 1H), 7.51-7.49 (m, 1H), 7.36 (d, J = 7.9 Hz, 1H), 5.92 - 5.83 (m, 1H), 5.34 - 5.23 (m, 2H), 4.69 (d, J = 5.8 Hz, 2H), 3.98 (d, J = 17.7 Hz, 1H), 3.21 (d, J = 17.7 Hz, 1H), 2.42 (s, 3H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -91.8 (dd, J = 250.7, 55.5 Hz, 1F), -93.4 (dd, J = 250.7, 55.5 Hz, 1F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 196.7, 168.1, 147.9, 138.8, 137.6, 133.1, 130.7, 125.9, 125.6, 120.3 (t, J = 270.7 Hz), 119.4, 67.5, 58.8, 39.1, 21.1 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2951, 1718, 1618, 1495, 1435, 1242, 1184, 1041, 937, 781 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{NaO}_3\text{S}$ 335.0529; Found 335.0529.

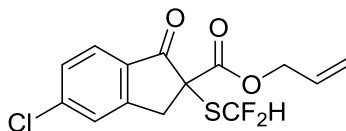
Allyl 2-((difluoromethyl)thio)-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5c)



5c was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.28. Pale yellow oil; **procedure A**: 149.1 mg; 64% yield. **procedure B**: 55.8 mg; 85% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.52 (t, J = 57.5 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.29 - 7.25 (m, 1H), 7.24 (s, 1H), 5.93 - 5.83 (m, 1H), 5.35 - 5.23 (m, 2H), 4.70 (d, J = 5.8 Hz, 2H), 3.95 (d, J = 17.7 Hz, 1H), 3.85 (s, 3H), 3.19 (d, J = 17.7 Hz, 1H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -91.9 (dd, J = 250.7, 55.5 Hz), -93.2 (dd, J = 251.7, 55.5 Hz) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 196.7, 168.0, 160.2, 143.4, 134.2, 130.7, 126.9, 125.9,

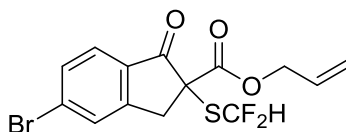
120.3 (t, $J = 271.6$ Hz), 119.4, 106.5, 67.5, 59.1, 55.7, 38.9 ppm. **IR** (NaCl): $\tilde{\nu} = 2947, 1714, 1616, 1495, 1435, 1279, 1230, 1184, 1028, 939, 781$ cm⁻¹. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd. for C₁₅H₁₄F₂NaO₄S 351.0479; Found 351.0478.

Allyl 5-chloro-2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5d)



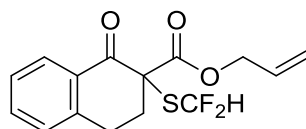
5d was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.26$. Pale yellow oil; **procedure A**: 347mg; >99% yield. **procedure B**: 59.4 mg; 89% yield. **¹H NMR** (500 MHz, CDCl₃): $\delta = 7.78$ (d, $J = 8.2$ Hz, 1H), 7.48 (t, $J = 55.5$ Hz, 1H), 7.48–7.44 (m, 1H), 5.88 (ddt, $J = 16.9, 11.1, 5.7$ Hz, 1 H), 5.37–5.22 (m, 2H), 4.71 (d, $J = 5.8$ Hz, 2H), 4.03 (d, $J = 18.1$ Hz, 1H), 3.26 (d, $J = 18.1$ Hz, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): $\delta = -91.7$ (dd, $J = 250.7, 55.5$ Hz, 1F), -93.3 (dd, $J = 250.7, 55.5$ Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): $\delta = 195.2, 167.6, 151.9, 143.0, 131.4, 130.6, 129.5, 126.8, 126.5, 120.1$ (t, $J = 271.6$ Hz), 119.7, 67.7, 58.6, 39.1 ppm. **IR** (NaCl): $\tilde{\nu} = 3089, 2952, 1722, 1599, 1423, 1319, 1242, 1184, 1068, 943, 895, 781$ cm⁻¹. **HRMS** (EI) m/z : $[M]^+$ Calcd. for C₁₄H₁₁ClF₂O₃S 332.0086; Found 332.0102.

Allyl 5-bromo-2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5e)



5e was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.36$. Yellow semi-solid; **procedure A**: 372.5mg; 99% yield. **procedure B**: 46.7 mg; 62% yield. **¹H NMR** (500 MHz, CDCl₃): $\delta = 7.72 - 7.64$ (m, 2H), 7.64 - 7.59 (m, 1H), 7.48 (t, $J = 55.0$ Hz, 1H), 5.93 - 5.83 (m, 1H), 5.37 - 5.22 (m, 2H), 4.70 (d, $J = 5.5$ Hz, 2H), 4.03 (d, $J = 18.0$ Hz, 1H), 3.26 (d, $J = 18.0$ Hz, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): $\delta = -91.7$ (dd, $J = 250.7, 55.5$ Hz, 1F), -93.3 (dd, $J = 250.7, 55.5$ Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): $\delta = 195.4, 167.5, 152.0, 132.3, 131.9, 131.8, 130.6, 129.6, 126.9, 120.1$ (t, $J = 271.6$ Hz), 119.6, 67.7, 58.5, 39.0 ppm. **IR** (KBr): $\tilde{\nu} = 3089, 2952, 1724, 1595, 1417, 1317, 1240, 1186, 1059, 883, 779$ cm⁻¹. **HRMS** (EI) m/z : $[M]^+$ Calcd. for C₁₄H₁₁BrF₂O₃ 375.9580; Found 375.9598.

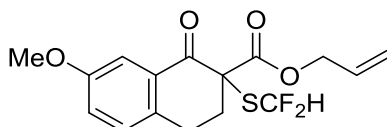
Allyl 2-((difluoromethyl)thio)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5f)



5f was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): $R_f = 0.49$. Colorless oil; 306.4 mg; 98% yield. **¹H NMR** (500 MHz, CDCl₃): $\delta = 8.08$ (d, $J = 7.9$ Hz, 1H), 7.58 - 7.51 (m, 1H), 7.39 (t, $J = 57.5$ Hz, 1H), 7.38 - 7.35 (m, 1H), 7.25 (d, $J = 8.2$ Hz, 1H), 5.85 (ddt, $J = 16.9, 11.1, 5.6$ Hz, 1H),

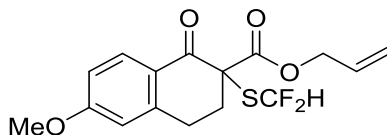
5.30 - 5.18 (m, 2H), 4.75 - 4.64 (m, 2H), 3.18 - 3.09 (m, 1H), 3.04 (ddd, $J = 17.7, 7.3, 4.9$ Hz, 1H), 3.00 - 2.90 (m, 1H), 2.44 - 2.34 (m, 1H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -91.7$ (dd, $J = 254.7, 57.5$ Hz, 1F), -94.2 (dd, $J = 254.7, 55.5$ Hz, 1F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 190.1, 168.4, 142.2, 134.5, 130.8, 130.2, 128.7, 128.7, 127.3, 120.8$ (dd, $J = 271.6, 268.8$ Hz), 119.2, 67.2, 61.3, 32.4, 25.8 ppm. IR (NaCl): $\tilde{\nu} = 3074, 2941, 1739, 1689, 1601, 1454, 1298, 1221, 1190, 1065, 966, 787, 737$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{NaO}_3\text{S}$ 335.0529; Found 335.0523.

Allyl 2-((difluoromethyl)thio)-7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5g)



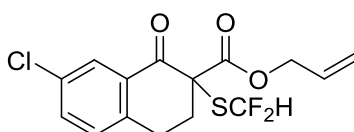
5g was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): $R_f = 0.47$. White semi-solid; 340.0mg; >99% yield. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.52$ (d, $J = 2.4$ Hz, 1H), 7.39 (dd, $J = 55.9, 57.4$ Hz, 1H), 7.16 (d, $J = 8.5$ Hz, 1H), 7.11 (dd, $J = 8.4, 2.6$ Hz, 1H), 5.86 (ddt, $J = 16.8, 11.0, 5.7$ Hz, 1H), 5.31 - 5.19 (m, 2H), 4.70 - 4.69 (m, 2H), 3.83 (s, 3H), 3.11 - 2.87 (m, 3H), 2.41 - 2.32 (m, 1H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -91.7$ (dd, $J = 254.7, 57.5$ Hz, 1F), -94.2 (dd, $J = 254.7, 55.5$ Hz, 1F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 190.1, 168.4, 158.7, 134.8, 131.0, 130.8, 130.0, 123.1, 120.8$ (dd, $J = 272.5, 268.8$ Hz), 119.2, 110.2, 67.2, 61.3, 55.5, 32.7, 25.1 ppm. IR (KBr): $\tilde{\nu} = 3354, 2956, 2835, 2048, 1905, 1691, 1452, 1281, 980, 783, 704$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{NaO}_4\text{S}$ 365.0635; Found 365.0633.

Allyl 2-((difluoromethyl)thio)-6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5h)



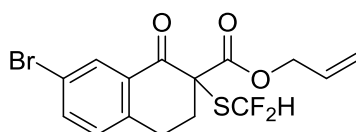
5h was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.48$. Colorless oil; 222.6 mg; 93% yield. ^1H NMR (500 MHz, CDCl_3): $\delta = 8.05$ (d, $J = 8.6$ Hz, 1H), 7.39 (t, $J = 56.5$ Hz, 1H), 6.88 (dd, $J = 8.9, 2.1$ Hz, 1H), 6.73 - 6.64 (m, 1H), 5.87 (ddt, $J = 16.9, 11.0, 5.6$ Hz, 1H), 5.33 - 5.18 (m, 2H), 4.74 - 4.64 (m, 2H), 3.87 (s, 3H), 3.14 - 3.06 (m, 1H), 3.03 - 2.89 (m, 2H), 2.39 - 2.32 (m, 1H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -91.7$ (dd, $J = 253.7, 57.5$ Hz, 1F), -94.2 (dd, $J = 254.7, 56.5$ Hz, 1F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 188.7, 168.6, 164.4, 144.8, 131.3, 130.9, 123.6, 120.9$ (dd, $J = 271.6, 268.9$ Hz), 119.1, 114.1, 112.4, 67.2, 61.1, 55.5, 32.5, 26.2 ppm. IR (NaCl): $\tilde{\nu} = 2945, 2844, 1738, 1674, 1601, 1446, 1261, 1065, 964, 787$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{NaO}_4\text{S}$ 365.0635; Found 365.0633.

Allyl 7-chloro-2-((difluoromethyl)thio)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5i)



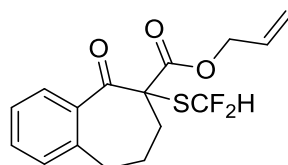
5i was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.34. White solid; 248.5mg; >99% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.04 (s, 1H), 7.50 (dd, J = 8.2, 1.2 Hz, 1H), 7.36 (t, J = 55.0 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 5.86 (ddt, J = 16.9, 11.1, 5.5 Hz, 1H), 5.32 - 5.22 (m, 2H), 4.70 (d, J = 5.5 Hz, 2H), 3.15 - 3.06 (m, 1H), 3.05 - 2.89 (m, 2H), 2.43 - 2.34 (m, 1H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -92.0 (dd, J = 255.6, 57.5 Hz, 1F), -93.9 (dd, J = 254.7, 55.5 Hz, 1F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 189.0, 168.1, 140.4, 134.4, 133.5, 131.5, 130.6, 130.3, 128.3, 120.6 (dd, J = 272.5, 269.8 Hz), 119.5, 67.4, 61.0, 32.2, 25.3 ppm. **IR** (KBr): $\tilde{\nu}$ = 3435, 3369, 3080, 2947, 1722, 1477, 1225, 1076, 924, 837, 791, 640 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{13}\text{ClF}_2\text{NaO}_3\text{S}$ 369.0140; Found 369.0142. **m.p.**: 45.7 - 46.9 $^{\circ}\text{C}$.

Allyl 7-bromo-2-((difluoromethyl)thio)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5j)



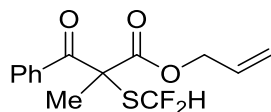
5j was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): R_f = 0.46. White solid; 268.9 mg; 73% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.18 (d, J = 2.1 Hz, 1H), 7.63 (dd, J = 8.24, 2.1 Hz, 1H), 7.36 (t, J = 56.5 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 5.91 - 5.79 (m, 1H), 5.33 - 5.19 (m, 2H), 4.70 (d, J = 5.8 Hz, 2H), 3.13 - 3.03 (m, 1H), 3.03 - 2.88 (m, 2H), 2.38 (ddd, J = 13.6, 7.0, 4.7 Hz, 1H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -92.2 (dd, J = 254.7, 56.5 Hz, 1F), -93.9 (dd, J = 254.7, 56.2 Hz, 1F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 188.9, 168.0, 140.8, 137.2, 131.6, 131.2, 130.6, 130.5, 121.2, 120.5 (dd, J = 269.8, 272.5 Hz), 119.4, 67.3, 61.0, 32.1, 25.3 ppm. **IR** (KBr): $\tilde{\nu}$ = 3076, 2945, 1722, 1691, 1589, 1477, 1180, 1082, 1018, 926, 789 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{13}\text{BrF}_2\text{NaO}_3\text{S}$ 412.9635; Found 412.9638. **m.p.**: 54.3 - 55.9 $^{\circ}\text{C}$.

Allyl 6-((difluoromethyl)thio)-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (5k)



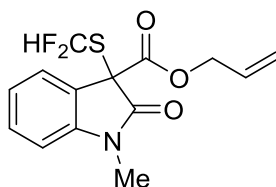
5k was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): R_f = 0.51. Colorless oil; 197.5 mg; 61% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.51 (dd, J = 7.4, 1.2 Hz, 1H), 7.45 - 7.39 (m, 1H), 7.33 - 7.27 (m, 1H), 7.24 (dd, J = 57.7, 54.9 Hz, 1H), 7.16 (d, J = 7.3 Hz, 1H), 5.74 (ddt, J = 16.9, 10.6, 5.9 Hz, 1H), 5.28 - 5.16 (m, 2H), 4.59 (dt, J = 5.8, 1.2 Hz, 2H), 3.00 - 2.88 (m, 2H), 2.65 - 2.54 (m, 1H), 2.15 - 1.93 (m, 3H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -91.1 (dd, J = 253.7, 57.5 Hz, 1F), -94.9 (dd, J = 253.7, 54.5 Hz, 1F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 199.7, 168.6, 138.4, 137.9, 132.2, 130.6, 129.8, 129.2, 126.8, 120.8 (dd, J = 272.5, 267.9 Hz), 119.6, 67.2, 65.0 (d, J = 1.8 Hz), 33.3, 32.4, 23.3 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2945, 1741, 1689, 1599, 1448, 1213, 1065, 960, 785, 742 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{NaO}_3\text{S}$ 349.0686; Found 349.0682.

Allyl 2-((difluoromethyl)thio)-2-methyl-3-oxo-3-phenylpropanoate (5l)



5l was prepared according to the **procedure A** at 40 °C; Eluent (*n*-hexane/CH₂Cl₂ = 7/3): *R_f* = 0.24. Colorless oil; 91.6mg; 31% yield. **¹H NMR** (500 MHz, CDCl₃): δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.89 (t, *J* = 57.5 Hz, 1H), 5.71 - 5.60 (m, 1H), 5.22 - 5.13 (m, 2H), 4.65 - 4.56 (m, 2H), 1.98 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -92.5 (d, *J* = 55.6 Hz, 2F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 191.6, 169.8, 133.7, 133.6, 130.2, 129.1, 128.6, 120.2 (t, *J* = 270.7 Hz), 120.0, 67.3, 61.5, 24.1 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3066, 2943, 1738, 1685, 1448, 1257, 1066, 960, 795 cm⁻¹. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd. for C₁₄H₁₄F₂NaO₃S 323.0529; Found 323.0529.

Allyl 3-((difluoromethyl)thio)-1-methyl-2-oxoindoline-3-carboxylate (5m)



5m was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): *R_f* = 0.57. Pale red oil; 201.0 mg; 51% yield. **¹H NMR** (500 MHz, CDCl₃): δ = 7.45 - 7.38 (m, 2H), 7.43 (dd, *J* = 58.6, 54.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 5.84 (ddt, *J* = 16.8, 11.0, 5.5 Hz, 1H), 5.29 - 5.19 (m, 2H), 4.68 (d, *J* = 5.8 Hz, 2H), 3.29 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -91.5 (dd, *J* = 254.7, 58.5 Hz, 1F), -97.5 (dd, *J* = 254.7, 54.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 171.2, 165.7, 143.3, 130.9, 130.5, 124.9, 123.6, 119.2, 119.1 (dd, *J* = 277.0, 269.8 Hz), 109.1, 67.5, 56.8 (d, *J* = 4.5 Hz), 27.0 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3062, 2943, 1722, 1608, 1471, 1348, 1227, 1065, 754 cm⁻¹. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd. for C₁₄H₁₃NF₂NaO₃S 336.0482; Found 336.0483.

Preparation of α-SCF₃-β-ketoallylesters **8**

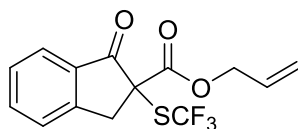
Trifluoromethylthio-β-ketoallylesters were prepared following a reported procedure.²

Procedure A: β-Ketoallylesters (1.0 equiv), *N*-trifluoromethylthiosaccharin (1.3 equiv), and DMAP (2.0 equiv) were added to toluene (0.1 M). The mixture was stirred at room temperature for 8 h. The reaction mixture was filtered through a pad of silica-gel and concentrated. The residue was purified by flash silica-gel column chromatography.

Procedure B: To a mixture of β -ketoallylesters (1.0 equiv), CuF_2 (20 mol %) and K_2CO_3 (20 mol %) in DMAc (0.08 M), 1-phenyl-2-(phenyl- λ^3 -iodaneylidene)-2-((trifluoromethyl)sulfonyl)ethan-1-one (2.0 equiv) was added at room temperature under nitrogen atmosphere. After stirring at room temperature for 12 h, the resulting mixture was then extracted with ethyl acetate. The organic layer was washed with water and brine once then dried over MgSO_4 . The solvent was removed by rotary evaporation and purified by flash silica gel column chromatography.

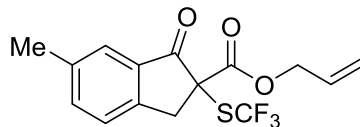
Procedure C: NaH (1.1 equiv, 60% dispersion in mineral oil) in THF (0.3 M) was added a solution of β -ketoesters (1.0 equiv) in THF (0.3 M) under nitrogen atmosphere. The mixture was stirred at room temperature for 0.5 h. The mixture was cooled to 0 °C and a solution of *N*-trifluoromethylthiosaccharin (1.3 equiv) in THF (0.3 M) was added. The mixture was stirred for 0.5 h at this temperature. The reaction was quenched by water, extracted with Et_2O . The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica-gel column chromatography.

Allyl 1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate (8a)



8a was prepared according to the **procedure B and C**; Eluent (*n*-hexane/ CH_2Cl_2 = 7/3): R_f = 0.28. Colorless oil; **procedure B**: 13.2 mg; 21% yield. **procedure C**: 663.6 mg; 84% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.84 (d, J = 7.9 Hz, 1H), 7.71 (t, J = 7.3 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 5.93 - 5.77 (m, 1H), 5.35 - 5.21 (m, 2H), 4.67 (d, J = 5.2 Hz, 2H), 4.20 (d, J = 17.7 Hz, 1H), 3.68 (d, J = 17.7 Hz, 1H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -37.5 (s, 3F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 194.7, 166.5, 151.6, 136.5, 132.8, 130.5, 129.8 (q, J = 309.1 Hz), 128.5, 126.2, 125.7, 119.4, 67.8, 63.5, 40.3 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2951, 1728, 1606, 1466, 1271, 1238, 1155, 1111, 993, 756 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NaO}_3\text{S}$ 339.0279; Found 339.0272.

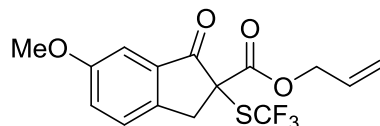
Allyl 6-methyl-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate (8b)



8b was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ether = 9/1): R_f = 0.24. Pale yellow oil; **procedure A**: 254 mg; 81% yield. **procedure B**: 30.7 mg; 46% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.62 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 5.84 (ddt, J = 16.7, 11.0, 5.4 Hz, 1H), 5.32 - 5.21 (m, 2H), 4.66 (d, J = 5.2 Hz, 2H), 4.13 (d, J = 17.7 Hz, 1H), 3.62 (d, J = 17.7 Hz, 1H), 2.42 (s, 3H) ppm. $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ = -37.5 (s, 3F) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 194.8, 166.6, 149.1, 138.7, 137.8, 133.0, 130.6, 129.8 (q, J = 309.1 Hz), 125.9, 125.4, 119.3, 67.7, 63.8, 40.0, 21.0 ppm. **IR**

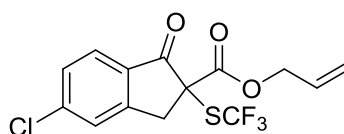
(NaCl): $\tilde{\nu}$ = 2951, 1724, 1618, 1495, 1439, 1279, 1238, 1153, 1111, 1020, 937, 820 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NaO}_3\text{S}$ 353.0435; Found 353.0437.

Allyl 6-methoxy-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-indene-2-carboxylate (8c)



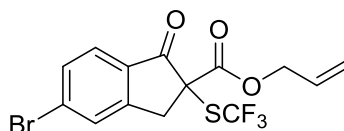
8c was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.26. Pale yellow oil; **procedure A**: 375.3 mg; 88% yield. **procedure B**: 25.0 mg; 36% yield. **^1H NMR** (300 MHz, CDCl_3): δ = 7.45 - 7.37 (m, 1H), 7.33 - 7.22 (m, 2H), 5.85 (ddt, J = 16.6, 10.9, 5.3 Hz, 1H), 5.34 - 5.21 (m, 2H), 4.67 (dd, J = 5.6, 1.2 Hz, 2H), 4.09 (d, J = 17.6 Hz, 1H), 3.87 - 3.83 (m, 3H), 3.59 (d, J = 17.6 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -37.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 194.8, 166.6, 160.1, 144.6, 134.1, 130.6, 129.7 (q, J = 309.4 Hz), 126.9, 126.2, 119.4, 106.3, 67.8, 64.1, 55.7, 39.7 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3074, 2947, 2841, 1724, 1618, 1495, 1435, 1279, 1236, 1155, 1111, 1024, 939, 758 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NaO}_4\text{S}$ 369.0384; Found 369.0373.

Allyl 5-chloro-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-indene-2-carboxylate (8d)



8d was prepared according to the **procedure A and B**; Eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.25. White solid; **procedure A**: 299 mg; 73% yield. **procedure B**: 52.6 mg; 75% yield. **^1H NMR** (500 MHz, CDCl_3): δ = 7.77 (d, J = 7.9 Hz, 1H), 7.52 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 5.91 - 5.76 (m, 1H), 5.35 - 5.18 (m, 2H), 4.67 (d, J = 5.2 Hz, 2H), 4.16 (d, J = 17.7 Hz, 1H), 3.65 (d, J = 18.0 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -37.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 193.4, 166.2, 53.0, 143.4, 131.3, 130.4, 129.7 (q, J = 309.7 Hz), 129.4, 126.7, 126.5, 119.7, 68.0, 63.5, 40.0 ppm. **IR** (KBr): $\tilde{\nu}$ = 3099, 2958, 1724, 1601, 1417, 1232, 1196, 1153, 1115, 1066, 993, 893, 858 cm^{-1} . **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd. for $\text{C}_{14}\text{H}_{10}\text{ClF}_3\text{O}_3\text{S}$ 349.9991; Found 349.9995. **m.p.**: 44.7 - 45.9 $^{\circ}\text{C}$.

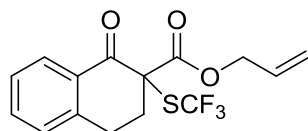
Allyl 5-bromo-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-indene-2-carboxylate (8e)



8e was prepared according to the **procedure A and B**; eluent (*n*-hexane/ether = 9/1): R_f = 0.32. Pale yellow solid; **Procedure A**: 157.9 mg; 80% yield. **Procedure B**: 3.5 mg; 4% yield. **^1H NMR** (500 MHz, CDCl_3): δ = 7.77 - 7.65 (m, 2H), 7.61 (d, J = 7.9 Hz, 1H), 5.85 (ddt, J = 17.1, 10.7, 5.5 Hz, 1H), 5.37 - 5.22 (m, 2H), 4.67 (d, J = 5.5 Hz, 2H), 4.16 (d, J = 18.0 Hz, 1H), 3.66 (d, J = 18.0 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -37.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 193.7, 166.1, 153.0, 132.3, 131.7, 130.4,

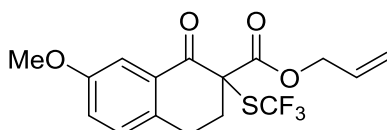
129.7 (q, $J = 309.4$ Hz), 129.6, 126.7, 119.7, 68.0, 63.4, 39.9 ppm. **IR** (KBr): $\tilde{\nu} = 3093, 2956, 1724, 1597, 1415, 1242, 1200, 1115, 1055, 993, 937, 883$ cm⁻¹. **HRMS** (EI) m/z : [M]⁺ Calcd. for C₁₄H₁₀BrF₃O₃S 393.9486; Found 393.9494. **m.p.**: 64.1 - 65.5 °C.

Allyl 1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8f)



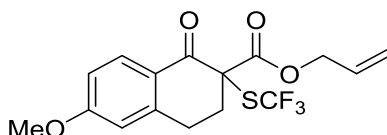
8f was prepared according to the **procedure C**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.32$. Pale yellow oil; 457.4 mg; 63% yield. **¹H NMR** (500 MHz, CDCl₃): $\delta = 8.03$ (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 7.6$ Hz, 1H), 5.89 - 5.73 (m, 1H), 5.28 - 5.14 (m, 2H), 4.70 - 4.62 (m, 2H), 3.34 - 3.20 (m, 1H), 3.16 - 3.07 (m, 2H), 2.63 - 2.47 (m, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): $\delta = -36.4$ (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl₃): $\delta = 188.9, 166.6, 142.5, 134.6, 130.6, 130.4, 129.8$ (q, $J = 309.4$ Hz), 128.8, 128.6, 127.2, 119.0, 67.2, 64.4, 32.7, 26.2 ppm. **IR** (NaCl): $\tilde{\nu} = 2941, 1741, 1691, 1601, 1454, 1298, 1221, 1188, 1107, 982, 964, 939, 889$ cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₅H₁₃F₃NaO₃S 353.0435; Found 353.0432.

Allyl 7-methoxy-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8g)



8g was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.28$. White solid; 198 mg; 69% yield. **¹H NMR** (300 MHz, CDCl₃): $\delta = 7.48$ (d, $J = 2.6$ Hz, 1H), 7.19 - 7.10 (m, 2H), 5.93 - 5.72 (m, 1H), 5.30 - 5.16 (m, 2H), 4.72 - 4.60 (m, 2H), 3.84 (s, 3H), 3.23 - 2.99 (m, 3H), 2.61 - 2.46 (m, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): $\delta = -36.4$ (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl₃): $\delta = 189.0, 166.7, 158.6, 135.1, 131.1, 130.7, 130.1, 129.8$ (q, $J = 309.4$ Hz), 123.4, 119.1, 110.0, 67.2, 64.3, 55.5, 33.0, 25.5 ppm. **IR** (KBr): $\tilde{\nu} = 3016, 2966, 2918, 2841, 1753, 1680, 1608, 1498, 1442, 1286, 1265, 1225, 1203, 1176, 1136, 1103, 1038, 910$ cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₆H₁₅F₃NaO₄S 383.0541; Found 383.0535. **m.p.**: 38.3 - 38.9 °C.

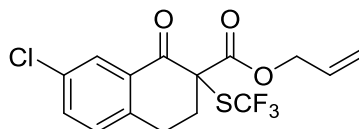
Allyl 6-methoxy-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8h)



8h was prepared according to the **procedure A**; Eluent (*n*-hexane/CH₂Cl₂ = 1/1): $R_f = 0.42$. White solid; 211.2 mg; 73% yield. **¹H NMR** (300 MHz, CDCl₃): $\delta = 8.00$ (d, $J = 8.8$ Hz, 1H), 6.92 - 6.79 (m, 1H), 6.68 (s, 1H), 5.92 - 5.75 (m, 1H), 5.33 - 5.15 (m, 2H), 4.66 (d, $J = 5.6$ Hz, 2H), 3.87 (s, 3H), 3.29 - 3.00 (m, 3H), 2.61 - 2.48 (m, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): $\delta = -36.5$ (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl₃):

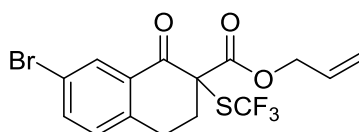
δ = 187.4, 166.8, 164.6, 145.3, 131.2, 130.8, 129.9 (q, J = 309.4 Hz), 123.7, 119.0, 114.2, 112.3, 67.1, 64.3, 55.6, 32.8, 26.6 ppm. **IR** (KBr): $\tilde{\nu}$ = 2983, 2949, 2848, 1734, 1666, 1597, 1444, 1356, 1263, 1215, 1109, 1034, 947, 849 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NaO}_4\text{S}$ 383.0541; Found 383.0544. **m.p.**: 65.8 - 66.7 $^{\circ}\text{C}$.

Allyl 7-chloro-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8i)



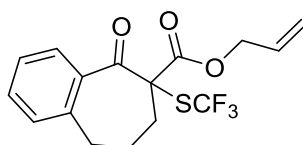
8i was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.33. White solid; 233.7 mg; 81% yield. **^1H NMR** (300 MHz, CDCl_3): δ = 7.99 (d, J = 2.1 Hz, 1H), 7.50 (dd, J = 8.2, 2.4 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 5.91 - 5.70 (m, 1H), 5.33 - 5.16 (m, 2H), 4.74 - 4.60 (m, 2H), 3.28 - 3.02 (m, 3H), 2.62 - 2.48 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -36.3 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 187.9, 166.4, 140.7, 134.6, 133.5, 131.6, 130.5, 130.4, 129.6 (q, J = 309.7 Hz), 128.2, 119.4, 67.4, 64.0, 32.5, 25.7 ppm. **IR** (KBr): $\tilde{\nu}$ = 3066, 2952, 1738, 1685, 1477, 1408, 1238, 1213, 1136, 1105, 949, 825 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{ClF}_3\text{NaO}_3\text{S}$ 387.0045; Found 387.0044. **m.p.**: 74.5 - 75.5 $^{\circ}\text{C}$.

Allyl 7-bromo-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8j)



8j was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.34. White solid; 205.6 mg; 63% yield. **^1H NMR** (300 MHz, CDCl_3): δ = 8.15 (d, J = 2.1 Hz, 1H), 7.65 (dd, J = 8.2, 2.4 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 5.93 - 5.70 (m, 1H), 5.35 - 5.15 (m, 2H), 4.73 - 4.60 (m, 2H), 3.26 - 2.99 (m, 3H), 2.62 - 2.49 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -36.3 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 187.8, 166.3, 141.2, 137.4, 131.8, 131.2, 130.6, 130.5, 129.6 (q, J = 309.4 Hz), 121.2, 119.4, 67.4, 64.0, 32.5, 25.8 ppm. **IR** (KBr): $\tilde{\nu}$ = 3062, 2952, 1738, 1682, 1587, 1441, 1402, 1271, 1238, 1213, 1134, 1105, 949, 823 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{BrF}_3\text{NaO}_3\text{S}$ 430.9540; Found 430.9548. **m.p.**: 77.6 - 78.5 $^{\circ}\text{C}$.

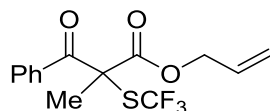
Allyl 5-oxo-6-((trifluoromethyl)thio)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (8k)



8k was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.40. Colorless oil; 180.2 mg; 52% yield. **^1H NMR** (300 MHz, CDCl_3): δ = 7.49 - 7.33 (m, 2H), 7.30 - 7.22 (m, 1H), 7.17

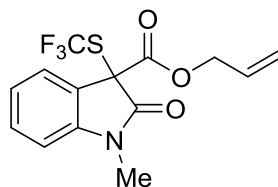
(d, $J = 7.6$ Hz, 1H), 5.65 - 5.46 (m, 1H), 5.23 - 5.06 (m, 2H), 4.44 (d, $J = 6.2$ Hz, 2H), 3.11 - 2.87 (m, 3H), 2.42 (ddd, $J = 14.4, 6.3, 4.8$ Hz, 1H), 2.25 - 2.12 (m, 1H), 2.08 - 1.94 (m, 1H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -37.3$ (s, 3F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 197.7, 167.5, 139.6, 137.2, 131.8, 130.5, 130.0, 129.9$ (q, $J = 309.1$ Hz), 129.7, 126.5, 119.5, 69.3, 67.2, 36.0, 33.6, 25.0 ppm. IR (NaCl): $\tilde{\nu} = 2947, 2868, 1745, 1689, 1446, 1254, 1215, 1115, 945, 739$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NaO}_3\text{S}$ 367.0592; Found 367.0589.

Allyl 2-methyl-3-oxo-3-phenyl-2-((trifluoromethyl)thio)propanoate (8l)



8l was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 9/1): $R_f = 0.42$. Colorless oil; 199.6 mg; 63% yield. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.94$ (d, $J = 7.9$ Hz, 2H), 7.64 - 7.53 (m, 1H), 7.50 - 7.40 (m, 2H), 5.74 - 5.57 (m, 1H), 5.25 - 5.12 (m, 2H), 4.61 (d, $J = 5.5$ Hz, 2H), 2.12 (s, 3H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -37.0$ (s, 3F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 190.7, 169.2, 133.7, 133.3, 130.1, 129.6$ (q, $J = 308.8$ Hz), 129.2, 128.7, 120.0, 67.5, 63.7, 24.3 ppm. IR (NaCl): $\tilde{\nu} = 3068, 2993, 2947, 1741, 1691, 1448, 1255, 1221, 1124, 964$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NaO}_3\text{S}$ 341.0435; Found 341.0430.

Allyl 1-methyl-2-oxo-3-((trifluoromethyl)thio)indoline-3-carboxylate (8m)



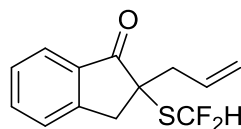
8m was prepared according to the **procedure A**; Eluent (*n*-hexane/ethyl acetate = 3/1): $R_f = 0.35$. Pale red oil; 169.7 mg; 51% yield. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.46 - 7.39$ (m, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.9$ Hz, 1H), 5.77 (ddt, $J = 16.8, 11.0, 5.5$ Hz, 1H), 5.22 - 5.15 (m, 2H), 4.64 (d, $J = 5.2$ Hz, 2H), 3.29 (s, 3H) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -38.4$ (s, 3F) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = 170.3, 164.7, 143.5, 131.0, 130.2, 128.7$ (q, $J = 310.0$ Hz), 124.9, 124.4, 123.5, 119.2, 109.1, 67.7, 27.2 ppm. IR (NaCl): $\tilde{\nu} = 2945, 1741, 1722, 1612, 1473, 1365, 1352, 1223, 1157, 1119, 995, 758$ cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NaO}_3\text{S}$ 354.0388; Found 354.0396.

General procedure for the DAAA reaction of 5

Procedure: Pd_2dba_3 (5 mol %) and Ligand (12.5 mol %) were dissolved in TBME (3.75 mL) and the mixture was stirred for 0.5 hour under nitrogen atmosphere. The mixture was cooled to -40 $^\circ\text{C}$ and a solution of substrate **5** (0.15 mmol) in TBME (3.75 mL) was added dropwise to the mixture. The resulting mixture was

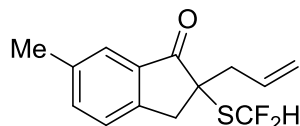
stirred at prescribed temperature. After completion of the reaction, solvent was removed under reduced pressure and the residue was purified by flash silica-gel column chromatography to give the desired product **4**.

2-Allyl-2-((difluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (**4a**)



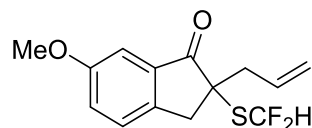
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.44. Pale yellow oil; 24.9 mg; 98% yield, 92% ee. $[\alpha]_D^{25} = -124.4$ (c = 0.83, CHCl_3 , 92% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 40.258 min for major isomer, t_R = 56.925 min for minor isomer. **¹H NMR** (500 MHz, CDCl_3): δ = 7.83 (d, J = 7.6 Hz, 1H), 7.68 - 7.61 (m, 1H), 7.45 - 7.39 (m, 2H), 7.33 (dd, J = 59.8, 53.4 Hz, 1H), 5.76 (ddt, J = 17.1, 10.0, 7.1 Hz, 1H), 5.24 - 5.13 (m, 2H), 3.44 (d, J = 18.3 Hz, 1H), 3.04 (d, J = 18.0 Hz, 1H), 2.84 - 2.69 (m, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -88.2 (dd, J = 257.6, 59.5 Hz, 1F), -98.1 (dd, J = 257.6, 52.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 202.5, 150.2, 135.9, 133.9, 131.7, 128.3, 126.3, 125.3, 120.3, 119.7 (dd, J = 274.3, 265.2 Hz), 55.0 (d, J = 3.6 Hz), 40.9, 38.9 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3081, 2922, 1709, 1608, 1433, 1277, 1213, 1036, 928, 791, 741 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{12}\text{F}_2\text{NaOS}$ 277.0475; Found 277.0471.

2-Allyl-2-((difluoromethyl)thio)-6-methyl-2,3-dihydro-1H-inden-1-one (**4b**)



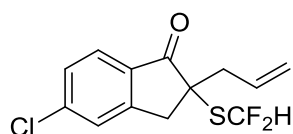
Eluent (*n*-hexane/ether = 9/1): R_f = 0.45. Pale yellow oil; 30.6 mg; 73% yield, 85% ee. $[\alpha]_D^{25} = -119.4$ (c = 1.02, CHCl_3 , 85% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 36.525 min for major isomer, t_R = 62.908 min for minor isomer. **¹H NMR** (500 MHz, CDCl_3): δ = 7.62 (s, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.33 (dd, J = 59.8, 53.4 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 5.74 (ddt, J = 17.1, 10.0, 7.2 Hz, 1H), 5.23 - 5.11 (m, 2H), 3.38 (d, J = 18.0 Hz, 1H), 2.99 (d, J = 18.0 Hz, 1H), 2.82 - 2.69 (m, 2H), 2.42 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -88.3 (dd, J = 258.6, 59.5 Hz, 1F), -98.1 (dd, J = 258.6, 53.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 202.6, 147.5, 138.4, 137.2, 134.0, 131.7, 126.0, 125.1, 120.2, 119.8 (dd, J = 274.3, 265.2 Hz), 55.4 (d, J = 2.7 Hz), 40.9, 38.5, 21.1 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2924, 1709, 1618, 1495, 1433, 1284, 1065, 926, 787 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{NaOS}$ 291.0631; Found 291.0630.

2-Allyl-2-((difluoromethyl)thio)-6-methoxy-2,3-dihydro-1H-inden-1-one (**4c**)



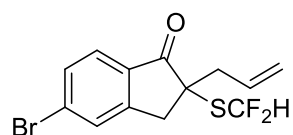
Eluent (*n*-hexane/ether = 9/1): R_f = 0.28. Yellow semi-solid; 22.7 mg; 53% yield, 93% ee. $[\alpha]_D^{25} = -99.6$ (c = 0.76, CHCl_3 , 93% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 26.408 min for major isomer, t_R = 41.067 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 7.32 (dd, J = 59.5, 53.4 Hz, 1H), 7.31 - 7.28 (m, 1H), 7.25 - 7.22 (m, 2H), 5.79 - 5.68 (m, 1H), 5.23 - 5.12 (m, 2H), 3.85 (s, 3H), 3.36 (d, J = 17.7, 1H), 2.97 (d, J = 17.7 Hz, 1H), 2.82 - 2.68 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -88.3 (dd, J = 257.6, 59.5 Hz, 1F), -97.9 (dd, J = 258.6, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 202.5, 160.0, 143.0, 135.1, 131.7, 127.1, 125.4, 120.3, 119.7, (dd, J = 274.3, 266.1 Hz), 106.1, 55.8 (d, J = 2.7 Hz), 55.6, 41.0, 38.3 ppm. **IR** (KBr): $\tilde{\nu}$ = 2925, 1707, 1616, 1493, 1435, 1281, 1232, 1030, 928, 787, 742 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{NaO}_2\text{S}$ 307.0580; Found 307.0577.

2-Allyl-5-chloro-2-((difluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (4d)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.49. Yellow solid; 39.9 mg; 92% yield, 92% ee. $[\alpha]_D^{25} = -146.7$ (c = 1.33, CHCl_3 , 92% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 19.633 min for major isomer, t_R = 27.425 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 7.78 - 7.72 (m, 1H), 7.44 - 7.40 (m, 2H), 7.28 (dd, J = 59.5, 53.4 Hz, 1H), 5.72 (ddt, J = 17.2, 10.0, 7.2 Hz, 1H), 5.24 - 5.13 (m, 2H), 3.41 (d, J = 18.0 Hz, 1H), 3.03 (d, J = 18.3 Hz, 1H), 2.82 - 2.69 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -88.3 (dd, J = 257.6, 59.5 Hz, 1F), -97.9 (dd, J = 257.6, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 201.1, 151.6, 142.5, 132.4, 131.4, 129.2, 126.6, 126.4, 120.6, 119.6 (dd, J = 275.2, 267.0 Hz), 55.2 (d, J = 3.6 Hz), 40.9, 38.6 ppm. **IR** (KBr): $\tilde{\nu}$ = 3082, 2924, 1712, 1601, 1431, 1321, 1267, 1209, 1066, 928, 785 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{11}\text{ClF}_2\text{NaOS}$ 311.0085; Found 311.0095. **m.p.**: 38.0 - 41.4 °C.

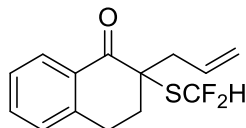
2-Allyl-5-bromo-2-((difluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (4e)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.40. Pale yellow oil; 42.3 mg; 87% yield, 94% ee. $[\alpha]_D^{25} = -115.2$ (c = 1.41, CHCl_3 , 94% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 25.917 min for major isomer, t_R = 31.333 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 7.68 (d, J = 7.9 Hz, 1H), 7.62 - 7.55 (m, 2H), 7.27 (dd, J = 59.5, 53.4 Hz, 1H), 5.77 - 5.65 (m, 1H), 5.24 - 5.13 (m, 2H), 3.42 (d, J = 18.3 Hz, 1H), 3.03 (d, J = 18.3 Hz, 1H), 2.82 - 2.69 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -88.3 (dd, J = 257.6, 59.5 Hz, 1F), -97.9 (dd, J = 257.6, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 201.3, 151.7, 132.8, 132.0, 131.3, 129.7, 126.4, 120.7, 119.6 (dd, J = 275.2, 267.0 Hz), 55.1 (d, J = 2.7 Hz), 40.9, 38.5 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3080, 2924, 1712, 1595,

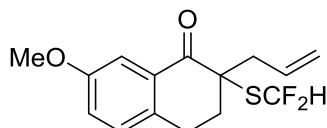
1431, 1319, 1265, 1207, 1059, 928, 872, 833, 785 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{11}\text{BrF}_2\text{NaOS}$ 354.9580; Found 354.9579.

2-Allyl-2-((difluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (4f)



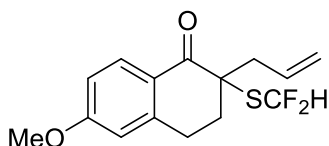
Eluent (*n*-hexane/ether = 9/1): R_f = 0.44. Yellow solid; 35.2 mg; 87% yield, 88% ee. $[\alpha]_{\text{D}}^{25}$ = +17.6 (c = 1.17, CHCl_3 , 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 28.117 min for major isomer, t_R = 44.742 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 8.10 - 8.01 (m, 1H), 7.43 (td, J = 7.5, 1.2 Hz, 1H), 7.30 - 7.25 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.88 (dd, J = 59.5, 53.4 Hz, 1H), 5.81 - 5.71 (m, 1H), 5.14 - 5.07 (m, 2H), 3.11 (ddd, J = 17.3, 12.6, 4.6 Hz, 1H), 2.83 - 2.72 (m, 3H), 2.34 - 2.24 (m, 1H), 2.15 - 2.08 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -87.4 (dd, J = 256.6, 59.5 Hz, 1F), -97.5 (dd, J = 259.6, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 192.5, 142.6, 133.9, 132.2, 130.2, 128.8, 128.6, 127.1, 120.7 (dd, J = 274.3, 265.2 Hz), 120.0, 55.1 (d, J = 2.7 Hz), 41.5, 32.4, 25.3 ppm. **IR** (KBr): $\tilde{\nu}$ = 3649, 2931, 1672, 1601, 1433, 1308, 1238, 1065, 922, 791, 746 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{NaOS}$ 291.0631; Found 291.0633. **m.p.**: 38.0 - 42.3 $^{\circ}\text{C}$.

2-Allyl-2-((difluoromethyl)thio)-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (4g)



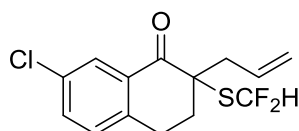
Eluent (*n*-hexane/ether = 9/1): R_f = 0.29. Pale yellow solid; 36.7 mg; 80% yield, 91% ee. $[\alpha]_{\text{D}}^{25}$ = +26.4 (c = 1.22, CHCl_3 , 91% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 20.933 min for major isomer, t_R = 33.350 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 7.59 (d, J = 2.8 Hz, 1H), 7.16 - 7.12 (m, 1H), 7.10 - 7.08 (m, 1H), 6.97 (dd, J = 59.5, 53.4 Hz, 1H), 5.89 - 5.79 (m, 1H), 5.21 - 5.15 (m, 2H), 3.85 (s, 3H), 3.11 (ddd, J = 17.3, 12.6, 4.6 Hz, 1H), 2.87 - 2.76 (m, 3H), 2.40 - 2.30 (m, 1H), 2.22 - 2.14 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -87.4 (dd, J = 255.6, 59.5 Hz, 1F), -97.5 (dd, J = 256.6, 56.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 192.5, 158.6, 135.2, 132.2, 130.9, 129.8, 122.4, 120.7 (dd, J = 274.3, 265.2 Hz), 120.0, 110.5, 55.5, 55.0 (d, J = 2.7 Hz), 41.5, 32.7, 24.6 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3086, 2954, 1658, 1500, 1421, 1329, 1284, 1012, 930, 791 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_2\text{NaO}_2\text{S}$ 321.0737; Found 321.0727. **m.p.**: 58.4 - 59.6 $^{\circ}\text{C}$.

2-Allyl-2-((difluoromethyl)thio)-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (4h)



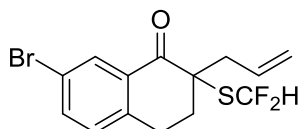
Eluent (*n*-hexane/ether = 9/1): R_f = 0.15. Yellow solid; 22.5 mg; 75% yield, 50% ee. $[\alpha]_D^{25}$ = -11.82 (c = 0.75, CHCl_3 , 50% ee). HPLC conditions: CHIRALCEL® OJ-H column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.4 mL/min, λ = 254 nm, t_R = 27.792 min for major isomer, t_R = 33.175 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 8.09 (dd, J = 8.9 Hz, 1H), 7.01 (dd, J = 59.5, 53.1 Hz, 1H), 6.89 - 6.84 (m, 1H), 6.67 (s, 1H), 5.89 - 5.78 (m, 1H), 5.21 - 5.13 (m, 2H), 3.86 (s, 3H), 3.17 (ddd, J = 17.1, 12.8, 4.3 Hz, 1H), 2.87 - 2.78 (m, 3H), 2.40 - 2.30 (m, 1H), 2.20 - 2.12 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -87.2 (dd, J = 256.6, 59.5 Hz, 1F), -97.6 (dd, J = 252.7, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 191.5, 164.0, 145.2, 132.4, 131.4, 123.6, 120.8 (dd, J = 274.3, 264.3 Hz), 119.8, 113.9, 112.3, 55.5, 54.9 (d, J = 2.7 Hz), 41.7, 32.6, 25.8 ppm. **IR** (KBr): $\tilde{\nu}$ = 3084, 3028, 2943, 2843, 1591, 1433, 1279, 1055, 897, 785 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_2\text{NaO}_2\text{S}$ 321.0737; Found 321.0734. **m.p.**: 51.6 - 56.1 $^\circ\text{C}$.

2-Allyl-7-chloro-2-((difluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (4i)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.37. Yellow solid; 37.6 mg; 80% yield, 93% ee. $[\alpha]_D^{25}$ = $+26.8$ (c = 1.25, CHCl_3 , 93% ee). HPLC conditions: CHIRALCEL® OJ-H column, eluent: *n*-hexane/*i*PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 14.533 min for major isomer, t_R = 23.675 min for minor isomer. **^1H NMR** (500 MHz, CDCl_3): δ = 8.09 (d, J = 2.14 Hz, 1H), 7.46 (dd, J = 8.1, 2.0 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 6.91 (dd, J = 59.2, 53.1 Hz, 1H), 5.82 (ddt, J = 17.1, 10.2, 7.1 Hz, 1H), 5.23 - 5.14 (m, 2H), 3.14 (ddd, J = 17.4, 12.7, 4.7 Hz, 1H), 2.90 - 2.80 (m, 3H), 2.40 - 2.30 (m, 1H), 2.24 - 2.15 (m, 1H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -87.6 (dd, J = 256.6, 58.5 Hz, 1F), -97.3 (dd, J = 256.6, 53.5 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 191.4, 140.7, 133.8, 133.3, 131.9, 131.5, 130.2, 128.5, 120.5 (dd, J = 274.3, 265.2 Hz), 120.3, 54.9 (d, J = 2.7 Hz), 41.3, 32.2, 24.8 ppm. **IR** (KBr): $\tilde{\nu}$ = 3080, 2927, 1676, 1595, 1479, 1410, 1306, 1219, 1065, 926, 791 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{ClF}_2\text{NaOS}$ 325.0241; Found 325.0240. **m.p.**: 48.6 - 52.4 $^\circ\text{C}$.

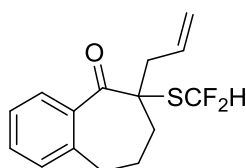
2-Allyl-7-bromo-2-((difluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (4j)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.40. Yellow solid; 31.7 mg; 60% yield, 93% ee. $[\alpha]_D^{25}$ = $+24.4$ (c = 1.06, CHCl_3 , 93% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 17.442 min for major isomer, t_R = 28.133 min for minor isomer. **^1H NMR**

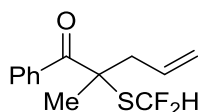
(500 MHz, CDCl₃): δ = 8.24 (s, 1H), 7.61 (dd, J = 8.1, 2.0 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 6.91 (dd, J = 59.2, 53.1 Hz, 1H), 5.87 - 5.74 (m, 1H), 5.24 - 5.11 (m, 2H), 3.16 - 3.04 (m, 1H), 2.88 - 2.75 (m, 3H), 2.40 - 2.28 (m, 1H), 2.24 - 2.13 (m, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -87.6 (dd, J = 256.6, 59.5 Hz, 1F), -97.3 (dd, J = 253.7, 52.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 191.2, 141.2, 136.7, 131.9, 131.7, 131.5, 130.4, 121.1, 120.5 (dd, J = 274.3, 265.2 Hz), 120.3, 54.8, 41.3, 32.1, 24.9 ppm. **IR** (KBr): $\tilde{\nu}$ = 3319, 3074, 2929, 1834, 1668, 1587, 1477, 1406, 1306, 1217, 1061, 914, 787, 742 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₄H₁₃BrF₂NaOS 368.9736; Found 368.9732. **m.p.**: 45.9 - 48.7 °C.

6-Allyl-6-((difluoromethyl)thio)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (4k)



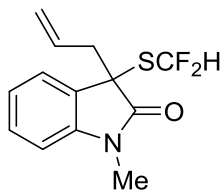
Eluent (*n*-hexane/ether = 9/1): R_f = 0.46. Pale yellow oil; 24.1 mg; >99% yield, 81% ee. $[\alpha]_D^{25}$ = +1.8 (c = 0.80, CHCl₃, 81% ee). HPLC conditions: CHIRALCEL[®] OJ-3 column, eluent: *n*-hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 15.908 min for major isomer, t_R = 19.233 min for minor isomer. **¹H NMR** (500 MHz, CDCl₃): δ = 7.36 - 7.28 (m, 2H), 7.25 - 7.20 (m, 1H), 7.15 (dd, J = 59.5, 53.4 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 5.88 - 5.75 (m, 1H), 5.17 - 5.06 (m, 2H), 2.94 - 2.84 (m, 1H), 2.80 (dd, J = 14.7, 6.1 Hz, 1H), 2.72 - 2.61 (m, 2H), 1.90 - 1.77 (m, 3H), 1.74 - 1.61 (m, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -88.6 (dd, J = 257.6, 59.5 Hz, 1F), -97.5 (dd, J = 257.6, 53.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 206.2, 139.2, 137.0, 131.9, 131.7, 128.5, 128.3, 126.8, 120.9 (dd, J = 274.3, 265.2 Hz), 119.9, 58.6 (d, J = 2.7 Hz), 40.4, 31.5, 30.9, 22.0 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3074, 2943, 1680, 1599, 1450, 1298, 1250, 1061, 926, 787 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₅H₁₆F₂NaOS 305.0788; Found 305.0782.

2-((difluoromethyl)thio)-2-methyl-1-phenylpent-4-en-1-one (4l)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.25. The reaction was carried at 40 °C; Colorless oil; 7.3 mg; 19% yield, 33% ee. $[\alpha]_D^{25}$ = +6.4 (c = 0.24, CHCl₃, 33% ee). HPLC conditions: CHIRALPAK[®] IG column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 22.225 min for major isomer, t_R = 31.550 min for minor isomer. **¹H NMR** (500 MHz, CDCl₃): δ = 8.00 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 6.80 (t, J = 55.9 Hz, 1H), 5.73 - 5.63 (m, 1H), 5.14 (d, J = 10.1 Hz, 1H), 5.05 (d, J = 17.1 Hz, 1H), 2.88 (dd, J = 14.0, 7.5 Hz, 1H), 2.68 (dd, J = 14.2, 7.5 Hz, 1H), 1.62 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -91.4 (dd, J = 255.6, 56.5 Hz, 1F), -93.1 (dd, J = 256.6, 55.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 199.9, 136.7, 132.0, 131.4, 129.0, 128.2, 120.4 (t, J = 271.6 Hz), 120.3, 55.4, 43.3, 24.0 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3078, 2929, 1674, 1448, 1242, 1066, 789 cm⁻¹. **HRMS** (EI) m/z : [M]⁺ Calcd. for C₁₃H₁₄F₂OS 256.0733; Found 256.0744.

3-Allyl-3-((difluoromethyl)thio)-1-methylindolin-2-one (4m)

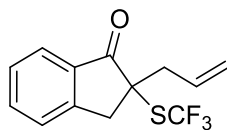


Eluent (*n*-hexane/ether = 9/1): R_f = 0.13. Yellow solid; 26.9 mg; 67% yield, 74% ee. $[\alpha]_D^{25} = -8.9$ (c = 0.90, CHCl_3 , 74% ee). HPLC conditions: CHIRALPAK[®] IC column, eluent: *n*-hexane/ethyl acetate = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 25.025 min for minor isomer, t_R = 27.150 min for major isomer. **¹H NMR** (500 MHz, CDCl_3): δ = 7.35 - 7.32 (m, 2H), 7.24 (dd, J = 70.2, 62.0 Hz, 1H), 7.15 - 7.11 (m, 1H), 6.87 (d, J = 7.9 Hz, 1H), 5.46 (ddt, J = 17.1, 9.8, 7.3 Hz, 1H), 5.11 - 4.99 (m, 2H), 3.24 (s, 3H), 2.96 - 2.80 (m, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -100.2 (dd, J = 258.6, 61.4 Hz, 1F), -94.0 (dd, J = 258.6, 52.5 Hz, 1F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 175.5, 142.9, 130.1, 129.8, 126.8, 124.3, 123.1, 120.7, 119.1 (dd, J = 277.0, 266.1 Hz), 108.6, 53.0 (d, J = 3.6 Hz), 41.1, 26.6 ppm. **IR** (KBr): $\tilde{\nu}$ = 3078, 2941, 1703, 1610, 1473, 1352, 1076, 1022, 931, 758 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{13}\text{NF}_2\text{NaOS}$ 292.0584; Found 292.0585. **m.p.**: 53.4 - 59.4 °C

General procedure for the DAAA reaction of 8

Procedure: Pd_2dba_3 (5 mol %) and Ligand (12.5 mol %) were dissolved in TBME (1.5 mL) and the mixture was stirred for 1 hour under nitrogen atmosphere. The mixture was cooled to -80 °C and a solution of **8** (0.15 mmol) in TBME (1.5 mL) was added dropwise to the mixture. The resulting mixture was stirred at prescribed temperature. After completion of the reaction, solvent was removed under reduced pressure and the residue was purified by flash silica-gel column chromatography to give the desired product **7**.

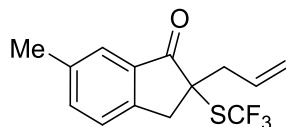
2-Allyl-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (7a)



Eluent (*n*-hexane/ CH_2Cl_2 = 7/3): R_f = 0.3. Pale yellow oil; 12.4 mg; 91% yield, 93% ee. $[\alpha]_D^{25} = -14.6$ (c = 0.62, CHCl_3 , 93% ee). HPLC conditions: CHIRALCEL[®] OJ-H column (x 2), eluent: *n*-hexane/*i*PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 23.183 min for major isomer, t_R = 25.667 min for minor isomer. **¹H NMR** (300 MHz, CDCl_3): δ = 7.83 (d, J = 8.2 Hz, 1H), 7.74 - 7.61 (m, 1H), 7.53 - 7.39 (m, 2H), 5.63 (ddt, J = 17.1, 9.9, 7.2, 7.2 Hz, 1H), 5.24 - 5.10 (m, 2H), 3.53 (s, 2H), 2.81 - 2.66 (m, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -36.4 (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 201.2, 150.3, 136.0, 134.1, 130.8, 130.0 (q, J = 309.1 Hz), 128.2, 126.2, 125.0, 120.7, 58.4, 41.7, 39.6 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3080, 2983, 2927, 1722, 1608, 1468, 1435, 1275, 1109, 993, 928 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NaOS}$

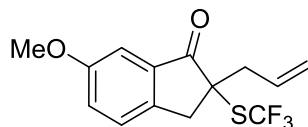
295.0380; Found 295.0383.

2-Allyl-6-methyl-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (7b)



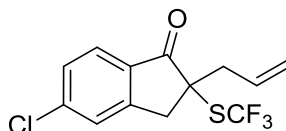
Eluent (*n*-hexane/ether = 9/1): R_f = 0.40. Pale yellow oil; 40.5 mg; 94% yield, 90% ee. $[\alpha]_D^{25}$ = -16.6 (c = 0.81, CHCl_3 , 90% ee). HPLC conditions: CHIRALPAK[®] IA column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 13.725 min for minor isomer, t_R = 17.633 min for major isomer. **¹H NMR** (300 MHz, CDCl_3): δ = 7.62 (s, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 5.72 - 5.51 (m, 1H), 5.25 - 5.05 (m, 2H), 3.48 (s, 2H), 2.82 - 2.64 (m, 2H), 2.42 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -36.5 (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 201.3, 147.7, 138.3, 137.3, 134.2, 130.9, 130.0 (q, J = 309.1 Hz), 125.9, 124.9, 120.6, 58.7, 41.7, 39.2, 21.1 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2981, 2925, 1722, 1618, 1495, 1435, 1282, 1111, 928, 820 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NaOS}$ 309.0537; Found 309.0539.

2-Allyl-6-methoxy-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (7c)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.27. Yellow oil; 43.5 mg; 96% yield, 90% ee. $[\alpha]_D^{25}$ = -25.3 (c = 0.87, CHCl_3 , 90% ee). HPLC conditions: CHIRALPAK[®] IG column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 27.792 min for major isomer, t_R = 32.725 min for minor isomer. **¹H NMR** (300 MHz, CDCl_3): δ = 7.38 - 7.29 (m, 1H), 7.27 - 7.22 (m, 2H), 5.78 - 5.49 (m, 1H), 5.25 - 5.08 (m, 2H), 3.85 (s, 3H), 3.45 (s, 2H), 2.81 - 2.65 (m, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -36.5 (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl_3): δ = 201.3, 159.9, 143.2, 135.3, 130.8, 130.0 (q, J = 309.1 Hz), 127.0, 125.6, 120.7, 105.8, 59.1, 55.6, 41.8, 39.0 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3008, 2943, 2839, 1720, 1493, 1435, 1281, 1230, 1111, 1028, 930 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NaO}_2\text{S}$ 325.0486; Found 325.0483.

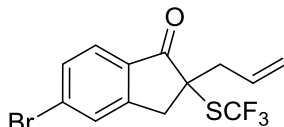
2-Allyl-5-chloro-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (7d)



Eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.36. Pale yellow oil; 42.3 mg; 92% yield, 91% ee. $[\alpha]_D^{25}$ = -19.5 (c = 0.83, CHCl_3 , 91% ee). HPLC conditions: CHIRALPAK[®] IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 19.367 min for minor isomer, t_R = 27.950 min for major isomer. **¹H NMR** (300 MHz, CDCl_3): δ = 7.76 (d, J = 8.2 Hz, 1H), 7.52 - 7.36 (m, 2H), 5.70 - 5.50 (m, 1H), 5.23 - 5.11 (m, 2H), 3.51 (s, 2H), 2.79 - 2.64 (m, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl_3): δ = -36.5 (s, 3F)

ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = 199.9, 151.8, 142.6, 132.6, 130.4, 129.9 (q, J = 309.4 Hz), 129.1, 126.5, 126.1, 121.1, 58.4, 41.7, 41.6, 39.2 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2989, 2906, 1712, 1643, 1597, 1576, 1435, 1417, 1319, 1263, 1207, 1115, 1036, 928, 885, 833 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{10}\text{ClF}_3\text{NaOS}$ 328.9991; Found 328.9994.

2-Allyl-5-bromo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (7e)

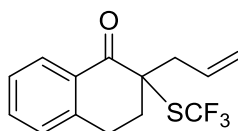


Eluent (*n*-hexane/ether = 9/1): R_f = 0.44. Colorless oil; 48.0 mg; 91% yield, 91% ee. $[\alpha]_{\text{D}}^{25}$ = -23.8 (c = 0.80, CHCl_3 , 91% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 19.692 min for minor isomer, t_R = 32.475 min for major isomer. ^1H NMR (300 MHz, CDCl_3): δ = 7.76–7.52 (m, 3H), 5.70 - 5.49 (m, 1H), 5.22 - 5.09 (m, 2H), 3.51 (s, 2H), 2.79 - 2.64 (m, 2H) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = -36.4 (s, 3F) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = 200.1, 151.8, 133.0, 132.0, 131.5, 130.4, 129.8 (q, J = 309.4 Hz), 129.6, 121.1, 58.3, 41.6, 39.1 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2989, 2900, 1714, 1593, 1577, 1415, 1317, 1263, 1207, 1163, 1109, 1057, 928, 829 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{13}\text{H}_{10}\text{BrF}_3\text{NaOS}$ 372.9486; Found 372.9480.

Reaction was also carried out using **8e** (1.29 g, 3.3 mmol), $\text{Pd}_2(\text{dba})_3$ (180 mg, 0.165 mmol) and **L7** (340 mg, 0.41 mmol) in TBME (80 mL, 0.05 M) at -80°C for 21 h.

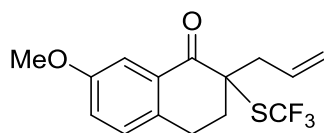
845.2 mg, 73% yield, 89% ee. The spectroscopic data is in agreement with the compound **7e**.

2-Allyl-2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (7f)



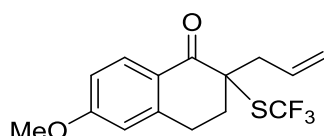
Eluent (*n*-hexane/ether = 9/1): R_f = 0.45. Colorless oil; 38.1 mg; 89% yield, 93% ee. $[\alpha]_{\text{D}}^{25}$ = $+23.7$ (c = 0.76, CHCl_3 , 93% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 17.508 min for major isomer, t_R = 24.450 min for minor isomer. ^1H NMR (300 MHz, CDCl_3): δ = 8.15 - 8.02 (m, 1H), 7.52 (td, J = 7.5, 1.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.9 Hz, 1H), 5.96 - 5.77 (m, 1H), 5.23 - 5.13 (m, 2H), 3.26 - 3.13 (m, 1H), 3.03 - 2.91 (m, 3H), 2.48 - 2.36 (m, 2H) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = -35.5 (s, 3F) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = 192.8, 141.9, 133.8, 132.2, 130.7, 129.9 (q, J = 309.1 Hz), 128.8, 128.6, 127.1, 120.0, 58.5, 40.4, 32.8, 25.4 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3078, 2929, 1689, 1601, 1454, 1433, 1290, 1234, 1223, 1105, 922, 746 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NaOS}$ 309.0537; Found 309.0540.

2-Allyl-7-methoxy-2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (7g)



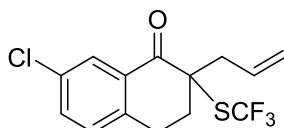
Eluent (*n*-hexane/ether = 9/1): R_f = 0.32. Yellow oil; 43.1 mg; 91% yield, 92% ee. $[\alpha]_D^{25}$ = +22.3 (c = 0.86, CHCl_3 , 92% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 23.167 min for major isomer, t_R = 45.525 min for minor isomer. **^1H NMR** (300 MHz, CDCl_3): δ = 7.55 (d, J = 2.6 Hz, 1H), 7.21 - 7.04 (m, 2H), 5.97 - 5.75 (m, 1H), 5.23 - 5.12 (m, 2H), 3.85 (s, 3H), 3.18 - 3.05 (m, 1H), 2.96 - 2.85 (m, 3H), 2.43 - 2.32 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -35.4 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 192.7, 158.6, 134.5, 132.2, 131.4, 130.0 (q, J = 309.1 Hz), 129.8, 122.5, 120.0, 110.3, 58.4, 55.5, 40.4, 33.1, 24.7 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3078, 3006, 2935, 2841, 1689, 1610, 1498, 1433, 1281, 1252, 1107, 1036, 926, 879, 820 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NaO}_2\text{S}$ 339.0643; Found 339.0649.

2-Allyl-6-methoxy-2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (7h)



Eluent (*n*-hexane/ether = 9/1): R_f = 0.21. Pale yellow oil; 44.1 mg; 93% yield, 91% ee. $[\alpha]_D^{25}$ = -1.1 (c = 0.88, CHCl_3 , 91% ee). HPLC conditions: CHIRALPAK® IC column, eluent: *n*-hexane/ethyl acetate = 49/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 25.883 min for minor isomer, t_R = 31.608 min for major isomer. **^1H NMR** (300 MHz, CDCl_3): δ = 8.06 (d, J = 8.8 Hz, 1H), 6.87 (dd, J = 8.8, 2.4 Hz, 1H), 6.67 (s, 1H), 5.96 - 5.74 (m, 1H), 5.21 - 5.09 (m, 2H), 3.87 (s, 3H), 3.25 - 3.11 (m, 1H), 2.99 - 2.88 (m, 3H), 2.47 - 2.31 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -35.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 191.5, 164.0, 144.6, 132.4, 131.3, 130.1 (q, J = 308.8 Hz), 124.1, 119.8, 113.9, 112.3, 58.7, 55.5, 40.6, 32.9, 25.9 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2954, 2924, 2895, 2848, 1676, 1599, 1496, 1352, 1261, 1225, 1103, 1022, 928 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NaO}_2\text{S}$ 339.0643; Found 339.0640.

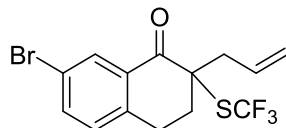
2-Allyl-7-chloro-2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (7i)



Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.44. Pale yellow oil; 41.5 mg; 86% yield, 95% ee. $[\alpha]_D^{25}$ = +18.3 (c = 0.83, CHCl_3 , 95% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 17.325 min for major isomer, t_R = 45.850 min for minor isomer. **^1H NMR** (300 MHz, CDCl_3): δ = 8.05 (d, J = 1.8 Hz, 1H), 7.47 (dd, J = 8.2, 2.1 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 5.95 - 5.72 (m, 1H), 5.24 - 5.14 (m, 2H), 3.22 - 3.08 (m, 1H), 2.99 - 2.85 (m, 3H), 2.45 - 2.32 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -35.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 191.6, 140.1, 133.8, 133.4, 131.9, 131.9, 130.2, 129.7 (q, J = 309.4 Hz), 128.4, 120.3, 57.9, 40.3, 32.6, 24.9 ppm. **IR**

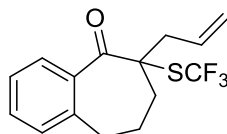
(NaCl): $\tilde{\nu}$ = 3080, 2929, 1693, 1597, 1479, 1433, 1304, 1219, 1107, 926, 835 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{ClF}_3\text{NaOS}$ 343.0147; Found 343.0153.

2-Allyl-7-bromo-2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (7j)



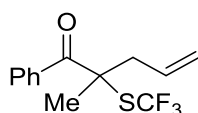
Eluent (*n*-hexane/ether = 9/1): R_f = 0.36. Pale yellow oil; 50.7 mg; 93% yield, 95% ee. $[\alpha]_D^{25}$ = +13.6 (c = 1.01, CHCl_3 , 95% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 20.375 min for major isomer, t_R = 66.508 min for minor isomer. **^1H NMR** (300 MHz, CDCl_3): δ = 8.21 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 5.92 - 5.72 (m, 1H), 5.25 - 5.14 (m, 2H), 3.19 - 3.06 (m, 1H), 2.99 - 2.87 (m, 3H), 2.44 - 2.33 (m, 2H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -35.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 191.5, 140.5, 136.6, 132.2, 131.8, 131.4, 130.4, 129.7 (q, J = 309.1 Hz), 121.1, 120.3, 57.9, 40.3, 32.5, 24.9 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3080, 2929, 1691, 1591, 1477, 1433, 1404, 1217, 1107, 995, 926, 833 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{BrF}_3\text{NaOS}$ 386.9642; Found 386.9652.

6-Allyl-6-((trifluoromethyl)thio)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (7k)



The reaction was carried at -20 °C; Eluent (*n*-hexane/ether = 20/1): R_f = 0.29. Pale yellow oil; 41.4 mg; 92% yield, 88% ee. $[\alpha]_D^{25}$ = +19.4 (c = 0.83, CHCl_3 , 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 16.792 min for major isomer, t_R = 21.233 min for minor isomer. **^1H NMR** (300 MHz, CDCl_3): δ = 7.47 - 7.27 (m, 3H), 7.14 (d, J = 7.3 Hz, 1H), 6.00 - 5.79 (m, 1H), 5.26 - 5.13 (m, 2H), 2.98 - 2.78 (m, 4H), 2.15 - 1.89 (m, 4H) ppm. **^{19}F NMR** (282 MHz, CDCl_3): δ = -35.9 (s, 3F) ppm. **^{13}C NMR** (126 MHz, CDCl_3): δ = 205.1, 139.4, 137.0, 132.1, 131.4, 129.7 (q, J = 309.1 Hz), 129.0, 128.8, 126.7, 120.1, 64.1, 41.3, 34.3, 33.3, 22.9 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3074, 2939, 2866, 1687, 1599, 1448, 1248, 1107, 958, 926, 758 cm^{-1} . **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NaOS}$ 323.0693; Found 323.0696.

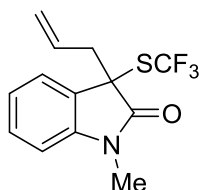
2-Methyl-1-phenyl-2-((trifluoromethyl)thio)pent-4-en-1-one (7l)



The reaction was carried at 40 °C; Eluent (*n*-hexane/ether = 20/1): R_f = 0.50. Pale yellow oil; 16.4 mg; 62% yield, 29% ee. $[\alpha]_D^{25}$ = +2.3 (c = 0.55, CHCl_3 , 29% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane = 100, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 81.350 min for major isomer, t_R = 104.275 min

for minor isomer. **¹H NMR** (300 MHz, CDCl₃): δ = 8.08 (dd, J = 8.4, 1.3 Hz, 2H), 7.61 - 7.49 (m, 1H), 7.49 - 7.38 (m, 2H), 5.71 (ddt, J = 17.1, 10.0, 7.3, 7.3 Hz, 1H), 5.19 - 5.03 (m, 2H), 2.88 (dd, J = 14.1, 7.0 Hz, 1H), 2.76 (dd, J = 14.2, 7.5 Hz, 1H), 1.71 (s, 3H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -36.5 (s, 3F) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 198.4, 136.1, 132.3, 131.0, 129.6 (q, J = 309.1 Hz), 129.4, 128.2, 120.7, 57.9, 43.0, 24.2 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3078, 2983, 2937, 1680, 1448, 1236, 1219, 1113, 993, 972, 928, 712 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₃H₁₃F₃NaOS 297.0537; Found 297.0536.

3-Allyl-1-methyl-3-((trifluoromethyl)thio)indolin-2-one (7m)

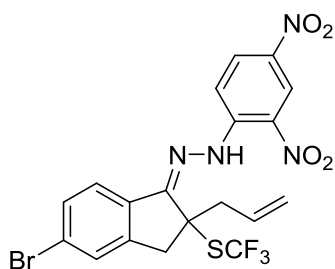


Eluent (*n*-hexane/ethyl acetate = 3/1): R_f = 0.48. Yellow oil; 12.5 mg; 87% yield, 49% ee. $[\alpha]_D^{25}$ = +14.1 (c = 0.76, CHCl₃, 49% ee). HPLC conditions: CHIRALPAK[®] IA column, eluent: *n*-hexane/ethyl acetate = 19/1, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 22.267 min for minor isomer, t_R = 27.400 min for major isomer. **¹H NMR** (300 MHz, CDCl₃): δ = 7.45 - 7.31 (m, 2H), 7.13 (td, J = 7.6, 0.9 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 5.51 - 5.38 (m, 1H), 5.14 - 5.03 (m, 2H), 3.24 (s, 3H), 2.76 (d, J = 7.3 Hz, 2H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -38.4 ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 174.5, 142.9, 129.8, 129.1, 129.0 (q, J = 309.7 Hz), 127.3, 124.8, 123.0, 121.3, 108.6, 55.6, 40.7, 26.7 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3060, 2937, 1726, 1612, 1493, 1471, 1371, 1348, 1250, 1111, 931, 752 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₃H₁₂F₃NNaOS 310.0489; Found 310.0490.

Preparation of 2,4-dinitrophenylhydrazone derivative 11

To a solution of 2,4-dinitrophenylhydrazine (59.4 mg, 0.30 mmol, 3.0 equiv) in EtOH (1.0 mL) was added 5 drops of conc. H₂SO₄ and **7e** (35.1 mg, 88% ee, 0.10 mmol). The resulting mixture was heated at 80 °C and stirred for 48 h. After completion of the reaction, silica-gel was added to the mixture and solvent was removed. The residue was purified by flash column chromatography to give the desired product **11**.

1-(2-Allyl-5-bromo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (11)



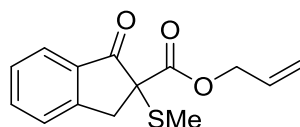
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.41. Yellow oil; 23.7 mg; 45% yield, 69% ee. $[\alpha]_D^{25}$ = +1.1 (c = 0.25, CHCl₃, 69% ee). HPLC conditions: CHIRALPAK[®] IA column, eluent: *n*-hexane/*i*PrOH = 80/20, flow

rate = 0.5 mL/min, λ = 254 nm, t_R = 6.092 min for minor isomer, t_R = 14.792 min for major isomer. **¹H NMR** (300 MHz, CDCl₃): δ = 12.3 (bs, 1H), 9.18 (d, J = 2.4 Hz, 1H), 8.40 (d, J = 7.0 Hz, 1H), 8.12 (d, J = 9.4 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.55 - 7.42 (m, 2H), 5.67 - 5.48 (m, 1H), 5.33 - 5.13 (m, 2H), 3.82 (d, J = 19.1 Hz, 1H), 3.68 (d, J = 18.5 Hz, 1H), 3.07 (dd, J = 14.5, 6.6 Hz, 1H), 2.88 (dd, J = 13.9, 7.8 Hz, 1H) ppm. **¹⁹F NMR** (282 MHz, CDCl₃): δ = -37.9 ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 154.0, 145.0, 144.3, 138.7, 135.4, 131.6, 130.3, 130.0, 129.1 (q, J = 310.6 Hz), 129.0, 128.2, 126.3, 123.4, 123.4, 122.2, 116.4, 55.4, 45.3, 40.0 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3273, 3097, 1618, 1593, 1502, 1425, 1336, 1271, 1221, 1107, 937, 829, 739 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₉H₁₄BrF₃N₄O₄S 552.9769; Found 552.9774. **m.p.**: 165.0 - 174.6 °C.

Preparation of α -SMe- β -ketoallylesters **12**

To a 0 °C suspension of NaH (60% in oil, 21 mg, 0.53 mmol, 1.05 equiv) in THF (2.0 mL) was added a solution of β -ketoallylester (108 mg, 0.5 mmol) in THF (1.0 mL). The resulting mixture was stirred for 20 min. at room temperature. To the mixture was added a solution of S-methyl methanethiosulfonate (57 μ L, 0.6 mmol, 1.2 equiv) in THF (1.0 mL). After stirring for 4 h, the reaction was quenched by water, extracted with EtOAc. The organic layer was dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography to give the desired product **12**.

Allyl 2-(methylthio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**12**)

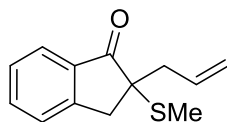


Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.29. Pink oil; 106.8 mg; 81% yield. **¹H NMR** (300 MHz, CDCl₃): δ = 7.84 (d, J = 7.9 Hz, 1H), 7.71 - 7.57 (m, 1H), 7.52 - 7.37 (m, 2H), 6.02 - 5.81 (m, 1H), 5.42 - 5.16 (m, 2H), 4.78 - 4.63 (m, 2H), 3.91 (d, J = 17.9 Hz, 1H), 3.15 (d, J = 17.9 Hz, 1H), 2.32 (s, 3H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 196.0, 168.8, 150.2, 135.3, 133.7, 131.2, 128.1, 126.1, 125.4, 118.8, 66.6, 57.8, 39.8, 13.5 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2927, 1711, 1649, 1606, 1464, 1431, 1273, 1178, 1076, 1011, 964, 787, 756 cm⁻¹. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd. for C₁₄H₁₄O₃NaS 285.0561; Found 285.0559.

DAAA transformation of non-fluorinated **12** into **13**

Pd₂dba₃ (5 mol %) and Ligand (12.5 mol %) were dissolved in TBME (0.5 mL) and the mixture was stirred for 1 hour under nitrogen atmosphere. The mixture was cooled to -40 °C and a solution of **12** (0.05 mmol) in TBME (0.5 mL) was added dropwise to the mixture. The resulting mixture was stirred at prescribed temperature. After completion of the reaction, solvent was removed under reduced pressure and the residue was purified by flash silica-gel column chromatography to give the desired product **13**.

2-Allyl-2-(methylthio)-2,3-dihydro-1H-inden-1-one (**13**)



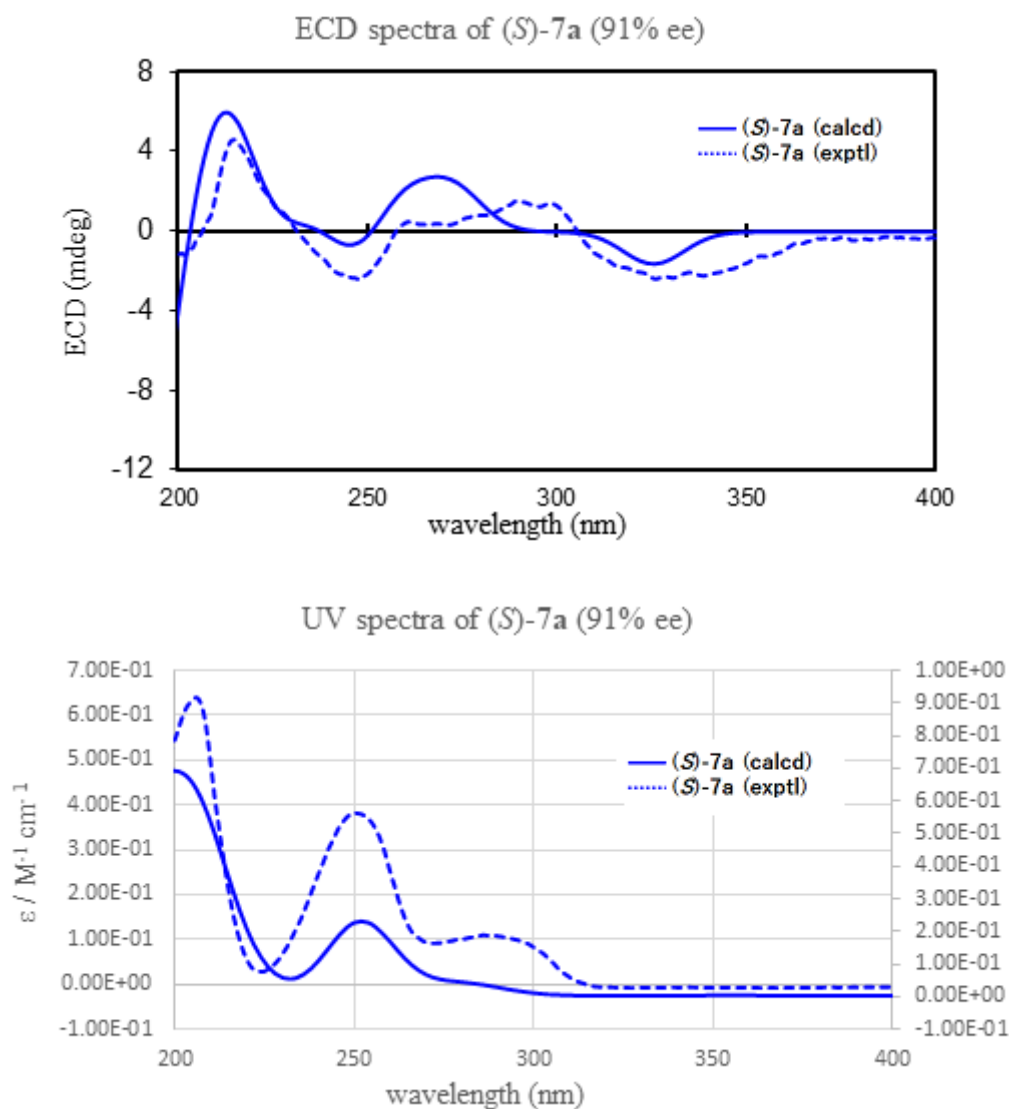
Eluent (CH₂Cl₂/*n*-hexane = 1/1): *R_f* = 0.46. Colorless oil; 10.7 mg; 84% yield, 65% ee. [α]_D²⁵ = −126.7 (*c* = 0.34, CHCl₃, 65% ee). HPLC conditions: CHIRALCEL[®] OJ-H column, eluent: *n*-hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, *t_R* = 13.667 min for minor isomer, *t_R* = 15.700 min for major isomer. **¹H NMR** (300 MHz, CDCl₃): δ = 7.79 (d, *J* = 7.9 Hz, 1H), 7.64 - 7.36 (m, 1H), 5.86 - 5.72 (m, 1H), 5.24 - 5.10 (m, 2H), 3.40 (d, *J* = 17.9 Hz, 1H), 2.94 (d, *J* = 17.9 Hz, 1H), 2.75 - 2.60 (m, 2H), 2.11 (s, 3H) ppm. **¹³C NMR** (126 MHz, CDCl₃): δ = 201.6, 150.3, 134.9, 134.8, 133.0, 127.8, 126.2, 124.9, 119.0, 53.3, 39.1, 37.1, 11.5 ppm. **IR** (NaCl): $\tilde{\nu}$ = 2921, 1707, 1608, 1464, 1431, 1327, 1273, 1211, 999, 920, 741 cm^{−1}. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd. for C₁₃H₁₄ NaOS 241.0663; Found 241.0667.

References

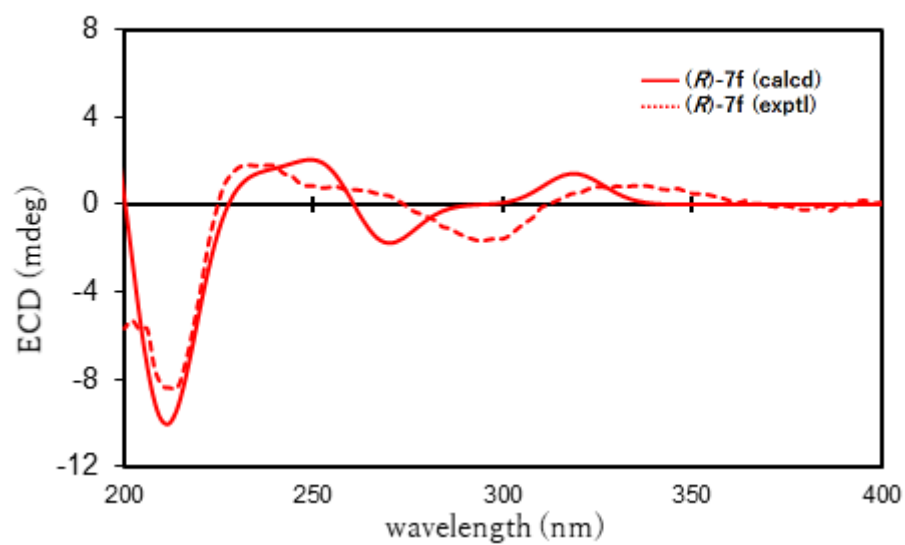
- (1) (a) Zhu, D.; Gu, Y.; Lu, L.; Shen, Q. *J. Am. Chem. Soc.* **2015**, *137*, 10547. (b) Arimori, S.; Matubara, O.; Takada, M.; Shiro, M.; Shibata, N. *R. Soc. Open sci.* **2016**, *3*, 160102.
- (2) Xu, C.; Ma, B.; Shen, Q. *Angew. Chem.* **2014**, *126*, 9470.

Experimental and calculated ECD and UV spectra

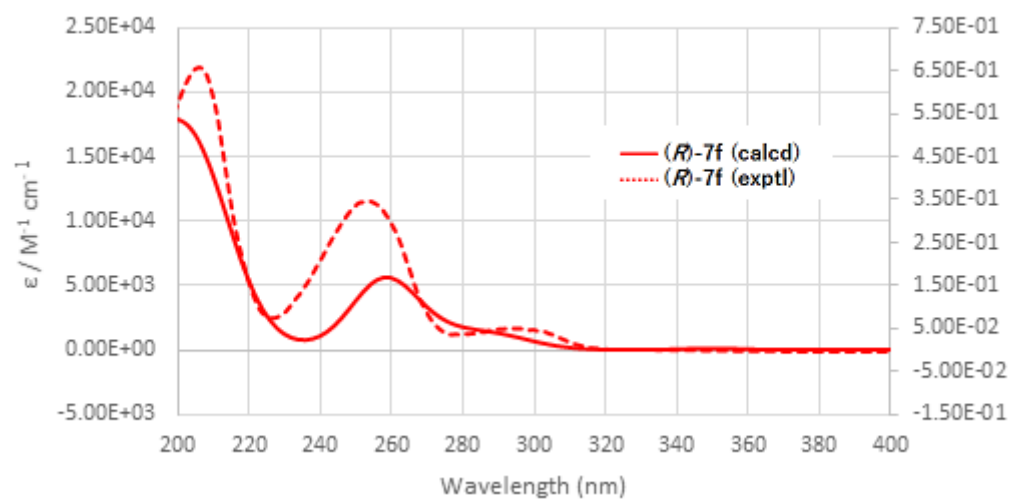
Molecular modeling calculations were performed on a PC (operating system: Windows7 Professional; CPU: Intel Xeon E5-1660 v2 processor, 3.70 GHz, 6 cores; RAM: 64 GB). Compound **7a** and **7f** were built on Spartan[®] 16 (Wavefunction Inc. Irvine, CA 92612 USA). Conformational search was performed with MMFF (ref. Halgren, T. A. Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94. *J. Comp. Chem.* **1996**, *17*, 490-519.) to give the candidate conformers. All of these were finely optimized with wB97X-D/6-31G* model. The conformers within 10 kcal/mol from the global minimum conformer were further subjected to geometry optimization, ECD calculation, and vibrational analysis with BHLYP/def2-TZVP model employing Turbomole 7.0.1 on a workstation (operating system: SUSE Linux Enterprise Desktop 12, CPU: Intel Xeon E5-2687W V4 (3.0 GHz, 12 cores) × 2, RAM: 512 GB). The free energy of each conformer was calculated by summing the SCF energy and the chemical potential. The ECD spectra were constructed based on frequencies and rotary strength using the NORMDIST function in Microsoft Excel 2016. The wavelengths for the spectra were corrected based on the experimental UV spectra. Theoretical ECD spectra were obtained after correction of the conformational distribution.



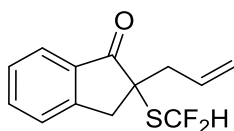
ECD spectra of (*R*)-7f (93% ee)



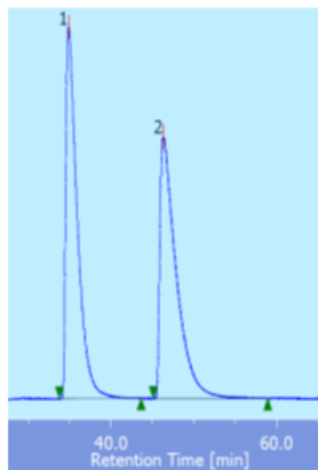
UV spectra of (*R*)-7f (93% ee)



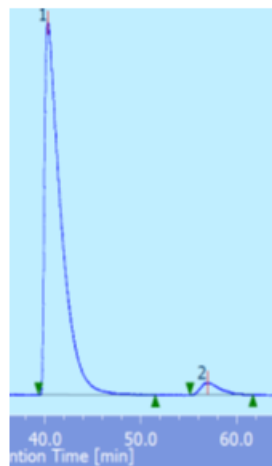
HPLC chromatographs of compounds 4 and 7



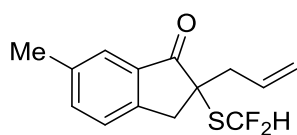
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



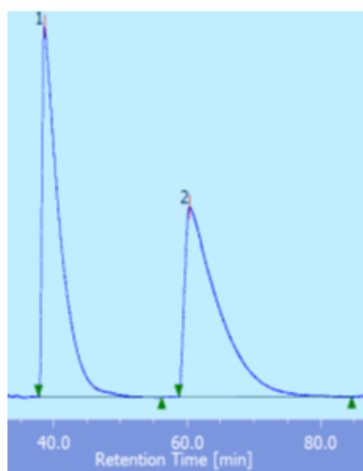
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	34.833	49.954	58.718
2	46.275	50.046	41.282



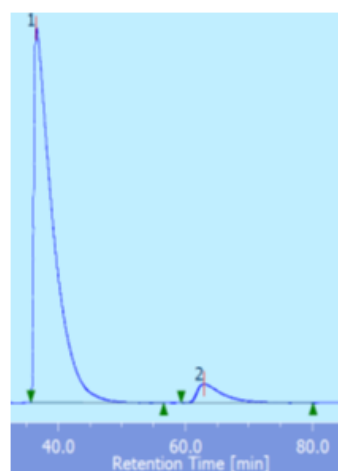
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	40.258	96.340	96.843
2	56.925	3.660	3.157



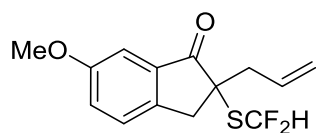
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



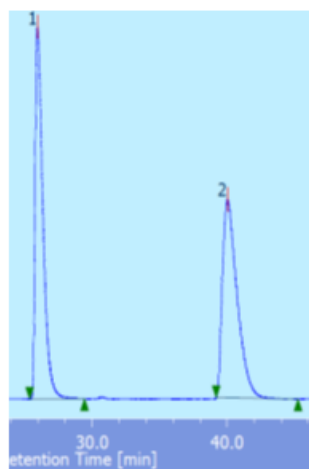
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	38.567	50.322	66.152
2	60.350	49.678	33.848



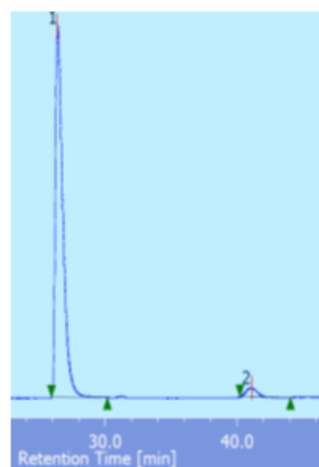
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	36.525	93.382	95.148
2	62.908	6.618	4.852



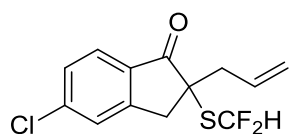
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



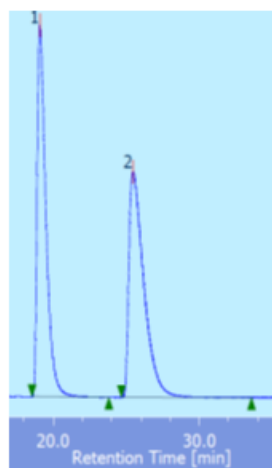
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	25.933	49.843	65.258
2	40.008	50.157	34.742



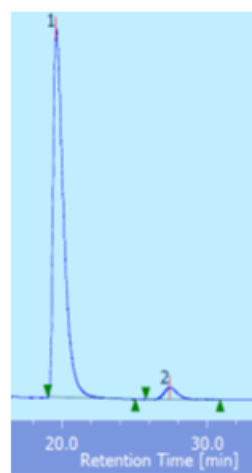
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	26.408	96.344	97.527
2	41.067	3.656	2.473



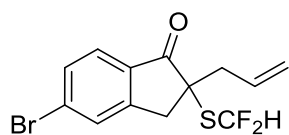
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



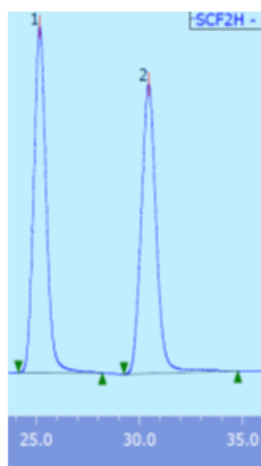
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	19.092	49.168	62.230
2	25.467	50.832	37.770



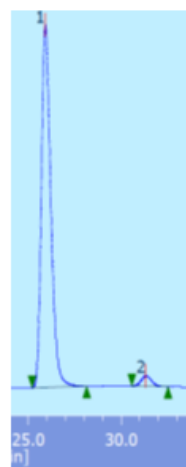
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	19.633	96.000	96.884
2	27.425	4.000	3.116



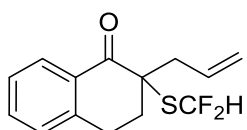
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



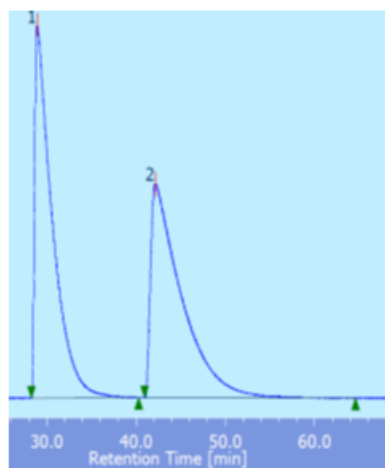
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	25.167	49.806	54.450
2	30.433	50.194	45.550



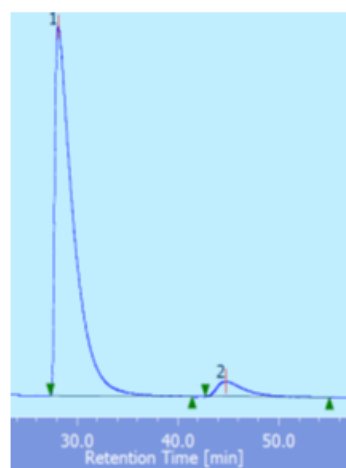
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	25.917	96.881	97.223
2	31.333	3.119	2.777



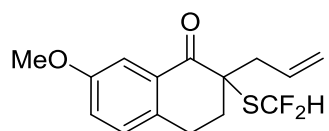
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



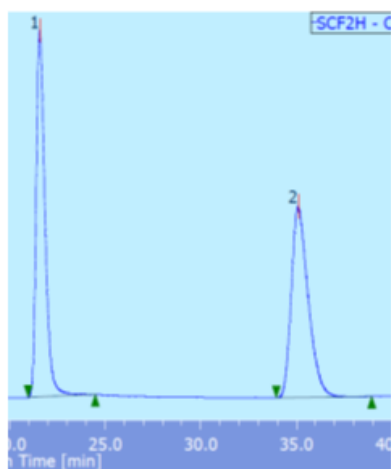
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	28.900	49.935	63.591
2	42.133	50.065	36.409



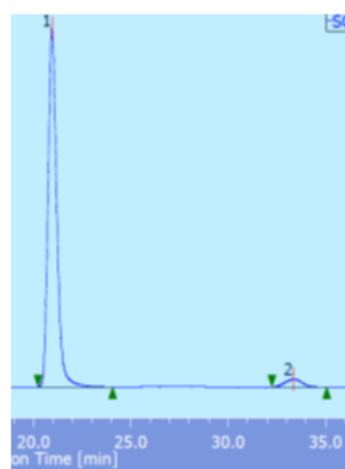
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	28.117	94.149	96.042
2	44.742	5.851	3.958



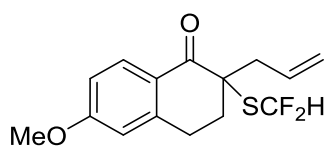
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



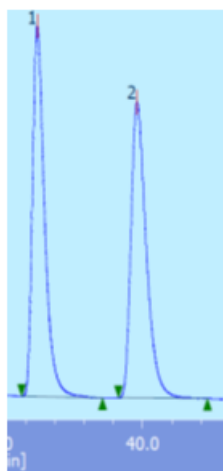
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	21.567	50.315	65.750
2	35.075	49.685	34.250



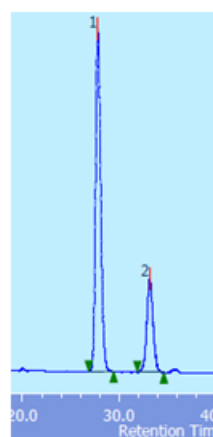
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	20.933	95.832	97.830
2	33.350	4.168	2.170



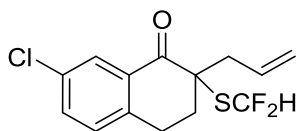
HPLC using a CHIRALCEL® OJ-H
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.4 ml/min, λ = 254 nm)



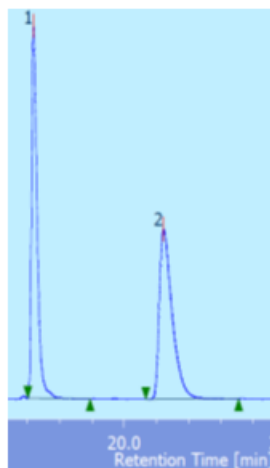
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	32.792	50.022	55.629
2	39.583	49.978	44.371



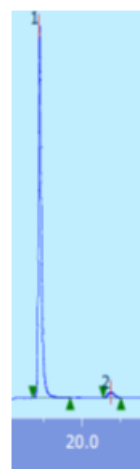
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	27.792	75.032	78.574
2	33.175	24.968	21.426



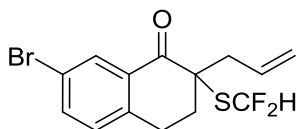
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



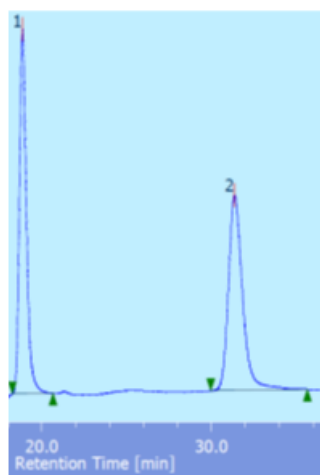
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	14.358	48.943	68.651
2	22.433	51.057	31.349



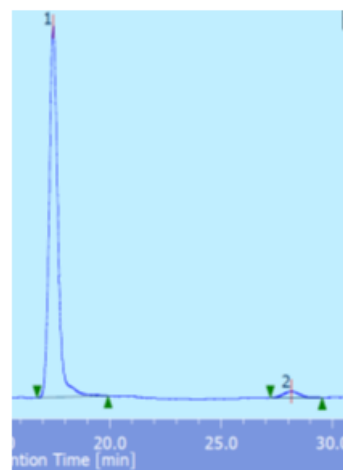
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	14.533	96.844	98.461
2	23.675	3.156	1.539



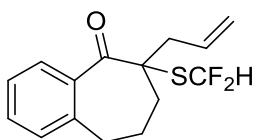
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	18.842	48.050	65.152
2	31.350	51.950	34.848



No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	17.442	96.936	98.338
2	28.133	3.064	1.662



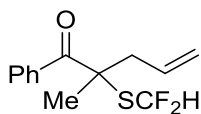
HPLC using a CHIRALCEL® OJ-3
(*n*-hexane/*i*PrOH = 99/1, flow rate 0.5 ml/min, λ = 254 nm)



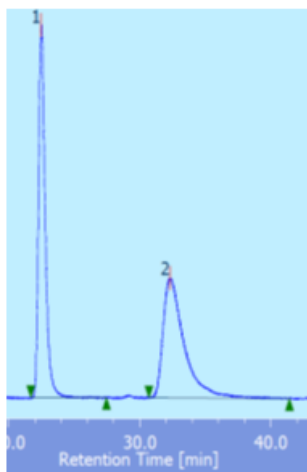
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	13.892	50.166	60.650
2	16.342	49.834	39.350



No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	15.908	90.711	91.088
2	19.233	9.289	8.912



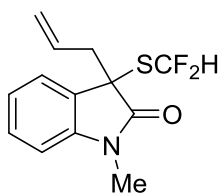
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



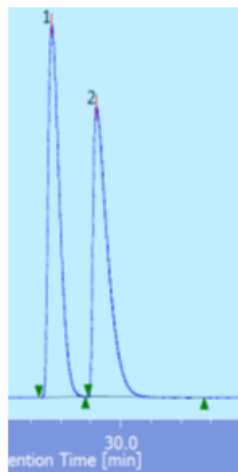
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	22.483	49.563	75.696
2	32.308	50.437	24.304



No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	22.225	66.265	85.296
2	31.550	33.735	14.704



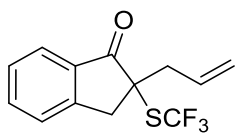
HPLC using a CHIRALPAK® IC
(*n*-hexane/ethyl acetate = 98/2, flow rate 1.0 ml/min, λ = 254 nm)



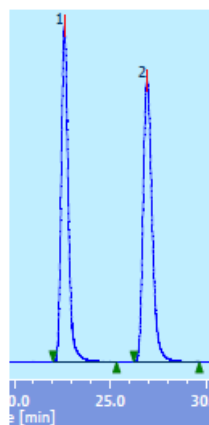
No.	t_R (min)	Area (%)	Height (%)
1	25.383	50.091	56.268
2	28.367	49.909	43.732



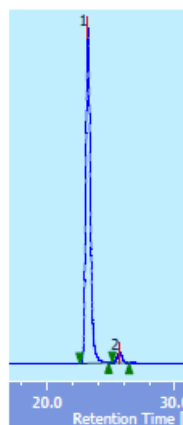
No.	t_R (min)	Area (%)	Height (%)
1	25.025	12.839	17.463
2	27.150	87.161	82.537



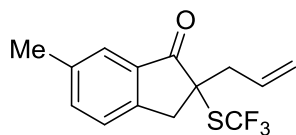
HPLC using a CHIRALCEL® OJ-H x 2
(*n*-hexane/*i*PrOH = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



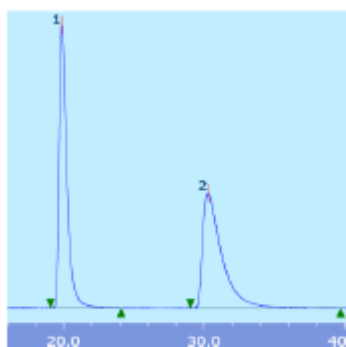
No.	t_R (min)	Area (%)	Height (%)
1	22.608	48.076	54.444
2	26.917	51.924	45.556



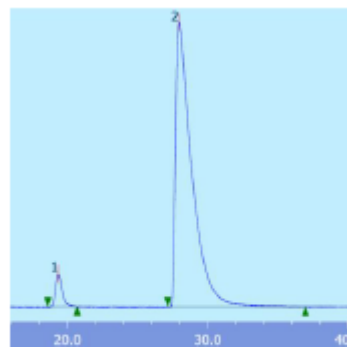
No.	t_R (min)	Area (%)	Height (%)
1	23.183	96.693	97.049
2	25.667	3.305	2.951



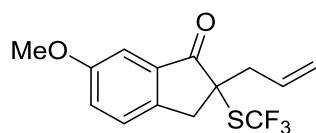
HPLC using a CHIRALPAK® IA
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



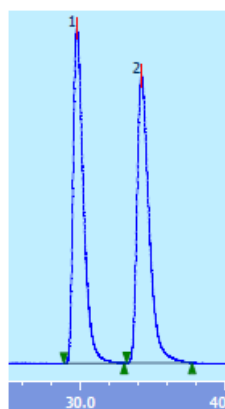
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	19.875	50.062	71.093
2	30.275	49.938	28.907



No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	19.367	4.382	10.156
2	27.950	95.618	89.844



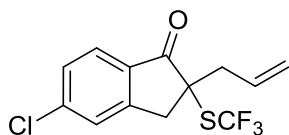
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



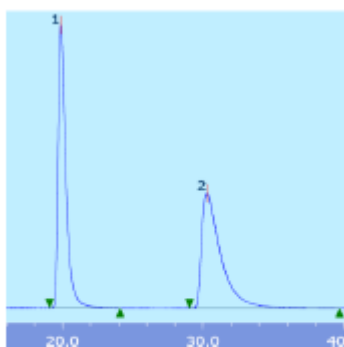
No.	<i>t</i> _R (min)	Area (%)	Height (%)
1	29.775	49.815	53.847
2	34.225	50.185	46.158



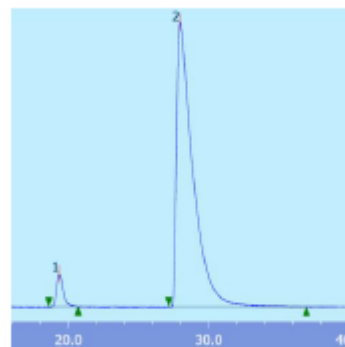
No.	<i>t</i> _R (min)	Area (%)	Height (%)
1	27.792	94.842	95.259
2	32.725	5.158	4.741



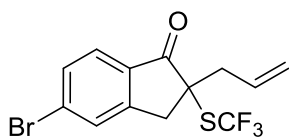
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



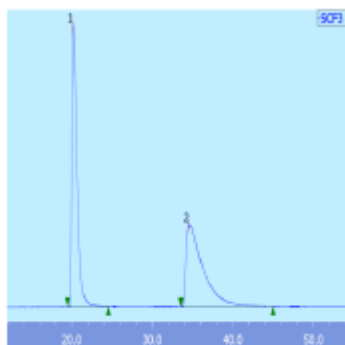
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	19.875	50.062	71.093
2	30.275	49.938	28.907



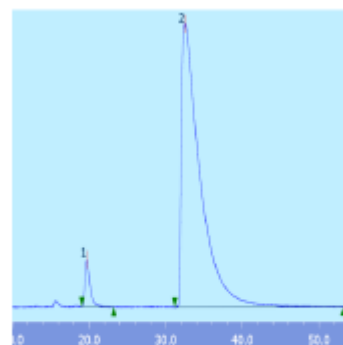
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	19.367	4.382	10.156
2	27.950	95.618	89.844



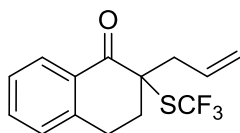
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



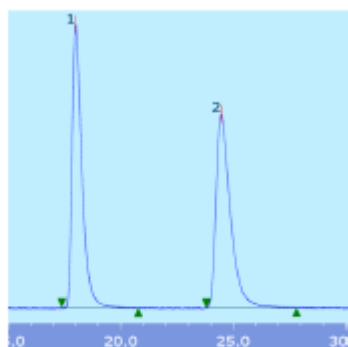
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	20.208	50.062	77.541
2	34.583	49.938	22.459



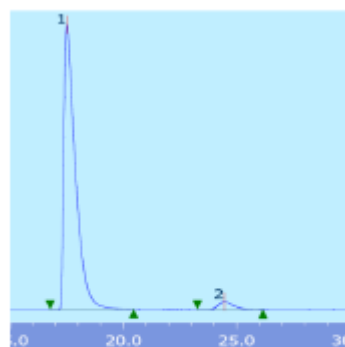
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	19.692	4.270	14.186
2	32.475	95.730	85.814



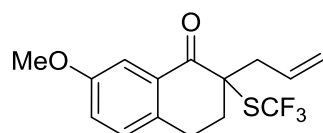
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



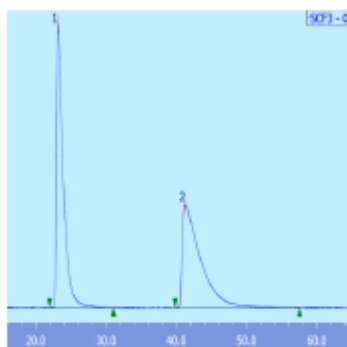
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	17.992	50.041	59.469
2	24.467	49.959	40.531



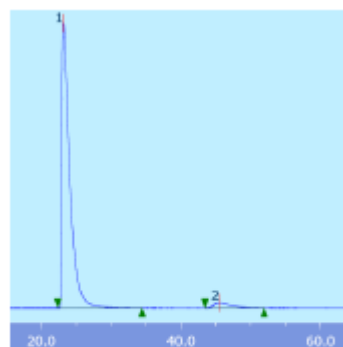
No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	17.508	96.649	97.378
2	24.450	3.351	2.622



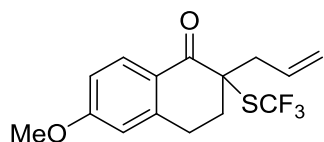
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	23.167	49.955	73.309
2	41.267	50.045	26.691

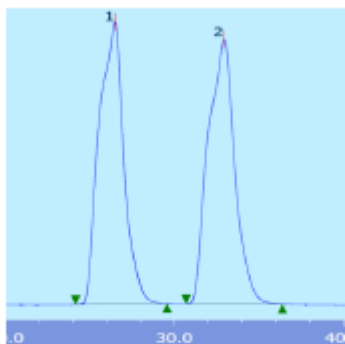


No.	<i>t</i> _R [min]	Area (%)	Height (%)
1	23.167	96.126	98.205
2	45.525	3.874	1.795

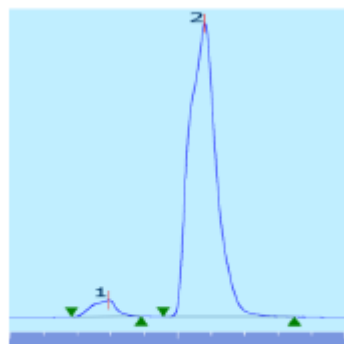


HPLC using a CHIRALPAK® IC

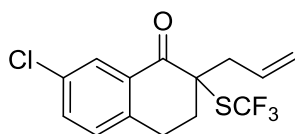
(*n*-hexane/ethyl acetate = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	26.475	49.915	51.586
2	32.925	50.085	48.414

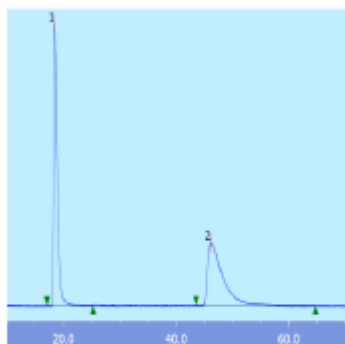


No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	25.883	4.733	5.309
2	31.608	95.267	94.691

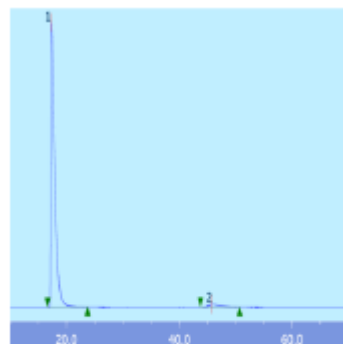


HPLC using a CHIRALPAK® IE

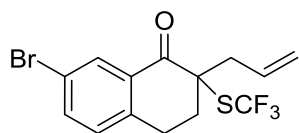
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



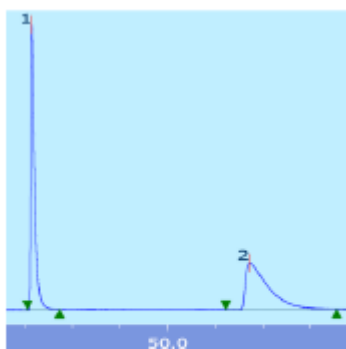
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	18.483	50.082	81.904
2	46.200	49.918	18.096



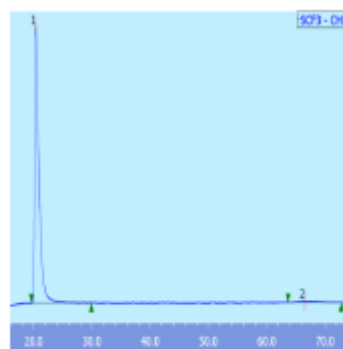
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	17.325	97.541	99.217
2	45.850	2.459	0.783



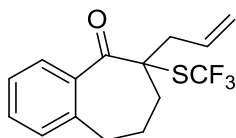
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



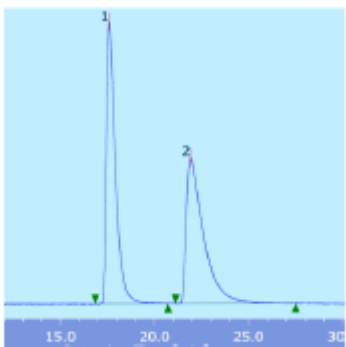
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	21.425	50.585	85.942
2	67.175	49.415	14.058



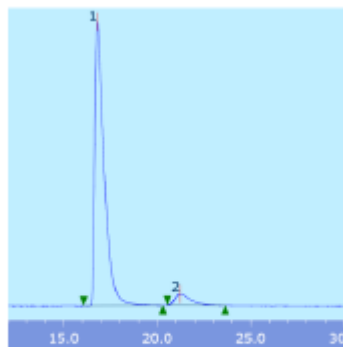
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	20.375	97.611	99.438
2	66.508	2.389	0.562



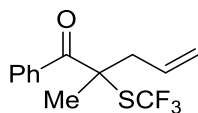
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



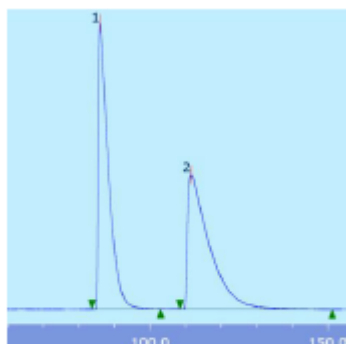
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	17.592	50.199	65.985
2	21.917	49.801	34.015



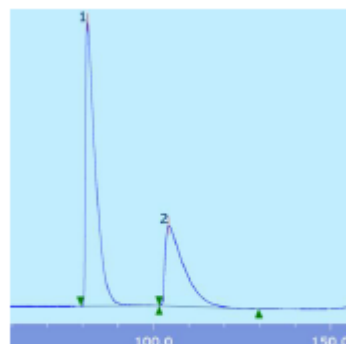
No.	<i>t_R</i> [min]	Area (%)	Height (%)
1	16.792	93.925	96.253
2	21.233	6.075	3.747



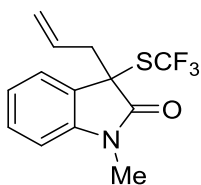
HPLC using a CHIRALPAK® IE
(*n*-hexane = 100, flow rate 0.3 ml/min, λ = 254 nm)



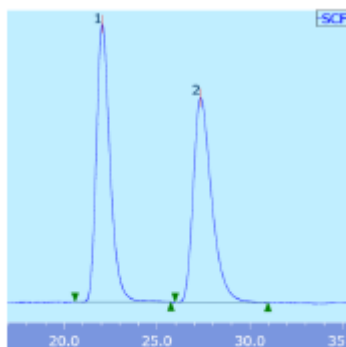
No.	t_R [min]	Area (%)	Height (%)
1	85.958	50.024	68.030
2	111.517	49.976	31.970



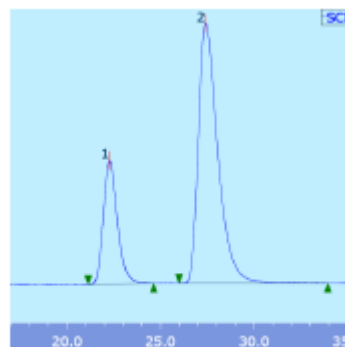
No.	t_R [min]	Area (%)	Height (%)
1	81.350	64.627	77.941
2	104.275	35.373	22.059



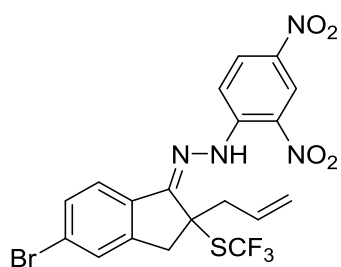
HPLC using a CHIRALPAK® IA
(*n*-hexane/ethyl acetate = 95/5, flow rate 0.5 ml/min, λ = 254 nm)



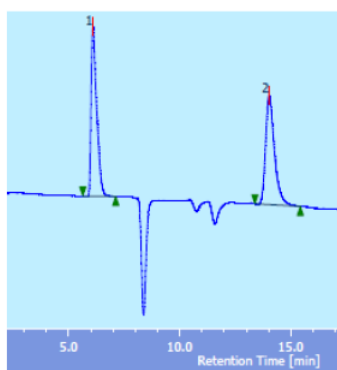
No.	t_R [min]	Area (%)	Height (%)
1	22.042	50.183	57.572
2	27.342	49.817	42.428



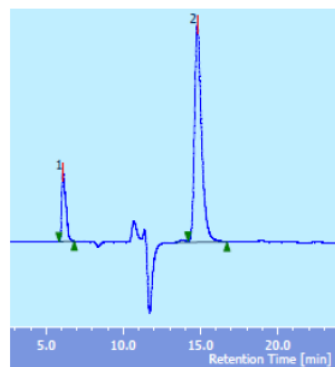
No.	t_R [min]	Area (%)	Height (%)
1	22.267	25.366	32.111
2	27.400	74.634	67.889



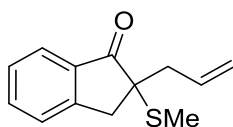
HPLC using a CHIRALPAK® IA
(*n*-hexane/*i*PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



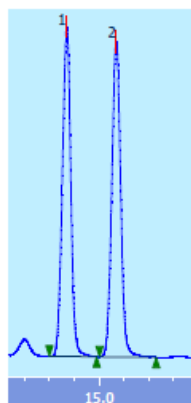
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	6.100	49.160	60.903
2	14.017	50.840	39.097



No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	6.092	15.364	24.293
2	14.792	84.639	75.707



HPLC using a CHIRALCEL® OJ-H
(*n*-hexane/*i*PrOH = 95/5, flow rate 0.5 ml/min, λ = 254 nm)

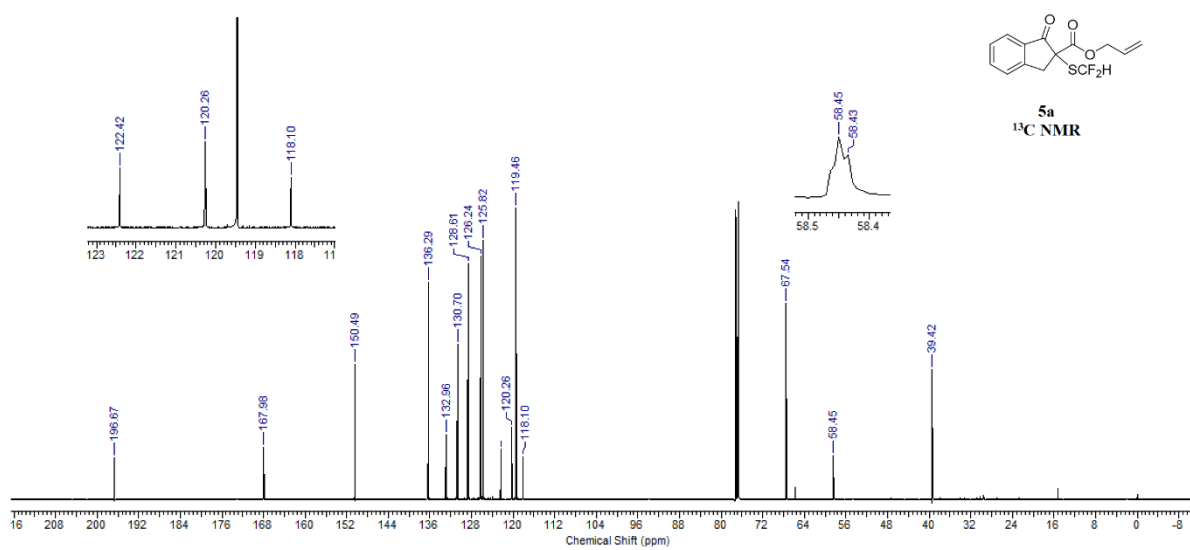
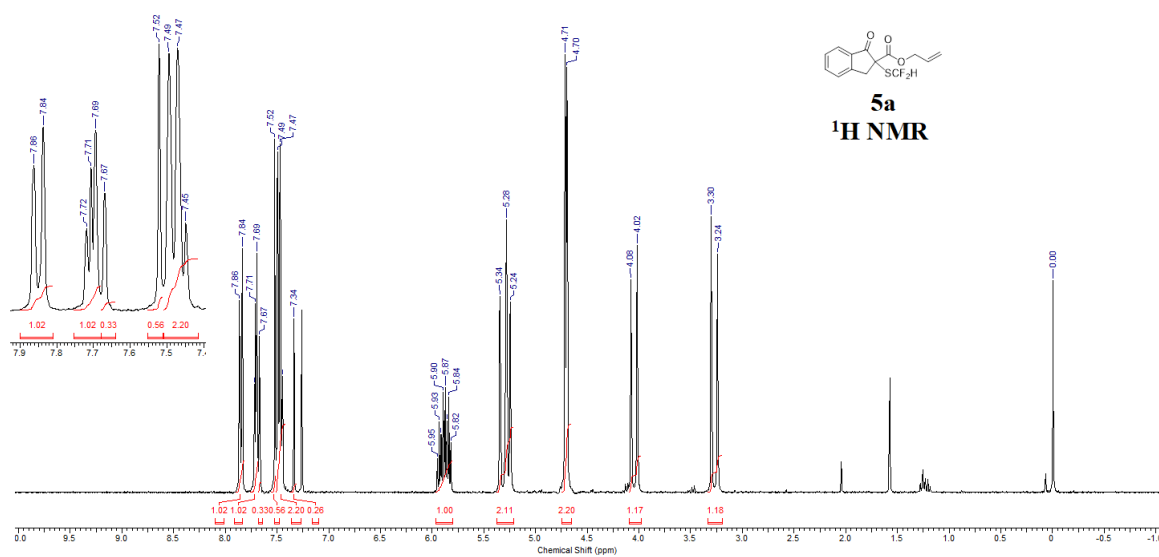


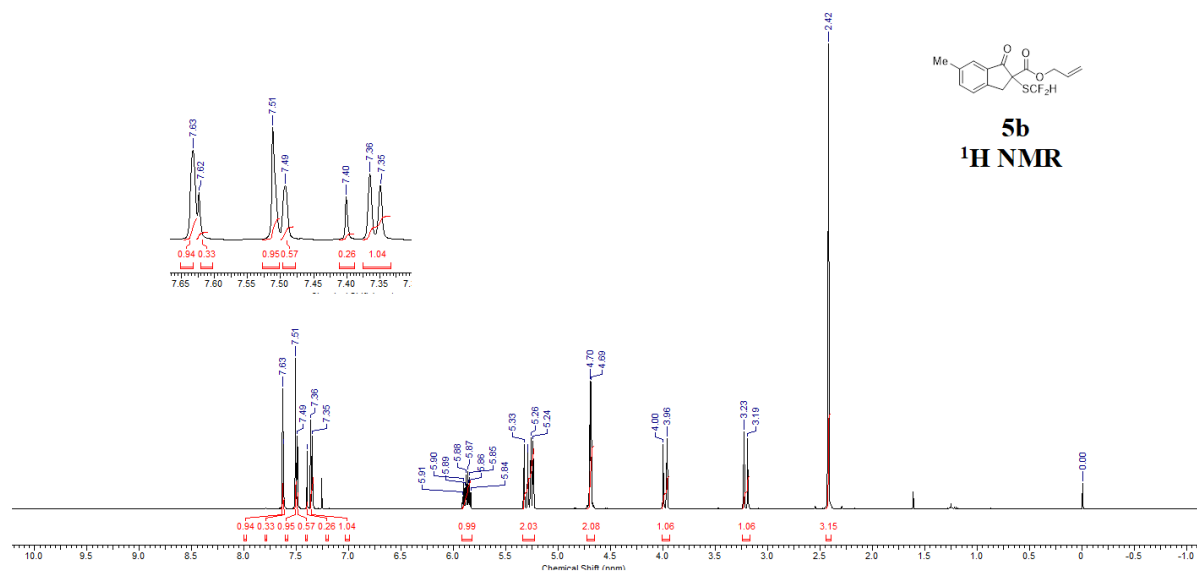
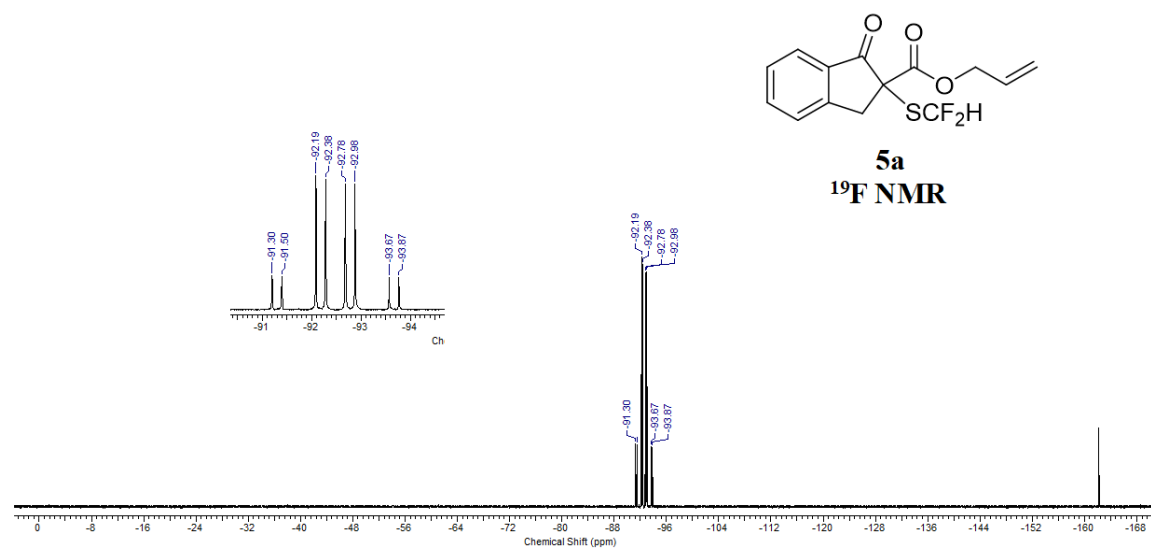
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	13.692	49.864	51.113
2	15.692	50.136	48.887

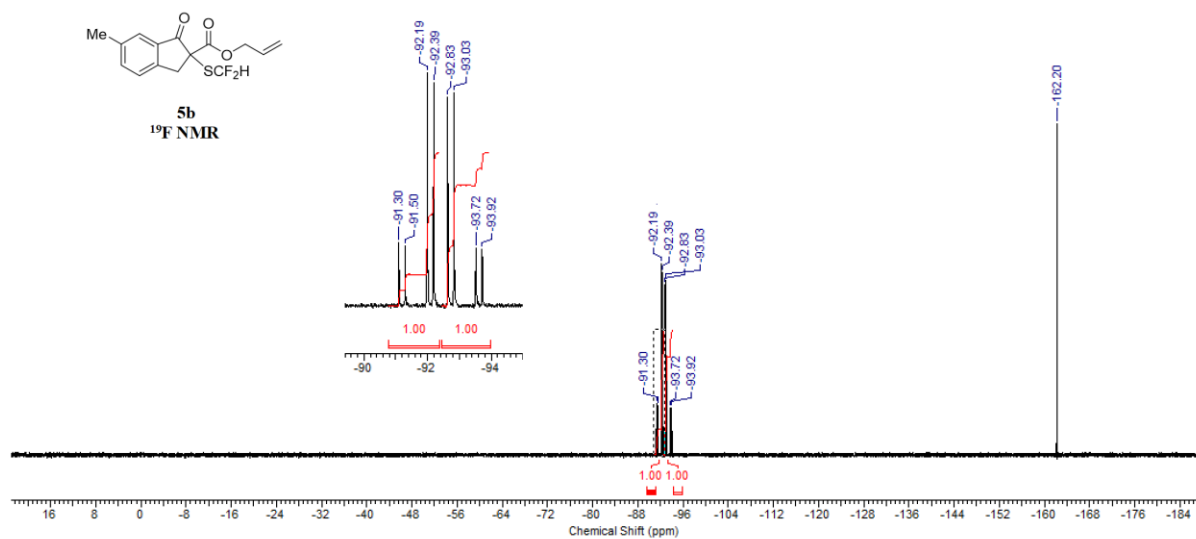
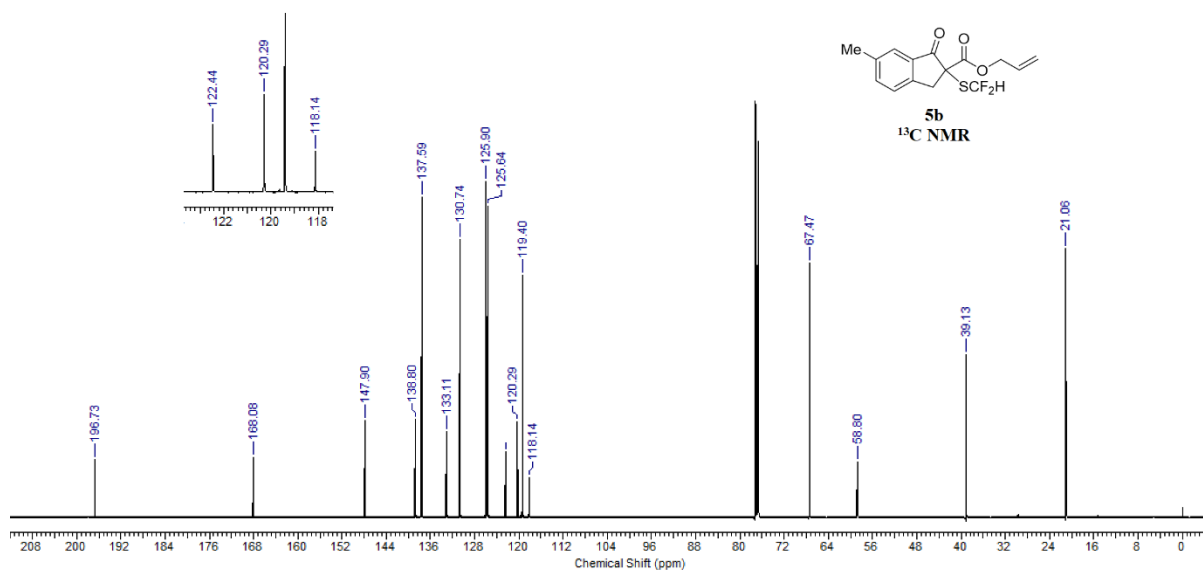


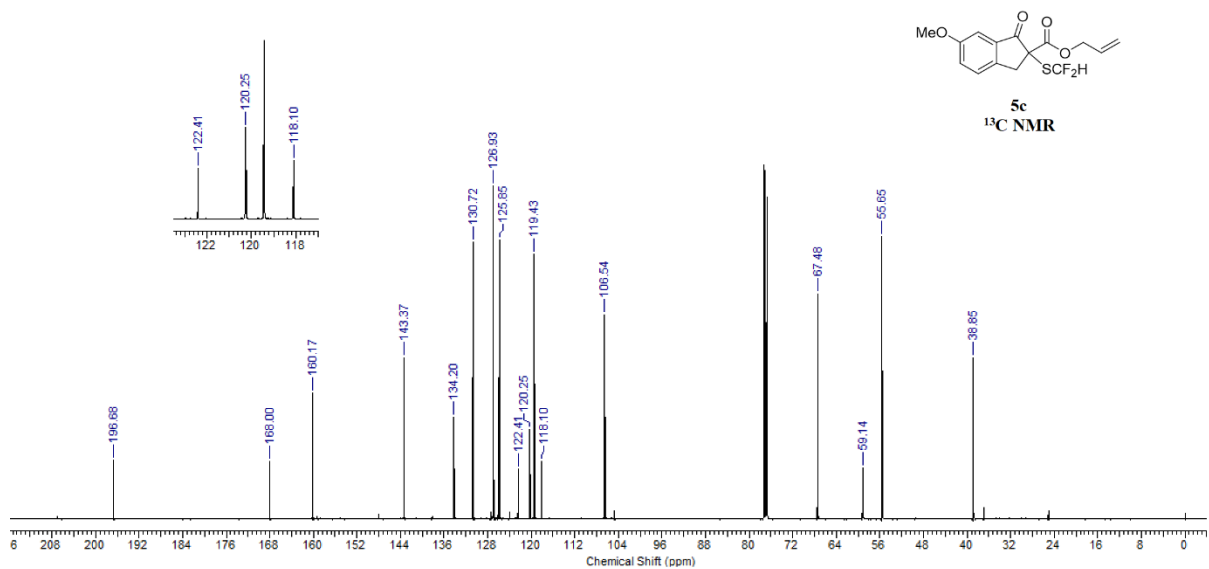
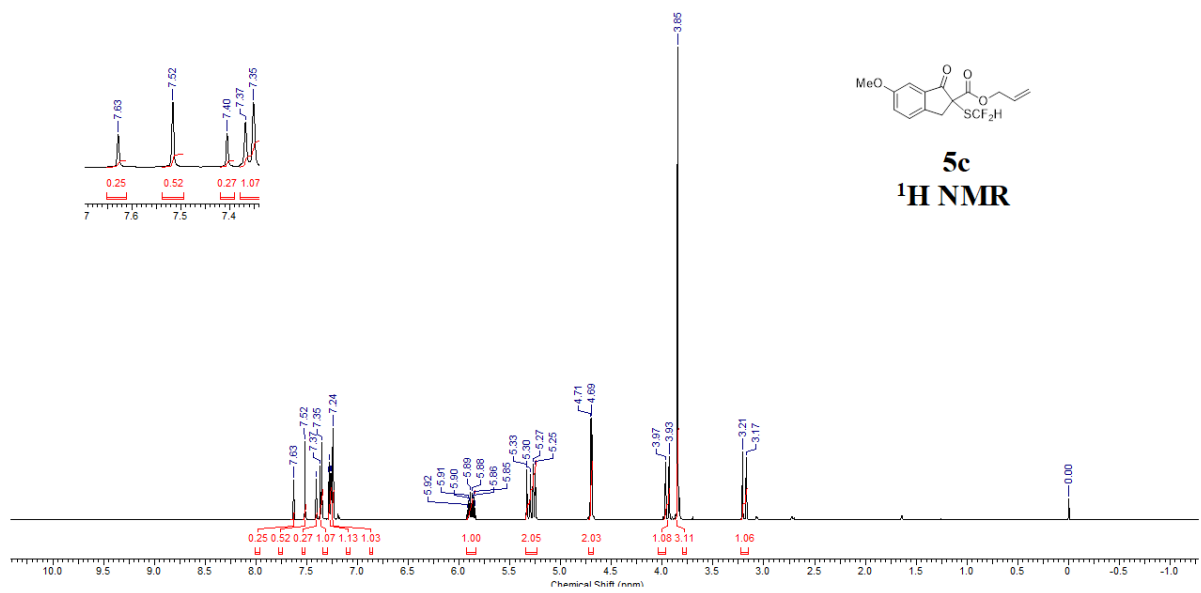
No.	<i>t_R</i> (min)	Area (%)	Height (%)
1	13.667	82.579	82.543
2	15.700	17.421	17.457

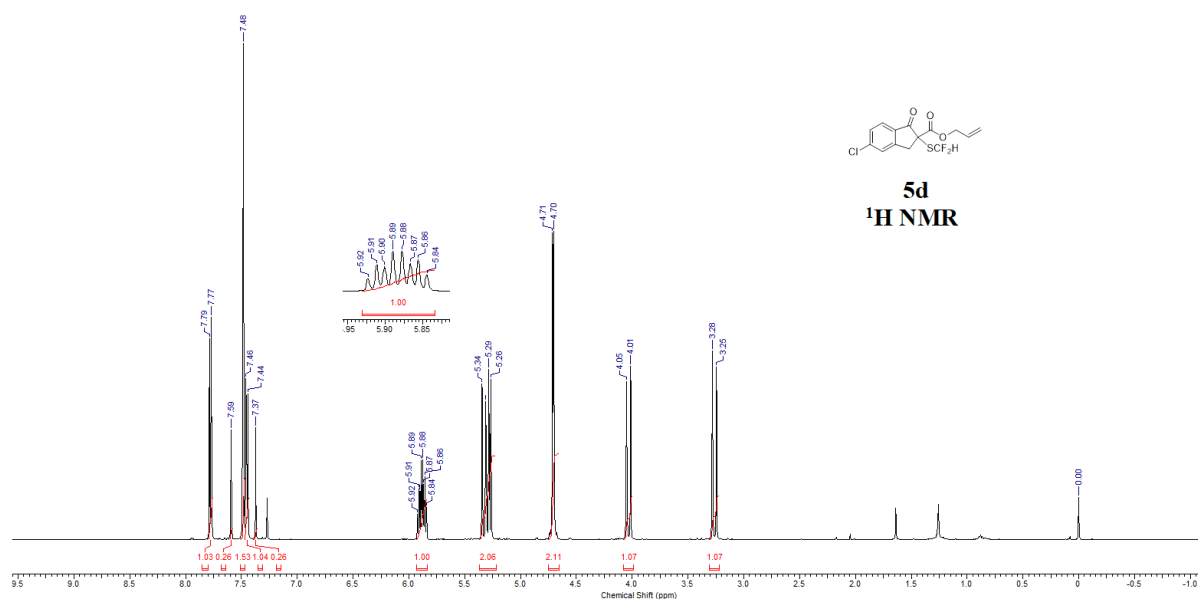
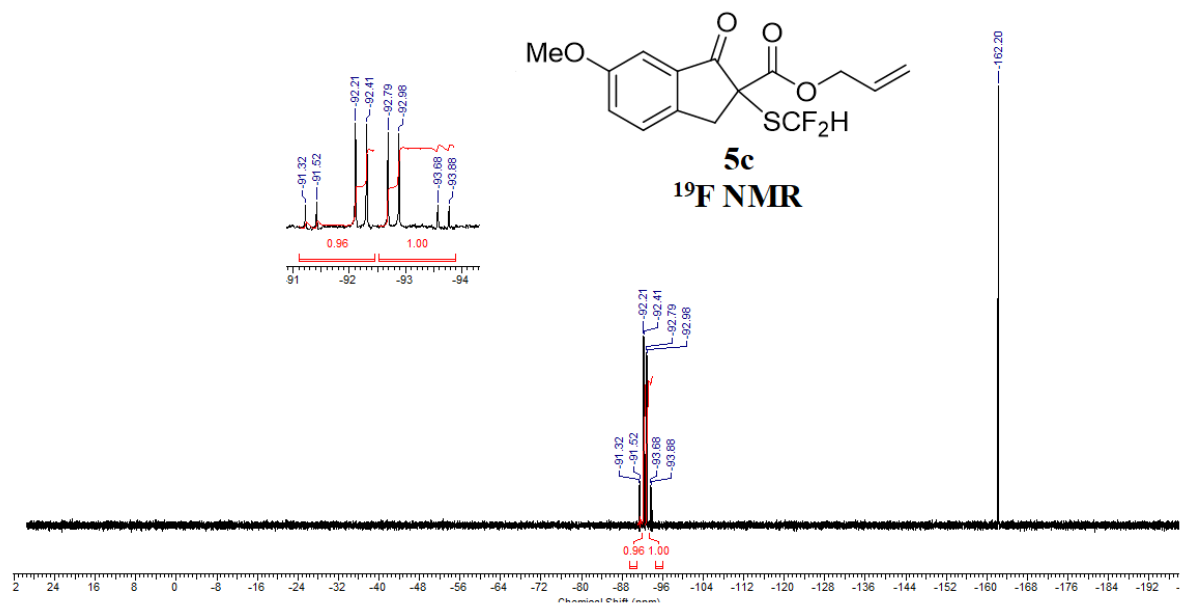
Copies of ^1H , ^{13}C , ^{19}F NMR

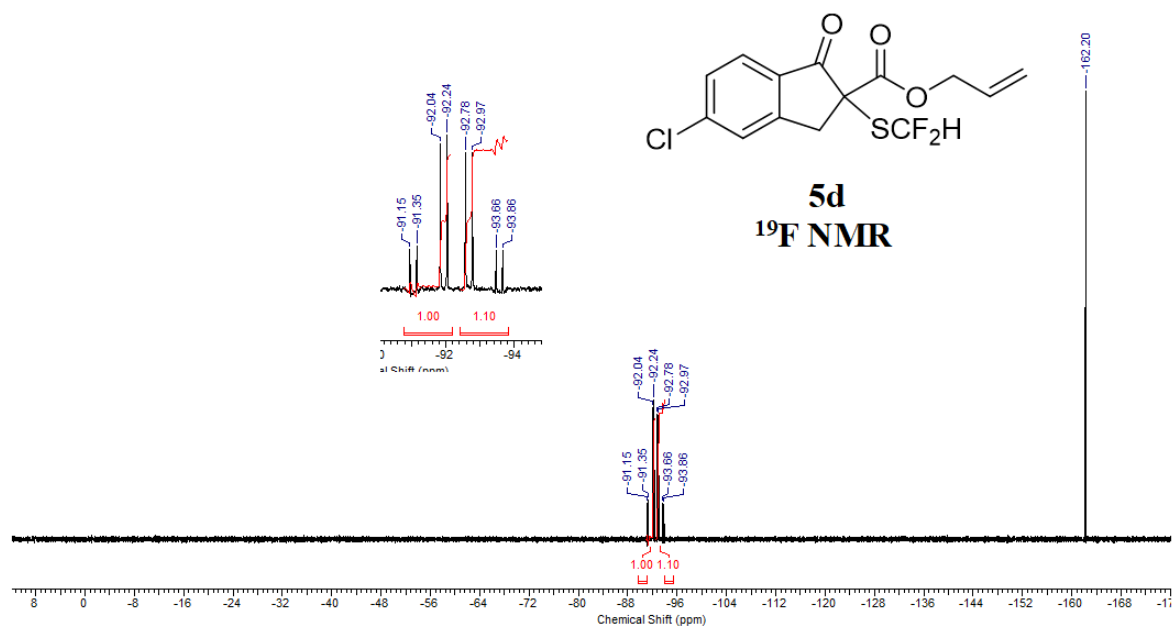
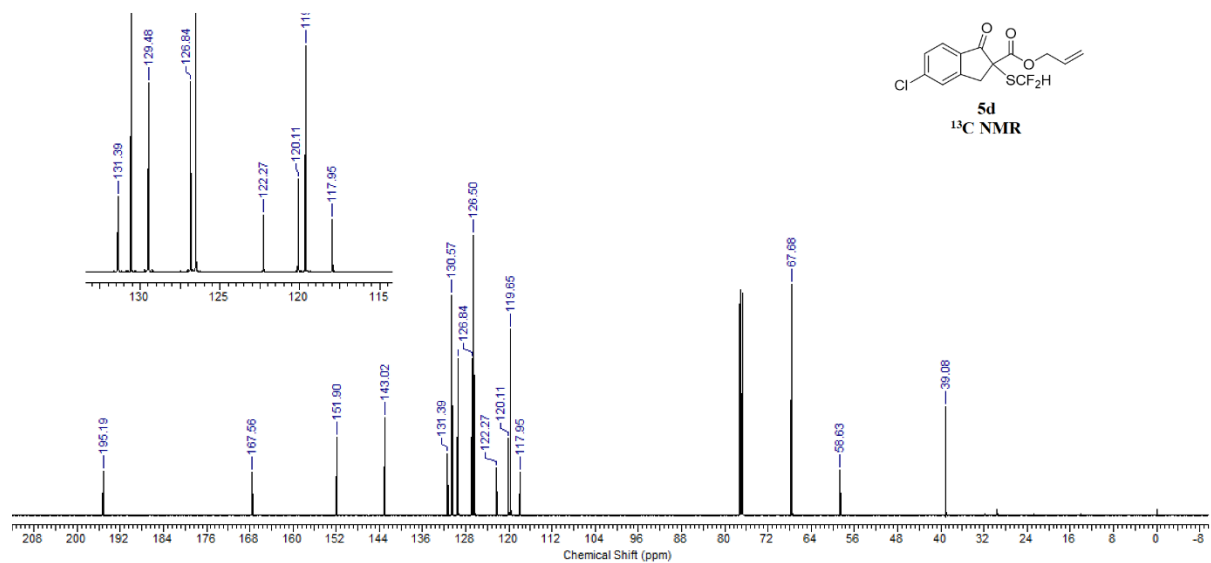


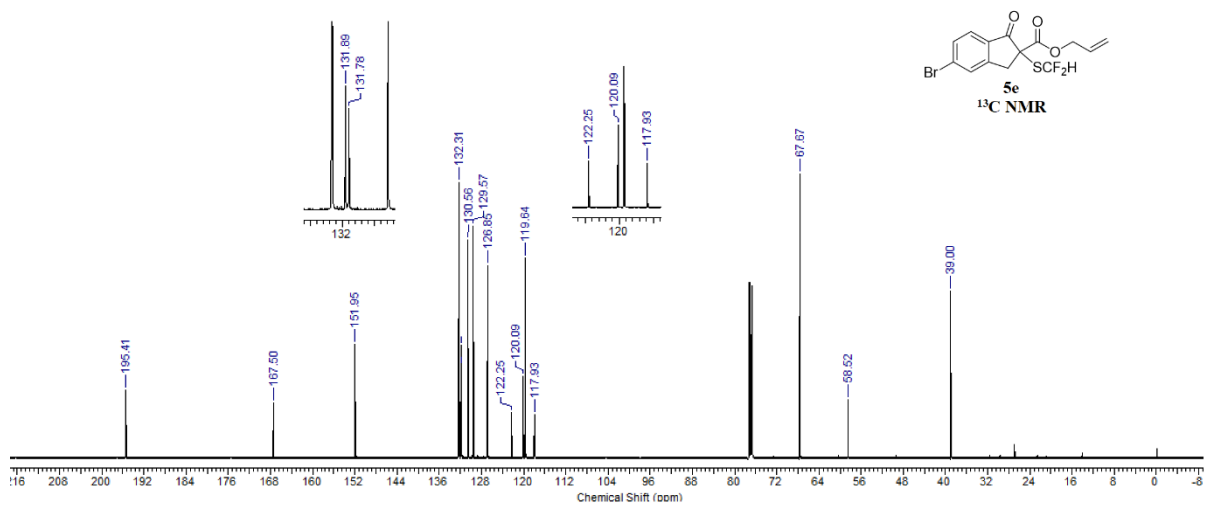
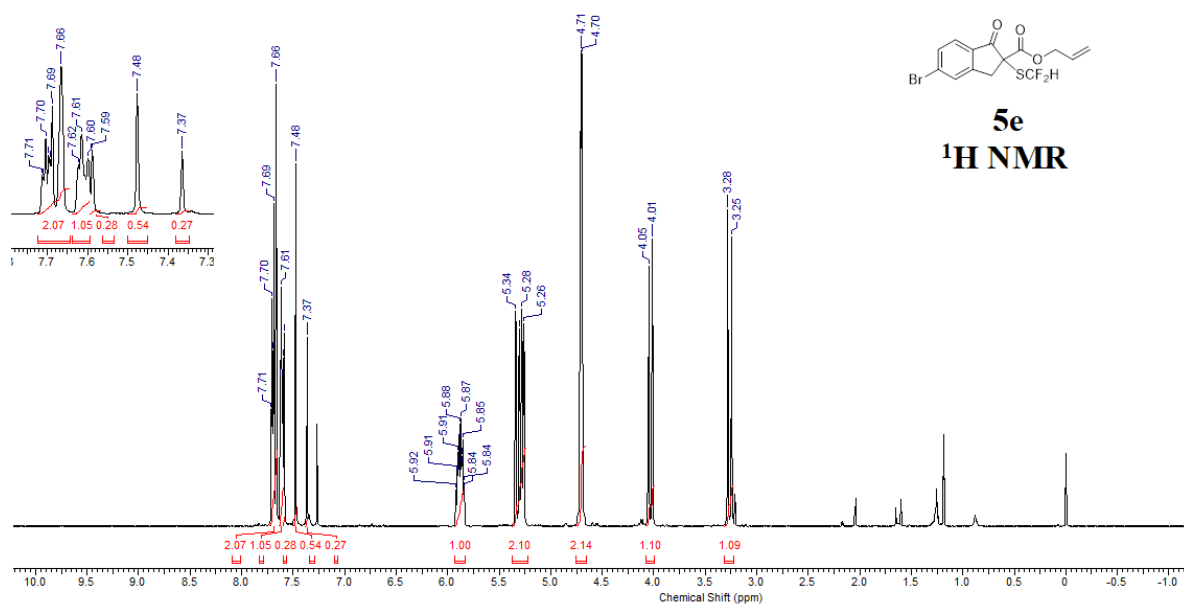


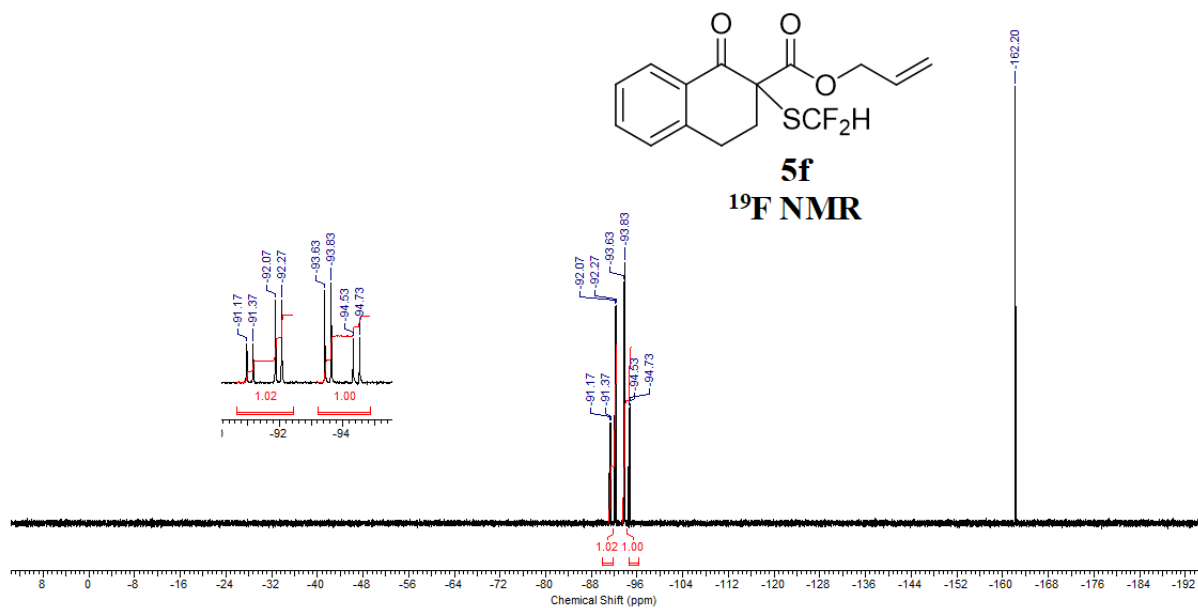
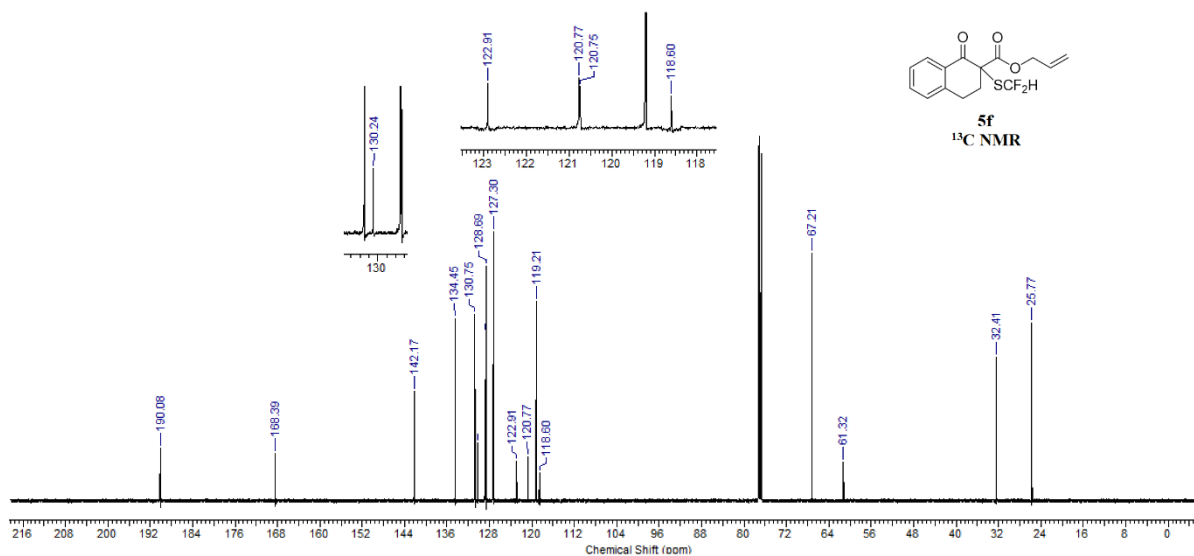


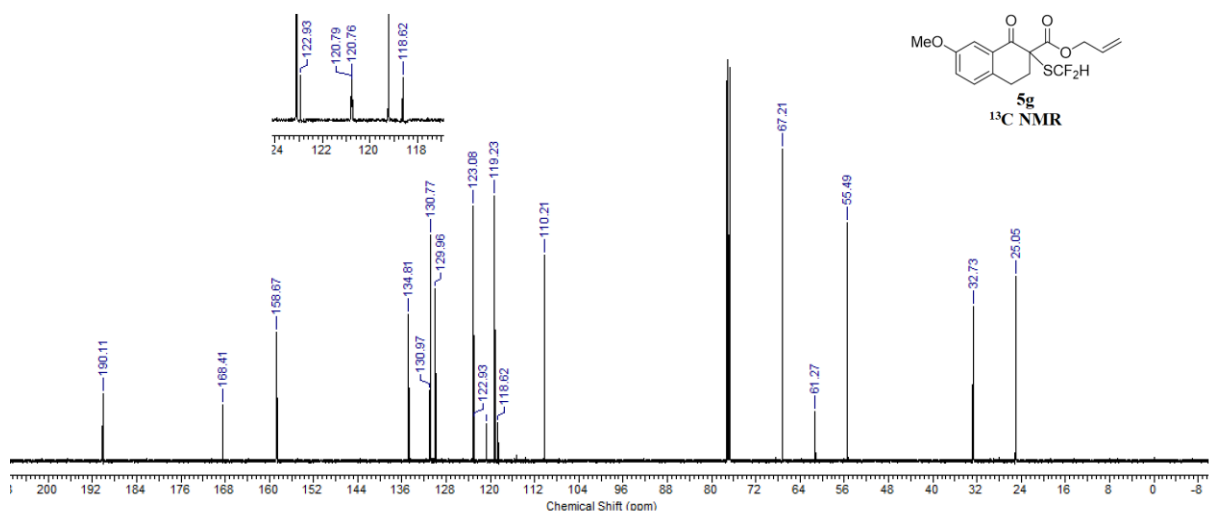
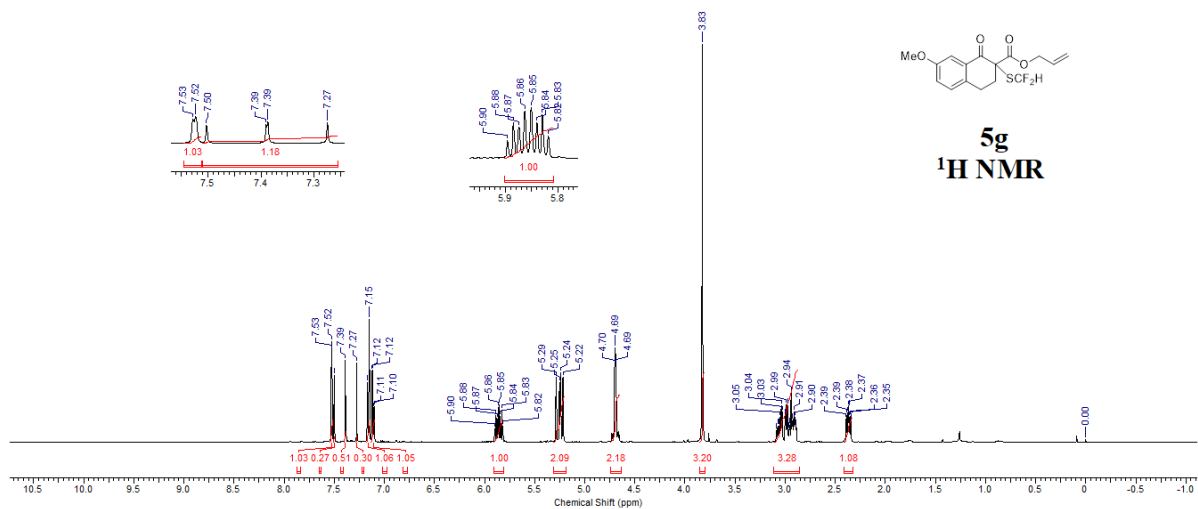


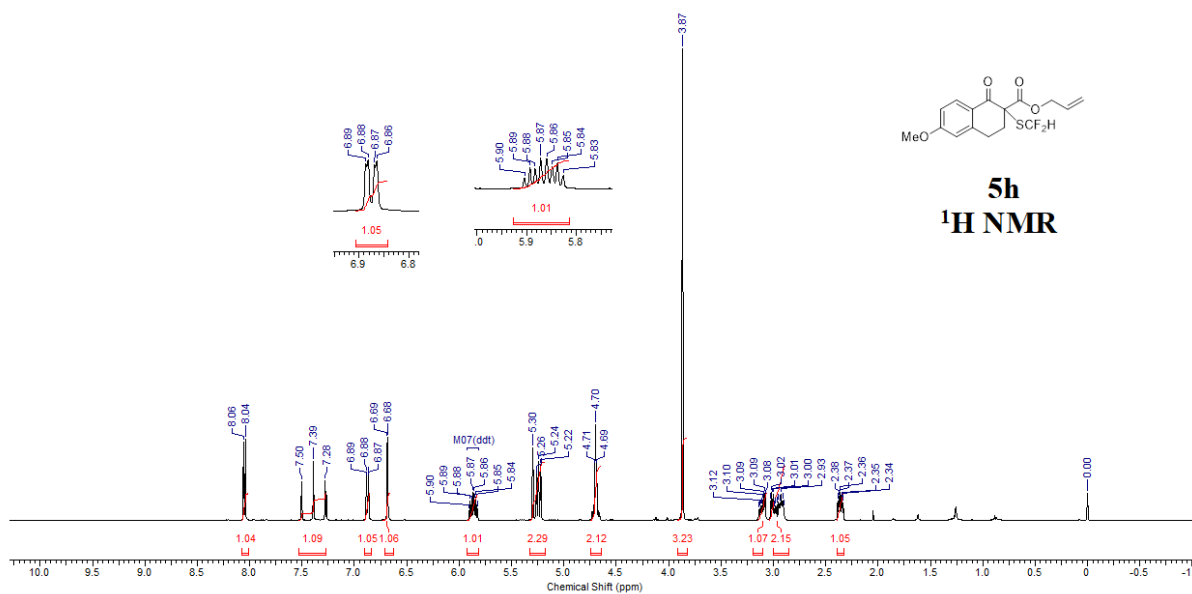
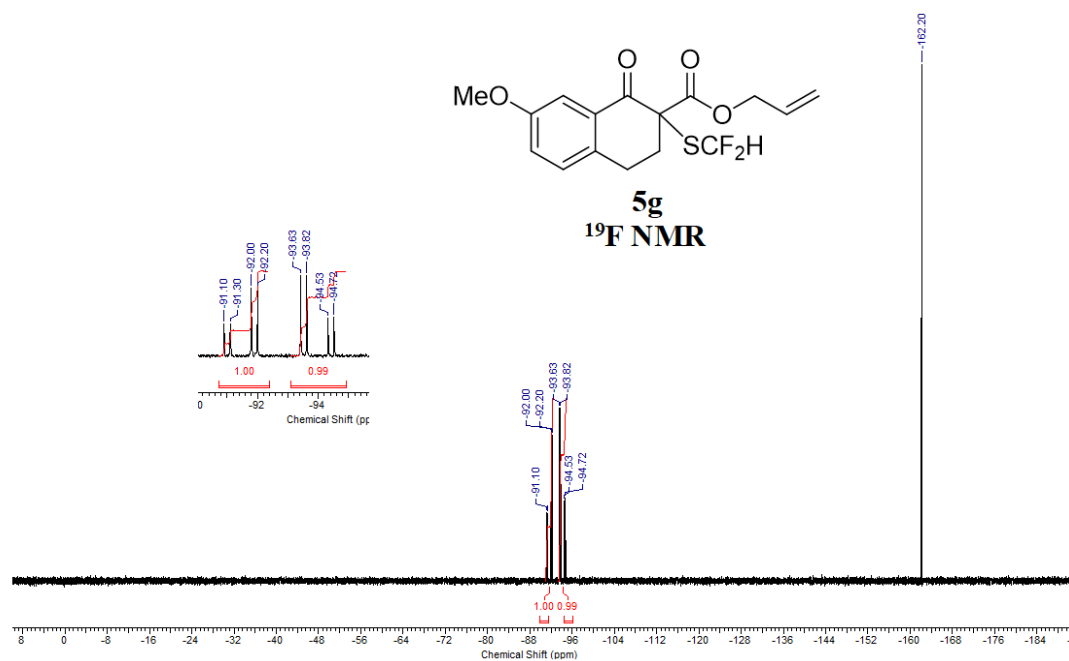


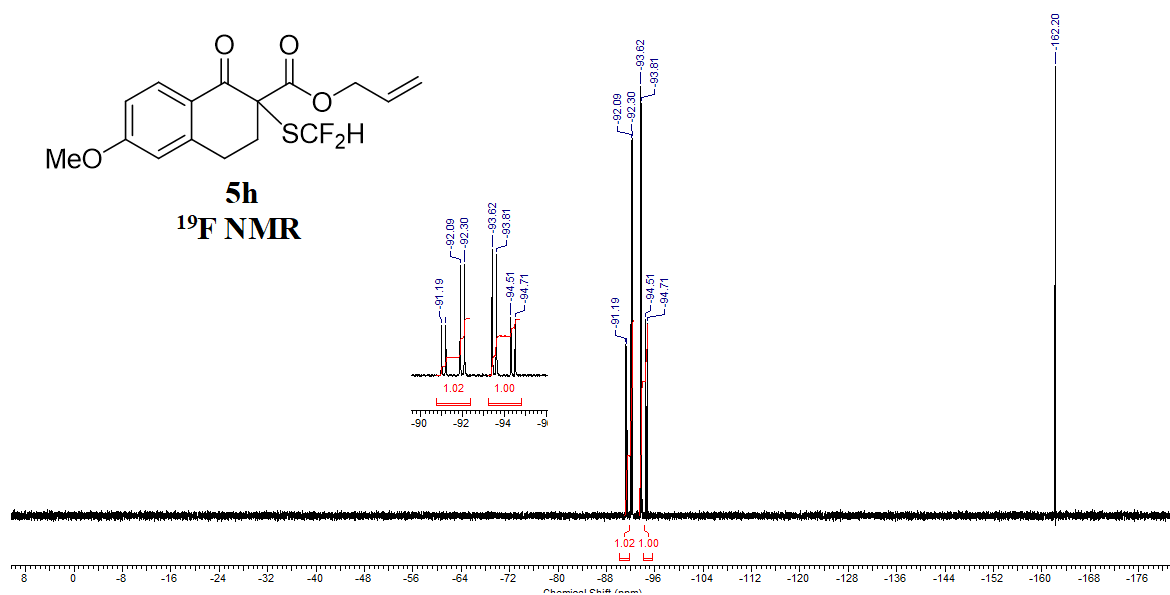
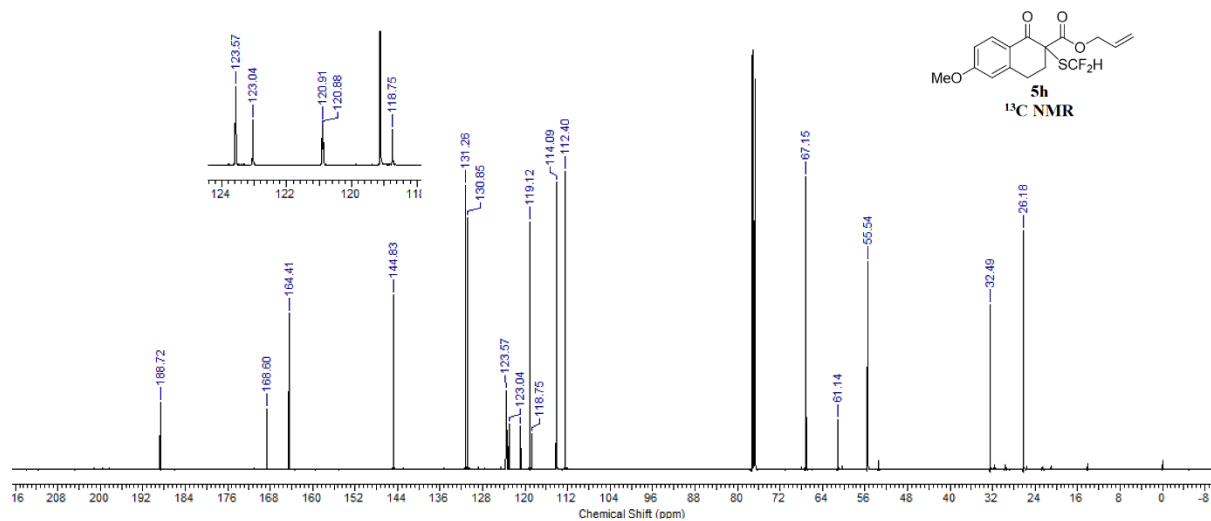


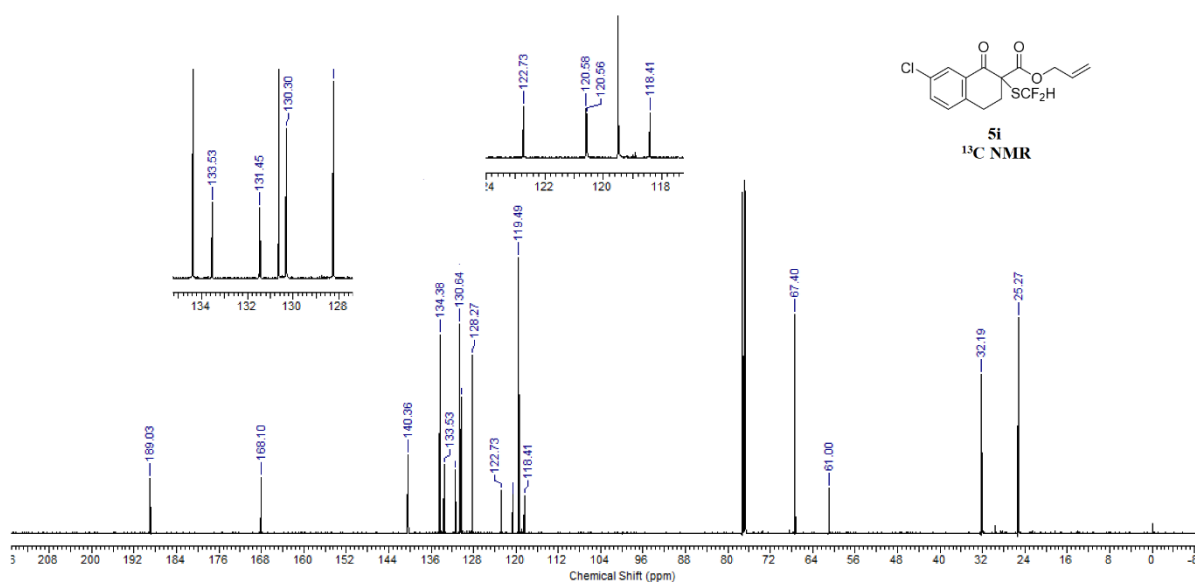
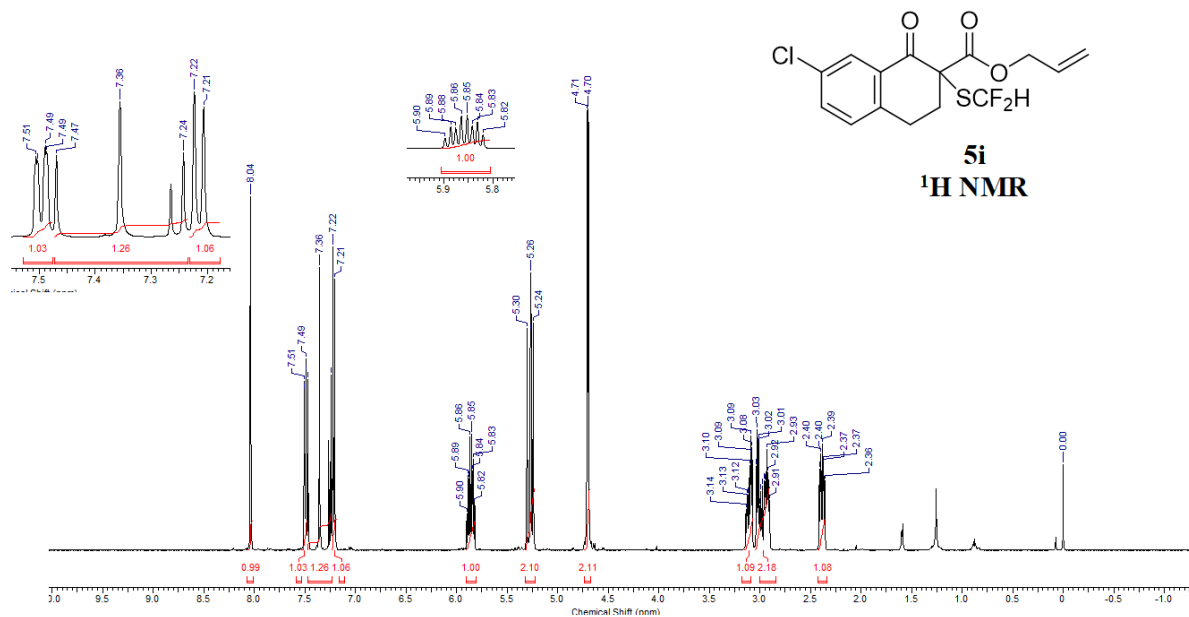


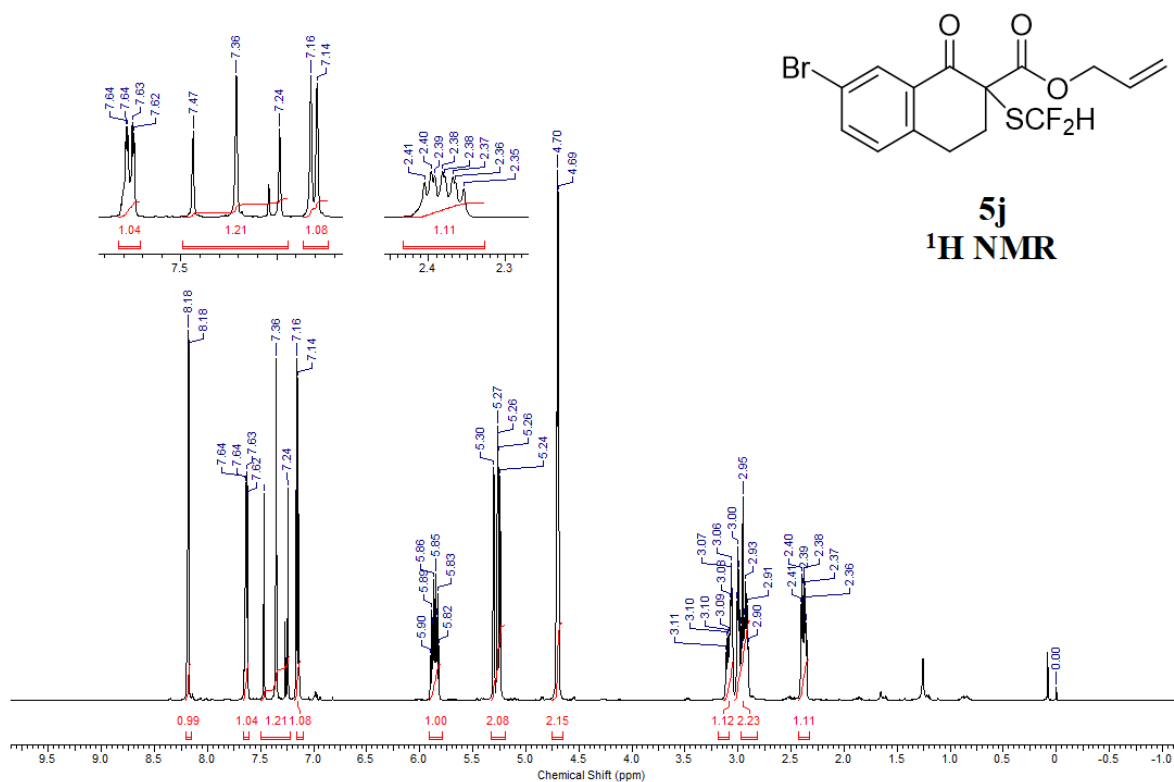
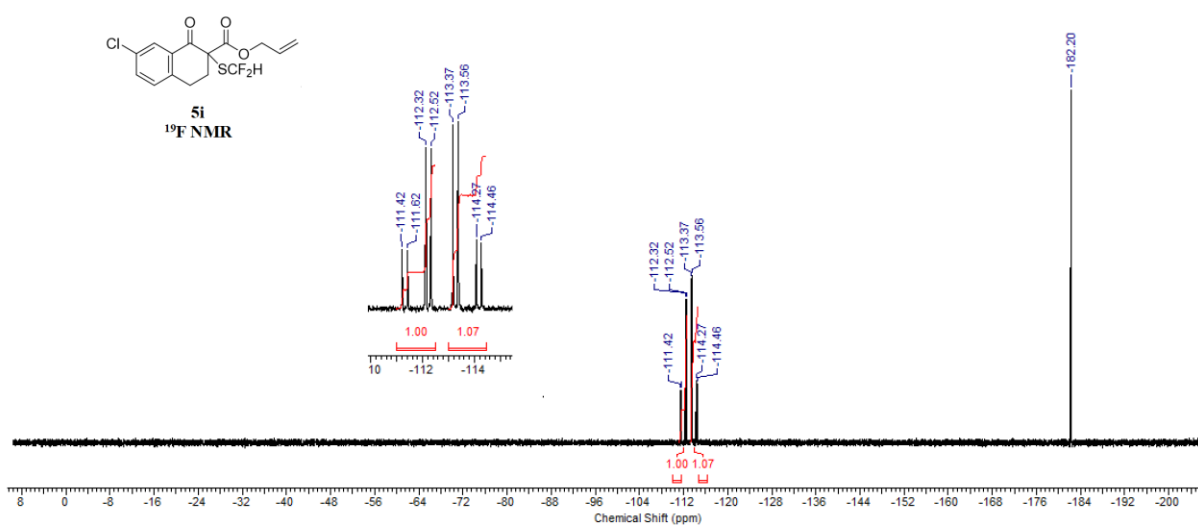


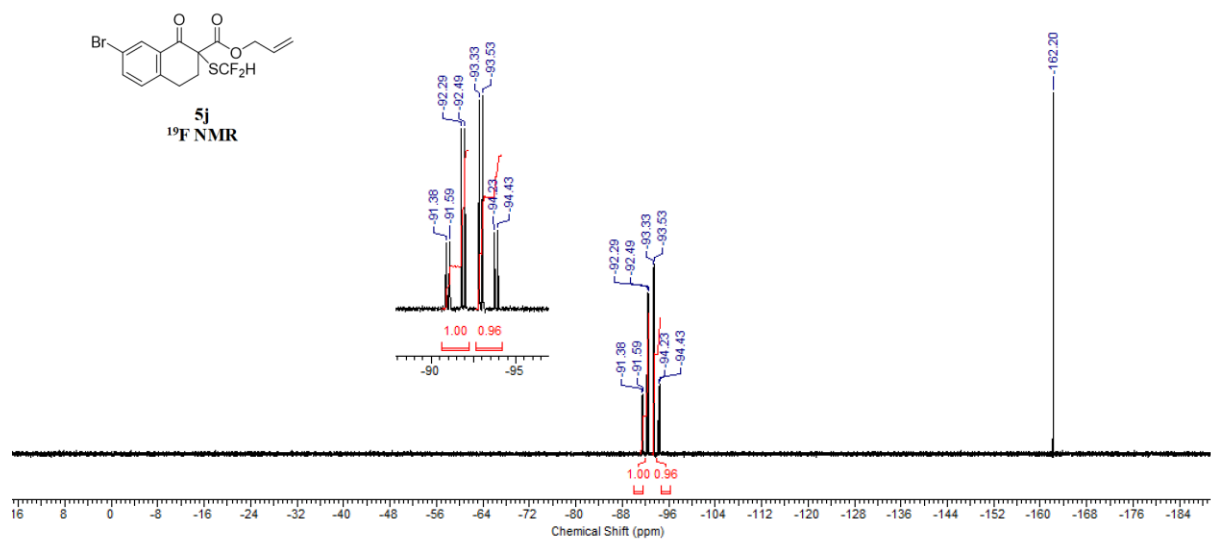
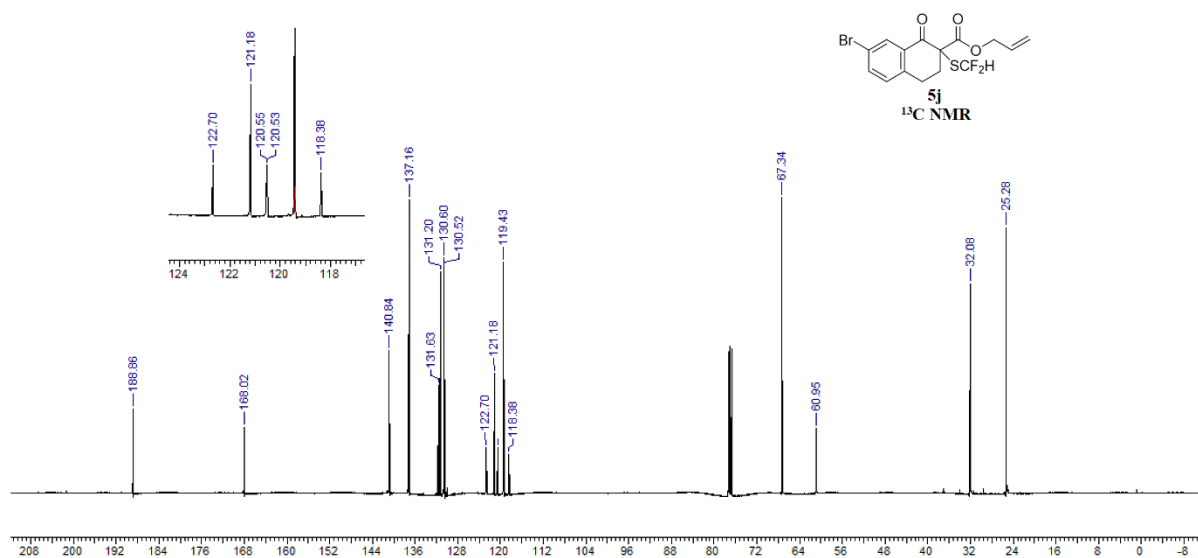


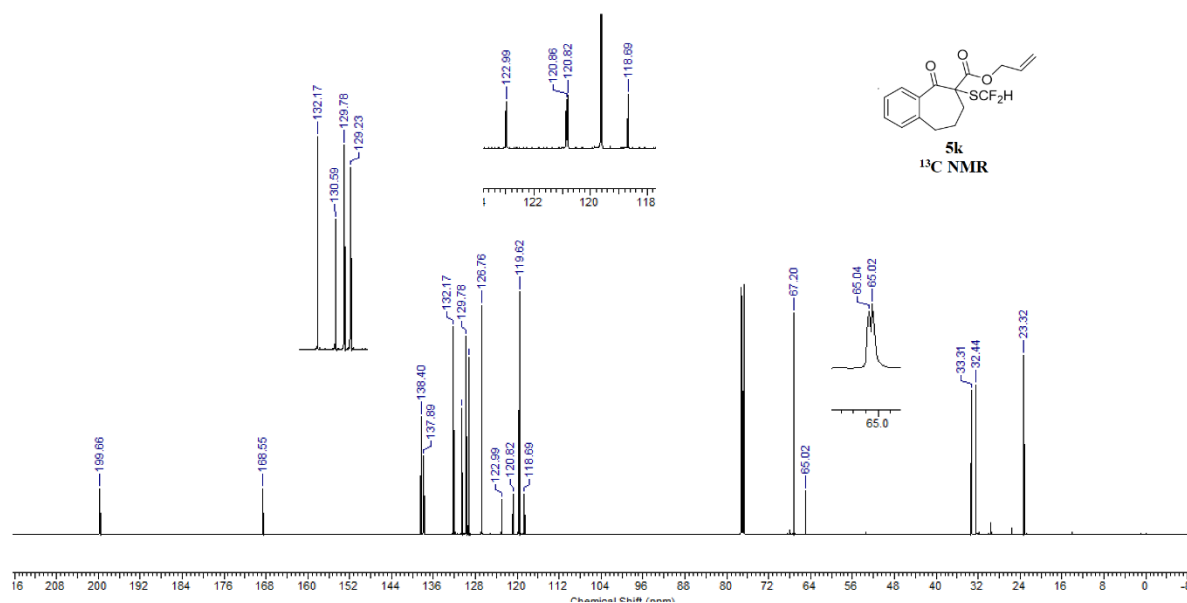
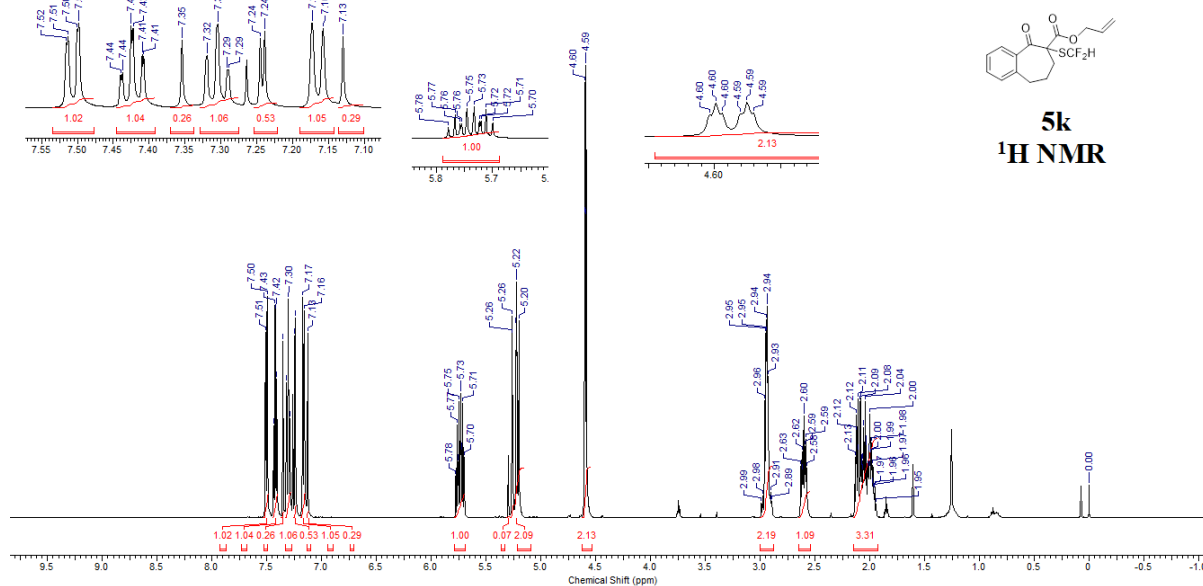


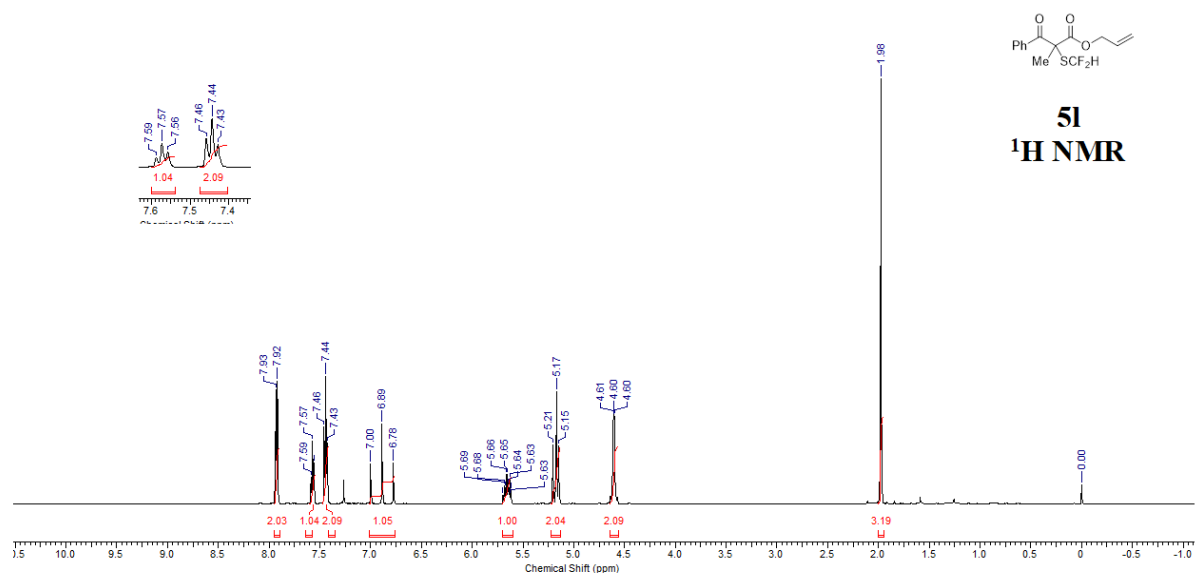
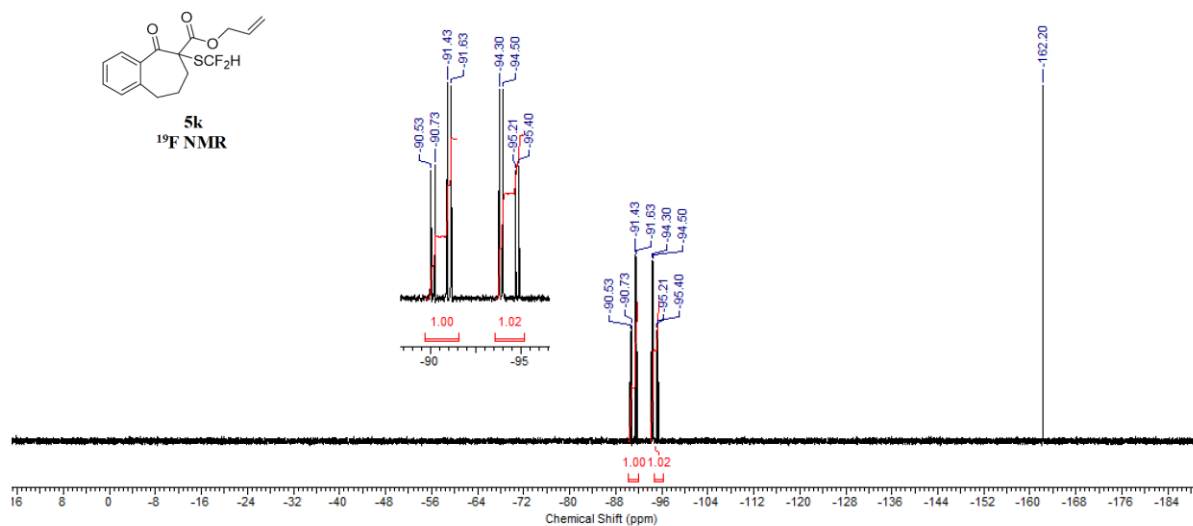


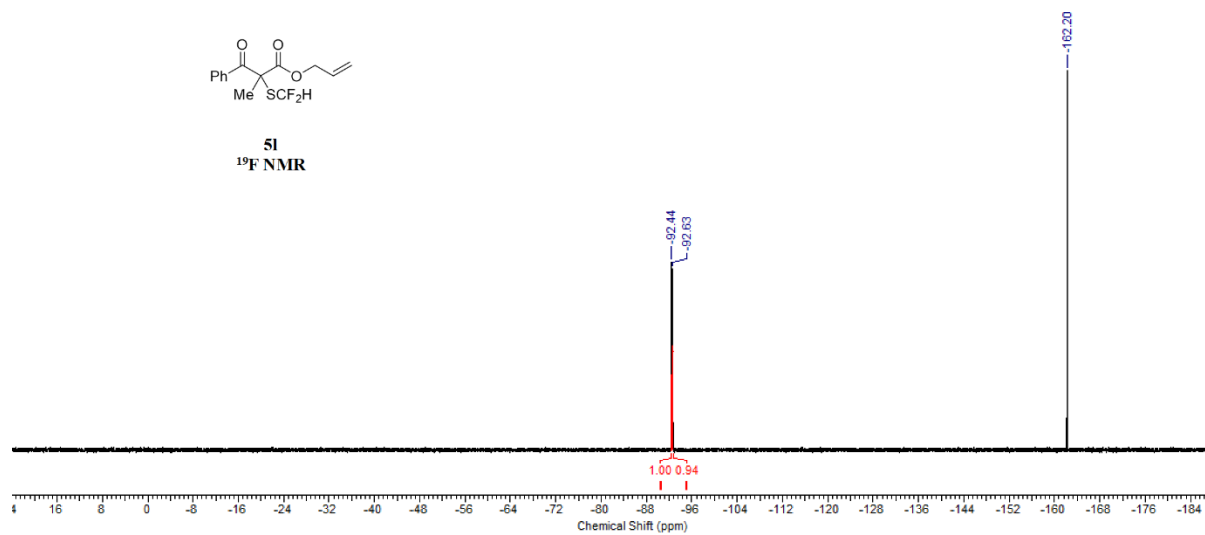
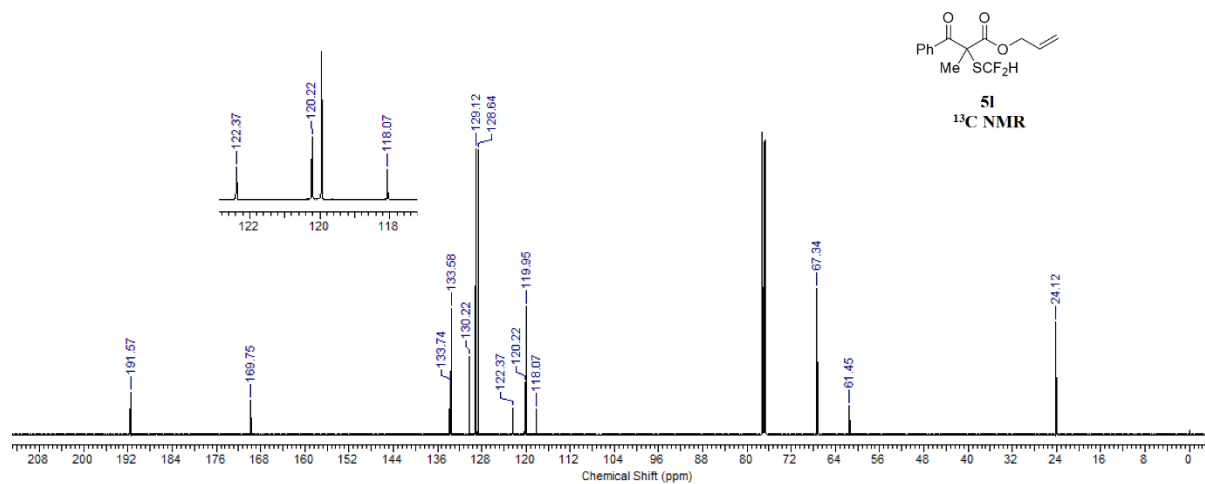


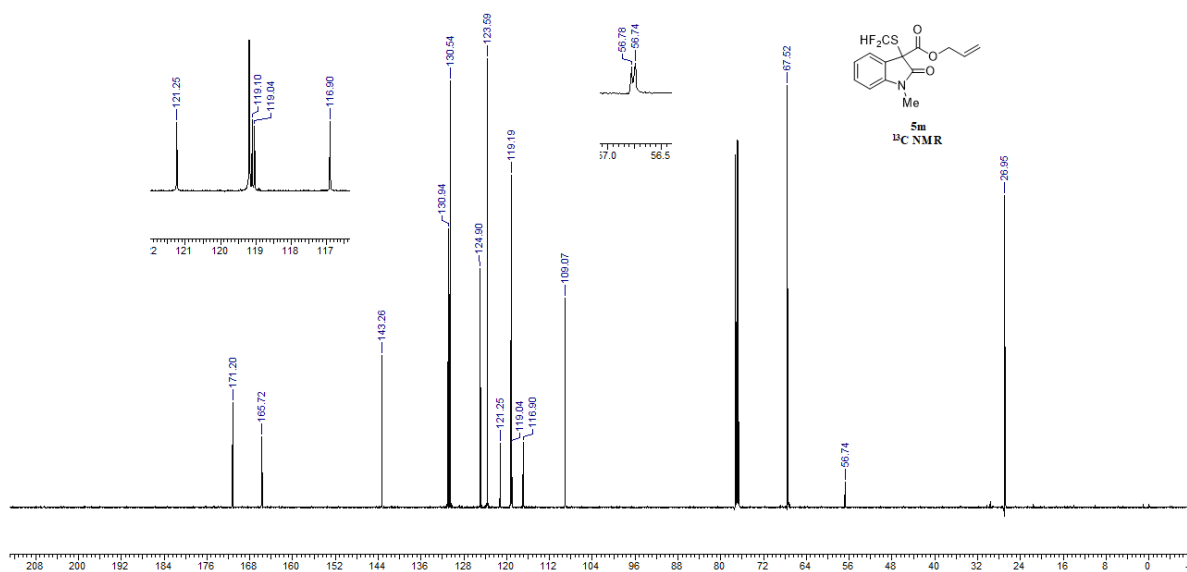
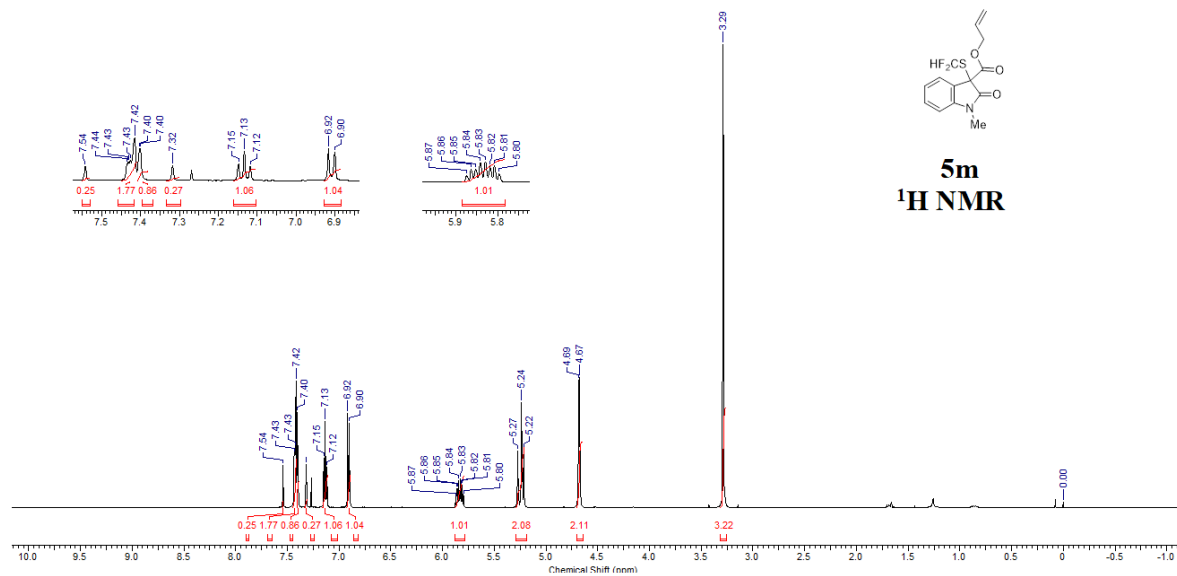


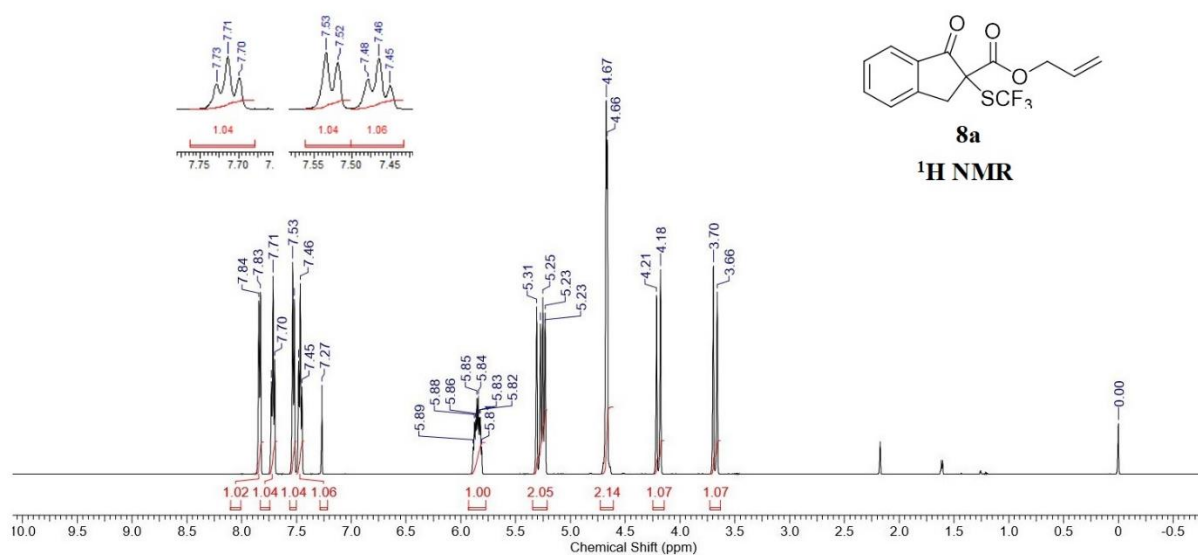
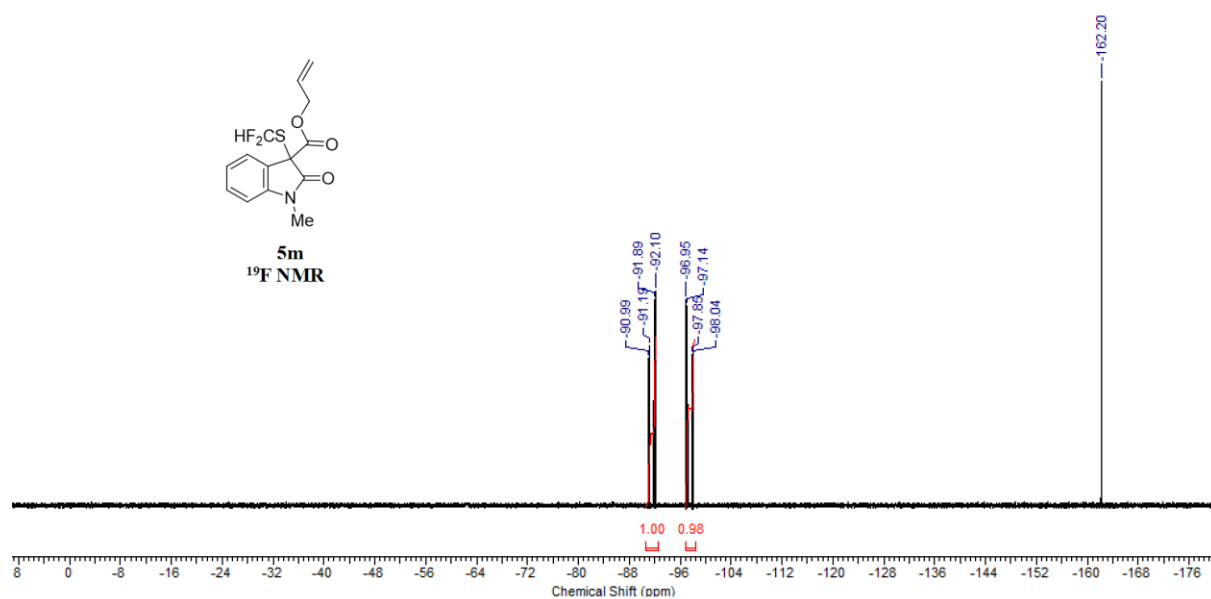


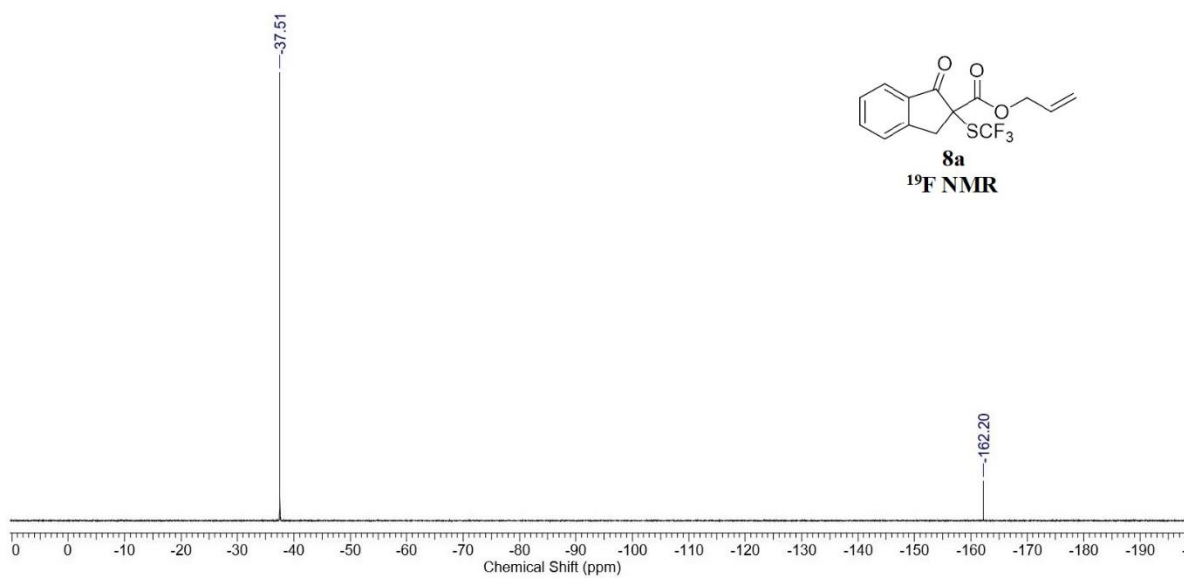
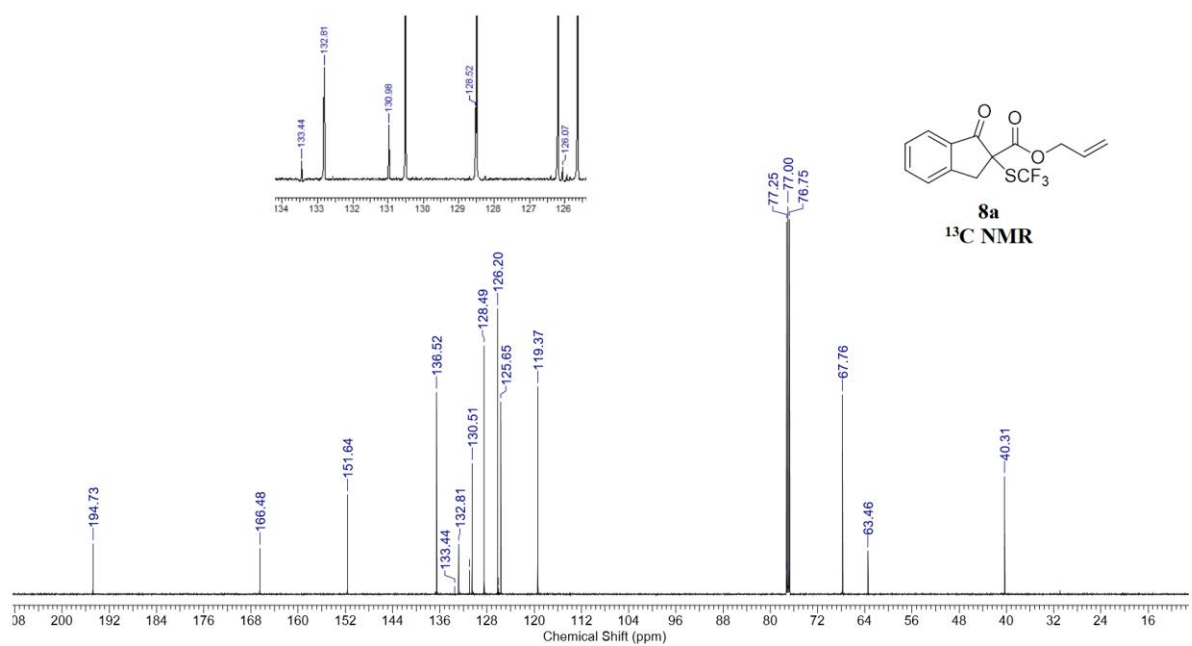


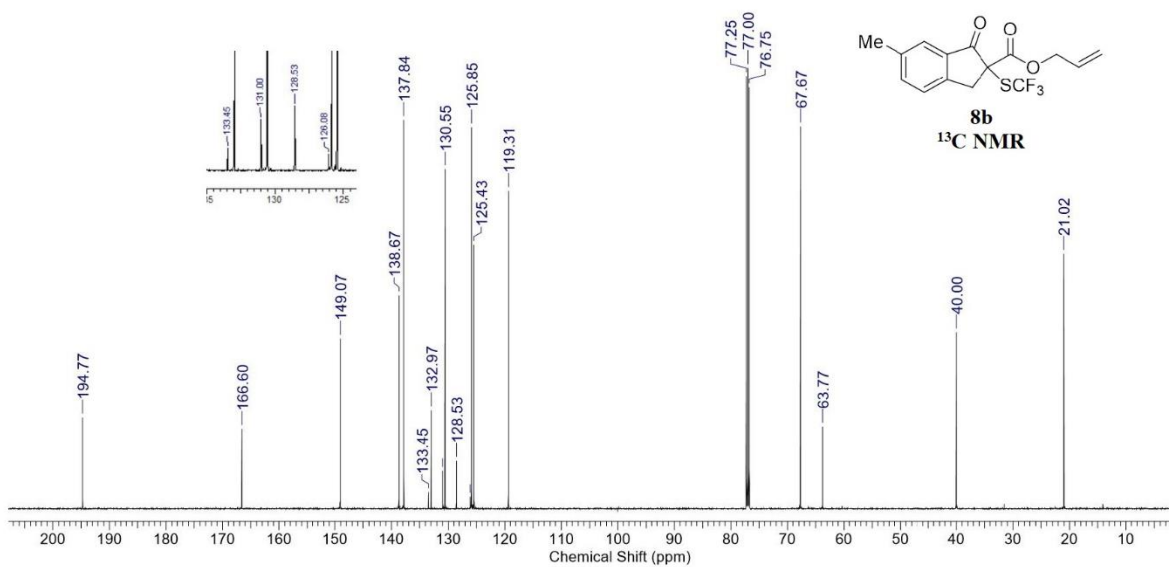
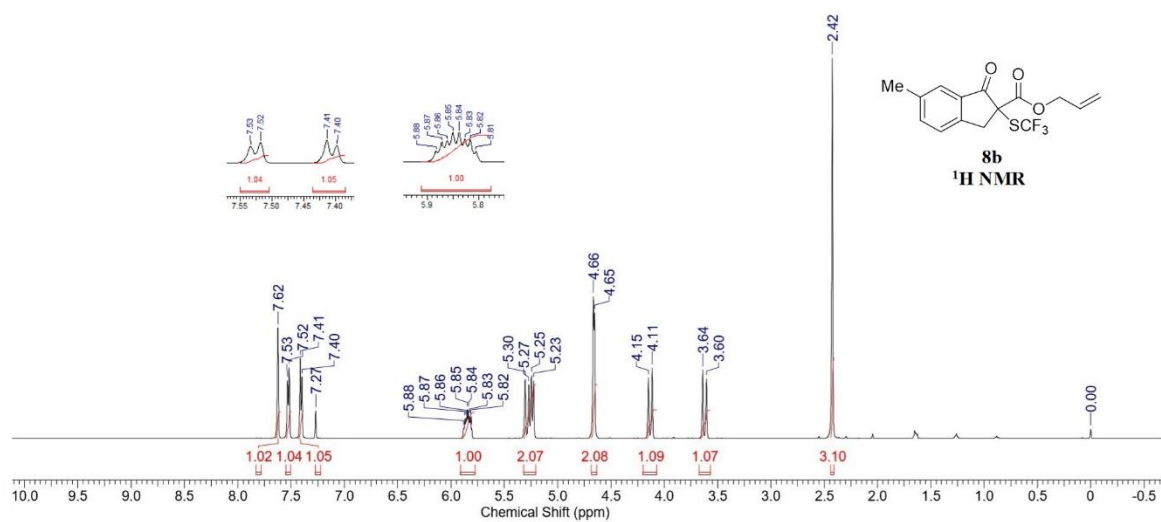


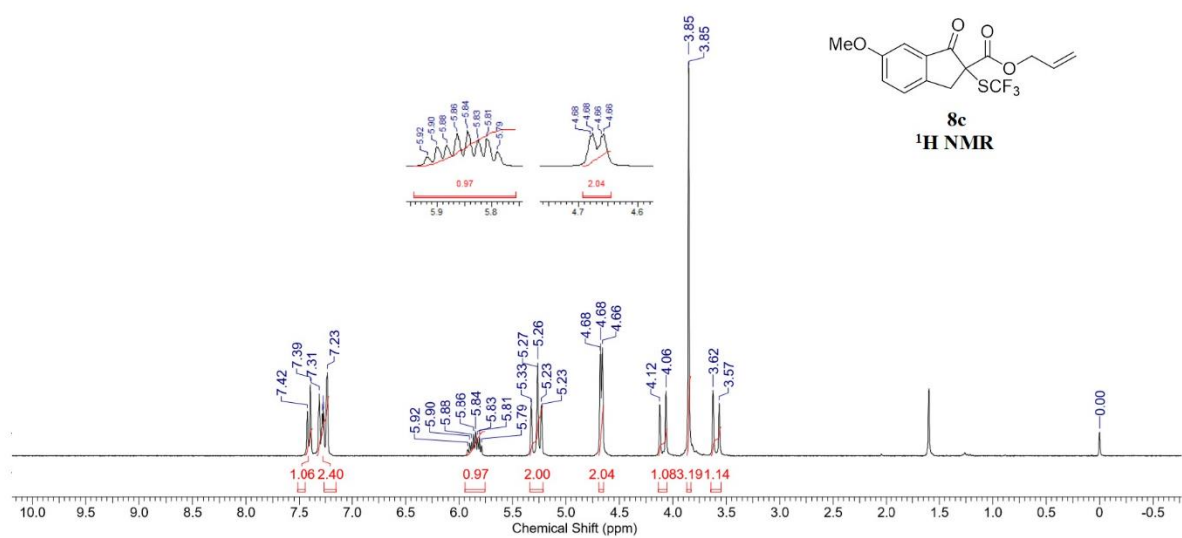
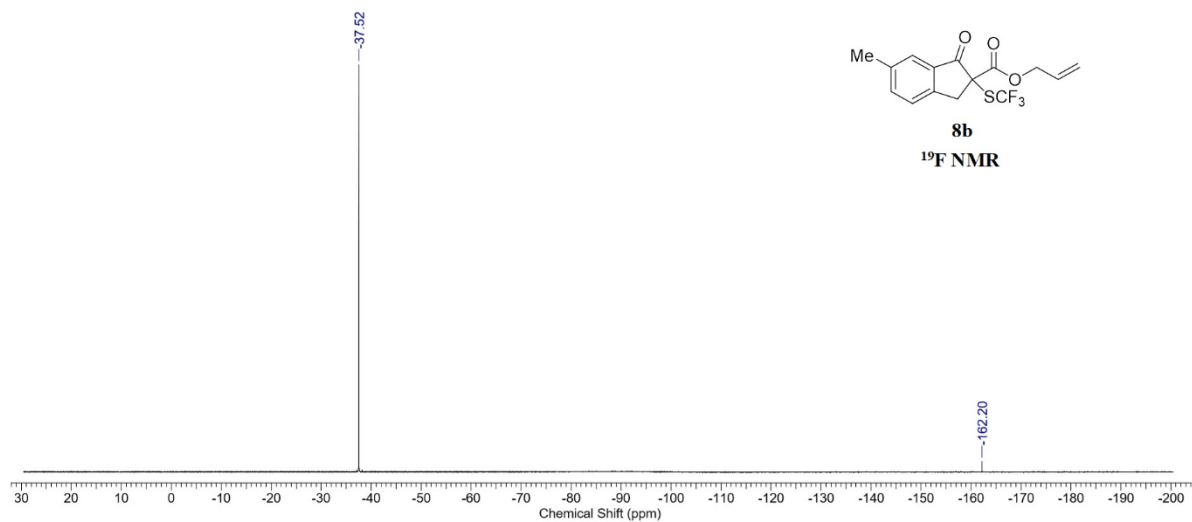


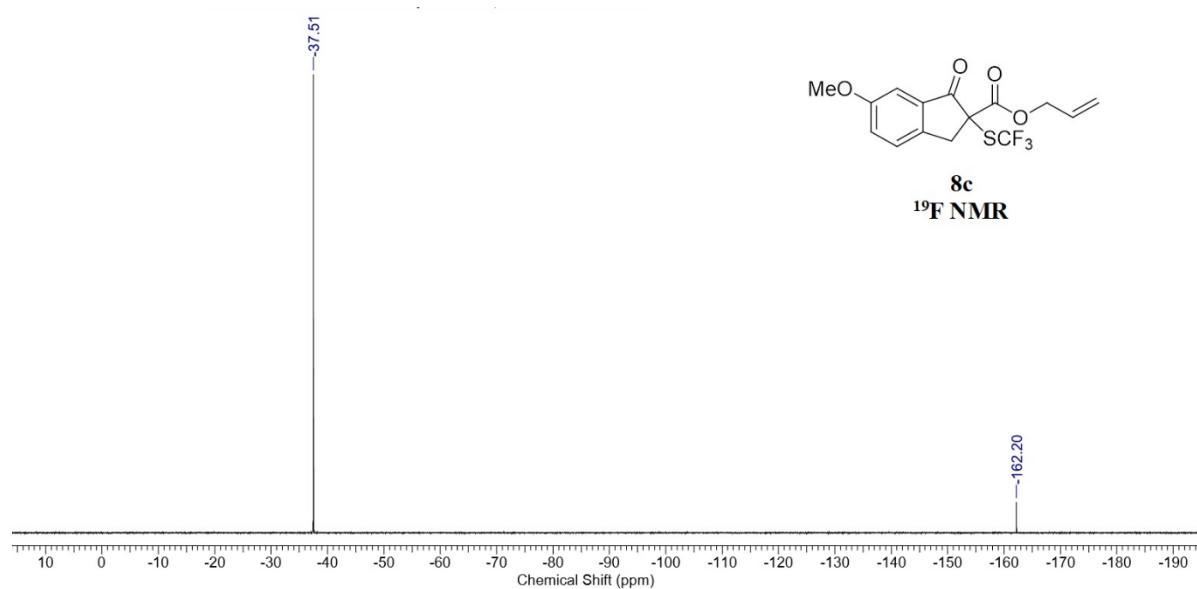
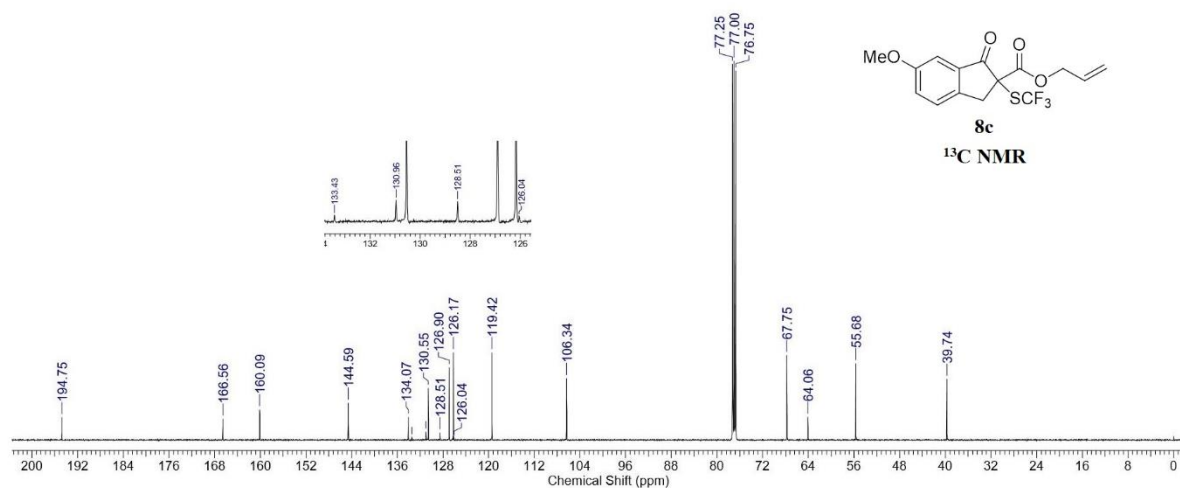


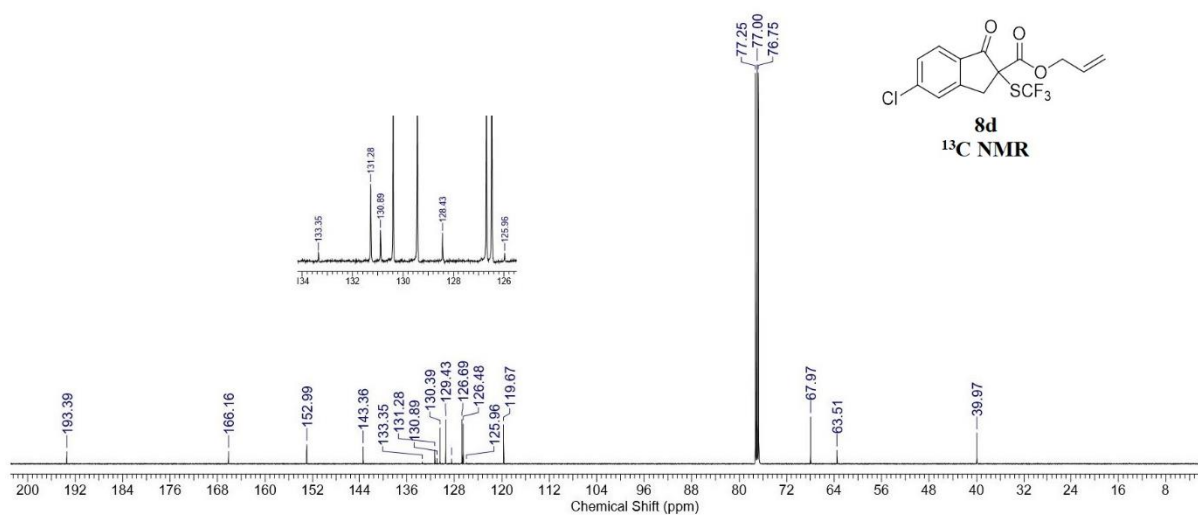
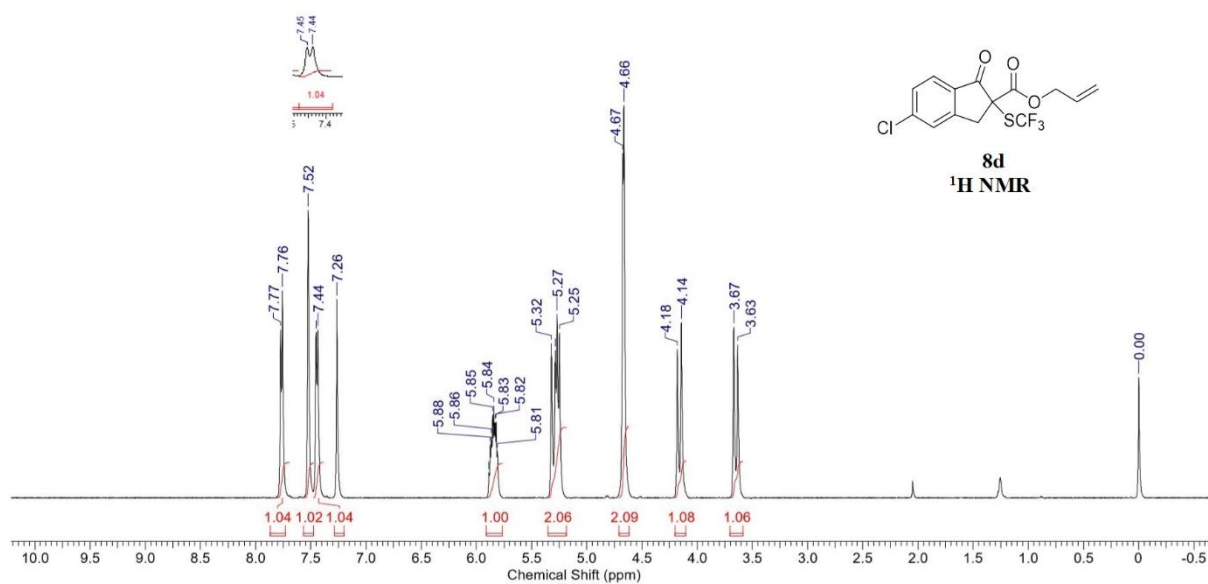


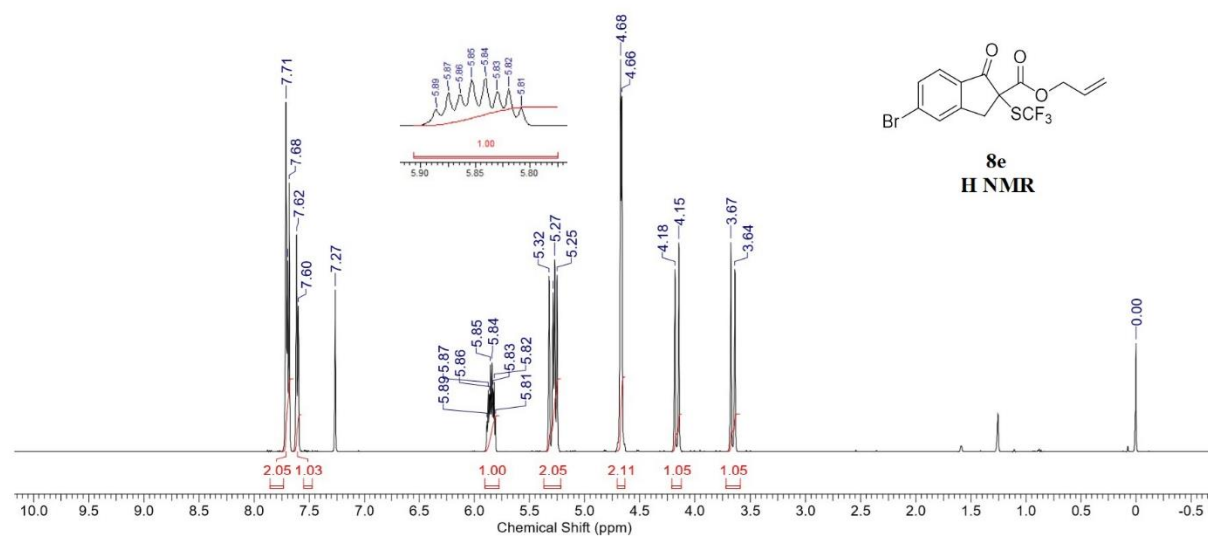
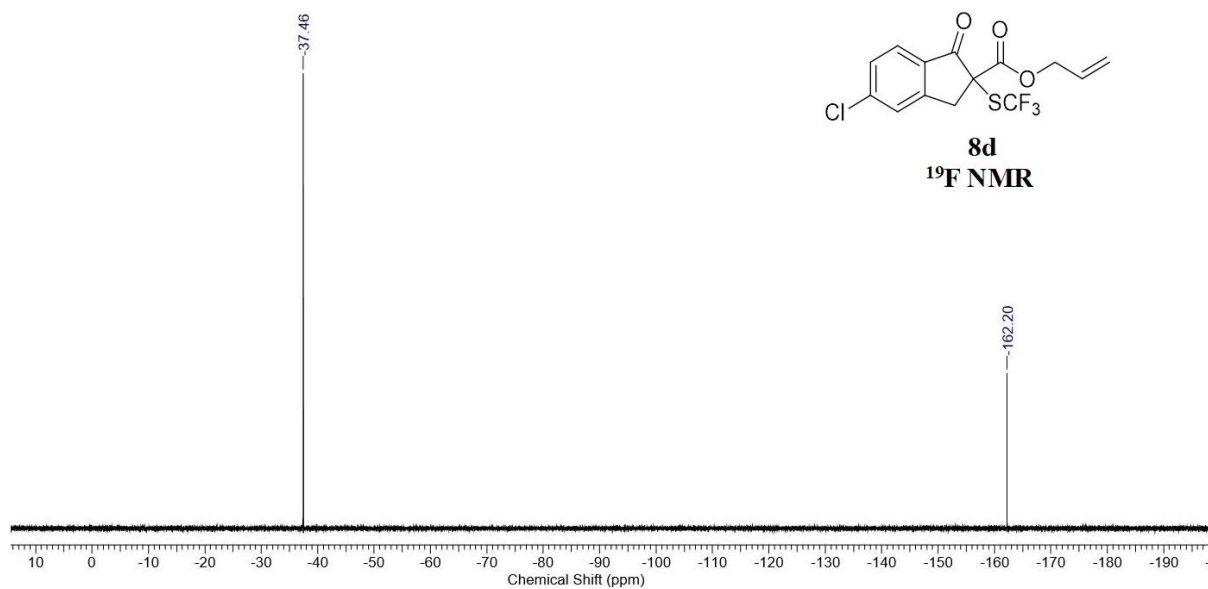


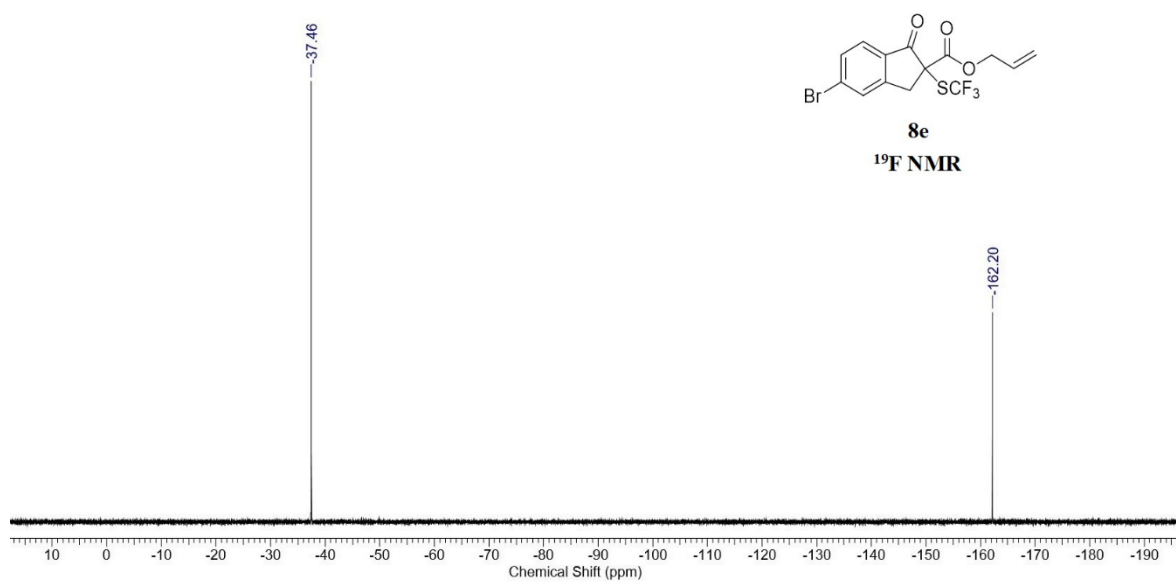
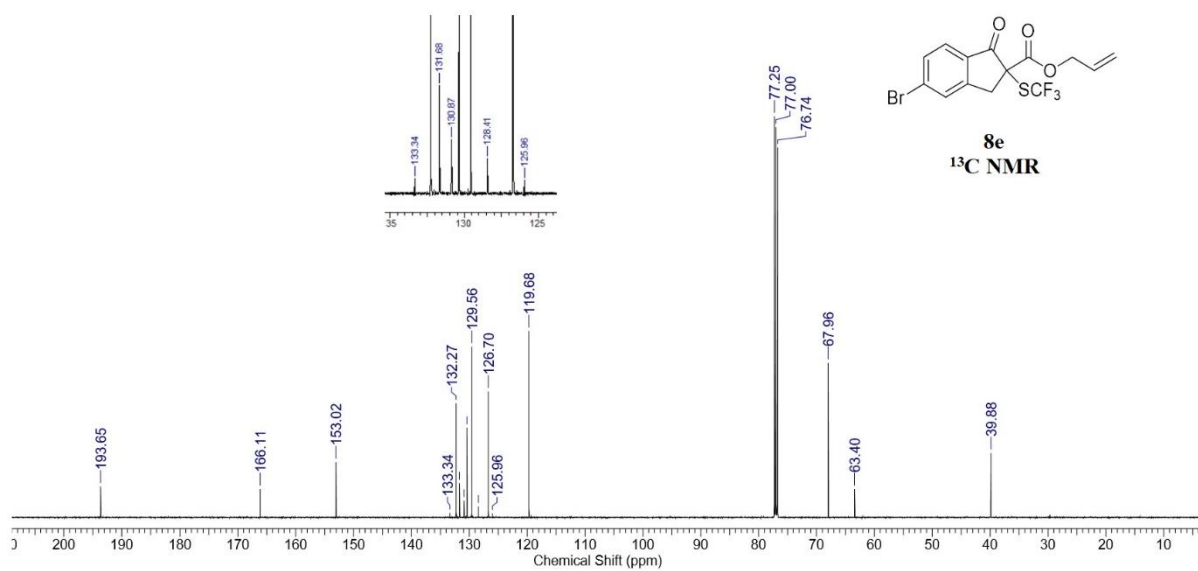


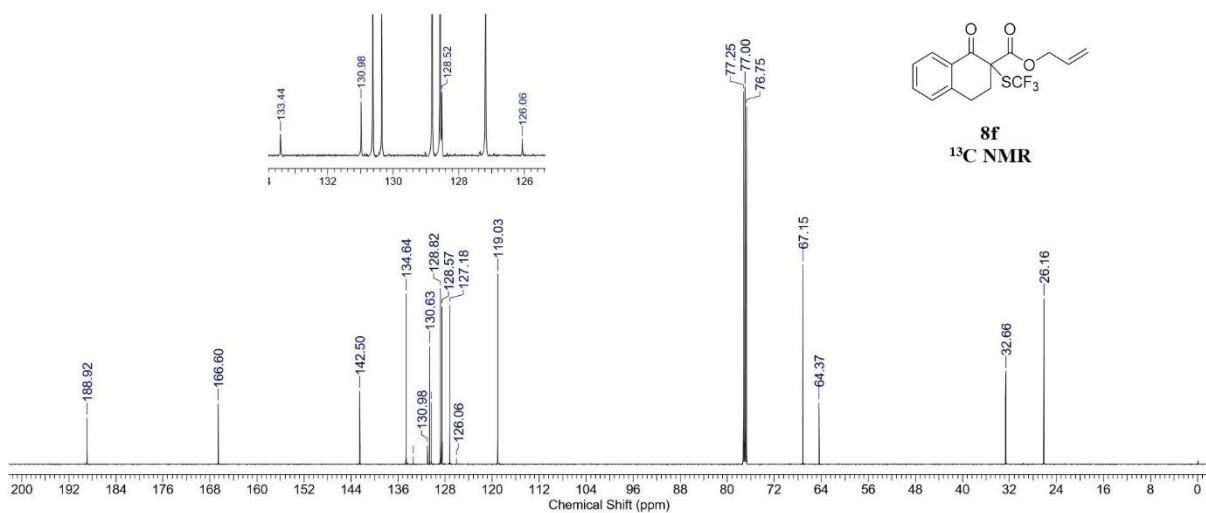
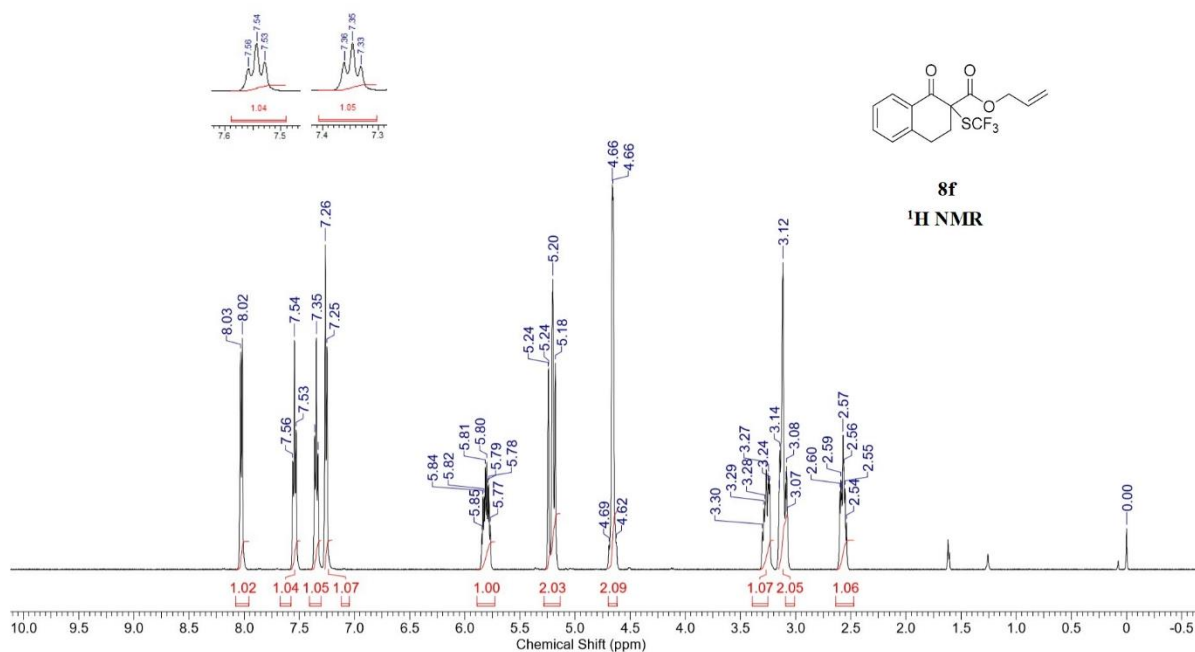


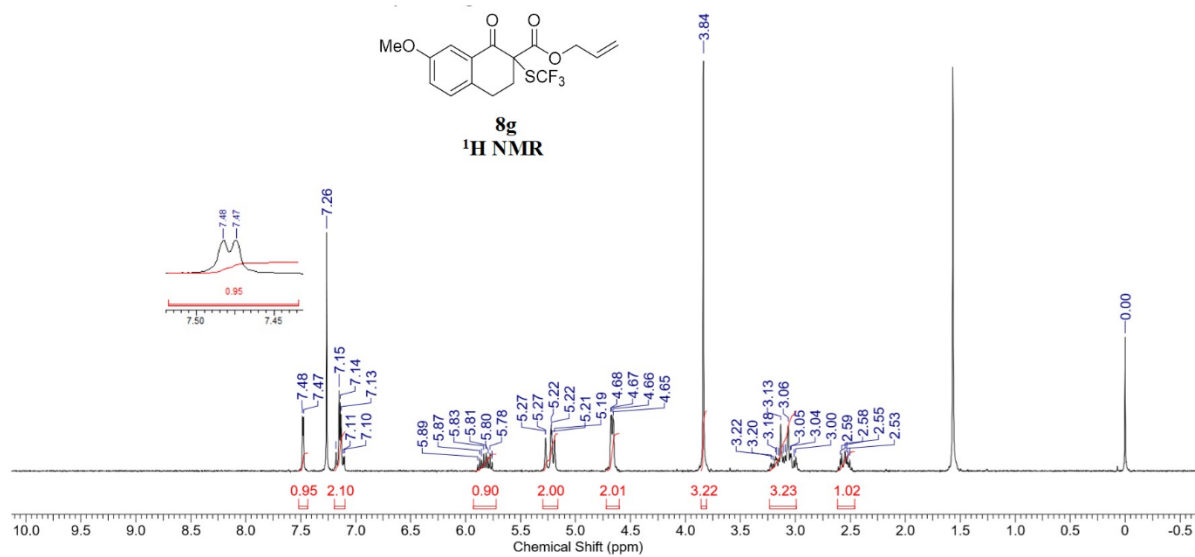
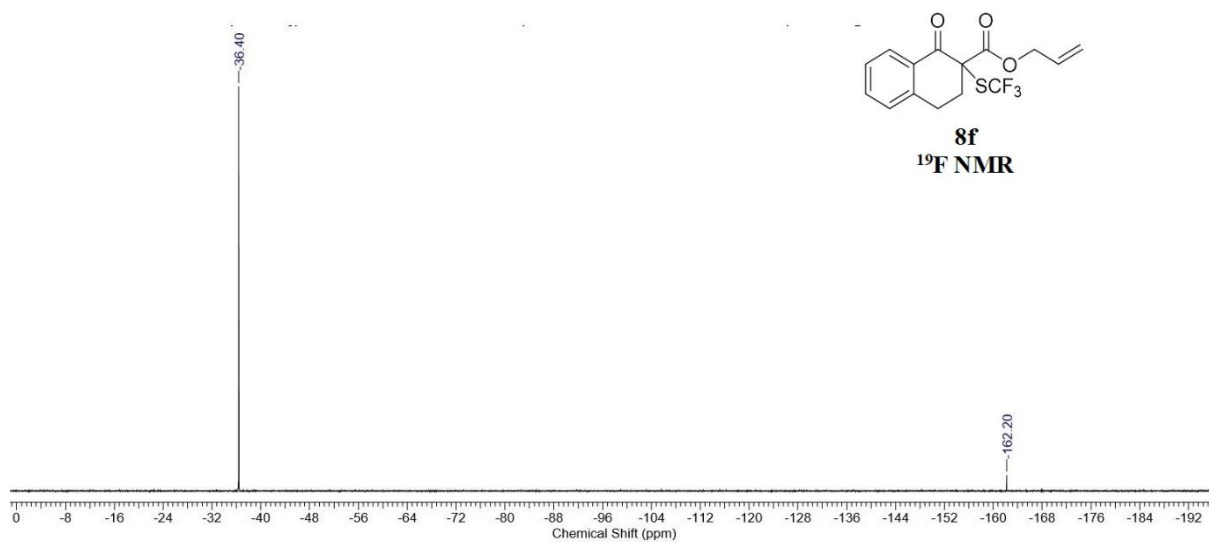


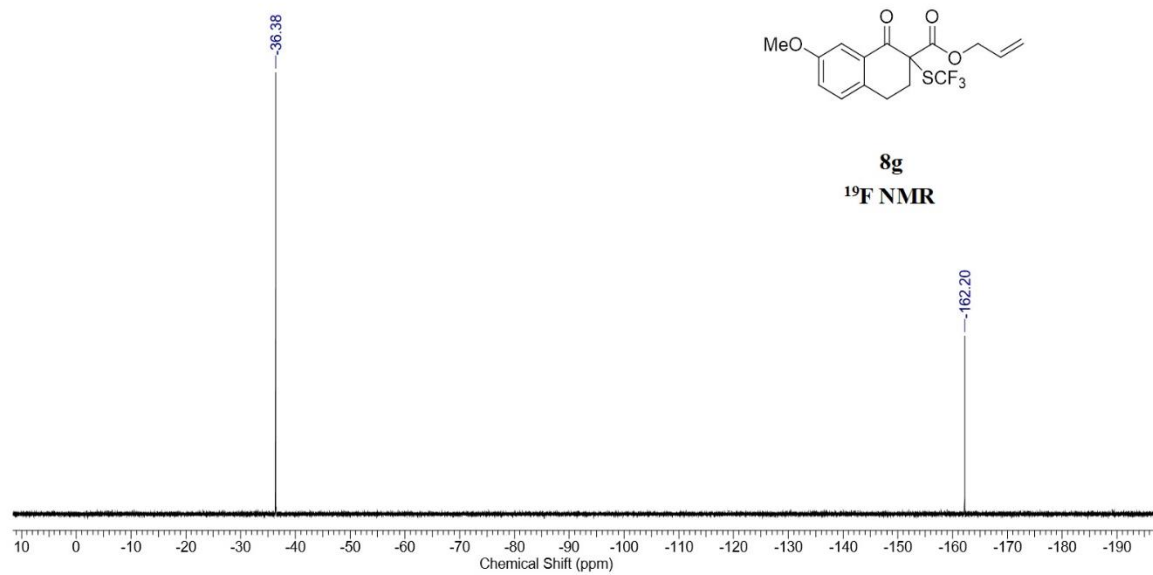
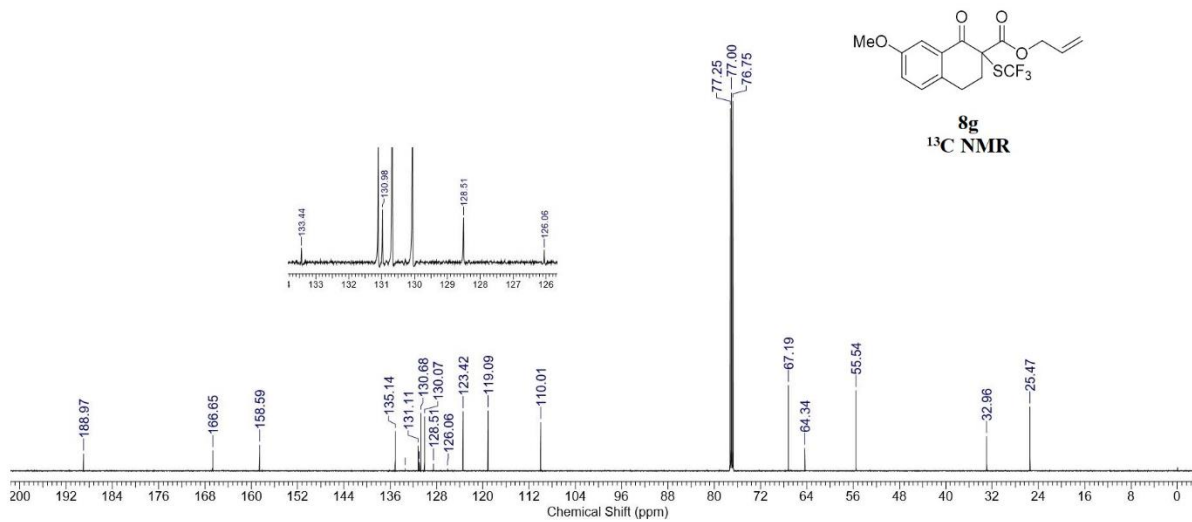


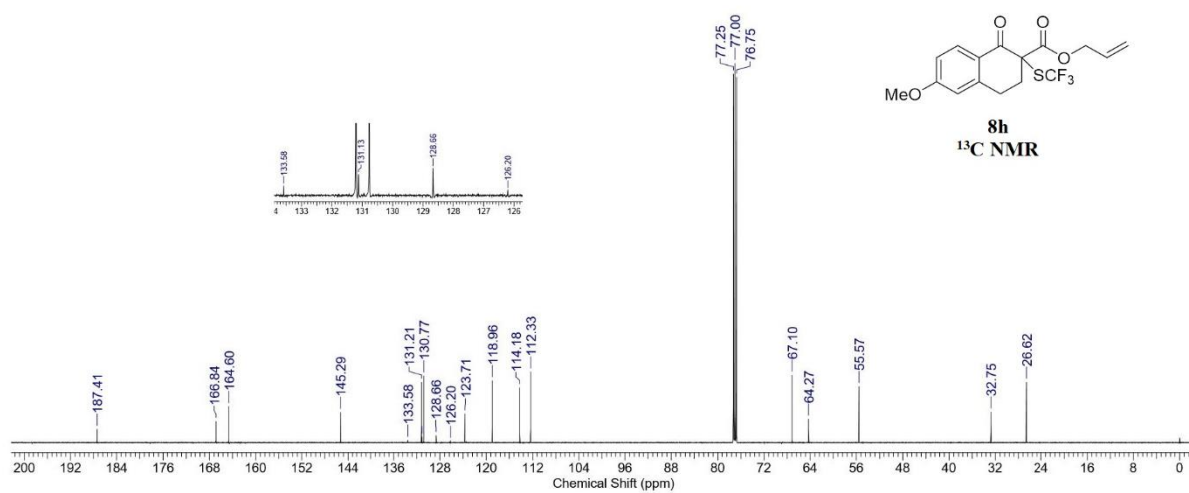
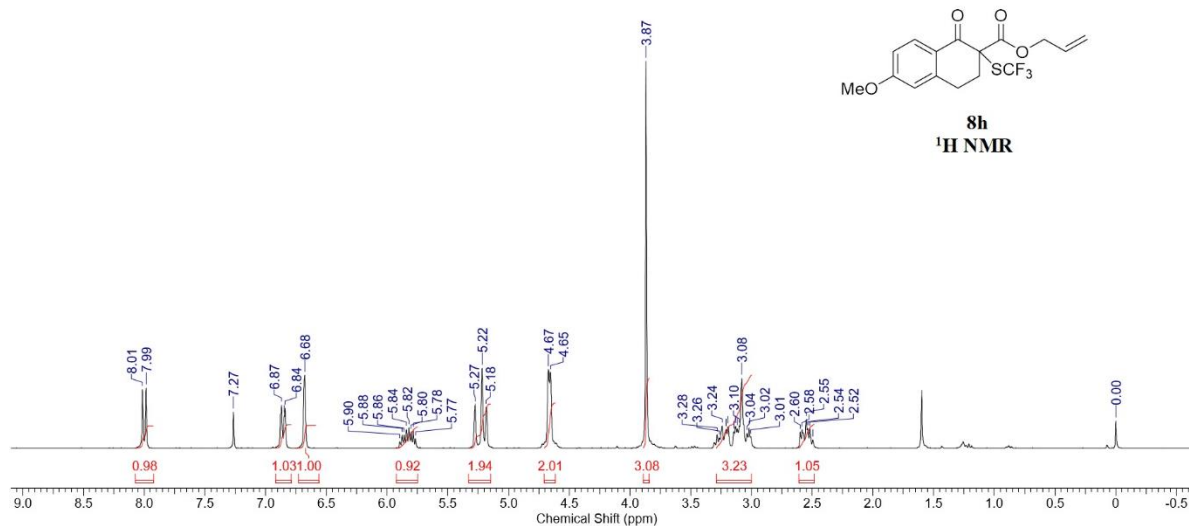


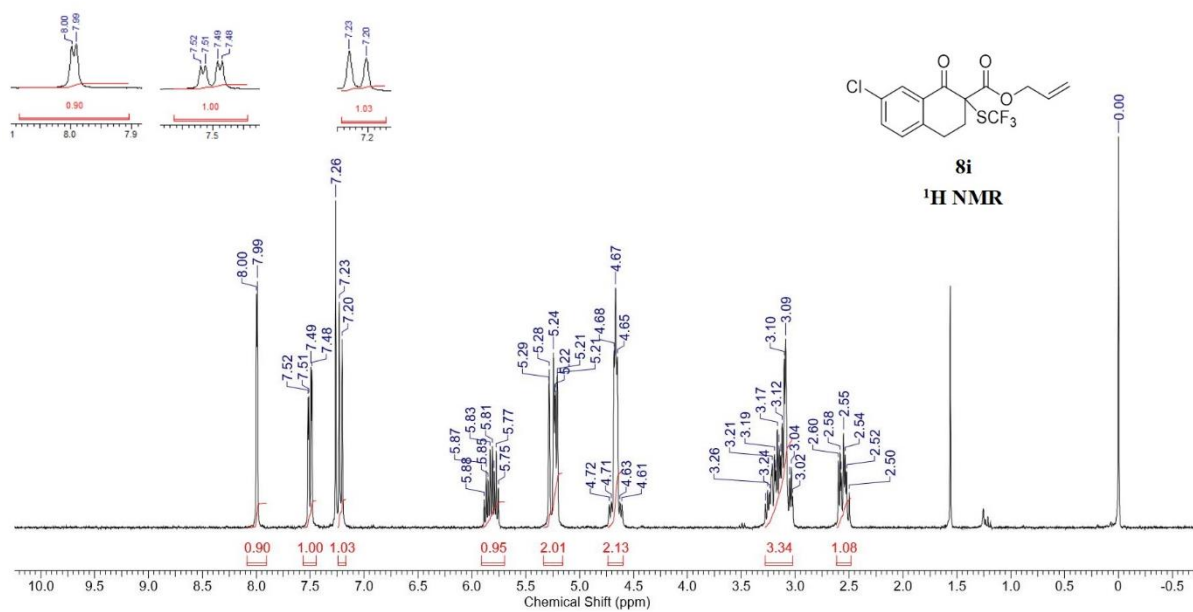
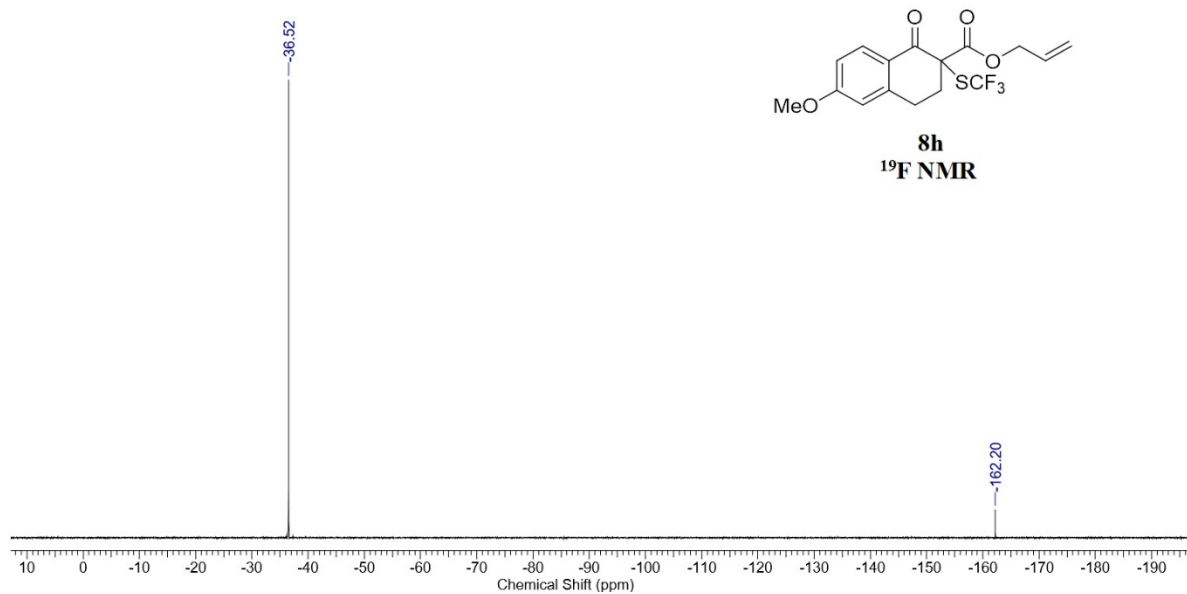


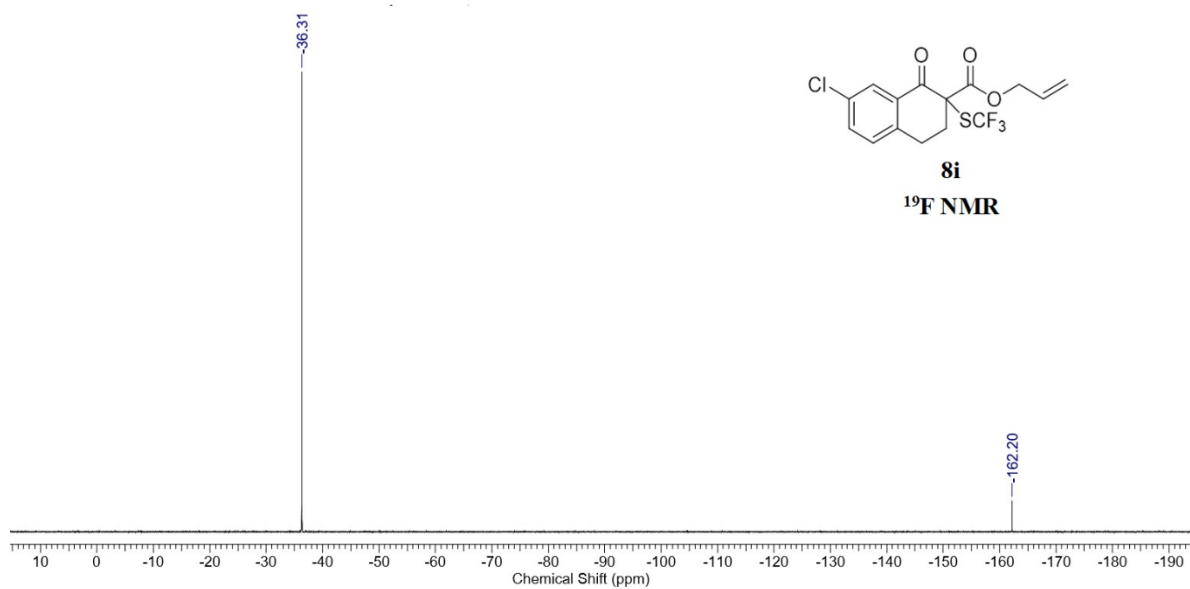
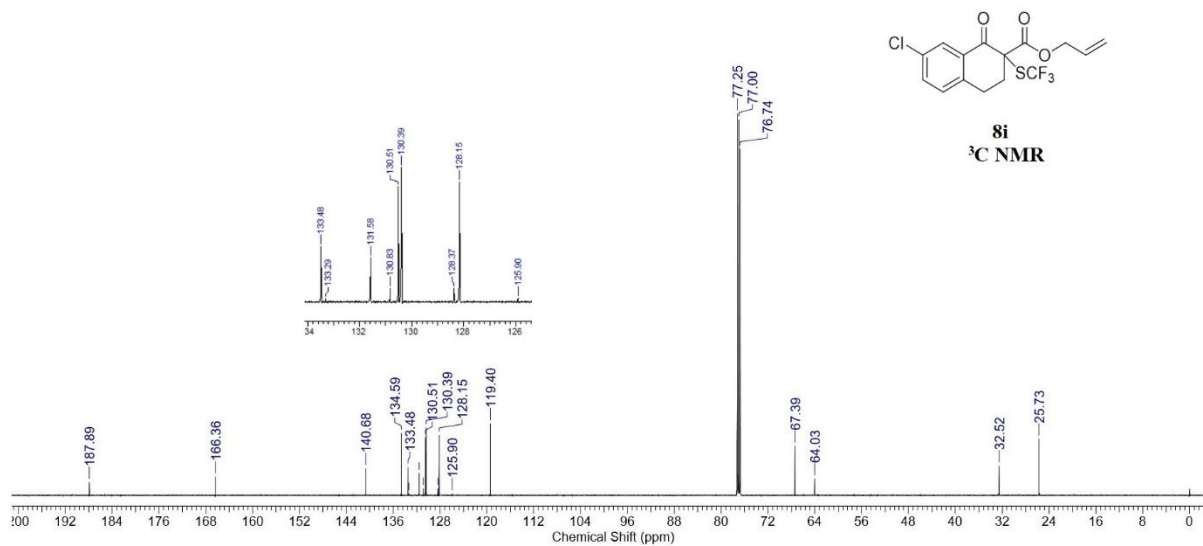


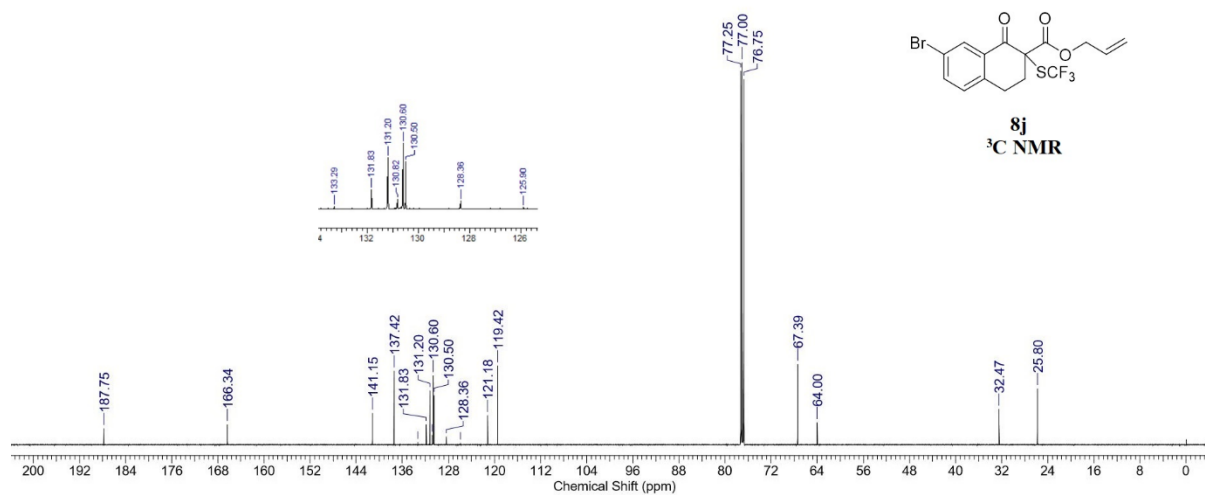
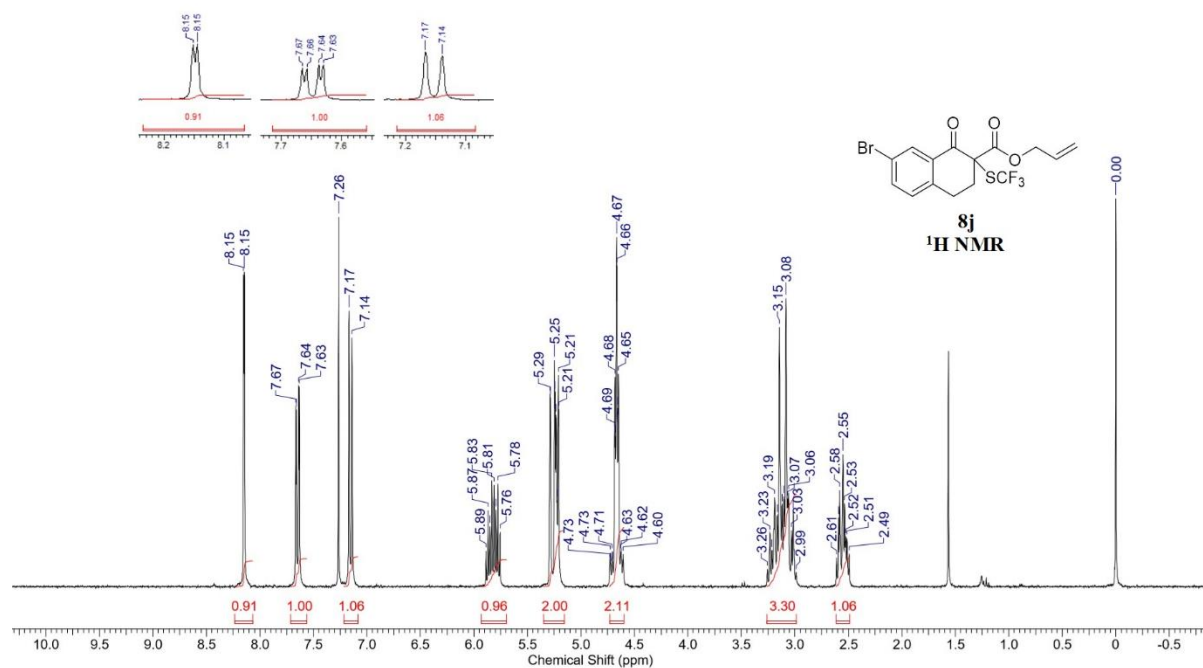


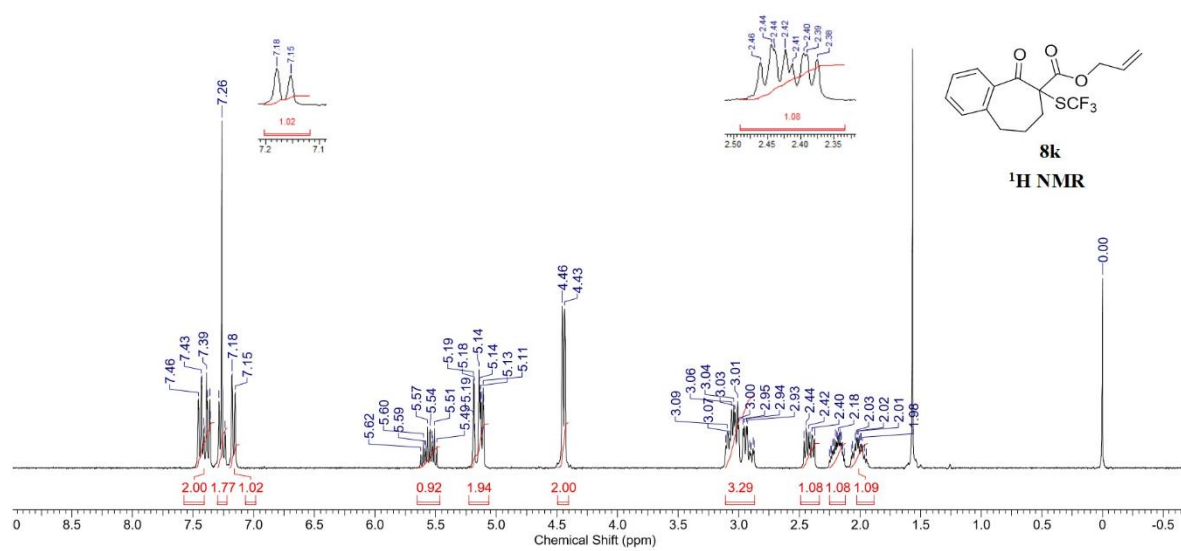
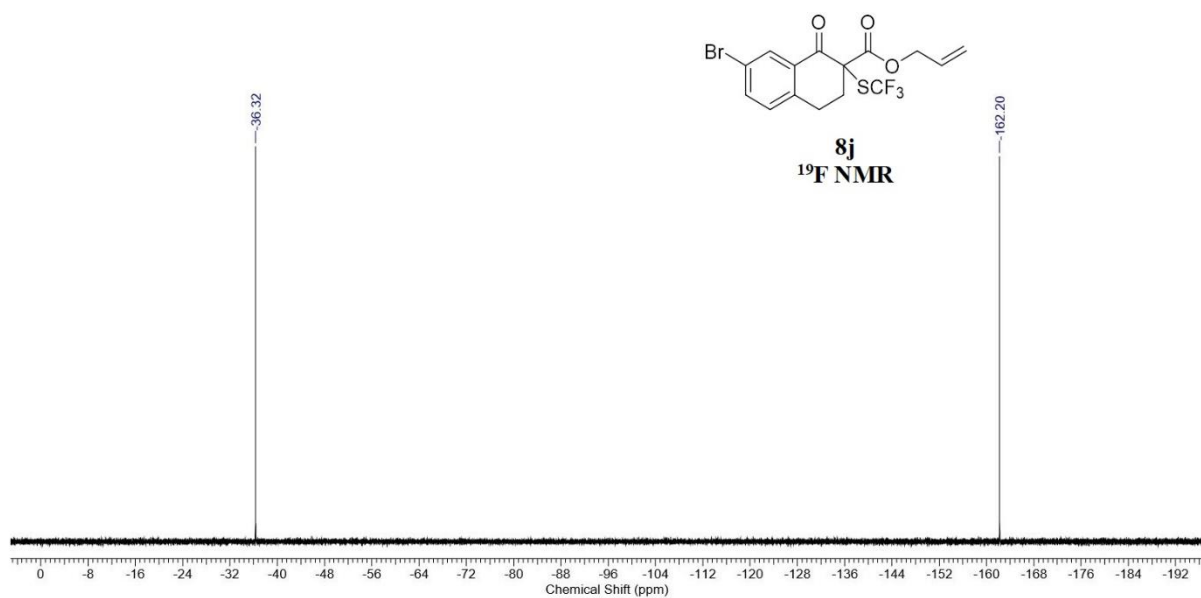


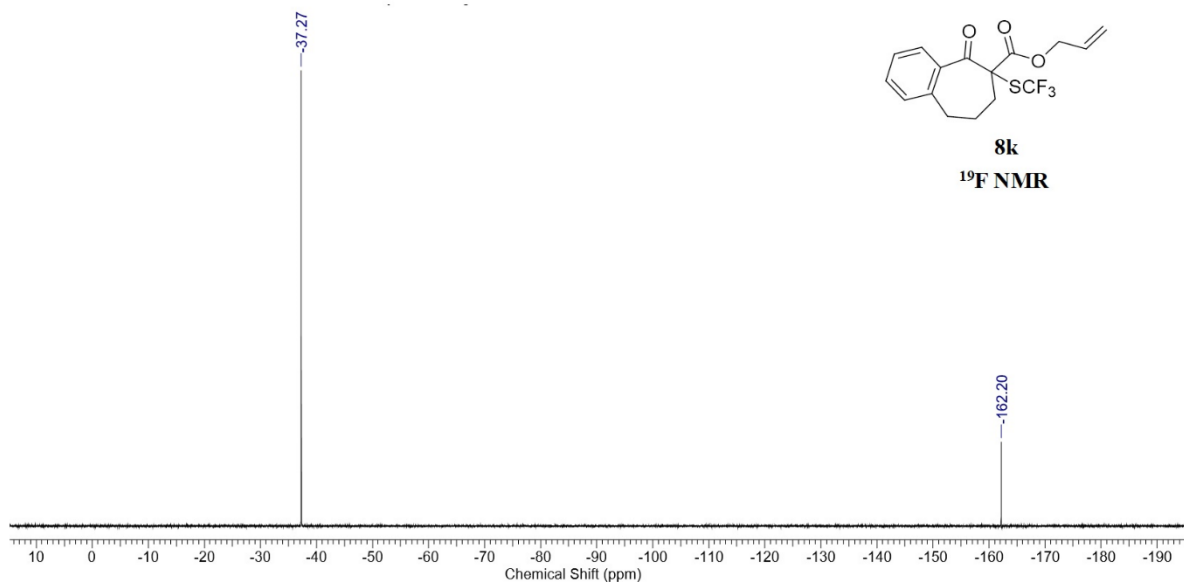
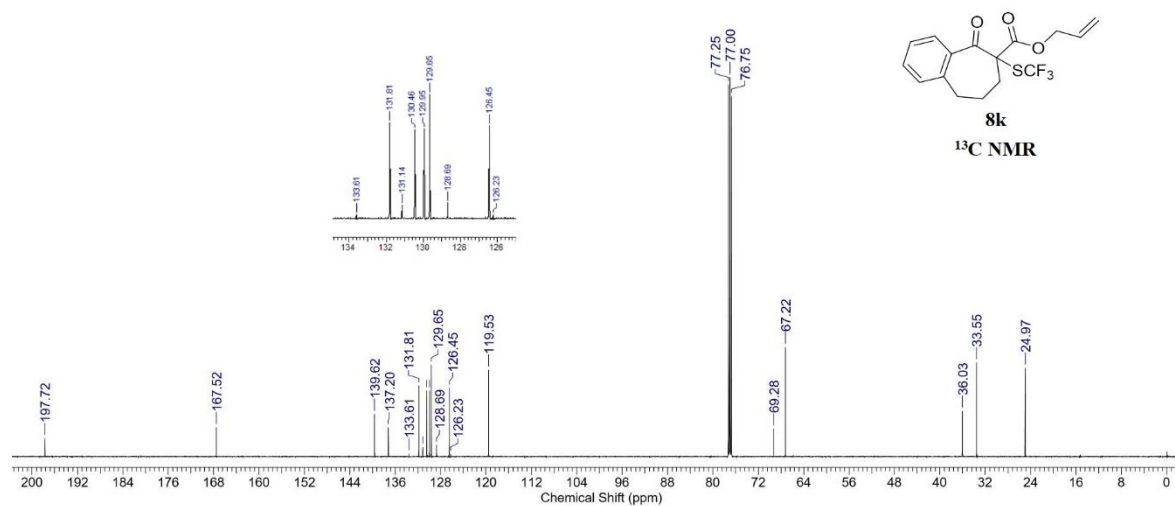


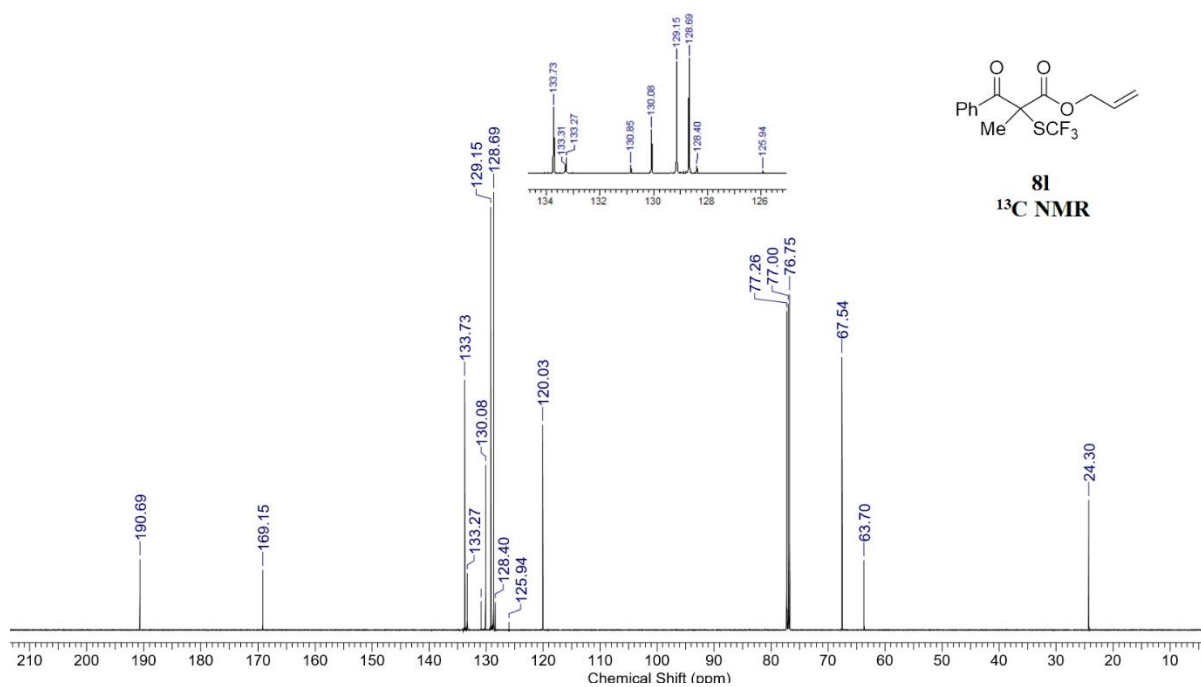
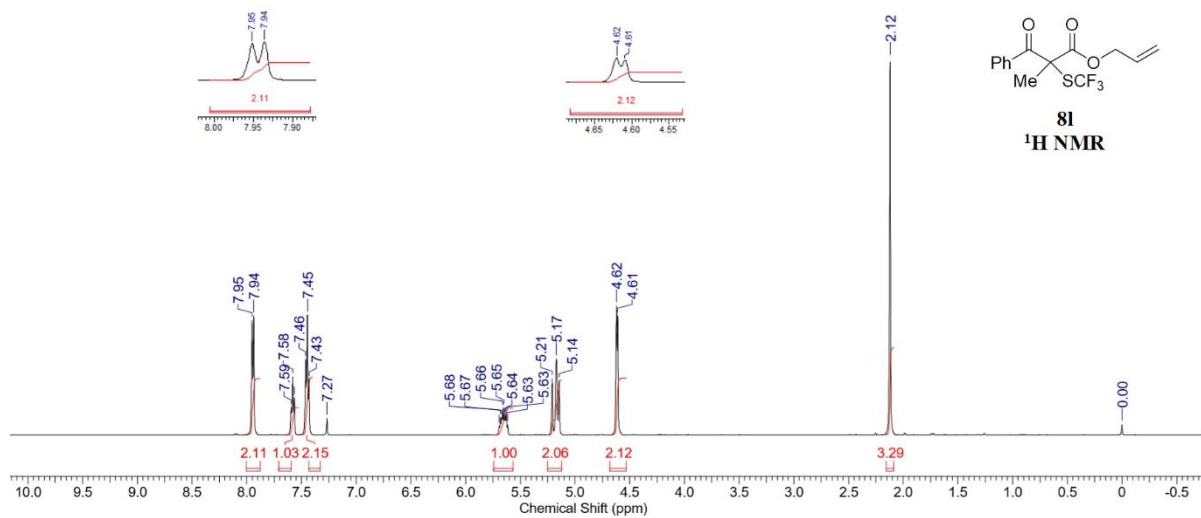


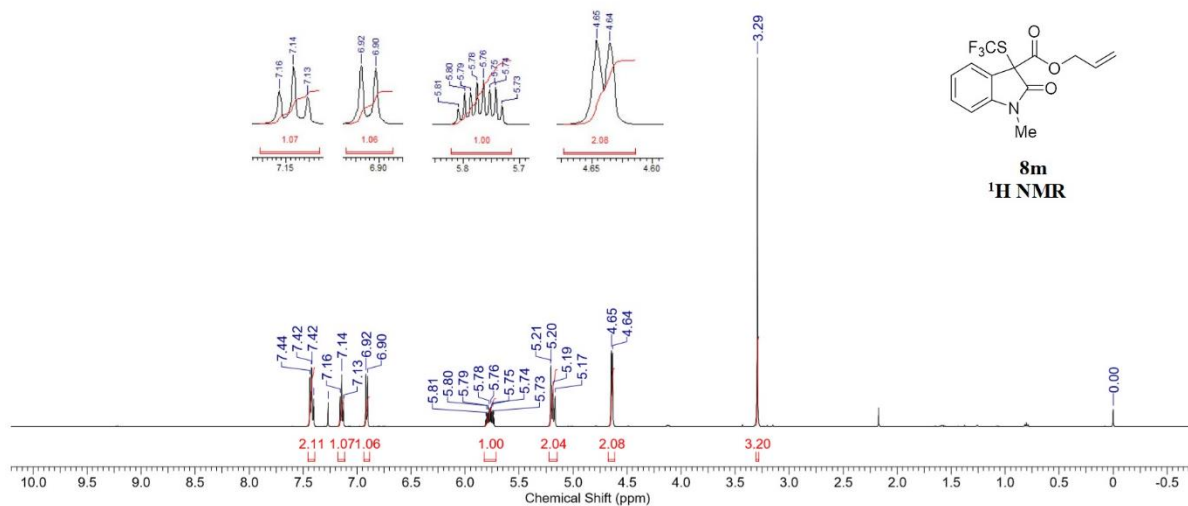
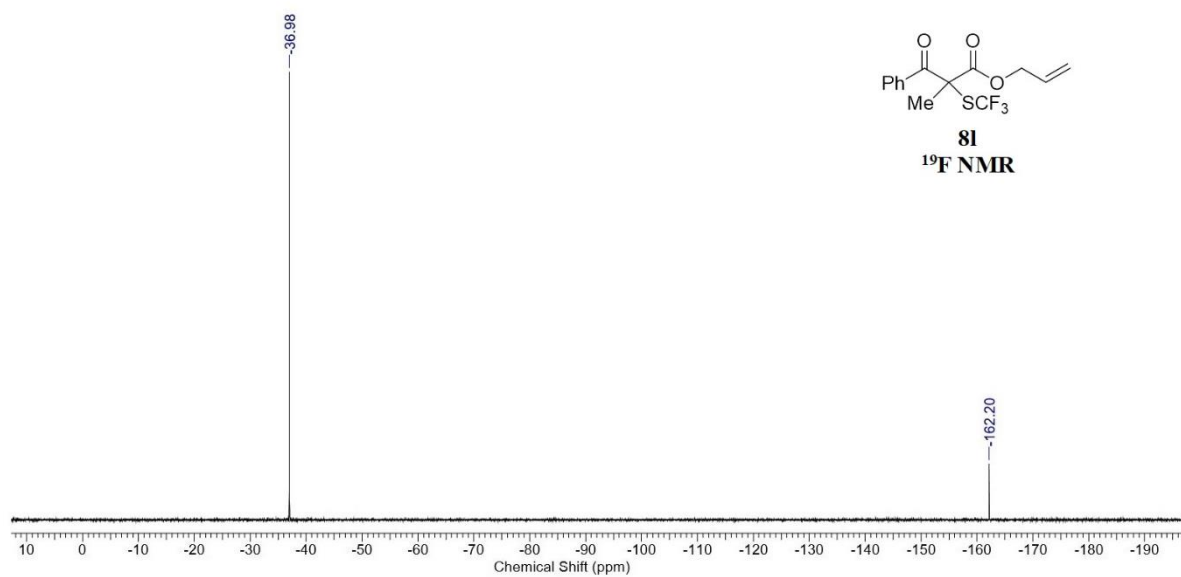


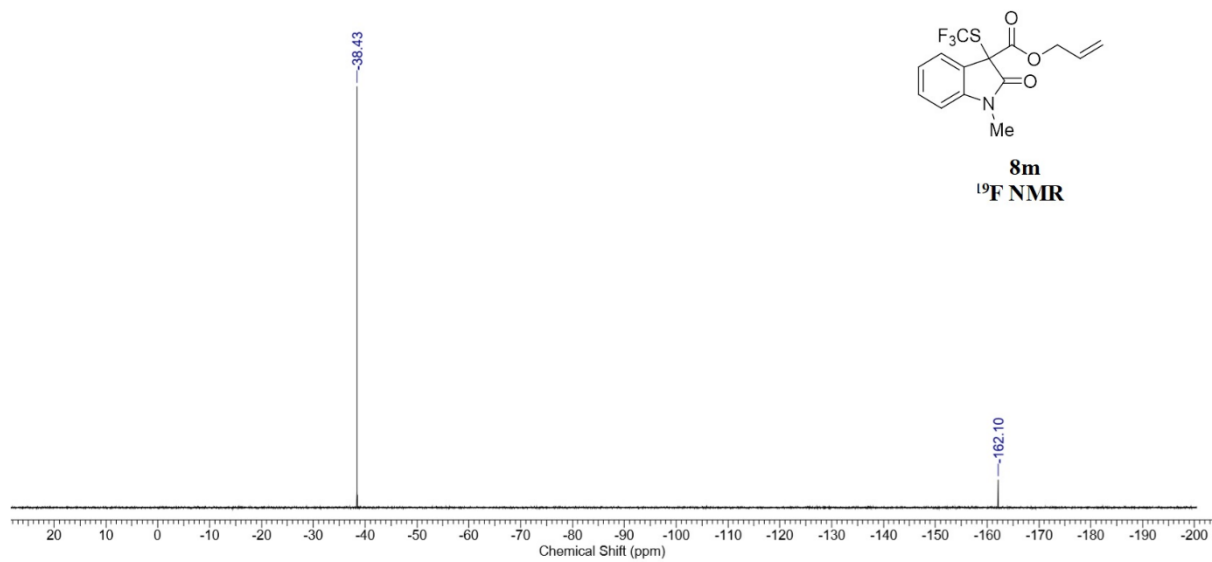
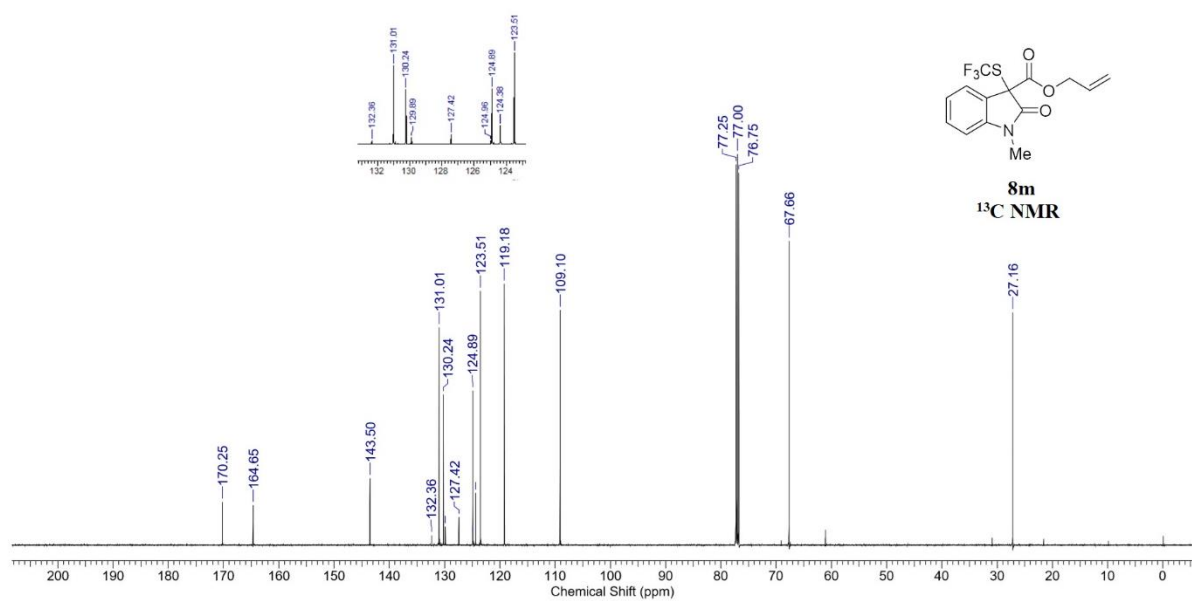


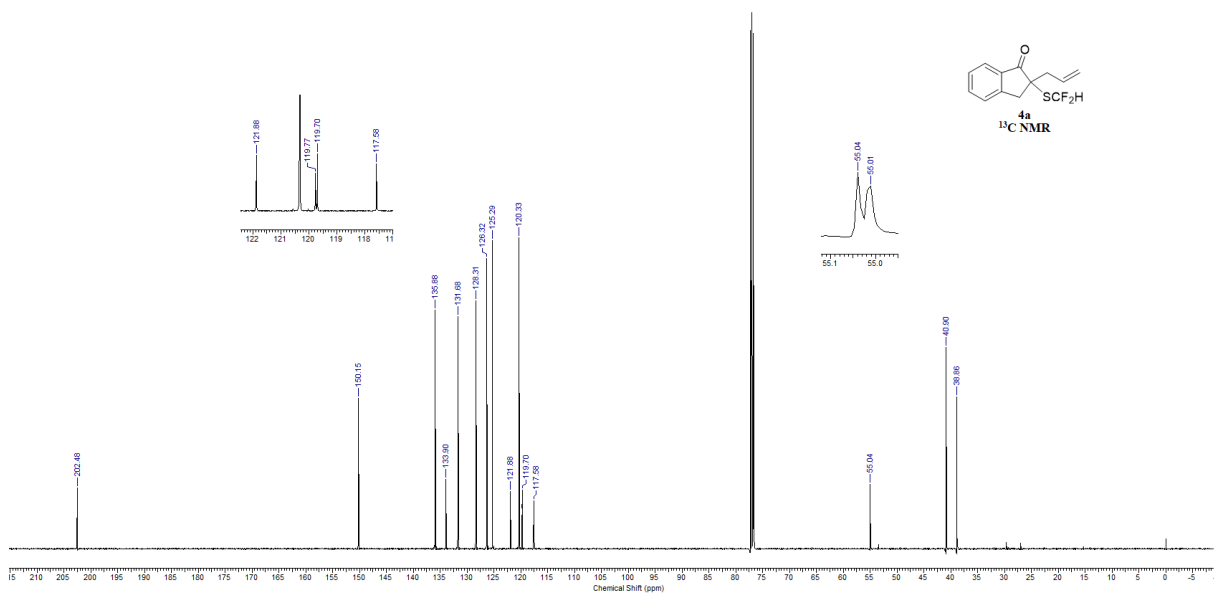
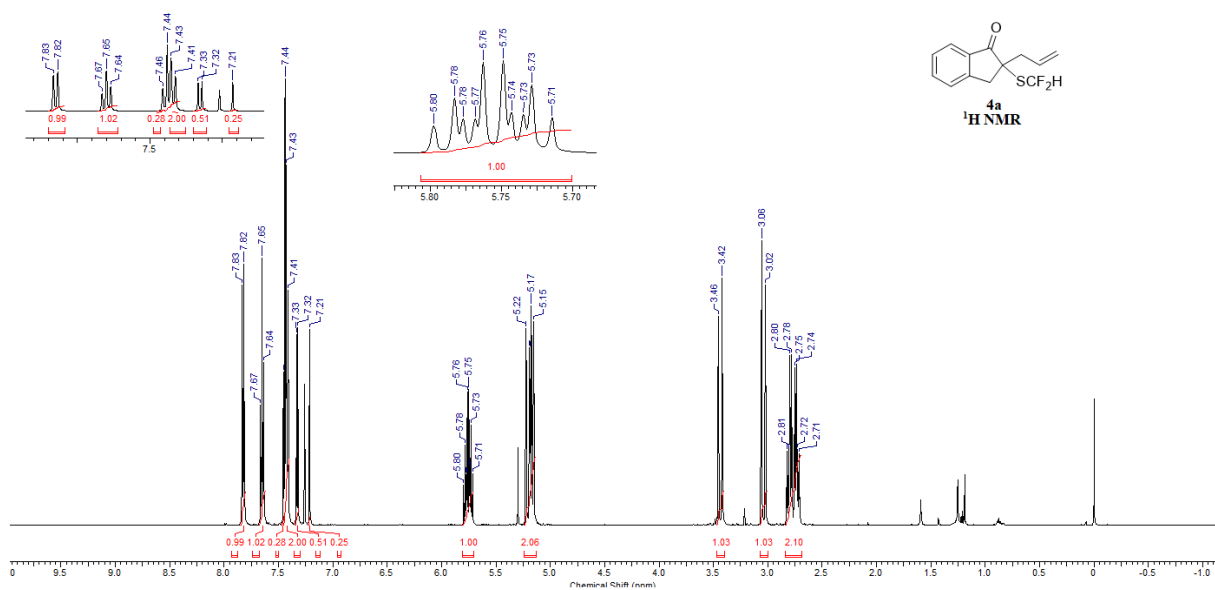


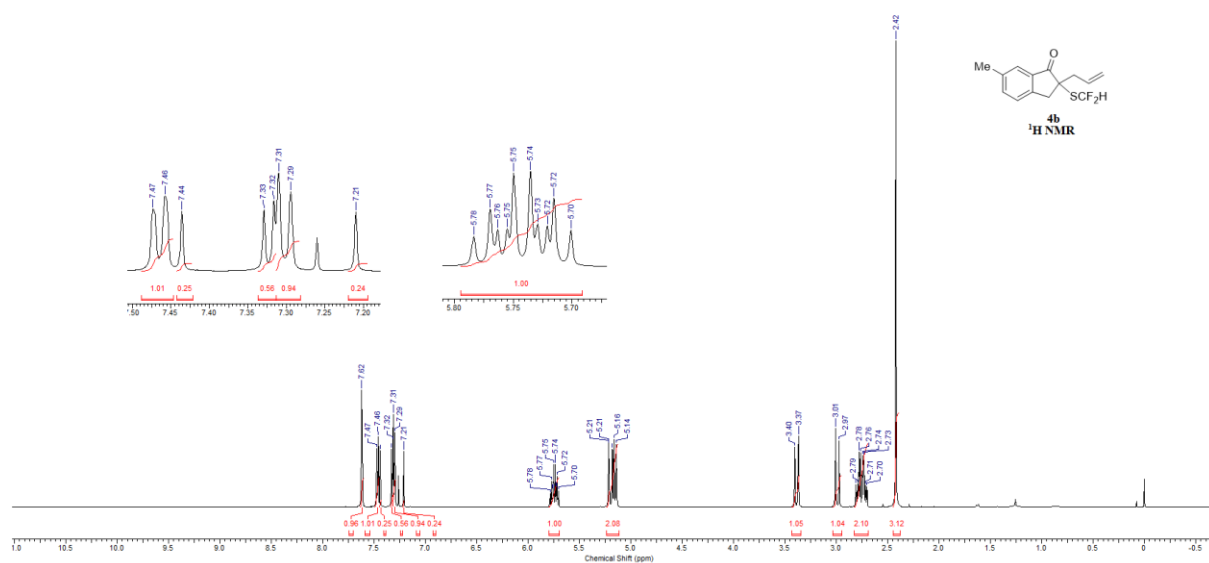
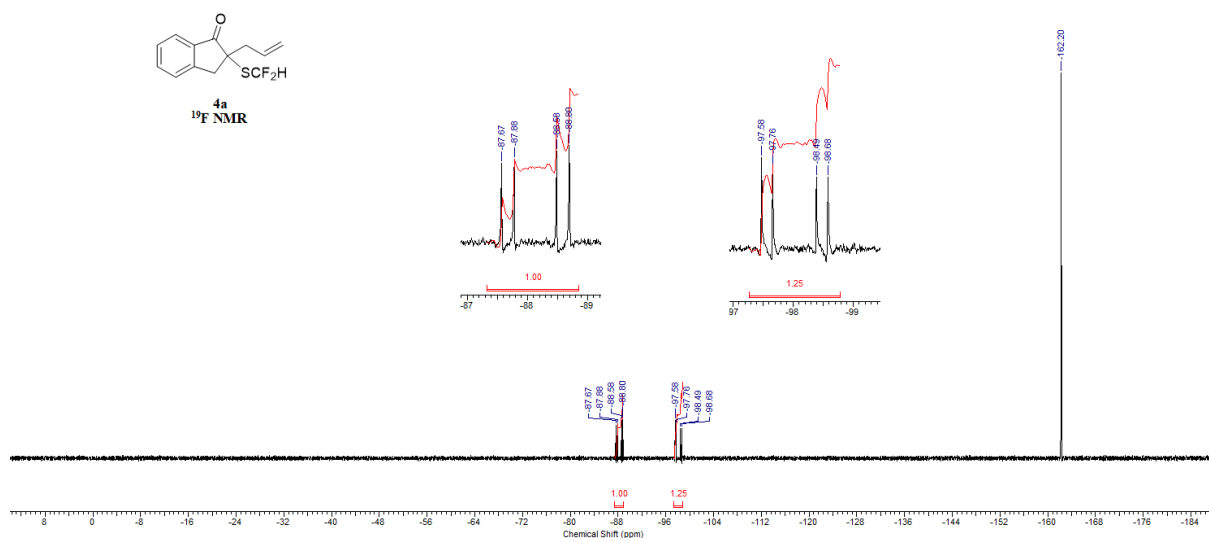


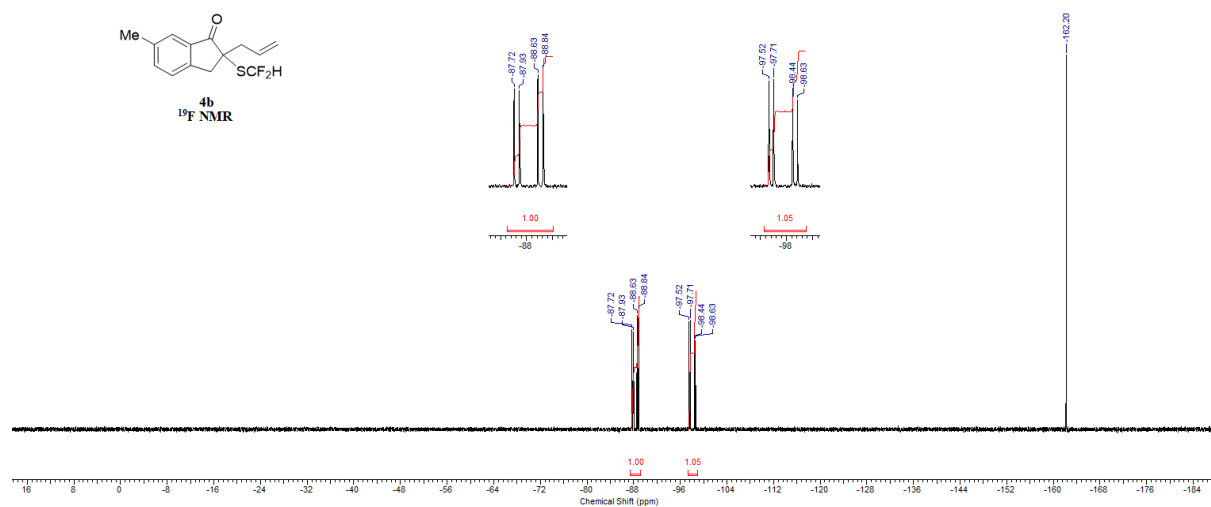
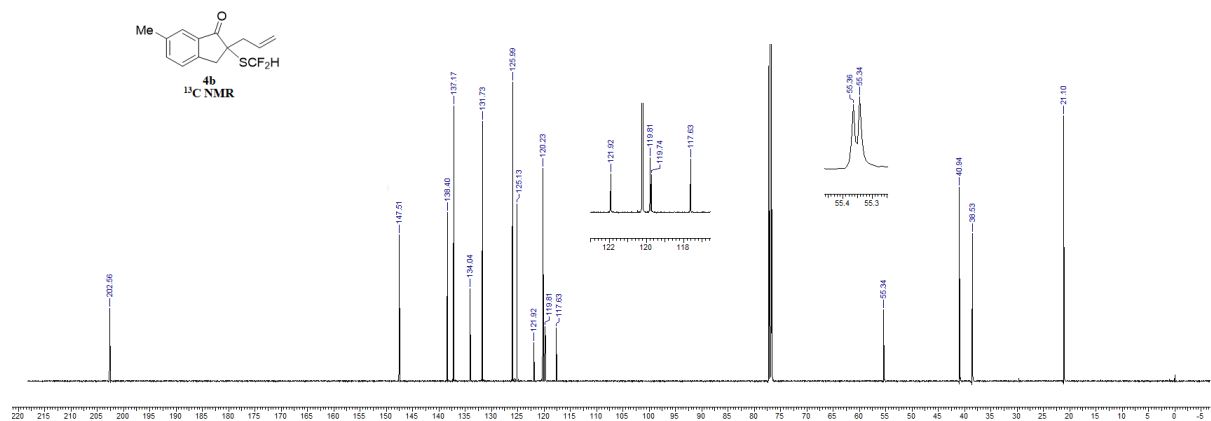


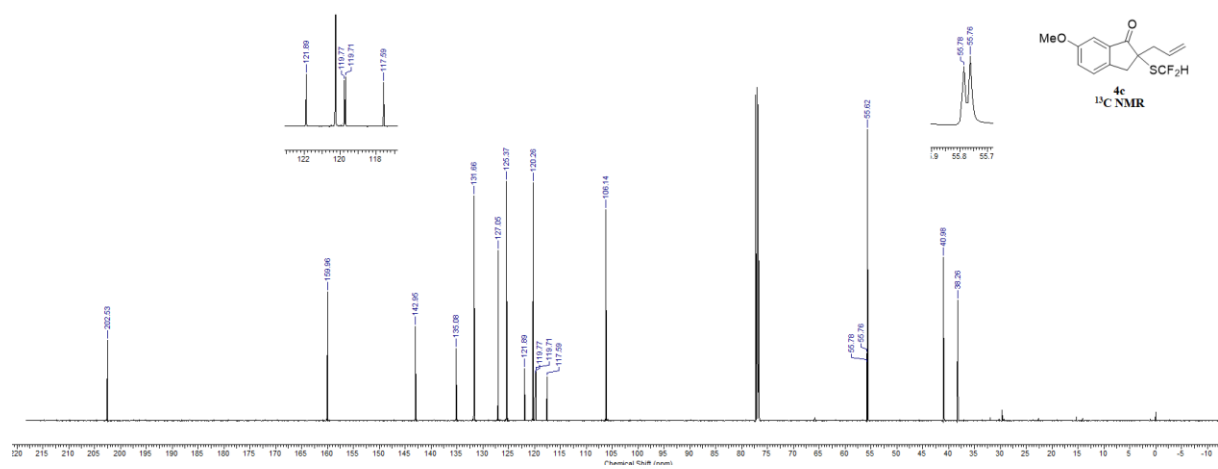
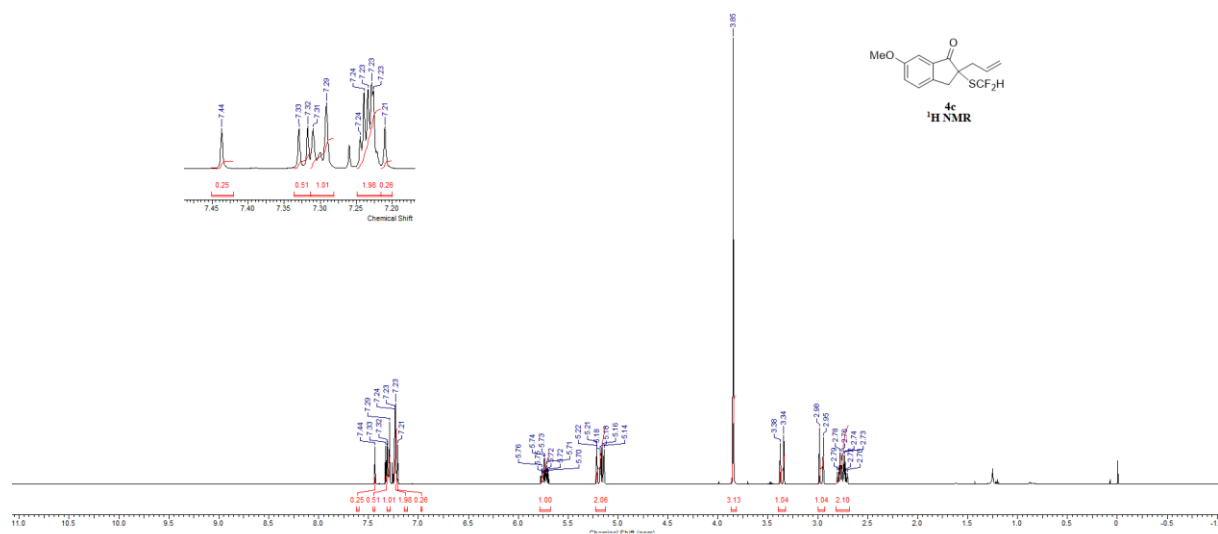


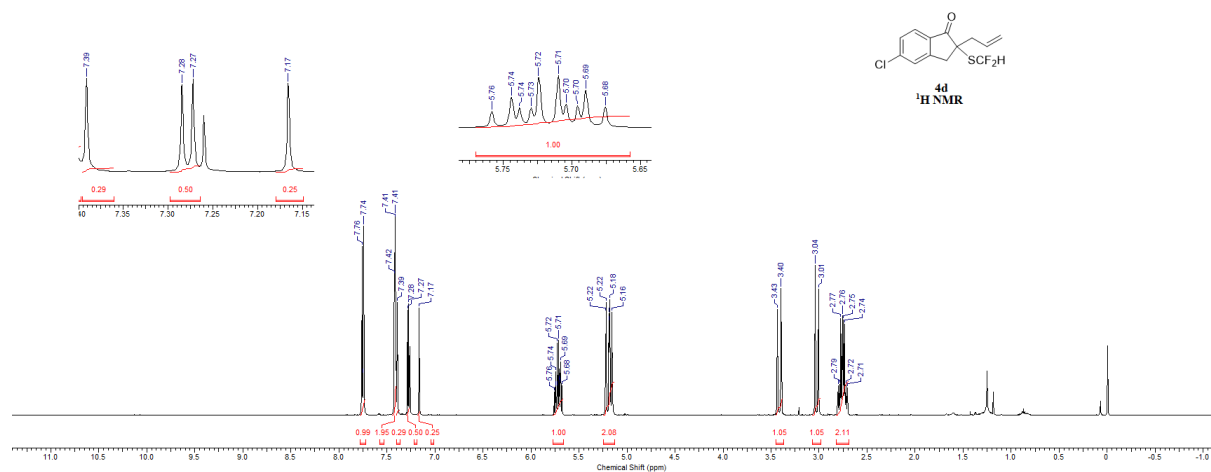
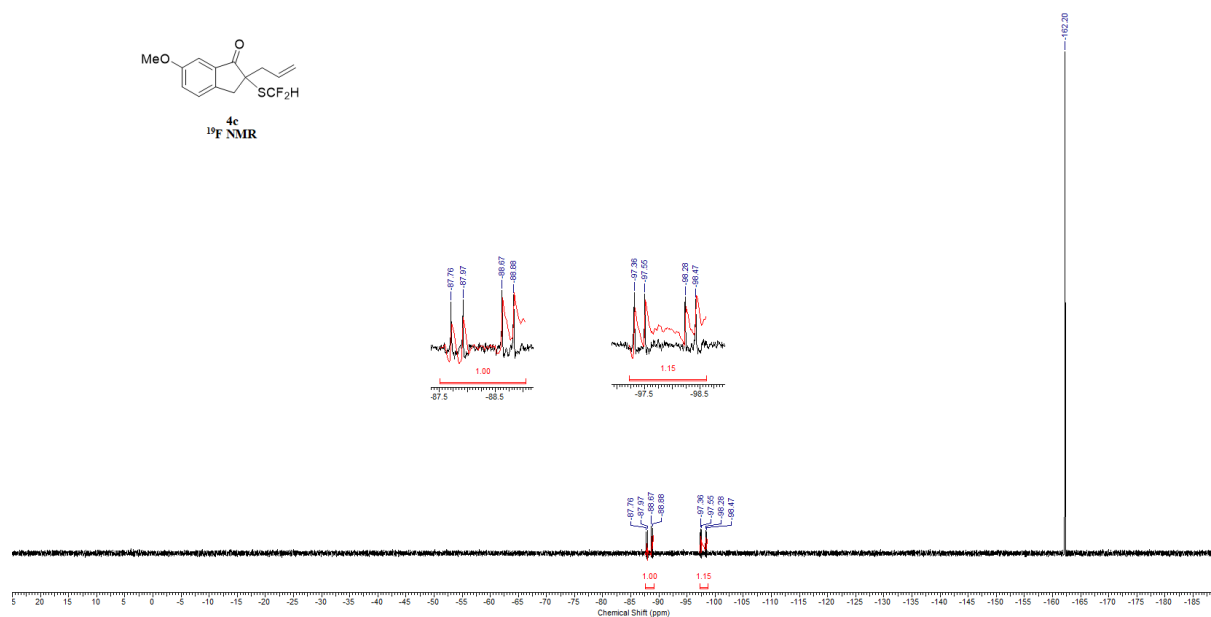


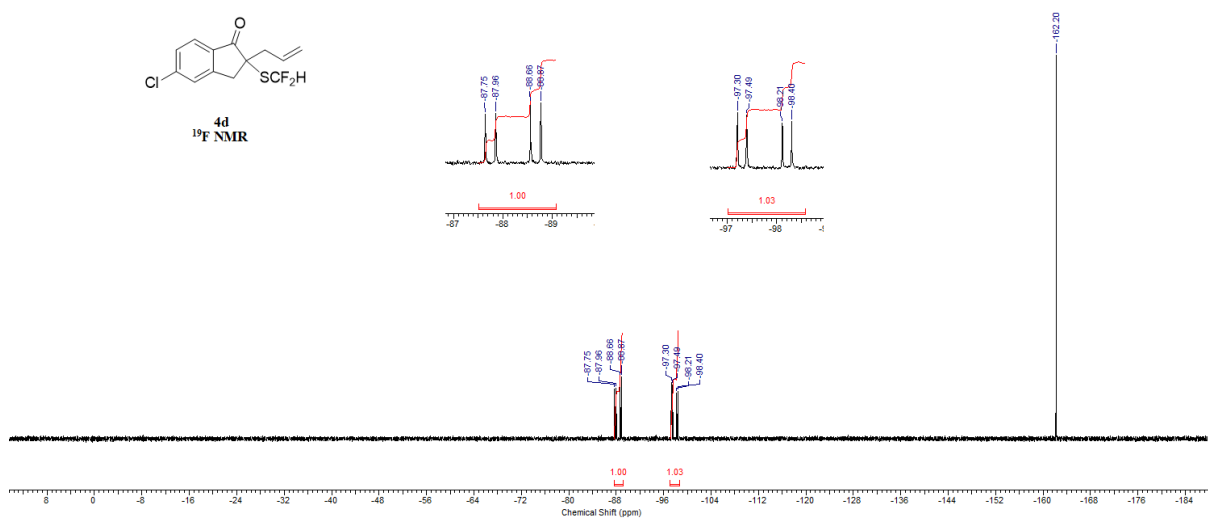
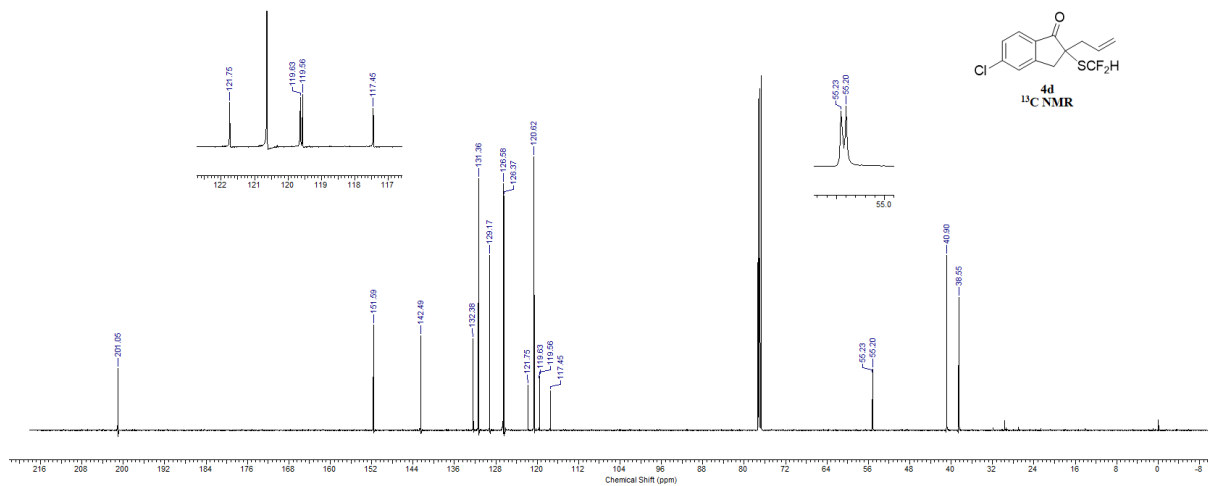


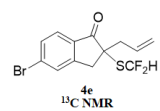
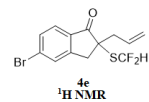


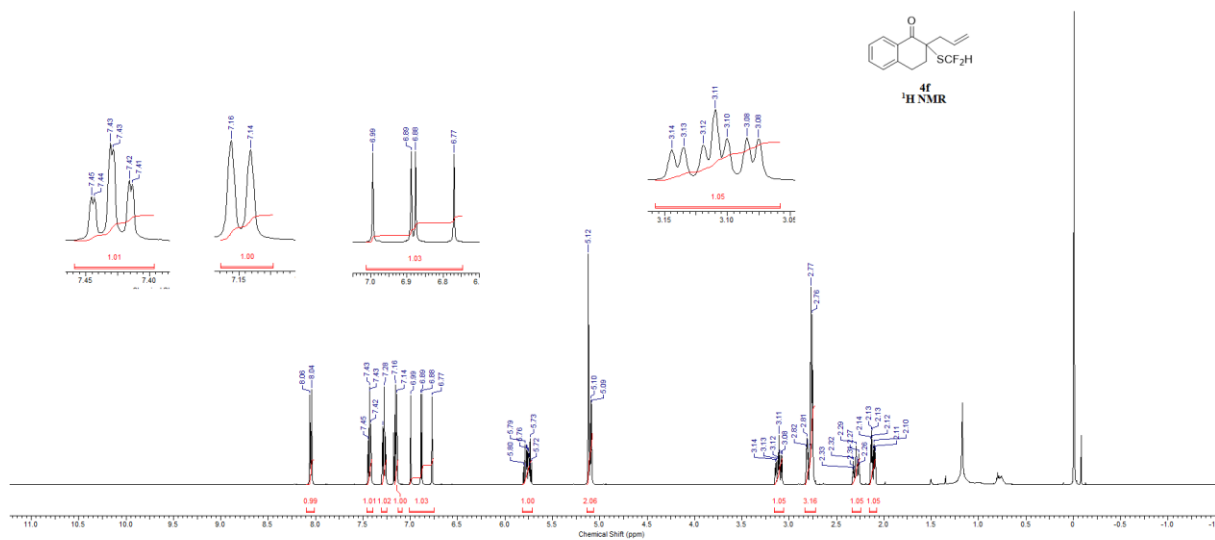
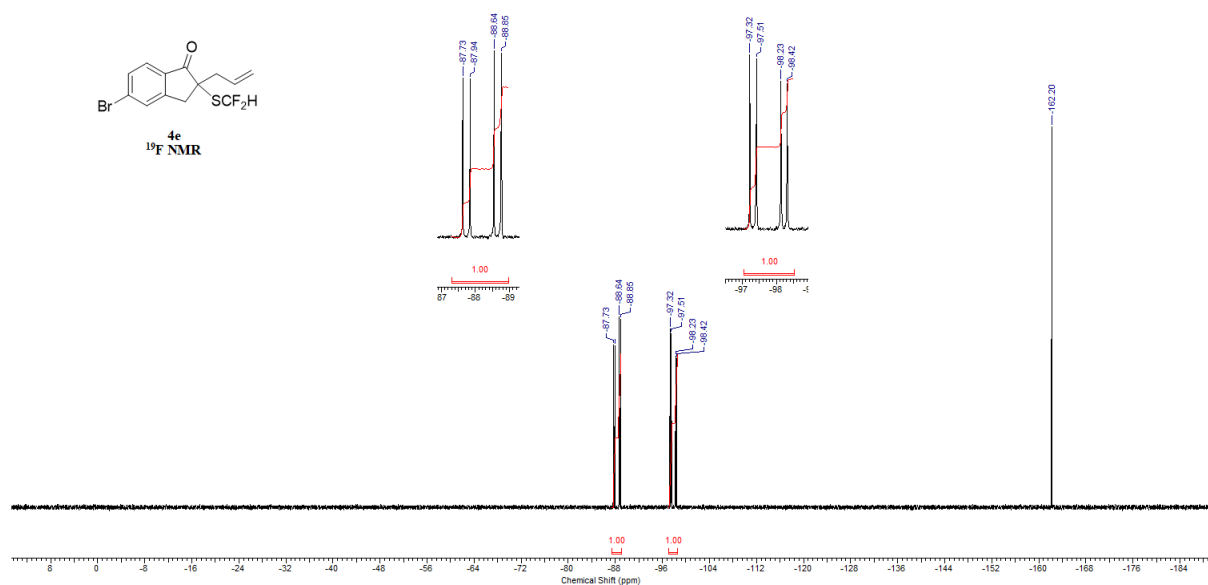


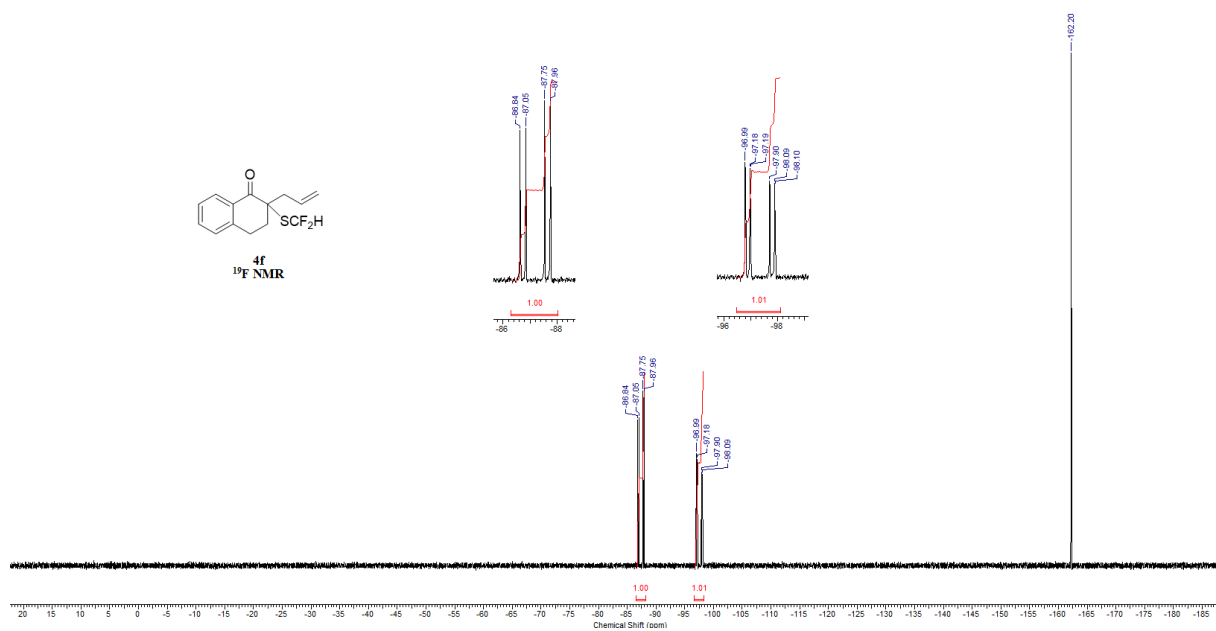
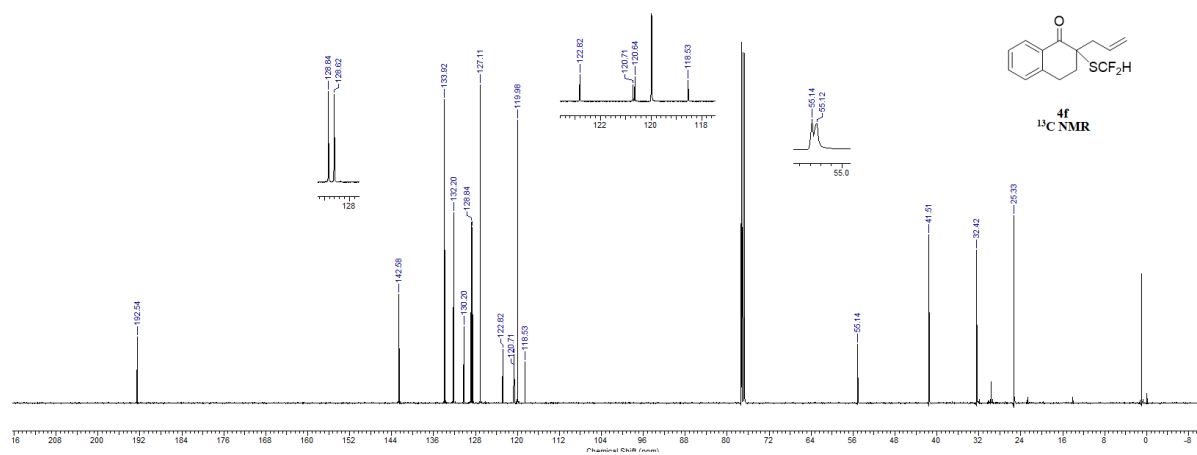


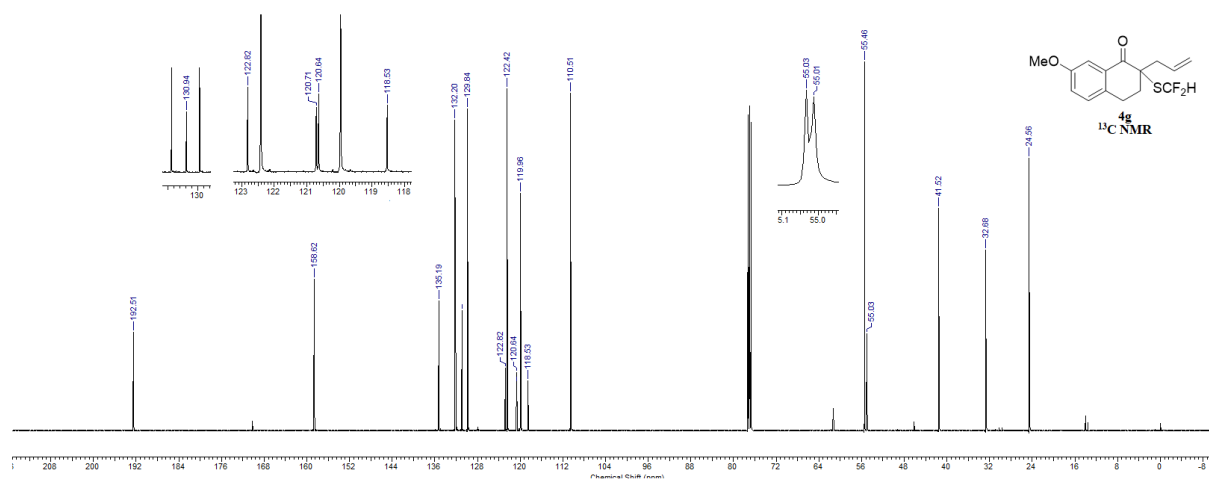
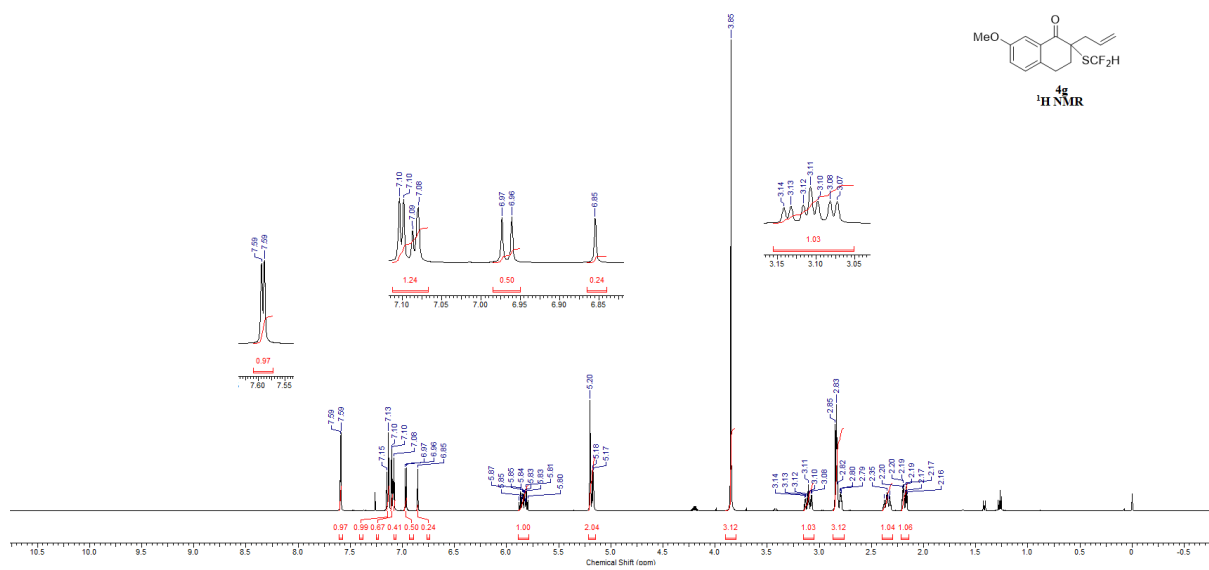


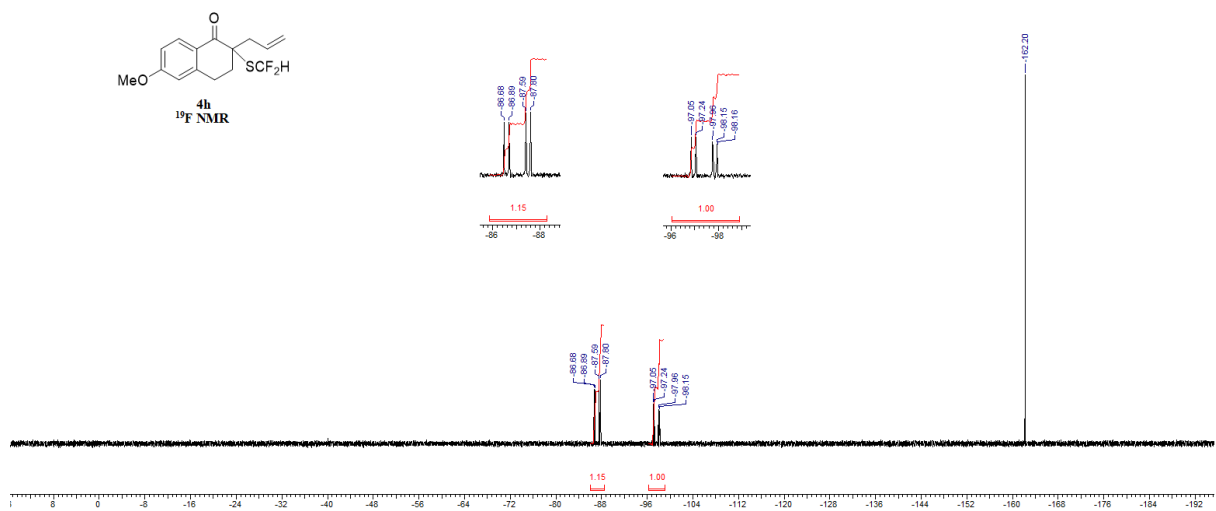
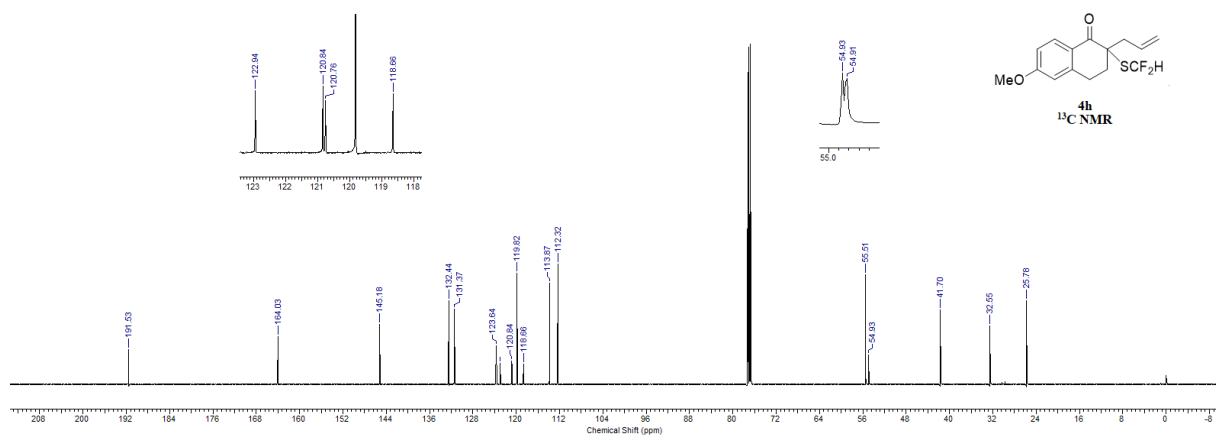


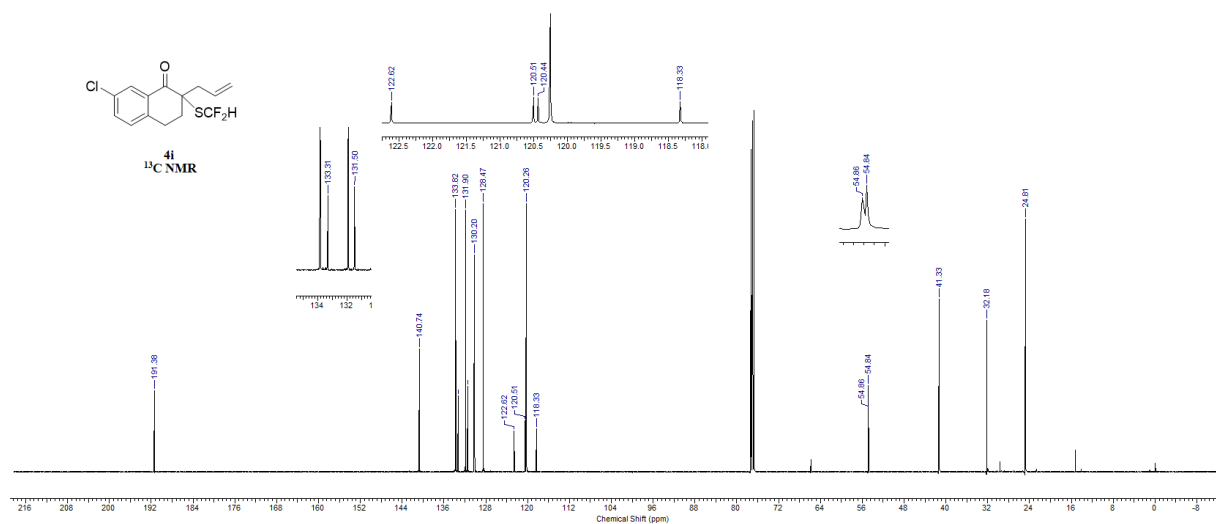
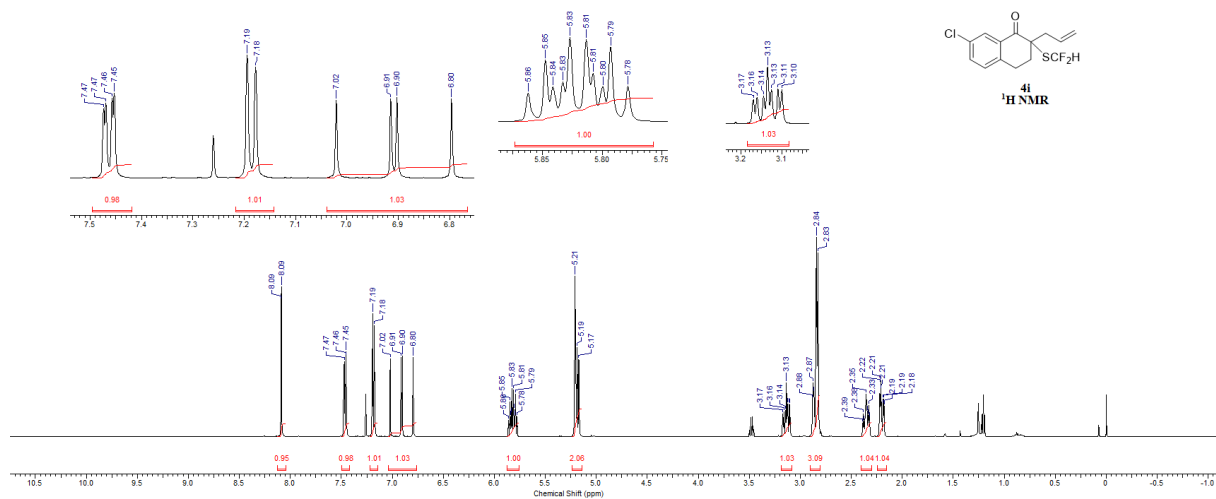


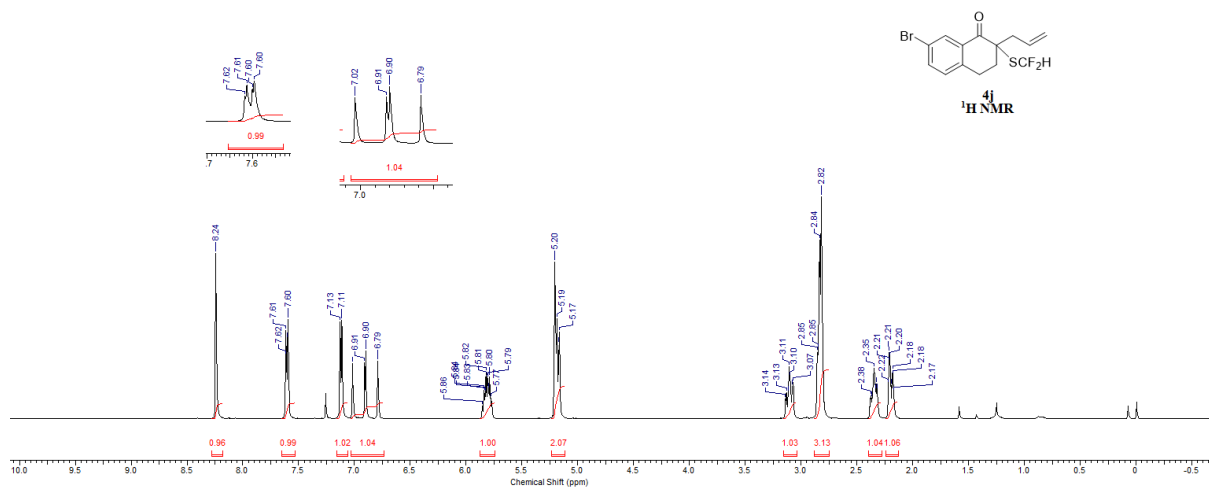
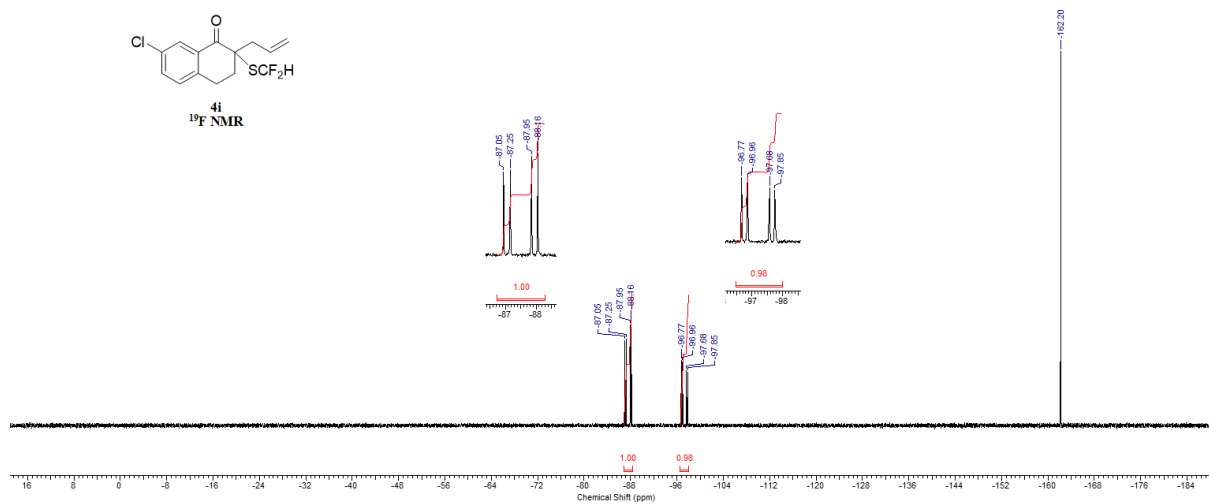


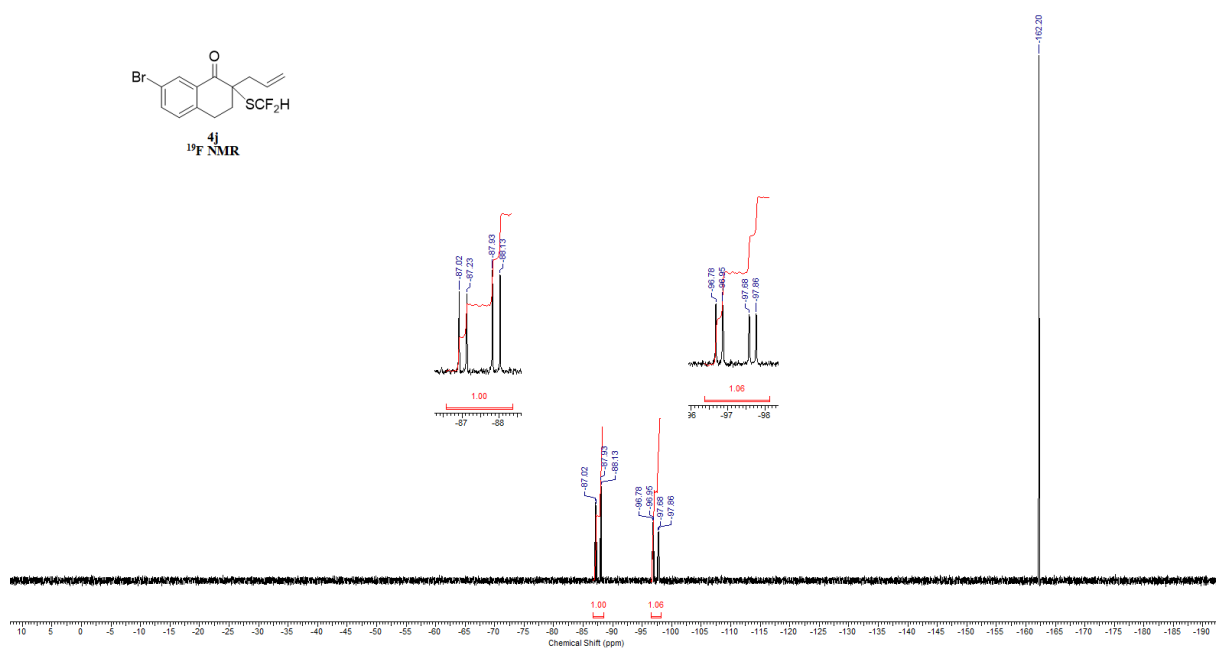
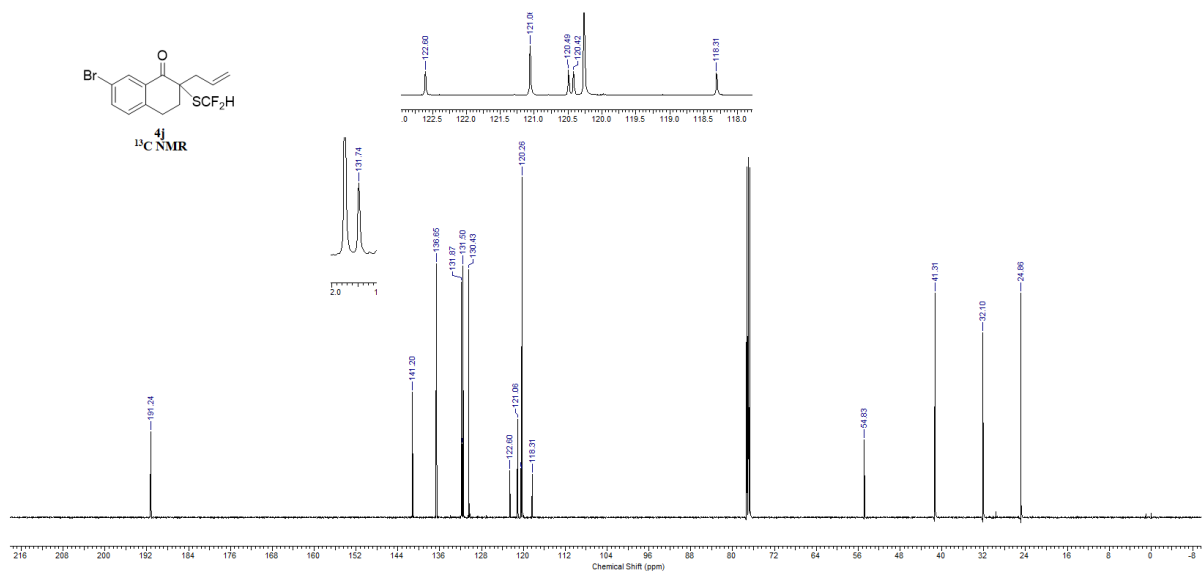


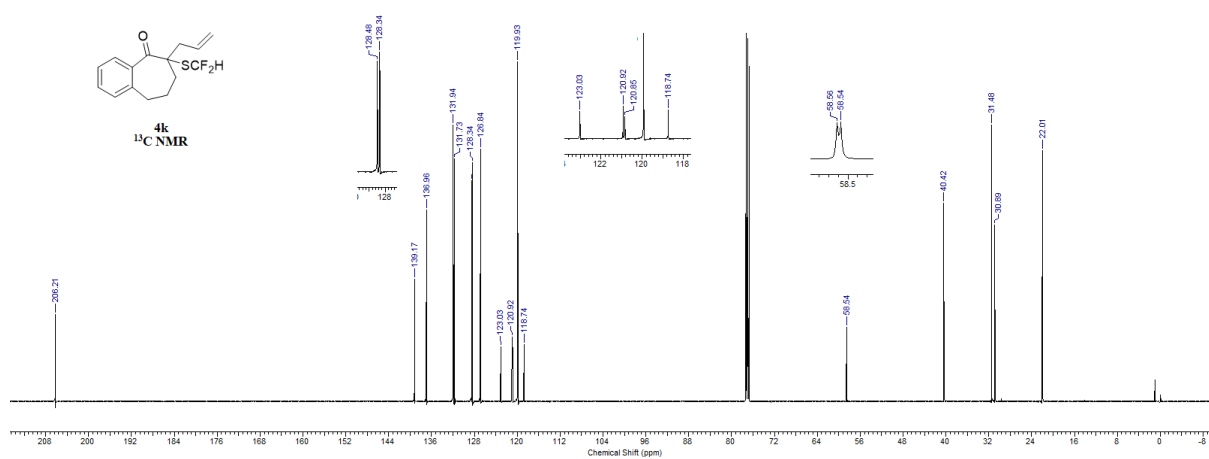
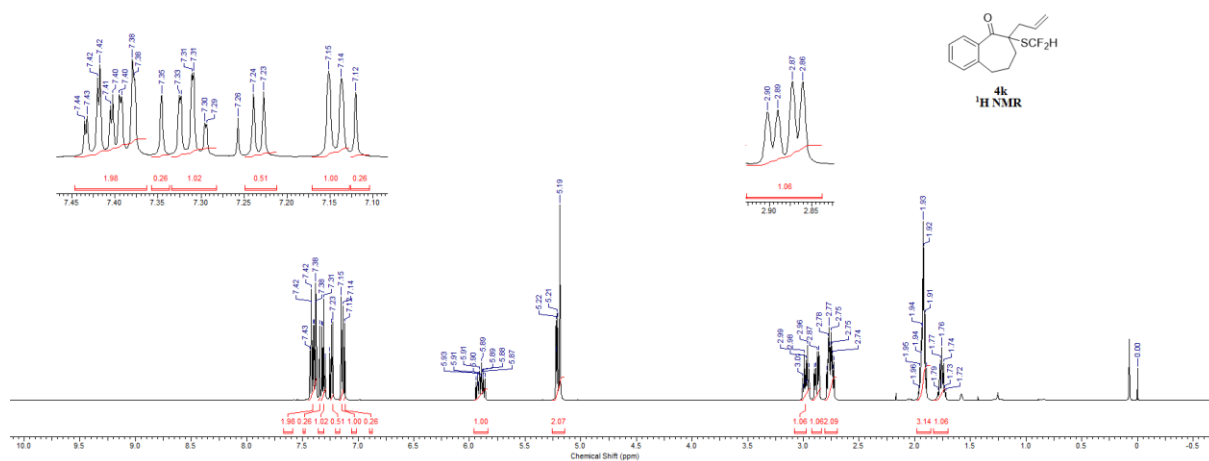


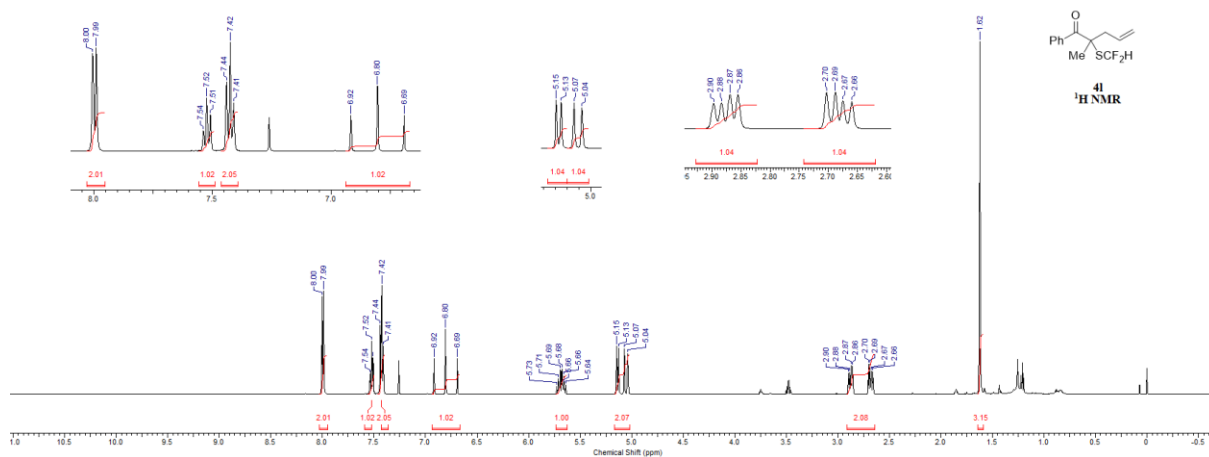
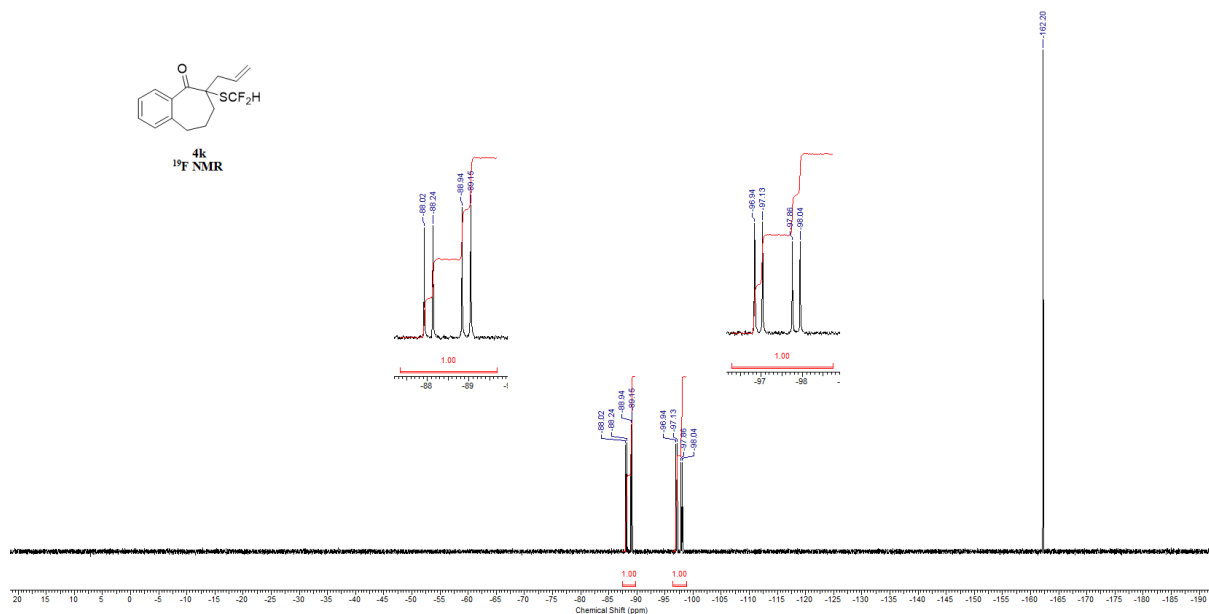


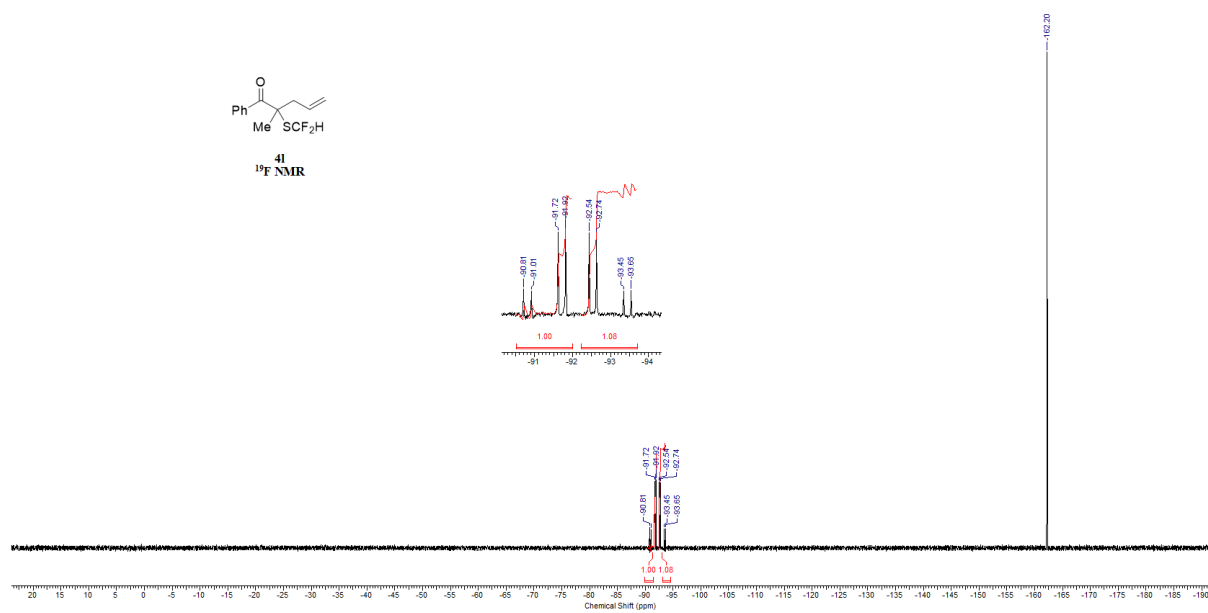
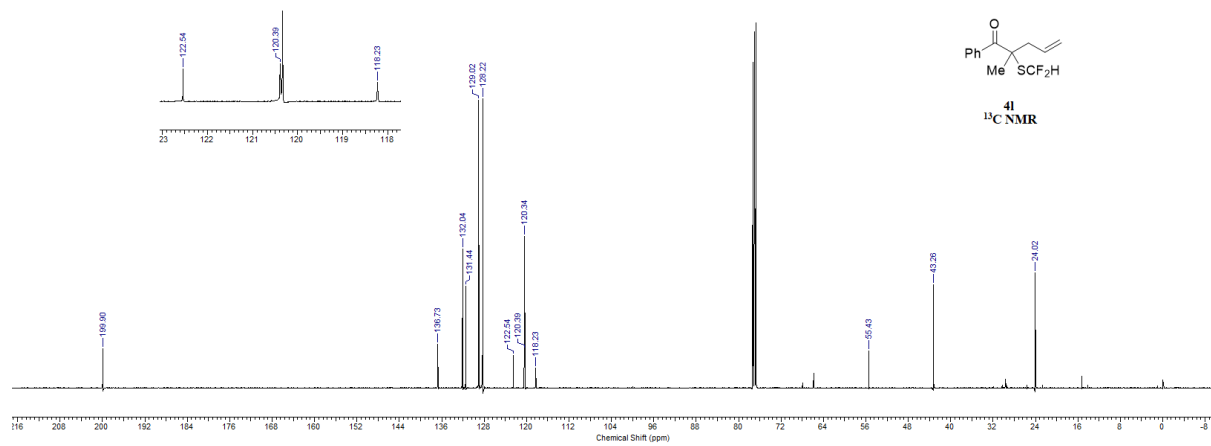


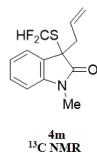
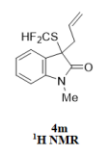


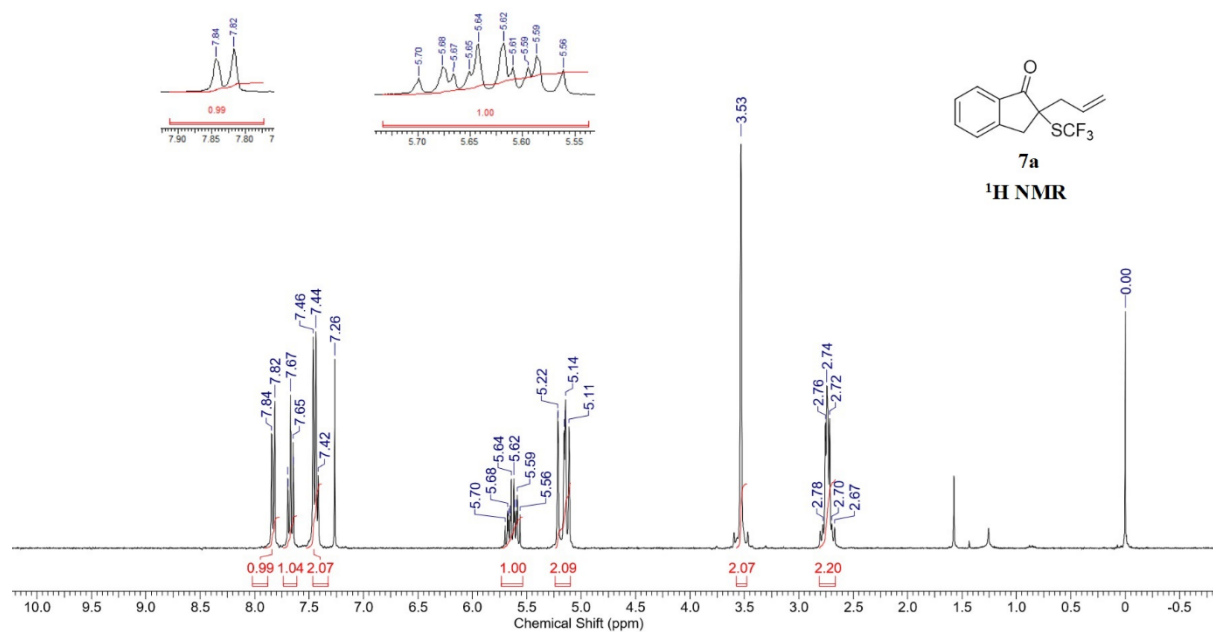
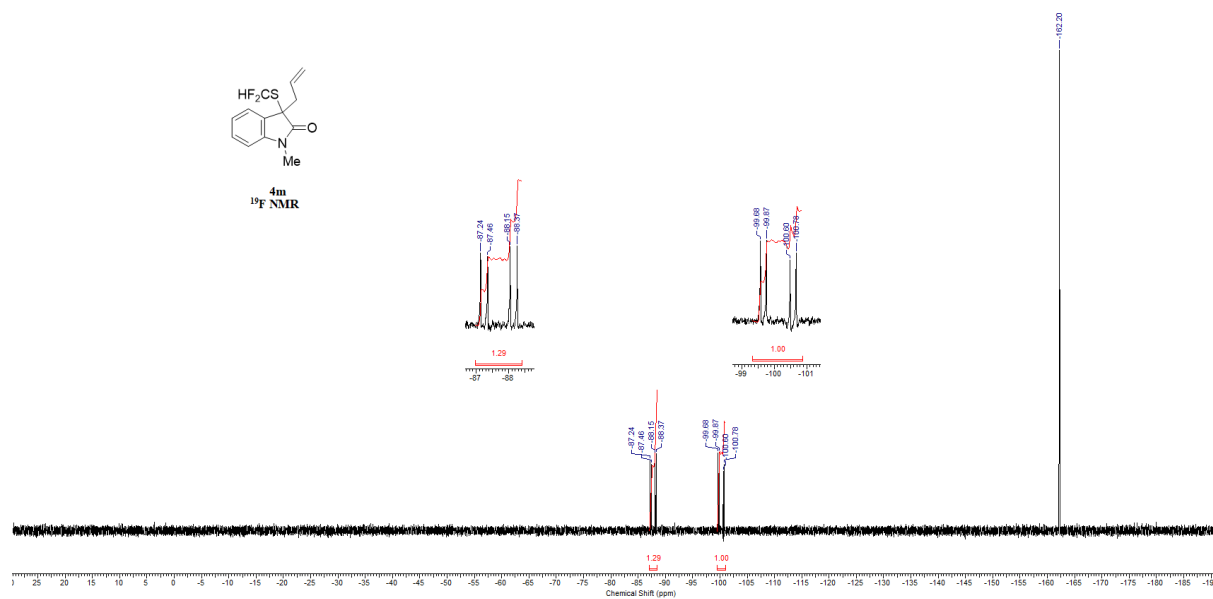


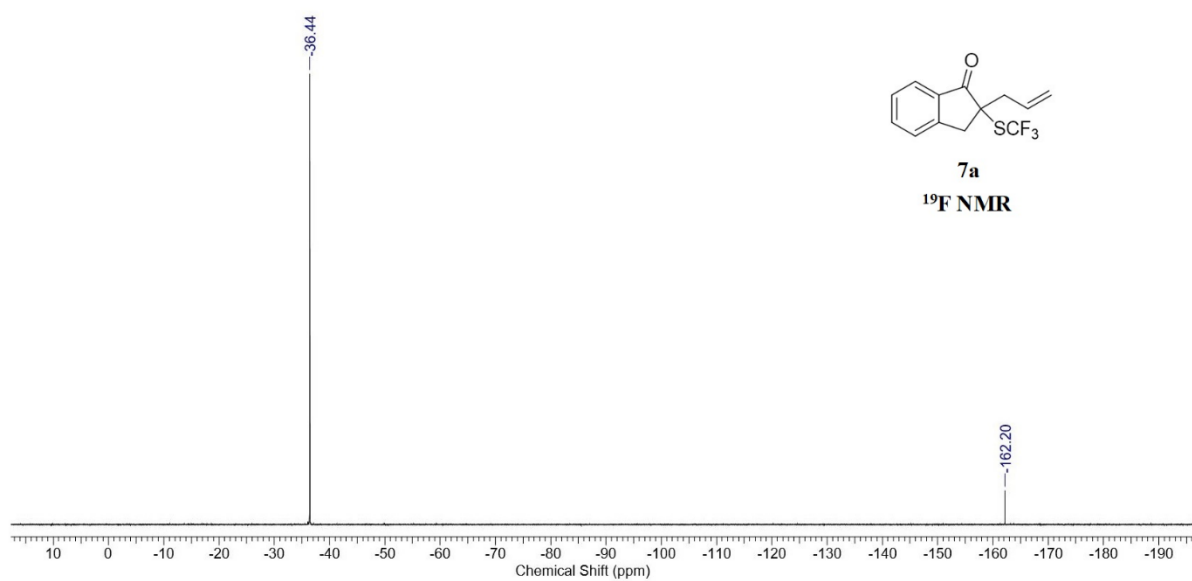
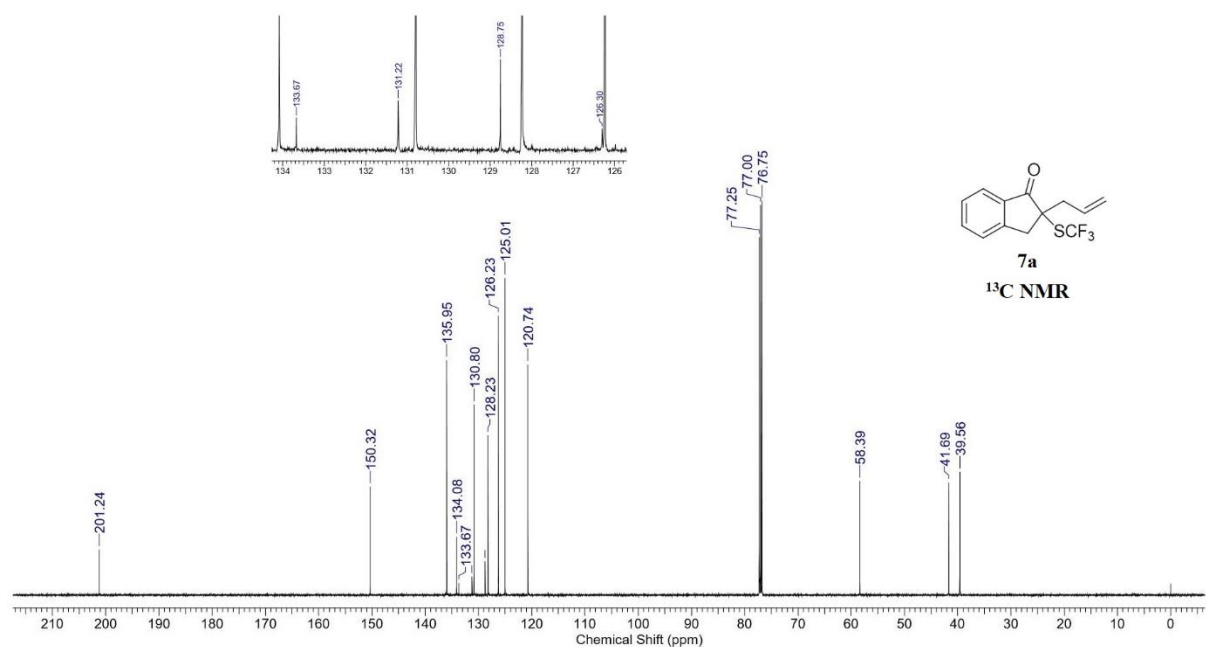


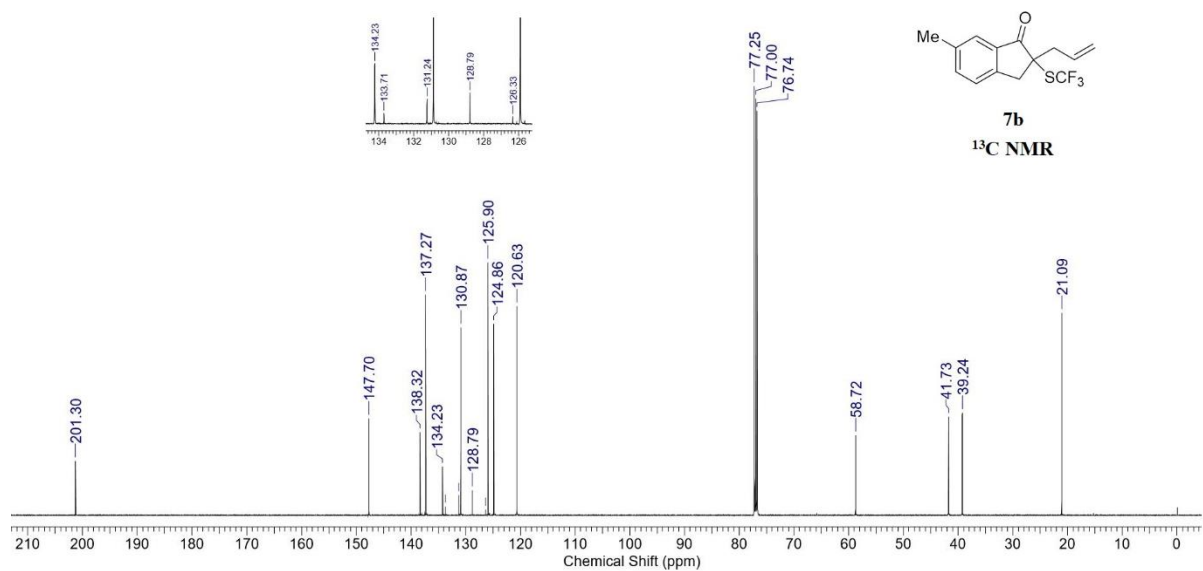
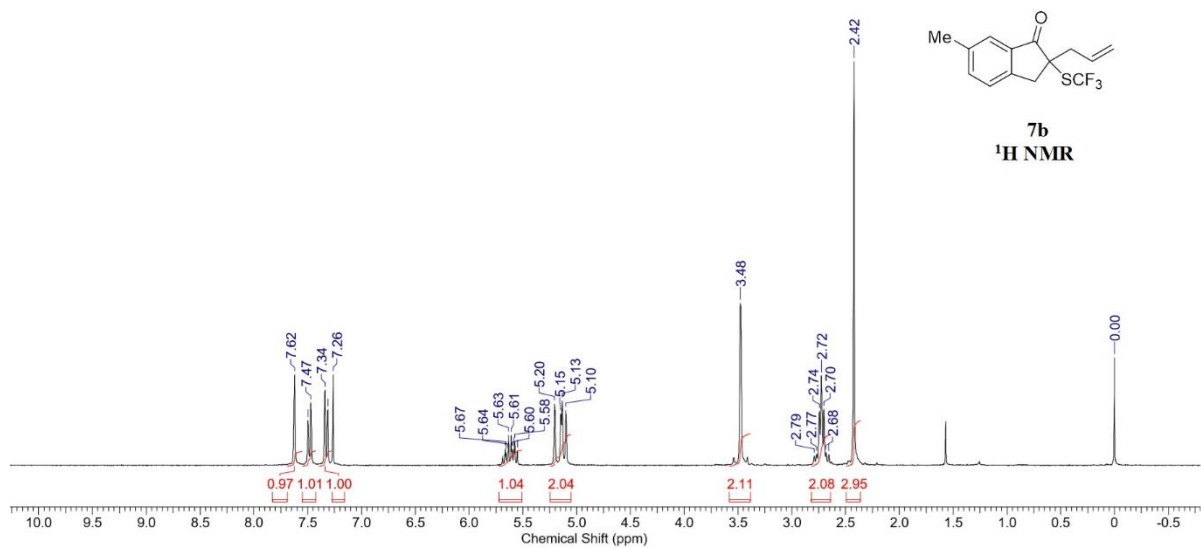


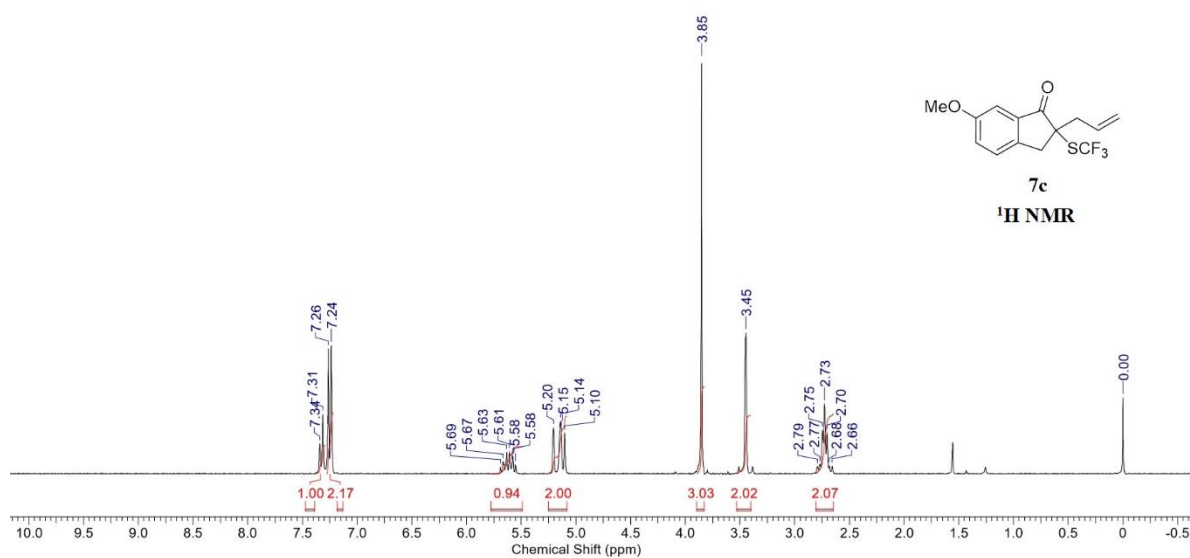
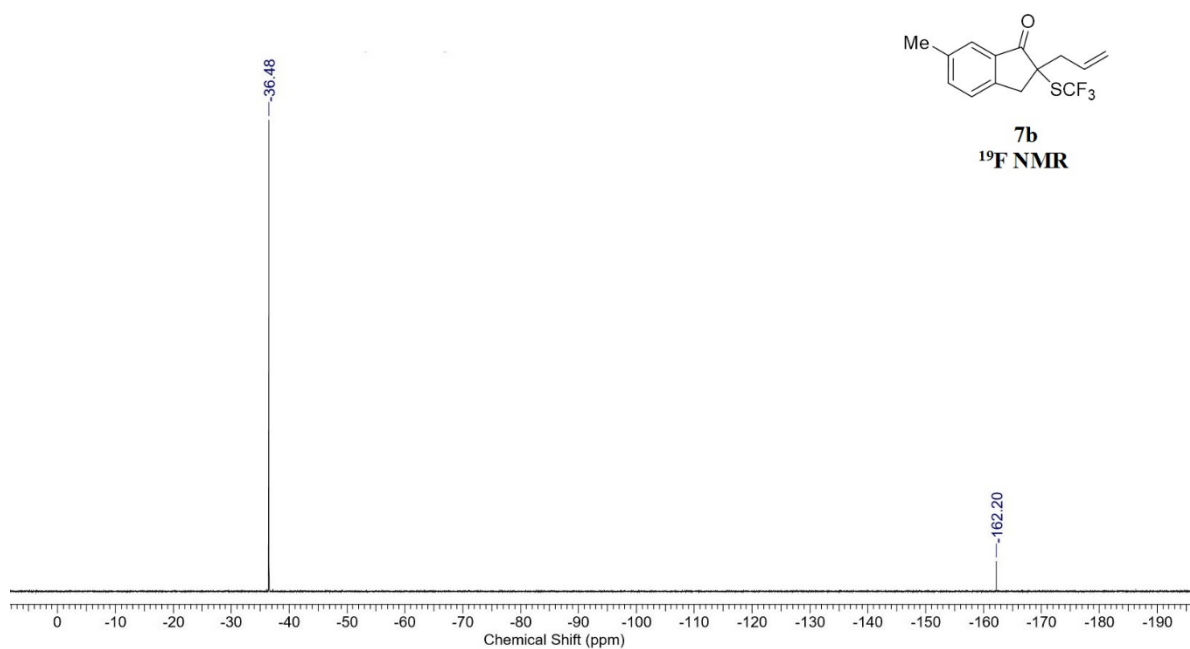


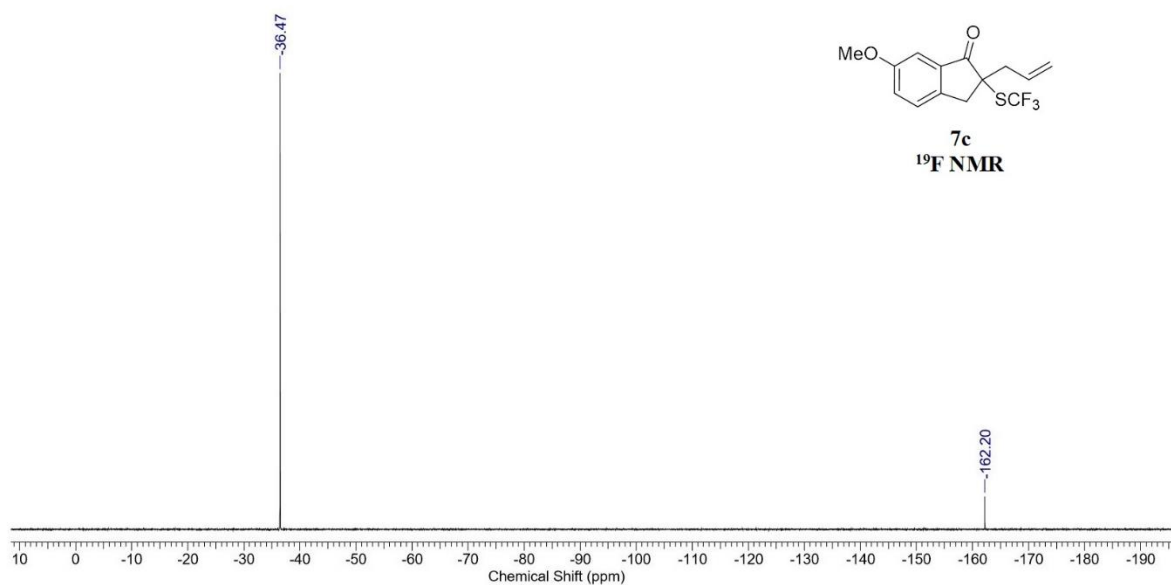
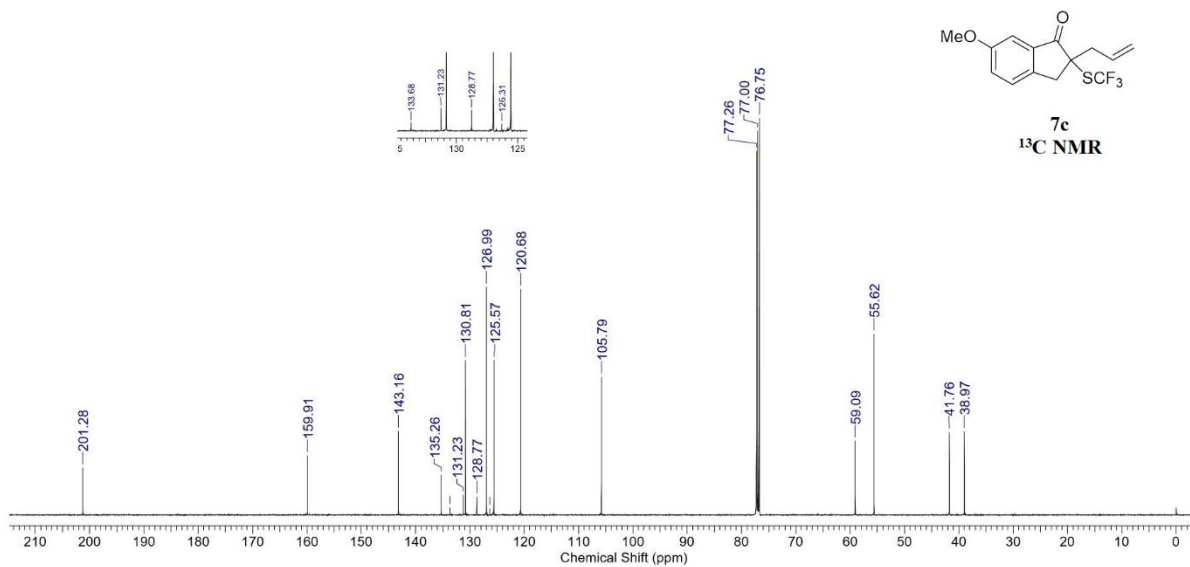


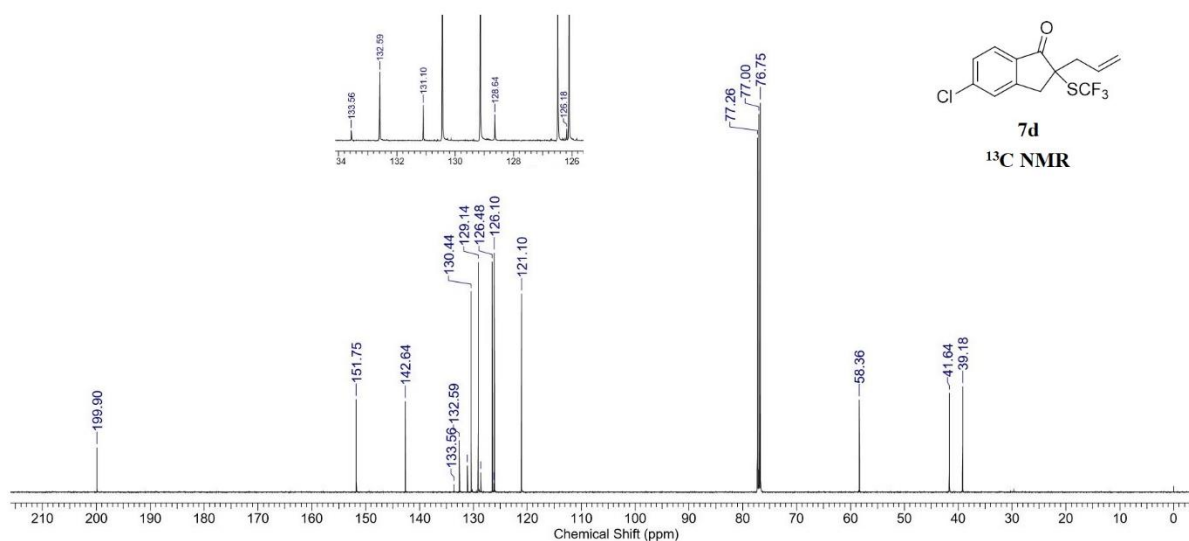
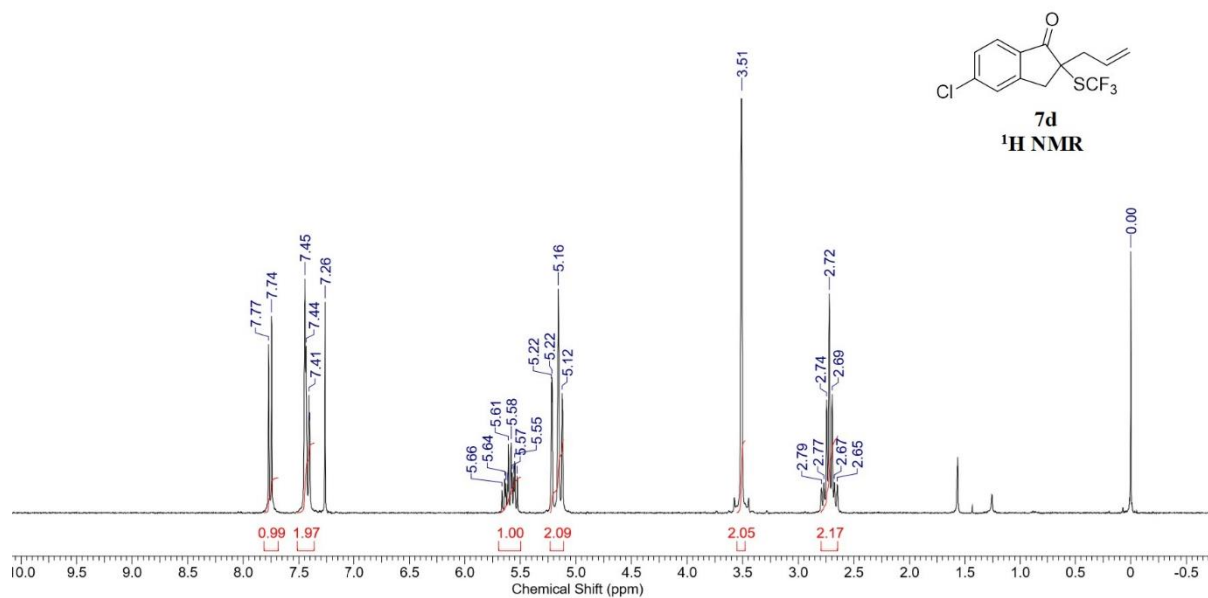


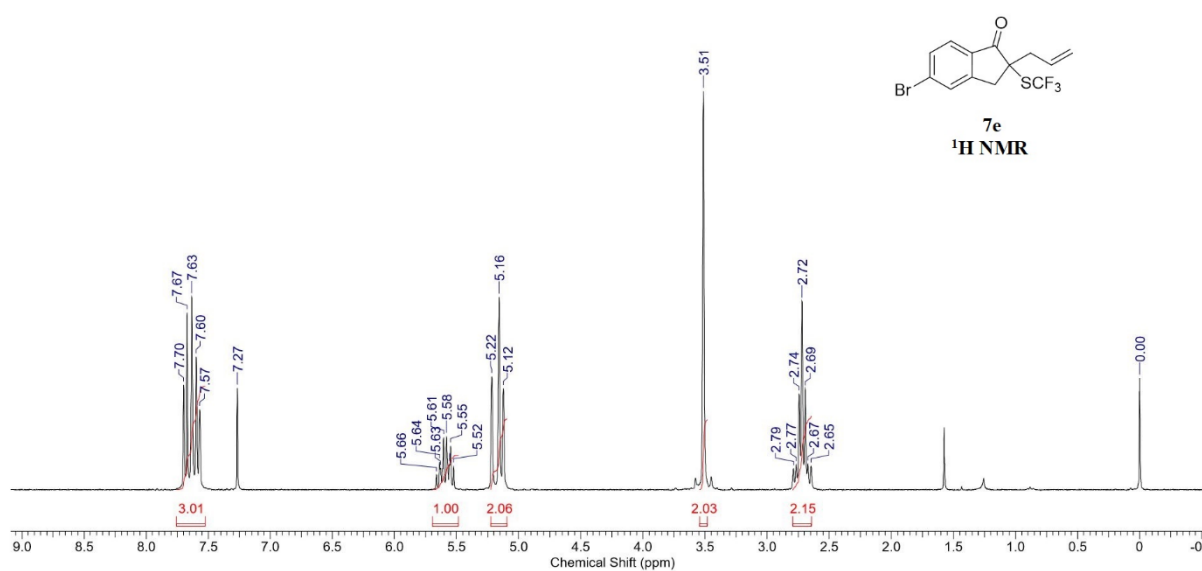
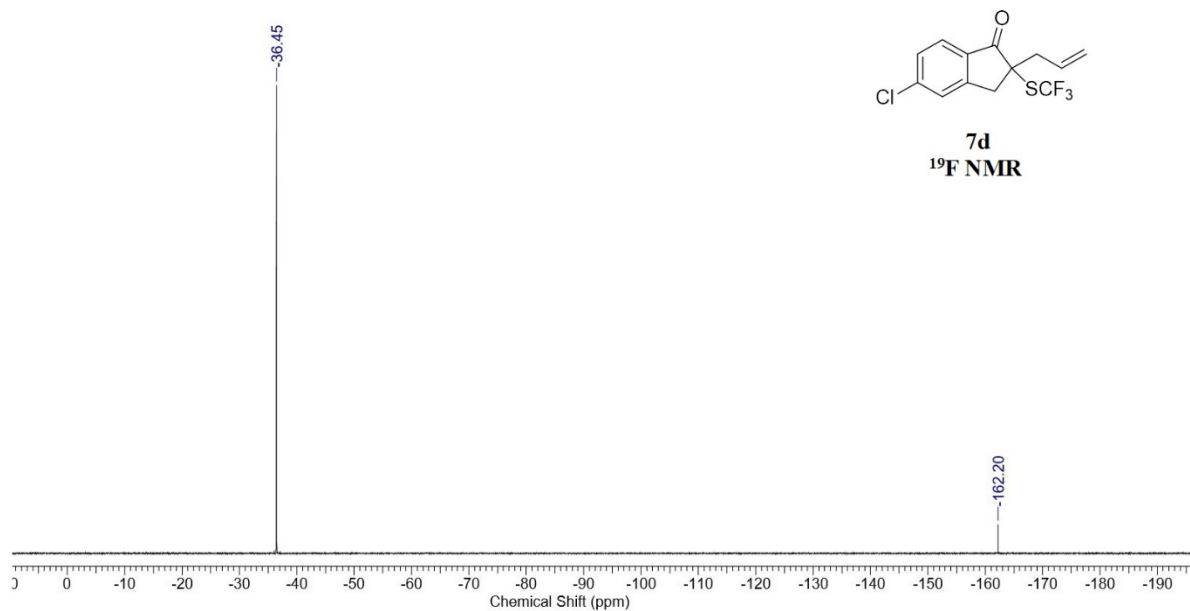


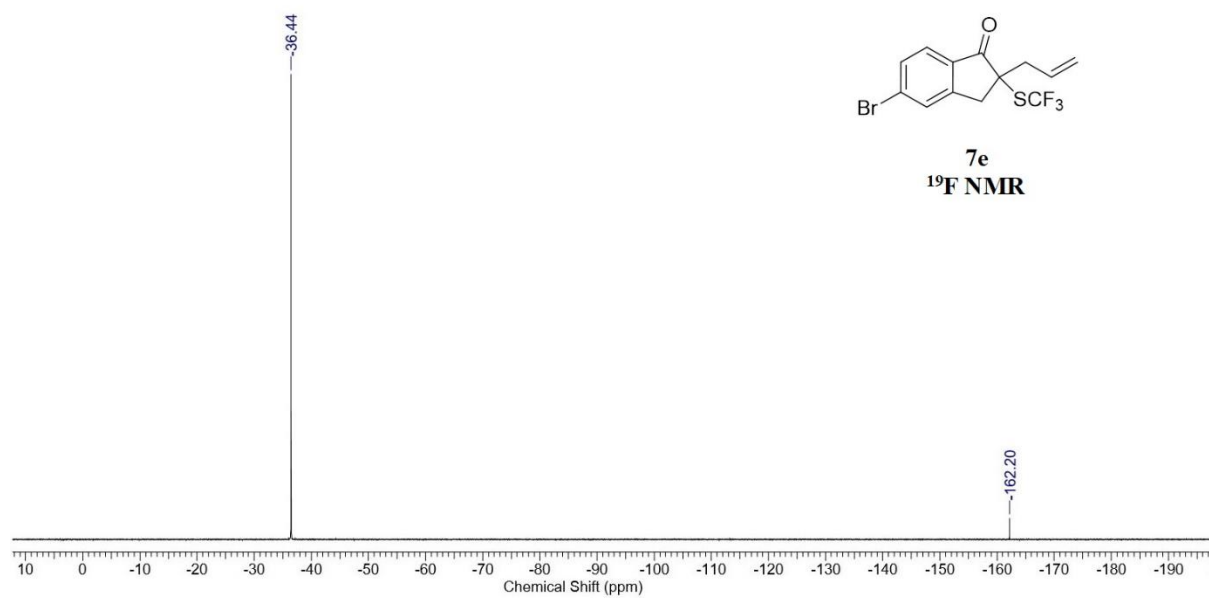
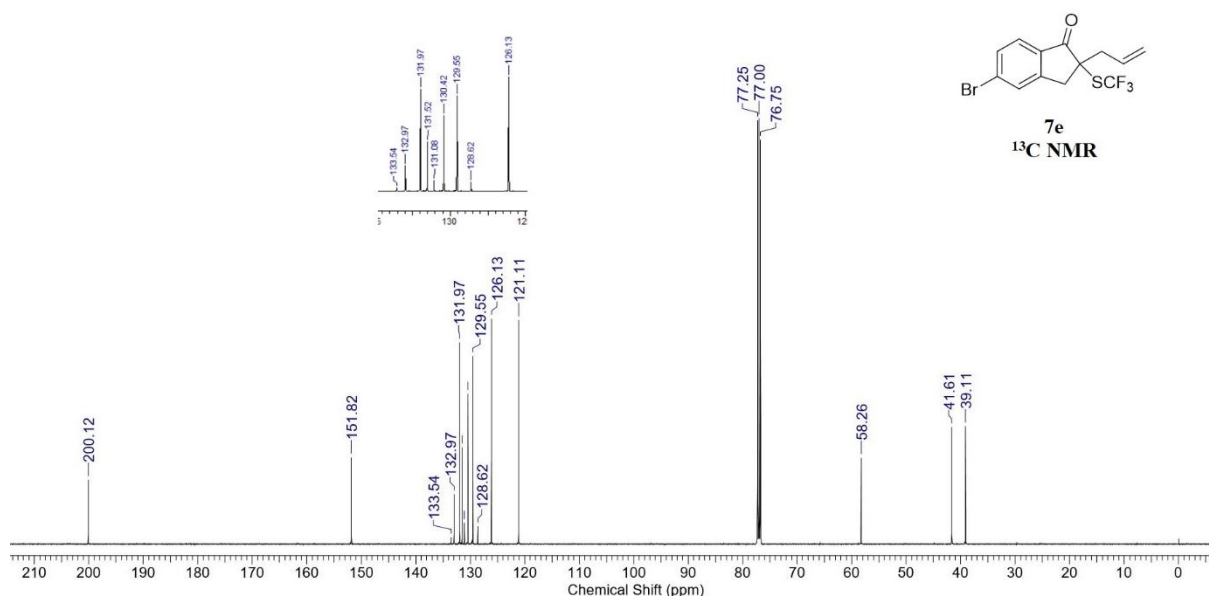


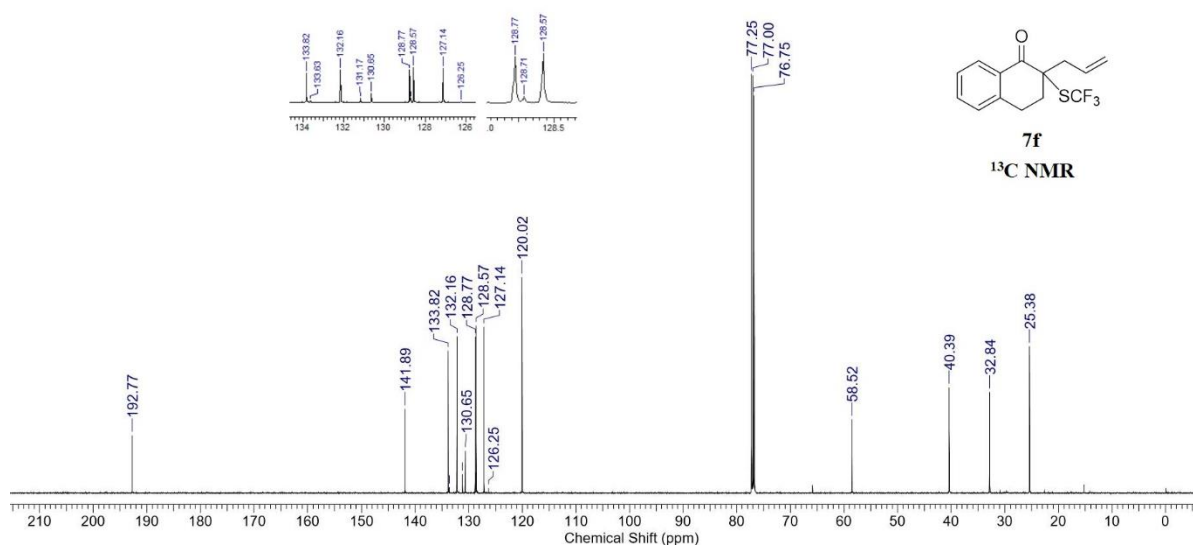
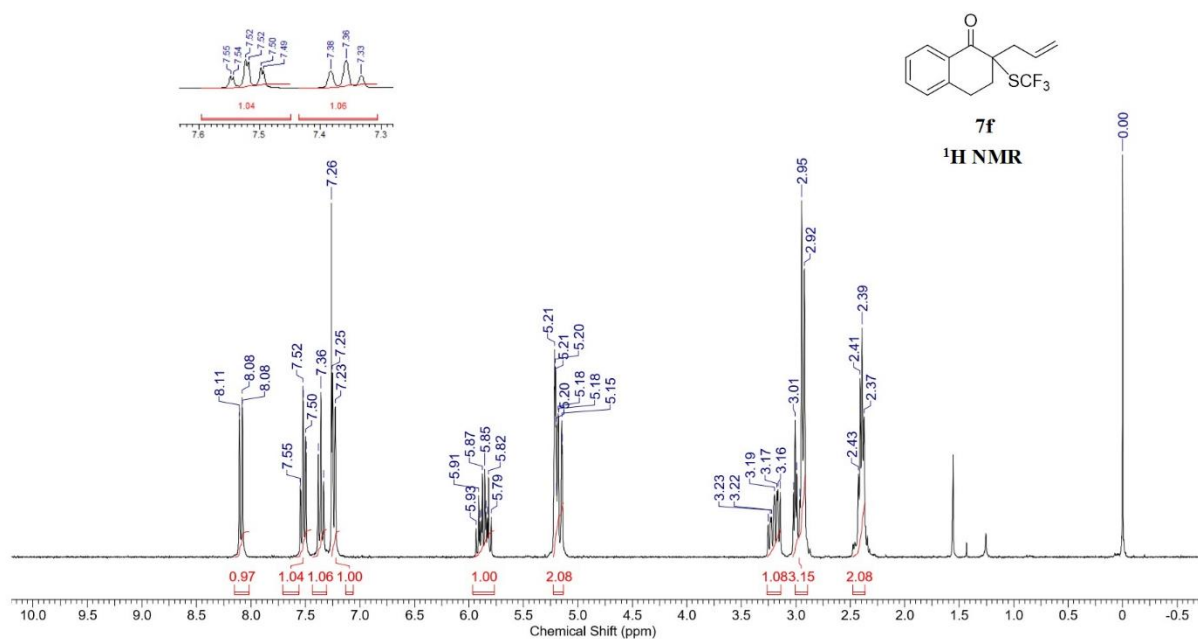


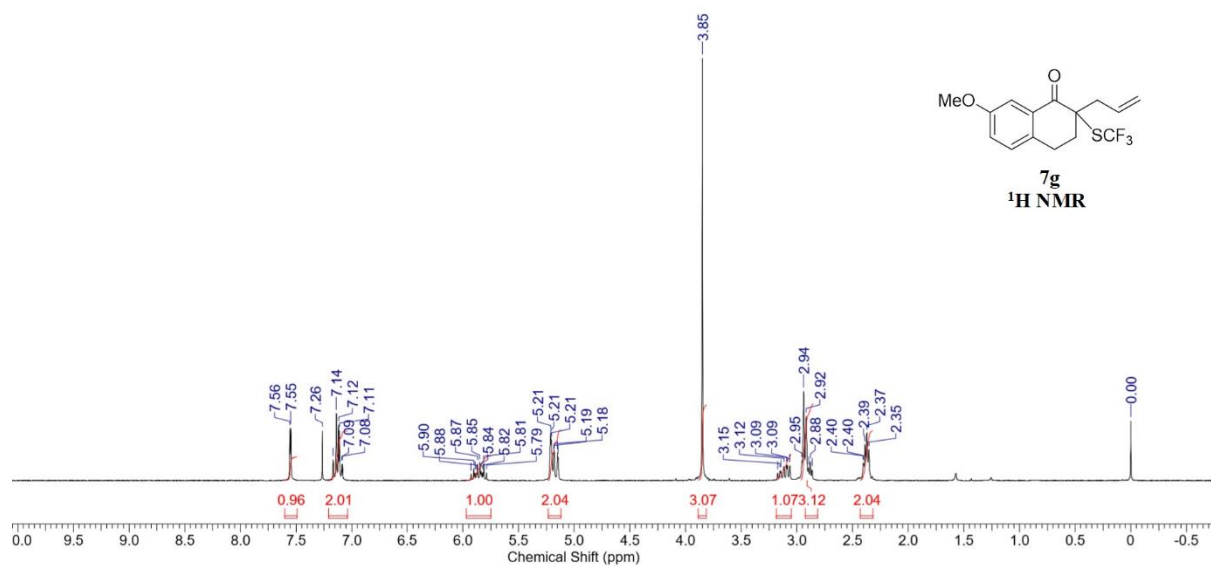
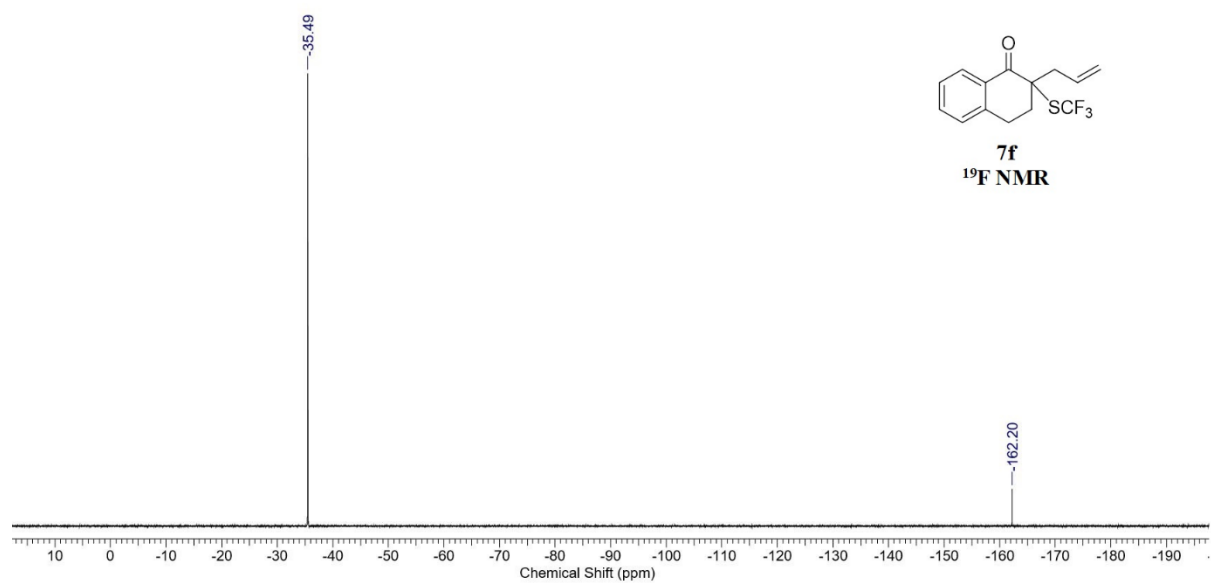


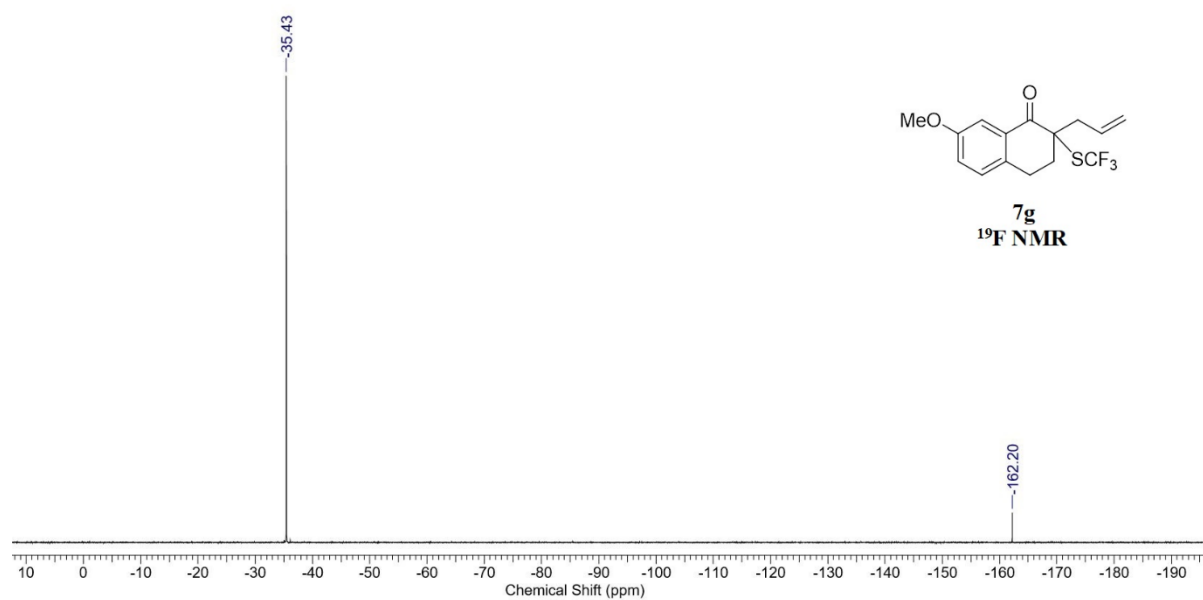
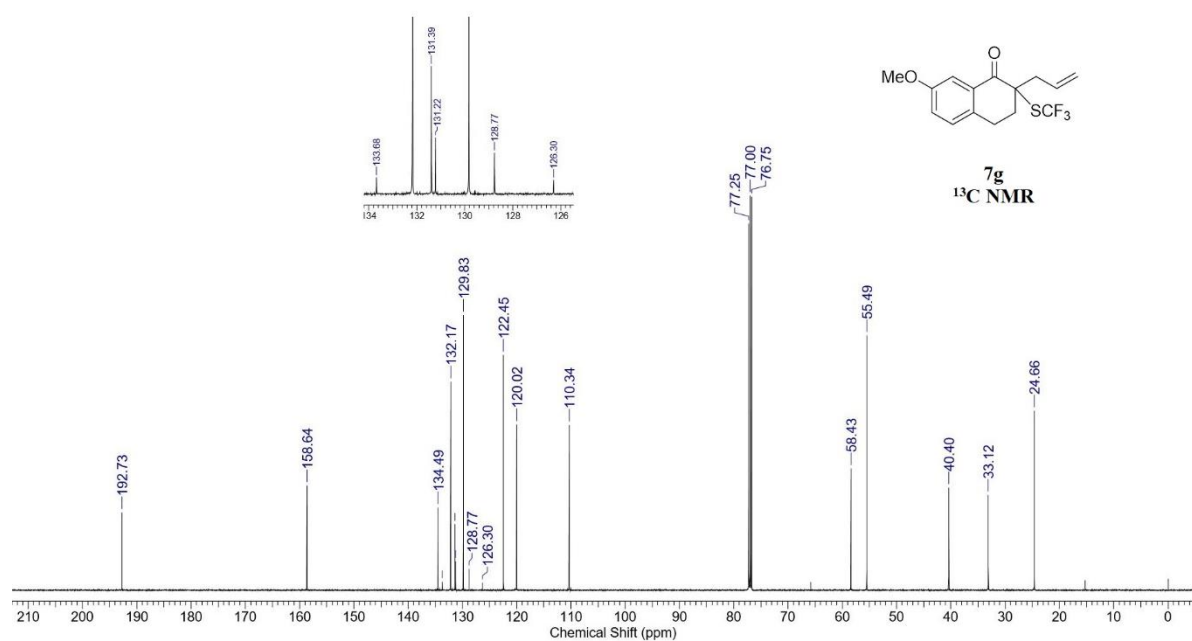


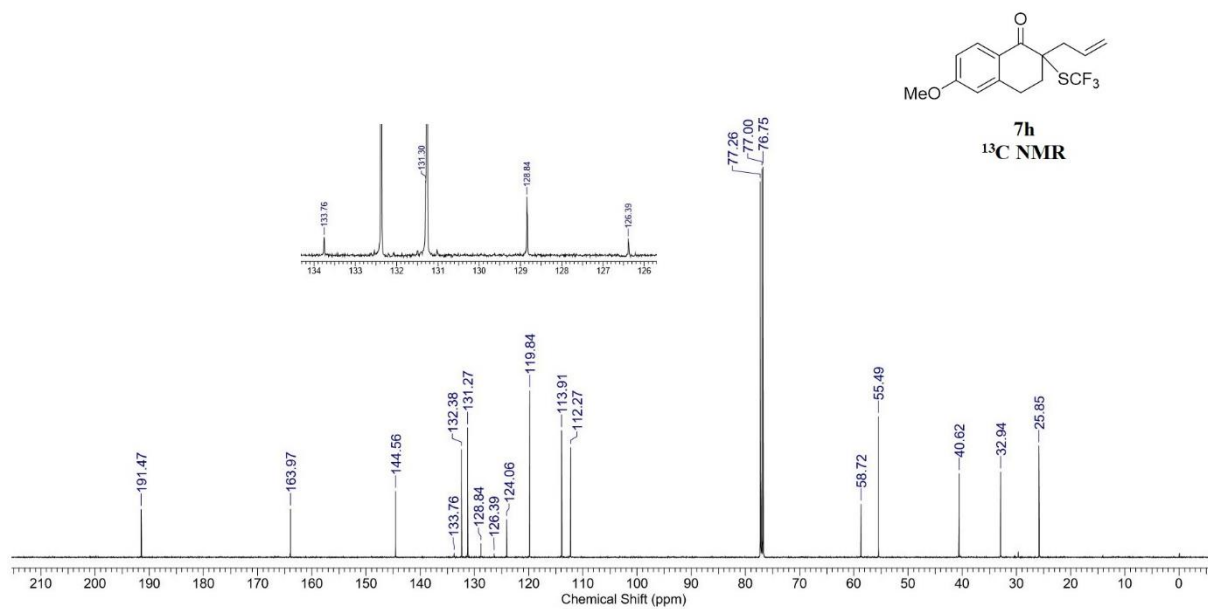
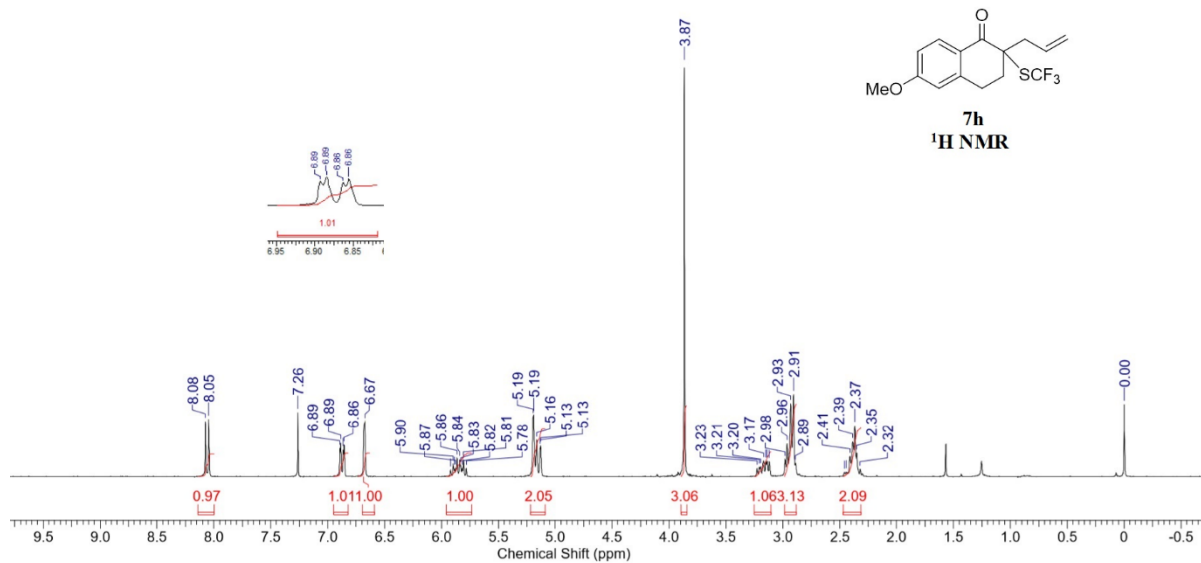


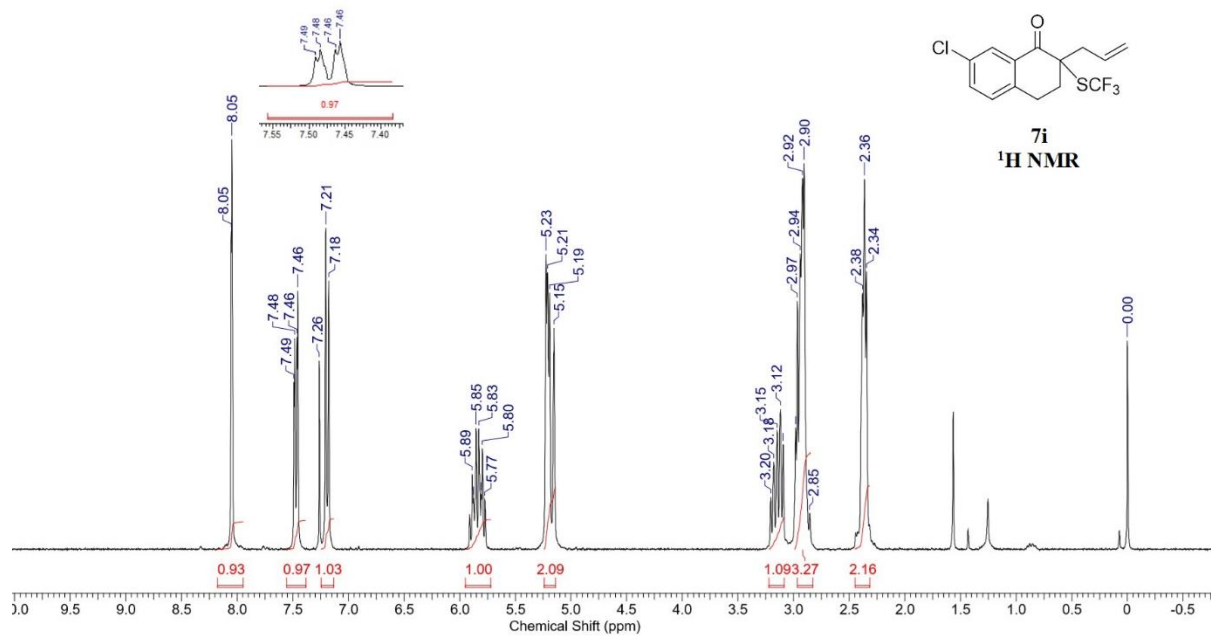
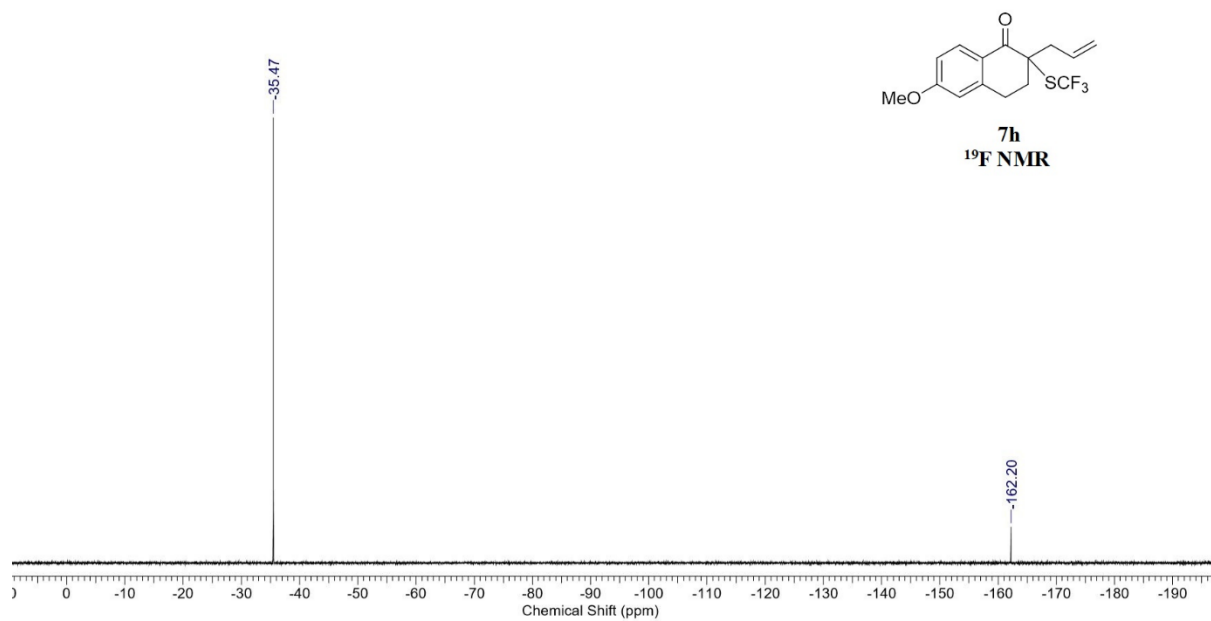


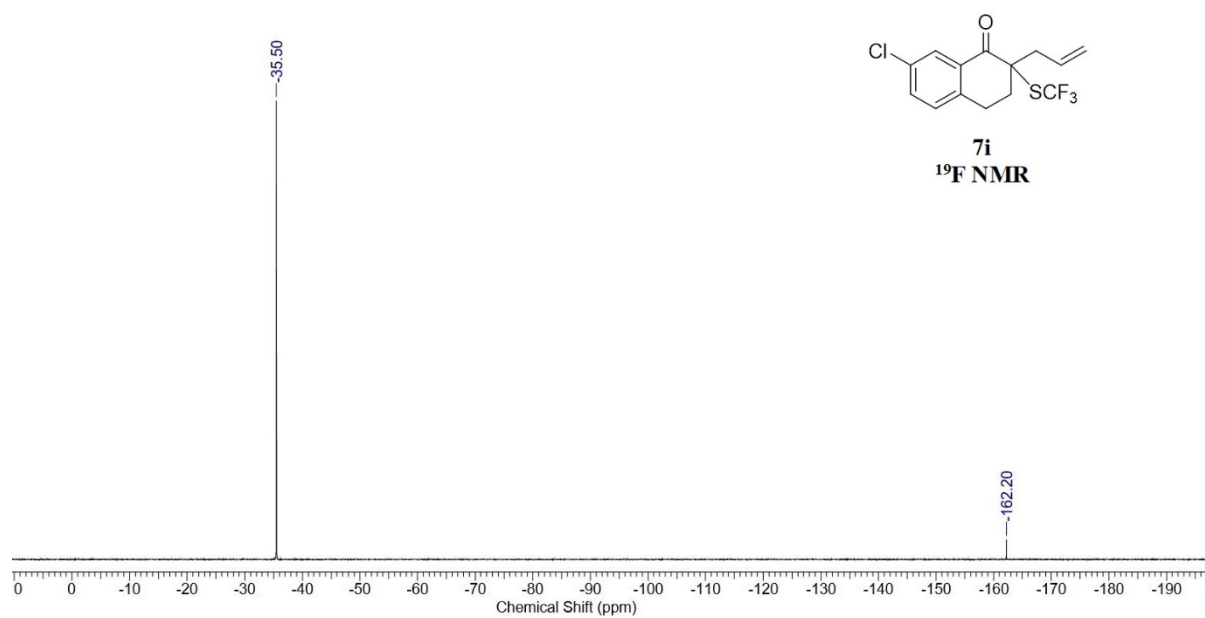
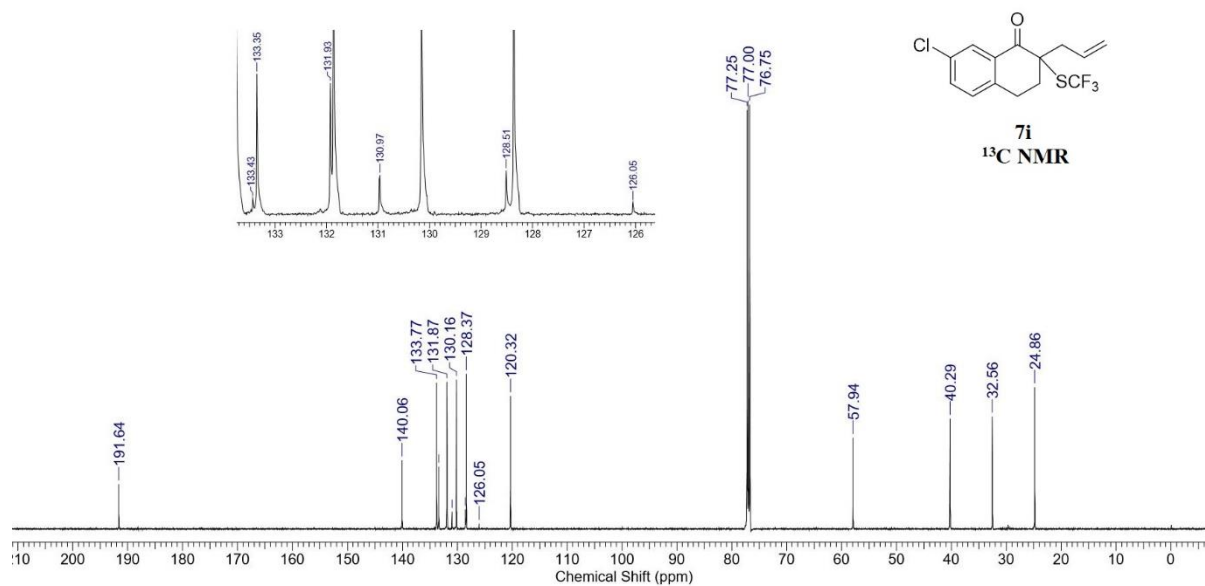


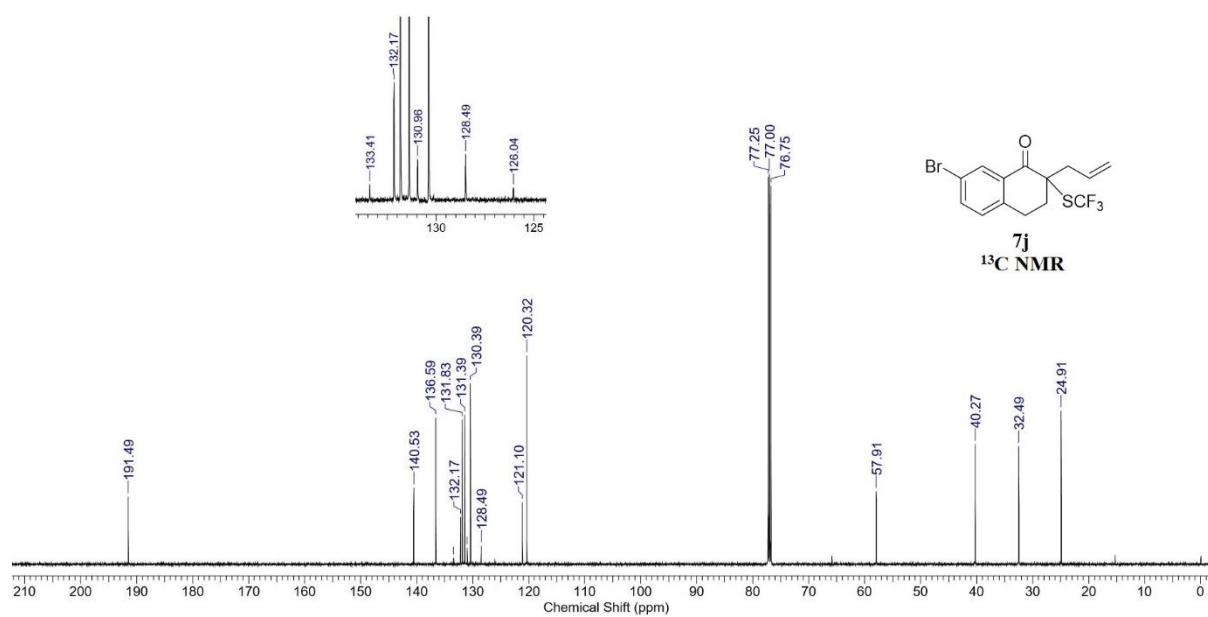
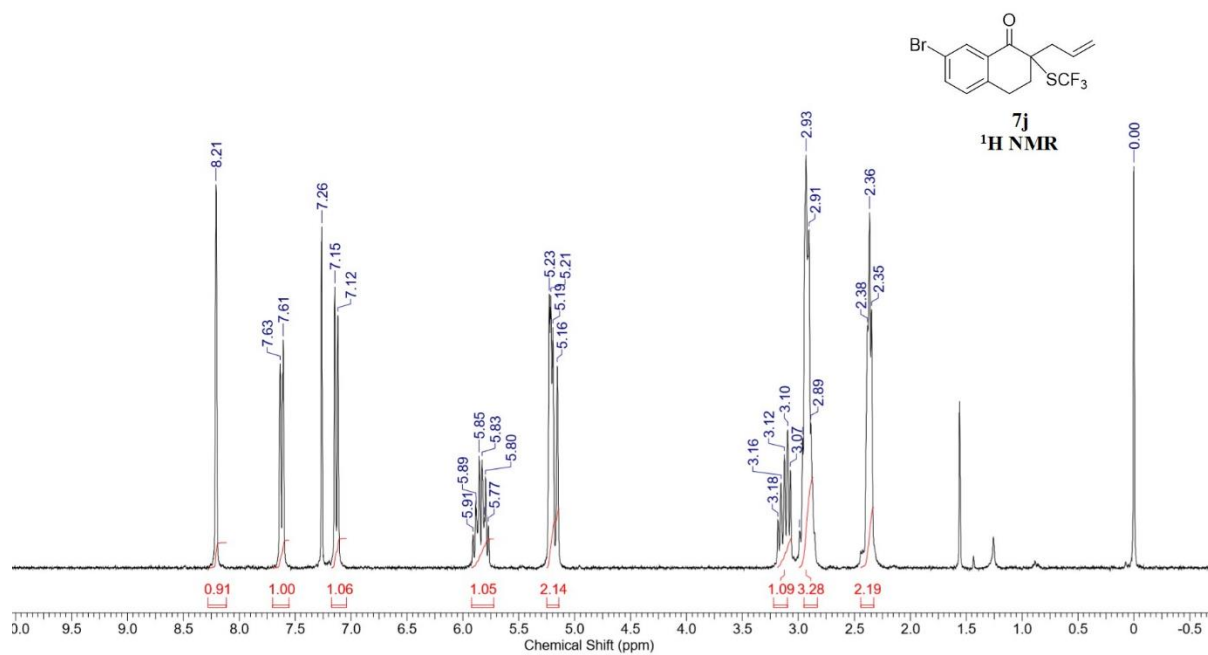


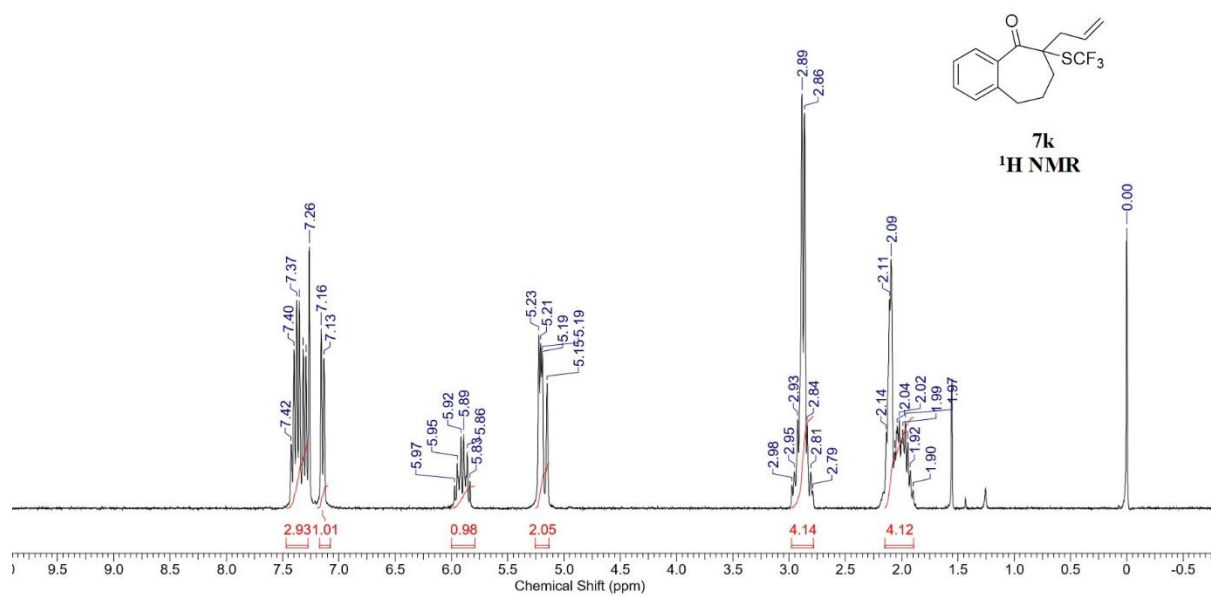
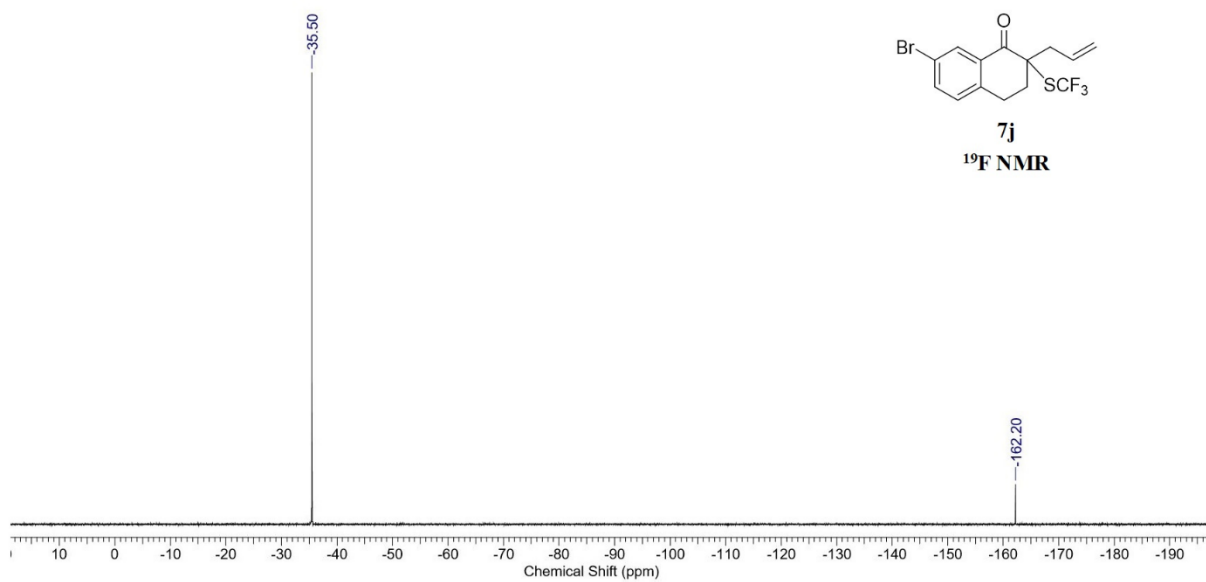


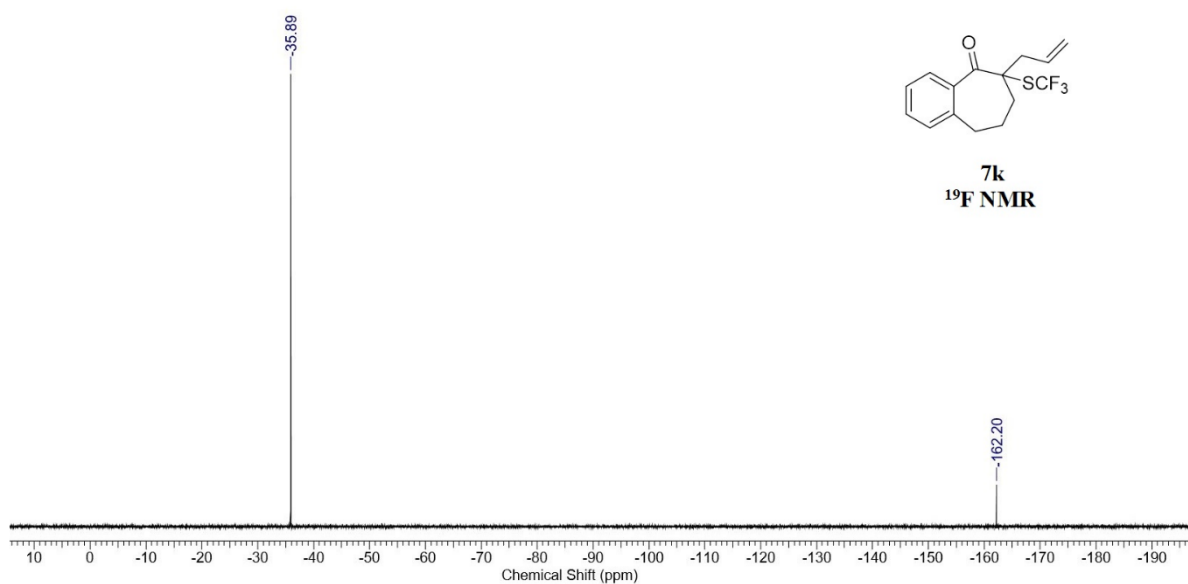
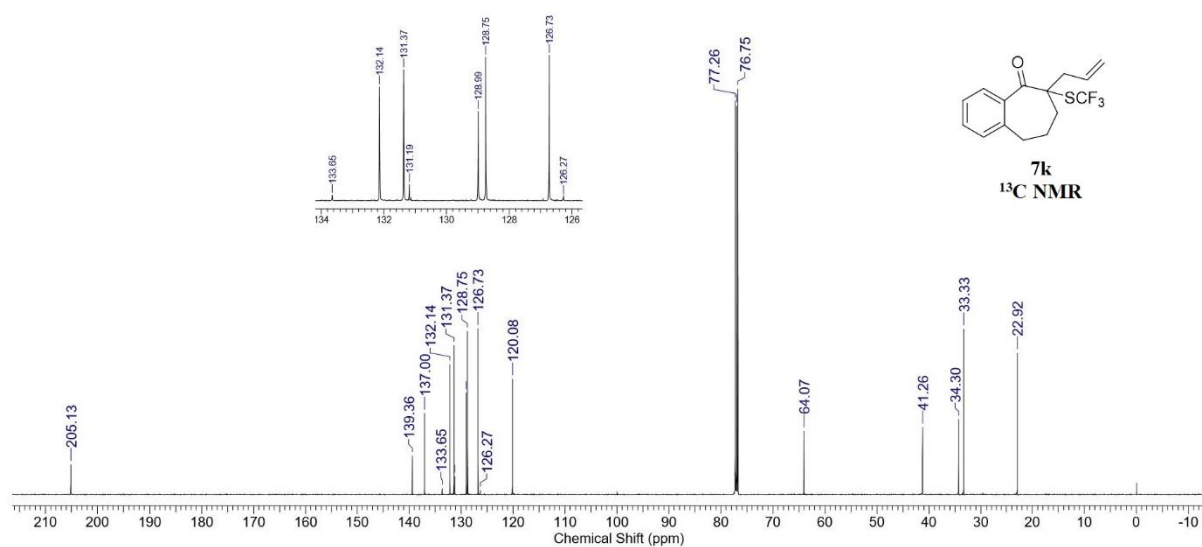


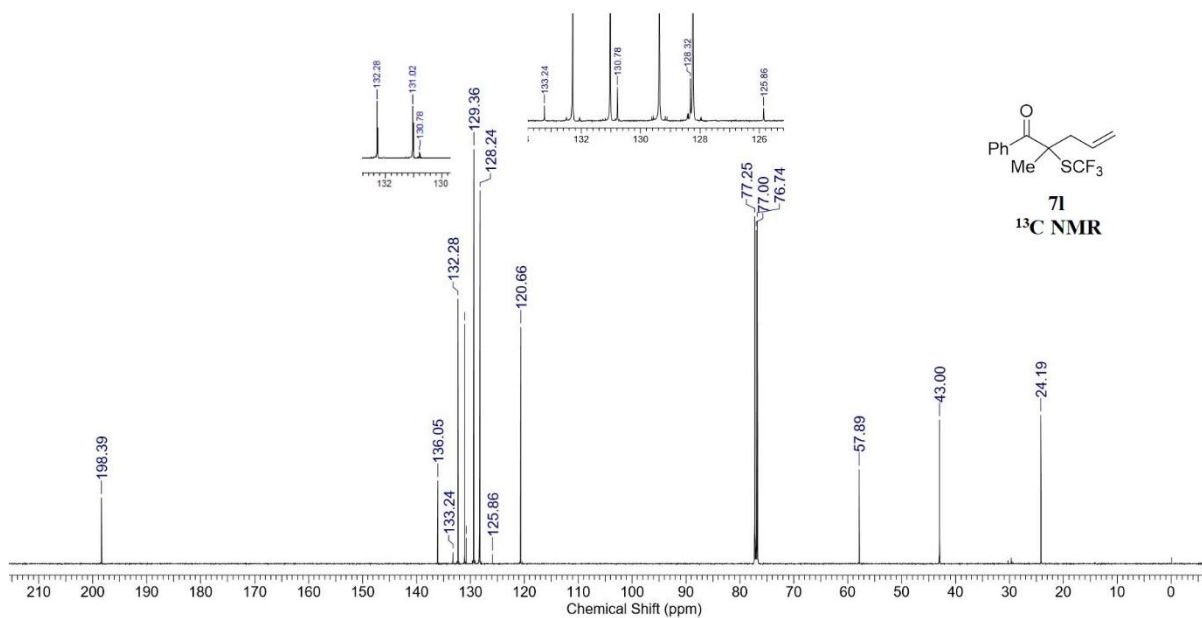
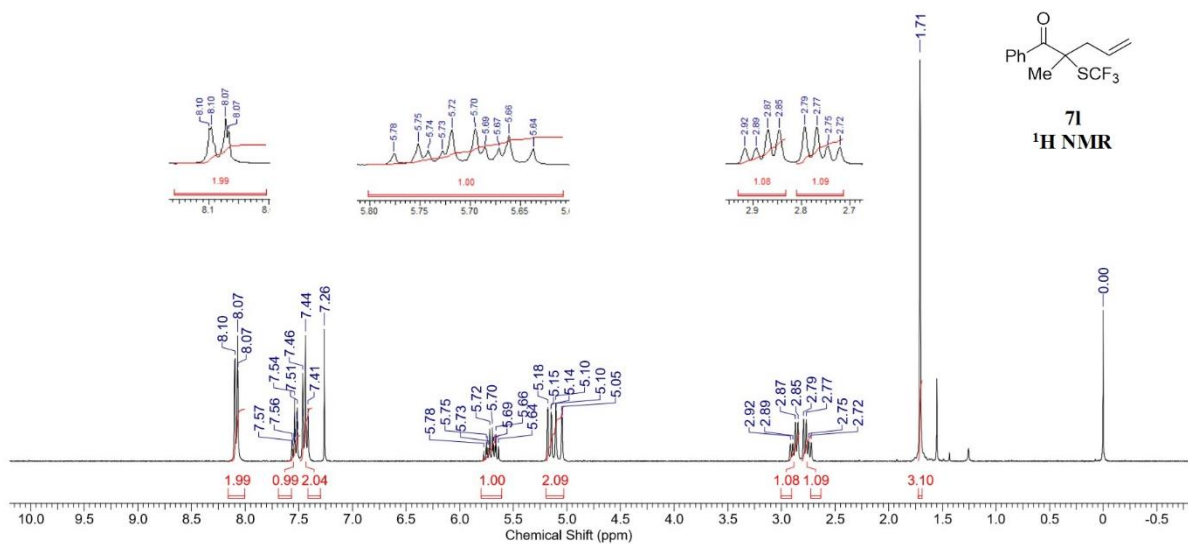


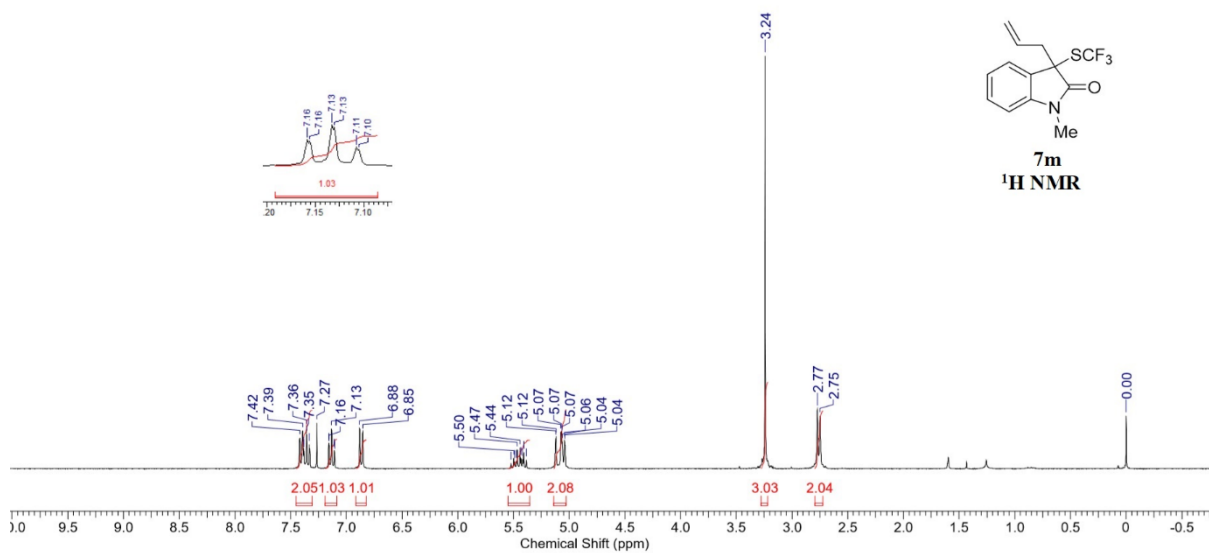
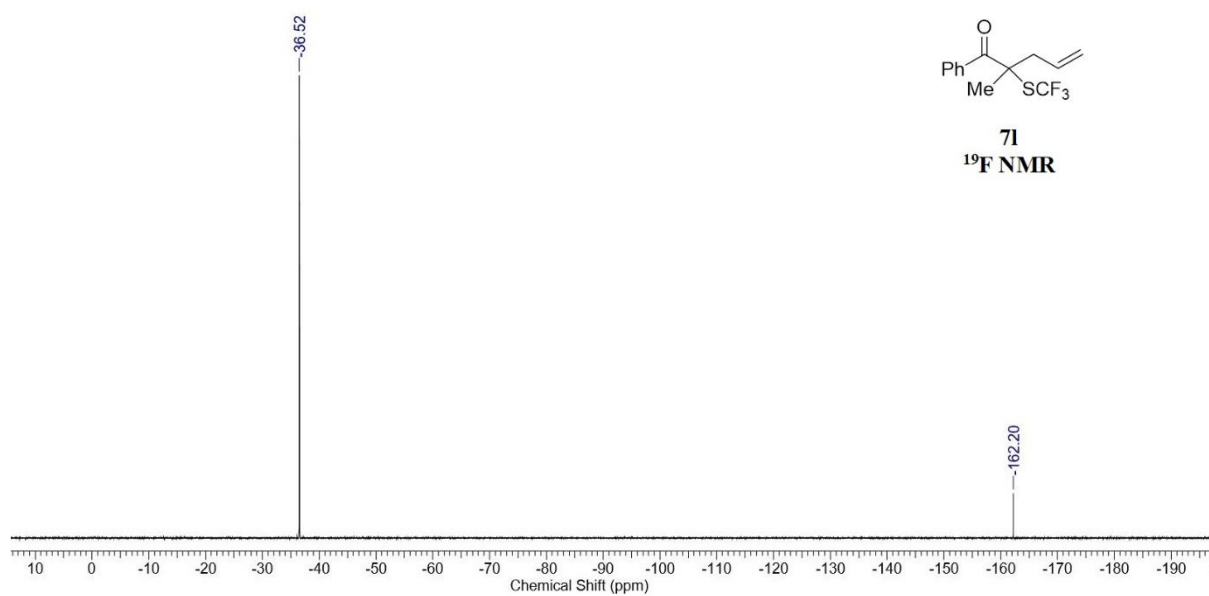


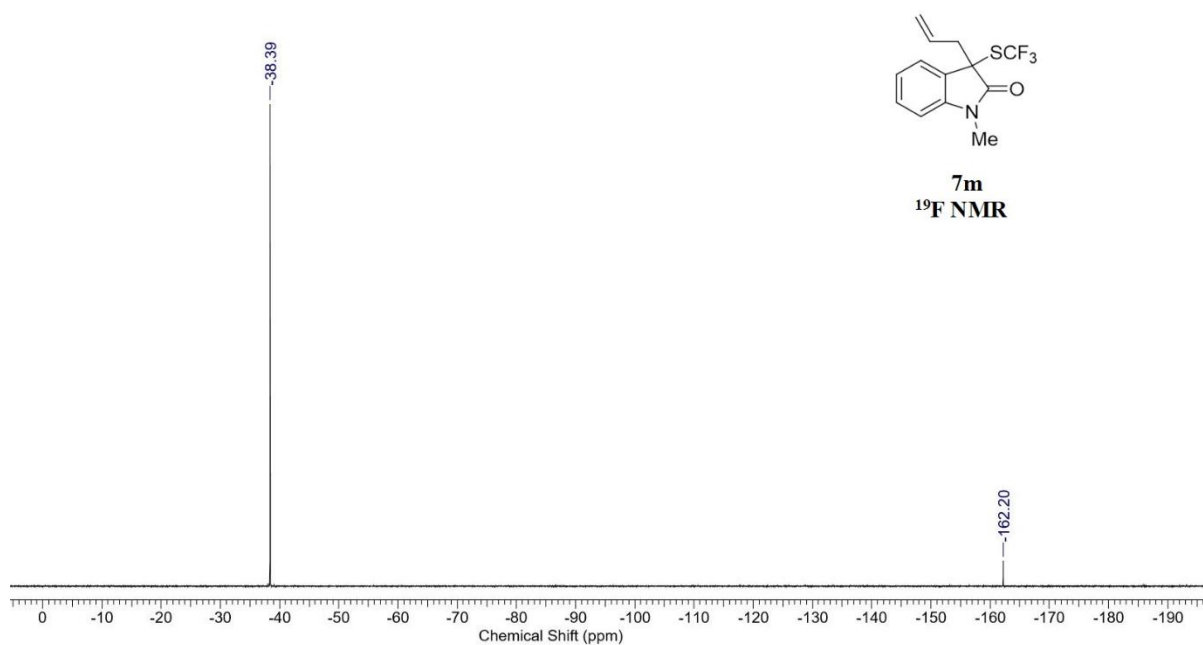
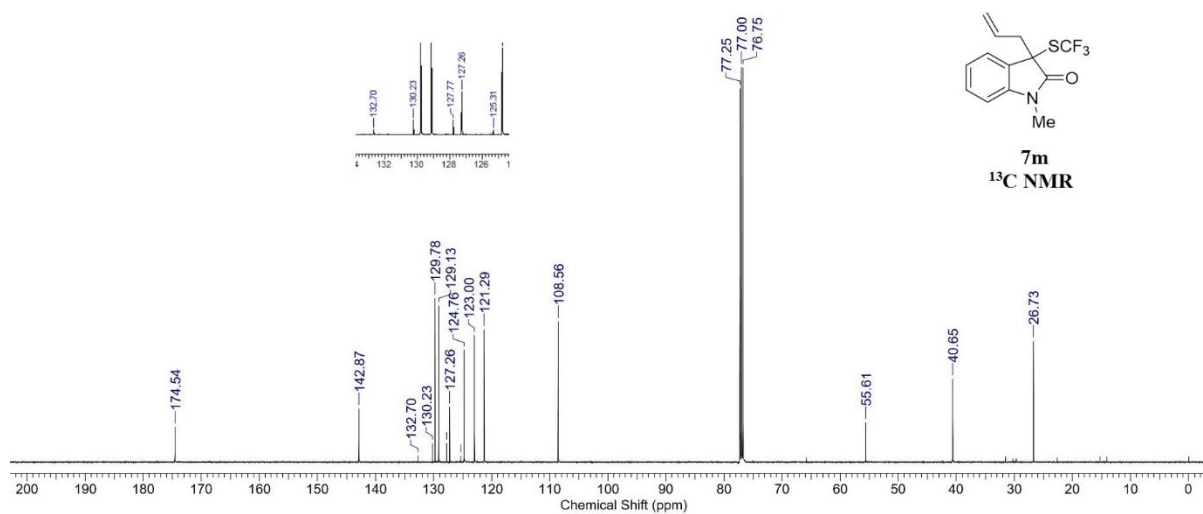


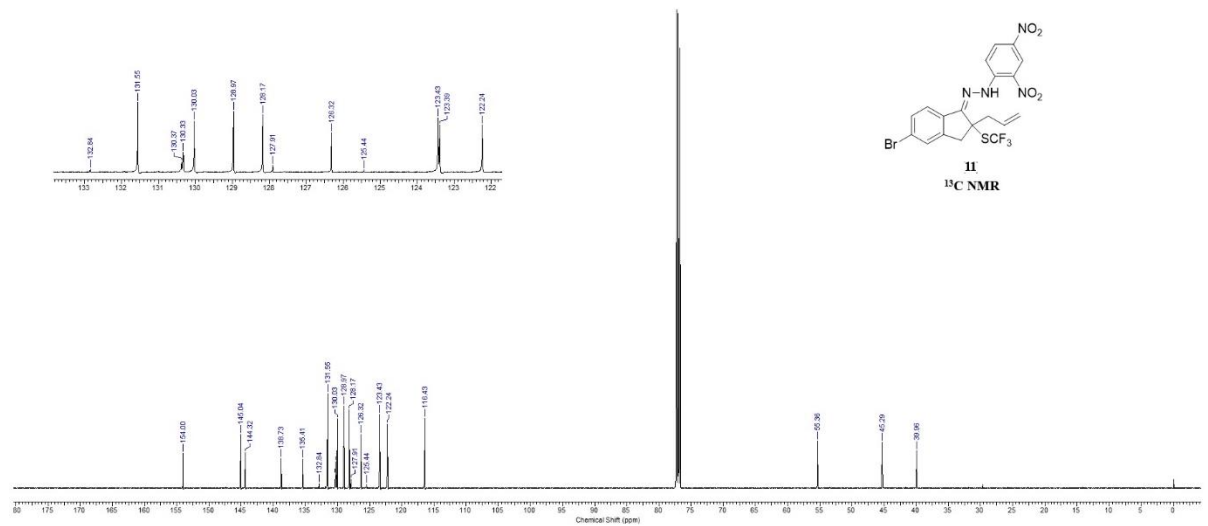
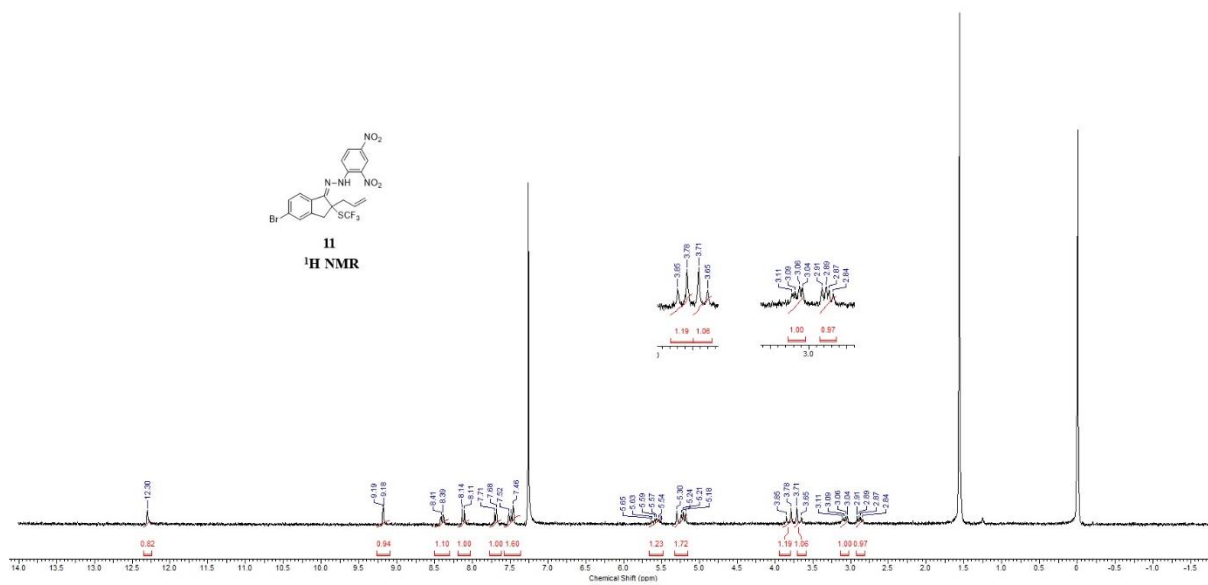


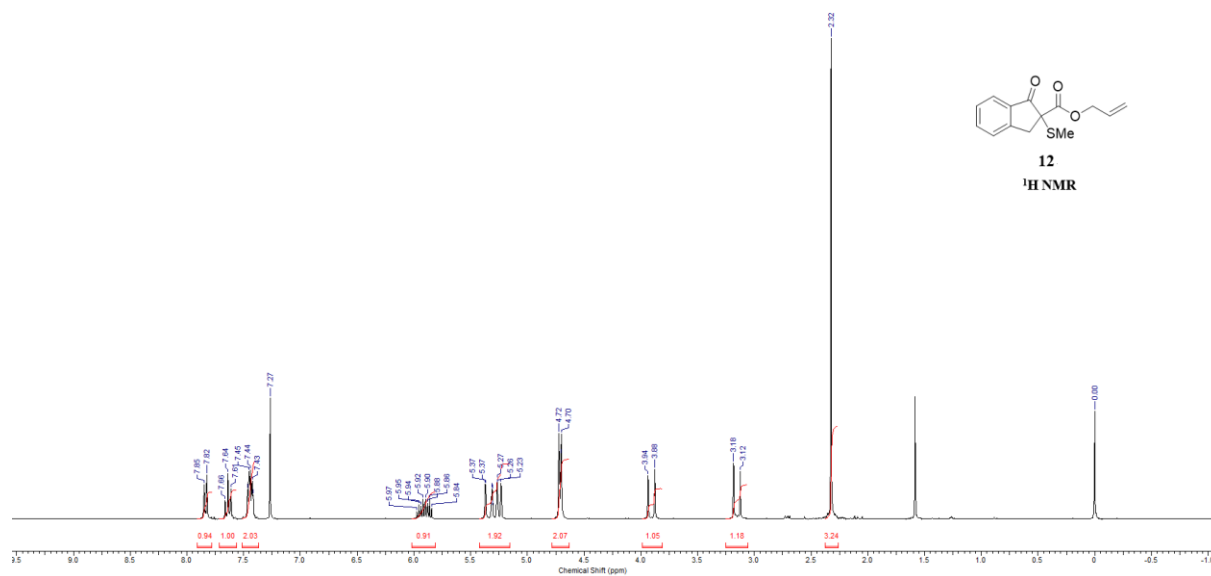
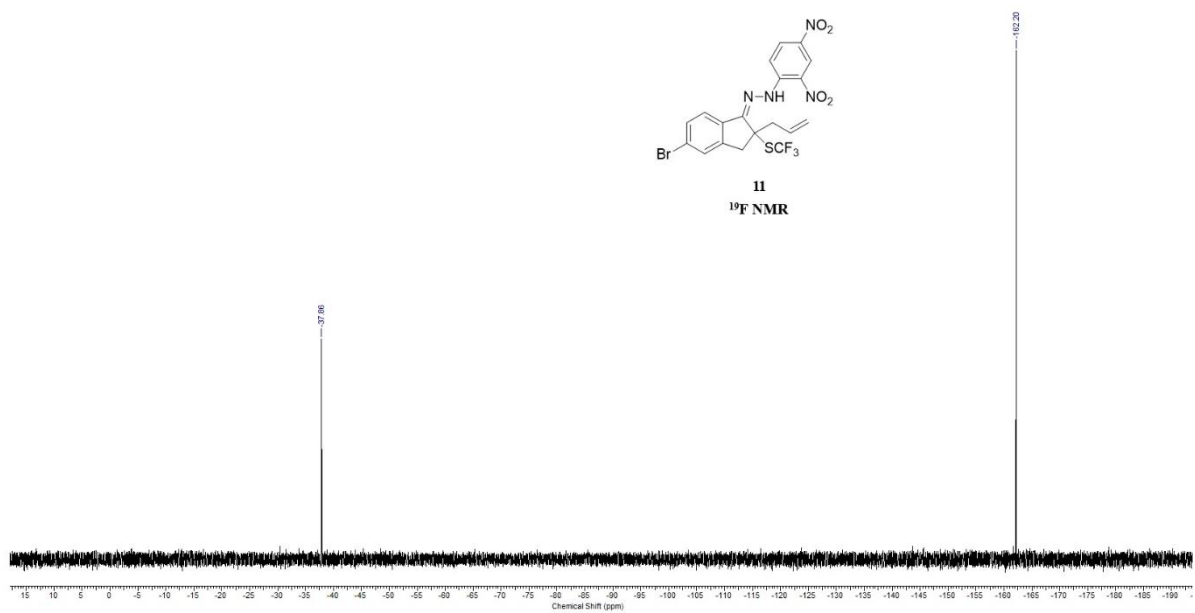


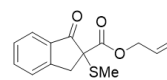




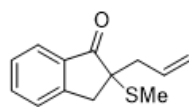
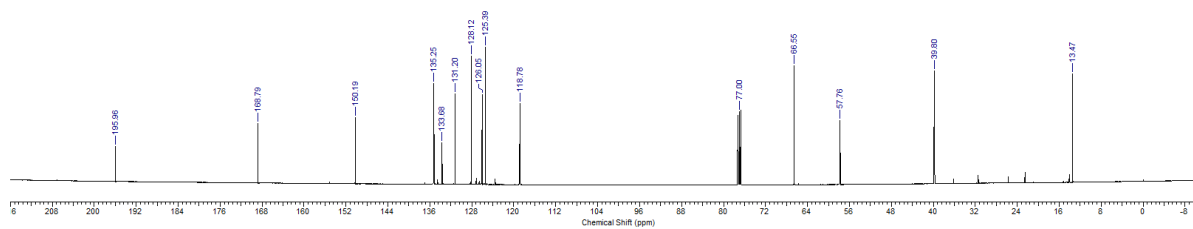








12
¹³C NMR



13
¹H NMR

