Electronic supplementary information

Asymmetric synthesis of α-trifluoromethoxy ketones with a tetrasubstituted α-stereogenic centre via the Palladium-catalyzed Decarboxylative Allylic Alkylation of Allyl Enol Carbonates

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Optimization of the reaction conditions for 1i

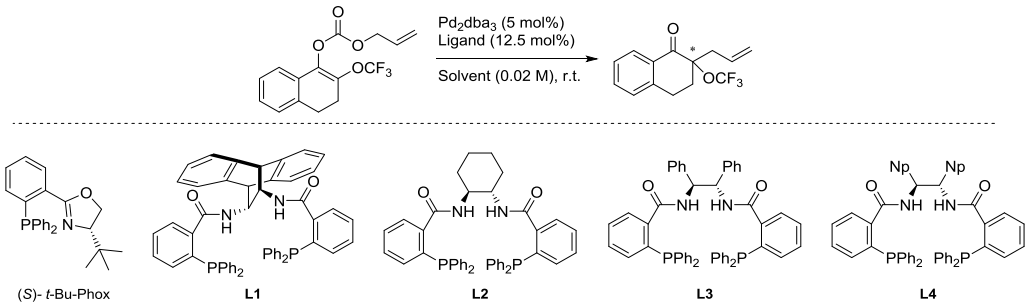


Table S1. Optimization of the reaction conditions for **1i**[a]

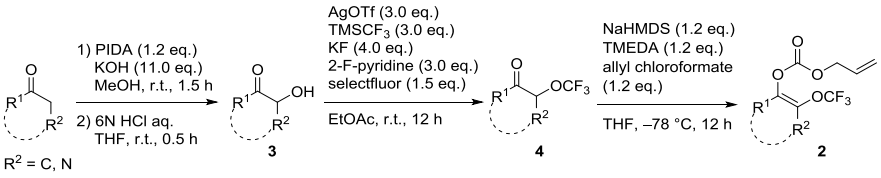
run	ligand	solvent	temp. (°C)	yield (%)	ee (%)
1	dppf	TBME	r.t.	61	–
2	(*S*)-*t*Bu-PHOX	TBME	r.t.	86	37
3	L1	TBME	r.t.	71	10
4	L2	TBME	r.t.	86	67
5	L3	TBME	r.t.	74	89
6	L4	TBME	r.t.	91	60
7	L3	THF	r.t.	81	86
8	L3	CH_2Cl_2	r.t.	81	82
9	L3	CH_2Cl_2	−30	84	75

[a] Reaction condition: **1i** (0.05 mmol, 1.0 eq.), Pd_2dba_3 (5 mol%), ligand (12.5 mol%) in TBME (0.02 M) at room temperature, unless otherwise noted.

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 Ark Pharm Inc., Aldrich Chemical Co., Nacalai Tesuque, 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 neutralize 40-63 μm. ^{1}H (300 MHz, 500 MHz and 700 MHz), ^{13}C (75 MHz, 126 MHz and 176 MHz) and ^{19}F (282 and 659 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 (δH = 0.00 ppm) or $CHCl_3$ (δC = 77.0 ppm) or hexafluorobenzene (δF = −162.2 ppm). The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, bs: broad singlet, dd: doublet of doublet, dt: doublet of triplet, dq: doublet of quartet, ddd: doublet of doublet of doublet, ddt: doublet of doublet of triplet, dtd: doublet of triplet of doublet, dddd: doublet of doublet of doublet of doublet, td: triplet of doublet, tt: triplet of triplet, tdd: triplet of doublet of doublet, qd: quartet 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 amicro-TOF analyzer. The wave numbers ($\tilde{\nu}$) of recorded IR-signals are quoted in cm^{-1} on a JASCO FT/IR-4100 spectrometer. HPLC analyses were performed on a JASCOLC-2000 Plus series using 4.6 x 250 mm CHIRALCEL® series or CHIRALPAK series. Melting points were recorded on a BUCHI M-565.

Scheme S1. OCF_3-substituted allyl enol carbonates were prepared by following procedure

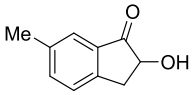


Preparation of hydroxyketones

Hydroxyketones were prepared by following a reported procedure.[1,3,5] Spectroscopic data of **3a**[1], **3i**[2], **3q**[3a], **3t**[4], **3u**[5], **3v**[6] were in agreement with the literature.

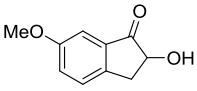
General Procedure A[1]**:** To a 0 °C solution of ketone in MeOH (0.2 M) was added KOH (11.0 eq.) and the mixture was stirred for 15 min at same temperature. PIDA (1.2 eq.) was added in one portion and the resulting mixture was stirred for 1 hour, then warmed to room temperature and stirred for additional 30 minutes. The mixture was concentrated, dissolved in ether, washed with 3% aqueous solution of $NaHCO_3$ and again concentrated. The residue was dissolved in THF (0.4 M) and conc. HCl (3.3 M), and stirred for 30 minutes. Then, the resulting mixture was extracted with ether and the combined organic layers were washed with saturated aqueous solution of $NaHCO_3$, water and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash silica-gel column chromatography.

2-Hydroxy-6-methyl-2,3-dihydro-1*H*-inden-1-one (3b)



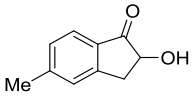
Recrystallized from *i*-PrOH. Slightly orange powder; 802.0 mg; 49% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 4.54 (ddd, *J* = 7.7, 5.1, 2.8 Hz, 1H), 3.54 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.30 - 3.24 (m, 1H), 2.97 (dd, *J* = 16.3, 5.0 Hz, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 206.6, 148.2, 138.0, 137.1, 134.1, 126.4, 124.3, 74.5, 34.8, 21.1 ppm. **IR** (KBr): ν̃ = 3427, 3028, 2920, 2862, 1693, 1257, 1099, 1036, 941, 823 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_{10}NaO_2$ 185.0578; Found 185.0579. **m.p.**: 87.8 - 88.4 °C.

2-Hydroxy-6-methoxy-2,3-dihydro-1*H*-inden-1-one (3c)



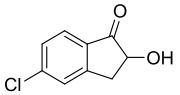
Eluent (*n*-hexane/ethyl acetate = 7/3): R_f = 0.48. White solid; 223.3 mg; 46% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.41 - 7.32 (m, 1H), 7.26 - 7.15 (m, 2H), 4.61 - 4.46 (m, 1H), 3.84 (s, 3H), 3.52 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.01 - 2.84 (m, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 206.6, 159.6, 143.7, 135.0, 127.5, 125.1, 105.6, 74.8, 55.6, 34.5 ppm. **IR** (KBr): ν̃ = 3411, 3016, 2956, 2850, 1712, 1496, 1211, 1088, 1022, 847, 771 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_{10}NaO_3$ 201.0528; Found 201.0515. **m.p.**: 72.1 - 73.5 °C.

2-Hydroxy-5-methyl-2,3-dihydro-1*H*-inden-1-one (3d)



Recrystallized from *i*-PrOH. Yellow powder; 770.0 mg; 62% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.9 Hz, 1H), 7.27 - 7.26 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.53 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.52 (dd, *J* = 16.5, 7.9 Hz, 1H), 3.36 (bs, 1H), 2.97 (dd, *J* = 16.5, 4.9 Hz, 1H), 2.45 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 206.0, 151.4, 147.3, 131.6, 129.2, 127.1, 124.3, 74.3, 35.0, 22.2 ppm. **IR** (KBr): ν̃ = 3396, 3041, 2916, 2875, 1693, 1610, 1255, 1093, 1032, 906, 802 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_{10}NaO_2$ 185.0578; Found 185.0589. **m.p.**: 137.5 - 138.3 °C.

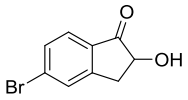
5-Chloro-2-hydroxy-2,3-dihydro-1*H*-inden-1-one (3e)



Recrystallized from *i*-PrOH. Slightly orange powder; 596.1 mg; 33% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 4.57 - 4.52 (m, 1H), 3.56 (dd, *J* = 17.0, 7.9 Hz, 1H), 3.04 - 2.97 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 205.0, 152.3, 142.4, 132.4, 128.9, 127.0, 125.6, 74.1, 34.9 ppm. **IR** (KBr): ν̃

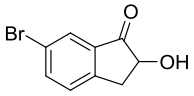
= 3406, 3064, 2972, 2881, 1709, 1304, 1209, 1103, 1066, 916, 833, 793 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_9H_7ClO_2$ 182.0135; Found 182.0127. **m.p.**: 142.5 - 143.2 °C.

5-Bromo-2-hydroxy-2,3-dihydro-1*H*-inden-1-one (3f)



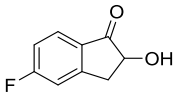
Recrystallized from *i*-PrOH. Slightly brown solid; 1.60 g; 47% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.75 - 7.49 (m, 3H), 4.53 (dd, *J* = 7.8, 5.1 Hz, 1H), 3.56 (dd, *J* = 16.7, 7.9 Hz, 1H), 3.01 (dd, *J* = 16.9, 4.8 Hz, 1H), 2.91 (bs, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 205.2, 152.4, 132.8, 131.7, 131.3, 130.1, 125.6, 74.0, 34.8 ppm. **IR** (KBr): ν̃ = 3413, 3060, 2972, 2929, 2883, 1709, 1599, 1304, 1250, 1103, 1055, 914 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_9H_7BrO_2$ 225.9629; Found 225.9611. **m.p.**: 153.8 - 154.5 °C.

6-Bromo-2-hydroxy-2,3-dihydro-1*H*-inden-1-one (3g)



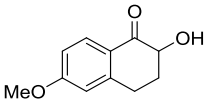
Eluent (*n*-hexane/ethyl acetate = 7/3): R_f = 0.19. Brown solid; 287 mg; 51% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 2.1 Hz, 1H), 7.74 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 4.58 (dd, *J* = 7.9, 5.2 Hz, 1H), 3.54 (dd, *J* = 16.6, 7.8 Hz, 1H), 3.27 (bs, 1H), 2.96 (ddd, *J* = 16.9, 5.3, 0.8 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 205.1, 149.4, 138.6, 135.8, 128.4, 127.3, 122.1, 74.4, 34.7 ppm. **IR** (KBr): ν̃ = 3411, 3074, 2956, 2898, 2827, 1709, 1595, 1207, 1192, 1095, 825, 793 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_9H_7BrO_2$ 225.9629; Found 225.9607. **m.p.**: 103.8 - 104.9 °C.

5-Fluoro-2-hydroxy-2,3-dihydro-1*H*-inden-1-one (3h)



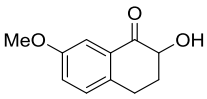
Eluent (*n*-hexane/ethyl acetate = 3/2): R_f = 0.29. White solid; 469.8 mg; 42% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 8.2, 5.3 Hz, 1H), 7.21 - 7.05 (m, 2H), 4.54 (ddd, *J* = 7.6, 5.2, 2.2 Hz, 1H), 3.57 (dd, *J* = 16.7, 7.9 Hz, 1H), 3.02 (dd, *J* = 16.7, 4.7 Hz, 1H), 2.92 - 2.91 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ= −100.8 (q, *J* = 6.6 Hz, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 204.5, 167.8 (d, *J* = 257.7 Hz), 153.9 (d, *J* = 10.9 Hz), 130.4 (d, *J* = 1.7 Hz), 126.9 (d, *J* = 10.9 Hz), 116.4 (d, *J* = 24.3 Hz), 113.5 (d, *J* = 22.6 Hz), 74.1, 35.1 (d, *J* = 2.5 Hz) ppm. **IR** (KBr): ν̃ = 3404, 3066, 2887, 1707, 1620, 1591, 1238, 1105, 1086, 879, 795 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_9H_7FNaO_2$ 189.0328; Found 189.0328. **m.p.**: 111.9 - 112.6 °C.

2-Hydroxy-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (3j)



Recrystallized from *i*-PrOH. Brown solid; 1.06 g; 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 1H), 6.90 - 6.82 (m, 1H), 6.74 - 6.66 (m, 1H), 4.33 (ddd, *J* = 13.4, 5.5, 1.8 Hz, 1H), 3.95 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 3H), 3.17 - 3.05 (m, 1H), 3.04 - 2.93 (m, 1H), 2.58 - 2.44 (m, 1H), 2.02 (qd, *J* = 13.0, 4.6 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 198.1, 164.2, 146.9, 130.0, 123.8, 113.6, 112.7, 73.5, 55.5, 31.8, 28.0 ppm. **IR** (KBr): ν̃ = 3479, 3006, 2968, 2929, 2837, 1664, 1601, 1250, 1147, 1092, 995, 933, 845, 791 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_{12}NaO_3$ 215.0684; Found 215.0692. **m.p.**: 83.2 - 84.6 °C.

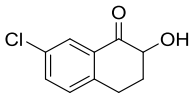
2-Hydroxy-7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (3k)



Eluent (*n*-hexane/EtOAc = 3/1): R_f = 0.32. Brown solid; 1.54 g; 69% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 2.6 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 8.5, 2.9 Hz, 1H), 4.37 (ddd, *J* = 13.6, 5.4, 1.9 Hz, 1H), 3.93 - 3.87 (m, 1H), 3.85 (s, 3H), 3.16 - 2.93 (m, 2H), 2.59 - 2.46 (m, 1H), 2.03 (qd, *J* = 12.9, 5.0 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 199.5, 158.3, 136.8, 131.1, 130.0, 122.4, 109.2, 73.8, 55.4, 32.0, 26.9 ppm. **IR** (KBr): ν̃ = 3427, 3072, 3012,

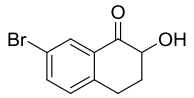
2939, 2833, 1689, 1610, 1325, 1244, 1095, 1030, 1007, 874, 742 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{11}H_{12}NaO_3$ 215.0684; Found 215.0677. **m.p.**: 134.6 - 135.3 °C.

7-Chloro-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (3l)



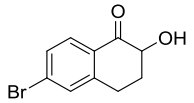
Recrystallized from *i*-PrOH. Off-white solid; 945.2 mg; 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 2.1 Hz, 1H), 7.48 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 4.38 (ddd, *J* = 13.4, 5.5, 1.8 Hz, 1H), 3.81 (d, *J* = 1.8 Hz, 1H), 3.18 - 2.97 (m, 2H), 2.60 - 2.47 (m, 1H), 2.04 (qd, *J* = 13.0, 4.9 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 198.5, 142.5, 134.0, 133.2, 131.7, 130.5, 127.2, 73.8, 31.6, 27.2 ppm. **IR** (KBr): ν̃ = 3489, 3076, 2954, 2866, 2821, 1685, 1475, 1369, 1255, 1221, 1147, 1109, 1005, 816 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_9ClNaO_2$ 219.0189; Found 219.0190. **m.p.**: 103.5 - 104.3 °C.

7-Bromo-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (3m)



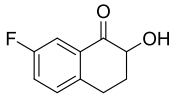
Recrystallized from *i*-PrOH. Off-white solid; 546.6 mg; 45% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 4.38 (ddd, *J* = 13.5, 5.4, 1.8 Hz, 1H), 3.81 (d, *J* = 1.8 Hz, 1H), 3.14 - 2.95 (m, 2H), 2.54 (dddd, *J* = 12.7, 5.4, 4.5, 2.8 Hz, 1H), 2.12 - 1.96 (m, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 198.4, 143.0, 136.9, 132.0, 130.7, 130.3, 120.9, 73.7, 31.5, 27.3 ppm. **IR** (KBr): ν̃ = 3473, 3068, 2947, 2825, 1687, 1473, 1375, 1261, 1217, 1147, 1103, 1001, 903 cm^{-1}. **HRMS** (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_9BrO_2$ 239.9786; Found 239.9776. **m.p.**: 113.9 - 114.6 °C.

6-Bromo-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (3n)



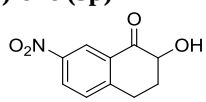
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.30. Off-white solid; 1.03 g; 81% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 - 7.41 (m, 2H), 4.37 (ddd, *J* = 13.4, 5.3, 1.7 Hz, 1H), 3.91 - 3.80 (m, 1H), 3.21 - 3.08 (m, 1H), 3.06 - 2.95 (m, 1H), 2.57 - 2.48 (m, 1H), 2.04 (qd, *J* = 13.1, 4.6 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 198.7, 145.9, 131.9, 130.4, 129.5, 129.2, 129.1, 73.7, 31.5, 27.4 ppm. **IR** (KBr): ν̃ = 3491, 2933, 2873, 2823, 1680, 1589, 1273, 1182, 1078, 991, 935 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_9BrNaO_2$ 262.9684.; Found 262.9694. **m.p.**: 72.7 - 73.9 °C.

7-Fluoro-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (3o)



Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.19. Off-white solid; 1.5 g; 59% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.33 - 7.17 (m, 2H), 4.39 (ddd, *J* = 13.6, 5.4, 1.8 Hz, 1H), 3.82 (s, 1H), 3.17 - 2.99 (m, 2H), 2.61 - 2.47 (m, 1H), 2.15 - 1.95 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −115.0 (q, *J* = 6.6 Hz, 1F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 198.6 (d, *J* = 1.7 Hz), 161.4 (d, *J* = 247.1 Hz), 139.9 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 6.6 Hz), 130.7 (d, *J* = 7.2 Hz), 121.4 (d, *J* = 22.7 Hz), 113.2 (d, *J* = 22.1 Hz), 73.7, 31.7, 27.0 ppm. **IR** (KBr): ν̃ = 3481, 3059, 2949, 2877, 2833, 1687, 1493, 1433, 1379, 1265, 1095, 891, 862 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{10}H_9FNaO_2$ 203.0484; Found 203.0492. **m.p.**: 66.9 - 67.4 °C.

2-Hydroxy-7-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3p)



Eluent (*n*-hexane/ethyl acetate = 3/2): R_f = 0.27. Yellow solid; 690.5 mg; 53% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.88 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 4.51 - 4.43 (m, 1H), 3.77 - 3.76 (m, 1H),

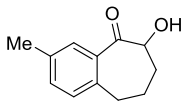
3.28 - 3.17 (m, 2H), 2.66 - 2.57 (m, 1H), 2.18 - 2.05 (m, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 197.7, 150.6, 147.1, 131.4, 130.4, 127.8, 122.9, 73.7, 31.0, 27.9 ppm. **IR** (KBr): ν̃ = 3508, 3084, 2937, 2848, 1699, 1610, 1518, 1348, 1259, 1144, 1072, 1005 cm^{-1}. **HRMS** (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{10}H_8NO_4$ 206.0453.; Found 206.0463. **m.p.**: 115.1 - 117.0 °C.

2-Hydroxy-1-phenylpropan-1-one (3s)

Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.25. Colorless oil; 1.10 g; 73% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.00 - 7.85 (m, 2H), 7.71 - 7.57 (m, 1H), 7.57 - 7.43 (m, 2H), 5.18 (quin, *J* = 6.9 Hz, 1H), 3.81 (d, *J* = 6.5 Hz, 1H), 1.46 (d, *J* = 7.0 Hz, 3H) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. For $C_9H_{10}NaO_2$ 173.0578; Found 173.0577. Spectroscopic data were in agreement with the literature.[3]

General Procedure B[3a]**:** To a solution of LDA (6.45 mmol) in THF (11 mL) at −78 °C was added ketone (750 mg, 4.30 mmol) in THF solution (2.1 mL) and the mixture was stirred for 1 h, then the solution of diethyl chlorophosphate (0.93 ml, 6.45 mmol) in THF (1 mL) was added dropwise at the same temperature. The reaction mixture was stirred and allowed to warm slowly to room temperature. After 1 h of stirring at ambient temperature, the solvent was removed and the mixture was extracted with ether. The combined organic layers were washed with saturated aqueous solution of NH_4Cl and water, dried over Na_2SO_4, filtered and concentrated. To a solution of crude product in CH_2Cl_2 (35 mL) was added a solution of *m*-chloroperbenzoic acid (3.4 g, 13.8 mmol) in CH_2Cl_2 (35 mL) at −20 °C. The reaction mixture was stirred at this temperature until enol phosphate disappeared (monitored by TLC). Then the reaction mixture was washed with 10% aqueous solution of sodium thiosulfate, saturated aqueous solution of $NaHCO_3$ and water. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The obtained crude product was dissolved in diethyl ether (13 mL). To the mixture was added trifluoroacetic acid (2.6 mL) in water (13 mL) at 5 °C. The reaction was stirred and monitored by TLC. After completion of the reaction, the mixture was diluted with chloroform, washed with saturated aqueous solution of $NaHCO_3$ and water and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the residue was purified by flash silica-gel column chromatography.

6-Hydroxy-3-methyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (3r)

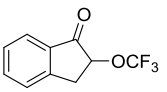


Eluent (*n*-hexane/ether = 3/1): R_f = 0.26. Yellow oil; 261.5 mg; 40% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.6 Hz, 1H), 7.40 - 7.28 (m, 1H), 7.25 - 7.18 (m, 1H), 4.59 - 4.45 (m, 1H), 3.84 (d, *J* = 4.4 Hz, 1H), 3.12 - 2.92 (m, 1H), 2.92 - 2.73 (m, 1H), 2.46 - 2.27 (m, 4H), 2.20 - 2.03 (m, 1H), 1.79 - 1.64 (m, 2H) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 205.8, 141.2, 136.6, 136.3, 134.5, 127.4, 126.2, 75.7, 32.6, 28.9, 23.1, 20.4 ppm. **IR** (NaCl): ν̃ = 3280, 2937, 2870, 1682, 1587, 1450, 1242, 1228, 1107, 1030, 985 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. For $C_{12}H_{14}NaO_2$ 213.0891; Found 213.0891.

Preparation of trifluoromethoxyketones

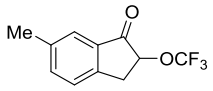
Trifluoromethoxyketones were prepared by following a reported procedure.[7] To a flask which contained hydroxyketone, AgOTf (3.0 eq.), KF (4.0 eq.) and selectfluor® (1.5 eq.) was added ethyl acetate (0.2 M), 2-fluoropyridine (3.0 eq.) and $TMSCF_3$ (3.0 eq.). The resulting mixture was stirred for 12 h at room temperature. The reaction mixture was filtered through a pad of silica-gel and concentrated. The residue was purified by flash silica-gel column chromatography.

2-(Trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4a)



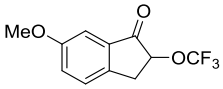
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.29. White solid; 1.15 g; 58% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.6 Hz, 1H), 7.72 - 7.64 (m, 1H), 7.51 - 7.40 (m, 2H), 4.96 - 4.91 (m, 1H), 3.68 (dd, *J* = 16.8, 7.9 Hz, 1H), 3.26 (dd, *J* = 16.9, 4.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.7 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 197.5, 149.5, 136.4, 133.6, 128.6, 126.6, 124.8, 121.9 (q, *J* = 256.7 Hz), 76.5 (q, *J* = 2.4 Hz), 33.7 ppm. **IR** (KBr): ν̃ = 3437, 3059, 2952, 2754, 1726, 1275, 1149, 1005, 862, 758 cm^{-1}. **HRMS** (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_7F_3O_2$ 216.0398; Found 216.0401. **m.p.**: 32.9 - 33.7 °C.

6-Methyl-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4b)



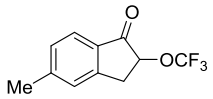
Eluent (*n*-hexane/ethyl acetate = 95/5): R_f = 0.39. Slightly yellow solid; 240 mg; 42% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.50 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 4.91 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.62 (dd, *J* = 16.8, 7.9 Hz, 1H), 3.19 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.42 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.7 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 197.5, 146.9, 138.7, 137.7, 133.7, 126.3, 124.7, 121.9 (q, *J* = 256.7 Hz), 76.8 (m), 33.4, 21.1 ppm. **IR** (KBr): ν̃ = 3437, 3016, 2960, 2931, 2868, 1728, 1493, 1277, 1149, 1090, 1018, 820 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_9F_3NaO_2$ 253.0452; Found 253.0458. **m.p.**: 54.8 - 55.3 °C.

6-Methoxy-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4c)



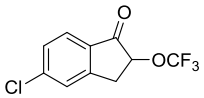
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.18. White solid; 223.3 mg; 46% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.5 Hz, 1H), 7.29 - 7.24 (m, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 4.93 (dd, *J* = 7.8, 4.7 Hz, 1H), 3.85 (s, 3H), 3.60 (dd, *J* = 16.6, 7.8 Hz, 1H), 3.17 (dd, *J* = 16.6, 4.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.7 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 197.5, 160.1, 142.3, 134.7, 127.4, 125.8, 121.9 (q, *J* = 256.7 Hz), 105.7, 77.0 (m), 55.7, 33.1 ppm. **IR** (KBr): ν̃ = 3408, 3016, 2956, 2844, 1714, 1496, 1273, 1213, 1165, 1088, 1022, 847 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{11}H_9F_3O_3$ 246.0504; Found 246.0503. **m.p.**: 61.2 - 62.7 °C.

5-Methyl-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4d)



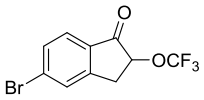
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.44. White solid; 224.5 mg; 28% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.2 Hz, 1H), 7.27 - 7.20 (m, 2H), 4.91 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.61 (dd, *J* = 17.0, 7.9 Hz, 1H), 3.20 (dd, *J* = 17.0, 4.7 Hz, 1H), 2.47 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.6 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 194.9, 134.0, 133.9, 128.9, 128.6, 121.5 (q, *J* = 256.6 Hz), 80.3 (q, *J* = 2.4 Hz), 26.1, 9.4 ppm. **IR** (KBr): ν̃ = 3427, 3041, 3014, 2960, 2862, 1722, 1614, 1308, 1223, 1144, 1086, 831, 802 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_9F_3NaO_2$ 253.0452; Found 253.0447. **m.p.**: 82.1 - 83.0 °C.

5-Chloro-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4e)



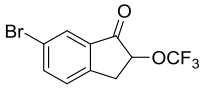
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.46. White solid; 284 mg; 45% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.48 (d, *J* = 0.6 Hz, 1H), 7.46 - 7.39 (m, 1H), 4.93 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.66 (dd, *J* = 17.4, 7.9 Hz, 1H), 3.24 (dd, *J* = 17.2, 4.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.8 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 196.0, 150.9, 143.0, 132.0, 129.4, 126.8, 126.0, 121.8 (q, *J* = 257.0 Hz), 76.2 (q, *J* = 2.4 Hz), 33.4 ppm. **IR** (KBr): ν̃ = 3406, 3064, 2972, 2881, 1709, 1304, 1209, 1103, 1066, 916, 833, 793 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{10}H_5ClF_3O_2$ 248.9930; Found 248.9932. **m.p.**: 76.7 - 77.9 °C.

5-Bromo-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4f)



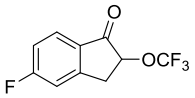
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.32. Slightly yellow solid; 465.7 mg; 32% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 - 7.50 (m, 3H), 4.95 - 4.91 (m, 1H), 3.67 (dd, *J* = 17.2, 8.1 Hz, 1H), 3.25 (dd, *J* = 17.3, 4.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.9 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 196.2, 151.0, 132.4, 132.3, 131.9, 129.9, 126.0, 121.8 (q, *J* = 257.0 Hz), 76.1 (q, *J* = 2.4 Hz), 33.3 ppm. **IR** (KBr): ν̃ = 3435, 3080, 2937, 1722, 1595, 1371, 1267, 1147, 1057, 868 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{10}H_5BrF_3O_2$ 292.9425; Found 292.9426. **m.p.**: 96.9 - 97.7 °C.

6-Bromo-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4g)



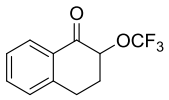
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.33. White solid; 132.8 mg; 45% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 2.1 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 4.95 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.64 (dd, *J* = 17.3, 7.9 Hz, 1H), 3.20 (dd, *J* = 17.2, 4.8 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.8 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 196.1, 148.0, 139.2, 135.3, 128.2, 127.7, 122.7, 121.8 (q, *J* = 257.0 Hz), 76.4 (m), 33.4 ppm. **IR** (KBr): ν̃ = 3431, 3068, 3028, 2922, 1728, 1599, 1437, 1275, 1225, 1147, 1092, 849 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{10}H_5BrF_3O_2$ 292.9425; Found 292.9421. **m.p.**: 120.9 - 121.3 °C.

5-Fluoro-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (4h)



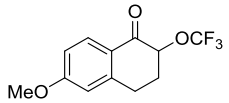
Eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.42. White semi-solid; 202.5 mg; 29% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.23 - 7.05 (m, 2H), 4.94 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.67 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.26 (dd, *J* = 17.0, 4.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.8 (s, 3F), −99.4 (s, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 195.5, 168.0 (d, *J* = 259.3 Hz), 152.5 (d, *J* = 10.9 Hz), 130.1, 127.4 (d, *J* = 10.9 Hz), 121.9 (q, *J* = 256.4 Hz), 117.0 (d, *J* = 23.4 Hz), 113.5 (d, *J* = 23.4 Hz), 76.2 (q, *J* = 2.3 Hz), 33.7 (d, *J* = 2.5 Hz) ppm. **IR** (KBr): ν̃ =3070, 2343, 1714, 1618, 1593, 1308, 1252, 1153, 1084, 889, 804 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{10}H_5F_4O_2$ 233.0226; Found 233.0222.

2-(Trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4i)



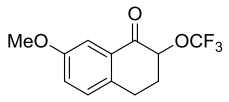
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.35. White solid; 1.10 g; 64% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 - 7.32 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 4.85 (dd, *J* = 12.2, 4.9 Hz, 1H), 3.16 (dd, *J* = 8.1, 4.4 Hz, 2H), 2.54 (dq, *J* = 12.9, 4.5 Hz, 1H), 2.39 (tt, *J* = 12.6, 8.2 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.1 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 190.8, 142.7, 134.3, 131.1, 128.6, 128.1, 127.2, 121.7 (q, *J* = 256.6 Hz), 77.8 (m), 30.0, 27.1 ppm. **IR** (KBr): ν̃ = 3386, 3078, 2914, 1707, 1601, 1288, 1230, 1147, 1092, 881, 752 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_9F_3NaO_2$ 253.0452; Found 253.0462. **m.p.**: 46.7 - 47.3 °C.

6-Methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4j)



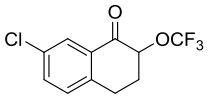
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.35. Slightly yellow solid; 388.0 mg; 36% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.1 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 - 6.62 (m, 1H), 4.79 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.87 (s, 3H), 3.10 (dd, *J* = 7.8, 4.5 Hz, 2H), 2.60 - 2.25 (m, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.9 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 189.3, 164.2, 145.3, 130.5, 124.5, 121.7 (q, *J* = 254.3 Hz), 113.9, 112.3, 77.6 (q, *J* = 2.0 Hz), 55.5, 30.0, 27.3 ppm. **IR** (KBr): ν̃ = 3359, 2974, 2949, 2846, 1691, 1603, 1302, 1255, 1228, 1126, 1078, 1026, 889, 833 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{12}H_{11}F_3NaO_3$ 283.0558; Found 283.0567. **m.p.**: 51.3 - 52.1 °C.

7-Methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4k)



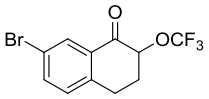
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.30. White solid; 137.1 mg; 34% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 2.6 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.83 (dd, *J* = 12.2, 4.8 Hz, 1H), 3.85 (s, 3H), 3.09 (dd, *J* = 7.9, 4.4 Hz, 2H), 2.58 - 2.46 (m, 1H), 2.45 - 2.29 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.1 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 190.7, 158.6, 135.3, 131.9, 129.9, 122.7, 121.7 (q, *J* = 254.5 Hz), 109.6, 77.9 (q, *J* = 2.8 Hz), 55.4, 30.3, 26.3 ppm. **IR** (KBr): ν̃ = 3373, 3020, 2968, 2844, 1697, 1612, 1496, 1294, 1271, 1246, 1126, 1030, 897, 822 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{12}H_{11}F_3NaO_3$ 283.0558; Found 283.0552. **m.p.**: 46.6 - 47.7 °C.

7-Chloro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4l)



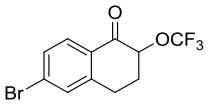
Eluent (*n*-hexane/CH_2Cl_2 = 1/1): R_f = 0.44. White powder; 602.9 mg; 64% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 2.1 Hz, 1H), 7.49 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 4.83 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.18 - 3.06 (m, 2H), 2.54 (dq, *J* = 13.2, 4.6 Hz, 1H), 2.39 (tdd, *J* = 12.6, 9.7, 6.1 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.2 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 189.7, 140.9, 134.2, 133.5, 132.4, 130.2, 127.7, 121.6 (q, *J* = 257.0 Hz), 77.5 (q, *J* = 2.1 Hz), 29.8, 26.5 ppm. **IR** (KBr): ν̃ = 3386, 3066, 2947, 2902, 2844, 1705, 1477, 1415, 1290, 125, 1144, 895, 816 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{11}H_7ClF_3O_2$ 263.0087; Found 263.0096. **m.p.**: 62.1 - 62.6 °C.

7-Bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4m)



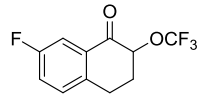
Eluent (*n*-hexane/CH_2Cl_2 = 1/1): R_f = 0.47. Slightly yellow solid; 368.6 mg; 52% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 4.83 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.18 - 3.01 (m, 2H), 2.53 (dq, *J* = 13.2, 4.5 Hz, 1H), 2.39 (tdd, *J* = 12.5, 10.1, 5.8 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.2 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 189.6, 141.4, 137.1, 132.6, 130.8, 130.5, 121.6 (q, *J* = 256.6 Hz), 121.3, 77.4 (q, *J* = 2.1 Hz), 29.7, 26.6 ppm. **IR** (KBr): ν̃ = 3386, 3062, 2949, 2904, 2844, 1703, 1591, 1410, 1292, 1223, 1144, 893, 812 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_8BrF_3NaO_2$ 330.9557; Found 330.9558. **m.p.**: 61.9 - 62.6 °C.

6-Bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4n)



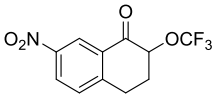
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.32. Slightly yellow solid; 902.4 mg; 75% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.5 Hz, 1H), 7.57 - 7.38 (m, 2H), 4.82 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.13 (dd, *J* = 7.3, 4.3 Hz, 2H), 2.55 - 2.51 (m, 1H), 2.43 - 2.35 (m, 1H) ppm. **^{19}F NMR** (659 MHz, $CDCl_3$): δ = −59.1 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 190.0, 144.2, 131.6, 130.8, 129.9, 129.7, 129.7, 121.6 (q, *J* = 257.0 Hz), 77.4 (q, *J* = 2.1 Hz), 29.8, 26.7 ppm. **IR** (KBr): ν̃ = 3087, 3060, 2958, 2902, 2846, 1705, 1589, 1265, 1227, 1174, 1092, 1063, 999, 887, 843, 825 cm^{-1}.**HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_8BrF_3NaO_2$ 330.9557; Found 330.9557. **m.p.**: 83.9 - 84.8 °C.

7-Fluoro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4o)



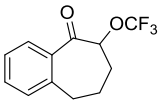
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.36. Slightly yellow solid; 452.9 mg; 27% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.73 - 7.69 (m, 1H), 7.32 - 7.20 (m, 2H), 4.84 (dd, *J* = 11.9, 4.8 Hz, 1H), 3.16 - 3.10 (m, 2H), 2.59 - 2.49 (m, 1H), 2.47 - 2.32 (m, 1H) ppm. **^{19}F NMR** (659 MHz, $CDCl_3$): δ = −59.1 (s, 3F), −114.5 (s, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 189.9, 161.7 (d, *J* = 247.6 Hz), 138.5 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 6.7 Hz), 130.6 (d, *J* = 7.5 Hz), 121.8 (d, *J* = 22.6 Hz), 121.7 (q, *J* = 256.4 Hz), 113.9 (d, *J* = 22.6 Hz), 77.5 (m), 30.0, 26.4 ppm. **IR** (KBr): ν̃ = 3082, 2958, 2850, 2505, 1705, 1495, 1441, 1282, 1234, 1163, 1126, 893 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_8F_4NaO_2$ 271.0358; Found 271.0352. **m.p.**: 59.8 - 61.1 °C.

7-Nitro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (4p)



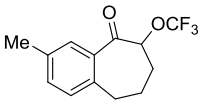
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.27. Yellow solid; 418.2 mg; 52% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 2.1 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 4.92 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.41 - 3.17 (m, 2H), 2.63 - 2.59 (m, 1H), 2.56 - 2.37 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.2 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 188.9, 149.0, 147.3, 132.0, 130.3, 128.0, 123.4, 121.5 (q, *J* = 257.9 Hz), 77.0 (m), 29.2, 27.0 ppm. **IR** (KBr): ν̃ = 3097, 2916, 2511, 2351, 1714, 1612, 1525, 1350, 1275, 1223, 1140, 1090, 893 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{11}H_7F_3NO_4$ 274.0327; Found 274.0314. **m.p.**: 94.9 - 98.1 °C.

6-(Trifluoromethoxy)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (4q)



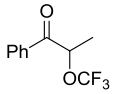
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.36. Slightly yellow oil; 459.4 mg; 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 4.99 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.11 - 2.93 (m, 2H), 2.38 - 2.25 (m, 1H), 2.18 - 2.02 (m, 2H), 1.95 - 1.82 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 198.7, 141.5, 136.2, 132.2, 130.1, 129.2, 126.8, 121.3 (q, *J* = 257.0 Hz), 80.8 (q, *J* = 2.1 Hz), 33.9, 30.6, 23.0 ppm. **IR** (NaCl): ν̃ = 3068, 3026, 2947, 2873, 1707, 1450, 1273, 1219, 1144, 970, 744 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{12}H_{11}F_3NaO_2$ 267.0609; Found 267.0614.

3-Methyl-6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (4r)



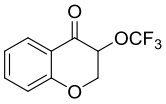
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.42. Off-white solid; 181.3 mg; 35% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 4.99 - 4.94 (m, 1H), 3.08 (dd, *J* = 17.3, 8.2 Hz, 1H), 2.83 (dd, *J* = 17.0, 10.3 Hz, 1H), 2.44 - 2.25 (m, 4H), 2.17 - 2.02 (m, 2H), 2.01 - 1.73 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.5 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 199.4, 140.1, 137.0, 136.6, 133.8, 127.0, 126.4, 121.3 (q, *J* = 257.0 Hz), 80.5, 30.9, 29.2, 22.7, 20.3 ppm. **IR** (KBr): ν̃ = 3074, 2941, 2873, 1707, 1454, 1279, 1255, 1240, 1217, 1138, 1028, 989 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}F_3NaO_2$ 281.0765; Found 281.0774. **m.p.**: 49.3 - 52.7 °C.

1-Phenyl-2-(trifluoromethoxy)propan-1-one (4s)



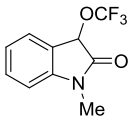
Eluent (*n*-hexane/CH_2Cl_2 = 3/1): R_f = 0.29. Colorless oil; 255.2 mg; 39% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 - 7.94 (m, 2H), 7.65 - 7.60 (m, 1H), 7.54 - 7.47 (m, 2H), 5.51 (q, *J* = 7.0 Hz, 1H), 1.65 (d, *J* = 7.0 Hz, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.3 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 194.9, 134.0, 133.5, 128.9, 128.7, 121.4 (q, *J* = 256.6 Hz), 75.2 (q, *J* = 2.5 Hz), 18.6 ppm. **IR** (NaCl): ν̃ = 3068, 2999, 2945, 1705, 1452, 1281, 1223, 1147, 968, 702 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{10}H_9F_3NaO_2$ 241.0452; Found 241.0457.

3-(Trifluoromethoxy)chroman-4-one (4t)



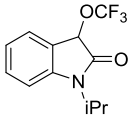
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.37. White powder; 358.9 mg; 42% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.12 - 7.09 (m, 1H), 7.05 - 6.98 (m, 1H), 4.93 (dd, *J* = 9.8, 4.9 Hz, 1H), 4.64 (dd, *J* = 11.6, 4.9 Hz, 1H), 4.51 (dd, *J* = 11.8, 9.9 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −59.7 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 185.4, 161.0, 136.9, 127.9, 122.4, 121.5 (q, *J* = 258.3 Hz), 119.4, 117.9, 72.4 (m), 68.6 ppm. **IR** (KBr): ν̃ = 3404, 3047, 2951, 2798, 1711, 1481, 1290, 1238, 1215, 1147, 1043, 835, 760 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{10}H_7F_3NaO_3$ 255.0245; Found 255.0243. **m.p.**: 91.3 - 100.7 °C.

1-Methyl-3-(trifluoromethoxy)indolin-2-one (4u)



Eluent (*n*-hexane/ethyl acetate = 3/2): R_f = 0.33. Slightly yellow solid; 37.0 mg; 32% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.49 - 7.34 (m, 2H), 7.14 (td, *J* = 7.6, 0.9 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.41 (s, 1H), 3.21 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 170.0, 144.4, 131.3, 126.0 (m), 123.4, 122.1, 121.9 (q, *J* = 257.9 Hz), 108.8, 72.4 (q, *J* = 2.5 Hz), 26.5 ppm. **IR** (KBr): ν̃ = 3446, 3068, 2941, 2368, 2318, 1716, 1616, 1473, 1267, 1225, 1153, 756 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{10}H_7F_3NO_2$ 230.0429; Found 230.0428. **m.p.**: 77.6 - 78.5 °C.

1-Isopropyl-3-(trifluoromethoxy)indolin-2-one (4v)

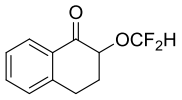


Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.25. Slightly yellow solid; 253.2 mg; 31% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.47 - 7.32 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.59 - 4.49 (m, 1H), 1.52 - 1.46 (m, 6H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.3 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 169.6, 143.2, 130.9, 126.1, 122.8, 122.4, 121.9 (q, *J* = 256.3 Hz), 110.2, 72.5 (q, *J* = 2.8 Hz), 44.5, 19.1, 19.0 ppm. **IR** (KBr): ν̃ = 3442, 3062, 2991, 2943, 2700, 2495, 1739, 1612, 1469, 1352, 1273, 1161, 1132, 756 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{12}H_{11}F_3NO_2$ 258.0742; Found 258.0736. **m.p.**: 43.4 - 46.9 °C.

Preparation of difluoromethoxyketone 13

Difluoromethoxyketone was prepared by following a reported procedure.[8] To a flask hydroxyketone (1.5 mmol, 243.2 mg, 1.0 eq.), then CH_2Cl_2 (0.3 mL) and aqueous NaOH solution (20 wt%, 8.0 eq.) were added subsequently. After being stirred at 0 °C for 10 min, $TMSCF_2Br$ (4.5 mmol, 3.0 eq.) was added into the mixture at 0 °C and the reaction mixture was stirred at this temperature for 2 h. Then the reaction mixture was treated with water and extracted with CH_2Cl_2. The organic layer was combined and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by flash silica-gel column chromatography.

2-(Difluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (13)

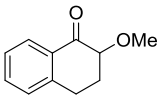


Eluent (*n*-hexane/ether = 10/1): R_f = 0.22. Off-white solid; 100.0 mg; 31% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 1H), 7.60 - 7.46 (m, 1H), 7.42 - 7.26 (m, 2H), 6.59 (dd, *J* = 77.4, 73.6 Hz, 1H), 4.80 (dd, *J* = 12.2, 4.8 Hz, 1H), 3.19 - 3.09 (m, 2H), 2.55 - 2.44 (m, 1H), 2.41 - 2.26 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −83.0 (dd, *J* = 161.0, 73.8 Hz, 1F), −83.8 (dd, *J* = 161.5, 78.3 Hz, 1F) ppm.**^{13}C NMR** (75 MHz, $CDCl_3$): δ = 193.4, 143.0, 134.1, 131.3, 128.6, 127.8, 127.0, 116.2 (dd, *J* = 262.2, 258.7 Hz), 75.2 (t, *J* = 3.4 Hz), 30.4, 27.4 ppm. **IR** (KBr): ν̃ = 3072, 3030, 2954, 2904, 2848, 1695, 1603, 1460, 1308, 1230, 1180, 1157, 1132, 1012, 939, 754 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_{10}F_2NaO_2$ 235.0547; Found 235.0549. **m.p.**: 48.4 - 51.7 °C.

Preparation of methoxyketone 14

Methoxyketone was prepared by following a reported procedure.[9a] Hydroxyketone (1.0 mmol, 1.0 eq.) was dissolved in iodomethane (2.7 mL). Calcium sulfate (4.0 eq.) and silver (I) oxide (3.0 eq.) were added, and the resulting mixture was stirredat room temperature for 16 h. The mixture was filtered, and the residue was washed with acetone, after which the filtrate was concentrated *in vacuo*. The residue was purified by flash silica-gel column chromatography.

2-Methoxy-3,4-dihydronaphthalen-1(2*H*)-one (14)

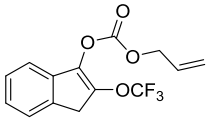


Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.26. White solid; 174.9 mg; 99% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.08 - 7.98 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 - 7.20 (m, 1H), 3.96 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.58 (s, 3H), 3.20 - 2.97 (m, 2H), 2.46 - 2.34 (m, 1H), 2.28 - 2.12 (m, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 196.6, 143.4, 133.5, 131.8, 128.5, 127.6, 126.7, 81.6, 58.2, 29.4, 27.2 ppm. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{11}H_{12}NaO_2$ 199.0735; Found 199.0738. Spectroscopic data were in agreement with the literature.[9b]

Preparation of trifluoromethoxy allyl enol carbonates

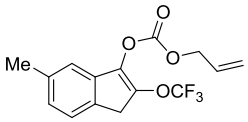
To a solution of NaHMDS (1.2 eq.) and TMEDA (1.2 eq.) in THF (0.15 M) at −78 °C was added a solution of trifluoromethoxyketone in THF (0.75 M) dropwise. After stirring for 1 h, a solution of allyl chloroformate (1.2 eq.) in THF (0.75 M) was added to the mixture, and the resulting mixture was stirred for overnight. Then the reaction was quenched by water and extracted with ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash silica-gel column chromatography.

Allyl (2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1a)



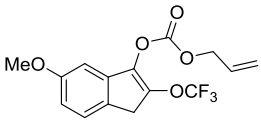
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.53. Slightly yellow oil; 97.2 mg; 70% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.42 - 7.21 (m, 4H), 6.12 - 5.89 (m, 1H), 5.57 - 5.29 (m, 2H), 4.87 - 4.72 (m, 2H), 3.62 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 151.4, 137.5, 136.0, 135.4, 134.1, 130.7, 127.1, 126.3, 124.0, 120.4 (q, *J* = 259.9 Hz), 119.8, 118.5, 69.8, 33.9 ppm. **IR** (NaCl): ν̃ = 3084, 3057, 3032, 2954, 1776, 1678, 1462, 1275, 1240, 1209, 989, 943 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{14}H_{10}F_3O_4$ 299.0531; Found 299.0522.

Allyl (5-methyl-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1b)



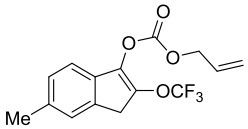
Eluent (*n*-hexane/ether = 95/5): R_f = 0.57. Slightly yellow oil; 240.2 mg; 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.2 Hz, 1H), 7.10 - 7.05 (m, 2H), 6.06 - 5.96 (m, 1H), 5.46 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.36 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.78 (dt, *J* = 5.9, 1.3 Hz, 2H), 3.57 (s, 2H), 2.38 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.4, 137.7 (q, *J* = 1.7 Hz), 136.9, 136.0, 135.3, 131.1, 130.7, 127.1, 123.8, 120.3 (q, *J* = 260.4 Hz), 119.8, 119.1, 69.8, 33.5, 21.5 ppm. **IR** (NaCl): ν̃ = 3087, 3026, 2952, 2925, 1776, 1678, 1479, 1300, 1273, 1213, 1190, 943, 806 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{13}F_3NaO_4$ 337.0664; Found 337.0657.

Allyl (5-methoxy-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1c)



Eluent (*n*-hexane/ether = 95/5): R_f = 0.34. Slightly yellow oil; 128.2 mg; 43% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.27 - 7.20 (m, 1H), 6.86 - 6.74 (m, 2H), 6.12 - 5.91 (m, 1H), 5.46 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.37 (dd, *J* = 10.6, 1.2 Hz, 1H), 4.79 (dt, *J* = 5.9, 1.2 Hz, 2H), 3.82 (s, 3H), 3.56 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 159.3, 151.3, 138.5 (m), 137.3, 135.2, 130.7, 126.0, 124.8, 120.3 (q, *J* = 259.9 Hz), 119.8, 112.3, 104.3, 69.8, 55.5, 33.2 ppm. **IR** (NaCl): ν̃ = 3089, 3003, 2956, 2839, 1776, 1676, 1481, 1275, 1207, 1032, 943 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{15}H_{12}F_3O_5$ 329.0637; Found 329.0635.

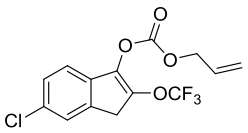
Allyl (6-methyl-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1d)



Eluent (*n*-hexane/ether = 95/5): R_f = 0.51. Slightly yellow oil; 99.8 mg; 32 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.19 (s, 1H), 7.14 (s, 2H), 6.00 (ddt, *J* = 16.9, 11.0, 5.7 Hz, 1H), 5.51 - 5.26 (m, 2H), 4.77 (d, *J* = 5.9 Hz, 2H), 3.57 (s, 2H), 2.38 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 151.3, 136.5 (q, *J* = 1.8 Hz), 136.3, 135.6, 134.3, 133.2, 130.7, 127.7, 124.9, 120.4 (q, *J* = 258.3 Hz), 119.7, 118.2, 69.7, 33.7, 21.5 ppm. **IR**

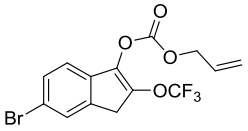
(NaCl): ν̃ = 3043, 2956, 2925, 2902, 1761, 1676, 1362, 1207, 987, 947 cm^{-1}. **HRMS** (ESI) *m*/*z*: [M+Na]$^+$ Calcd. for $C_{15}H_{13}F_3NaO_4$ 337.0664; Found 337.0665.

Allyl (6-chloro-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1e)



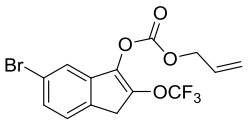
Eluent (*n*-hexane/ether = 95/5): R_f = 0.31. White solid; 177.4 mg; 35% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.60 - 7.41 (m, 1H), 7.37 - 7.28 (m, 1H), 7.21 - 7.06 (m, 1H), 6.09 - 5.91 (m, 1H), 5.50 - 5.32 (m, 2H), 4.78 (d, *J* = 5.9 Hz, 2H), 3.61 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 151.2, 137.5, 135.6, 135.0, 134.6, 132.4, 130.6, 127.4, 124.6, 120.3 (q, *J* = 260.5 Hz), 120.0, 119.6, 69.9, 33.7 ppm. **IR** (KBr): ν̃ = 3060, 2939, 1757, 1668, 1323, 1275, 1230, 1211, 939, 822 cm^{-1}. **HRMS** (ESI) *m*/*z*: [M−H]$^-$ Calcd. for $C_{14}H_9ClF_3O_4$ 333.0141; Found 333.0142. **m.p.**: 44.5 - 48.1 °C.

Allyl (6-bromo-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1f)



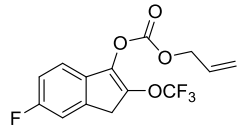
Eluent (*n*-hexane/ether = 95/5): R_f = 0.31. Slightly yellow solid; 282.3 mg; 50% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.59 - 7.41 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.12 - 5.88 (m, 1H), 5.53 - 5.31 (m, 2H), 4.78 (dd, *J* = 5.9, 0.9 Hz, 2H), 3.61 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.4 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 151.2, 137.5 (m), 135.9, 135.1, 135.0, 130.6, 130.3, 127.4, 120.3 (q, *J* = 260.5 Hz), 120.2, 120.0, 119.9, 70.0, 33.7 ppm. **IR** (KBr): ν̃ = 3089, 3057, 2939, 2900, 1761, 1668, 1275, 1228, 1198, 937, 818 cm^{-1}. **HRMS** (ESI) *m*/*z*: [M−H]$^-$ Calcd. for $C_{14}H_9BrF_3O_4$ 376.9636; Found 376.9637. **m.p.**: 46.2 - 48.0 °C.

Allyl (5-bromo-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1g)



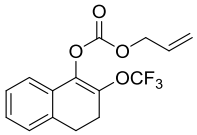
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.44. Slightly yellow semi-solid; 43.7 mg; 32% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.44 - 7.35 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 6.11 - 5.91 (m, 1H), 5.51 - 5.35 (m, 2H), 4.79 (d, *J* = 5.9 Hz, 2H), 3.58 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.3 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 151.2, 138.6 (m), 138.1, 134.3, 132.7, 130.6, 129.3, 125.5, 121.8, 121.2, 120.3 (q, *J* = 260.5 Hz), 120.1, 70.0, 33.6 ppm. **IR** (KBr): ν̃ = 3089, 2943, 1766, 1678, 1292, 1267, 1194, 991, 943 cm^{-1}. **HRMS** (ESI) *m*/*z*: [M+H]$^+$ Calcd. for $C_{14}H_{11}BrF_3O_4$ 378.9793; Found 378.9781.

Allyl (6-fluoro-2-(trifluoromethoxy)-1*H*-inden-3-yl) carbonate (1h)



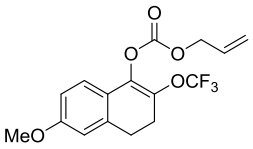
Eluent (*n*-hexane/ether = 30/1): R_f = 0.27. Colorless semi-solid; 95.4 mg; 41% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.19 (dd, *J* = 8.4, 5.0 Hz, 1H), 7.15 - 7.07 (m, 1H), 7.07 - 6.98 (m, 1H), 6.00 (ddt, *J* = 17.0, 10.8, 5.8 Hz, 1H), 5.45 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.37 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.78 (dt, *J* = 5.9, 1.3 Hz, 2H), 3.61 (s, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −58.5 (s, 3F), −115.5 (m, 1F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 162.0 (d, *J* = 245.2 Hz), 151.3, 136.7 (quin, *J* = 1.8 Hz), 136.1 (d, *J* = 9.1 Hz), 135.0, 131.9 (d, *J* = 1.8 Hz), 130.6, 120.3 (q, *J* = 261.2 Hz), 120.0, 119.7 (d, *J* = 8.2 Hz), 114.2 (d, *J* = 23.6 Hz), 112.1 (d, *J* = 24.5 Hz), 69.9, 33.9 ppm. **IR** (KBr): ν̃ = 3089, 2956, 1776, 1680, 1481, 1363, 1271, 1238, 1209, 991, 939, 858, 820 cm^{-1}. **HRMS** (ESI) *m*/*z*: [M−H]$^-$ Calcd. for $C_{14}H_9F_4O_4$ 317.0437; Found 317.0429.

Allyl (2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1i)



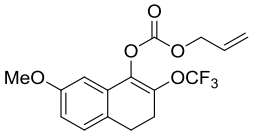
Eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.32. Slightly yellow oil; 463 mg; 76% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26 - 7.18 (m, 3H), 7.18 - 7.12 (m, 1H), 5.98 (ddt, *J* = 17.3, 10.5, 5.8 Hz, 1H), 5.43 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.33 (dq, *J* = 10.6, 1.1 Hz, 1H), 4.74 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.08 - 3.01 (m, 2H), 2.79 - 2.70 (m, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.7 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 152.0, 136.7, 136.1, 133.6, 130.9, 129.1, 128.5, 127.4, 126.8, 121.4, 120.5 (q, *J* = 260.4 Hz), 119.5, 69.5, 27.7, 24.9 ppm. **IR** (NaCl): ν̃ = 3074, 3028, 2952, 2898, 2844, 1772, 1689, 1263, 1201, 993, 943, 773, 750 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{15}H_{13}F_3O_4$ 314.0766; Found 314.0751.

Allyl (6-methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1j)



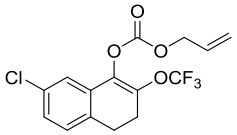
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.40. Slightly yellow oil; 240.9 mg; 91% yield. **^{1}H NMR** (700 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 8.4 Hz, 1H), 6.75 - 6.70 (m, 2H), 6.03 - 5.92 (m, 1H), 5.45 - 5.38 (m, 1H), 5.36 - 5.31 (m, 1H), 4.74 - 4.72 (m, 2H), 3.80 (s, 3H), 3.01 (t, *J* = 8.2 Hz, 2H), 2.72 (t, *J* = 8.2 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −57.0 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 159.9, 152.0, 136.3, 135.7, 134.4, 130.9, 122.8, 121.8, 120.6 (q, *J* = 259.9 Hz), 119.3, 114.0, 111.4, 69.4, 55.3, 28.1, 25.0 ppm. **IR** (NaCl): ν̃ = 3001, 2954, 2904, 2841, 1770, 1612, 1502, 1254, 1205, 1169, 1039, 993, 943 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{16}H_{15}F_3NaO_5$ 367.0769; Found 367.0764.

Allyl (7-methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1k)



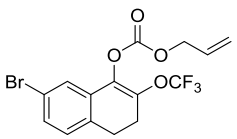
Eluent (*n*-hexane/CH_2Cl_2 = 1/1): R_f = 0.37. Slightly yellow oil; 165.0 mg; 81% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.2 Hz, 1H), 6.81 - 6.71 (m, 2H), 6.09 - 5.87 (m, 1H), 5.47 - 5.31 (m, 2H), 4.75 (dd, *J* = 5.6, 1.2 Hz, 2H), 3.79 (s, 3H), 2.98 (t, *J* = 8.2 Hz, 2H), 2.72 (t, *J* = 8.1 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.7 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 158.7, 151.9, 137.3, 136.0, 130.9, 130.3, 128.4, 125.7, 120.5 (q, *J* = 259.3 Hz), 119.4, 113.3, 107.8, 69.5, 55.4, 26.8, 25.3 ppm. **IR** (NaCl): ν̃ = 3086, 2951, 2841, 2351, 1772, 1610, 1498, 1263, 1201, 1176, 1041, 1011, 943, 814 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{16}H_{15}F_3NaO_5$ 367.0769; Found 367.0766.

Allyl (7-chloro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1l)



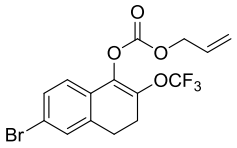
Eluent (*n*-hexane/CH_2Cl_2 = 3/1): R_f = 0.30. White solid; 204.2 mg; 77% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.23 - 7.13 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.06 - 5.93 (m, 1H), 5.44 (dq, *J* = 17.2, 1.3 Hz, 1H), 5.35 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.76 (dt, *J* = 5.8, 1.2 Hz, 2H), 3.01 (t, *J* = 8.2 Hz, 2H), 2.74 (t, *J* = 8.2 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.6 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.8, 137.8, 135.1, 132.9, 131.9, 130.9, 130.7, 128.7, 128.3, 121.6, 120.4 (q, *J* = 260.8 Hz), 119.7, 69.7, 27.1, 24.8 (d, *J* = 1.8 Hz) ppm. **IR** (KBr): ν̃ = 3095, 3078, 2972, 2904, 2841, 2370, 2318, 1774, 1236, 1198, 1105, 1003, 947, 874, 825, 777 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{12}ClF_3NaO_4$ 371.0274; Found 371.0275. **m.p.**: 55.0 - 56.3 °C.

Allyl (7-bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1m)



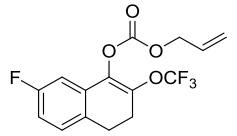
Eluent (*n*-hexane/CH_2Cl_2 = 3/1): R_f = 0.27. White solid; 102.2 mg; 80% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.38 - 7.29 (m, 2H), 7.06 - 6.99 (m, 1H), 5.99 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.44 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.36 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.76 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.99 (t, *J* = 8.2 Hz, 2H), 2.74 (t, *J* = 8.2 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.8, 137.7, 135.0, 132.4, 131.2, 131.2, 130.7, 129.0, 124.5, 120.7, 120.4 (q, *J* = 260.8 Hz), 119.7, 69.7, 27.2, 24.7 ppm. **IR** (KBr): ν̃ = 3095, 2970, 2904, 2839, 2370, 2345, 2318, 1768, 1265, 1198, 1001, 947, 876, 823 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{15}H_{12}BrF_3O_4$ 391.9871; Found 391.9850. **m.p.**: 50.6 - 51.7 °C.

Allyl (6-bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1n)



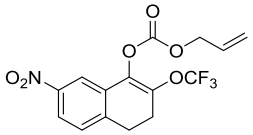
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.49. Off-white solid; 650.4 mg; 64% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 6.7 Hz, 1H), 7.31 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.03 - 5.91 (m, 1H), 5.47 - 5.38 (m, 1H), 5.38 - 5.29 (m, 1H), 4.76 - 4.70, (m, 2H), 3.02 (t, *J* = 8.1 Hz, 2H), 2.73 (t, *J* = 8.1 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.6 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.8, 136.9, 135.6, 135.6, 130.7, 130.5, 129.9, 128.2, 123.0, 122.3, 120.4 (q, *J* = 260.4 Hz), 119.6, 69.7, 27.4, 24.8 ppm. **IR** (KBr): ν̃ = 3097, 2947, 2428, 2183, 1765, 1689, 1444, 1427, 1367, 1201, 1082, 984, 943, 816 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{12}BrF_3NaO_4$ 414.9769; Found 414.9777. **m.p.**: 37.7 - 39.3 °C.

Allyl (7-fluoro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1o)



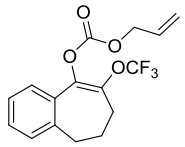
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.42. White semi-solid; 288.9 mg; 53% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8.1, 5.4 Hz, 1H), 6.99 - 6.84 (m, 2H), 6.09 - 5.89 (m, 1H), 5.48 - 5.32 (m, 2H), 4.77 - 4.73 (m, 2H), 3.01 (t, *J* = 8.1 Hz, 2H), 2.74 (t, *J* = 8.2 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.5 (s, 3F), −115.9 (s, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 162.0 (d, *J* = 244.3 Hz), 151.9, 137.9 (d, *J* = 1.7 Hz), 135.3 (d, *J* = 1.7 Hz), 131.2 (d, *J* = 8.4 Hz), 130.8, 129.1 (d, *J* = 3.4 Hz), 128.8 (d, *J* = 8.4 Hz), 120.4 (q, *J* = 259.9 Hz), 119.6, 114.8 (d, *J* = 21.8 Hz), 109.0 (d, *J* = 25.1 Hz), 69.7, 26.9, 25.0 ppm. **IR** (KBr): ν̃ = 3087, 2954, 2900, 2844, 1774, 1587, 1495, 1315, 1263, 1194, 1018, 943, 872, 820 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{12}F_4NaO_4$ 355.0569; Found 355.0563.

Allyl (7-nitro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (1p)



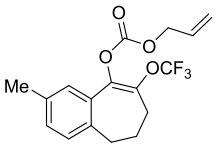
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.24. Yellow solid; 599.9 mg; 78% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.15 - 8.01 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 6.07 - 5.94 (m, 1H), 5.52 - 5.42 (m, 1H), 5.42 - 5.33 (m, 1H), 4.80 - 4.76 (m, 2H), 3.17 (t, *J* = 8.1 Hz, 2H), 2.83 (t, *J* = 8.1 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.4 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.7, 147.4, 140.7, 138.6 (d, *J* = 1.8 Hz), 134.6, 131.0, 130.5, 128.4, 123.4, 120.3 (q, *J* = 261.2 Hz), 119.9, 116.5, 69.9, 27.7, 24.3 ppm. **IR** (KBr): ν̃ = 3086, 2960, 2920, 2426, 1778, 1687, 1525, 1350, 1171, 1038, 1016, 989, 941, 741 cm^{-1}. **HRMS** (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{15}H_{11}F_3NO_6$ 358.0538; Found 358.0537. **m.p.**: 51.9 - 54.3 °C.

Allyl (8-(trifluoromethoxy)-6,7-dihydro-5*H*-benzo[7]annulen-9-yl) carbonate (1q)



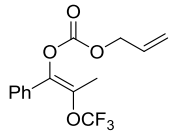
Eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.33. Yellow oil; 303.2 mg; 90% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.45 - 7.39 (m, 1H), 7.30 - 7.26 (m, 2H), 7.25 - 7.20 (m, 1H), 5.98 - 5.84 (m, 1H), 5.36 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.65 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.85 - 2.82 (m, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 2.26 - 2.20 (m, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −57.2 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 152.4, 141.1, 139.4, 138.1, 132.0, 130.9, 129.3, 129.2, 126.5, 126.2, 120.5 (q, *J* = 259.1 Hz), 119.2, 69.3, 32.3, 32.1, 27.9 ppm. **IR** (NaCl): ν̃ = 3070, 3026, 2945, 2870, 1768, 1450, 1365, 1261, 1203, 1171, 989, 945, 771 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{15}F_3NaO_4$ 351.0820; Found 351.0819.

Allyl (2-methyl-8-(trifluoromethoxy)-6,7-dihydro-5*H*-benzo[7]annulen-9-yl) carbonate (1r)



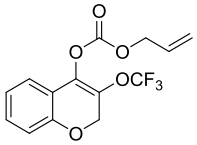
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.45. Slightly yellow oil; 108 mg; 55% yield. **^{1}H NMR** (700 MHz, $CDCl_3$): δ = 7.26 - 7.24 (m, 1H), 7.18 - 7.14 (m, 2H), 5.96 - 5.87 (m, 1H), 5.38 - 5.32 (m, 1H), 5.31 - 5.25 (m, 1H), 4.65 - 4.63 (m, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 2.28 - 2.22 (m, 4H) ppm. **^{19}F NMR** (659 MHz, $CDCl_3$): δ = −57.4 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 152.5, 139.2, 138.3, 138.2, 135.9, 133.1, 131.0, 131.0, 125.9, 124.0, 120.6 (q, *J* = 258.1 Hz), 119.1 (d, *J* = 1.7 Hz), 69.3, 33.1, 27.2, 26.7, 20.1 ppm. **IR** (NaCl): ν̃ = 3070, 3026, 2945, 2870, 1766, 1452, 1365, 1259, 1201, 1169, 1130, 945, 783 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{17}H_{17}F_3NaO_4$ 365.0977; Found 365.0970.

(*E*)-Allyl (1-phenyl-2-(trifluoromethoxy)prop-1-en-1-yl) carbonate (1s)



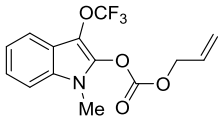
Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.38. Colorless oil; 108.9 mg; 52% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.58 - 7.45 (m, 2H), 7.42 - 7.31 (m, 3H), 5.91 (ddt, *J* = 16.8, 11.0, 5.6 Hz, 1H), 5.40 - 5.26 (m, 2H), 4.68 - 4.62 (m, 2H), 2.14 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −56.6 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 152.4, 141.5, 138.6, 131.5, 130.8, 129.0, 128.3, 127.5, 120.6 (q, *J* = 260.0 Hz), 119.5, 69.4, 14.7 (q, *J* = 2.1 Hz) ppm. **IR** (NaCl): ν̃ = 3062, 3030, 2958, 1768, 1446, 1234, 1194, 945, 694 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_4$ 325.0664; Found 325.0654.

Allyl (3-(trifluoromethoxy)-2*H*-chromen-4-yl) carbonate (1t)



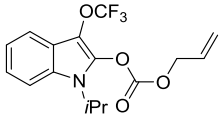
Eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.54. Colorless oil; 229.0 mg; 72% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.26 - 7.13 (m, 2H), 7.03 - 6.94 (m, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.07 - 5.89 (m, 1H), 5.49 - 5.29 (m, 2H), 4.97 (s, 2H), 4.75 (dt, *J* = 5.6, 1.3 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −57.8 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 153.1, 151.3, 134.1, 130.6, 130.6, 128.0, 122.1, 122.1, 120.5 (q, *J* = 259.5 Hz), 119.7, 117.9, 116.2, 69.9, 65.1 (q, *J* = 2.3 Hz) ppm. **IR** (NaCl): ν̃ = 3086, 2956, 2858, 1776, 1462, 1261, 1201, 1047, 943, 756 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd. for $C_{14}H_{12}F_3O_5$ 317.0637; Found 317.0636.

Allyl (1-methyl-3-(trifluoromethoxy)-1*H*-indol-2-yl) carbonate (1u)



Eluent (*n*-hexane/ether = 3/1): R_f = 0.36. Yellow solid; 124.6 mg; 46% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.2 Hz, 1H), 7.31 - 7.27 (m, 2H), 7.23 - 7.18 (m, 1H), 6.00 (ddt, *J* = 16.9, 10.6, 5.9 Hz, 1H), 5.47 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.43 - 5.36 (m, 1H), 4.81 (dt, *J* = 5.8, 1.2 Hz, 2H), 3.61 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −60.4 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 151.4, 133.3, 130.2, 129.1, 122.7, 121.3 (q, *J* = 258.7 Hz), 121.0, 120.4, 119.1, 117.5, 113.7 (q, *J* = 2.9 Hz), 109.3, 70.5, 28.4 ppm. **IR** (KBr): ν̃ = 3062, 2949, 1770, 1631, 1373, 1252, 1219, 1201, 1173, 947, 735 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{12}F_3NNaO_4$ 338.0616; Found 338.0620. **m.p.**: 31.7 - 33.6 °C.

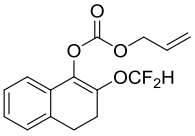
Allyl (1-isopropyl-3-(trifluoromethoxy)-1*H*-indol-2-yl) carbonate (1v)



Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.39. Yellow semi-solid; 151.4 mg; 52% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.25 - 7.15 (m, 2H), 6.10 - 5.81 (m, 1H), 5.50 - 5.31 (m, 2H), 4.85 -

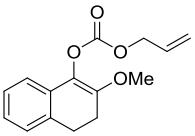
4.76 (m, 2H), 4.65 - 4.53 (m, 1H), 1.58 (d, *J* = 7.0 Hz, 6H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −60.1 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 151.4, 133.0, 130.3, 127.3, 122.2, 121.3 (q, *J* = 256.3 Hz), 120.6, 120.3, 119.6, 117.6, 114.0, 110.8, 70.4, 47.0, 21.4 ppm. **IR** (KBr): ν̃ = 3060, 2987, 2943, 2885, 1786, 1631, 1458, 1362, 1259, 1223, 945, 741 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{16}H_{16}F_3NNaO_4$ 366.0929; Found 366.0913.

Allyl (2-(difluoromethoxy)-3,4-dihydronaphthalen-1-yl) carbonate (9)



Eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.39. Colorless oil; 114.4 mg; 82% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.22 - 7.11 (m, 4H), 6.45 (t, *J* = 73.9 Hz, 1H), 6.07 - 5.89 (m, 1H), 5.47 - 5.29 (m, 2H), 4.73 (dt, *J* = 5.8, 1.2 Hz, 2H), 3.02 (t, *J* = 8.1 Hz, 2H), 2.71 (t, *J* = 8.2 Hz, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.0 (d, *J* = 74.3 Hz) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 152.3, 138.4, 134.2, 133.4, 130.9, 129.6, 127.9, 127.4, 126.7, 120.9, 119.4, 115.8 (t, *J* = 262.3 Hz), 69.5, 27.6, 25.8 ppm. **IR** (NaCl): ν̃ = 3072, 3026, 2951, 2897, 2841, 1766, 1687, 1367, 1248, 1117, 1055, 943, 769 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{14}F_2NaO_4$ 319.0758; Found 319.0761.

Allyl (2-methoxy-3,4-dihydronaphthalen-1-yl) carbonate (10)



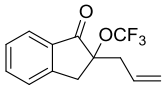
Eluent (*n*-hexane/CH_2Cl_2 = 2/3): R_f = 0.38. White solid; 779.8 mg; 88% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.18 - 7.14 (m, 1H), 7.11 - 7.04 (m, 3H), 6.05 - 5.94 (m, 1H), 5.42 (dq, *J* = 17.3, 1.4 Hz, 1H), 5.31 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.73 (dt, *J* = 5.7, 1.5 Hz, 2H), 3.72 (s, 3H), 2.96 (t, *J* = 8.1 Hz, 2H), 2.61 (t, *J* = 8.2 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 153.1, 145.9, 131.8, 131.4, 131.3, 128.1, 126.9, 126.6, 125.9, 119.4, 119.0, 69.0, 56.0, 27.8, 23.2 ppm. **IR** (KBr): ν̃ = 3064, 3022, 2981, 2952, 2891, 2852, 1757, 1664, 1572, 1485, 1462, 1371, 1246, 1147, 987, 910 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{16}NaO_4$ 283.0946; Found 283.0950. **m.p.**: 44.7 - 46.5 °C.

General procedure for the DcAA reaction

Procedure A: Pd_2dba_3 (5 mol%) and ligand (12.5 mol%) were dissolved in CH_2Cl_2 (2.5 mL) and the mixture was stirred for 2 hours under nitrogen atmosphere. The mixture was cooled to −30 °C and a solution of substrate (0.05 mmol) in CH_2Cl_2 (2.5 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.

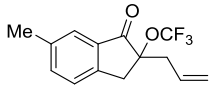
Procedure B: Pd_2dba_3 (5 mol%) and ligand (12.5 mol%) were dissolved in TBME (1.2 mL) and the mixture was stirred for 2 hours under nitrogen atmosphere. A solution of substrate (0.05 mmol) in TBME (1.3 mL) was added dropwise to the mixture. The resulting mixture was stirred at prescribed temperature. 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.

2-Allyl-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2a)



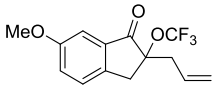
2a was prepared according to the **procedure A**; eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.51. Colorless oil; 9.3 mg; 73% yield, 81% ee. **$[\alpha]_D^{25}$** = −22.5 (*c* = 0.25, $CHCl_3$, 81% ee). HPLC conditions: CHIRALCEL® OJ-H column, eluent: *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, tR = 11.708 min for major isomer, tR = 13.758 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.9 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 - 7.36 (m, 2H), 5.67 (ddt, *J* = 17.1, 10.1, 7.1, 7.1 Hz, 1H), 5.22 - 5.09 (m, 2H), 3.54 (d, *J* = 17.9 Hz, 1H), 3.40 (d, *J* = 17.6 Hz, 1H), 2.75 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.55 (dd, *J* = 13.9, 7.5 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 199.7, 149.5, 136.3, 133.4, 130.1, 128.4, 126.4, 125.0, 121.2 (q, *J* = 259.1 Hz), 120.7, 86.4, 41.2, 36.3 (m) ppm. **IR** (NaCl): ν̃ = 3082, 2929, 2858, 1732, 1610, 1265, 1213, 1151, 1063, 928, 742 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{11}F_3NaO_2$ 279.0609; Found 279.0611.

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



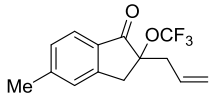
2b was prepared according to the **procedure A**; eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.40. Colorless oil; 10.4 mg; 77% yield, 82% ee. $[\alpha]_D^{25}$ = −33.3 (*c* = 0.32, $CHCl_3$, 82% ee). HPLC conditions: CHIRALCEL® OJ-3 column, eluent: *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate = 0.5 mL/min, λ = 254 nm, tR = 13.267 min for major isomer, tR = 15.533 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 5.76 - 5.55 (m, 1H), 5.19 - 5.07 (m, 2H), 3.49 (d, *J* = 17.6 Hz, 1 H), 3.35 (d, *J* = 17.6 Hz, 1 H), 2.80 - 2.64 (m, 1H), 2.59 - 2.46 (m, 1H), 2.42 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 199.6, 146.9, 138.5, 137.6, 133.6, 130.2, 126.1, 124.8, 121.2 (q, *J* = 258.7 Hz), 120.5, 86.7, 41.3, 36.0, 21.1 ppm. **IR** (NaCl): ν̃ = 3082, 3022, 2983, 2929, 1730, 1495, 1431, 1263, 1201, 1153, 930, 822 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_2$ 293.0765; Found 293.0765.

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



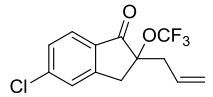
2c was prepared according to the **procedure A**; eluent (*n*-hexane/ether = 3/1): R_f = 0.36. Slightly yellow oil; 37.3 mg; 87% yield, 74% ee. $[\alpha]_D^{25}$ = −35.1 (*c* = 1.24, $CHCl_3$, 74% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 20.642 min for major isomer, tR = 24.858 min for minor isomer. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.38 - 7.30 (m, 1H), 7.28 - 7.20 (m, 2H), 5.73 - 5.55 (m, 1H), 5.23 - 5.06 (m, 2H), 3.85 (s, 3H), 3.46 (d, *J* = 17.4 Hz, 1H), 3.33 (d, *J* = 17.4 Hz, 1H), 2.73 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.56 (dd, *J* = 13.7, 7.3 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 199.7, 159.9, 142.3, 134.5, 130.2, 127.2, 125.8, 121.2 (q, *J* = 259.1 Hz), 120.6, 105.8, 87.0, 55.6, 41.4, 35.7 (m) ppm. **IR** (NaCl): ν̃ = 3086, 3012, 2949, 2910, 2843, 2688, 2320, 1724, 1495, 1468, 1435, 1261, 931, 773 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_3$ 309.0714; Found 309.0719.

2-Allyl-5-methyl-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2d)



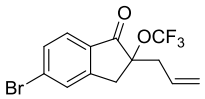
2d was prepared according to the **procedure A**; eluent (*n*-hexane/ether = 95/5): R_f = 0.21. Colorless oil; 11.2 mg; 83% yield, 77% ee. $[\alpha]_D^{25}$ = −10.8 (*c* = 0.37, $CHCl_3$, 77% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 11.508 min for major isomer, tR = 13.158 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 1H), 7.21 - 7.12 (m, 2H), 5.58 (ddt, *J* = 17.0, 9.9, 7.3 Hz, 1H), 5.12 - 5.02 (m, 2H), 3.41 (d, *J* = 17.9 Hz, 1H), 3.27 (d, *J* = 17.9 Hz, 1H), 2.73 - 2.59 (m, 1H), 2.51 - 2.43 (m, 1H), 2.39 (s, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.8 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 199.0, 150.0, 147.9, 131.2, 130.3, 129.6, 126.7, 124.9, 121.2 (q, *J* = 258.7 Hz), 120.5, 86.6, 41.3, 36.2, 22.3 ppm. **IR** (NaCl): ν̃ = 3082, 3016, 2983, 2927, 2862, 1730, 1612, 1441, 1265, 1211, 1153, 928, 829 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_2$ 293.0765; Found 293.0768.

2-Allyl-5-chloro-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2e)



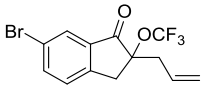
2e was prepared according to the **procedure A**; eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.32. Colorless oil; 30.3 mg; 69% yield, 83% ee. $[\alpha]_D^{25}$ = −4.52 (*c* = 1.01, $CHCl_3$, 83% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 14.817 min for minor isomer, tR = 17.400 min for major isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.83 - 7.66 (m, 1H), 7.52 - 7.34 (m, 2H), 5.74 - 5.49 (m, 1H), 5.24 - 5.04 (m, 2H), 3.51 (d, *J* = 17.9 Hz, 1H), 3.38 (d, *J* = 17.9 Hz, 1H), 2.74 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.55 (dd, *J* = 13.9, 7.5 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 198.2, 150.9, 142.9, 131.9, 129.8, 129.3, 126.7, 126.1, 121.2 (q, *J* = 259.3 Hz), 121.0, 86.2, 41.2, 36.1 ppm. **IR** (NaCl): ν̃ = 3084, 2983, 2931, 2856, 1736, 1601, 1421, 1263, 1211, 1153, 1072, 926, 831 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{10}ClF_3NaO_2$ 313.0219; Found 313.0228.

2-Allyl-5-bromo-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2f)



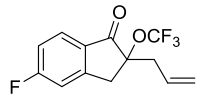
2f was prepared according to the **procedure A**; eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.26. Colorless oil; 36.6 mg; 73% yield, 84% ee. **[α]$_D^{25}$** = +3.71 (*c* = 1.22, $CHCl_3$, 86% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 15.400 min for minor isomer, tR = 19.042 min for major isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.72 - 7.56 (m, 3H), 5.63 (ddt, *J* = 17.1, 10.0, 7.1 Hz, 1H), 5.21 - 5.12 (m, 2H), 3.52 (d, *J* = 17.9 Hz, 1H), 3.39 (d, *J* = 17.9 Hz, 1H), 2.74 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.55 (dd, *J* = 13.9, 7.5 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 198.4, 151.0, 132.3, 132.1, 131.8, 129.8, 129.8, 126.2, 121.2 (q, *J* = 258.7 Hz), 121.0, 86.1, 41.2, 36.0 ppm. **IR** (NaCl): ν̃ = 3084, 2983, 2931, 2856, 1736, 1597, 1577, 1263, 1211, 1153, 1059, 926, 868, 829 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{13}H_{10}BrF_3O_2$ 333.9816; Found 333.9839.

2-Allyl-6-bromo-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2g)



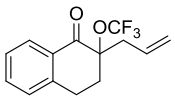
2g was prepared according to the **procedure A**; eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.44. Colorless oil; 9.5 mg; 57% yield, 89% ee. **[α]$_D^{25}$** = −42.2 (*c* = 0.32, $CHCl_3$, 89% ee). HPLC conditions: CHIRALPAK® IA column, eluent: *n*-hexane/*i*-PrOH = 99.7/0.3, flow rate = 0.5 mL/min, λ = 254 nm, tR = 16.200 min for major isomer, tR = 18.875 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.81 - 7.67 (m, 1H), 7.48 - 7.34 (m, 2H), 5.73 - 5.51 (m, 1H), 5.23 - 5.02 (m, 2H), 3.51 (d, *J* = 17.9 Hz, 1H), 3.38 (d, *J* = 17.9 Hz, 1H), 2.74 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.55 (dd, *J* = 13.9, 7.5 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −52.0 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 198.3, 148.0, 139.1, 135.2, 129.8, 128.0, 127.8, 122.5, 121.2 (q, *J* = 258.7 Hz), 121.0, 86.4, 41.2, 36.1 ppm. **IR** (NaCl): ν̃ = 3084, 2927, 2856, 1738, 1601, 1468, 1442, 1419, 1265, 1205, 1153, 1059, 930, 820 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{13}H_{10}BrF_3O_2$ 333.9816; Found 333.9797.

2-Allyl-5-fluoro-2-(trifluoromethoxy)-2,3-dihydro-1*H*-inden-1-one (2h)



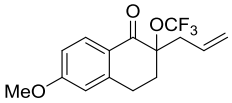
2h was prepared according to the **procedure A**; eluent (*n*-hexane/ethyl acetate = 19/1): R_f = 0.36. Colorless oil; 27.2 mg; 67% yield, 71% ee. **[α]$_D^{25}$** = −23.9 (*c* = 0.92, $CHCl_3$, 71% ee). HPLC conditions: CHIRALPAK® IF column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR =13.242 min for major isomer, tR = 15.200 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.21 - 6.97 (m, 2H), 5.64 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.22 - 5.04 (m, 2H), 3.53 (d, *J* = 17.9 Hz, 1H), 3.39 (d, *J* = 17.9 Hz, 1H), 2.75 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.56 (dd, *J* = 14.1, 7.3 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F), −99.7 (q, *J* = 6.6 Hz, 1F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 197.7, 168.0 (d, *J* = 258.9 Hz), 152.4 (d, *J* = 10.9 Hz), 129.9, 127.6 (d, *J* = 10.0 Hz), 121.2 (q, *J* = 259.1 Hz), 120.9, 117.0, 116.8, 113.3 (d, *J* = 22.7 Hz), 86.2, 41.2, 36.3 (t, *J* = 1.8 Hz) ppm. **IR** (NaCl): ν̃ = 3084, 2927, 1736, 1618, 1595, 1263, 1219, 1155, 941, 864 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{10}F_4NaO_2$ 297.0515; Found 297.0513.

2-Allyl-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2i)



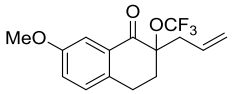
2i was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 30/1): R_f = 0.28. Colorless oil; 20.0 mg; 74% yield, 88% ee. **[α]$_D^{25}$** = +0.71 (*c* = 0.67, $CHCl_3$, 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 10.992 min for major isomer, tR = 15.900 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.9 Hz, 1H), 7.63 - 7.44 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 - 7.25 (m, 1H), 5.89 (dddd, *J* = 16.8, 10.4, 7.9, 6.2 Hz, 1H), 5.31 - 5.15 (m, 2H), 3.22 - 3.00 (m, 2H), 2.78 - 2.55 (m, 3H), 2.37 (dt, *J* = 13.6, 5.2 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.1 (s, 3F) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 192.4, 142.2, 134.1, 130.8, 130.6, 128.7, 128.5, 127.1, 121.1 (q, *J* = 256.5 Hz), 120.1, 85.1, 38.3, 31.0, 25.7 ppm. **IR** (NaCl): ν̃ = 3078, 3026, 2951, 1703, 1603, 1454, 1261, 1223, 1147, 926, 904, 741 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_2$ 293.0765; Found 293.0769.

2-Allyl-6-methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2j)



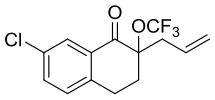
2j was prepared according to the **procedure B**; eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.24. Colorless oil; 10.4 mg; 61% yield, 77% ee. **[α]$_D^{25}$** = +1.25 (*c* = 0.35, $CHCl_3$, 77% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 18.608 min for major isomer, tR = 26.567 min for minor isomer. **^{1}H NMR** (700 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.73 - 6.65 (m, 1H), 5.88 (dddd, *J* = 16.9, 10.4, 8.1, 6.1 Hz, 1H), 5.25 - 5.17 (m, 2H), 3.87 (s, 3H), 3.11 - 3.05 (m, 1H), 3.03 - 2.95 (m, 1H), 2.73 (dd, *J* = 14.8, 5.8 Hz, 1H), 2.63 (dd, *J* = 14.7, 8.1 Hz, 1H), 2.59 - 2.52 (m, 1H), 2.34 (dt, *J* = 13.5, 5.4 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.0 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 191.1, 164.2, 144.8, 131.1, 124.1, 124.1, 121.2 (q, *J* = 258.1 Hz), 120.0, 113.9, 112.4, 85.0, 55.5, 38.6, 31.1, 26.1 ppm. **IR** (NaCl): ν̃ = 3080, 3012, 2949, 2844, 2600, 1691, 1603, 1496, 1448, 1340, 1265, 1227, 1147, 926, 904 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{15}F_3NaO_3$ 323.0871; Found 323.0870.

2-Allyl-7-methoxy-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2k)



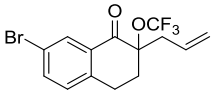
2k was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 9/1): R_f = 0.33. Colorless oil; 71% yield, 80% ee. **[α]$_D^{25}$** = −17.3 (*c* = 0.73, $CHCl_3$, 80% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 12.800 min for major isomer, tR = 22.450 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 2.6 Hz, 1H), 7.22 - 7.04 (m, 2H), 5.99 - 5.78 (m, 1H), 5.27 - 5.16 (m, 2H), 3.85 (s, 3H), 3.11 - 2.90 (m, 2H), 2.76 - 2.52 (m, 3H), 2.36 (dt, *J* = 13.5, 5.1 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.0 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 192.4, 158.7, 134.8, 131.4, 130.9, 130.0, 122.8, 121.2 (q, *J* = 258.1 Hz), 120.1, 110.1, 85.2, 55.5, 38.4, 31.2, 25.0 ppm. **IR** (NaCl): ν̃ = 3093, 3014, 2947, 2843, 2372, 2322, 1701, 1498, 1338, 1282, 1263, 1248, 1198, 1147, 1032, 908 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{15}F_3NaO_3$ 323.0871; Found 323.0873.

2-Allyl-7-chloro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2l)



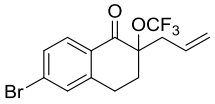
2l was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 30/1): R_f = 0.38. White solid; 28.2 mg; 93% yield, 89% ee. **[α]$_D^{25}$** = −21.2 (*c* = 0.70, $CHCl_3$, 89% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 10.967 min for major isomer, tR = 30.992 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.14 - 7.94 (m, 1H), 7.49 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 5.97 - 5.74 (m, 1H) 5.35 - 5.08 (m, 2H), 3.22 - 3.05 (m, 1H), 3.05 - 2.89 (m, 1H), 2.82 - 2.49 (m, 3H), 2.44 - 2.24 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.2 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 191.3, 140.5, 134.1, 133.5, 131.9, 130.6, 130.3, 128.2, 121.1 (q, *J* = 258.1 Hz), 120.4, 84.6, 38.2, 31.0, 25.1 ppm. **IR** (KBr): ν̃ = 3089, 3022, 2952, 2916, 2850, 1705, 1595, 1477, 1444, 1412, 1261, 1215, 1153, 926, 910, 833 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{14}H_{12}ClF_3O_2$ 304.0478; Found 304.0454. **m.p.**: 34.9 - 36.4 °C.

2-Allyl-7-bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2m)



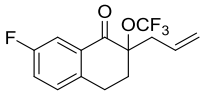
2m was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 30/1): R_f = 0.27. Slightly yellow solid; 278.4 mg; 92% yield, 89% ee. **[α]$_D^{25}$** = −23.0 (*c* = 0.94, $CHCl_3$, 89% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 70/30, flow rate = 0.5 mL/min, λ = 254 nm, tR = 10.017 min for major isomer, tR = 25.583 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 5.98 - 5.73 (m, 1H), 5.27 - 5.16 (m, 2H), 3.15 - 2.89 (m, 2H), 2.77 - 2.53 (m, 3H), 2.41 - 2.23 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.2 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 191.3, 141.0, 136.9, 132.1, 131.2, 130.6, 130.5, 121.2, 121.1 (q, *J* = 259.1 Hz), 120.4, 84.6, 38.2, 30.9, 25.2 ppm. **IR** (KBr): ν̃ = 3089, 3024, 2952, 2924, 1705, 1589, 1475, 1448, 1267, 1213, 1151, 926, 912, 833 cm^{-1}. **HRMS** (EI) *m*/*z*: $[M]^+$ Calcd. for $C_{14}H_{12}BrF_3O_2$ 347.9973; Found 347.9951. **m.p.**: 34.9 - 39.4 °C.

2-Allyl-6-bromo-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(*2H*)-one (2n)



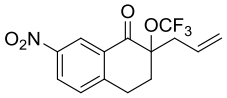
2n was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 30/1): R_f = 0.25. White solid; 30.4 mg; 87% yield, 87% ee. **[α]$_D^{25}$** = +1.89 (*c* = 0.48, $CHCl_3$, 87% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 16.950 min for major isomer, tR = 23.058 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.5 Hz, 1H), 7.58 - 7.37 (m, 2H), 5.86 (dddd, *J* = 16.9, 10.3, 7.9, 6.5 Hz, 1H), 5.30 - 5.13 (m, 2H), 3.13 (dt, *J* = 17.6, 5.7 Hz, 1H), 2.98 (ddd, *J* = 17.5, 8.6, 5.0 Hz, 1H), 2.78 - 2.52 (m, 3H), 2.33 (dt, *J* = 13.7, 5.6 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.2 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 191.6, 143.9, 131.6, 130.7, 130.6, 130.2, 129.5, 129.5, 121.1 (q, *J* = 258.1 Hz), 120.4, 84.6, 38.2, 31.0, 25.3 ppm. **IR** (KBr): ν̃ = 3080, 2954, 1701, 1589, 1446, 1327, 1265, 1223, 1200, 1144, 928, 903, 843, 833 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{12}BrF_3NaO_2$ 370.9870; Found 370.9856. **m.p.**: 38.9 - 42.6 °C.

2-Allyl-7-fluoro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (2o)



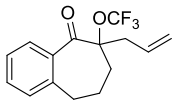
2o was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 10/1): R_f = 0.47. Colorless oil; 13.6 mg, 94% yield, 88% ee. **[α]$_D^{25}$** = +1.66 (*c* = 0.45, $CHCl_3$, 88% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 10.683 min for major isomer, tR = 20.117 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 9.1, 1.2 Hz, 1H), 7.33 - 7.18 (m, 2H), 5.97 - 5.77 (m, 1H), 5.31 - 5.15 (m, 2H), 3.18 - 2.93 (m, 2H), 2.78 - 2.54 (m, 3H), 2.44 - 2.27 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.2 (s, 3F), −114.6 (q, *J* = 7.3 Hz, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 191.5, 161.8 (d, *J* = 247.6 Hz), 138.0 (d, *J* = 3.3 Hz), 132.3 (d, *J* = 5.9 Hz), 130.7, 130.6, 121.7 (d, *J* = 22.6 Hz), 121.1 (q, *J* = 258.7 Hz), 120.4, 114.3 (d, *J* = 22.6 Hz), 84.6, 38.2, 31.2, 25.0 ppm. **IR** (NaCl): ν̃ = 3080, 2951, 2856, 2490, 1707, 1495, 1427, 1263, 1215, 1151, 928, 889, 823 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{12}F_4NaO_2$ 311.0671; Found 311.0667.

2-Allyl-7-nitro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(*2H*)-one (2p)



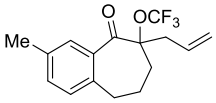
2p was prepared according to the **procedure B**; eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.22. Yellow solid; 28.2 mg; 89% yield, 91% ee. **[α]$_D^{25}$** = −22.5 (*c* = 0.59, $CHCl_3$, 91% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, tR = 7.642 min for major isomer, tR = 53.592 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 5.93 - 5.77 (m, 1H), 5.32 - 5.13 (m, 2H), 3.30 (dt, *J* = 18.3, 6.1 Hz, 1H), 3.18 - 3.00 (m, 1H), 2.91 - 2.75 (m, 1H), 2.75 - 2.56 (m, 2H), 2.43 - 2.24 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 190.5, 148.8, 147.4, 131.6, 130.3, 130.2, 127.8, 123.8, 121.0 (q, *J* = 260.0 Hz), 120.8, 84.0, 38.0, 30.9, 25.6 ppm. **IR** (KBr): ν̃ = 3101, 2952, 2925, 2856, 1709, 1610, 1531, 1421, 1350, 1267, 1213, 1147, 1088, 937 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{12}F_3NNaO_4$ 338.0616; Found 338.0609. **m.p.**: 73.5 - 80.7 °C.

6-Allyl-6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (2q)



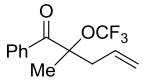
2q was prepared according to the **procedure B**; eluent (*n*-hexane/ethyl acetate = 9/1): R_f = 0.46. Colorless oil; 9.2 mg; 73% yield, 85% ee. **[α]$_D^{25}$** = −24.7 (*c* = 0.31, $CHCl_3$, 85% ee). HPLC conditions: CHIRALPAK® IA column, eluent: *n*-hexane/*i*-PrOH = 99.7/0.3, flow rate = 0.5 mL/min, λ = 254 nm, tR = 12.950 min for major isomer, tR = 14.092 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.49 - 7.34 (m, 2H), 7.29 (d, *J* = 6.5 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 5.96 - 5.77 (m, 1H), 5.25 - 5.15 (m, 2H), 3.14 - 3.03 (m, 1H), 2.95 - 2.73 (m, 3H), 2.31 - 2.06 (m, 2H), 1.96 (dt, *J* = 14.4, 5.2 Hz, 1H), 1.88 - 1.74 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −50.9 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 203.2, 140.1, 137.8, 131.4, 131.0, 129.6, 129.1, 126.4, 121.1 (q, *J* = 258.1 Hz), 120.2, 91.3, 39.5, 35.4, 33.8, 23.4 ppm. **IR** (NaCl): ν̃ = 3076, 3024, 2939, 2870, 1697, 1446, 1282, 1271, 1230, 1151, 926, 735 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{15}F_3NaO_2$ 307.0922; Found 307.0916.

6-Allyl-3-methyl-6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (2r)



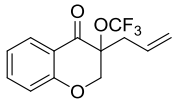
2r was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 9/1): R_f = 0.44. Colorless oil; 13.7 mg; 92% yield, 83% ee. **[α]$_D^{25}$** = −24.3 (*c* = 0.46, $CHCl_3$, 83% ee). HPLC conditions: CHIRALPAK® IA column, eluent: *n*-hexane = 100, flow rate = 0.5 mL/min, λ = 254 nm, tR = 23.017 min for major isomer, tR = 29.617 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.32 - 7.26 (m, 2H), 7.23 - 7.13 (m, 1H), 5.96 - 5.74 (m, 1H), 5.27 - 5.10 (m, 2H), 2.97 - 2.84 (m, 3H), 2.82 - 2.70 (m, 1H), 2.32 (s, 3H), 2.25 - 1.93 (m, 3H), 1.89 - 1.69 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.1 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 203.6, 139.0, 138.0, 135.7, 133.1, 131.0, 127.5, 126.1, 121.0 (q, *J* = 258.1 Hz), 120.1, 91.5, 39.6, 35.0, 29.1, 22.8, 20.0 ppm. **IR** (NaCl): ν̃ = 3072, 3024, 2962, 2931, 2868, 2362, 1687, 1454, 1281, 1232, 1203, 1188, 937, 796, 733 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{16}H_{17}F_3NaO_2$ 321.1078; Found 321.1082.

2-Methyl-1-phenyl-2-(trifluoromethoxy)pent-4-en-1-one (2s)



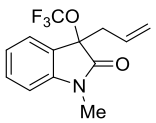
2s was prepared according to the **procedure A**; eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.49. Colorless oil; 28.6 mg; 74% yield, 55% ee. **[α]$_D^{25}$** = −29.6 (*c* = 0.95, $CHCl_3$, 55% ee). HPLC conditions: CHIRALPAK® IB-3 column, eluent: *n*-hexane = 100, flow rate = 0.5 mL/min, λ = 254 nm, tR = 13.233 min for major isomer, tR = 14.392 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.23 - 8.03 (m, 2H), 7.67 - 7.52 (m, 1H), 7.52 - 7.35 (m, 2H), 5.87 - 5.61 (m, 1H), 5.29 - 5.02 (m, 2H), 2.91 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.72 (dd, *J* = 14.4, 7.9 Hz, 1H), 1.71 (d, *J* = 1.5 Hz, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.7 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 197.9, 134.2, 133.1, 130.3, 129.7, 128.4, 121.3 (q, *J* = 258.1 Hz), 120.6, 89.4, 43.4, 21.4 ppm. **IR** (NaCl): ν̃ = 3080, 3010, 2987, 2954, 1689, 1448, 1385, 1261, 1213, 1157, 985, 928 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}F_3NaO_2$ 281.0765; Found 281.0762.

3-Allyl-3-(trifluoromethoxy)chroman-4-one (2t)



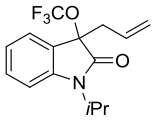
2t was prepared according to the **procedure B**; eluent (*n*-hexane/CH_2Cl_2 = 3/1): R_f = 0.37. Colorless oil; 40% yield, 84% ee. **[α]$_D^{20}$** = +5.85 (*c* = 0.36, MeOH, 84% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 99.5/0.5, flow rate = 0.5 mL/min, λ = 254 nm, tR = 37.450 min for major isomer, tR = 46.867 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.0, 1.8 Hz, 1H), 7.18 - 7.06 (m, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.84 (ddt, *J* = 17.2, 10.0, 7.1 Hz, 1H), 5.36 - 5.12 (m, 2H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 2.90 - 2.66 (m, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.9 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 187.1, 160.6, 136.7, 129.6, 128.2, 122.4, 121.2, 121.0 (q, *J* = 259.9 Hz), 119.2, 117.9, 80.7, 70.8, 36.1 ppm. **IR** (NaCl): ν̃ = 3084, 3018, 2987, 2927, 1707, 1610, 1479, 1468, 1327, 1252, 1217, 1157, 1045, 930, 760 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M-H]^-$ Calcd. for $C_{13}H_{10}F_3O_3$ 271.0582; Found 271.0584.

3-Allyl-1-methyl-3-(trifluoromethoxy)indolin-2-one (2u)



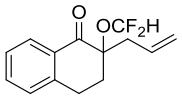
2u was prepared according to the **procedure A**; eluent (*n*-hexane/ether = 3/1): R_f = 0.21. White solid; 12.0 mg; 88% yield, 44% ee. **[α]$_D^{25}$** = +0.41 (*c* = 0.38, $CHCl_3$, 44% ee). HPLC conditions: CHIRALPAK® IC column, eluent: *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, tR = 18.225 min for major isomer, tR = 22.458 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.50 - 7.30 (m, 2H), 7.17 - 7.06 (m, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.58 - 5.41 (m, 1H), 5.14 - 4.99 (m, 2H), 3.21 (s, 3H), 2.90 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.68 (dd, *J* = 13.5, 8.2 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −53.8 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 172.5, 143.3, 130.9, 128.6, 125.6 (m), 124.1, 122.9, 121.4, 120.7 (q, *J* = 259.6 Hz), 108.7, 81.6, 41.5, 26.4 ppm. **IR** (KBr): ν̃ = 3064, 2941, 1739, 1616, 1473, 1254, 1213, 1165, 1070, 930, 754 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{13}H_{12}F_3NNaO_2$ 294.0718; Found 294.0721. **m.p.**: 67.1 - 69.4 °C.

3-Allyl-1-isopropyl-3-(trifluoromethoxy)indolin-2-one (2v)



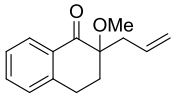
2v was prepared according to the **procedure A**; eluent (*n*-hexane/CH_2Cl_2 = 7/3): R_f = 0.27. Slightly yellow semi-solid; 13.2 mg; 88% yield, 32% ee. **[α]$_D^{25}$** = −1.44 (*c* = 0.34, $CHCl_3$, 32% ee). HPLC conditions: CHIRALPAK® IA-3 column, eluent: *n*-hexane/ethyl acetate = 97/3, flow rate = 0.5 mL/min, λ = 254 nm, tR = 12.867 min for minor isomer, tR = 14.817 min for major isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.45 - 7.30 (m, 2H), 7.12 - 6.98 (m, 2H), 5.50 - 5.32 (m, 1H), 5.11 - 5.04 (m, 2H), 4.63 - 4.47 (m, 1H), 2.87 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.71 (dd, *J* = 13.2, 8.2 Hz, 1H), 1.45 (dd, *J* = 6.9, 1.6 Hz, 6H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −53.6 (s, 3F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 172.1, 142.3, 130.7, 128.5, 125.8, 124.4, 122.3, 121.3, 120.7 (q, *J* = 259.9 Hz), 110.2, 81.4, 44.4, 41.5, 19.2, 18.9 ppm. **IR** (KBr): ν̃ = 3084, 3062, 2981, 2939, 2883, 1730, 1612, 1485, 1469, 1254, 1221, 1163, 1074, 930, 752 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{15}H_{16}F_3NNaO_2$ 322.1031; Found 322.1031.

2-Allyl-2-(difluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (11)



11 was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 9/1): R_f = 0.42. Colorless oil; 8.1 mg; 82% yield, 72% ee. **[α]$_D^{25}$** = +13.4 (*c* = 0.27, $CHCl_3$, 72% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, tR = 15.683 min for major isomer, tR = 17.208 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.6 Hz, 1H), 7.58 - 7.49 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28 - 7.25 (m, 1H), 6.54 (t, *J* = 75.0 Hz, 1H), 5.98 - 5.78 (m, 1H), 5.24 - 5.15 (m, 2H), 3.17 (dt, *J* = 17.4, 5.8 Hz, 1H), 3.05 - 2.91 (m, 1H), 2.74 - 2.57 (m, 2H), 2.47 - 2.26 (m, 2H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −77.9 (dd, *J* = 169.9, 74.8 Hz, 1F), −78.6 (dd, *J* = 169.4, 75.3 Hz, 1F) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 194.6, 143.1, 134.3, 131.0, 130.8, 128.8, 128.4, 127.1, 120.0, 115.6 (dd, *J* = 253.0, 251.4 Hz), 81.7, 38.2, 32.6 (d, *J* = 1.7 Hz), 25.4 ppm. **IR** (NaCl): ν̃ = 3078, 3020, 2933, 2852, 1693, 1603, 1454, 1396, 1227, 1117, 1034, 926, 744 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{14}F_2NaO_2$ 275.0860; Found 275.0862.

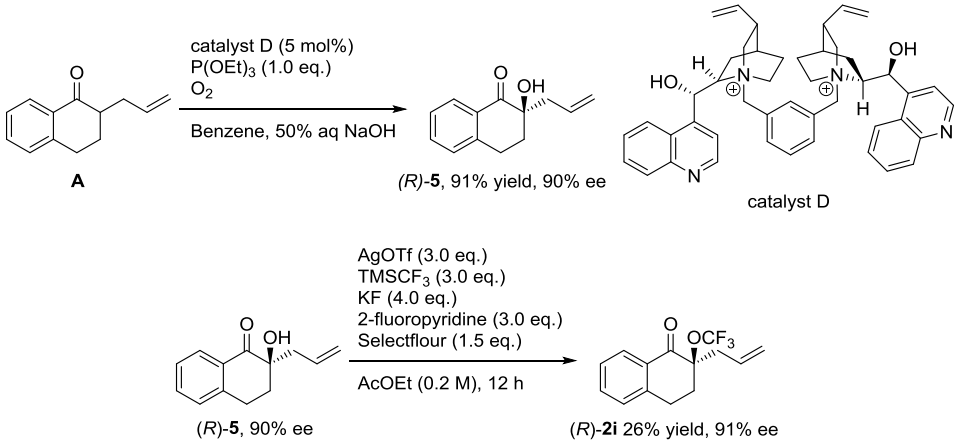
2-Allyl-2-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (12)



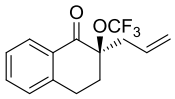
12 was prepared according to the **procedure B**; eluent (*n*-hexane/ether = 30/1): R_f = 0.17. Colorless oil; 7.2 mg; 94% yield, 80% ee. **[α]$_D^{25}$** = +25.6 (*c* = 0.24, $CHCl_3$, 80% ee). HPLC conditions: CHIRALPAK® IG column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 15.217 min for major isomer, tR = 20.892 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.17 - 7.89 (m, 1H), 7.57 - 7.37 (m, 1H), 7.35 - 7.21 (m, 2H), 5.95 - 5.70 (m, 1H), 5.22 - 5.08 (m, 2H), 3.28 - 3.16 (m, 4H), 2.87 (dt, *J* = 17.2, 5.3 Hz, 1H), 2.73 (dd, *J* = 14.8, 6.6 Hz, 1H), 2.59 - 2.33 (m, 2H), 2.17 - 1.97 (m, 1H) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 196.1, 143.8, 133.4, 132.8, 131.6, 128.6, 128.1, 126.6, 118.6, 78.5, 51.4, 36.2, 31.9, 25.2 ppm. **IR** (NaCl): ν̃ = 3074, 2937, 2831, 1687, 1601, 1454, 1288, 1223, 1080, 995, 922, 744 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{14}H_{16}NaO_2$ 239.1048; Found 239.1051.

The absolute configuration of 2i

Scheme S2. The absolute configuration of **2i** was determined by HPLC comparison with (*R*)-**2i** which synthesized from (*R*)-**5** reported in the literature. [11] **A** and (*R*)-**5** were prepared according to the reported procedure, and spectral data of **A** and(*R*)-**5** were in agreement with the literature. [10,11]

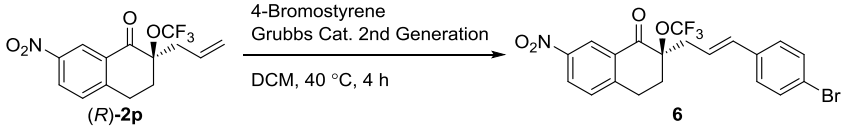


(*R*)-2-Allyl-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one ((*R*)-2i)



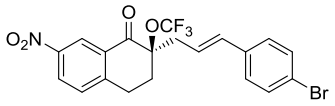
(*R*)-**2i** was prepared according to the reported procedure[7]; colorless oil; 44.7 mg; 26% yield, 91% ee. $[\alpha]_D^{25}$ = +0.79 (*c* = 0.61, $CHCl_3$, 91% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/TBME = 80/20, flow rate = 0.5 mL/min, λ = 254 nm, tR = 11.025 min for major isomer, tR = 14.675 min for minor isomer. Spectral data for (*R*)-**2i** (^{1}H NMR, ^{19}F NMR, ^{13}C NMR, IR, HRMS) corresponded to **2i**.

Olefin metathesis reaction of 2p[12]



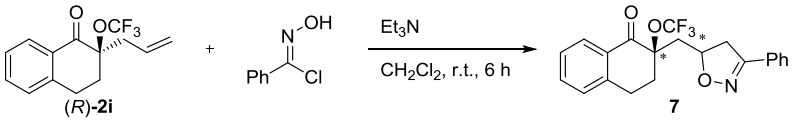
To a solution of α-trifluoromethoxylated ketone (*R*)-**2p** (0.27 mmol, 1.0 eq., 91% ee), Grubbs Cat. 2nd Generation (3.0 mol%) in CH_2Cl_2 (2.7 mL) was added 4-Bromstyrene (0.54 mmol, 2.0 eq.) and the mixture was stirred at 40 °C for 4 h under nitrogen atmosphere. Then the solvent was removed under reduced pressure and the crude product was purified by flash silica-gel column chromatography to afford **6** (49 mg; 39% yield, 91% ee) as white solid.

(*R*,*E*)-2-(3-(4-Bromophenyl)allyl)-7-nitro-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (6)



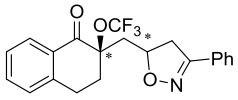
Eluent (*n*-hexane/ethyl acetate = 4/1): R_f = 0.33. $[\alpha]_D^{25}$ = −66.8 (*c* = 0.69, $CHCl_3$, 91% ee). HPLC conditions: CHIRALPAK® IA column, eluent: *n*-hexane/TBME = 60/40, flow rate = 0.5 mL/min, λ = 254 nm, tR = 31.092 min for major isomer, tR = 57.508 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.54 - 7.40 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.27 - 6.15 (m, 1H), 3.41 - 3.25 (m, 1H), 3.18 - 3.03 (m, 1H), 3.02 - 2.81 (m, 2H), 2.74 - 2.59 (m, 1H), 2.44 - 2.28 (m, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.5 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 190.4, 148.8, 147.4, 135.4, 134.3, 131.7, 131.6, 130.3, 127.9, 127.8, 121.1 (q, *J* = 260.0 Hz), 123.9, 122.3, 121.7, 84.1, 37.3, 31.3, 25.6 ppm. **IR** (KBr): ν̃ = 3082, 3033, 2925, 2870, 1711, 1612, 1529, 1487, 1419, 1248, 1215, 1146, 987, 931, 823, 739 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{20}H_{15}BrF_3NNaO_4$ 492.0034; Found 492.0035. **m.p.**: 157.3 - 162.6 °C.

1,3-Dipolar cycloaddition reaction of 2i[13]



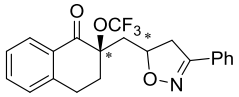
To a round bottomed flask, benzohydroximinoyl chloride (5.0 eq.) was dissolved in dry CH_2Cl_2 (2.0 mL) under a nitrogen atmosphere. Then, triethyl amine (5.0 eq.) was added and the reaction mixture was stirred for 15-30 min at room temperature. α-trifluoromethoxylated ketone (*R*)-**2i** (0.185 mmol, 1.0 eq., 86% ee) in dry CH_2Cl_2 (1.7 mL) was then added to the reaction mixture and stirred 6 h at room temperature. Then the solvent was removed and the crude product was purified by flash silica-gel column chromatography to afford **7** (64.6 mg; 90% yield, d.r. = 1.6:1) as an off-white solid.

2-((3-Phenyl-4,5-dihydroisoxazol-5-yl)methyl)-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (7-less polar)



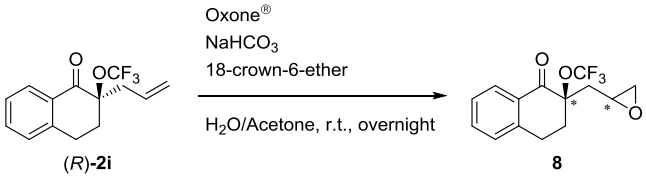
A diastereomerically pure sample could be purified by flash silica-gel column chromatography from *n*-hexane/CH_2Cl_2 to afford **7-less polar** (36.3 mg; 50% yield, 88% ee) as an off-white semi-solid. TLC (*n*-hexane/CH_2Cl_2 = 2/3): R_f = 0.49. $[\alpha]_D^{25}$ = +89.6 (*c* = 0.72, $CHCl_3$, 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 34.158 min for major isomer, tR = 74.025 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.9 Hz, 1H), 7.69 - 7.59 (m, 2H), 7.58 - 7.49 (m, 1H), 7.44 - 7.31 (m, 4H), 7.29 (s, 1H), 5.15 (dtd, *J* = 10.6, 8.2, 2.6 Hz, 1H), 3.58 (dd, *J* = 16.7, 10.3 Hz, 1H), 3.39 - 3.10 (m, 2H), 3.00 (dd, *J* = 16.9, 8.1 Hz, 1H), 2.81 - 2.68 (m, 2H), 2.34 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.19 (dd, *J* = 15.3, 2.6 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −50.8 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 192.9, 156.8, 142.7, 134.4, 130.3, 130.3, 129.1, 128.9, 128.7, 128.5, 127.1, 126.6, 121.0 (q, *J* = 259.1 Hz), 85.5, 76.4, 41.4, 39.7, 30.7, 26.5 ppm. **IR** (KBr): ν̃ = 3062, 2952, 2927, 2854, 1703, 1603, 1448, 1358, 1265, 1227, 1151, 1090, 910, 737 cm^{-1}. **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd. for $C_{21}H_{18}F_3NNaO_3$ 412.1136; Found 412.1141.

2-((3-Phenyl-4,5-dihydroisoxazol-5-yl)methyl)-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (7-polar)



A diastereomerically pure sample could be purified by flash silica-gel column chromatography from *n*-hexane/CH_2Cl_2 to afford **7-polar** (28.3 mg; 39% yield, 88% ee) as an off-white solid. TLC (*n*-hexane/CH_2Cl_2 = 2/3): R_f = 0.30. **[α]$_D^{25}$** = −24.9 (*c* = 0.77, $CHCl_3$, 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, tR = 47.575 min for minor isomer, tR = 74.175 min for major isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.9 Hz, 1H), 7.71 - 7.61 (m, 2H), 7.59 - 7.51 (m, 1H), 7.44 - 7.35 (m, 4H), 7.29 (s, 1H), 4.86 - 4.68 (m, 1H), 3.60 (dd, *J* = 17.0, 10.3 Hz, 1H), 3.30 - 3.05 (m, 3H), 2.83 - 2.69 (m, 1H), 2.58 - 2.47 (m, 3H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −50.6 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 191.7, 157.1, 142.0, 134.4, 130.6, 130.2, 129.3, 128.7, 128.7, 128.7, 127.3, 126.7, 121.1 (q, *J* = 259.1 Hz), 84.8, 77.1, 41.4, 39.7, 33.2, 25.9 ppm. **IR** (KBr): ν̃ = 2962, 2925, 1693, 1603, 1362, 1267, 1232, 1211, 1186, 1146, 1055, 904, 768 cm^{-1}. Spectral data for **7-polar** (HRMS) corresponded to **7-less polar**. **m.p.**: 109.0 - 110.6 °C.

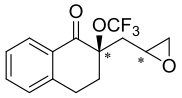
Epoxidation of 2i using dimethyldioxirane[14]



(*R*)-**2i** **8**

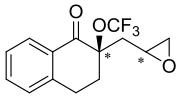
To a solution of α-trifluoromethoxylated ketone (*R*)-**2i** (270 mg, 1.0 mmol, 1.0 eq., 86% ee) in acetone (17 mL) was added solid $NaHCO_3$ (1.26 g, 15.0 mmol) and 18-crown-6-ether (26.4 mg, 0.10 mmol). Then, a solution of Oxone® (3.07 g, 10.0 mmol) in water (17 mL) was added slowly to the reaction mixture. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was dissolved in ether and washed with water. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash silica-gel column chromatography to afford **8** (208.2 mg; 73% yield, d.r. = 1.1:1) as a slightly yellow oil.

2-(Oxiran-2-ylmethyl)-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (8-less polar)



A diastereomerically pure sample could be purified by flash silica-gel column chromatography from benzene only to afford **8-less polar** (109.0 mg; 38% yield, 86% ee) as a slightly yellow oil. TLC (*n*-hexane/ethyl acetate = 4/1): R_f = 0.46. **[α]$_D^{25}$** = −4.05 (*c* = 0.69, $CHCl_3$, 86% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/*i*-PrOH = 70/30, flow rate = 0.5 mL/min, λ = 254 nm, tR = 10.175 min for major isomer, tR = 11.608 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.9 Hz, 1H), 7.59 - 7.49 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 - 7.24 (m, 1H), 3.31 - 3.23 (m, 1H), 3.21 - 3.14 (m, 2H), 2.84 (t, *J* = 4.5 Hz, 1H), 2.80 - 2.69 (m, 1H), 2.59 (dt, *J* = 13.4, 4.9 Hz, 1H), 2.47 - 2.38 (m, 2H), 1.73 (dd, *J* = 15.3, 7.9 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.0 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 191.7, 142.2, 134.2, 130.6, 128.7, 128.6, 127.2, 121.2 (q, *J* = 259.1 Hz), 84.5, 47.7, 46.8, 37.6, 32.9, 25.4 ppm. **IR** (NaCl): ν̃ = 3059, 2954, 2927, 1703, 1603, 1456, 1263, 1225, 1151, 1093, 918, 737 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_3NaO_3$ 309.0714; Found 309.0710.

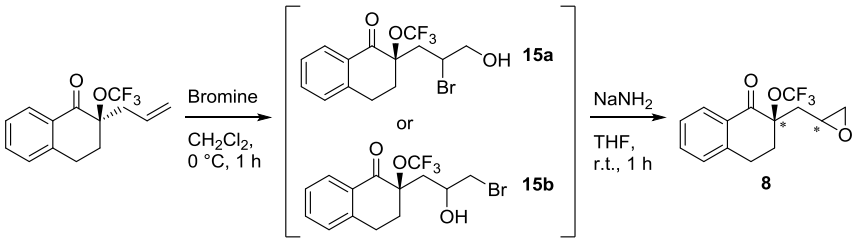
2-(Oxiran-2-ylmethyl)-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (8-polar)



A diastereomerically pure sample could be purified by flash silica-gel column chromatography from benzene only to afford **8-polar** (99.2 mg; 35% yield, 88% ee) as a slightly yellow oil. TLC (n-hexane/ethyl acetate = 4/1): R_f = 0.41. **[α]$_D^{25}$** = −16.2 (*c* = 0.62, $CHCl_3$, 88% ee). HPLC conditions: CHIRALPAK® IE column, eluent: *n*-hexane/*i*-PrOH = 70/30, flow rate = 0.5 mL/min, λ = 254 nm, tR = 11.558 min for major isomer, tR = 13.033 min for minor isomer. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.9 Hz, 1H), 7.62 - 7.47 (m, 1H), 7.44 - 7.33 (m, 1H), 7.30 - 7.23 (m, 1H), 3.33 - 3.21 (m, 1H),

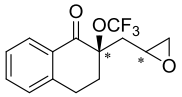
3.09 - 2.95 (m, 2H), 2.81 (t, *J* = 4.4 Hz, 1H), 2.75 - 2.64 (m, 1H), 2.57 - 2.44 (m, 3H), 2.03 (dd, *J* = 14.7, 6.7 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.1 (s, 3F) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 191.7, 142.2, 134.2, 130.6, 128.7, 128.6, 127.2, 121.1 (q, *J* = 259.1 Hz), 84.5, 47.6, 46.7, 37.5, 32.8, 25.4 ppm. **IR** (NaCl): $\tilde{\nu}$ = 3059, 2929, 1703, 1603, 1456, 1363, 1261, 1151, 951, 926, 744 cm^{-1}. Spectral data for **8-polar** (HRMS) corresponded to **8-less polar**.

Stereoselective synthesis of 8



To a solution of (*R*)-**2i** (150 mg, 0.56 mmol) in CH_2Cl_2 (11.0 mL) was added bromine (0.072 mL, 1.39 mmol, 2.5 eq.) dropwisely at 0 °C. The resulting mixture was stirred for 1 h, then quenched by aqueous solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography to give the mixture of regioisomer **15a** and **15b** (174.8 mg; 86% yield). The mixture was directly use for the next step without characterization.
A mixture of **15a** and **15b** (33.8 mg) was dissolved in THF (0.60 mL) and a solution of $NaNH_2$ (35.9 mg, 0.92 mmol) in THF (0.60 mL) was added to the solution. After stirring for 1 h, reaction was quenched by water, extracted with ether, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by Flash silica-gel column chromatography (*n*-hexane/ethyl acetate = 4/1) to give **8** (slightly yellow oil; 26.1 mg, 85% yield) as a single isomer.

2-(Oxiran-2-ylmethyl)-2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (8)



TLC (*n*-hexane/ethyl acetate = 4/1): R_f = 0.40. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.9 Hz, 1H), 7.62 - 7.47 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30 - 7.26 (m, 1H), 3.34 - 3.20 (m, 1H), 3.08 - 2.95 (m, 2H), 2.85 - 2.79 (m, 1H), 2.75 - 2.65 (m, 1H), 2.56 - 2.44 (m, 3H), 2.04 (dd, *J* = 14.7, 6.5 Hz, 1H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −51.1 (s, 3F) ppm. Spectroscopic data for **8** were in good agreement with that of **8-polar**.

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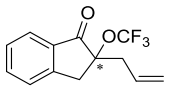
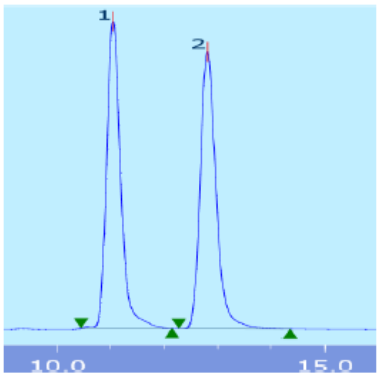
HPLC chromatographs of trifluoromethoxy allyl ketones



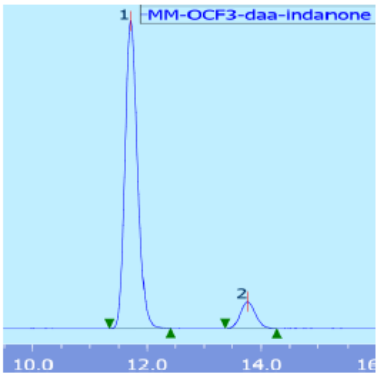
2a

HPLC using a CHIRALCEL® OJ-H

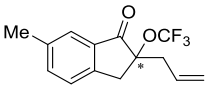
(*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	11.042	49.948	52.578
2	12.808	50.052	47.422



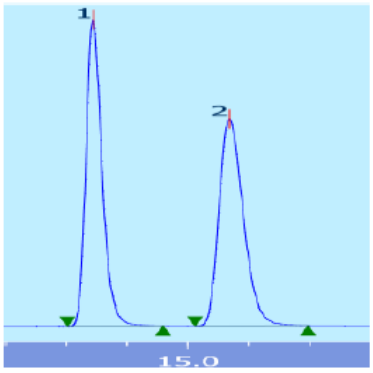
No.	tR [min]	Area (%)	Height (%)
1	11.708	90.475	91.983
2	13.758	9.525	8.017



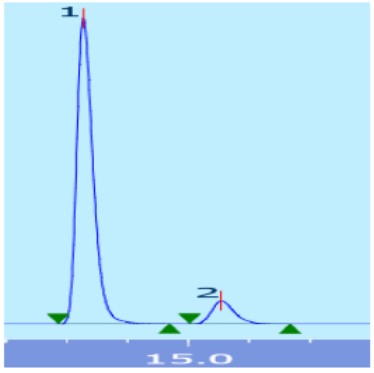
2b

HPLC using a CHIRALCEL® OJ-3

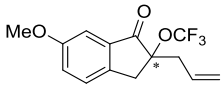
(*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	13.433	50.042	59.756
2	15.683	49.958	40.244



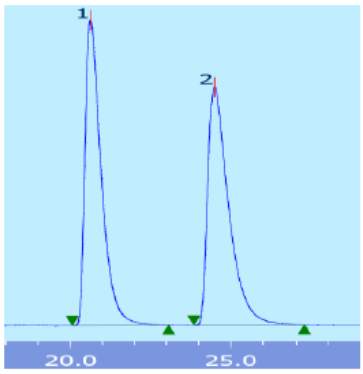
No.	tR [min]	Area (%)	Height (%)
1	13.267	90.757	93.016
2	15.533	9.243	6.984



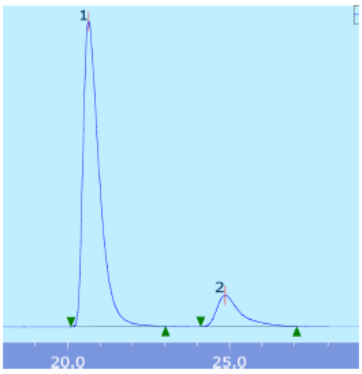
2c

HPLC using a CHIRALPAK® IE

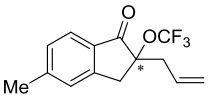
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



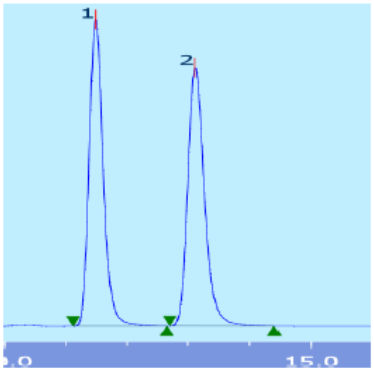
No.	tR [min]	Area (%)	Height (%)
1	20.625	50.061	56.254
2	24.483	49.939	43.746



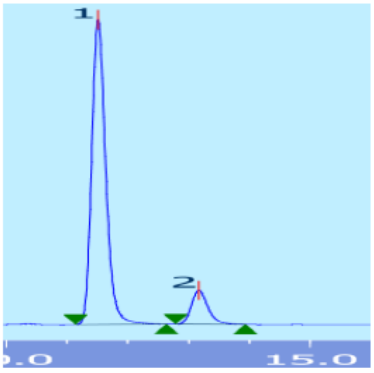
No.	tR [min]	Area (%)	Height (%)
1	20.642	86.862	90.655
2	24.858	13.138	9.345



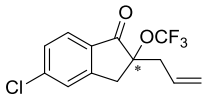
2d
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



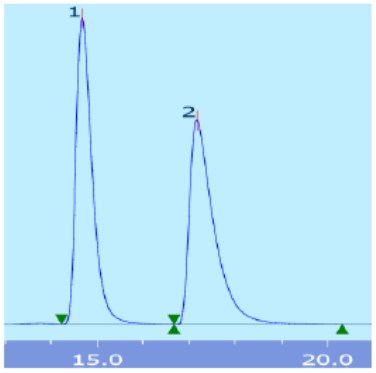
No.	tR [min]	Area (%)	Height (%)
1	11.483	50.053	54.275
2	13.117	49.947	45.725

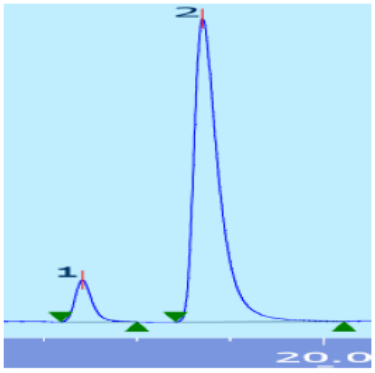


No.	tR [min]	Area (%)	Height (%)
1	11.508	88.484	90.021
2	13.158	11.516	9.979



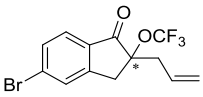
2e
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



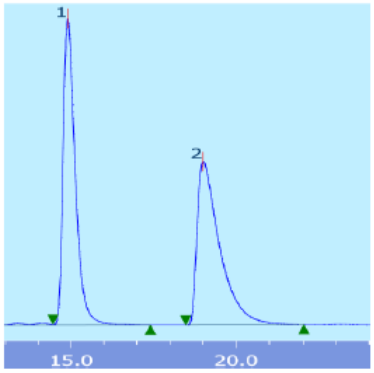


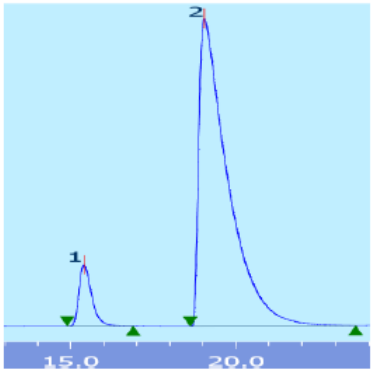
No.	tR [min]	Area (%)	Height (%)
1	14.675	49.979	60.012
2	17.175	50.021	39.988

No.	tR [min]	Area (%)	Height (%)
1	14.817	8.628	12.131
2	17.400	91.372	87.869



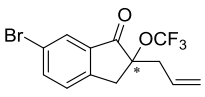
2f
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



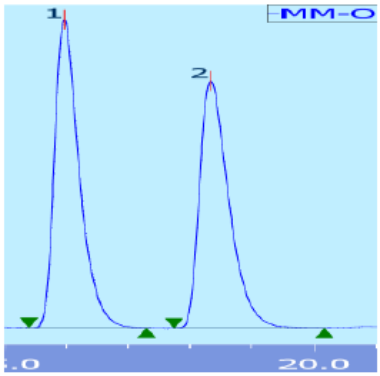


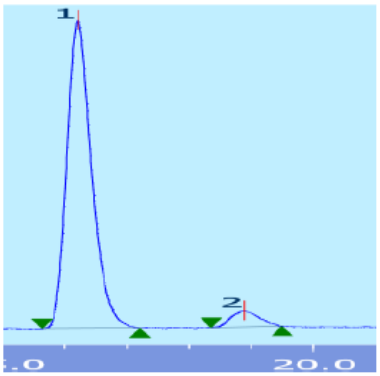
No.	tR [min]	Area (%)	Height (%)
1	14.900	50.089	65.057
2	19.008	49.911	34.943

No.	tR [min]	Area (%)	Height (%)
1	15.400	8.064	16.729
2	19.042	91.936	83.271



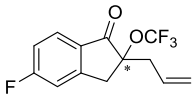
2g
HPLC using a CHIRALPAK® IA
(*n*-hexane/*i*-PrOH = 99.7/0.3, flow rate 0.5 ml/min, λ = 254 nm)



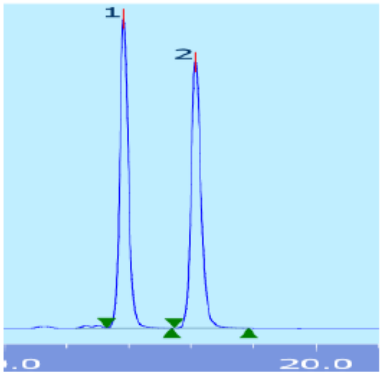


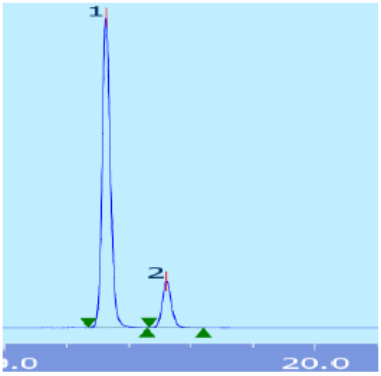
No.	tR [min]	Area (%)	Height (%)
1	15.967	51.357	55.531
2	18.333	48.643	44.469

No.	tR [min]	Area (%)	Height (%)
1	16.200	94.253	94.913
2	18.875	5.747	5.087



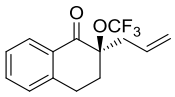
2h
HPLC using a CHIRALPAK® IF
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



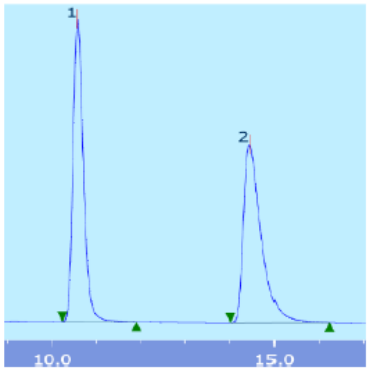


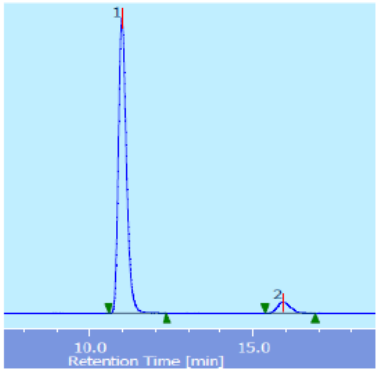
No.	tR [min]	Area (%)	Height (%)
1	13.825	49.962	53.772
2	16.142	50.038	46.228

No.	tR [min]	Area (%)	Height (%)
1	13.242	85.668	86.896
2	15.200	14.332	13.104



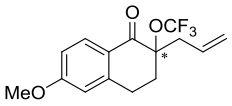
(*R*)-**2i**
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



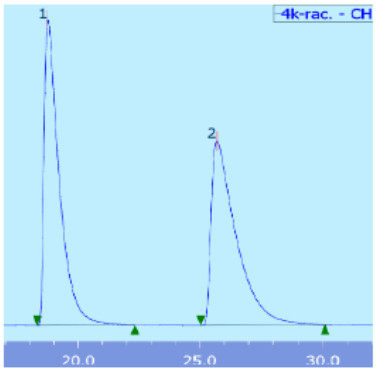


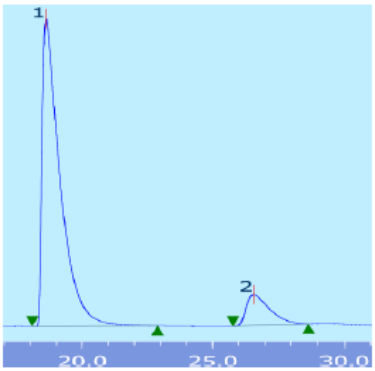
No.	tR [min]	Area (%)	Height (%)
1	10.575	50.073	62.869
2	14.450	49.927	37.131

No.	tR [min]	Area (%)	Height (%)
1	10.992	93.782	96.379
2	15.900	6.218	3.621



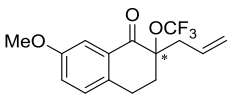
2j
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



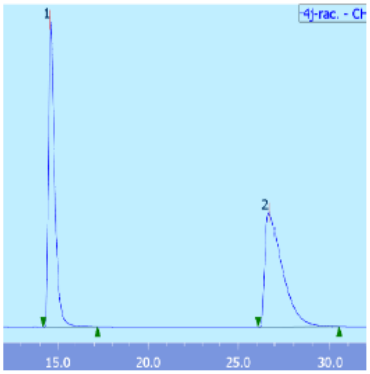


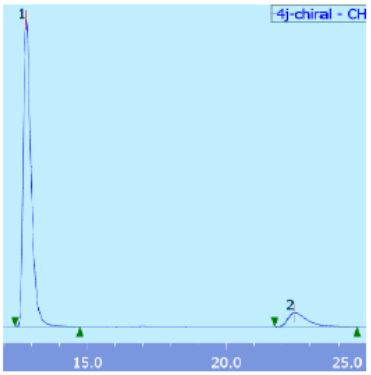
No.	tR [min]	Area (%)	Height (%)
1	18.750	49.998	62.481
2	25.692	50.002	37.519

No.	tR [min]	Area (%)	Height (%)
1	18.608	88.352	90.831
2	26.567	11.648	9.169



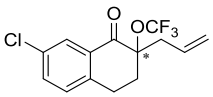
2k
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)





No.	tR [min]	Area (%)	Height (%)
1	14.600	50.183	72.772
2	26.675	49.817	27.228

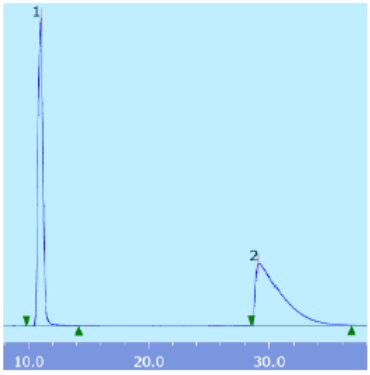
No.	tR [min]	Area (%)	Height (%)
1	12.800	89.769	95.563
2	22.450	10.231	4.437

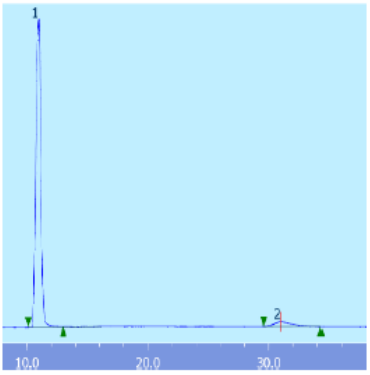


2l

HPLC using a CHIRALPAK® IE

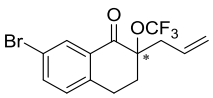
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)





No.	tR [min]	Area (%)	Height (%)
1	11.008	49.529	83.121
2	29.167	50.471	16.879

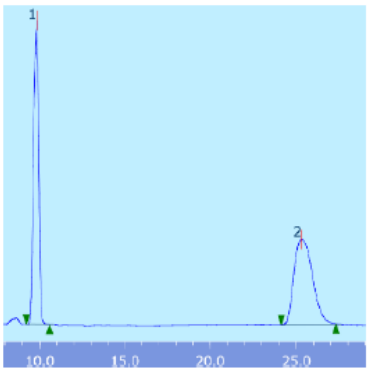
No.	tR [min]	Area (%)	Height (%)
1	10.967	94.662	98.473
2	30.992	5.338	1.527

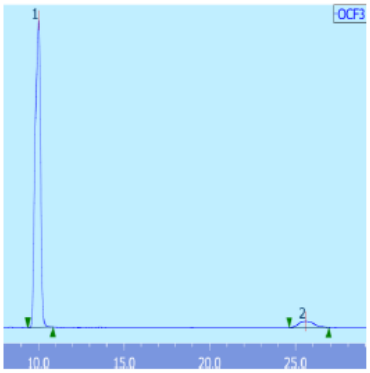


2m

HPLC using a CHIRALPAK® IG

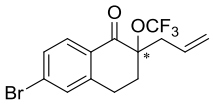
(*n*-hexane/TBME = 70/30, flow rate 0.5 ml/min, λ = 254 nm)



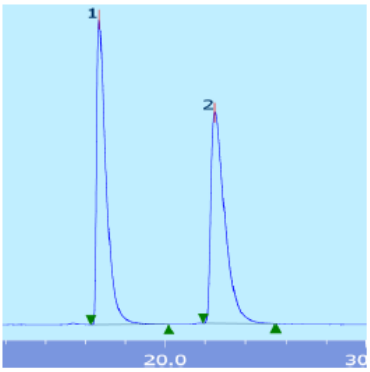


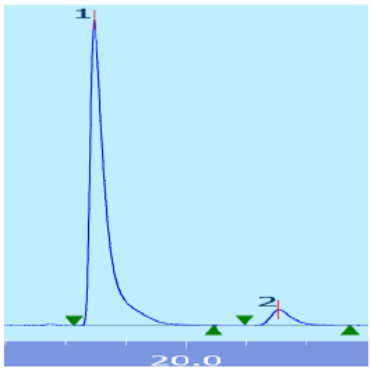
No.	tR [min]	Area (%)	Height (%)
1	9.817	49.862	78.029
2	25.283	50.138	21.971

No.	tR [min]	Area (%)	Height (%)
1	10.017	94.420	98.013
2	25.583	5.580	1.987



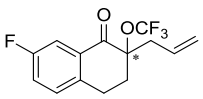
2n
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



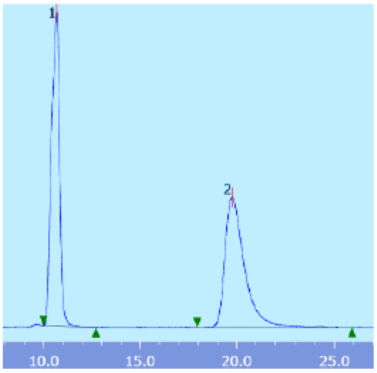


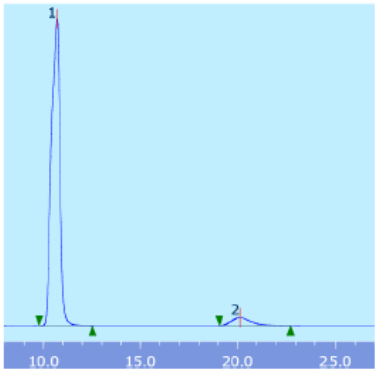
No.	tR [min]	Area (%)	Height (%)
1	16.675	49.893	58.979
2	22.475	50.107	41.021

No.	tR [min]	Area (%)	Height (%)
1	16.950	93.537	95.067
2	23.058	6.463	4.933



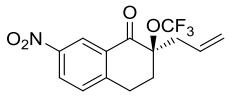
2o
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



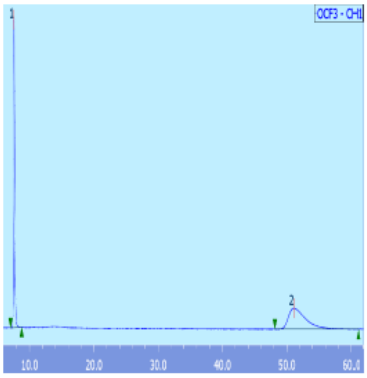


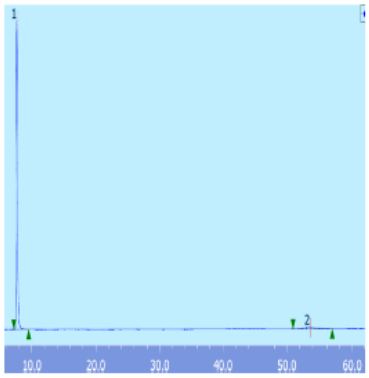
No.	tR [min]	Area (%)	Height (%)
1	10.667	50.119	70.607
2	19.767	49.881	29.393

No.	tR [min]	Area (%)	Height (%)
1	10.683	94.042	97.397
2	20.117	5.958	2.603



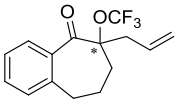
(*R*)-**2p**
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 60/40, flow rate 1.0 ml/min, λ = 254 nm)



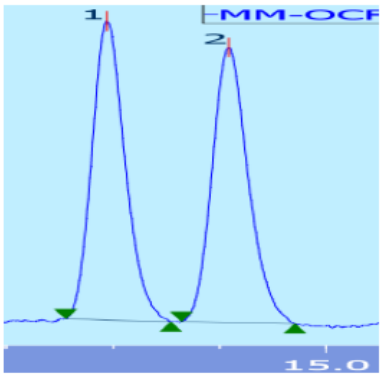


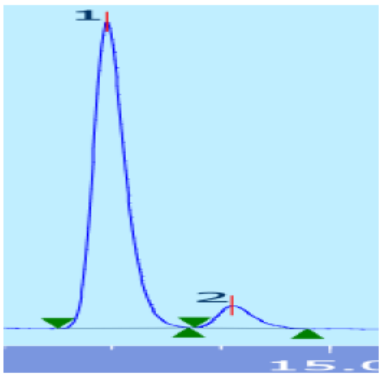
No.	tR [min]	Area (%)	Height (%)
1	7.583	49.979	93.589
2	51.092	50.021	6.411

No.	tR [min]	Area (%)	Height (%)
1	7.642	95.550	99.608
2	53.592	4.450	0.392



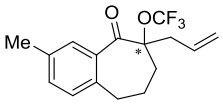
2q
HPLC using a CHIRALPAK® IA
(*n*-hexane/*i*-PrOH = 99.7/0.3, flow rate 0.5 ml/min, λ = 254 nm)



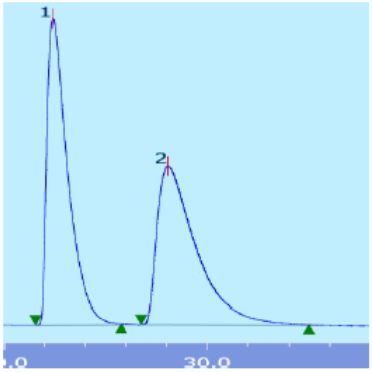


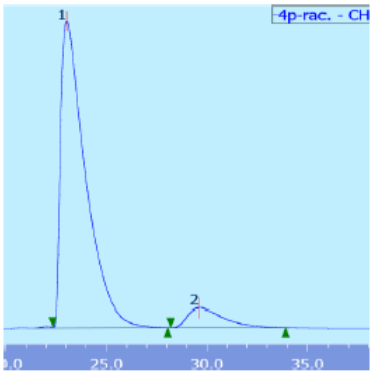
No.	tR [min]	Area (%)	Height (%)
1	12.933	50.014	52.095
2	14.083	49.986	47.905

No.	tR [min]	Area (%)	Height (%)
1	12.950	92.546	93.162
2	14.092	7.454	6.838



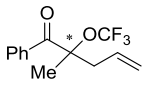
2r
HPLC using a CHIRALPAK® IA
(*n*-hexane = 100, flow rate 0.5 ml/min, λ = 254 nm)



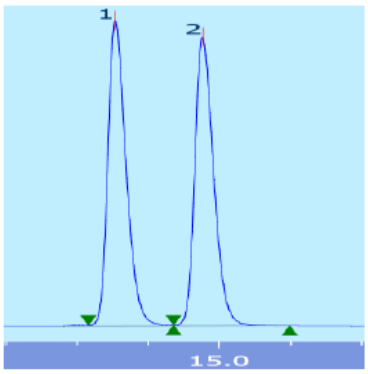


No.	tR [min]	Area (%)	Height (%)
1	22.400	50.761	65.987
2	28.075	49.239	34.013

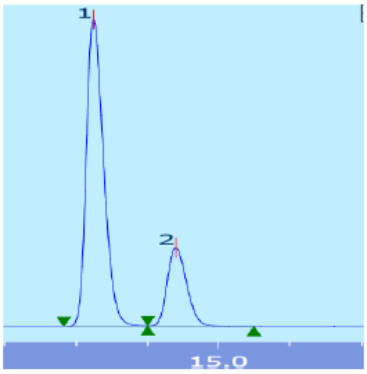
No.	tR [min]	Area (%)	Height (%)
1	23.017	91.604	94.123
2	29.617	8.396	5.877



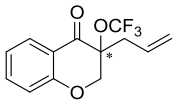
2s
HPLC using a CHIRALPAK® IB-3
(*n*-hexane = 100, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	13.533	50.605	51.438
2	14.767	49.395	48.562



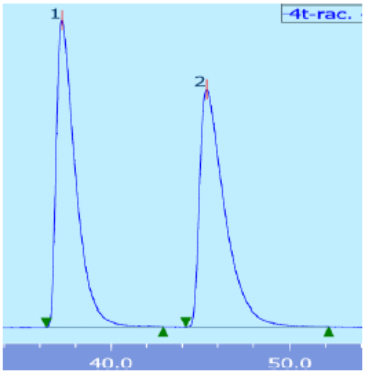
No.	tR [min]	Area (%)	Height (%)
1	13.233	77.389	79.515
2	14.392	22.611	20.485



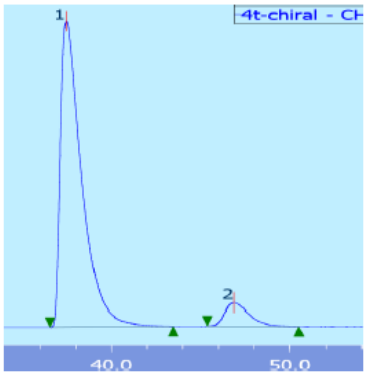
2t

HPLC using a CHIRALPAK® IE

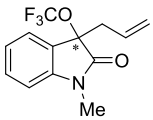
(*n*-hexane/TBME = 99.5/0.5, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	37.233	50.054	56.443
2	45.367	49.946	43.557



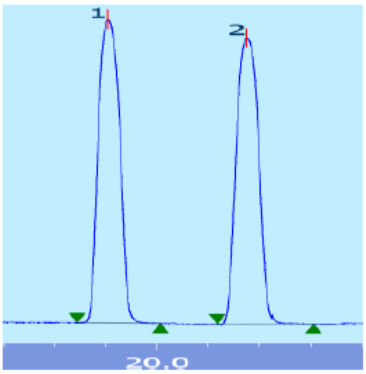
No.	tR [min]	Area (%)	Height (%)
1	37.450	91.945	93.007
2	46.867	8.055	6.993



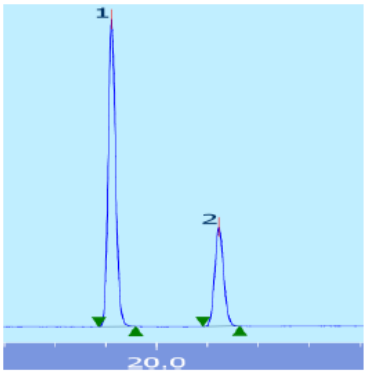
2u

HPLC using a CHIRALPAK® IC

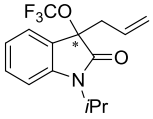
(*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	18.075	50.192	51.508
2	23.508	49.808	48.492



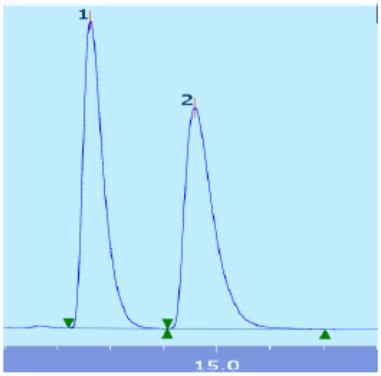
No.	tR [min]	Area (%)	Height (%)
1	18.225	72.082	75.568
2	22.458	27.918	24.432



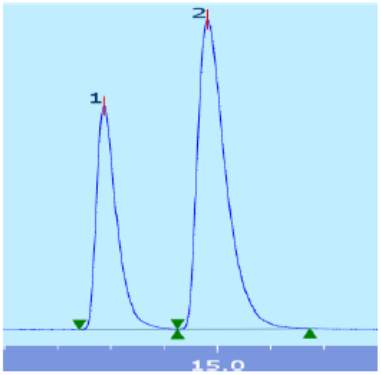
2v

HPLC using a CHIRALPAK® IA-3

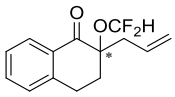
(*n*-hexane/ethyl acetate = 97/3, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	12.617	49.767	58.218
2	14.575	50.233	41.782



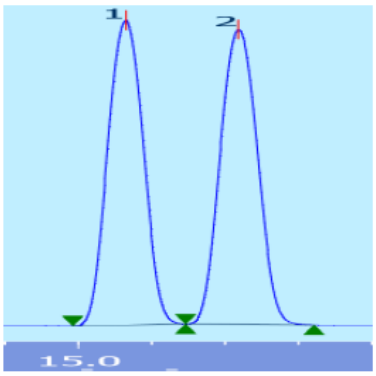
No.	tR [min]	Area (%)	Height (%)
1	12.867	34.191	41.899
2	14.817	65.809	58.101



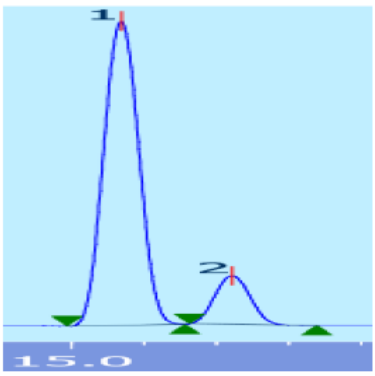
11

HPLC using a CHIRALPAK® IG

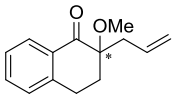
(*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 ml/min, λ = 254 nm)



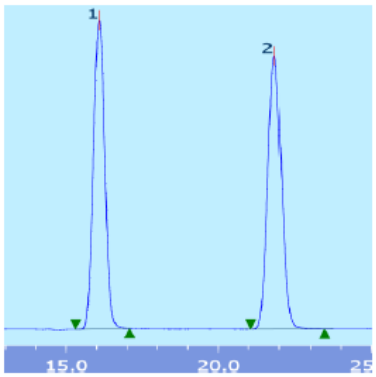
No.	tR [min]	Area (%)	Height (%)
1	15.642	50.028	50.823
2	17.175	49.972	49.177



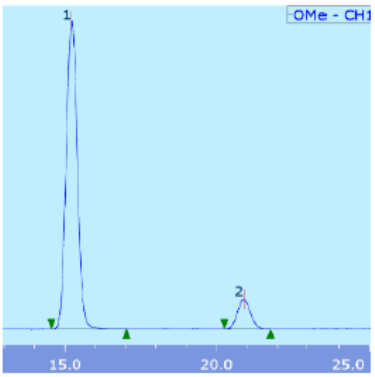
No.	tR [min]	Area (%)	Height (%)
1	15.683	86.228	86.268
2	17.208	13.772	13.732



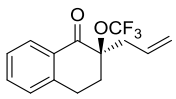
12
HPLC using a CHIRALPAK® IG
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)



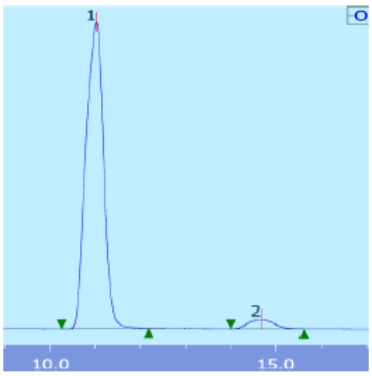
No.	tR [min]	Area (%)	Height (%)
1	16.083	50.165	53.102
2	21.817	49.835	46.898



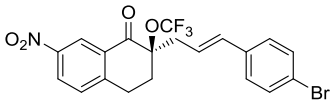
No.	tR [min]	Area (%)	Height (%)
1	15.217	90.110	91.183
2	20.892	9.890	8.817



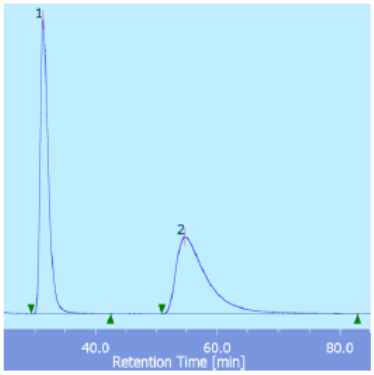
(*R*)-**2i**
HPLC using a CHIRALPAK® IE
(*n*-hexane/TBME = 80/20, flow rate 0.5 ml/min, λ = 254 nm)

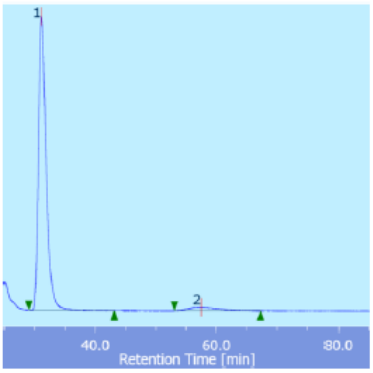


No.	tR [min]	Area (%)	Height (%)
1	11.025	95.559	97.055
2	14.675	4.441	2.945



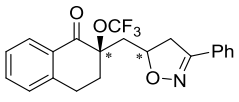
(*R*)-**6**
HPLC using a CHIRALPAK® IA
(*n*-hexane/TBME = 60/40, flow rate 0.5 ml/min, λ = 254 nm)



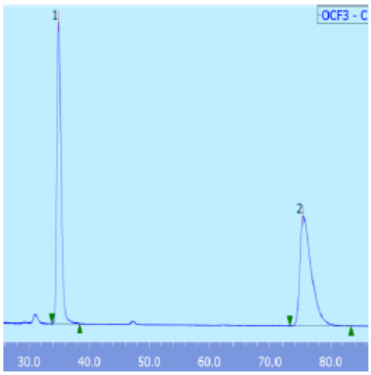


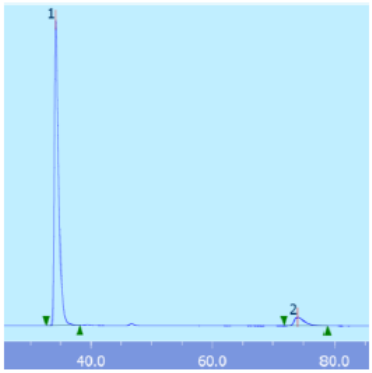
No.	tR [min]	Area (%)	Height (%)
1	31.350	50.298	79.322
2	54.725	49.702	20.678

No.	tR [min]	Area (%)	Height (%)
1	31.092	95.539	98.756
2	57.508	4.461	1.244



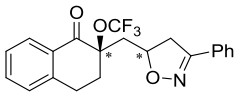
7-less polar
HPLC using a CHIRALPAK® IE
(*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



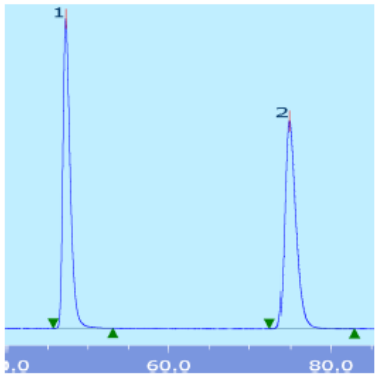


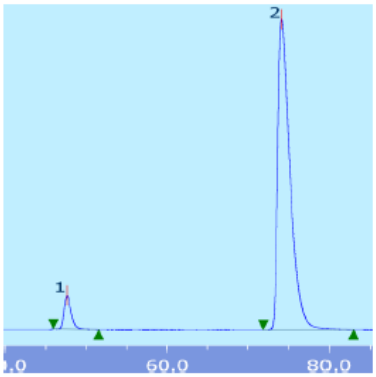
No.	tR [min]	Area (%)	Height (%)
1	34.900	49.996	73.372
2	75.383	50.004	26.628

No.	tR [min]	Area (%)	Height (%)
1	34.158	93.851	97.290
2	74.025	6.149	2.710



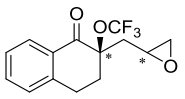
7-polar
HPLC using a CHIRALPAK® IE
(*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 ml/min, λ = 254 nm)



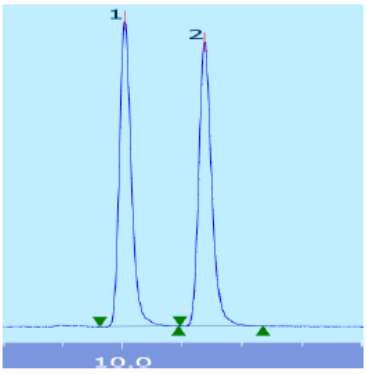


No.	tR [min]	Area (%)	Height (%)
1	47.200	49.969	59.850
2	74.808	50.031	40.150

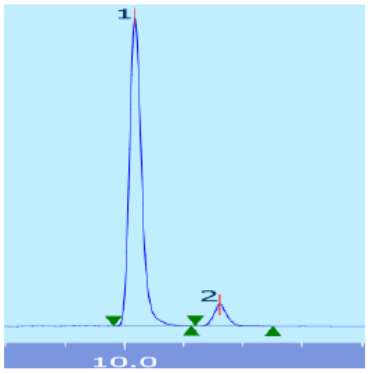
No.	tR [min]	Area (%)	Height (%)
1	47.575	6.051	9.865
2	74.175	93.949	90.135



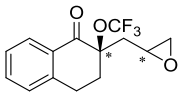
8-less polar
HPLC using a CHIRALPAK® IE
(*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 ml/min, λ = 254 nm)



No.	tR [min]	Area (%)	Height (%)
1	10.033	49.982	51.908
2	11.375	50.018	48.092



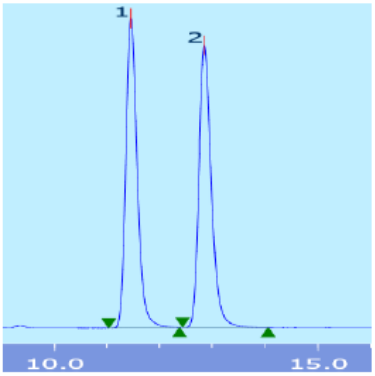
No.	tR [min]	Area (%)	Height (%)
1	10.175	92.956	93.792
2	11.608	7.044	6.208



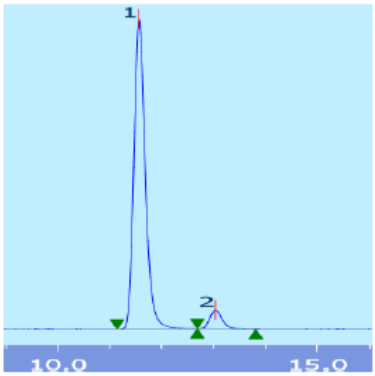
8-polar

HPLC using a CHIRALPAK® IE

(*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 ml/min, λ = 254 nm)

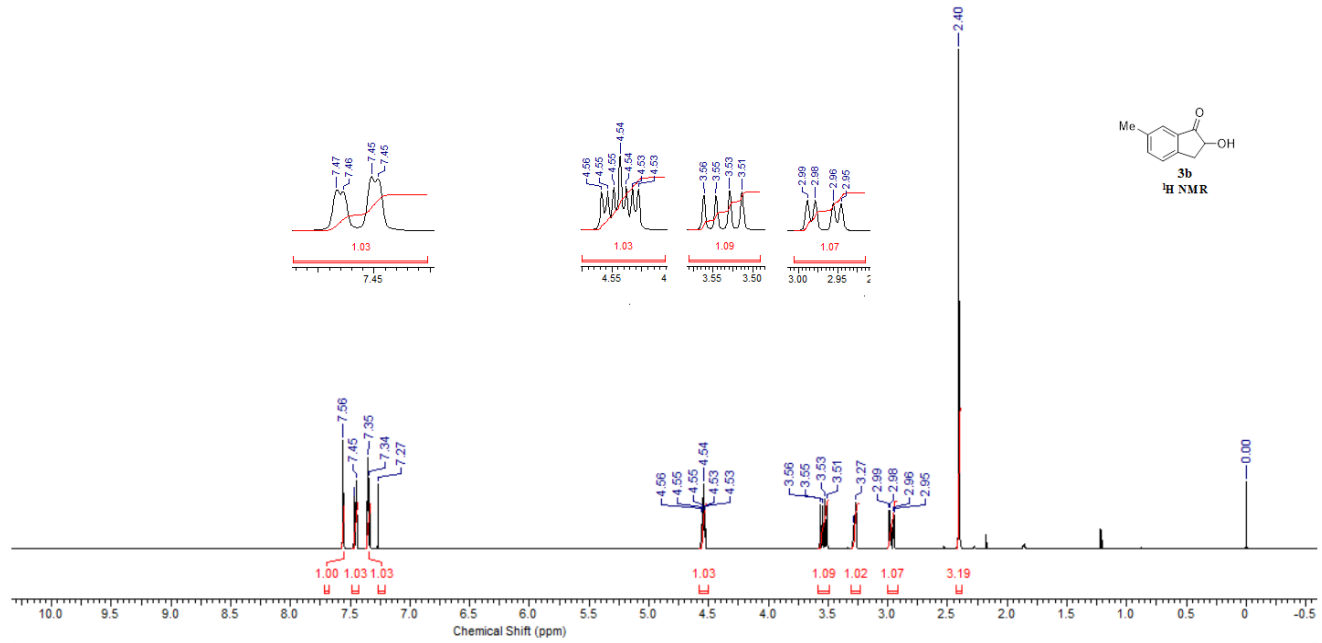


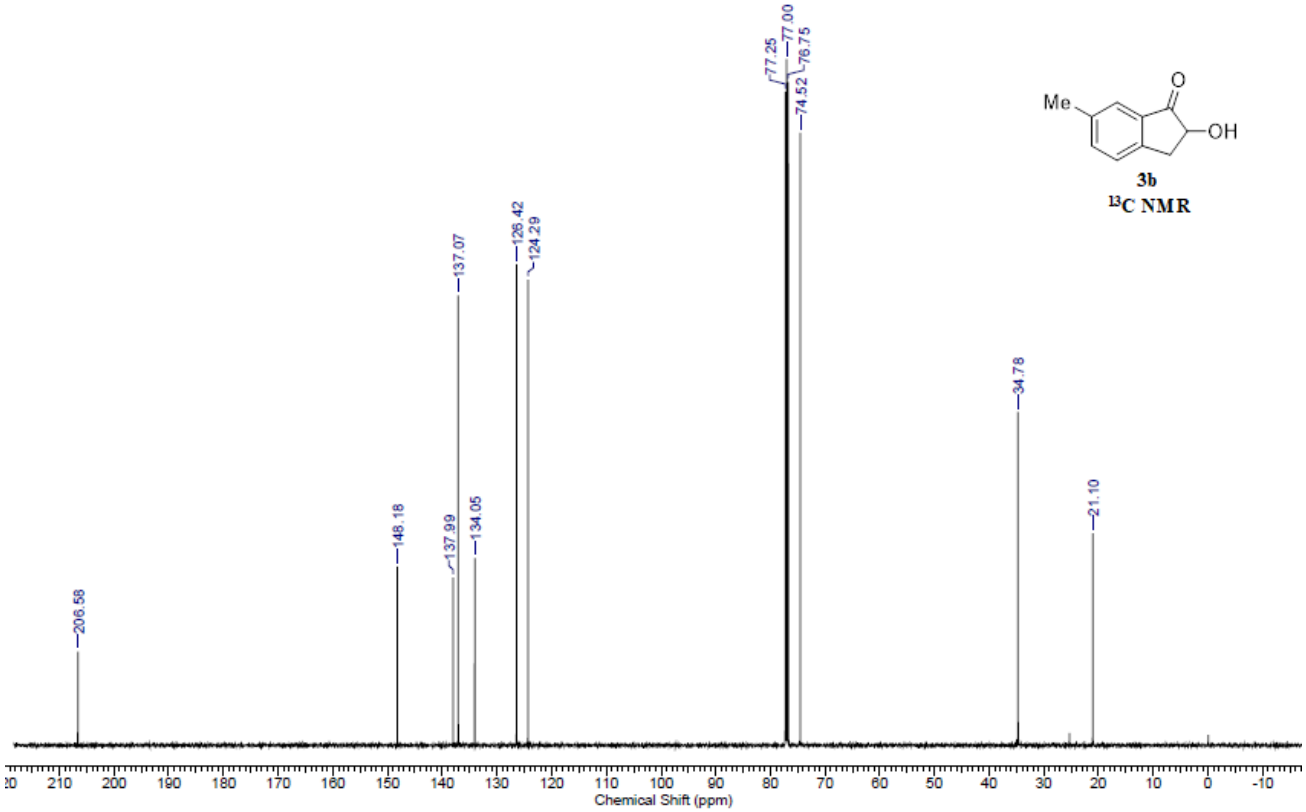
No.	tR [min]	Area (%)	Height (%)
1	11.450	49.959	52.348
2	12.858	50.041	47.652

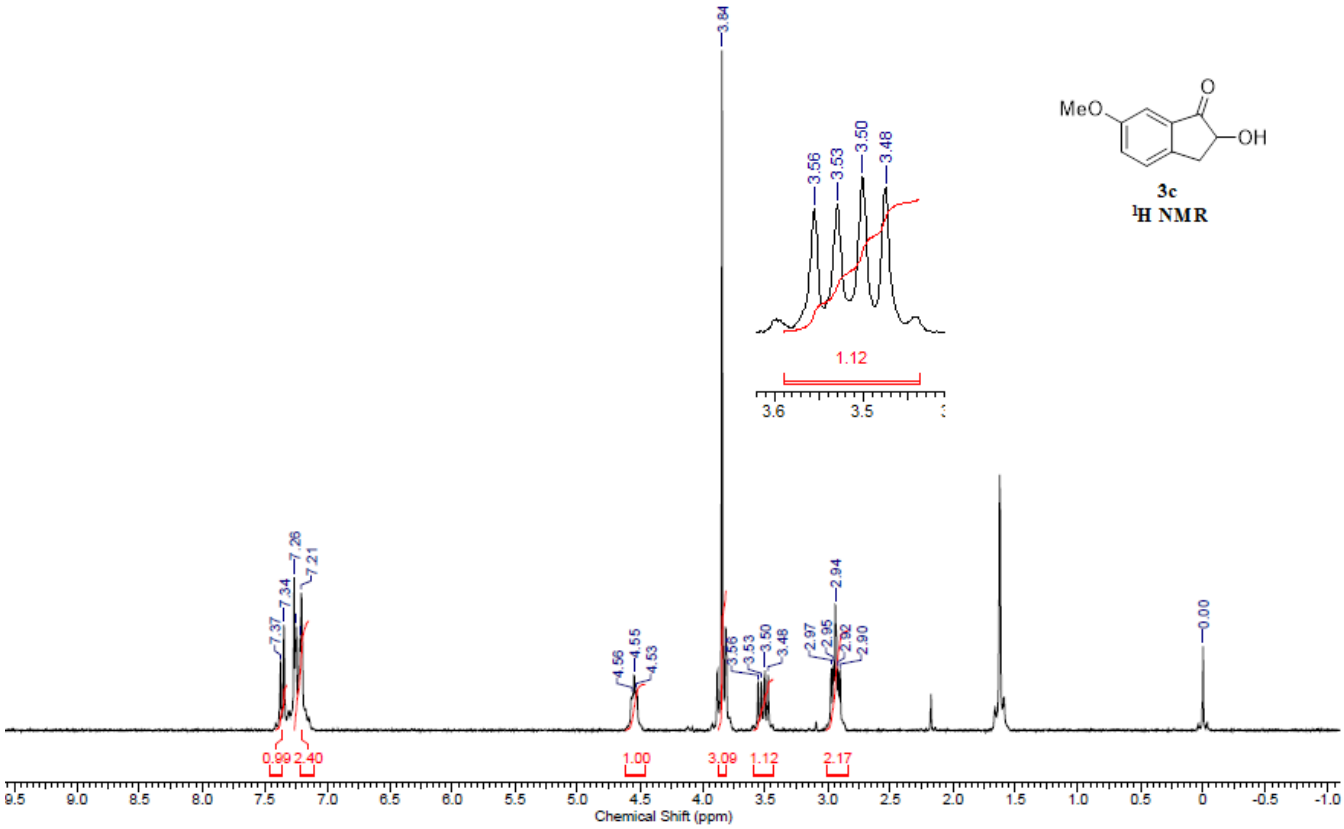


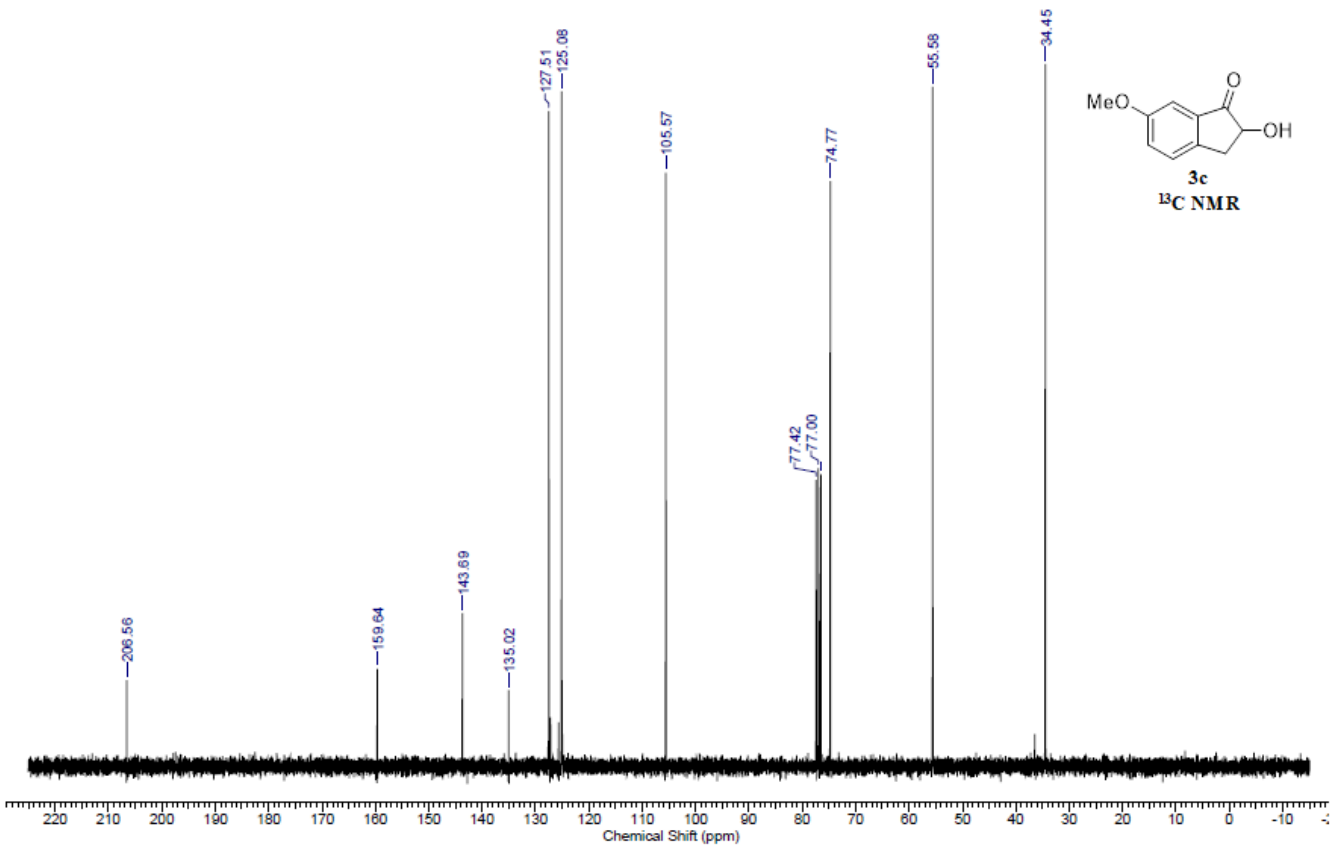
No.	tR [min]	Area (%)	Height (%)
1	11.558	93.885	94.324
2	13.033	6.115	5.676

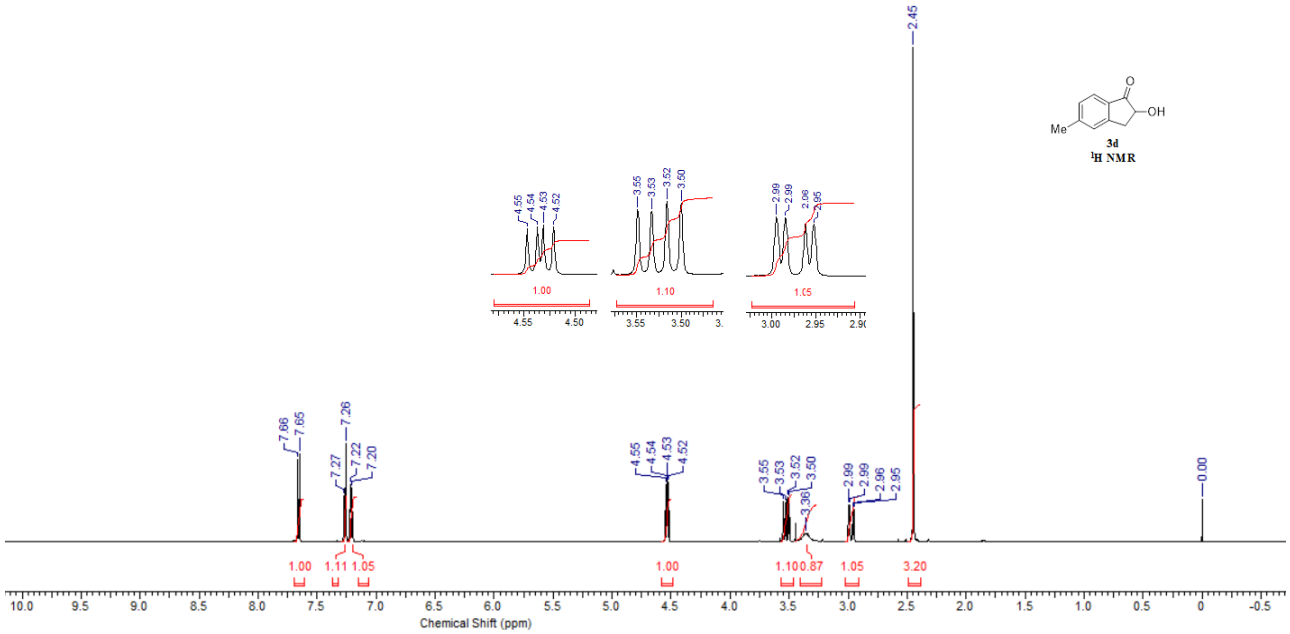
Copies of ^{1}H, ^{19}F, ^{13}C NMR

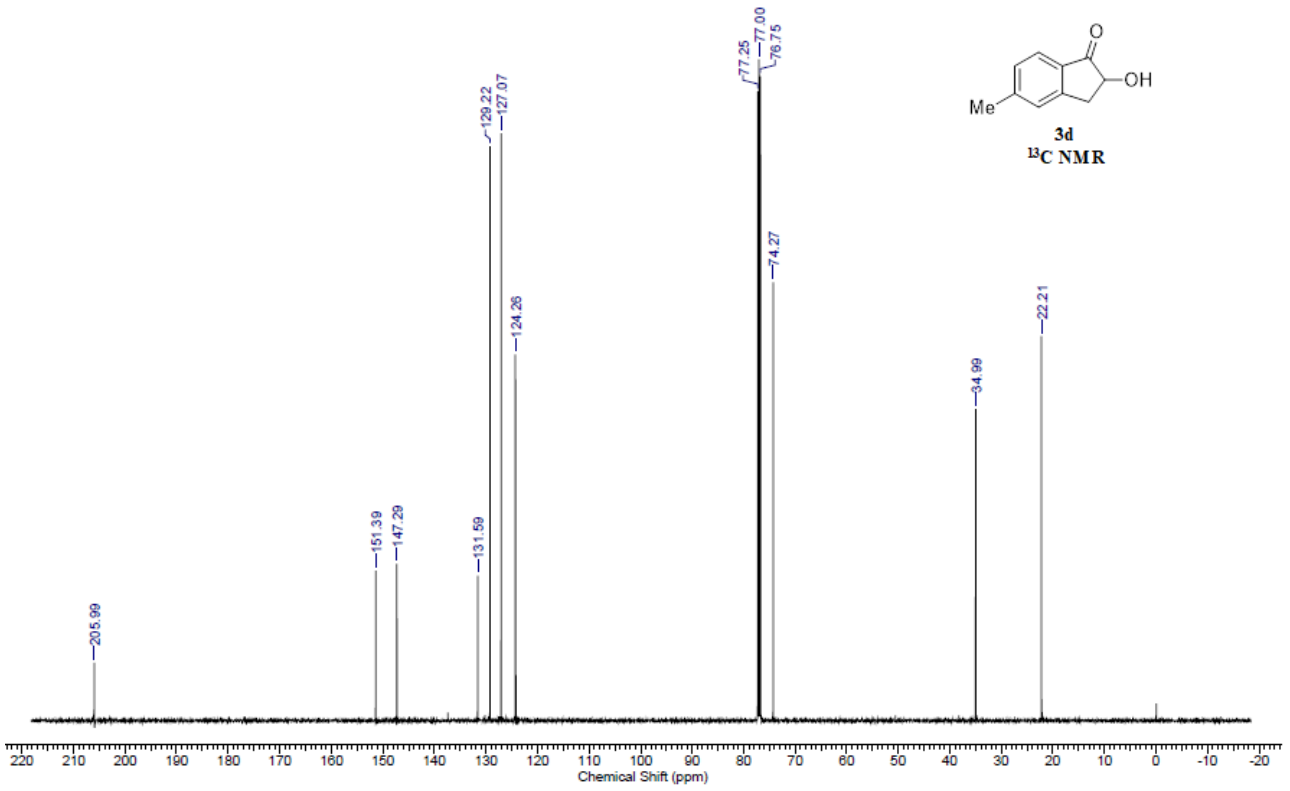


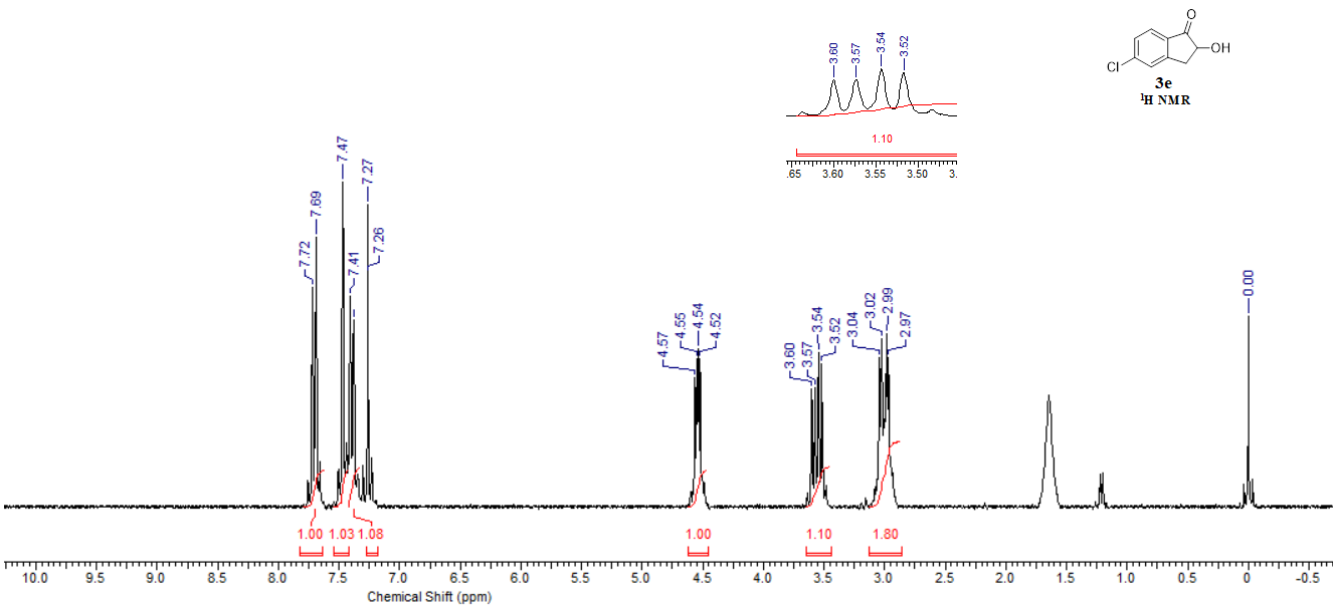


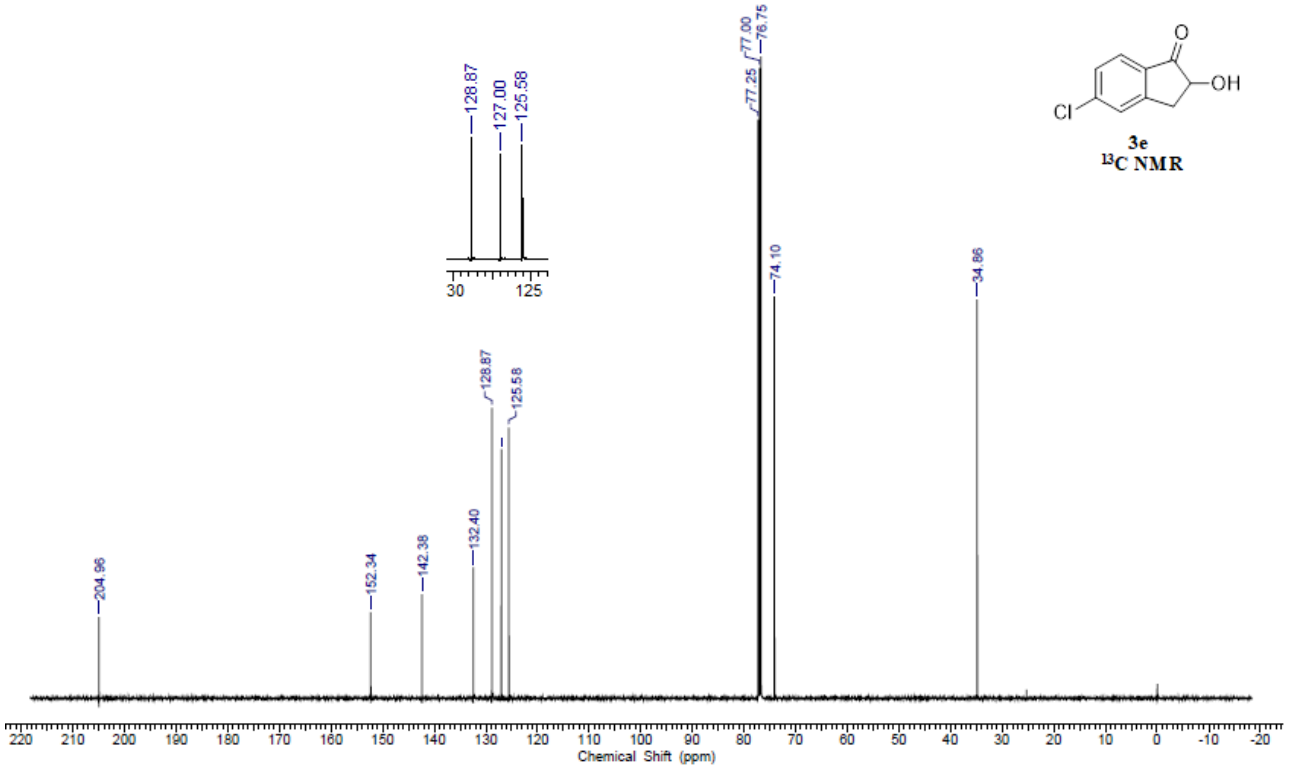

3.84
3.56
3.53
3.50
3.48
1.12
3.6
3.5
MeO
O
OH
3c
1H NMR
7.37
7.34
7.26
7.21
4.56
4.55
4.53
3.56
3.53
3.50
3.48
2.97
2.95
2.92
2.90
2.94
0.00
0.99
2.40
1.00
3.09
1.12
2.17
Chemical Shift (ppm)

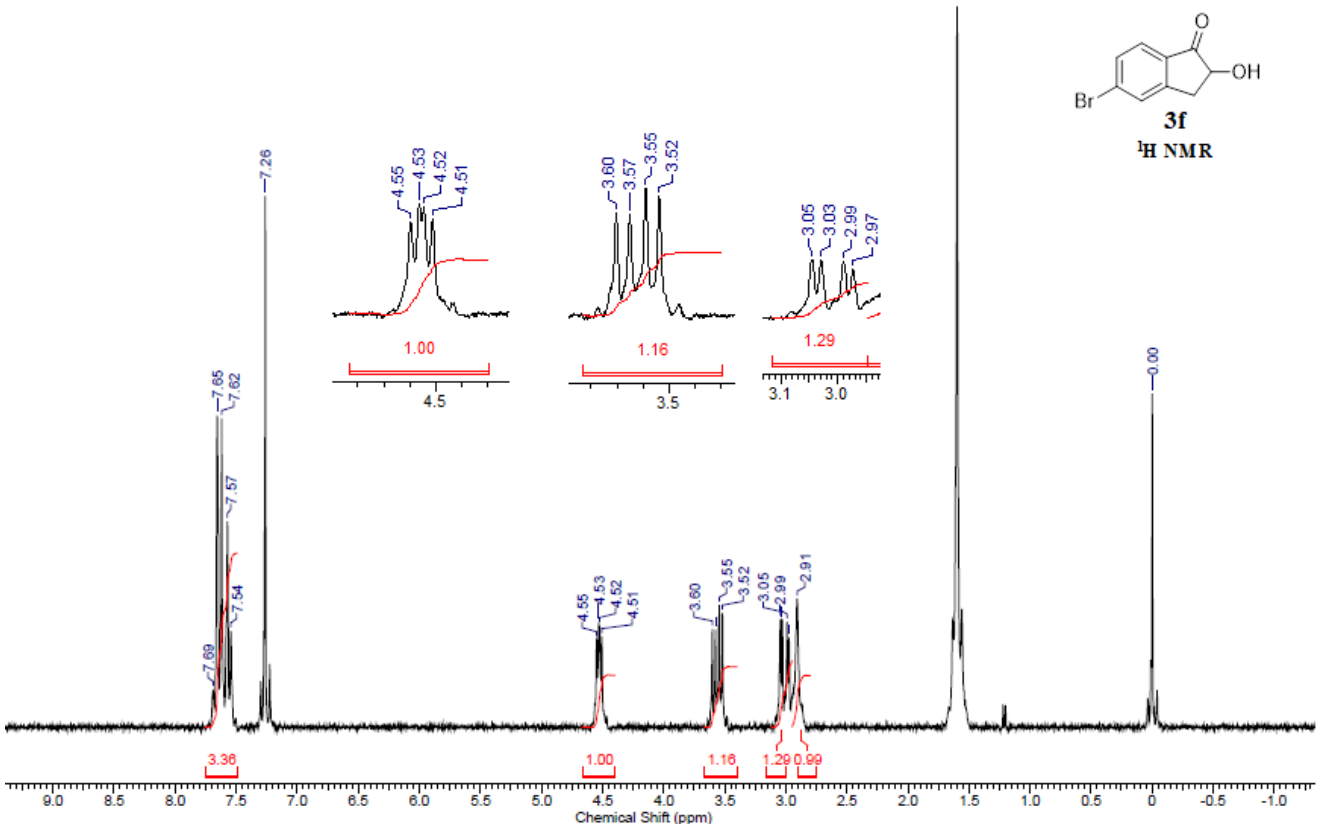

127.51
125.08
105.57
74.77
55.58
34.45
77.42
77.00
206.56
159.64
143.69
135.02
MeO
O
OH
3c
13C NMR
Chemical Shift (ppm)

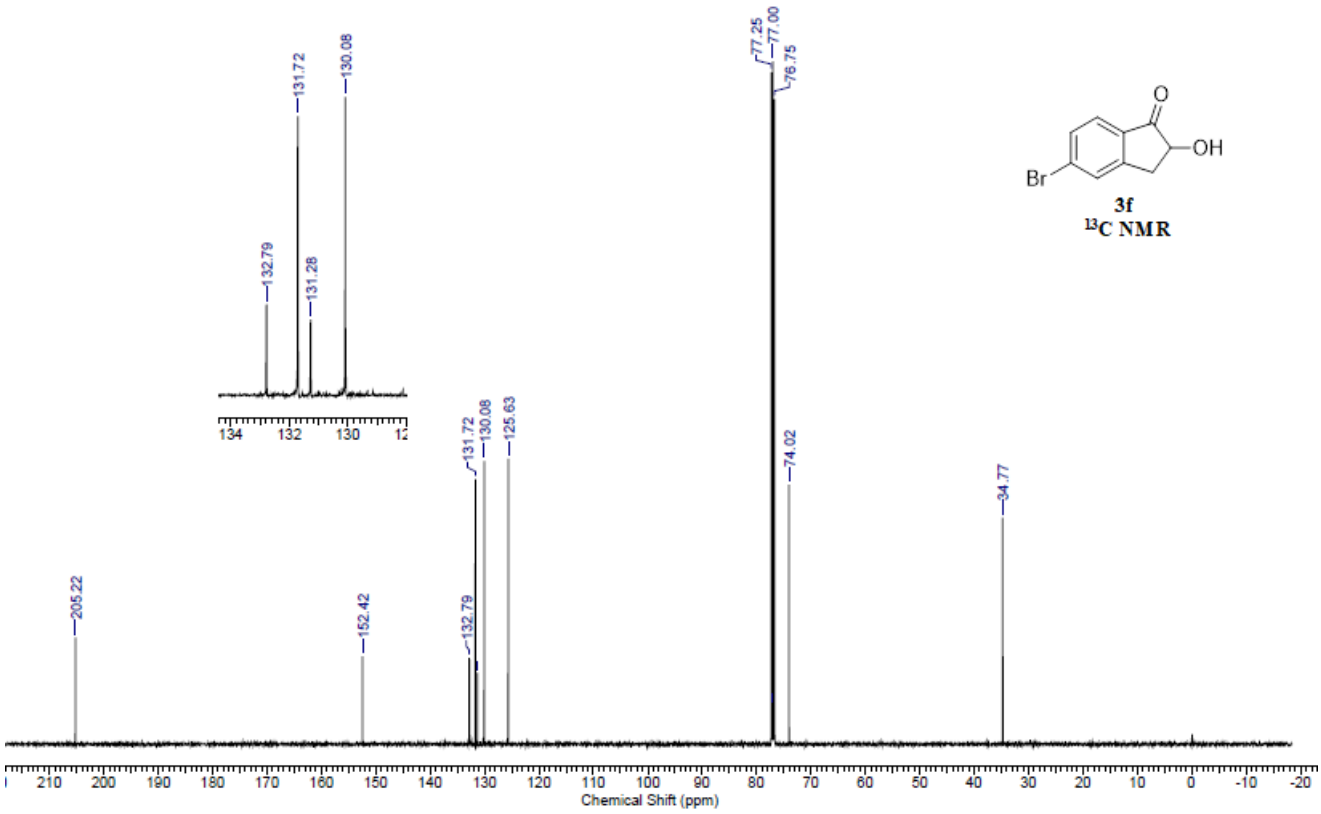

Me
OH
3d
¹H NMR
Chemical Shift (ppm)

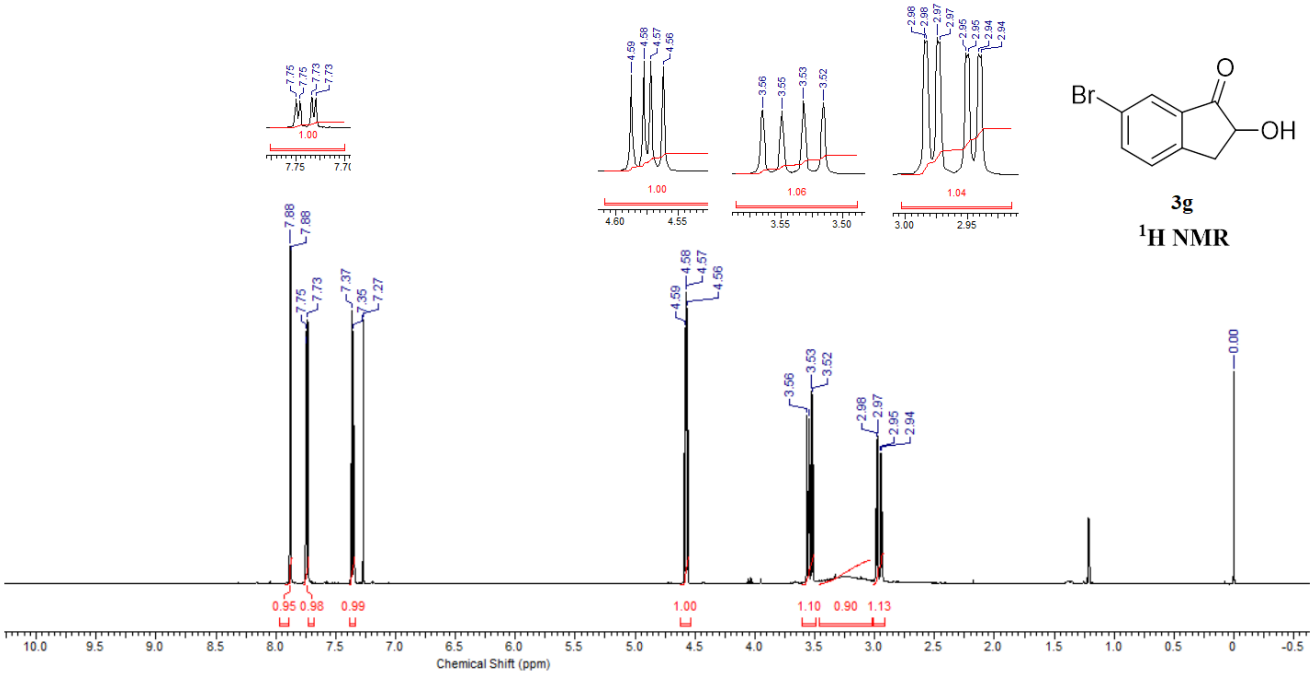

Me
OH
3d
¹³C NMR
Chemical Shift (ppm)

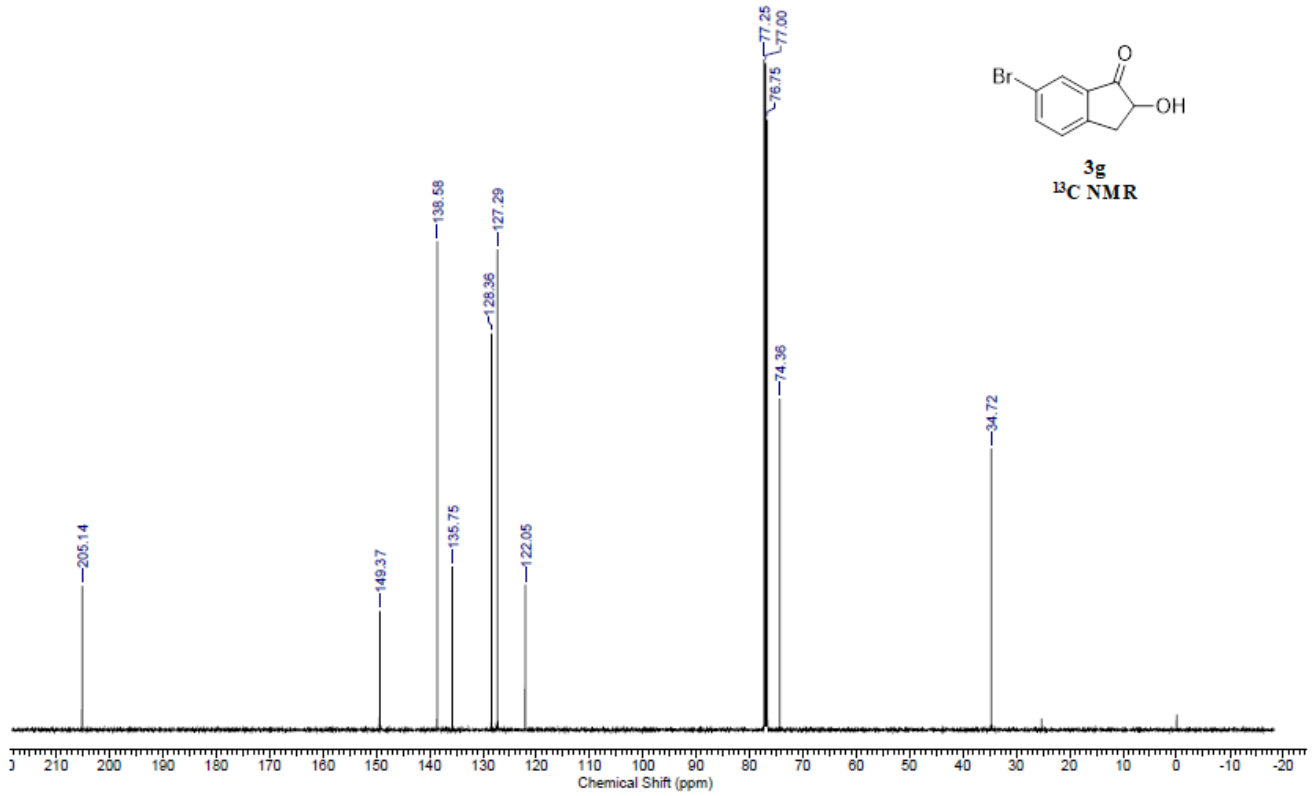

3e
1H NMR
Chemical Shift (ppm)

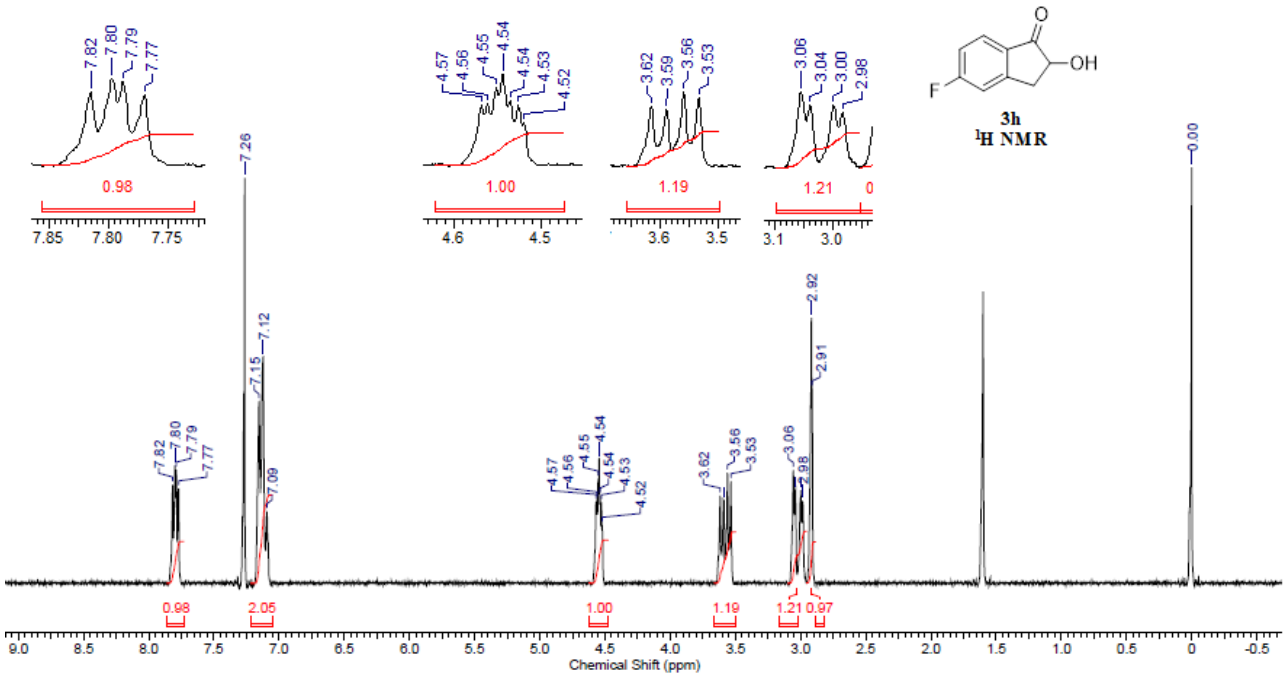

3e
13C NMR
Chemical Shift (ppm)

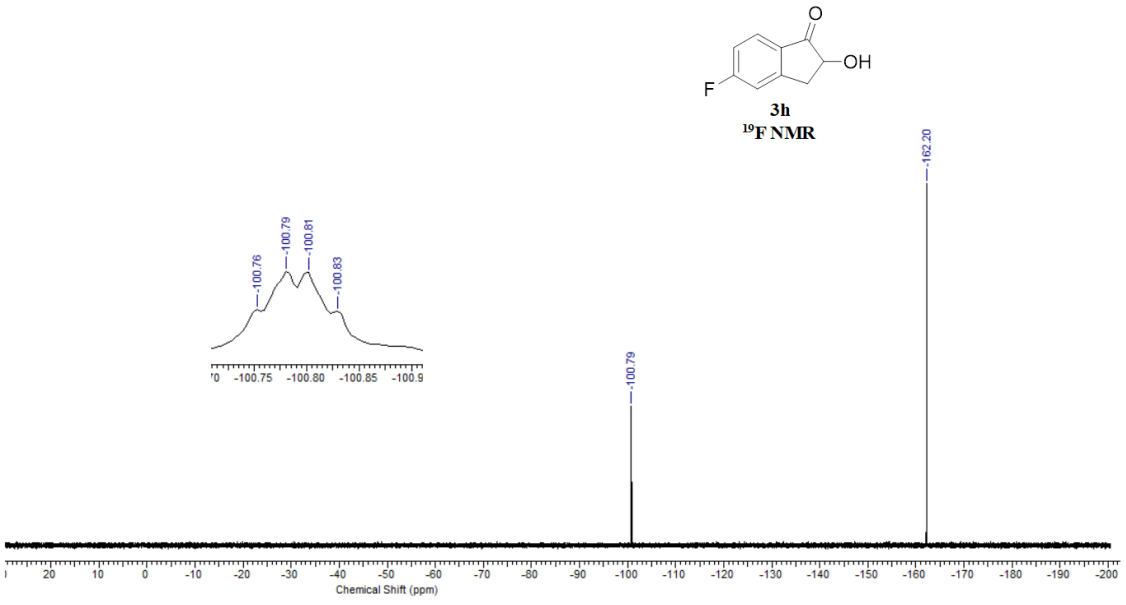

3f
1H NMR
Chemical Shift (ppm)

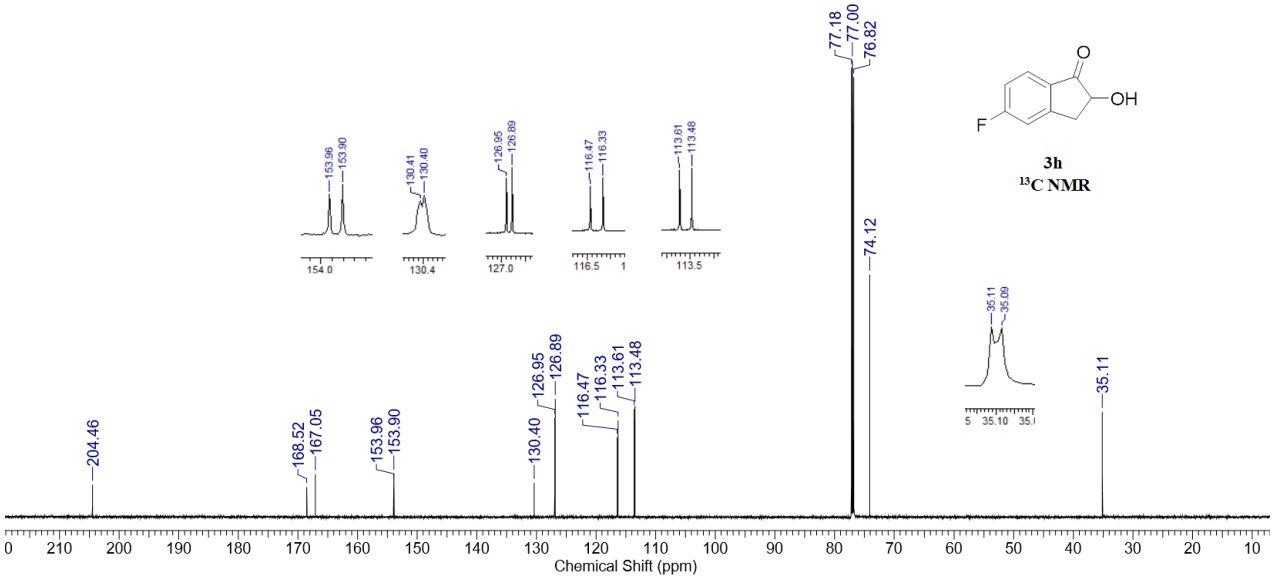

3f
13C NMR
Chemical Shift (ppm)

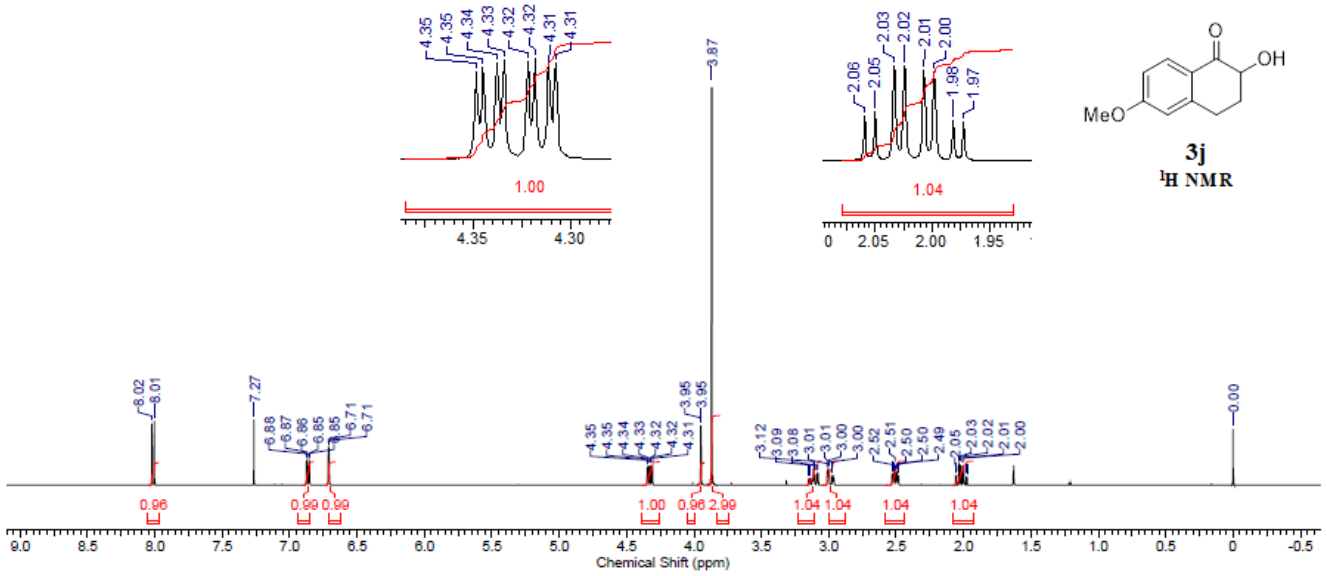

Br
O
OH
3g
1H NMR
Chemical Shift (ppm)

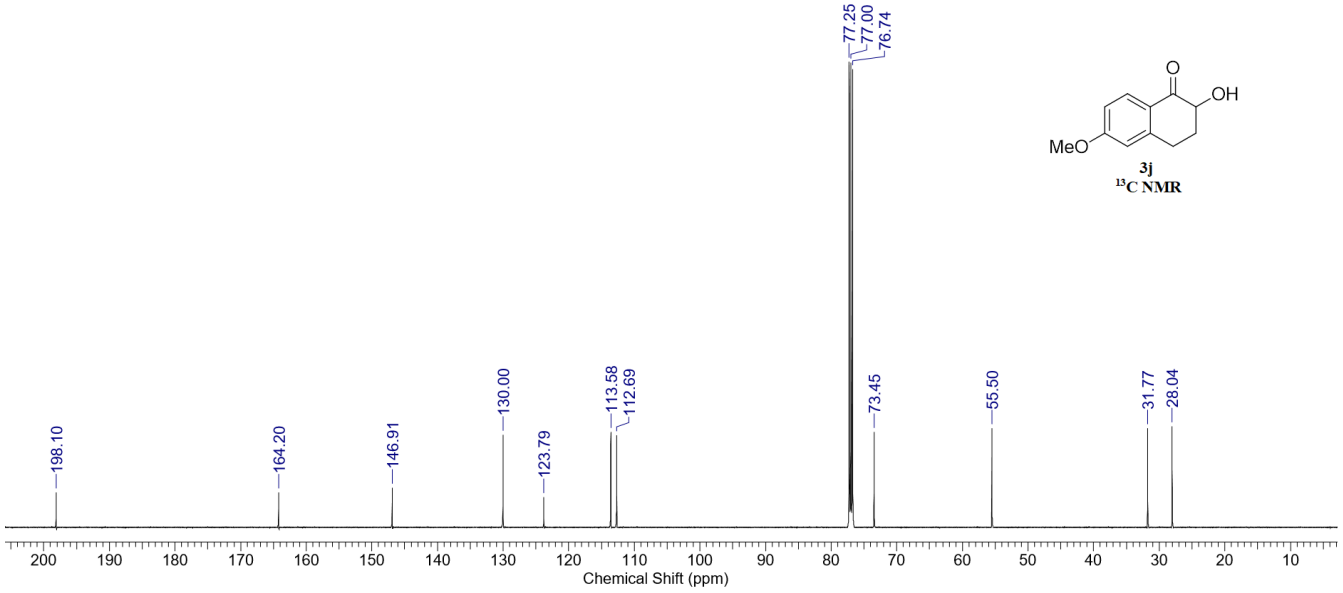

Br
O
OH
3g
13C NMR
Chemical Shift (ppm)

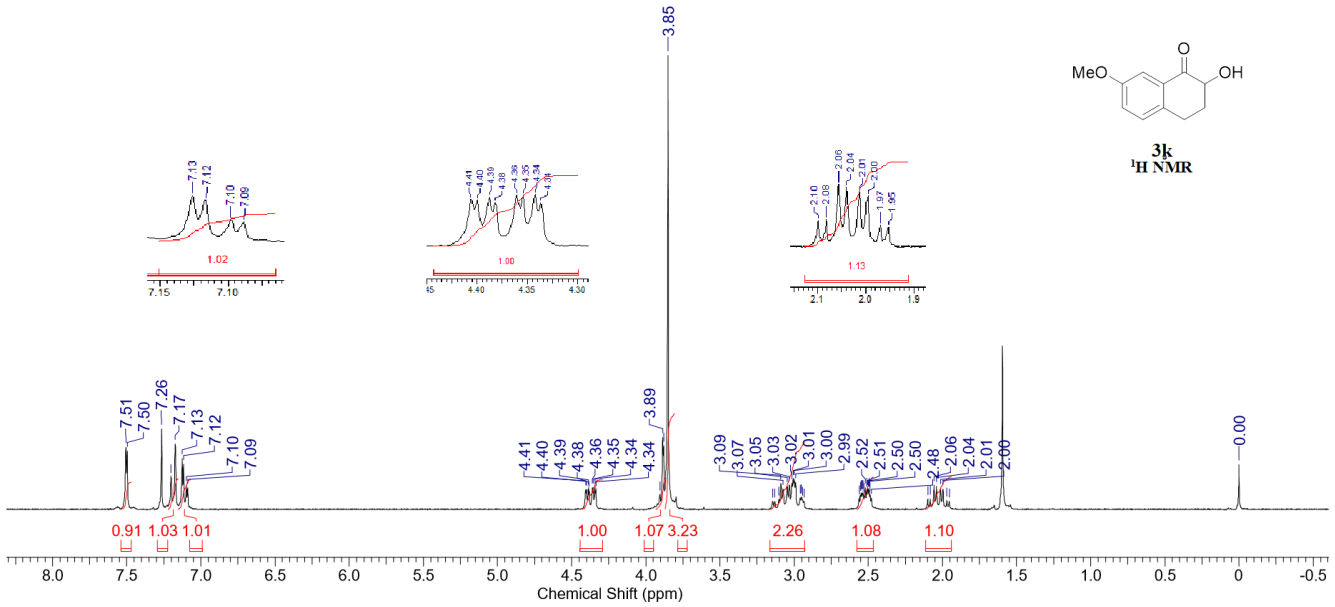

3h
1H NMR
Chemical Shift (ppm)


3h
19F NMR
Chemical Shift (ppm)

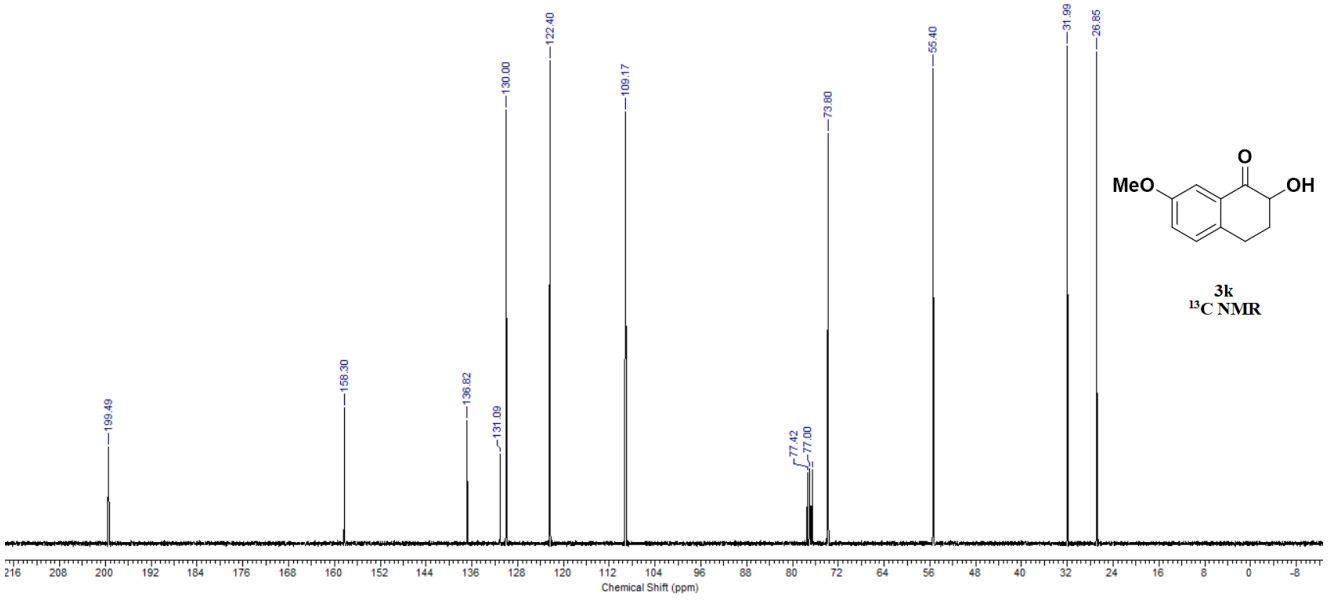

77.18
77.00
76.82
74.12
204.46
168.52
167.05
153.96
153.90
130.40
126.95
126.89
116.47
116.33
113.61
113.48
35.11
Chemical Shift (ppm)
3h
13C NMR


4.35
4.34
4.33
4.32
4.31
3.87
2.06
2.05
2.03
2.02
2.01
2.00
1.98
1.97
1.00
1.04
MeO
OH
3j
1H NMR
8.02
8.01
7.27
6.88
6.87
6.86
6.85
6.71
6.71
3.95
3.12
3.09
3.08
3.01
3.00
2.52
2.51
2.50
2.49
2.05
2.03
2.02
2.01
2.00
0.00
Chemical Shift (ppm)

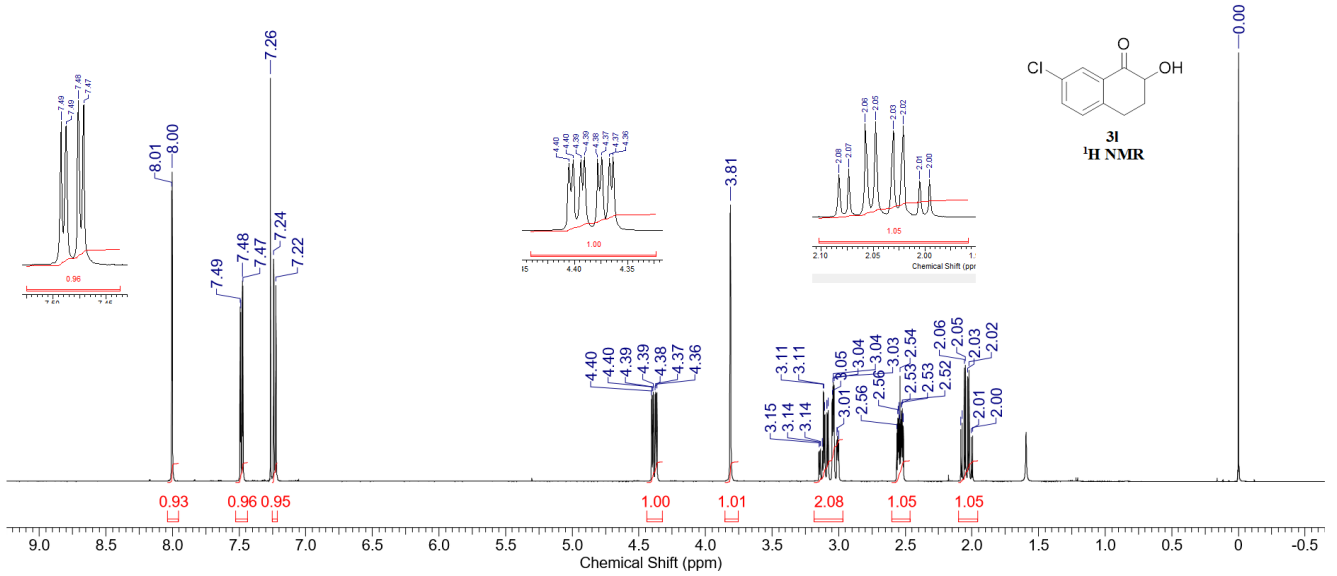

77.25
77.00
76.74
198.10
164.20
146.91
130.00
123.79
113.58
112.69
73.45
55.50
31.77
28.04
MeO
OH
3j
13C NMR
Chemical Shift (ppm)

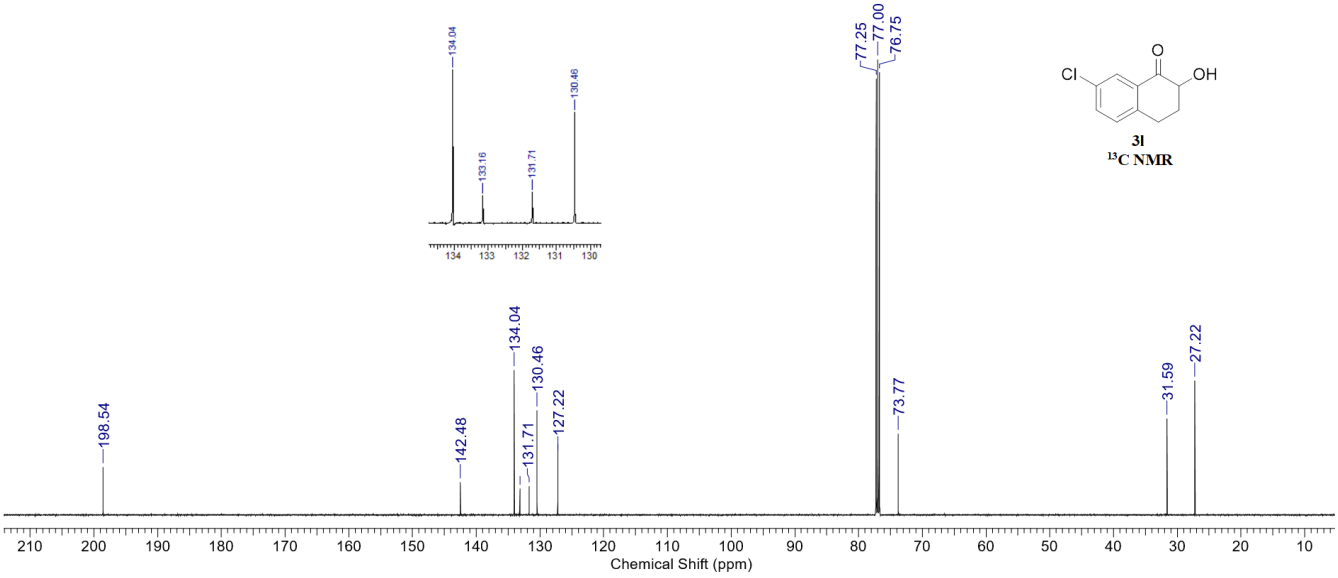


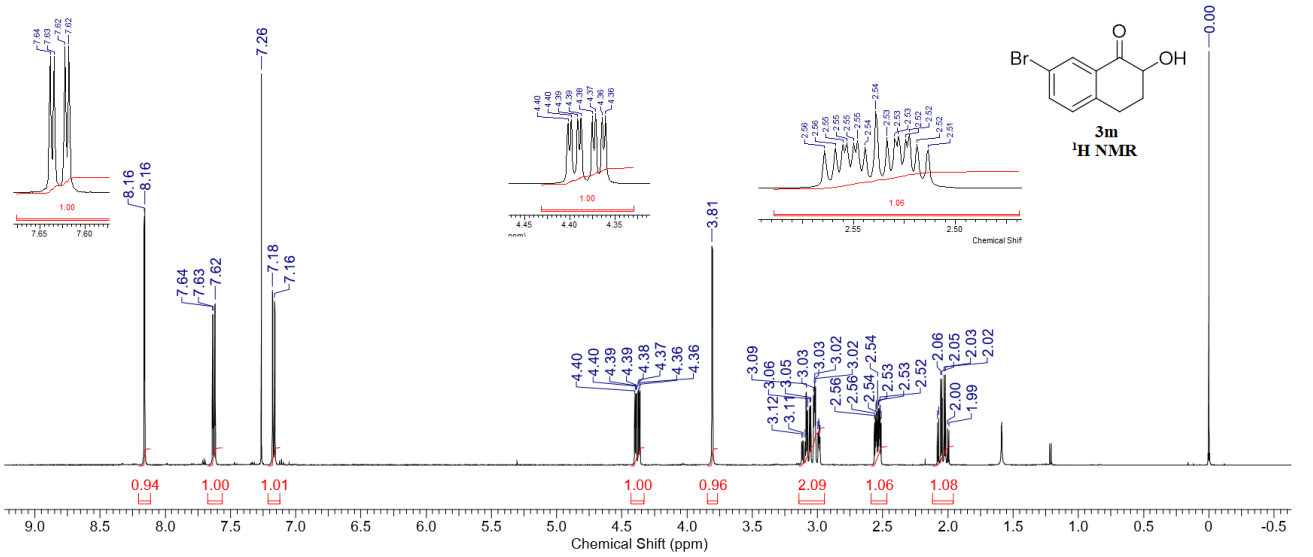
3k
^{1}H NMR

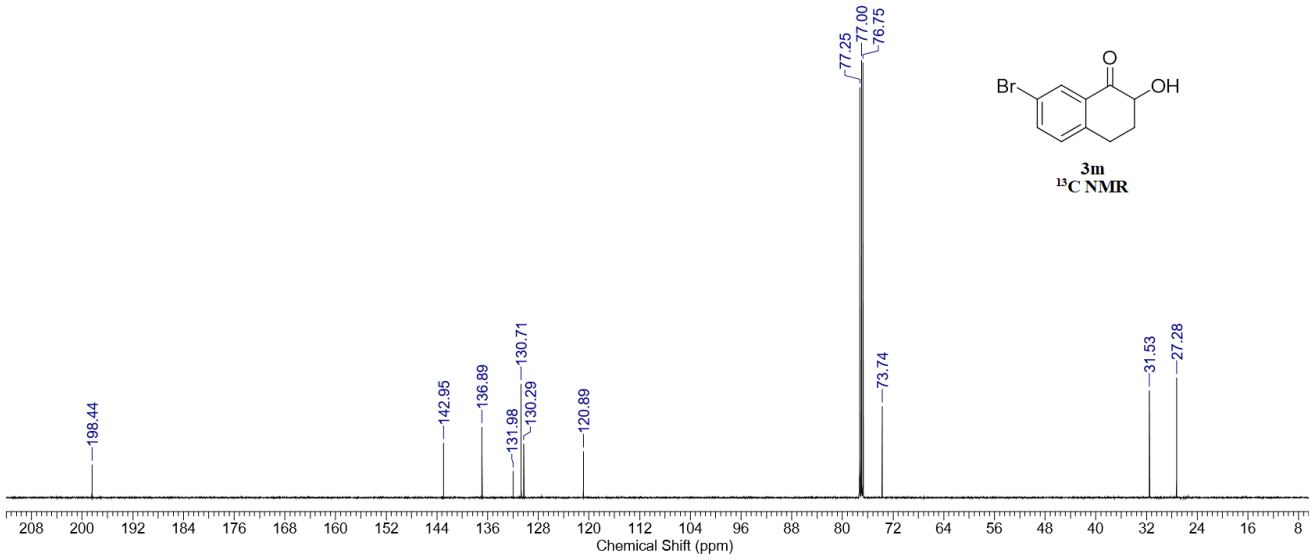


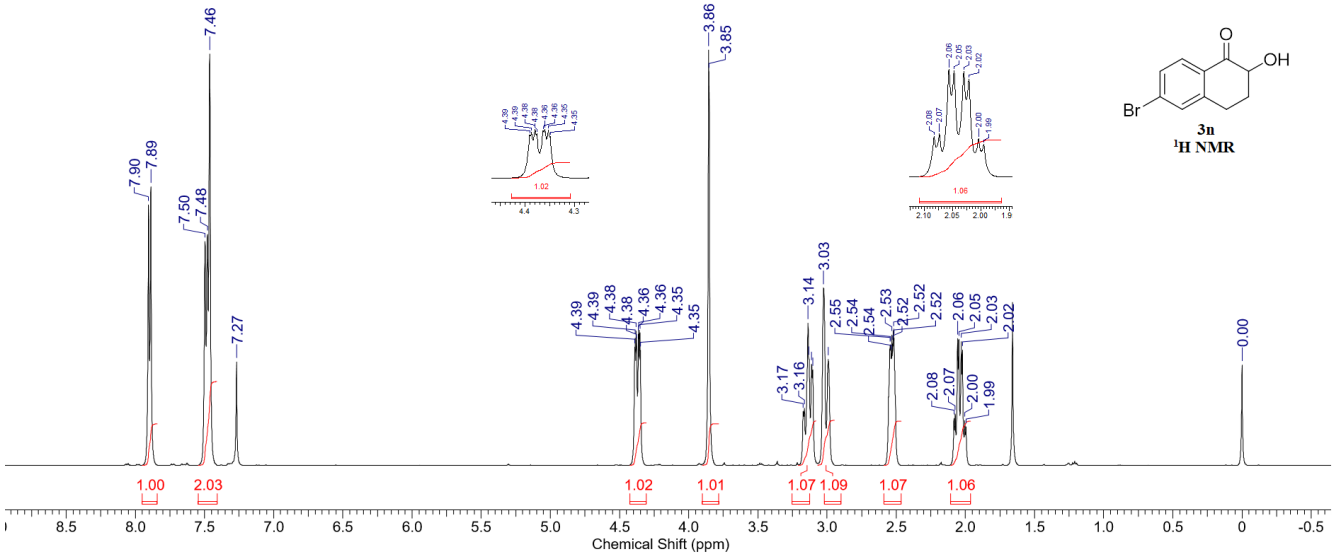
3k
^{13}C NMR

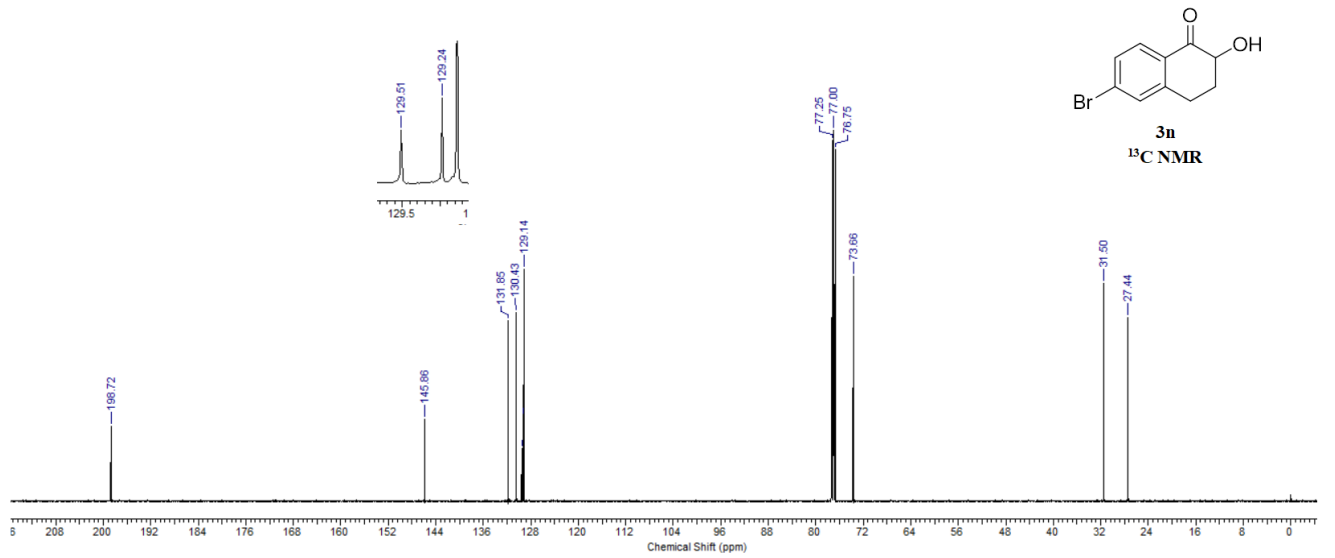

Cl
O
OH
3l
^{1}H NMR
Chemical Shift (ppm)

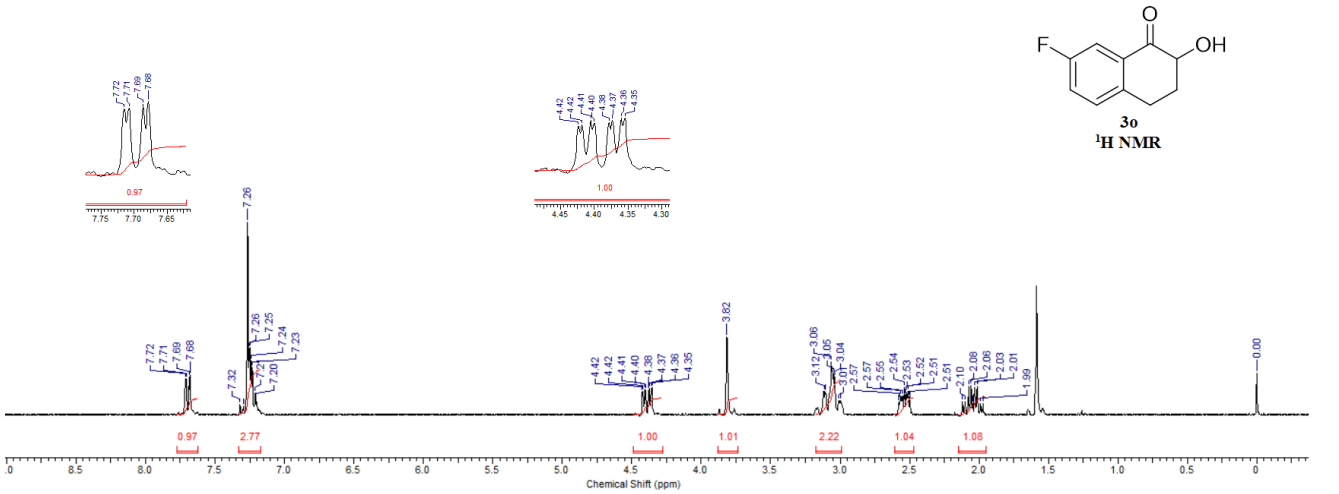

Cl
O
OH
3l
^{13}C NMR
Chemical Shift (ppm)

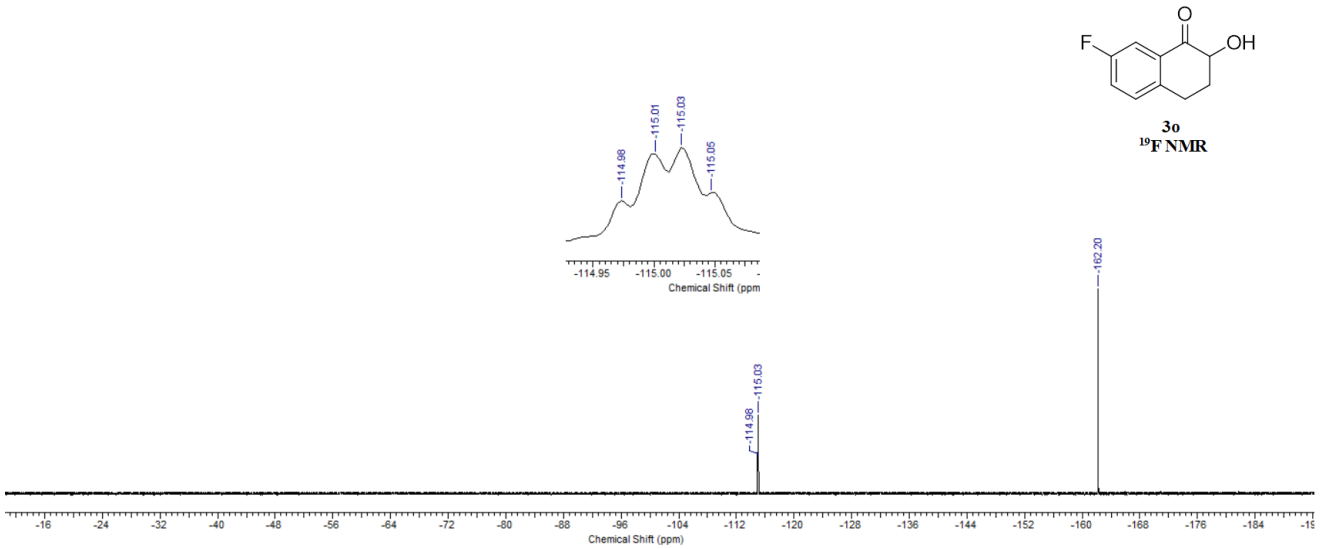

3m
1H NMR
Chemical Shift (ppm)

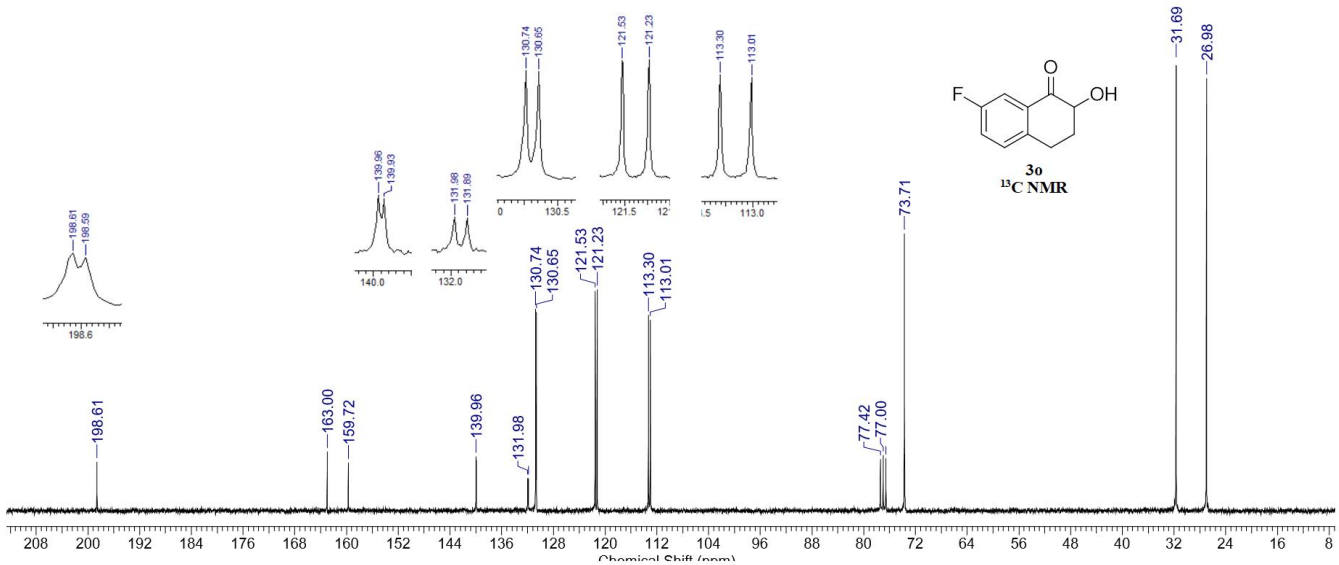

3m
13C NMR
Chemical Shift (ppm)

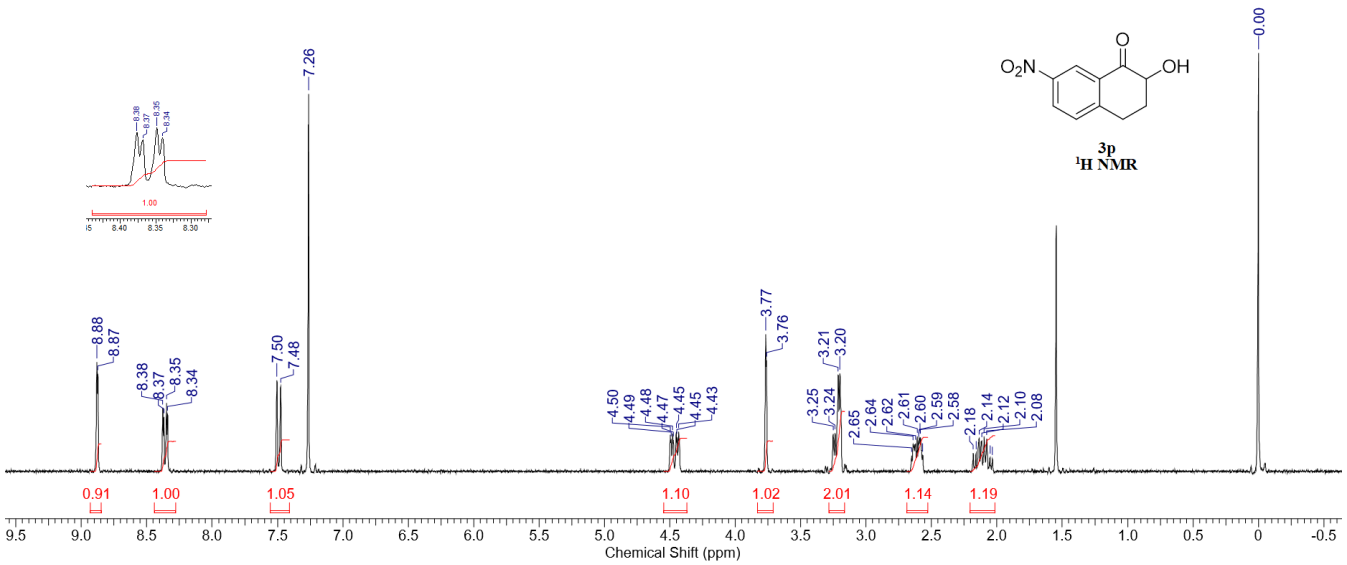

7.90
7.89
7.50
7.48
7.46
7.27
4.39
4.38
4.36
4.35
3.86
3.85
3.17
3.16
3.14
3.03
2.55
2.54
2.53
2.52
2.08
2.07
2.06
2.05
2.03
2.02
2.00
1.99
0.00
1.00
2.03
1.02
1.01
1.07
1.09
1.07
1.06
Chemical Shift (ppm)
O
OH
Br
3n
1H NMR

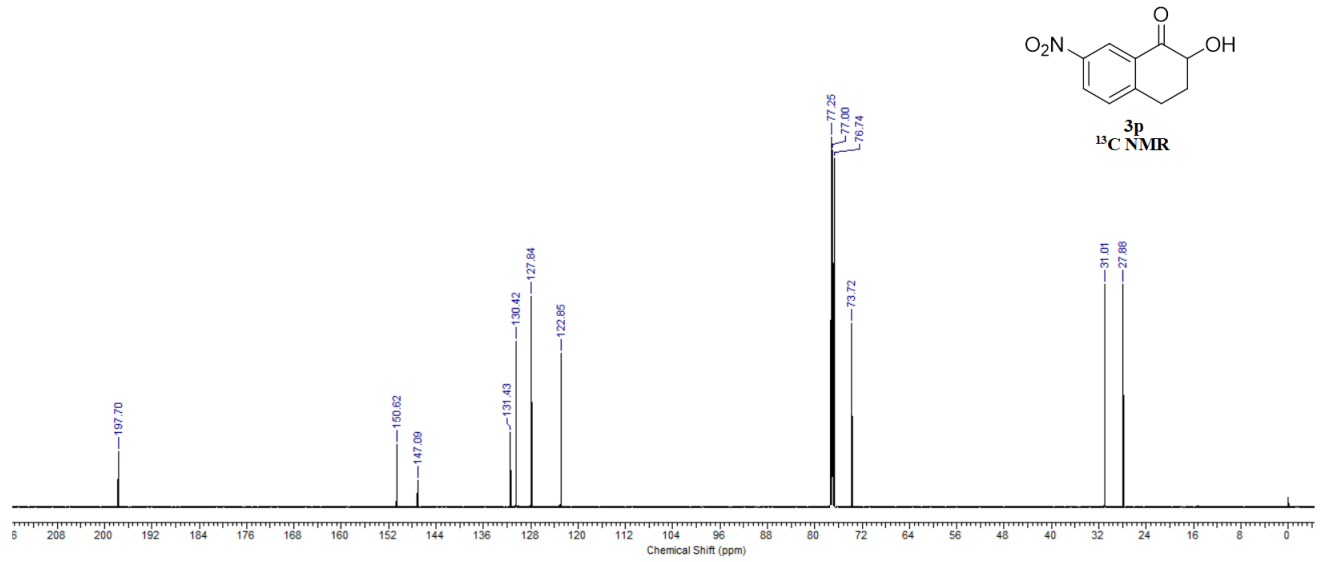

129.51
129.24
198.72
145.86
131.85
130.43
129.14
77.25
77.00
76.75
73.66
31.50
27.44
Chemical Shift (ppm)
O
OH
Br
3n
13C NMR

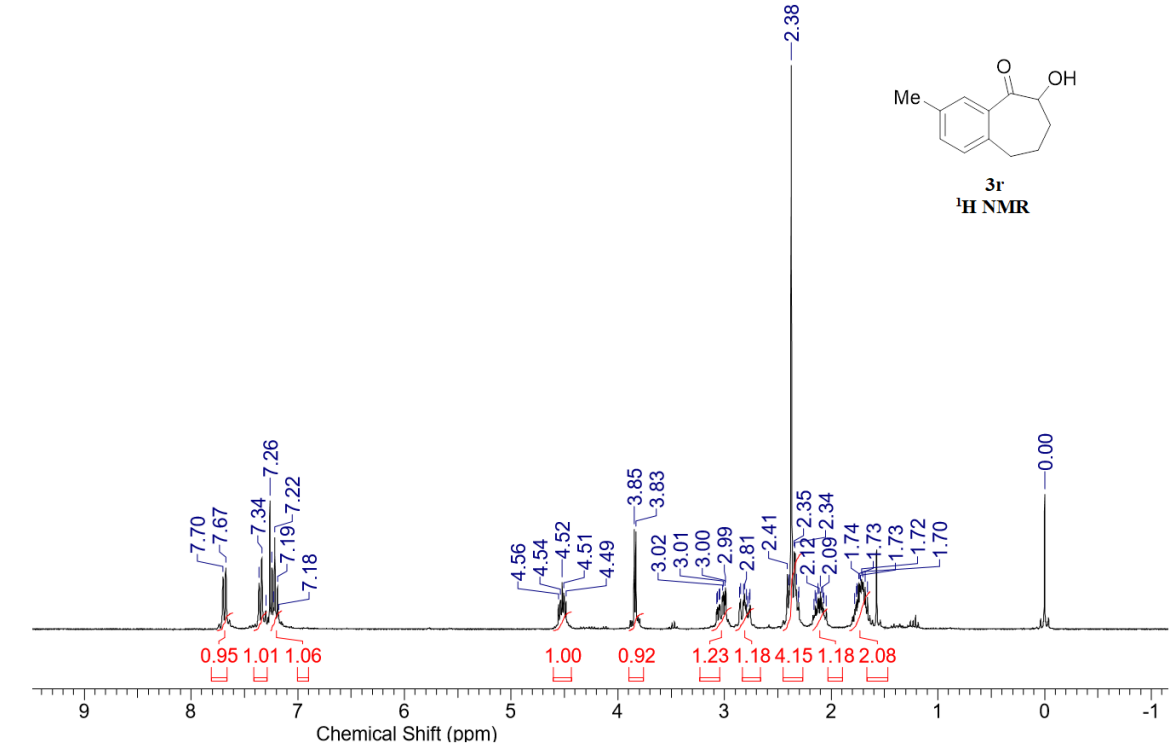

F
O
OH
3o
1H NMR
Chemical Shift (ppm)

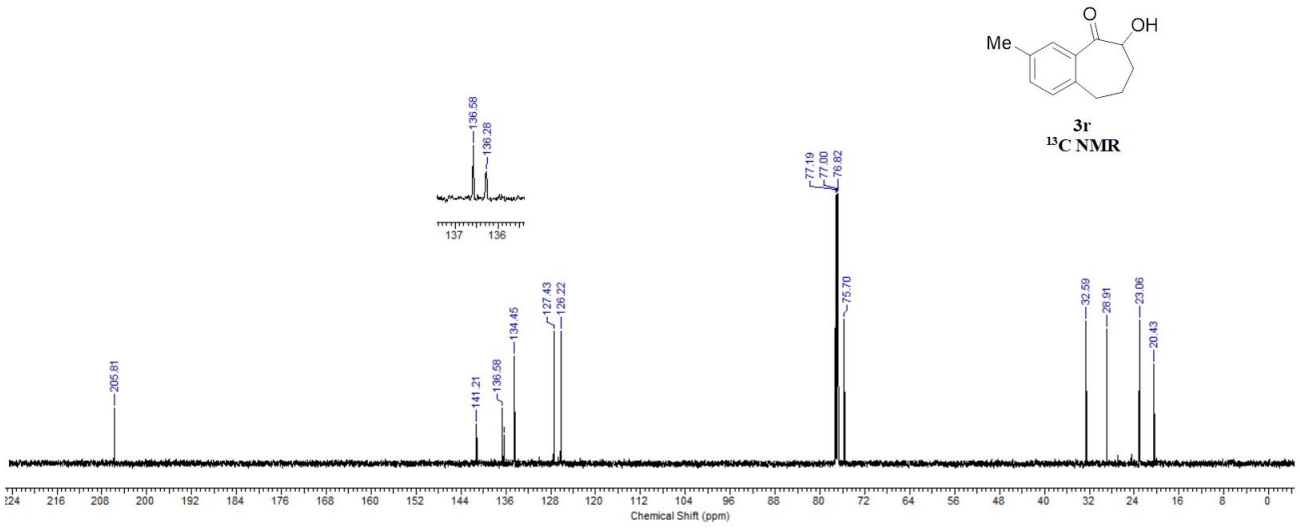

F
O
OH
3o
19F NMR
Chemical Shift (ppm)

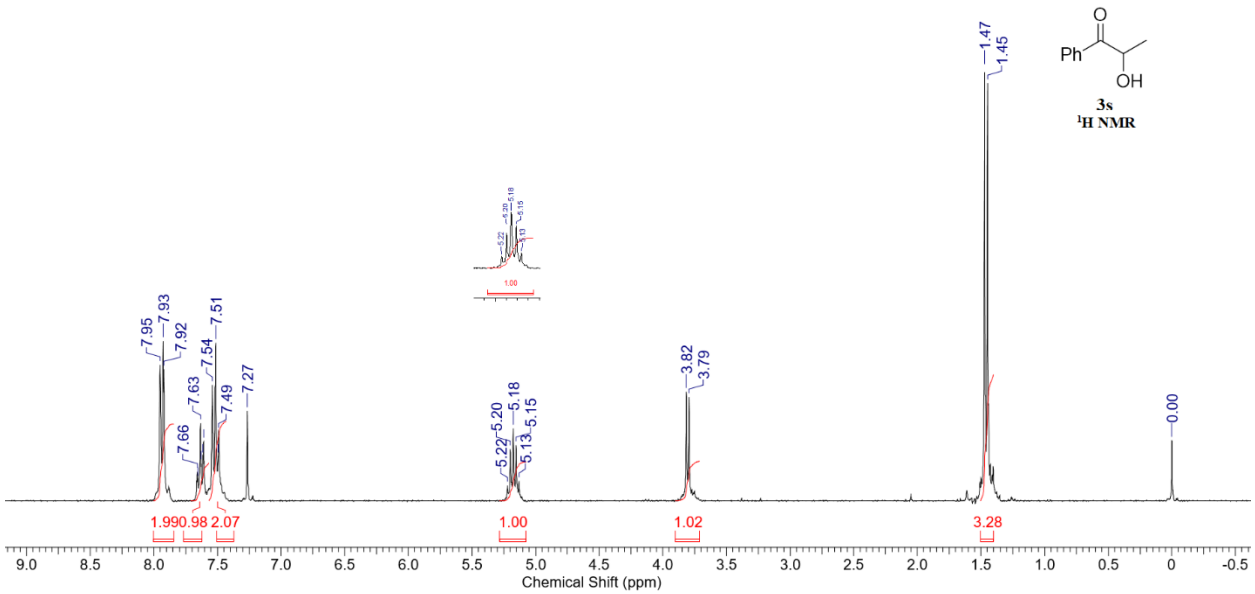

F
O
OH
3o
13C NMR
Chemical Shift (ppm)

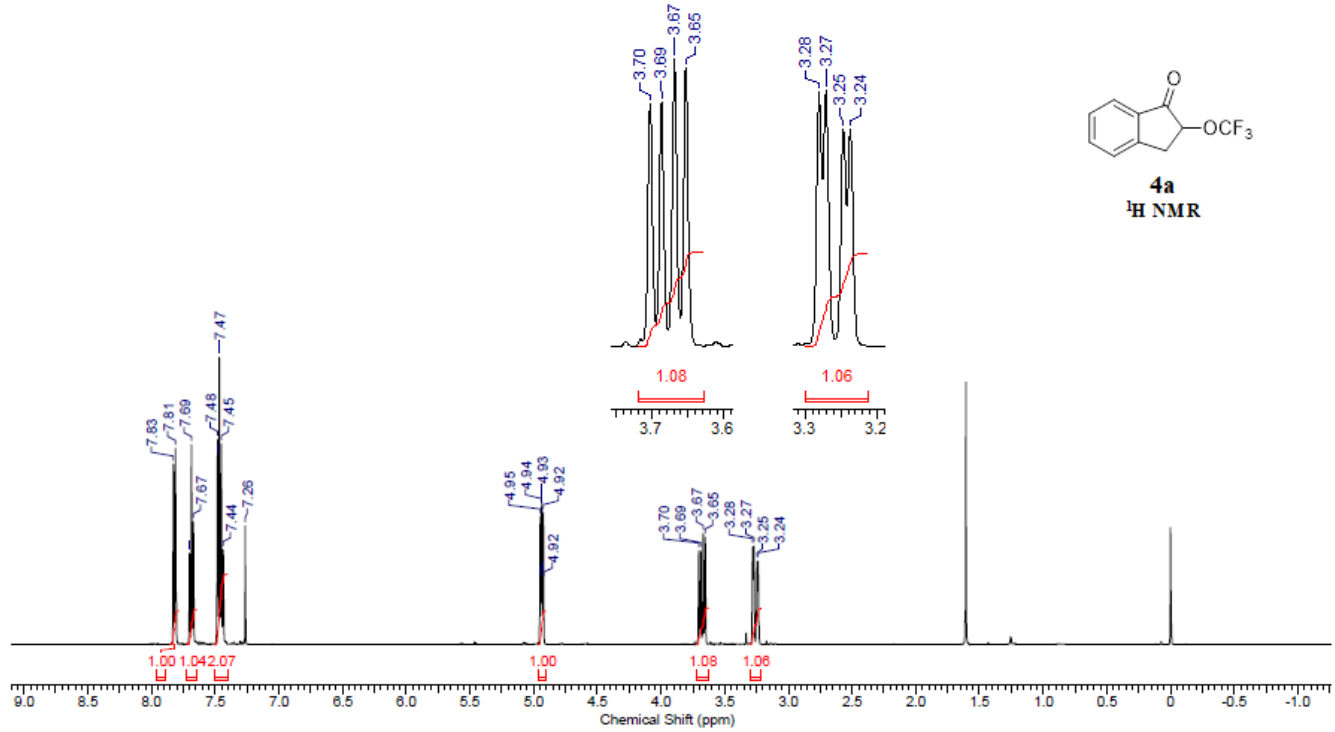

O2N
O
OH
3p
1H NMR
Chemical Shift (ppm)

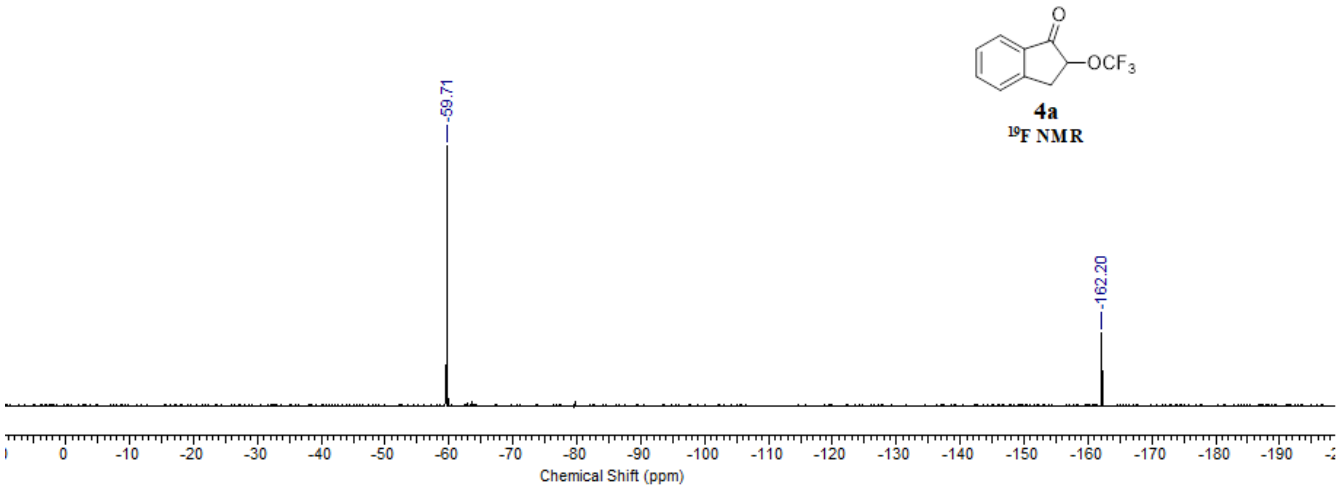

O2N
O
OH
3p
13C NMR
Chemical Shift (ppm)


2.38
O
OH
Me
3r
1H NMR
7.70
7.67
7.34
7.26
7.22
7.19
7.18
4.56
4.54
4.52
4.51
4.49
3.85
3.83
3.02
3.01
3.00
2.99
2.81
2.41
2.35
2.12
2.09
2.34
1.74
1.73
1.72
1.70
0.00
0.95 1.01 1.06
1.00
0.92
1.23 1.18 4.15 1.18 2.08
Chemical Shift (ppm)


O
OH
Me
3r
13C NMR
136.58
136.28
77.19
77.00
76.82
205.81
141.21
136.58
134.45
127.43
126.22
75.70
32.59
28.91
23.06
20.43
Chemical Shift (ppm)

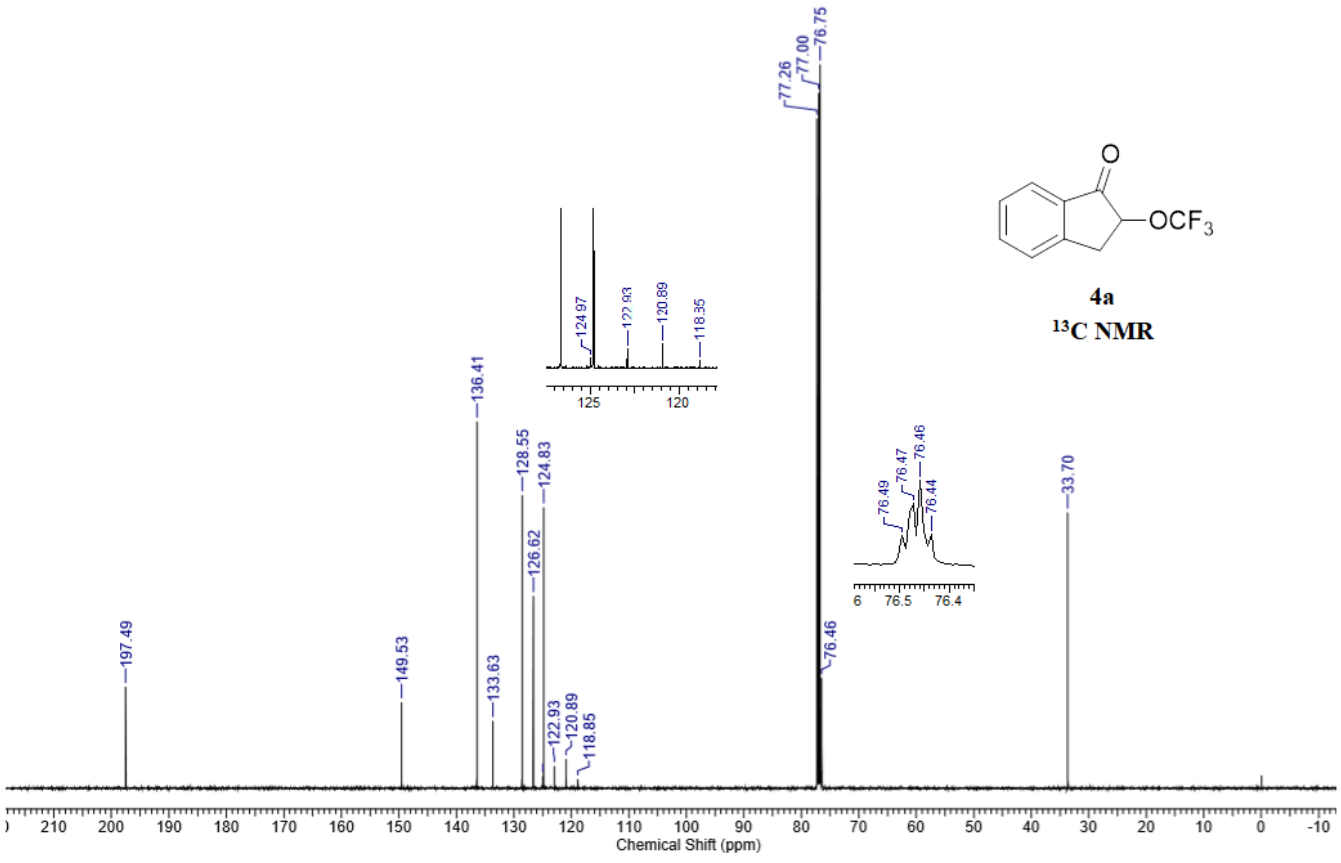

Ph
O
OH
3s
¹H NMR
Chemical Shift (ppm)


OCF3
O
4a
¹H NMR
Chemical Shift (ppm)



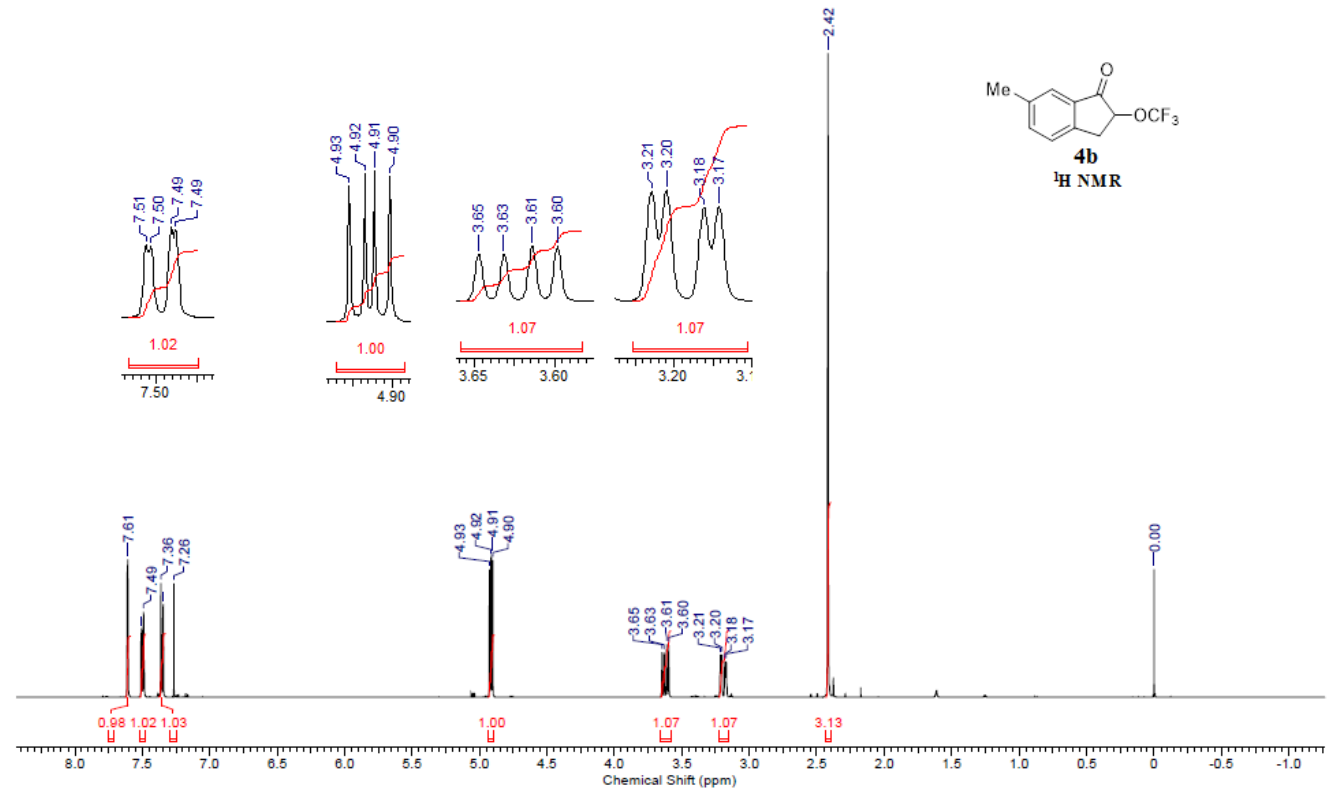
4a

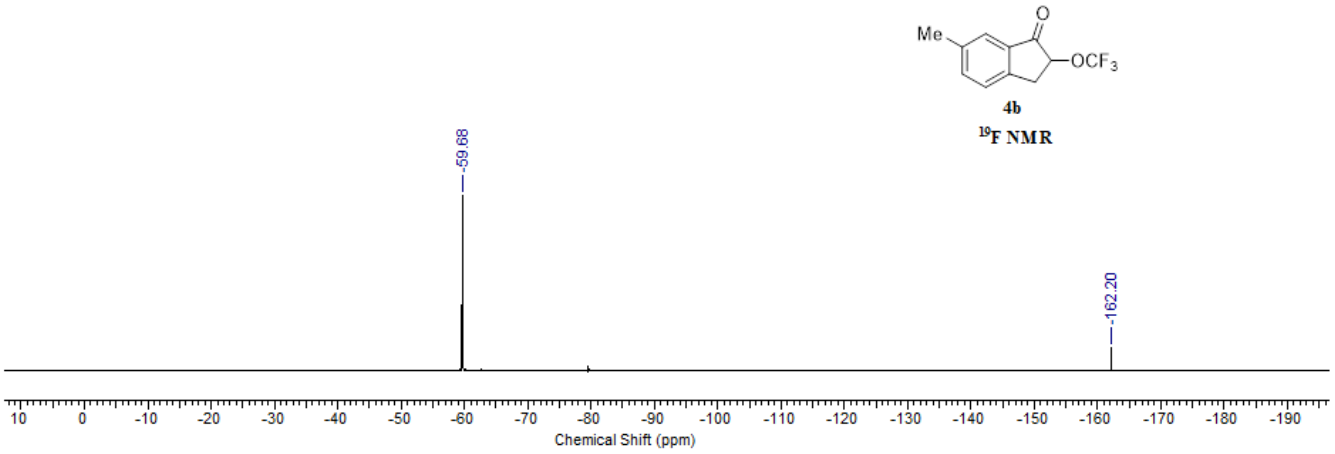
^{19}F NMR

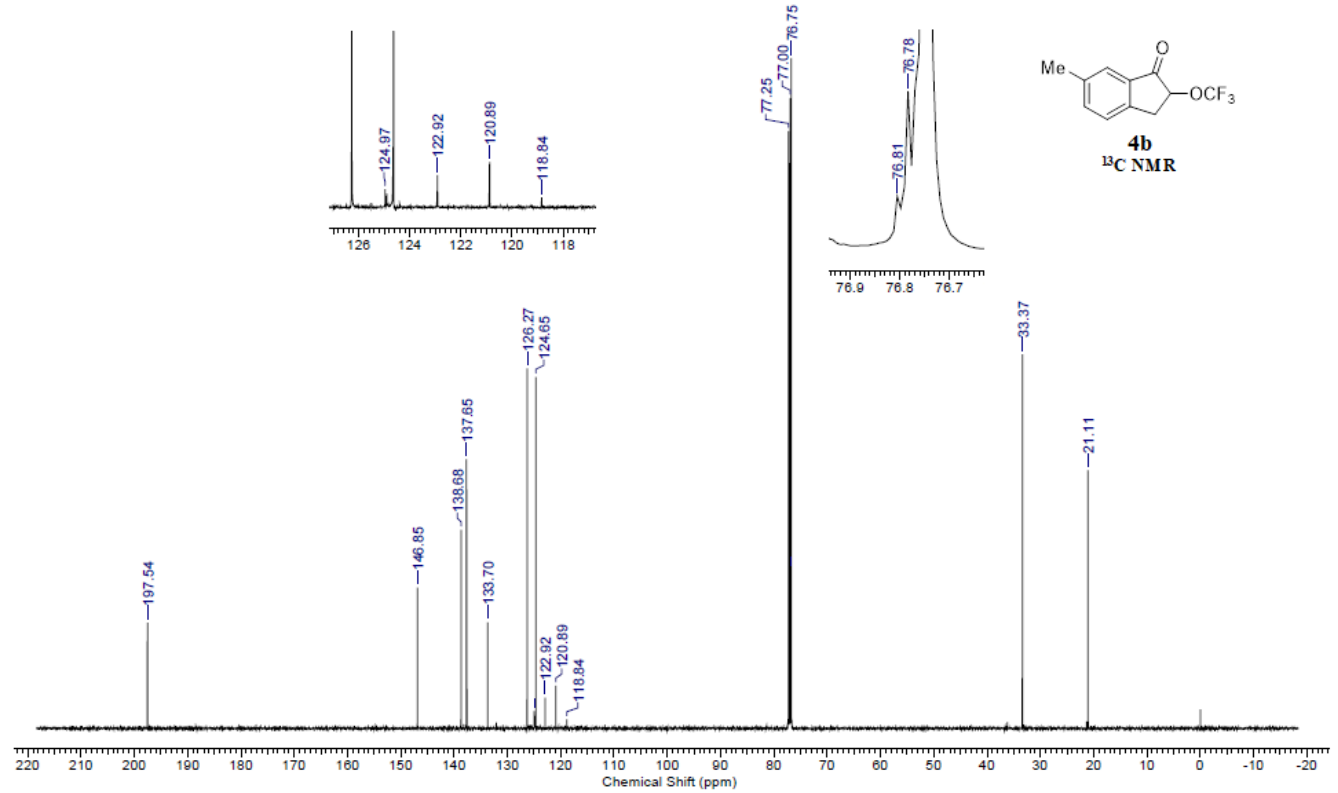


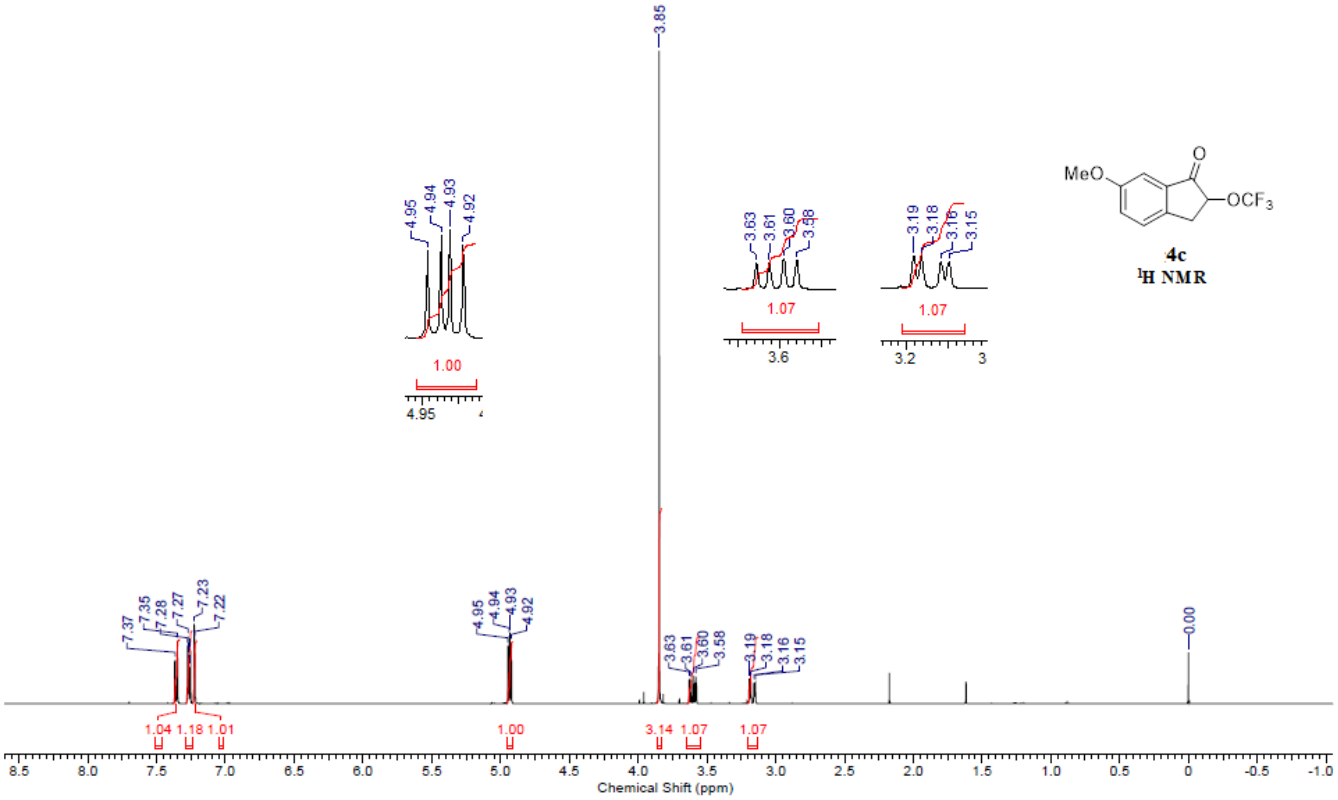
4a

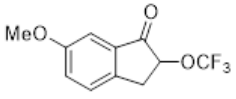
^{13}C NMR


Me
O
OCF3
4b
1H NMR
Chemical Shift (ppm)


Me
O
OCF3
4b
19F NMR
Chemical Shift (ppm)

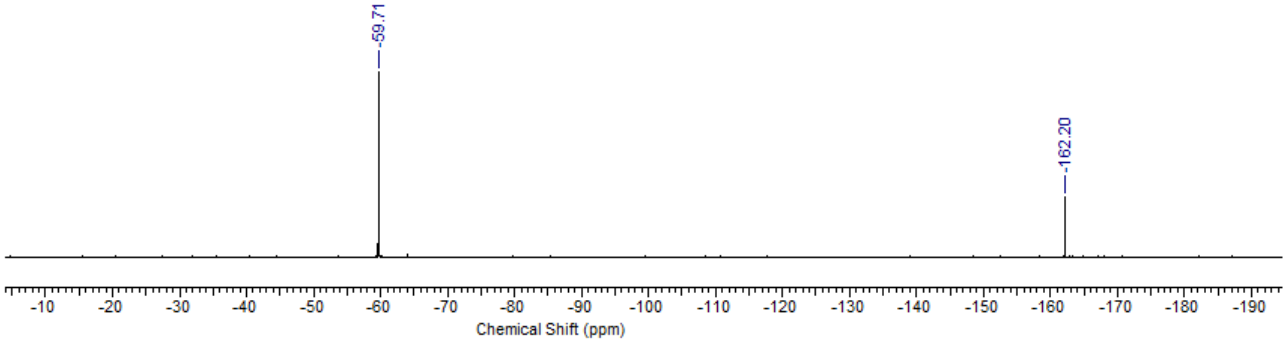

Me
O
OCF3
4b
13C NMR
Chemical Shift (ppm)

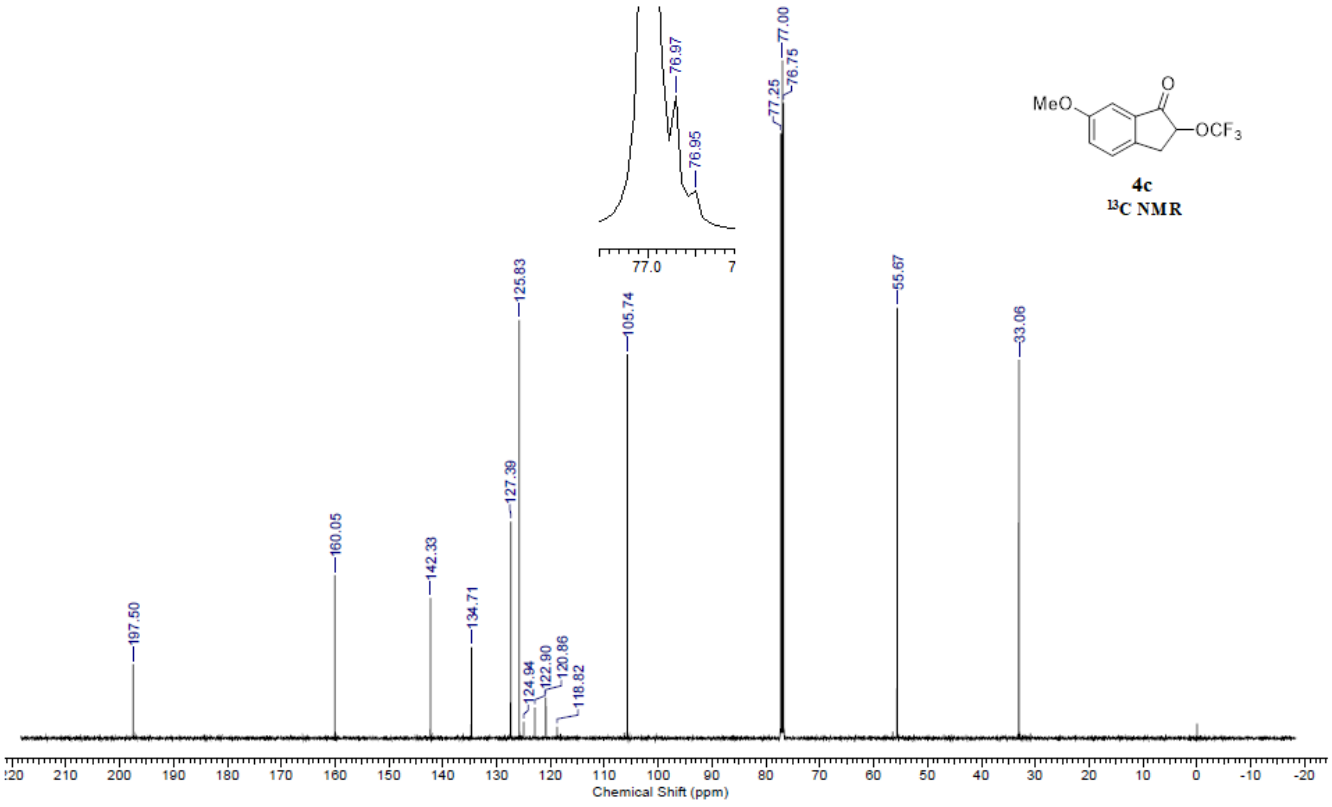

MeO
O
OCF3
4c
1H NMR
Chemical Shift (ppm)



4c

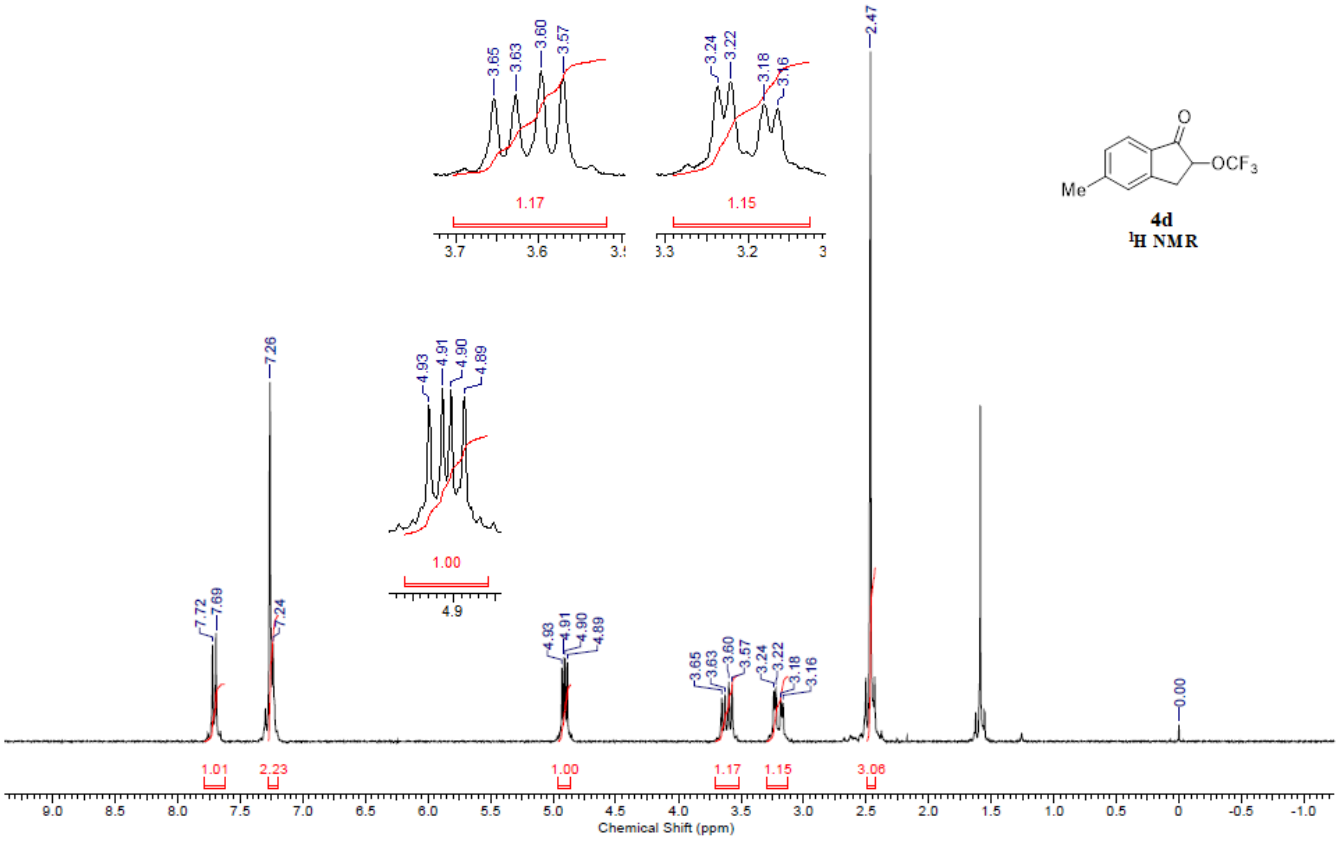
^{19}F NMR

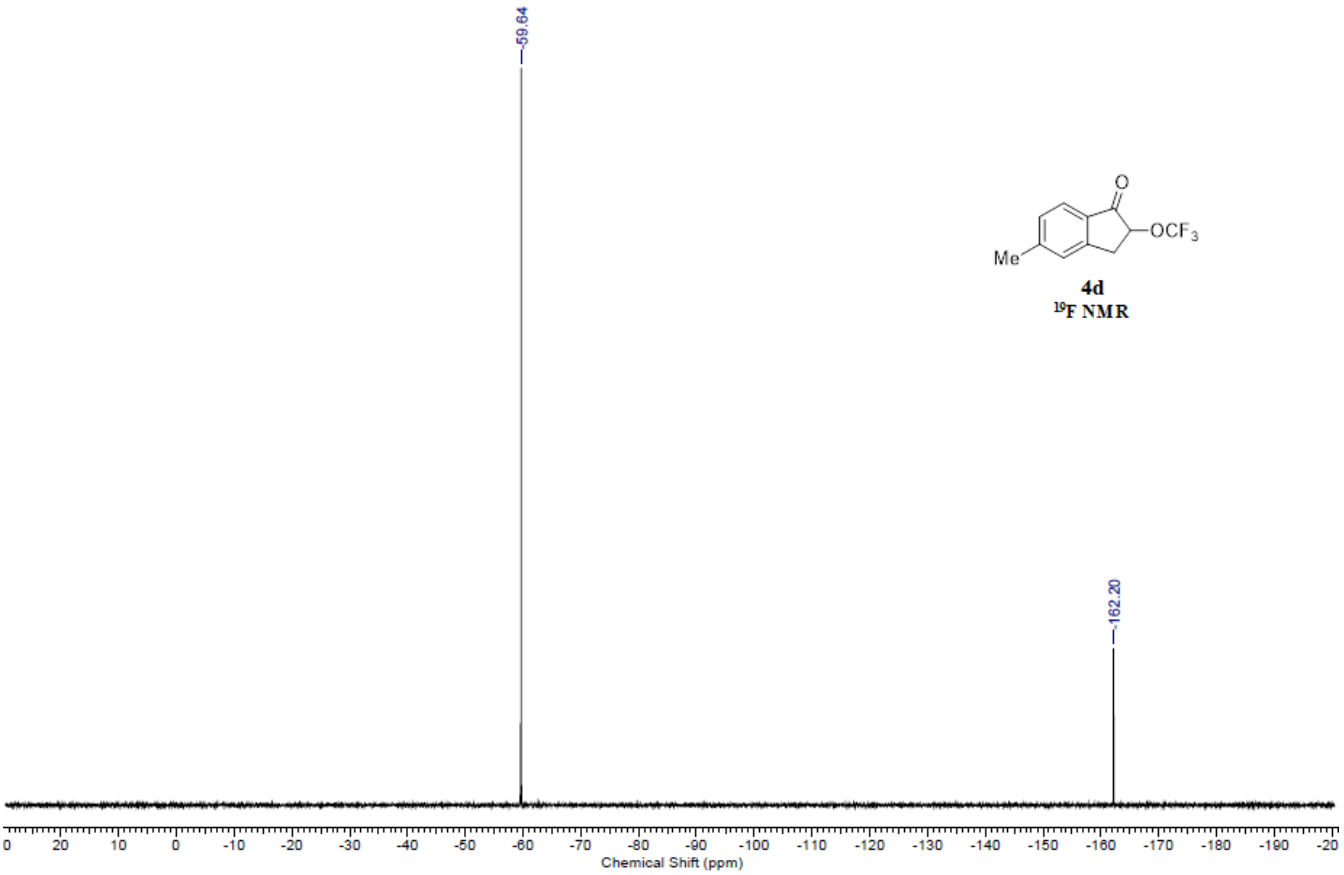


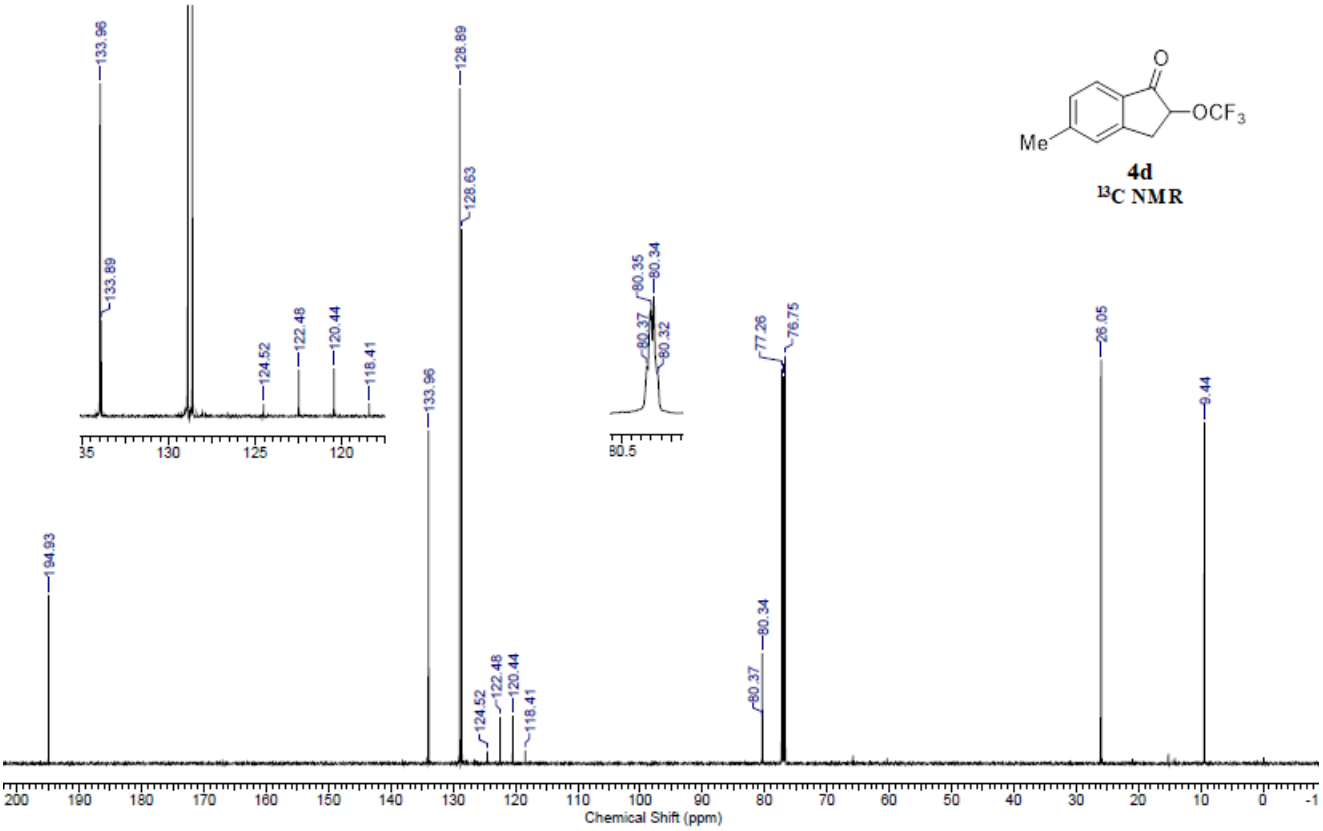


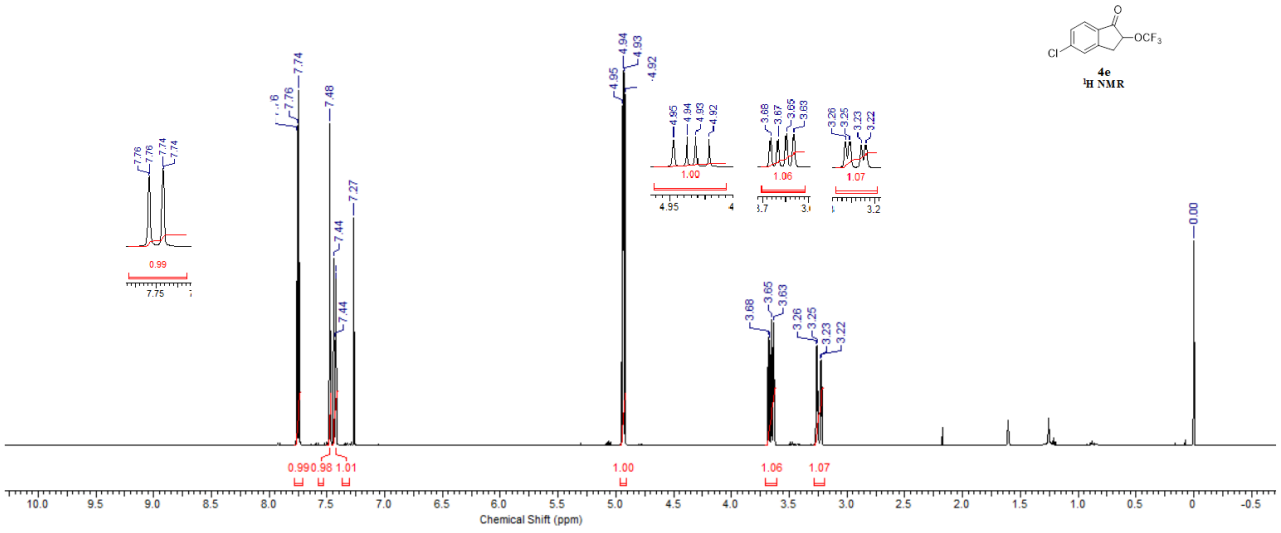
4c

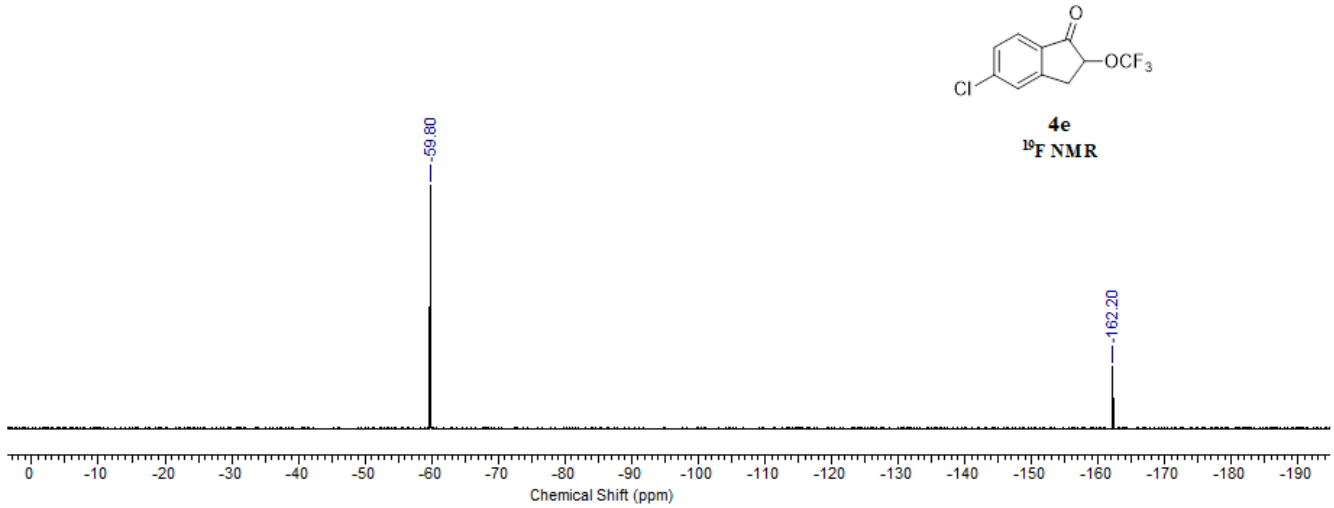
^{13}C NMR

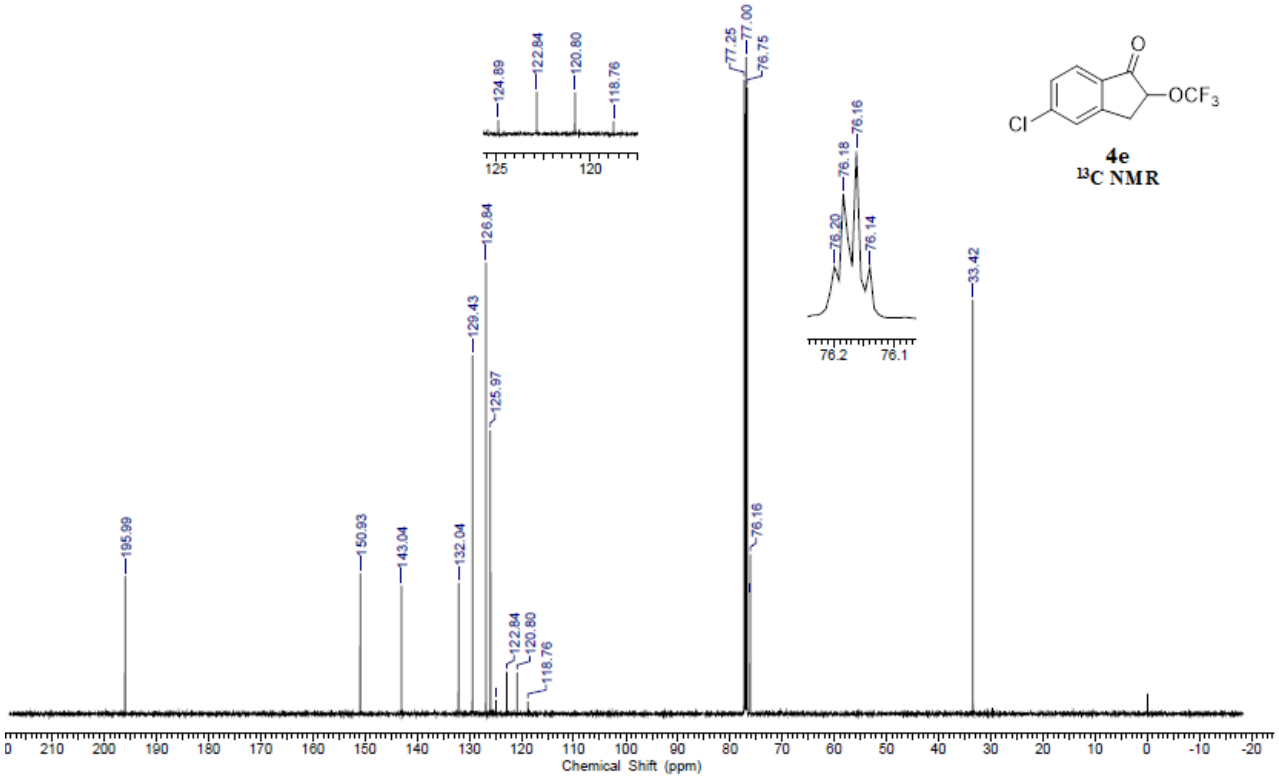

3.65
3.63
3.60
3.57
3.24
3.22
3.18
3.16
2.47
1.17
1.15
7.26
4.93
4.91
4.90
4.89
1.00
7.72
7.69
7.24
0.00
1.01
2.23
3.06
Chemical Shift (ppm)
O
OCF3
Me
4d
1H NMR

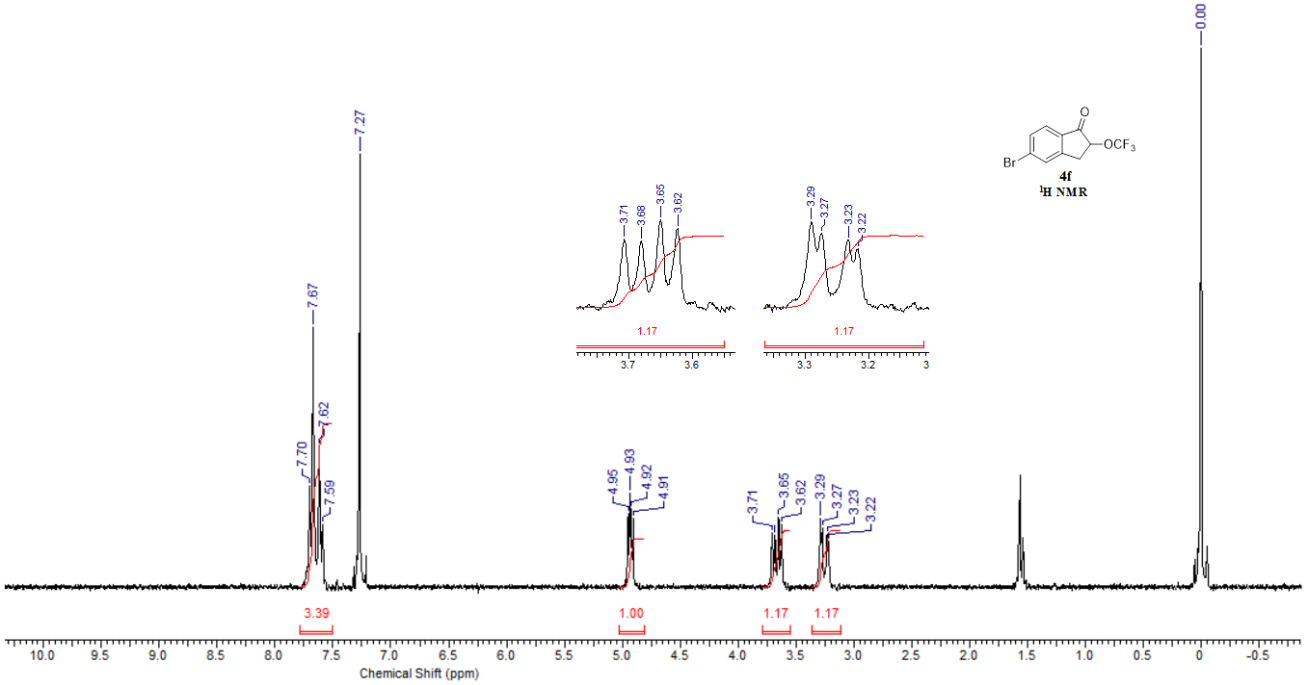

-59.64
-162.20
Chemical Shift (ppm)
O
OCF3
Me
4d
19F NMR

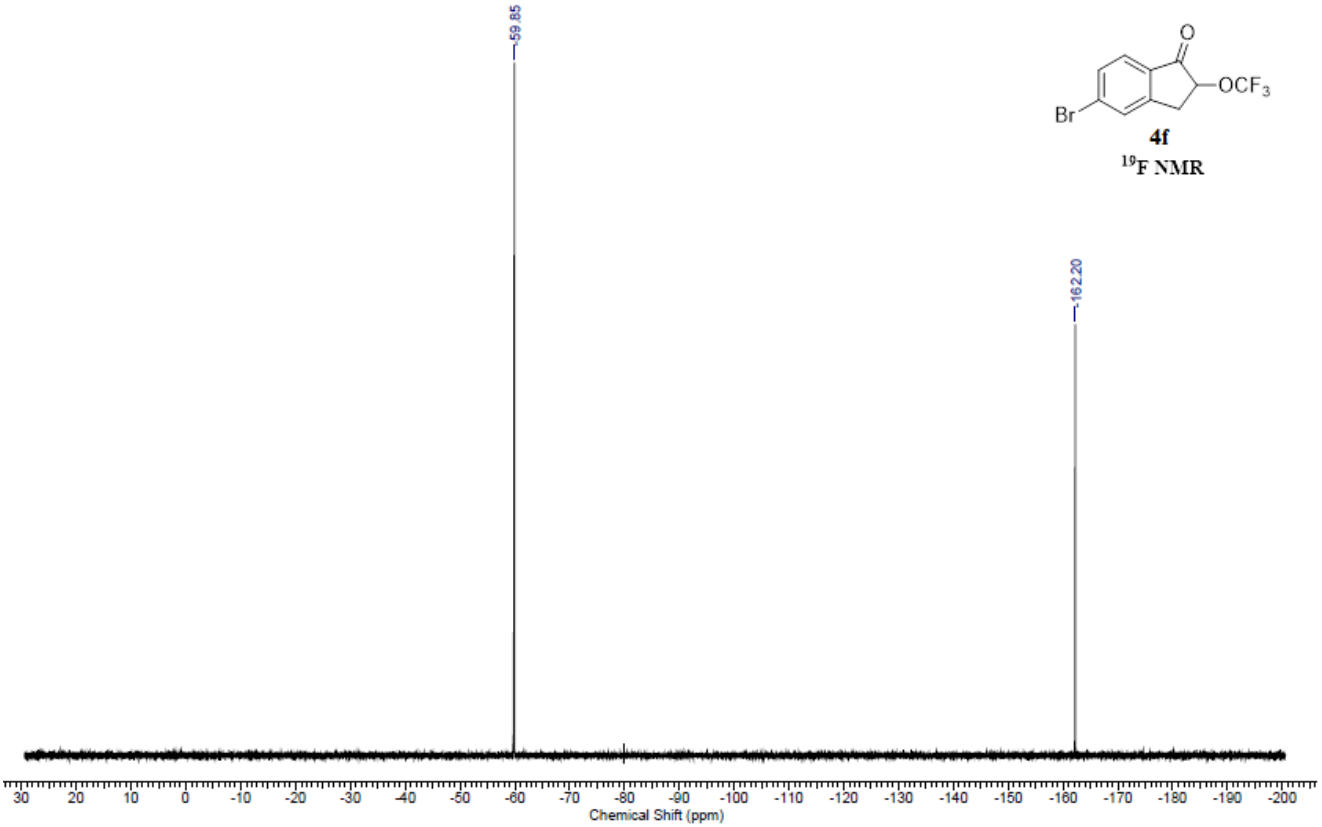

Me
OCF3
4d
13C NMR
Chemical Shift (ppm)

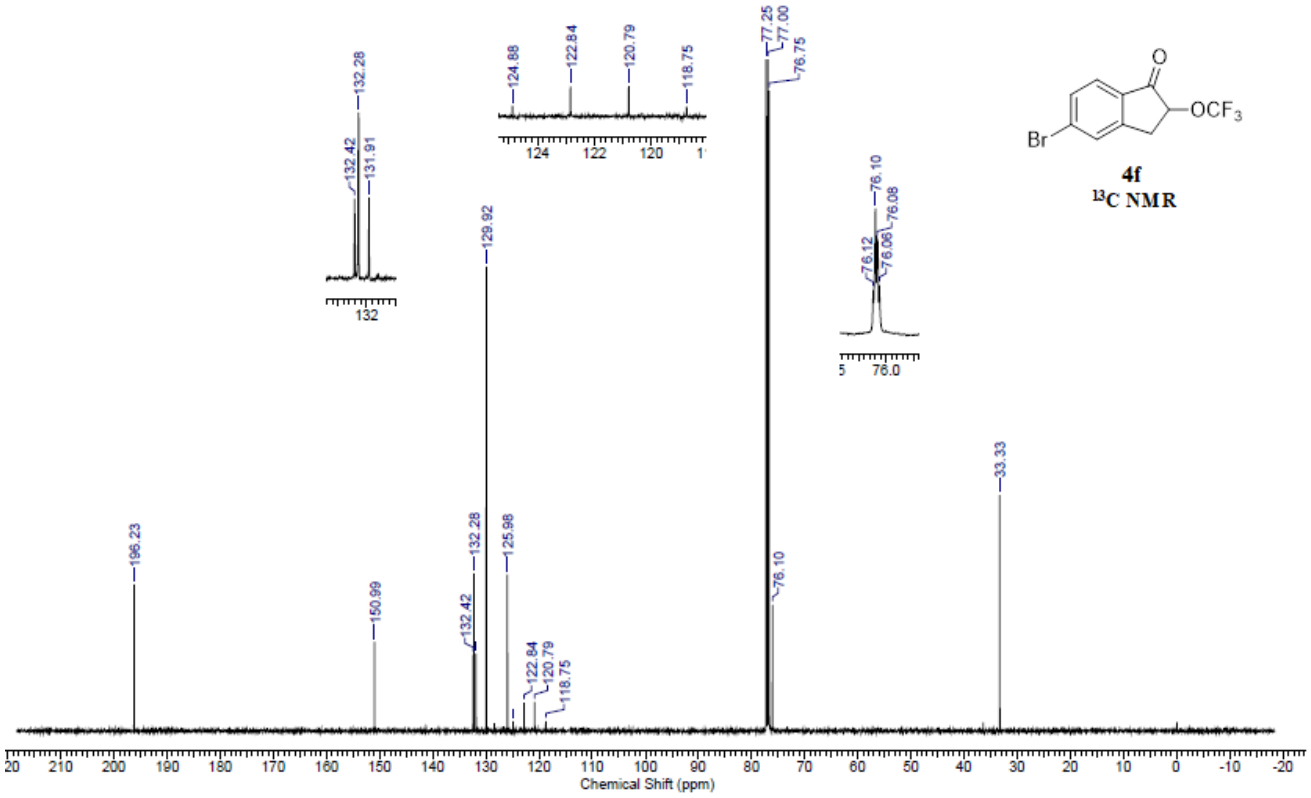

Cl
OCF3
4e
1H NMR
Chemical Shift (ppm)

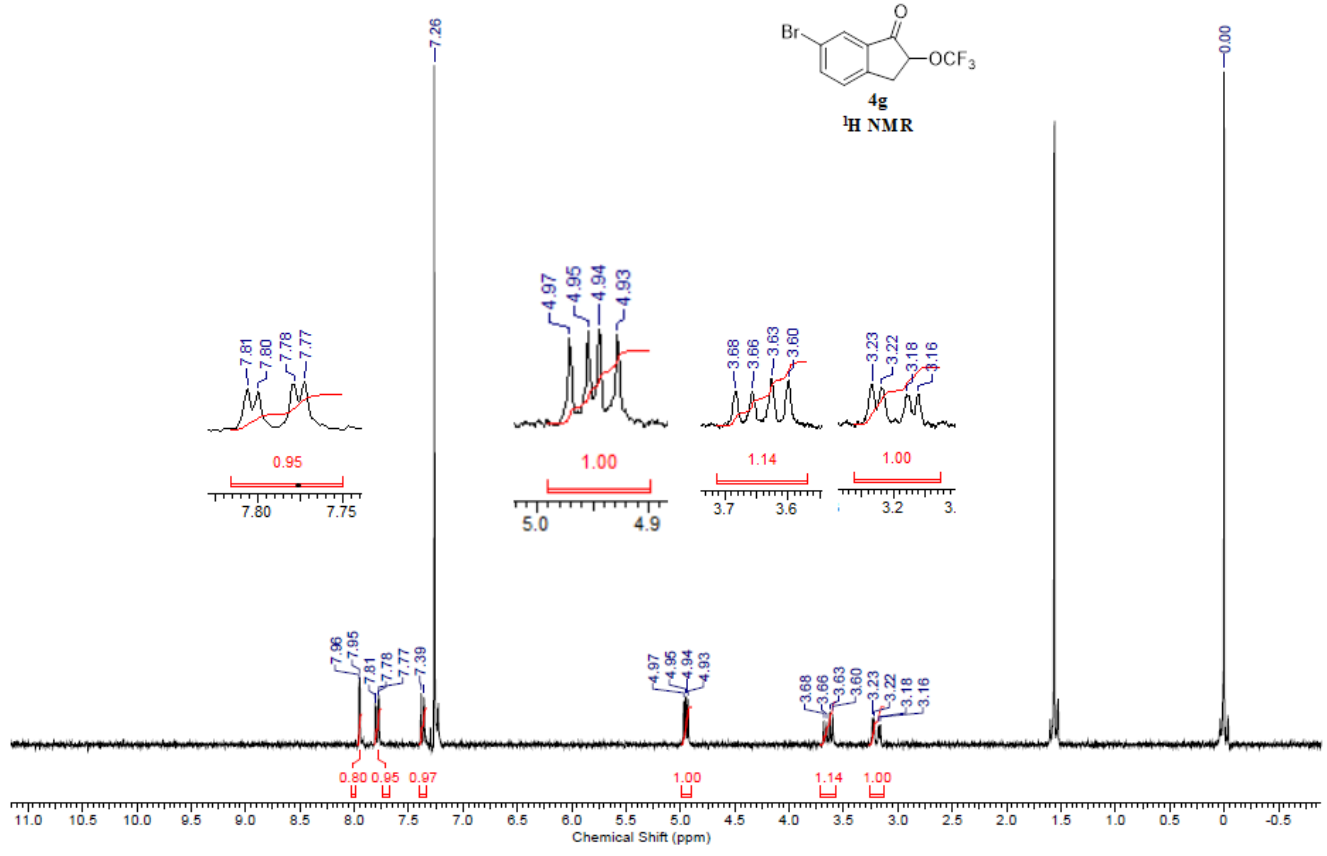

O
OCF3
Cl
4e
19F NMR
-59.80
-162.20
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift (ppm)

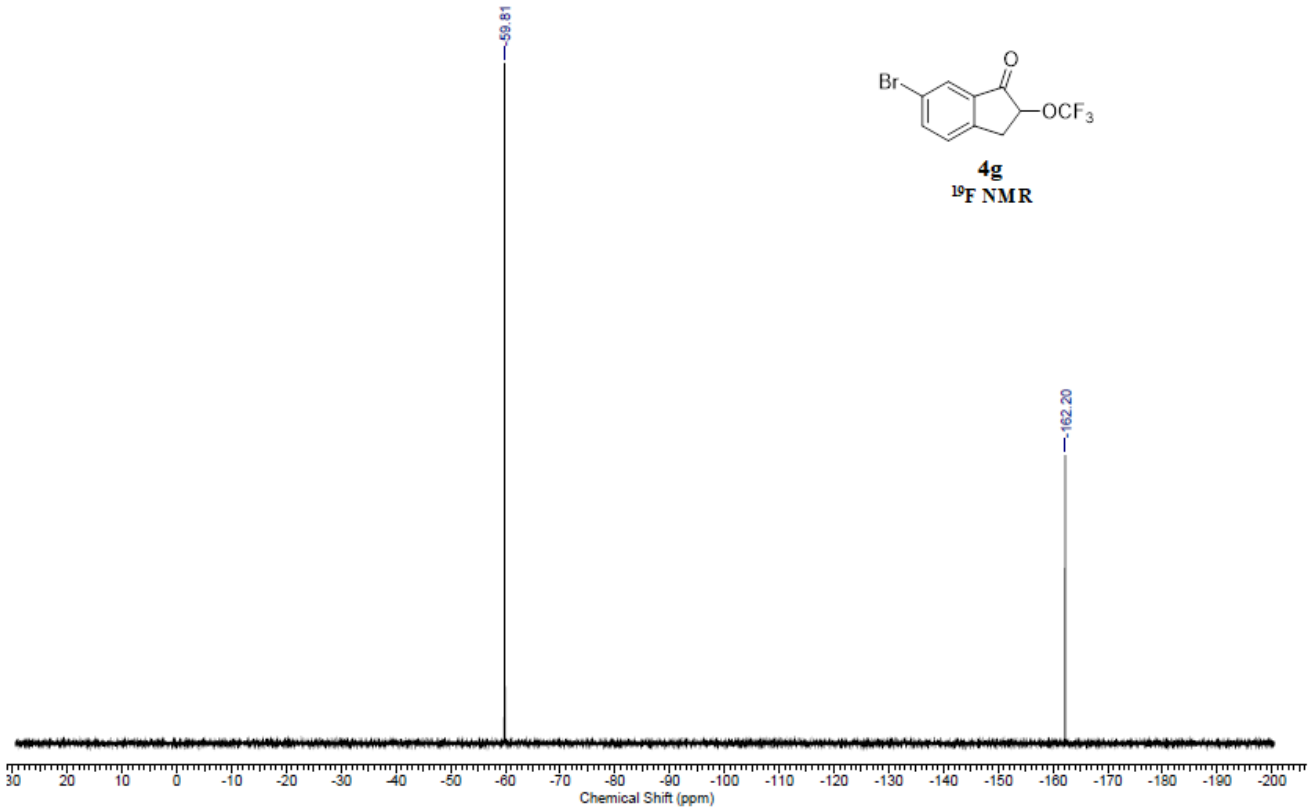

O
OCF3
Cl
4e
13C NMR
124.89
122.84
120.80
118.76
125
120
77.25
77.00
76.75
76.18
76.16
76.20
76.14
76.2
76.1
126.84
129.43
125.97
33.42
195.99
150.93
143.04
132.04
76.16
122.84
120.80
118.76
0 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)


4f
^{1}H NMR
Chemical Shift (ppm)


4f
^{19}F NMR
Chemical Shift (ppm)

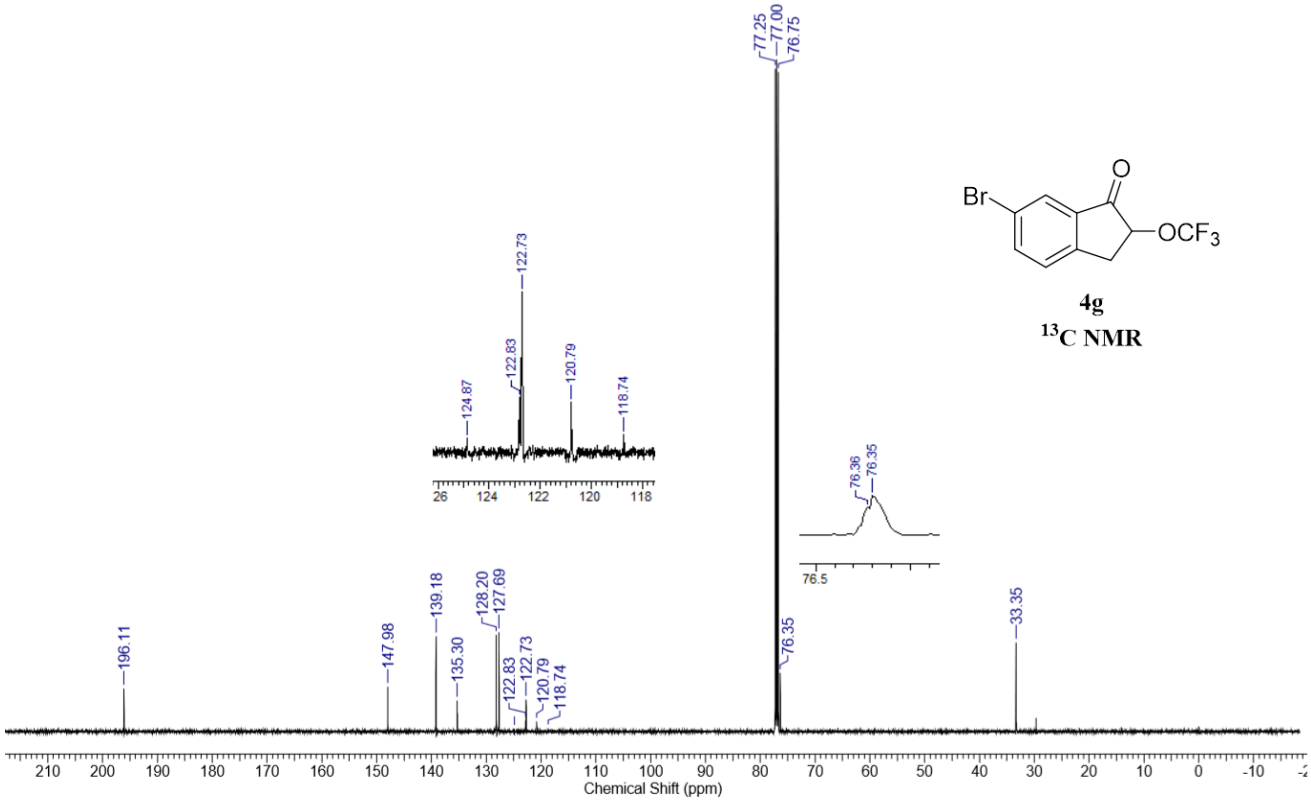

Br
O
OCF3
4f
13C NMR
Chemical Shift (ppm)


Br
O
OCF3
4g
1H NMR
Chemical Shift (ppm)



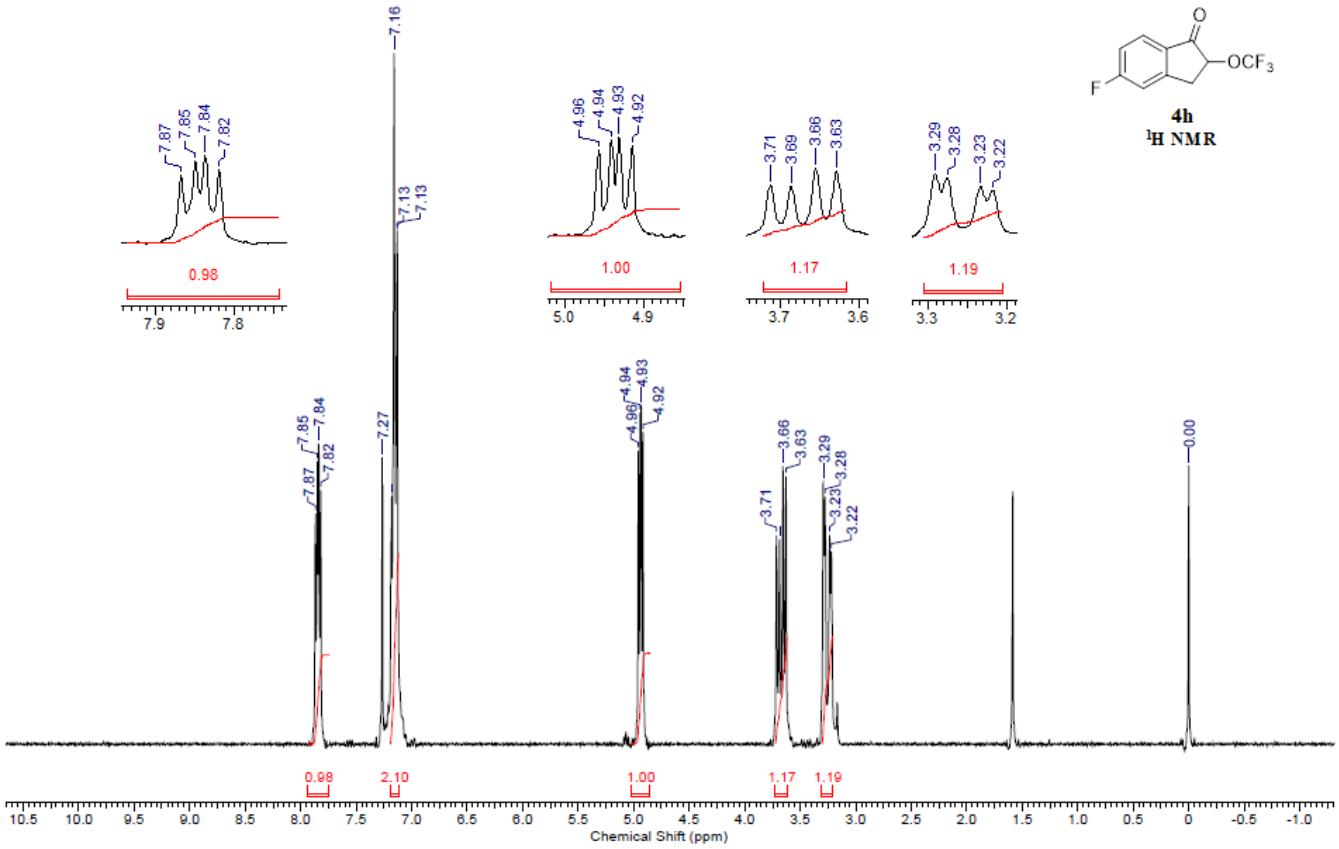
4g

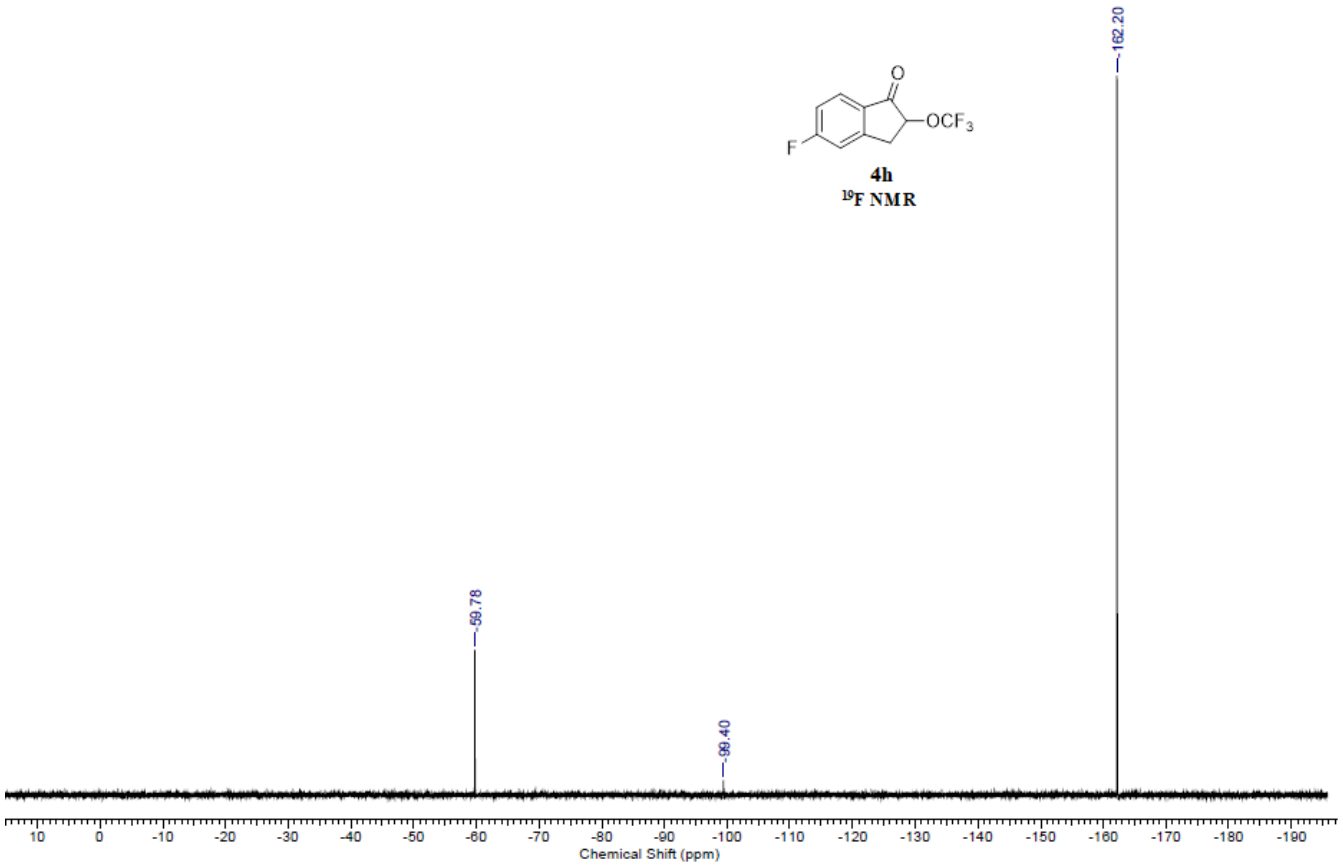
^{19}F NMR

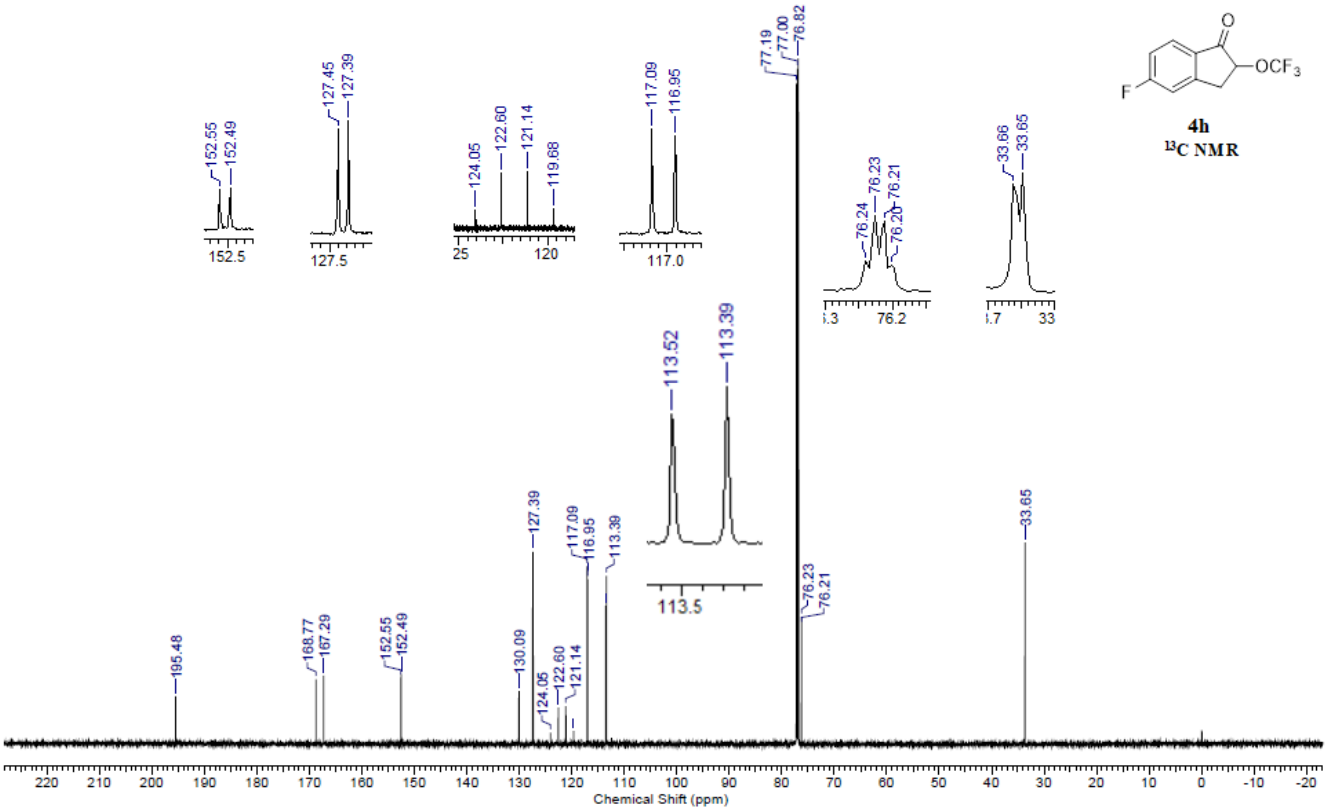


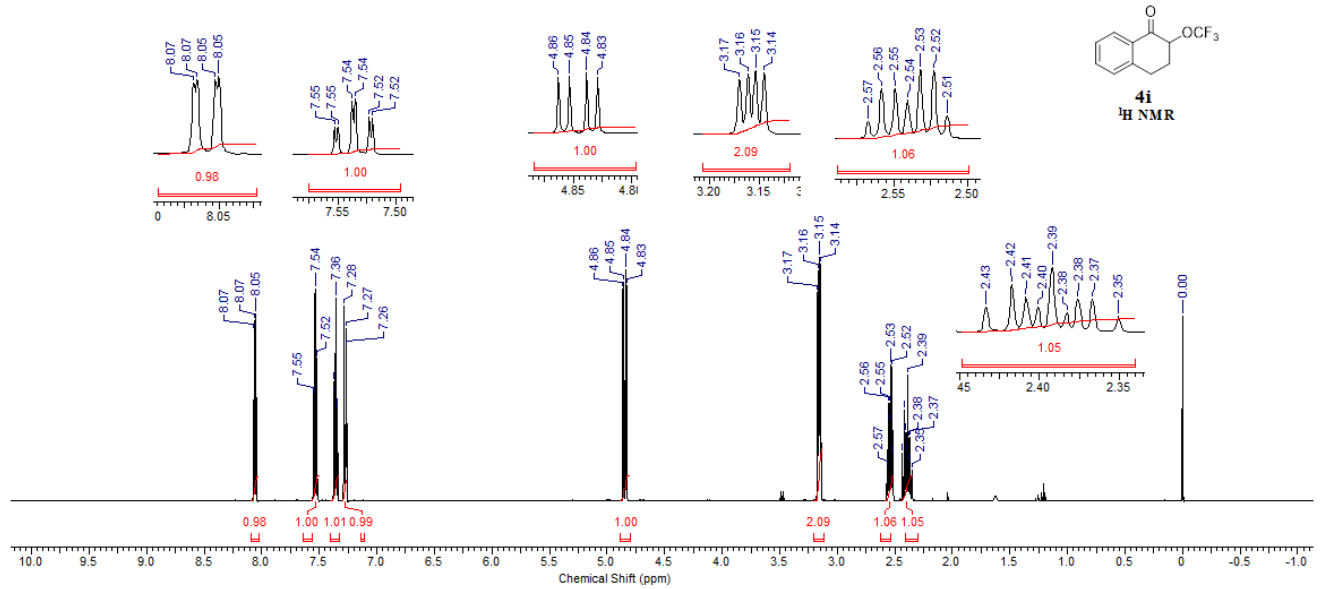
4g

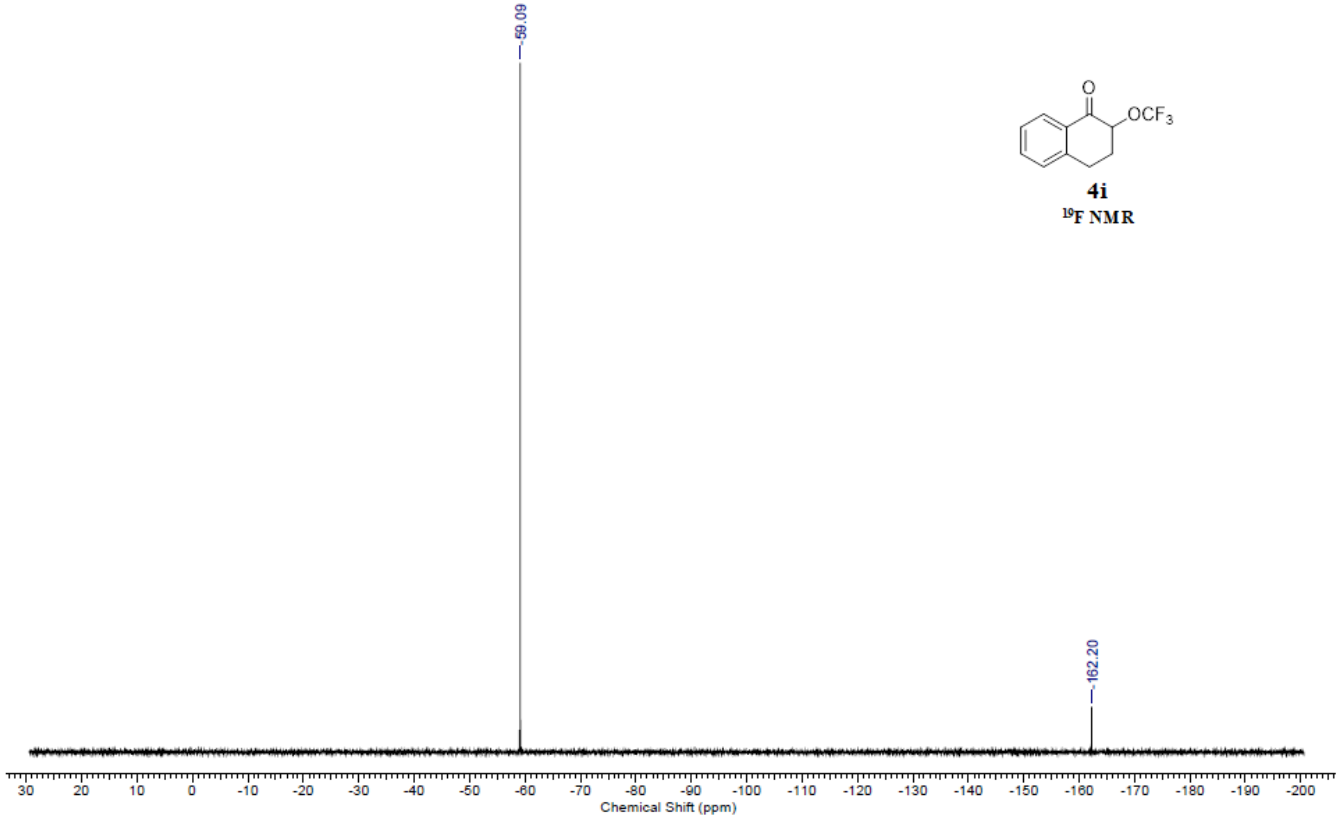
^{13}C NMR


4h
^{1}H NMR
Chemical Shift (ppm)


O
OCF3
F
4h
19F NMR
-162.20
-59.78
-99.40
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical Shift (ppm)

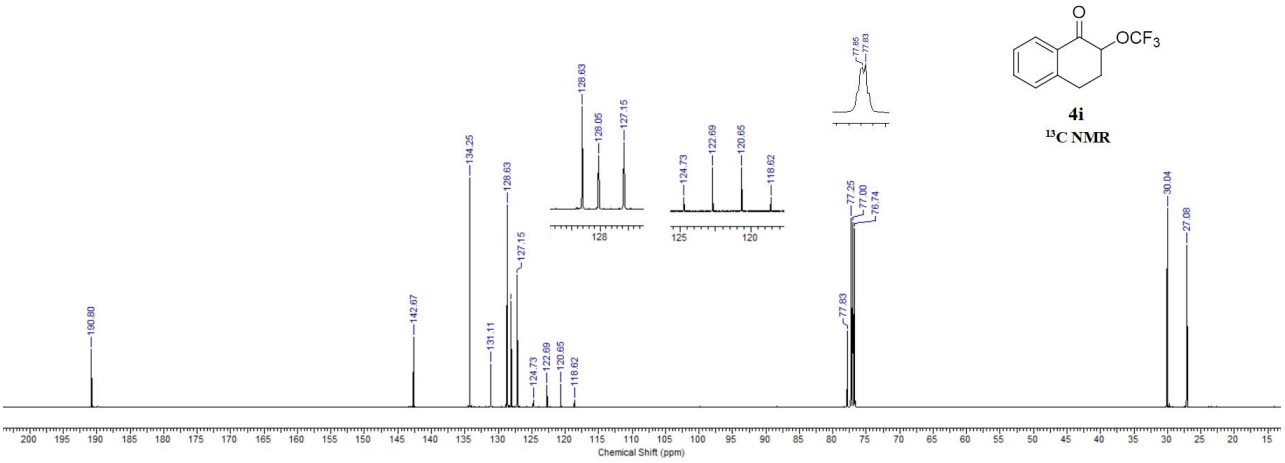

4h
^{13}C NMR
Chemical Shift (ppm)


4i
^{1}H NMR
Chemical Shift (ppm)



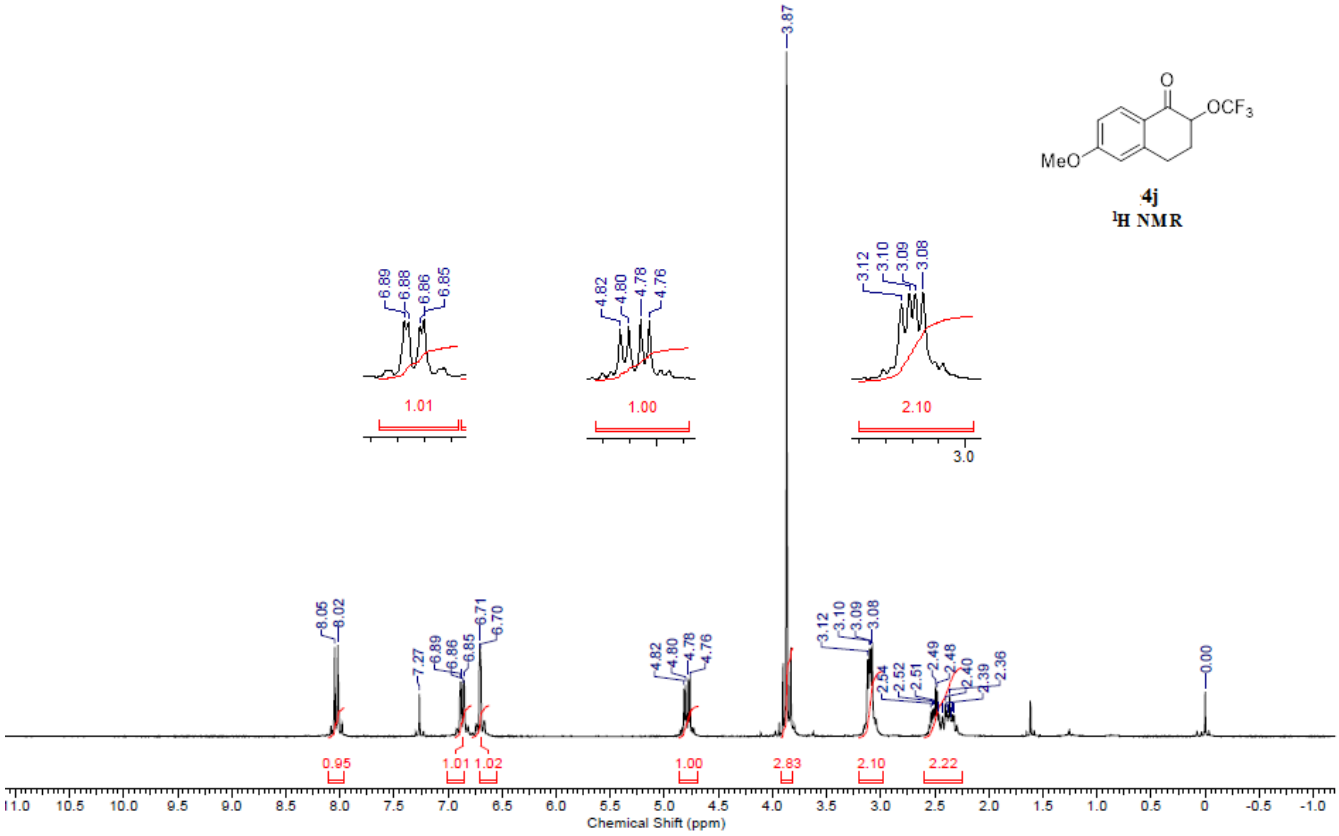
4i

^{19}F NMR

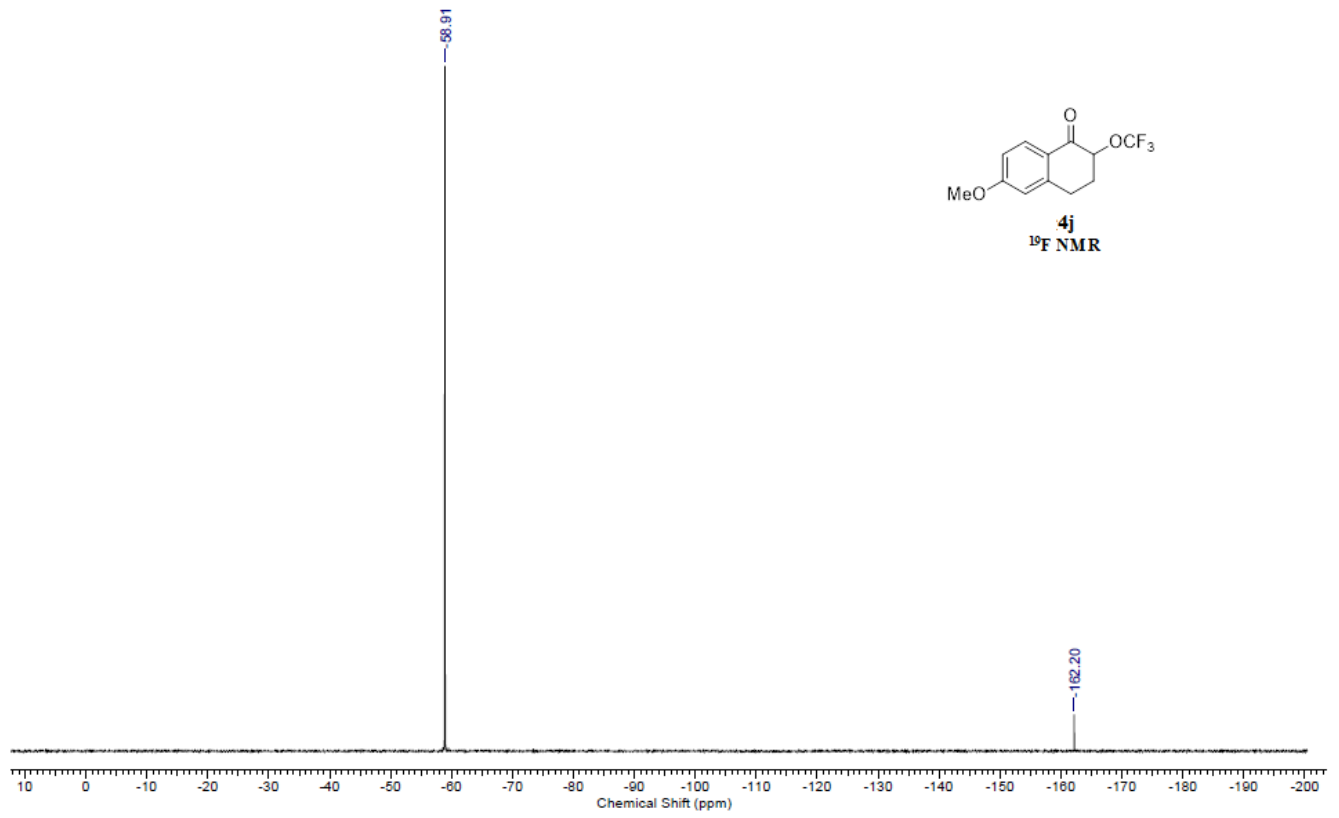


4i

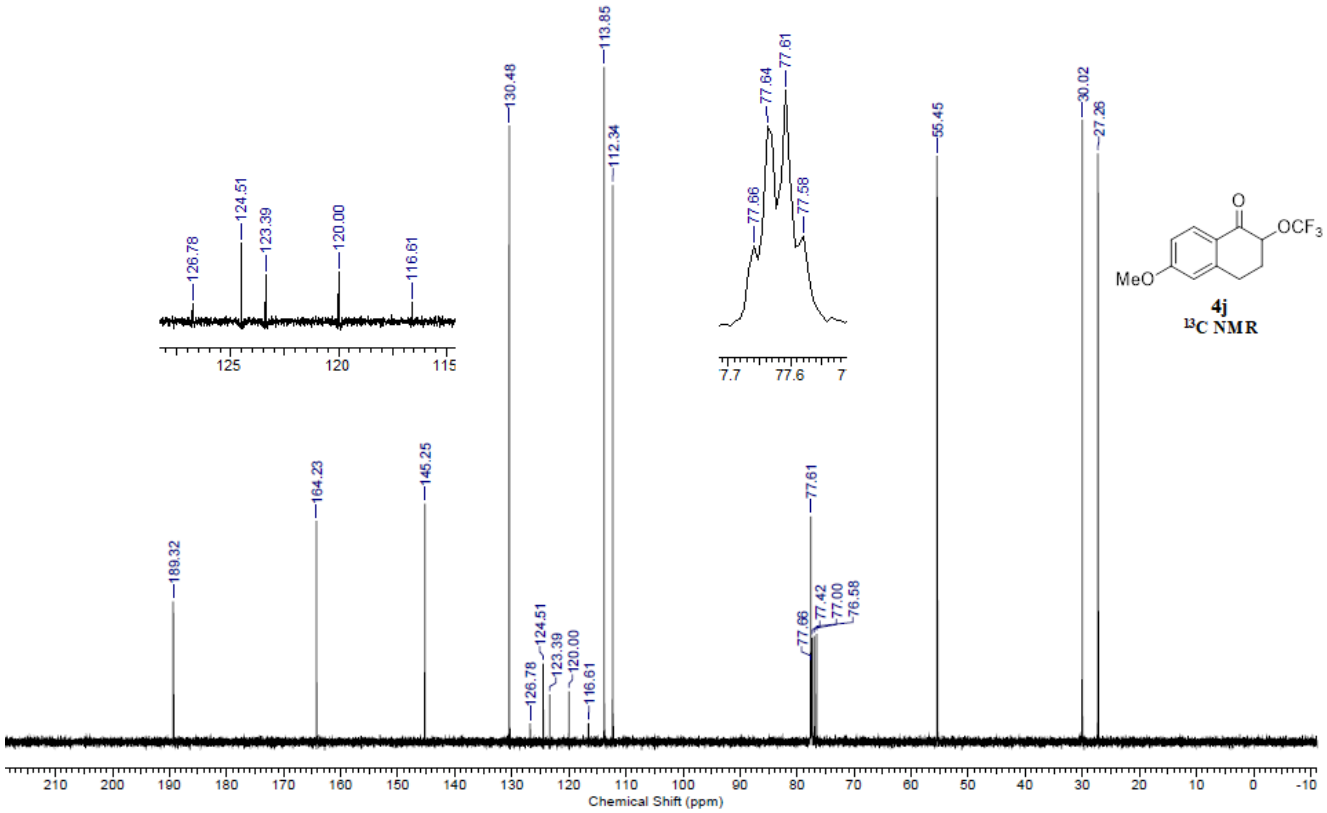
^{13}C NMR

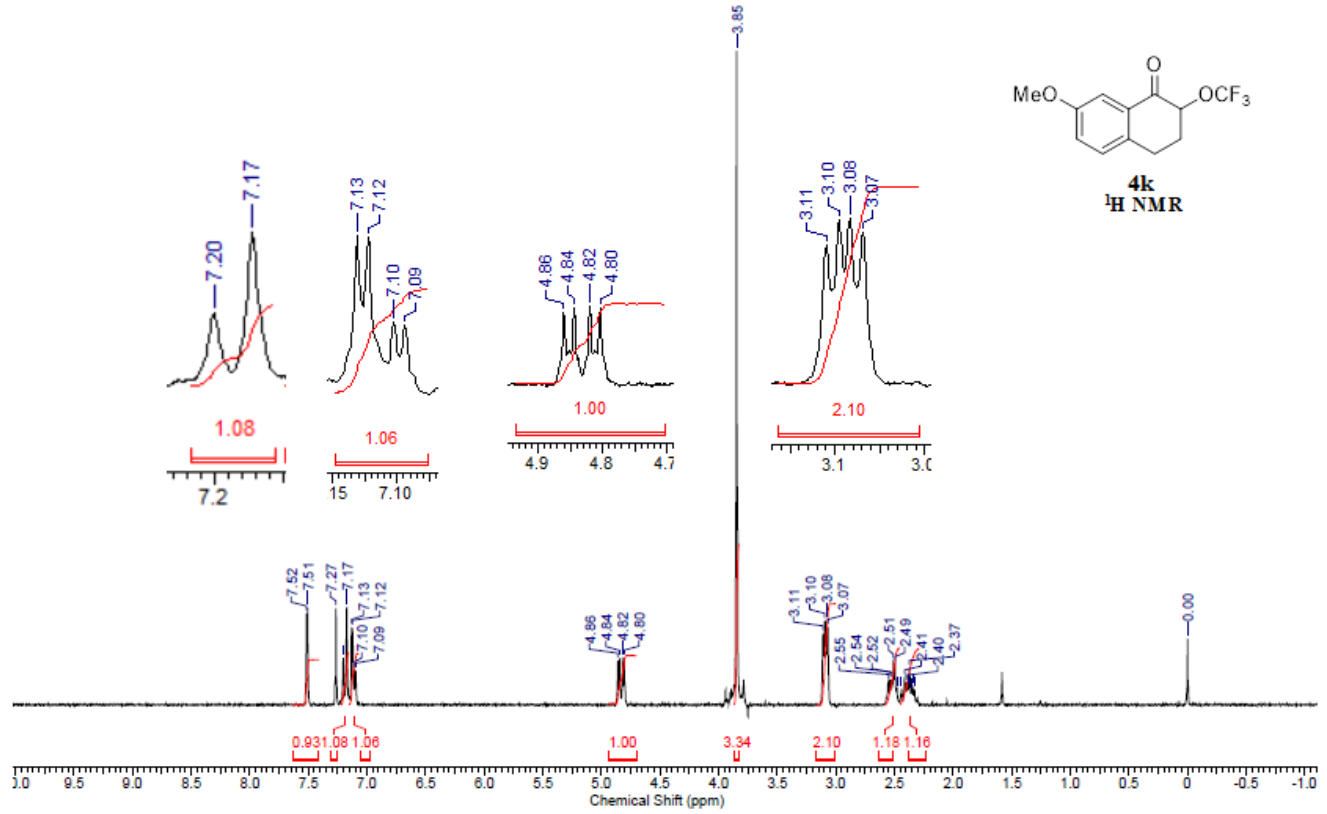


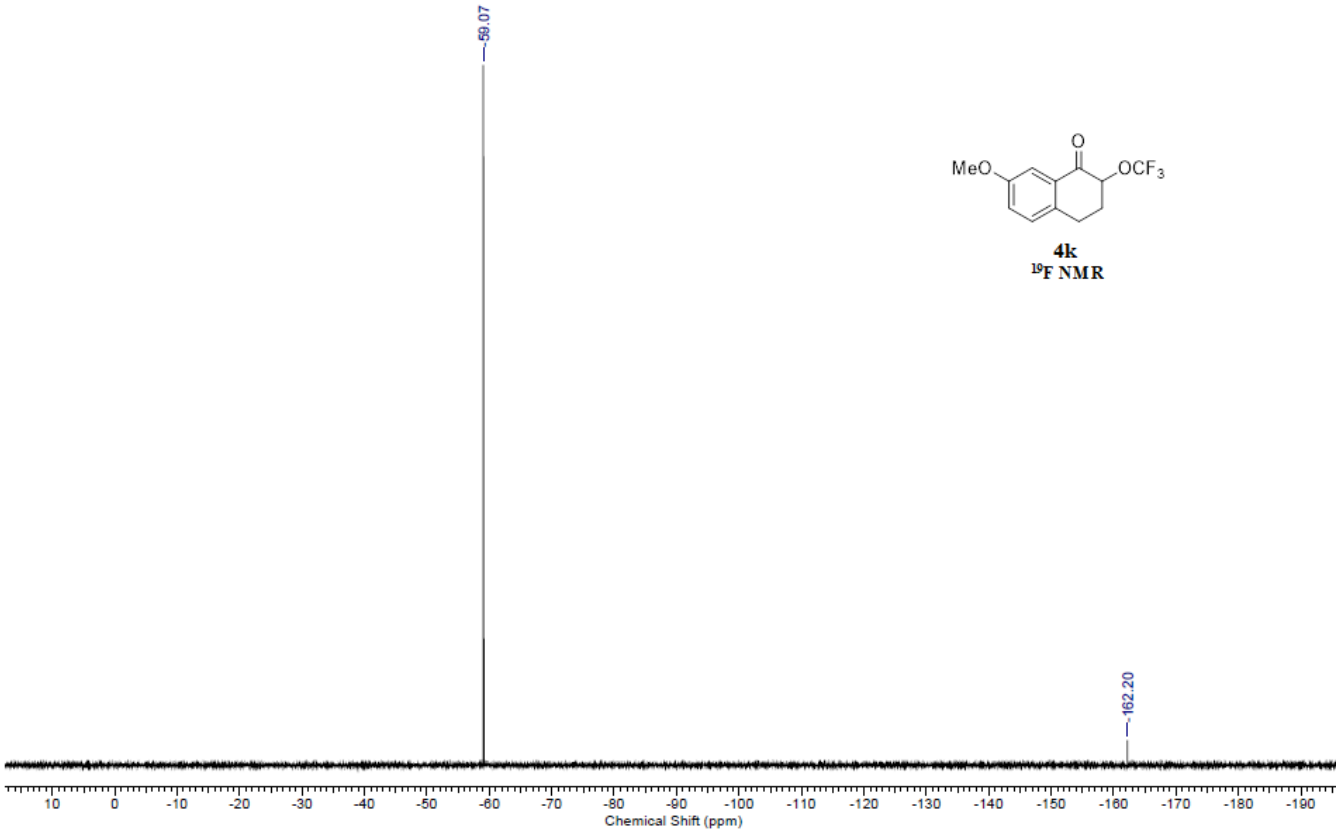
4j
^{1}H NMR



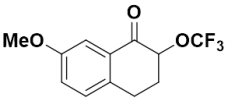
4j
^{19}F NMR


126.78
124.51
123.39
120.00
116.61
130.48
113.85
112.34
77.64
77.61
77.66
77.58
55.45
30.02
27.26
O
OCF3
MeO
4j
13C NMR
189.32
164.23
145.25
77.61
77.66
77.42
77.00
76.58
126.78
124.51
123.39
120.00
116.61
Chemical Shift (ppm)

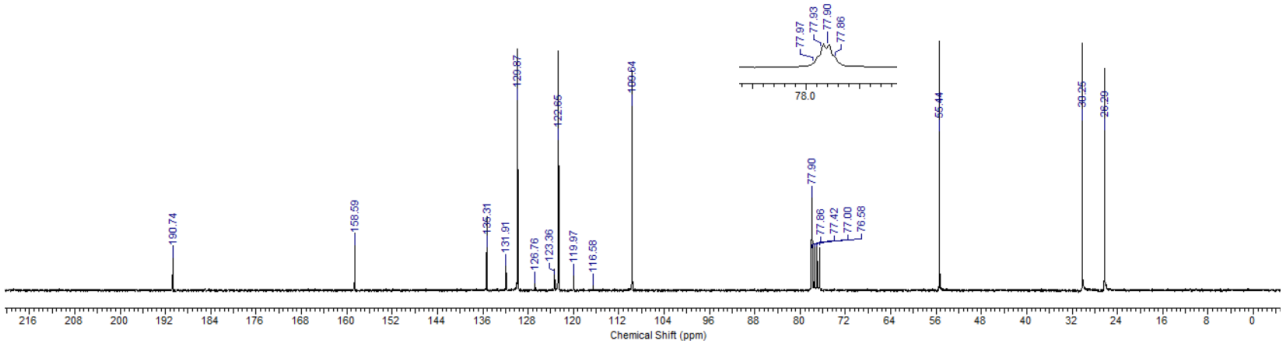

3.85
7.17
7.20
7.13
7.12
7.10
7.09
4.86
4.84
4.82
4.80
3.11
3.10
3.08
3.07
1.08
1.06
1.00
2.10
MeO
OCF3
4k
1H NMR
7.52
7.51
7.27
7.17
7.13
7.12
7.10
7.09
4.86
4.84
4.82
4.80
3.11
3.10
3.08
3.07
2.55
2.54
2.52
2.51
2.49
2.41
2.40
2.37
0.00
0.93
1.08
1.06
1.00
3.34
2.10
1.18
1.16
Chemical Shift (ppm)

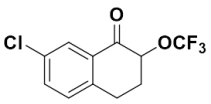


4k
^{19}F NMR



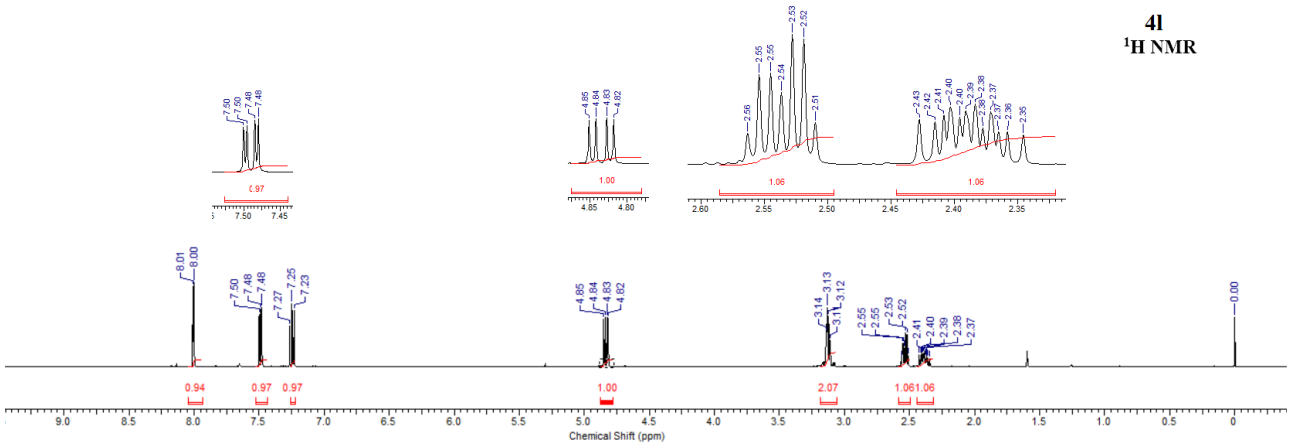
4k
^{13}C NMR

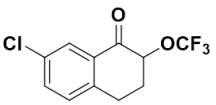




4l

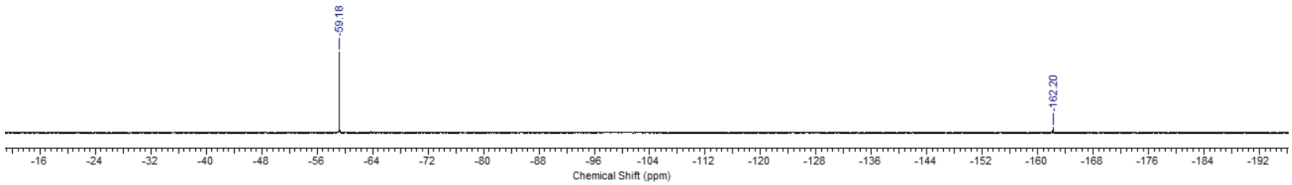
^{1}H NMR

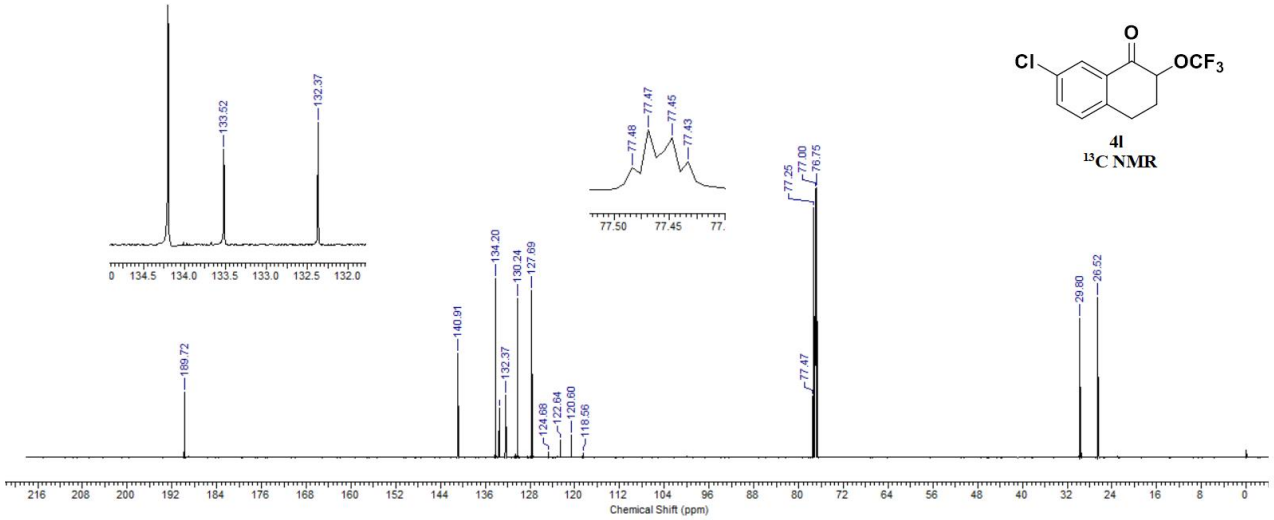


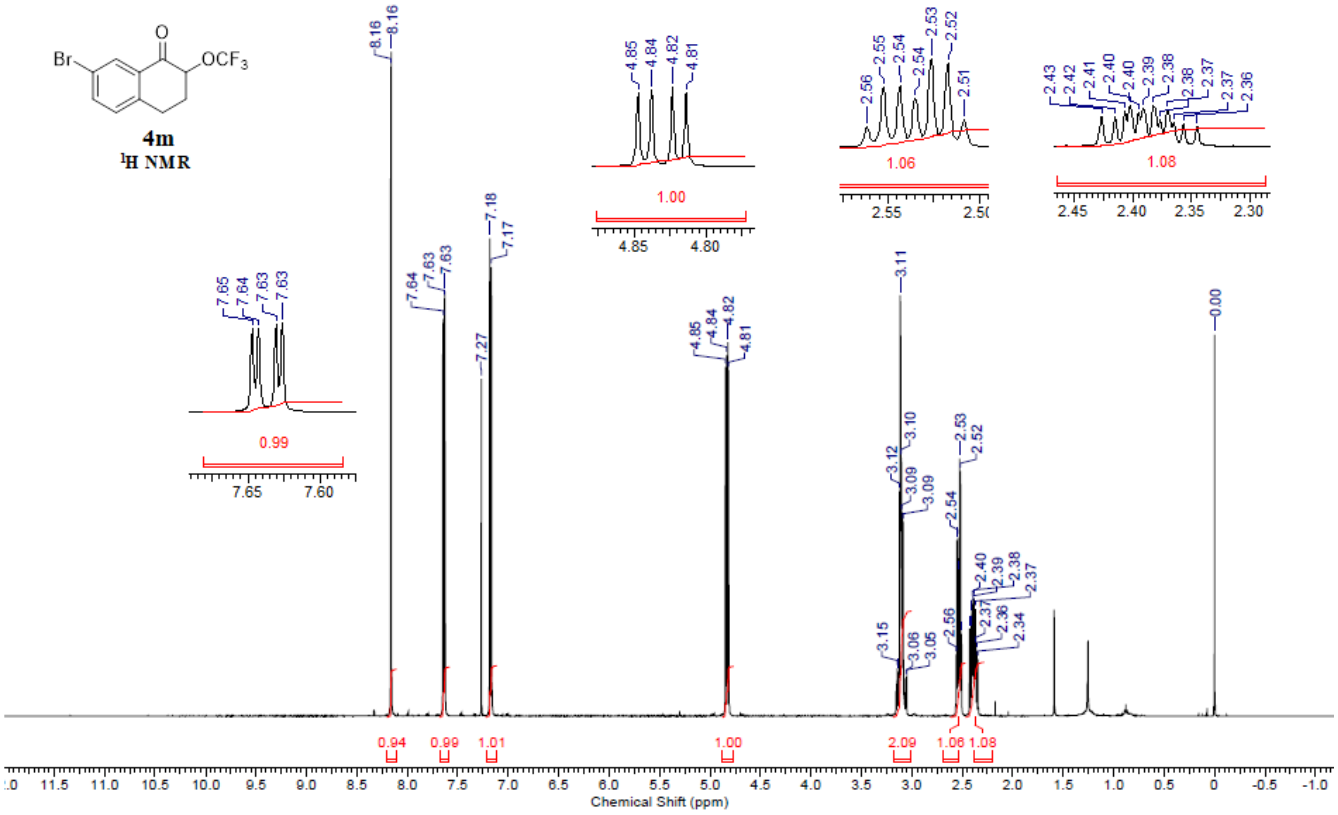


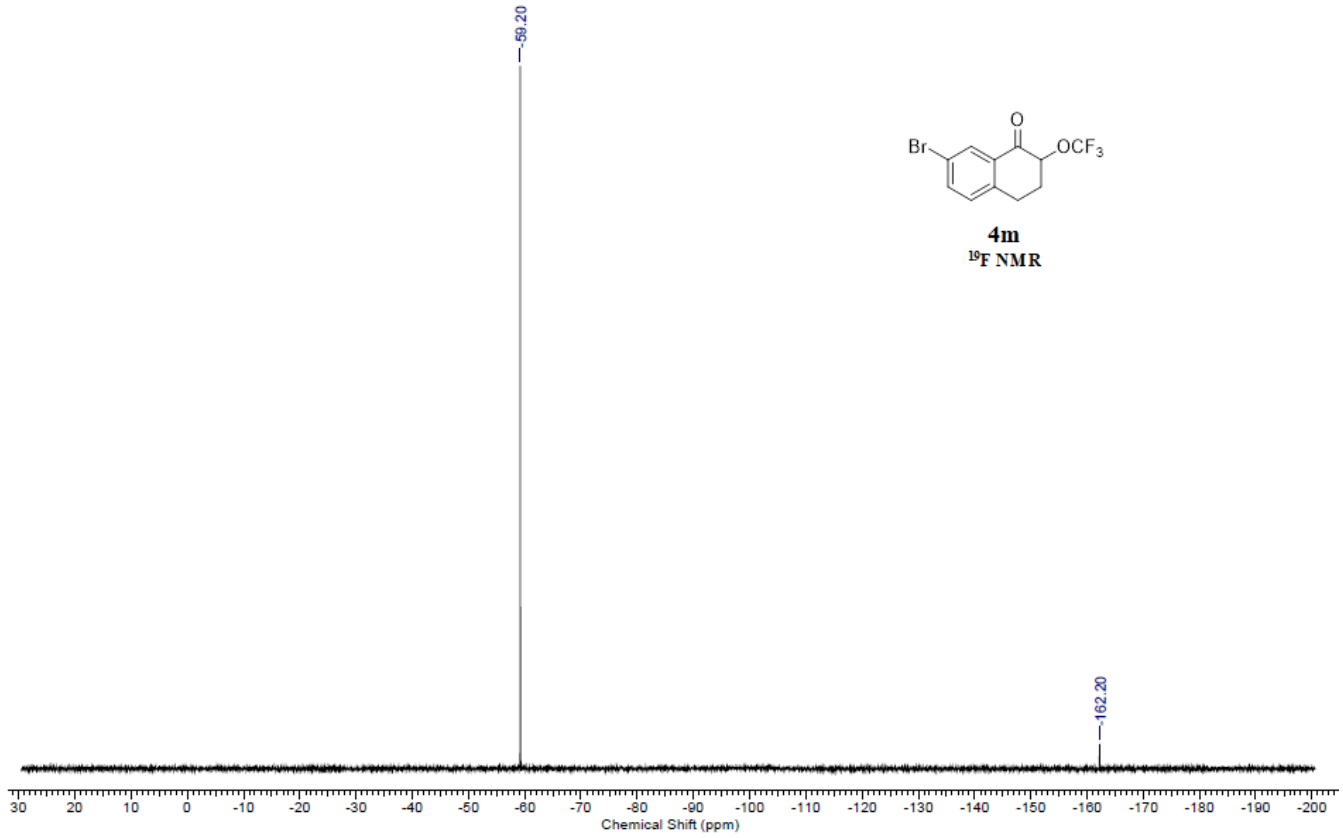
4l

^{19}F NMR



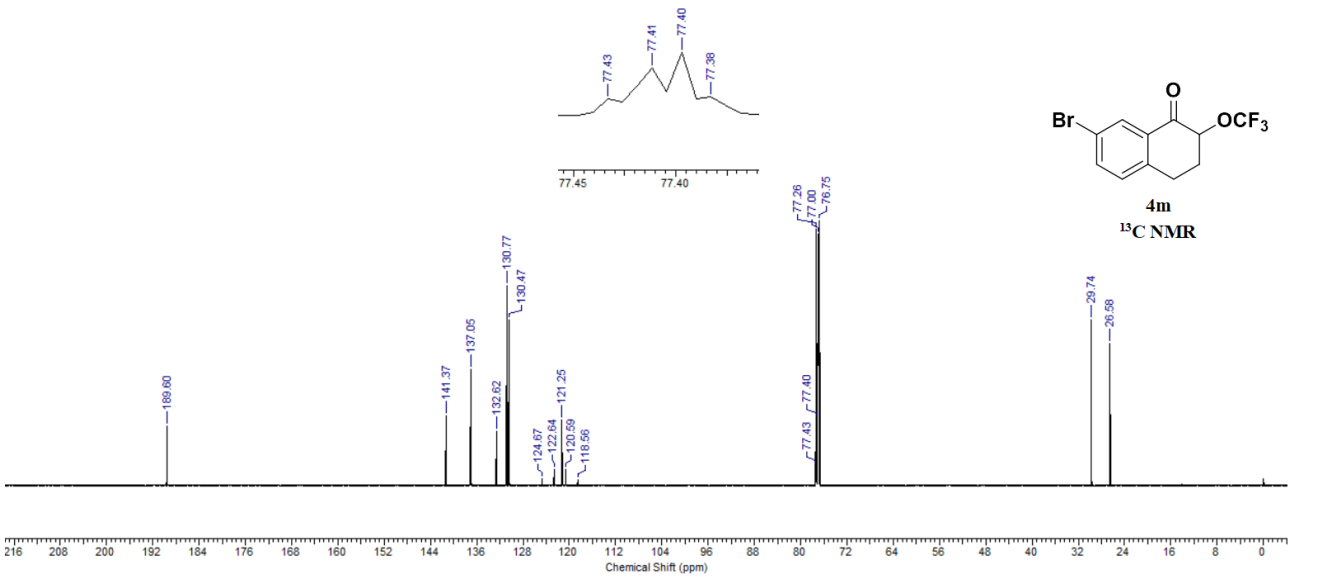

Cl
O
OCF3
4l
13C NMR
Chemical Shift (ppm)


Br
O
OCF3
4m
1H NMR
0.99
1.00
1.06
1.08
0.94
0.99
1.01
1.00
2.09
1.06
1.08
Chemical Shift (ppm)



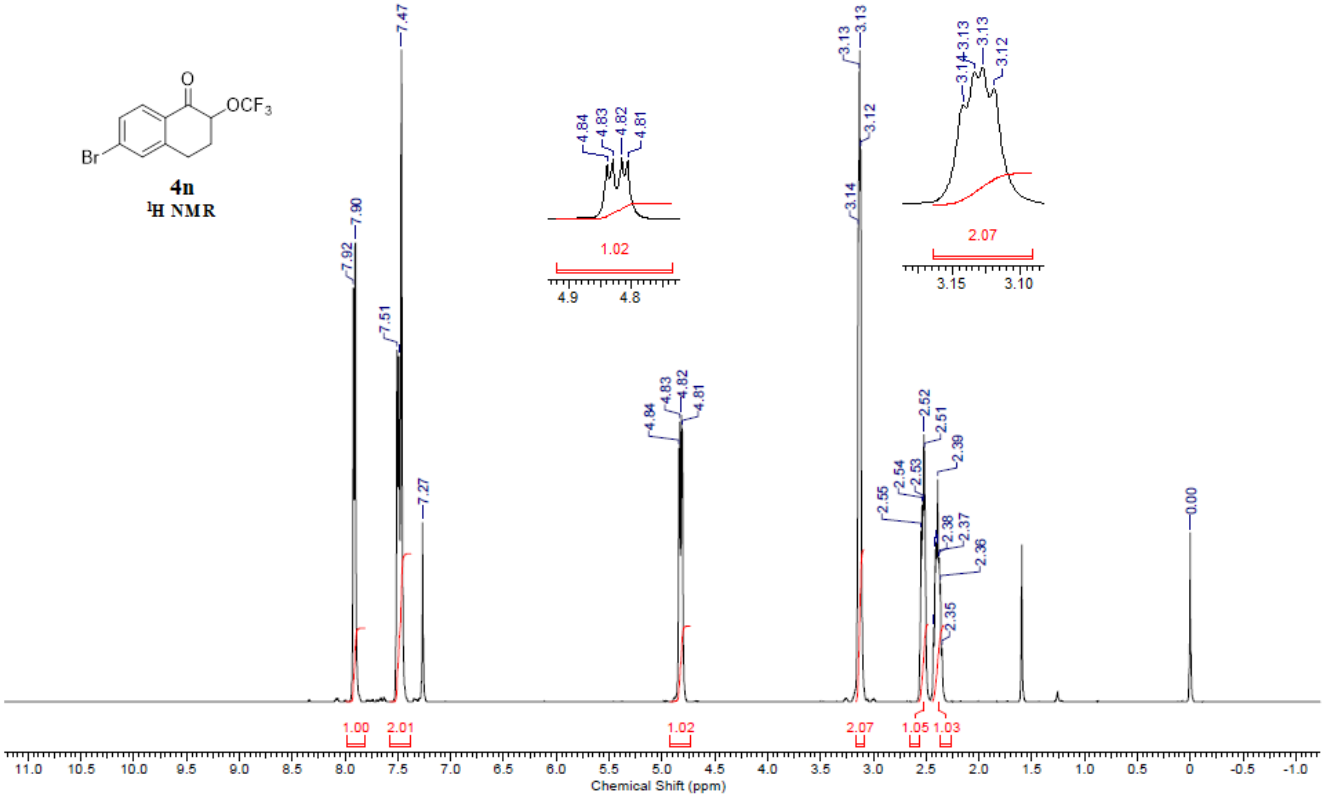
4m

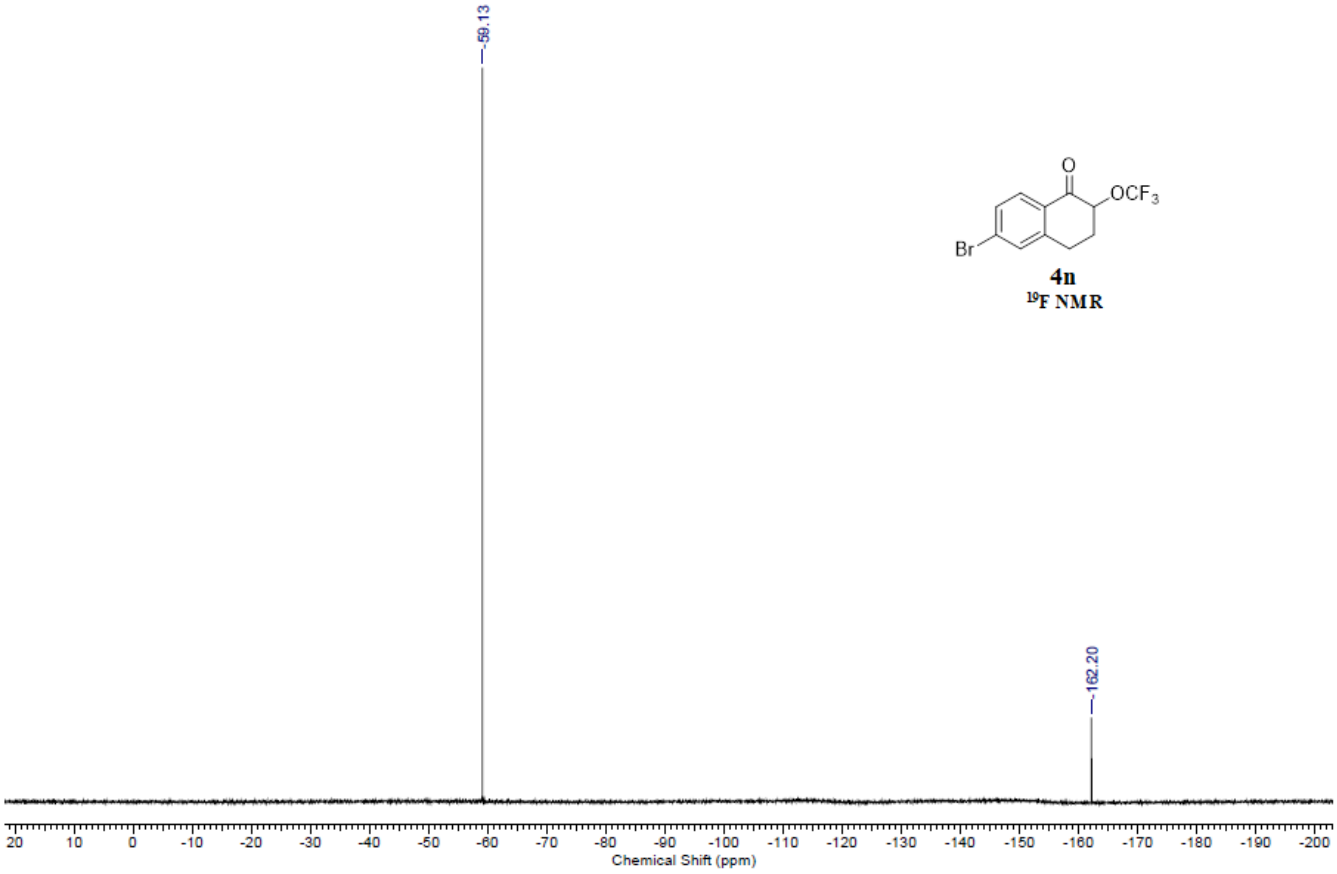
^{19}F NMR

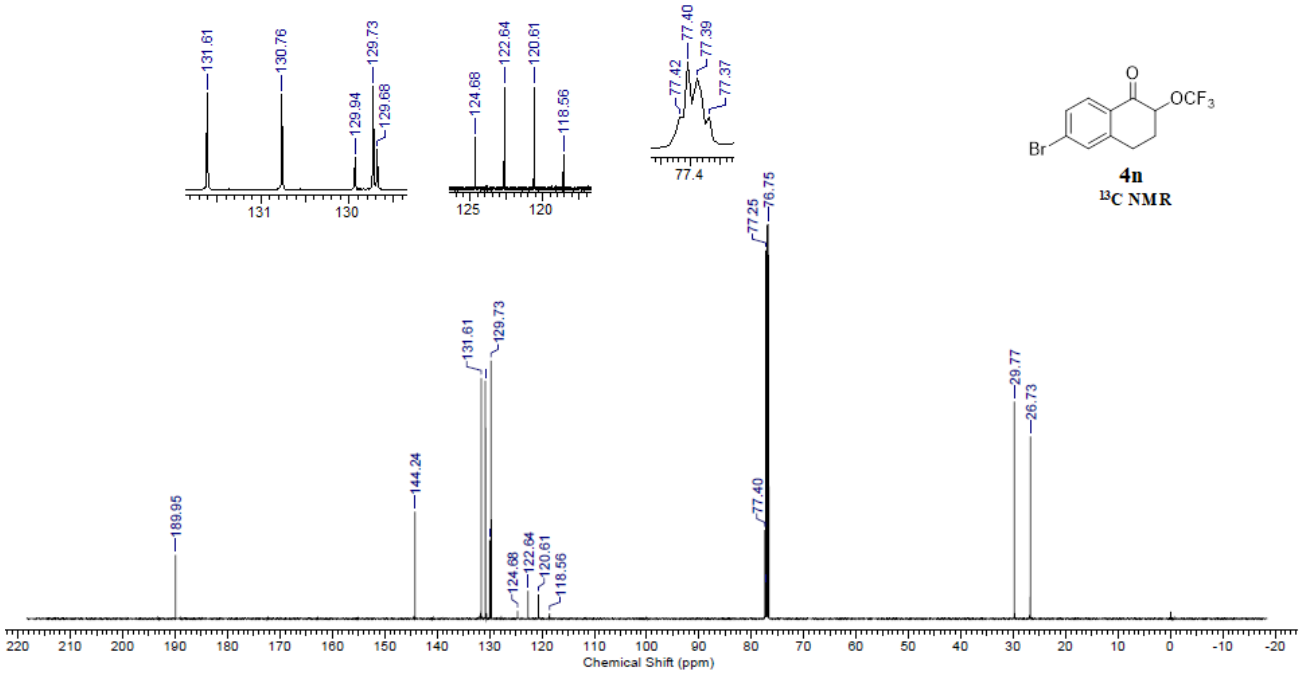


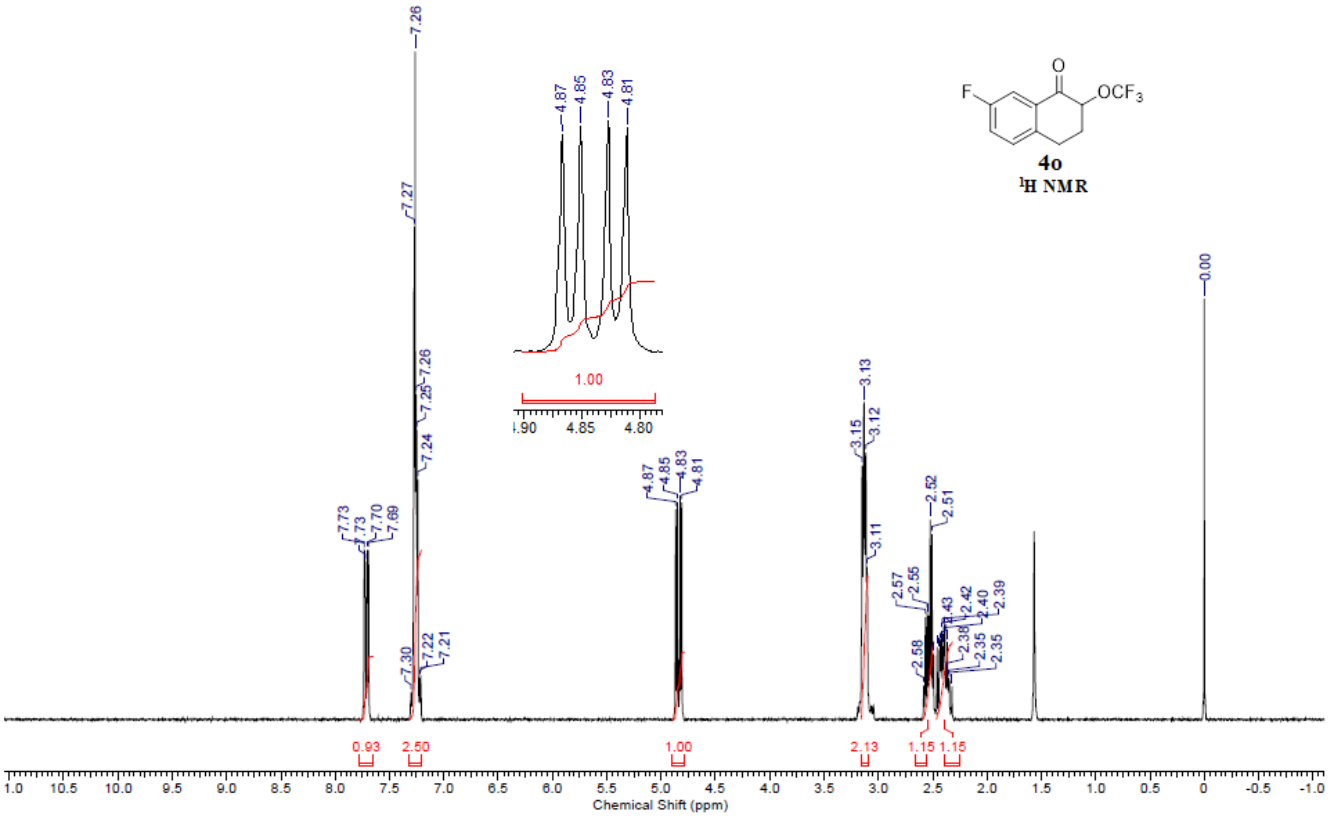
4m

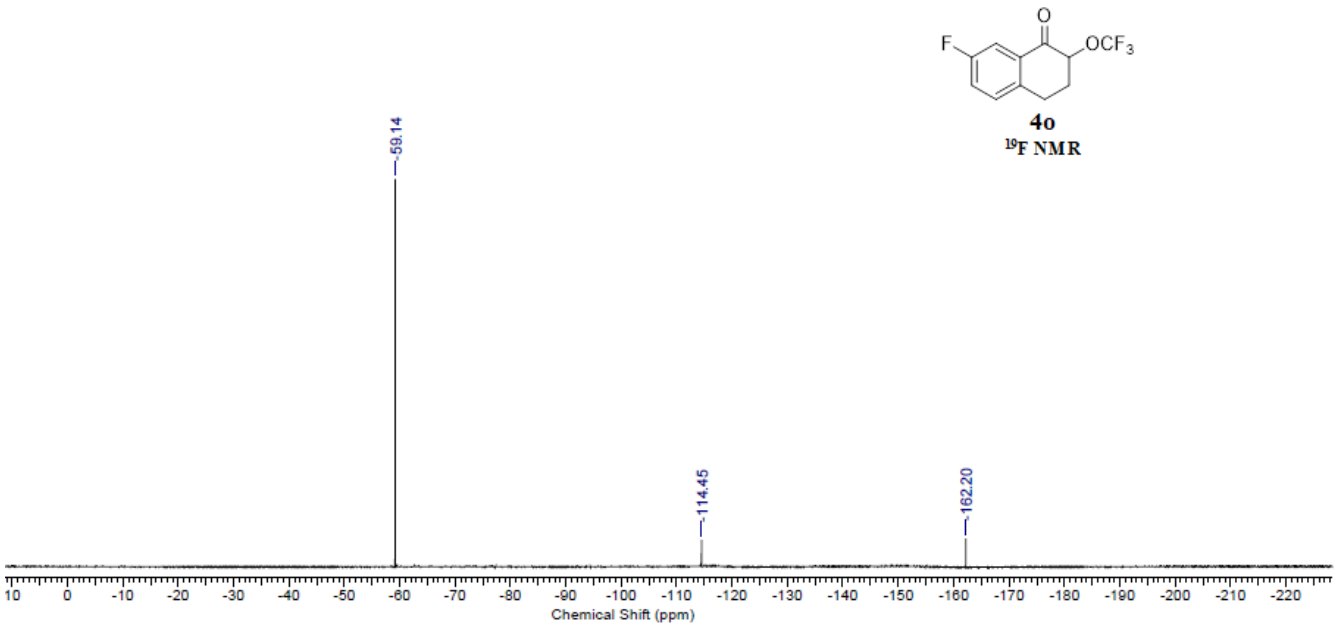
^{13}C NMR

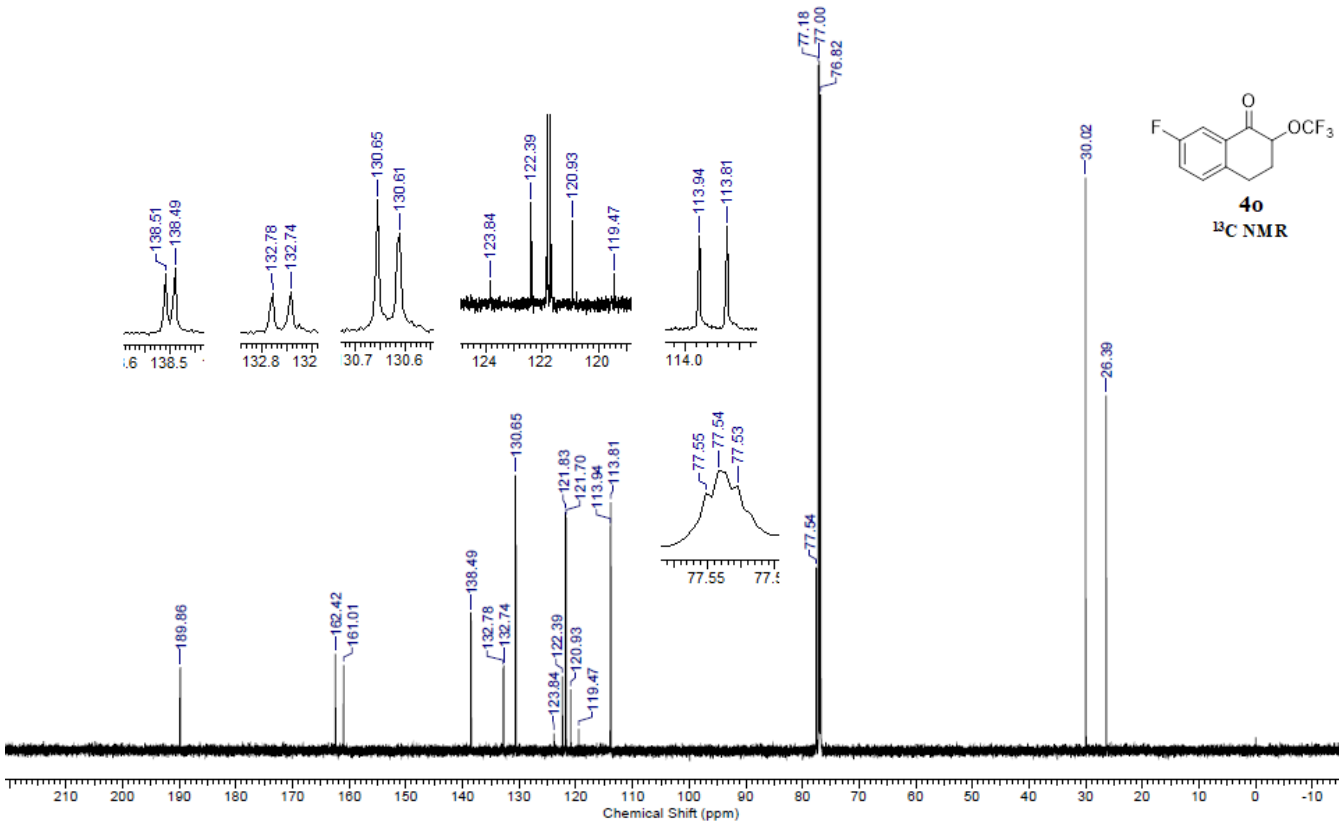

O
OCF3
Br
4n
1H NMR
7.92
7.90
7.51
7.47
7.27
4.84
4.83
4.82
4.81
3.13
3.12
3.14
2.52
2.51
2.39
2.55
2.54
2.53
2.38
2.37
2.36
2.35
0.00
1.02
2.07
1.00
2.01
1.05
1.03
Chemical Shift (ppm)


-59.13
-162.20
O
OCF3
Br
4n
19F NMR
Chemical Shift (ppm)


131.61
130.76
129.94
129.73
129.68
124.68
122.64
120.61
118.56
77.42
77.40
77.39
77.37
77.4
O
OCF3
Br
4n
13C NMR
77.25
76.75
131.61
129.73
144.24
189.95
124.68
122.64
120.61
118.56
77.40
29.77
26.73
Chemical Shift (ppm)


7.26
7.27
4.87
4.85
4.83
4.81
1.00
O
F
OCF3
4o
1H NMR
0.00
3.13
3.12
3.15
3.11
2.52
2.51
2.57
2.55
2.43
2.42
2.40
2.39
2.38
2.35
2.58
7.73
7.70
7.69
7.30
7.25
7.24
7.22
7.21
0.93
2.50
1.00
2.13
1.15
1.15
Chemical Shift (ppm)


O
F
OCF3
4o
19F NMR
-59.14
-114.45
-162.20
Chemical Shift (ppm)


O
F
OCF3
4o
13C NMR
77.18
77.00
76.82
30.02
26.39
138.51
138.49
132.78
132.74
130.65
130.61
123.84
122.39
120.93
119.47
113.94
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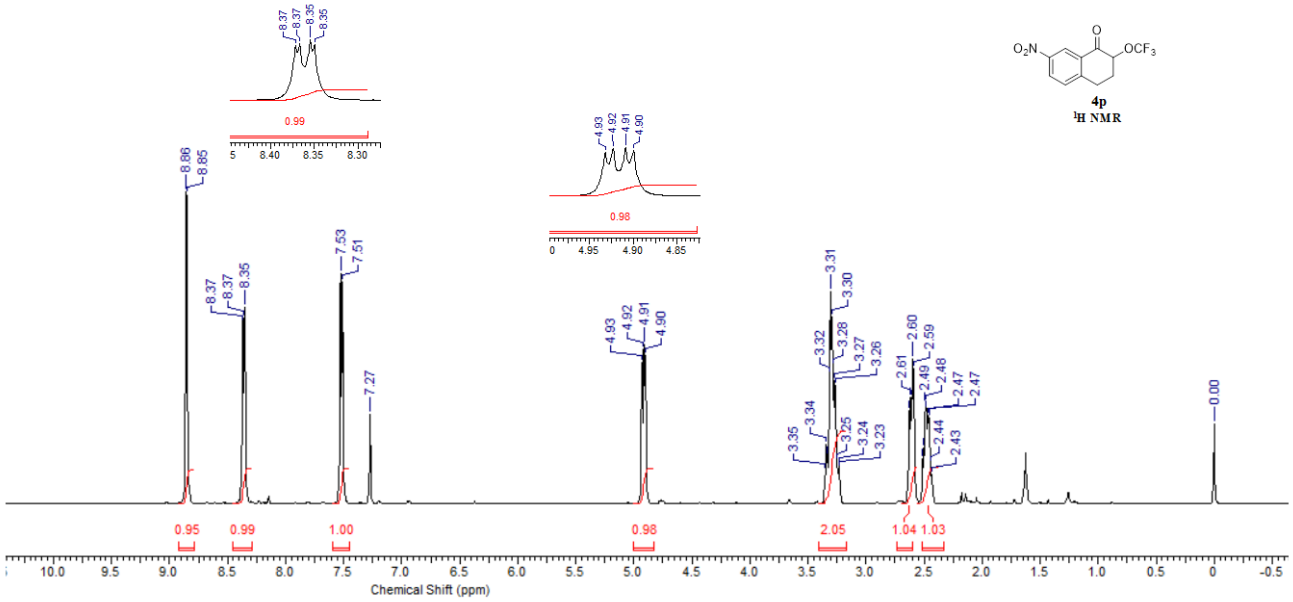
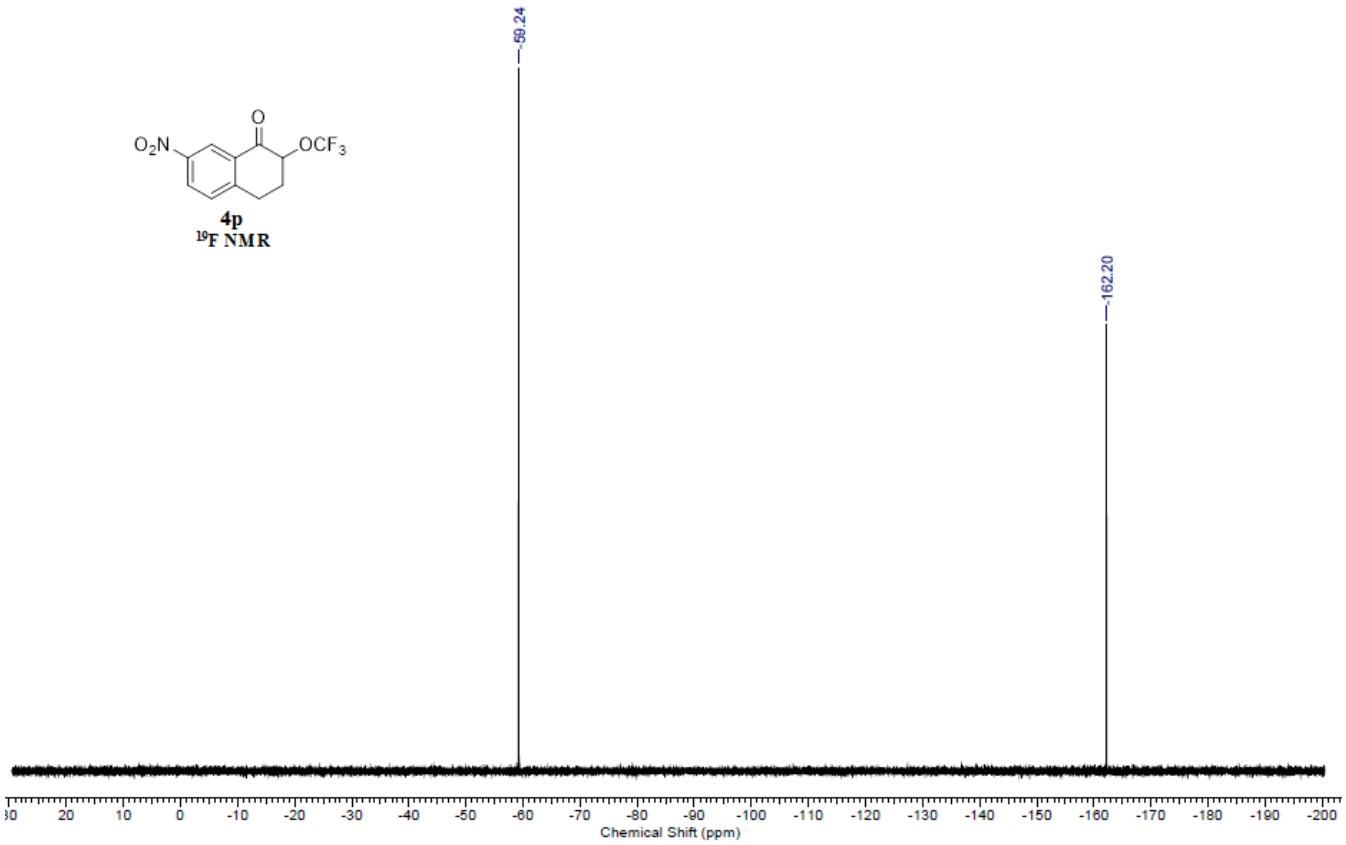
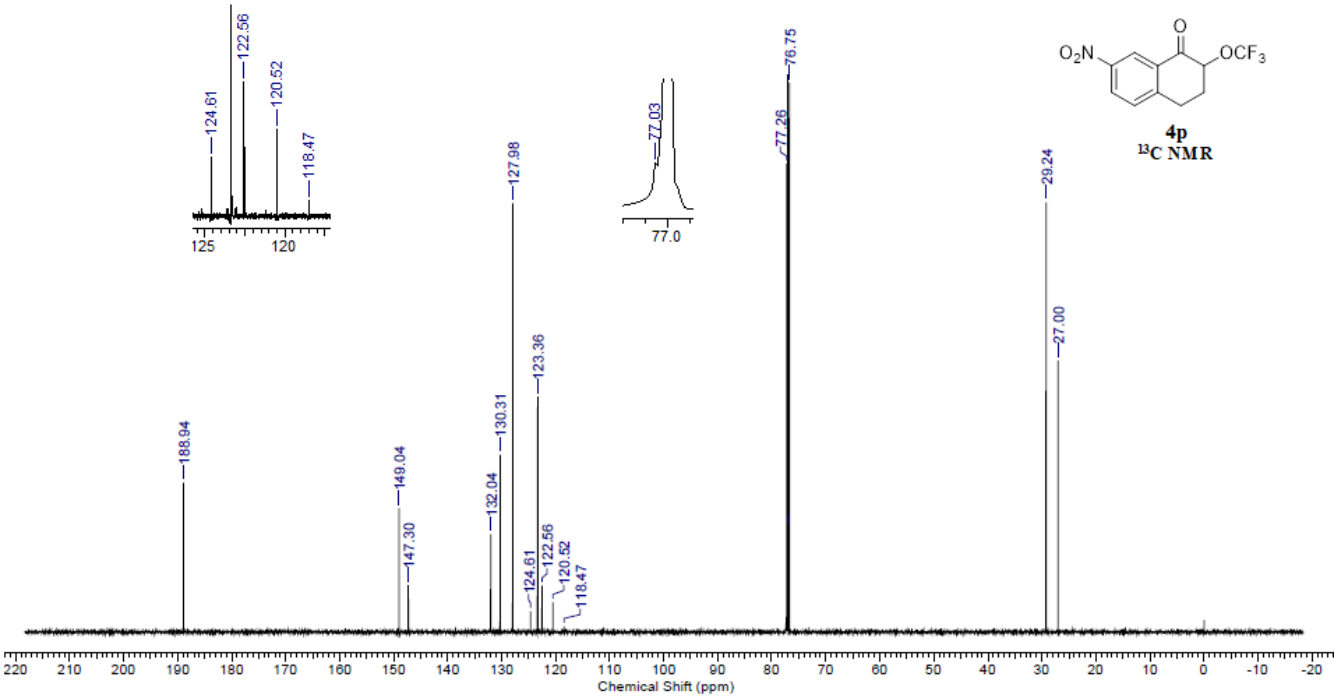
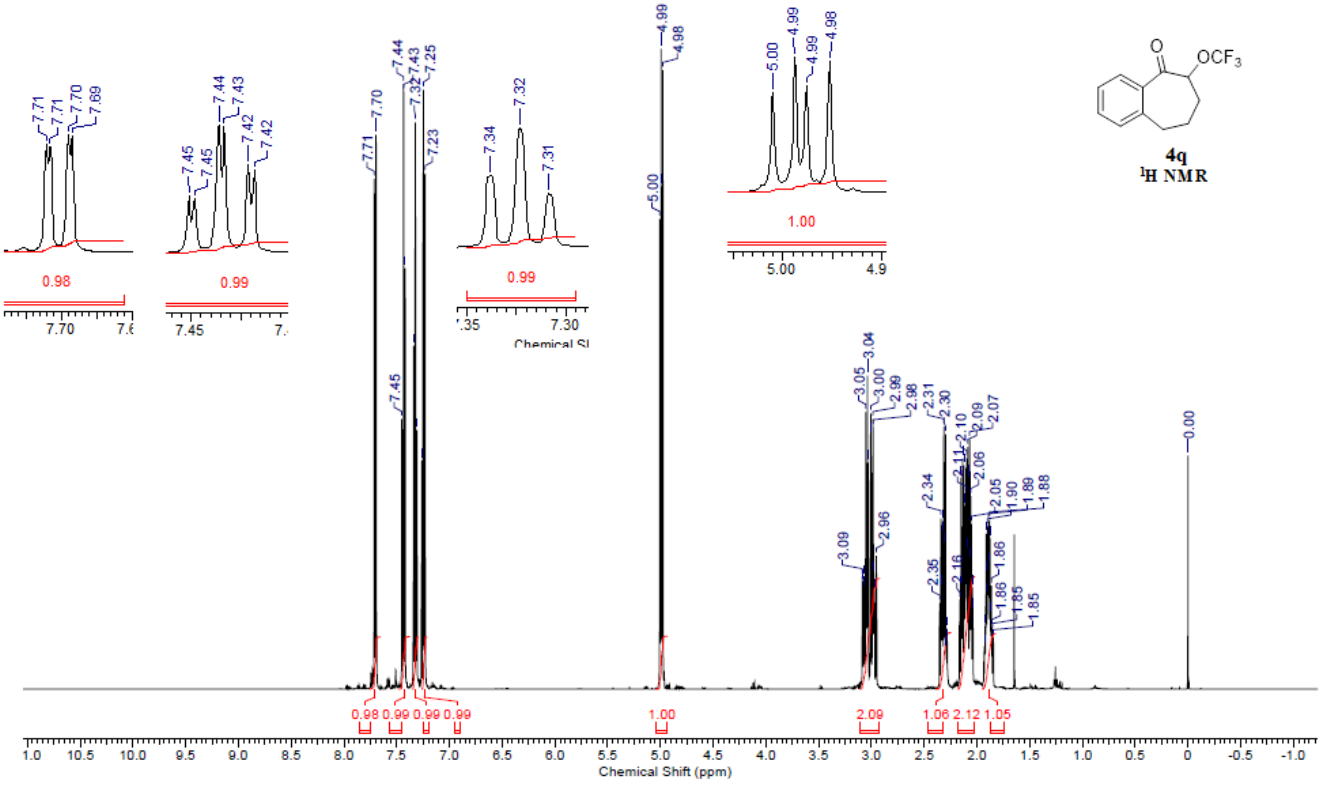
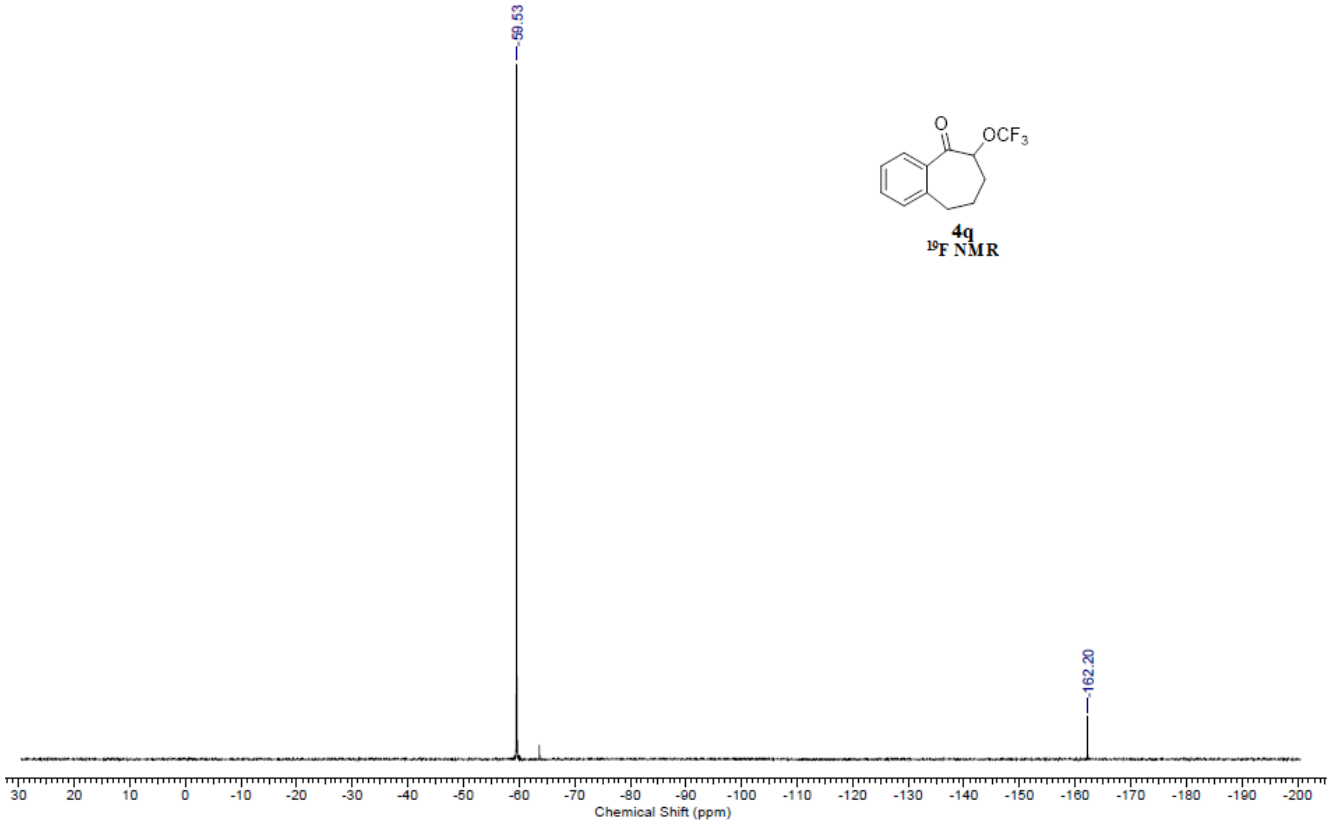
77.55
77.54
77.53
189.86
162.42
161.01
121.83
121.70
Chemical Shift (ppm)


4p
1H NMR
Chemical Shift (ppm)

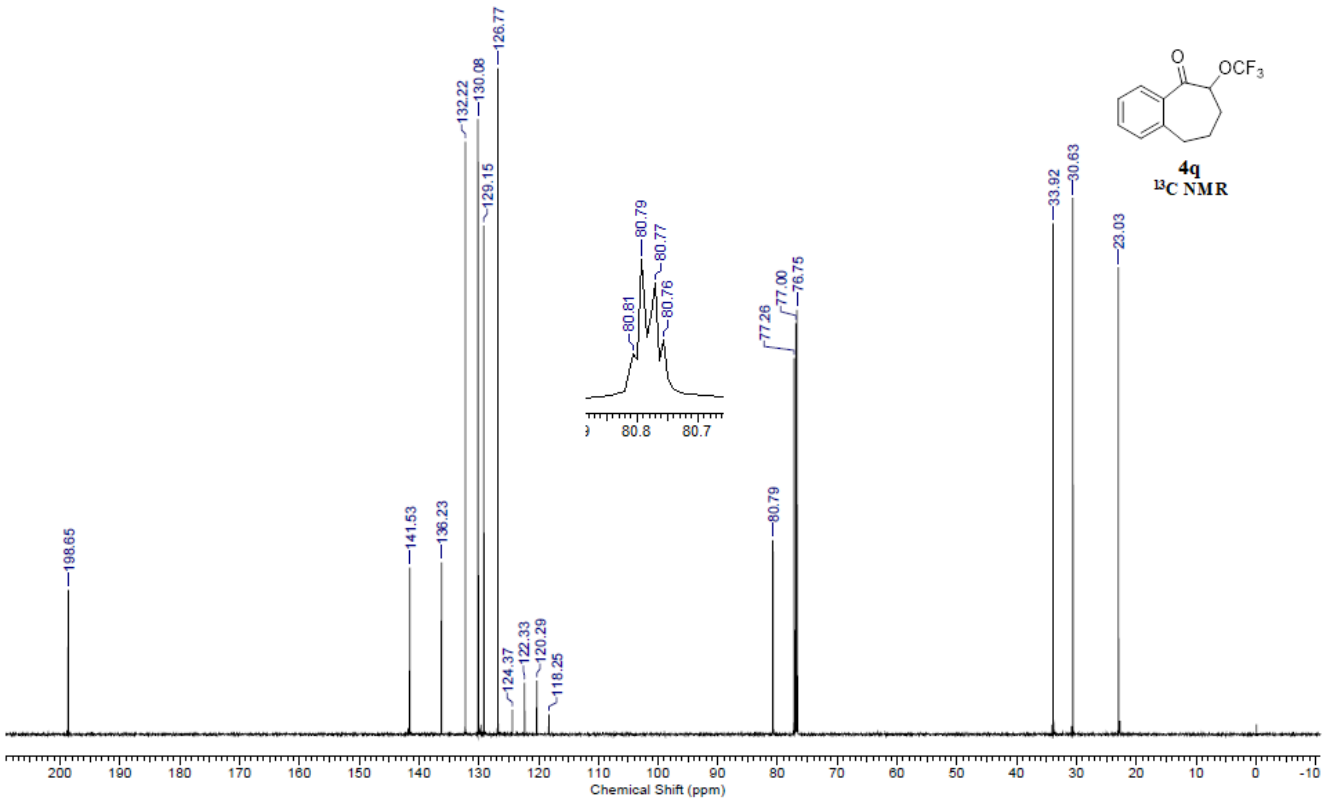

4p
19F NMR
Chemical Shift (ppm)


4p
13C NMR
Chemical Shift (ppm)

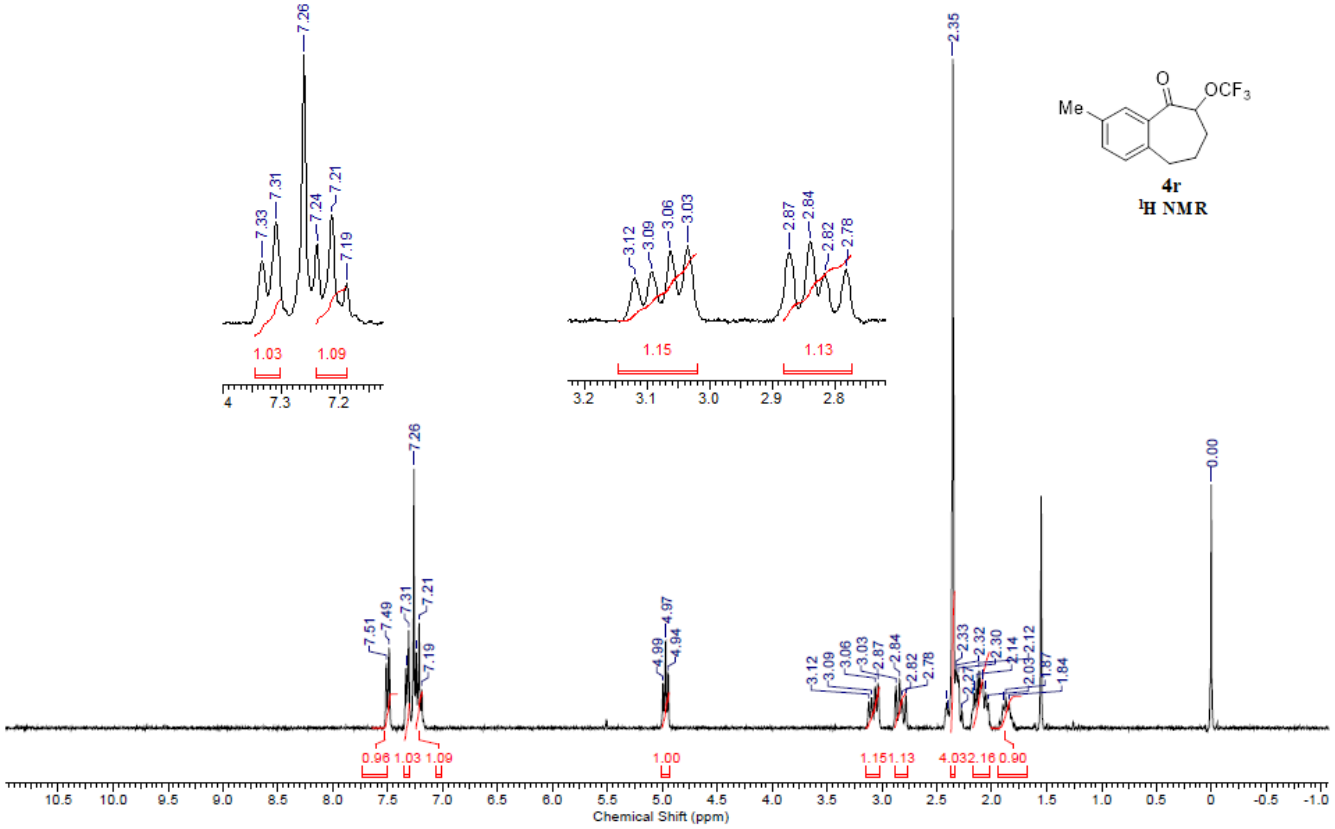

4q
1H NMR
Chemical Shift (ppm)

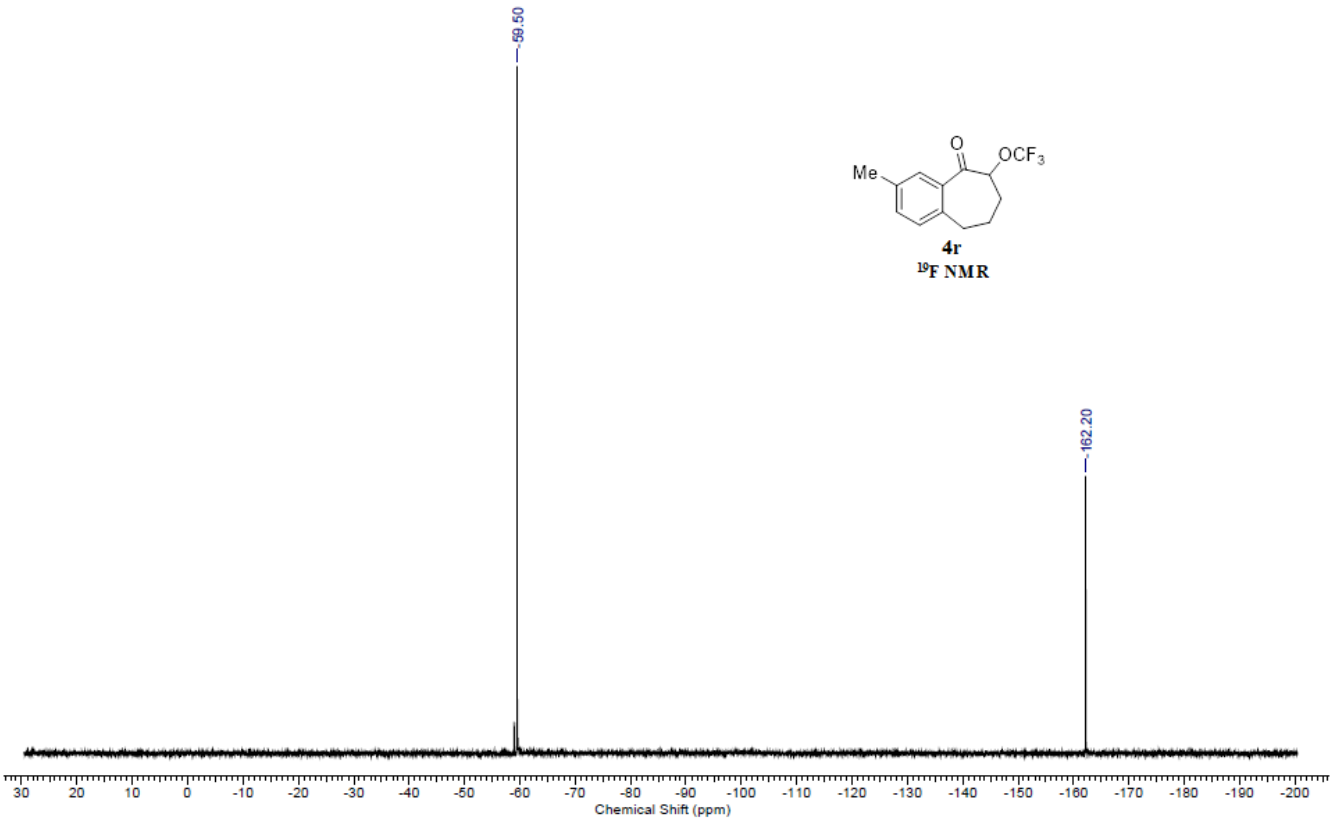


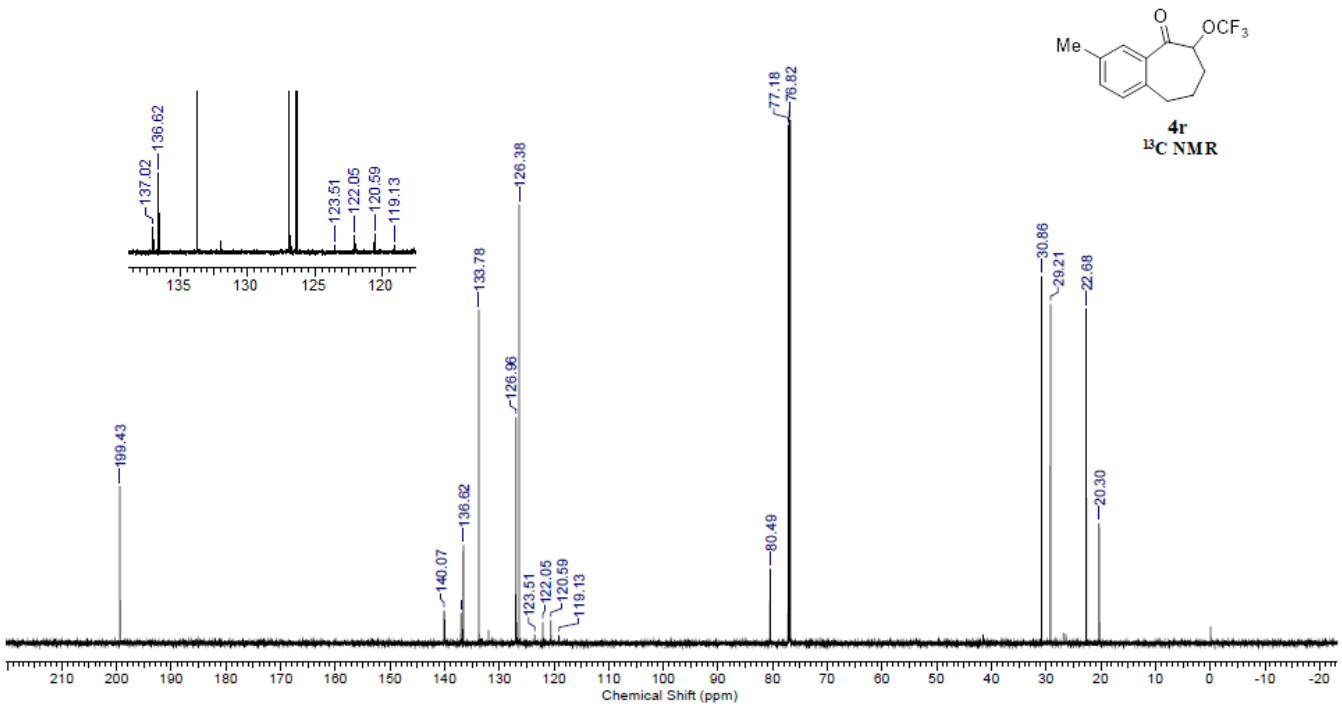
4q
^{19}F NMR

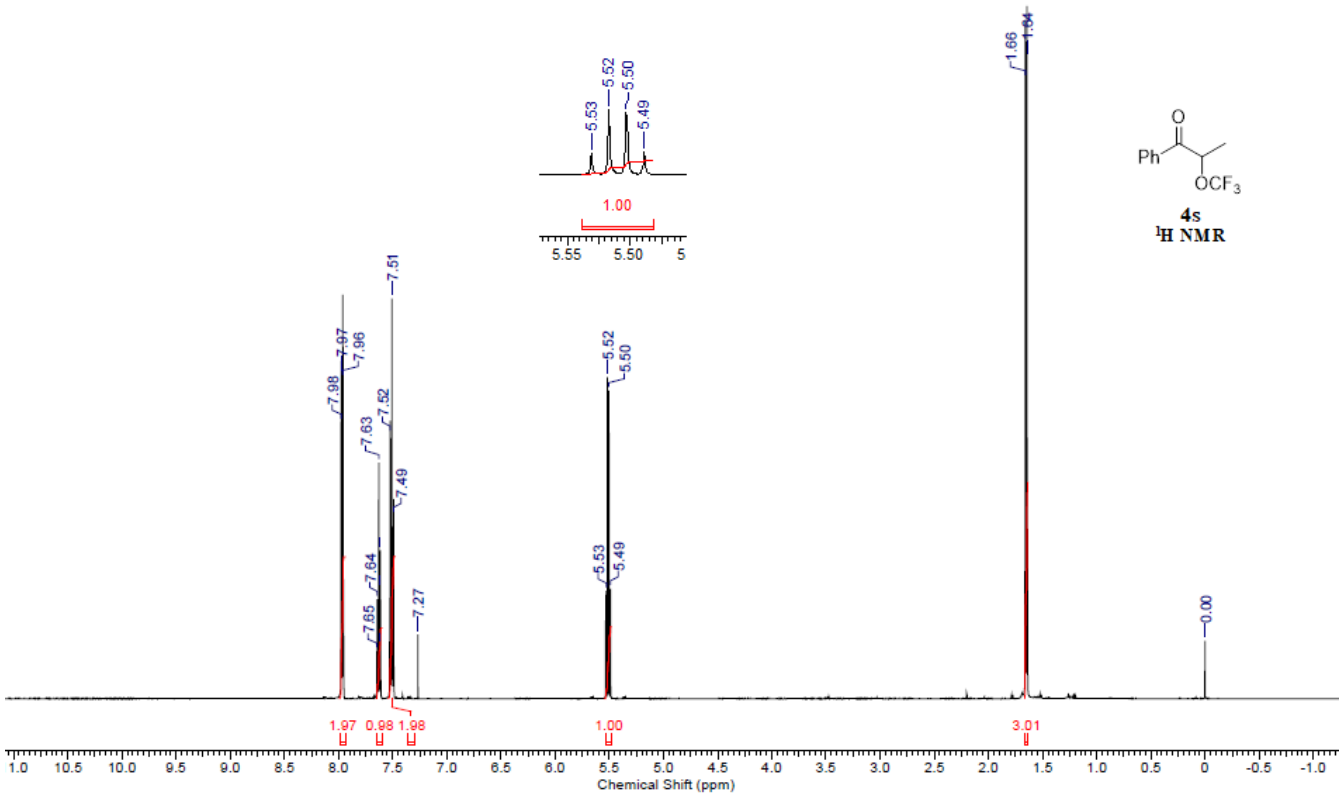


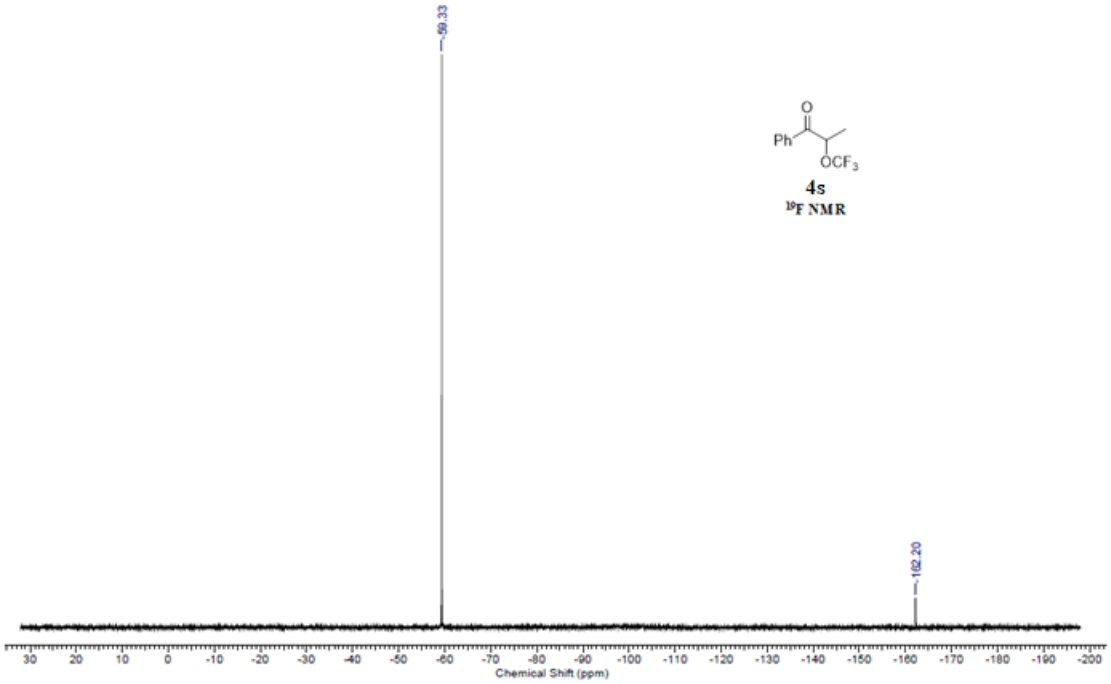
4q
^{13}C NMR


7.26
7.33
7.31
7.24
7.21
7.19
1.03
1.09
3.12
3.09
3.06
3.03
2.87
2.84
2.82
2.78
1.15
1.13
2.35
O
OCF3
Me
4r
1H NMR
0.00
7.51
7.49
4.99
4.97
4.94
2.33
2.32
2.30
2.14
2.03
2.12
1.87
1.84
0.96
1.00
1.15
1.13
4.03
2.16
0.90
Chemical Shift (ppm)


59.50
162.20
O
OCF3
Me
4r
19F NMR
Chemical Shift (ppm)

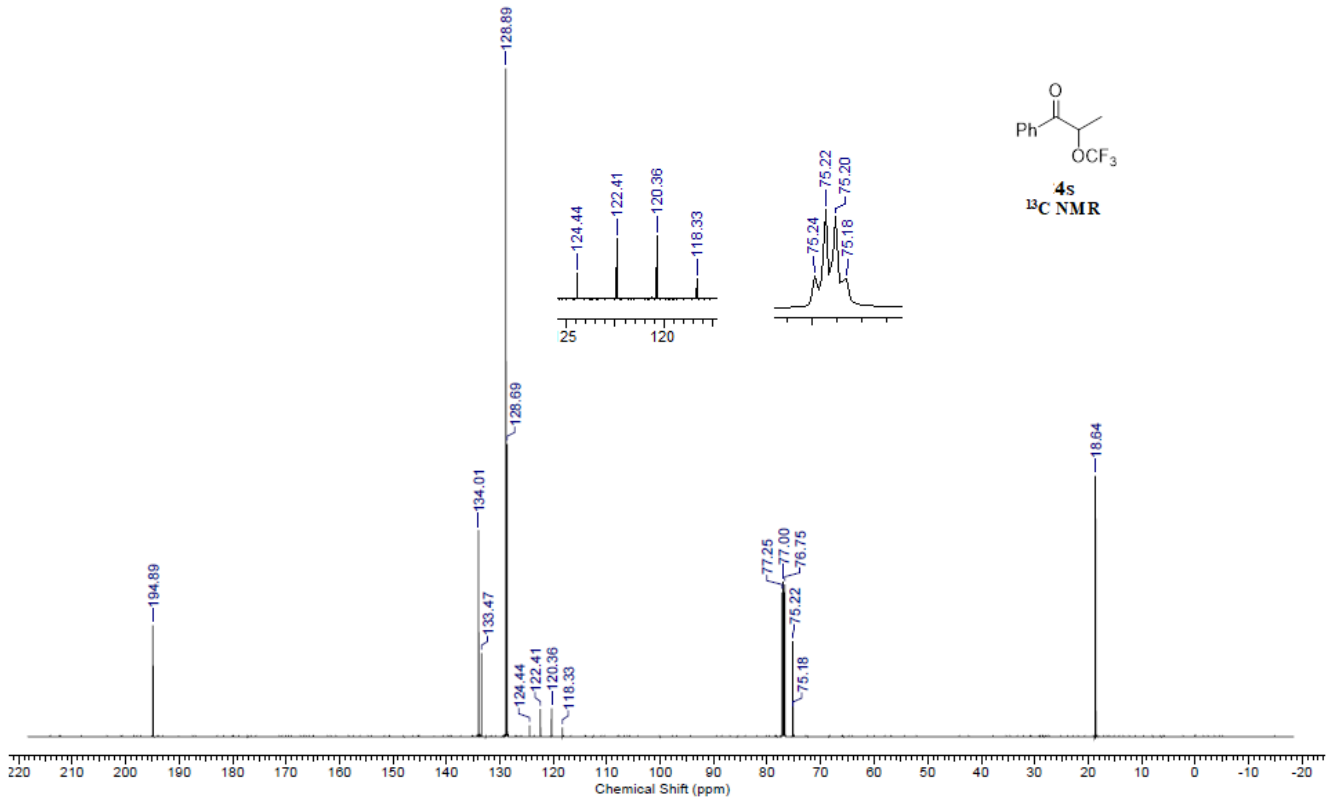

Me
O
OCF3
4r
13C NMR
Chemical Shift (ppm)


Ph
O
OCF3
4s
1H NMR
1.97
0.98
1.98
1.00
3.01
Chemical Shift (ppm)



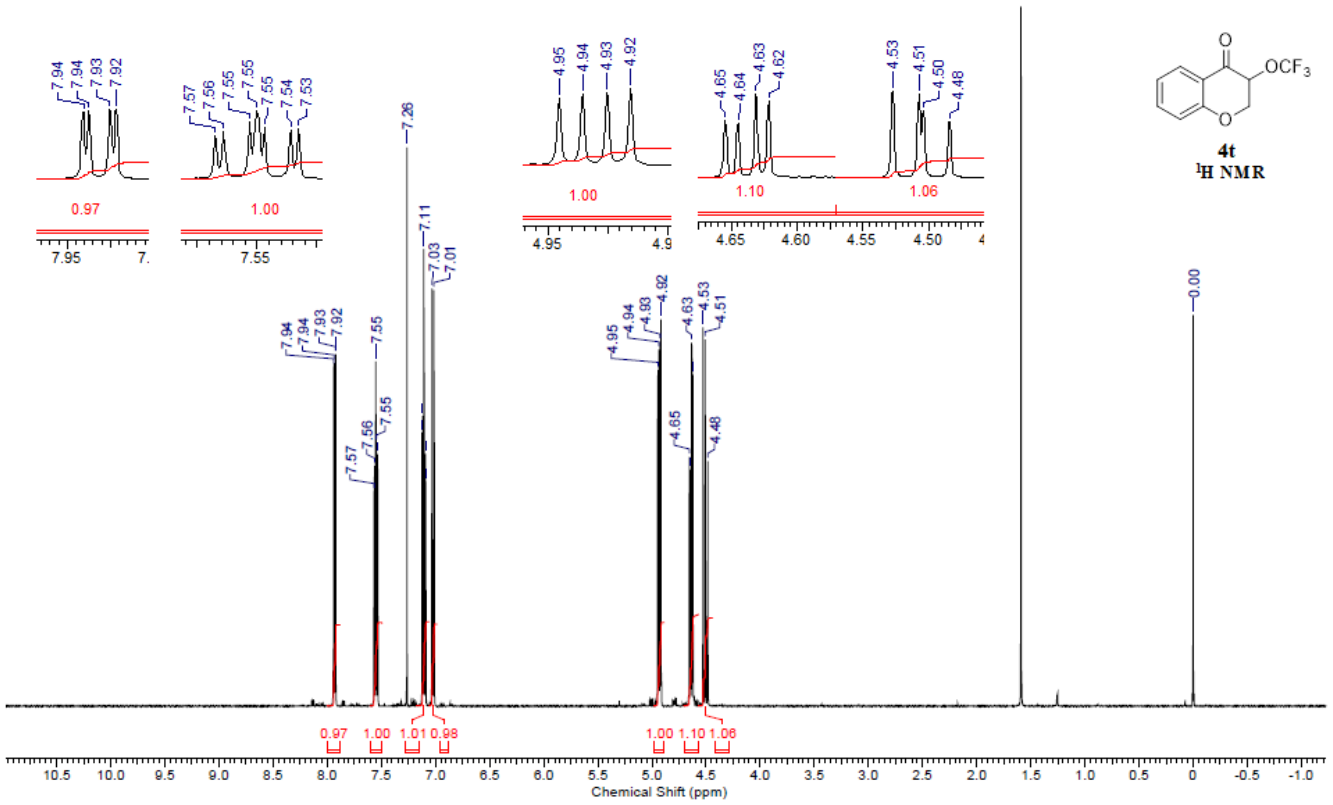
4s

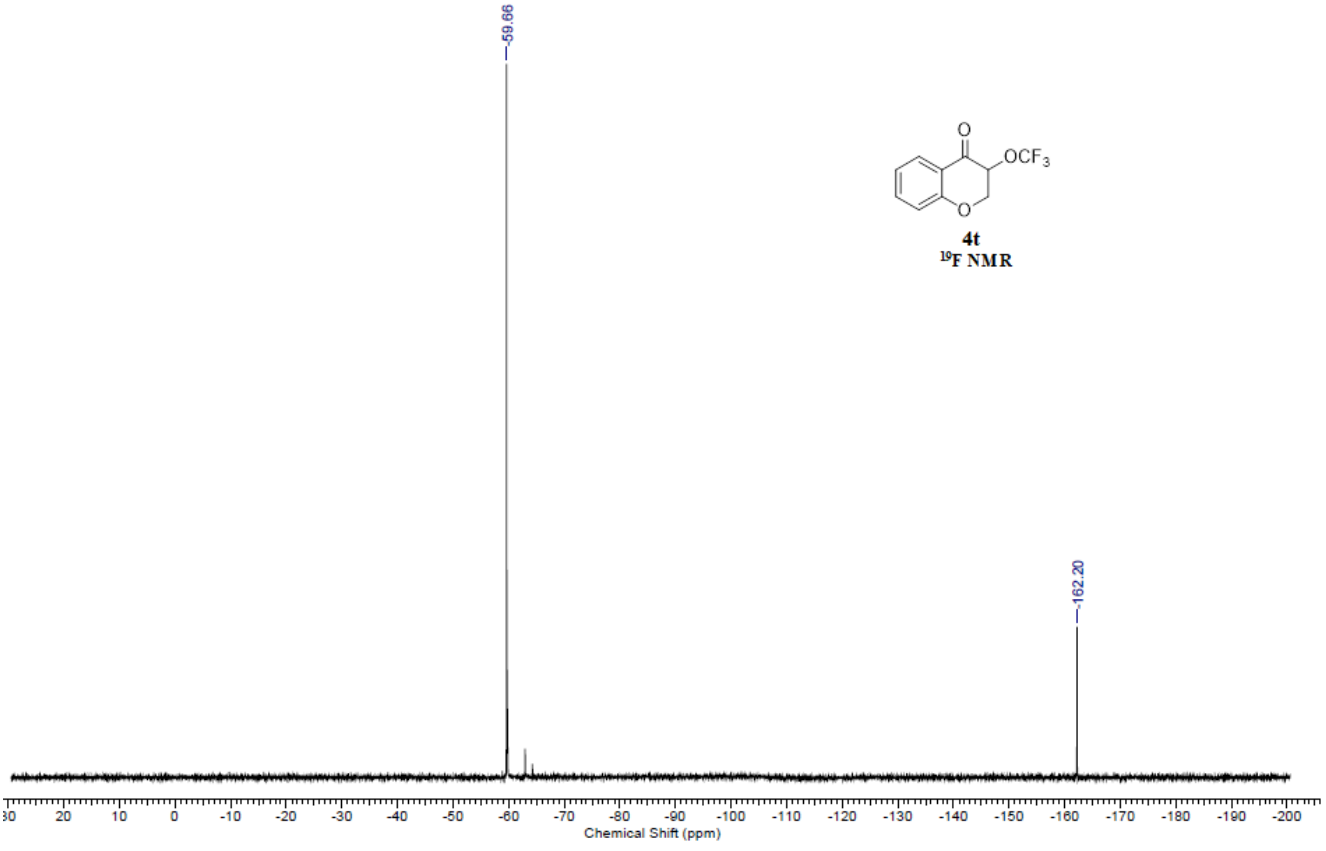
^{19}F NMR

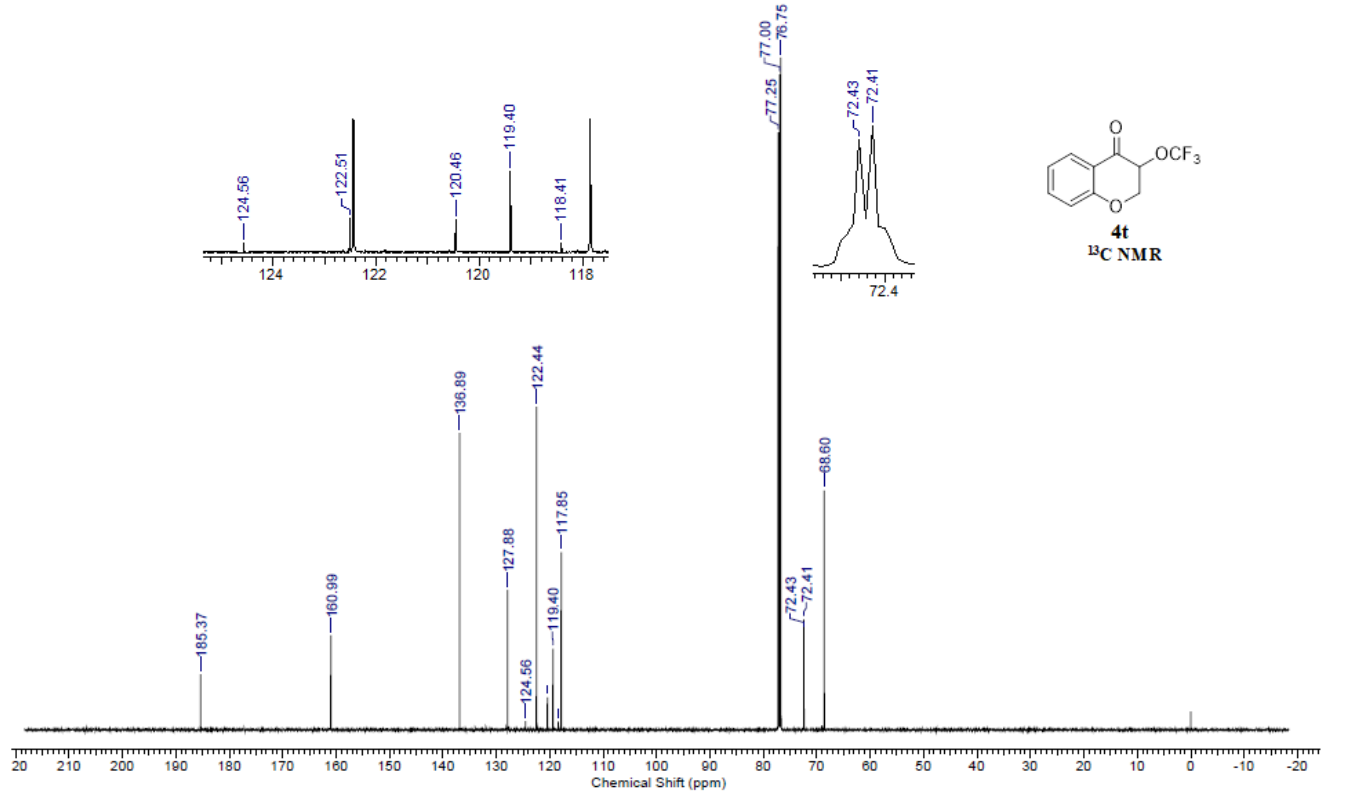


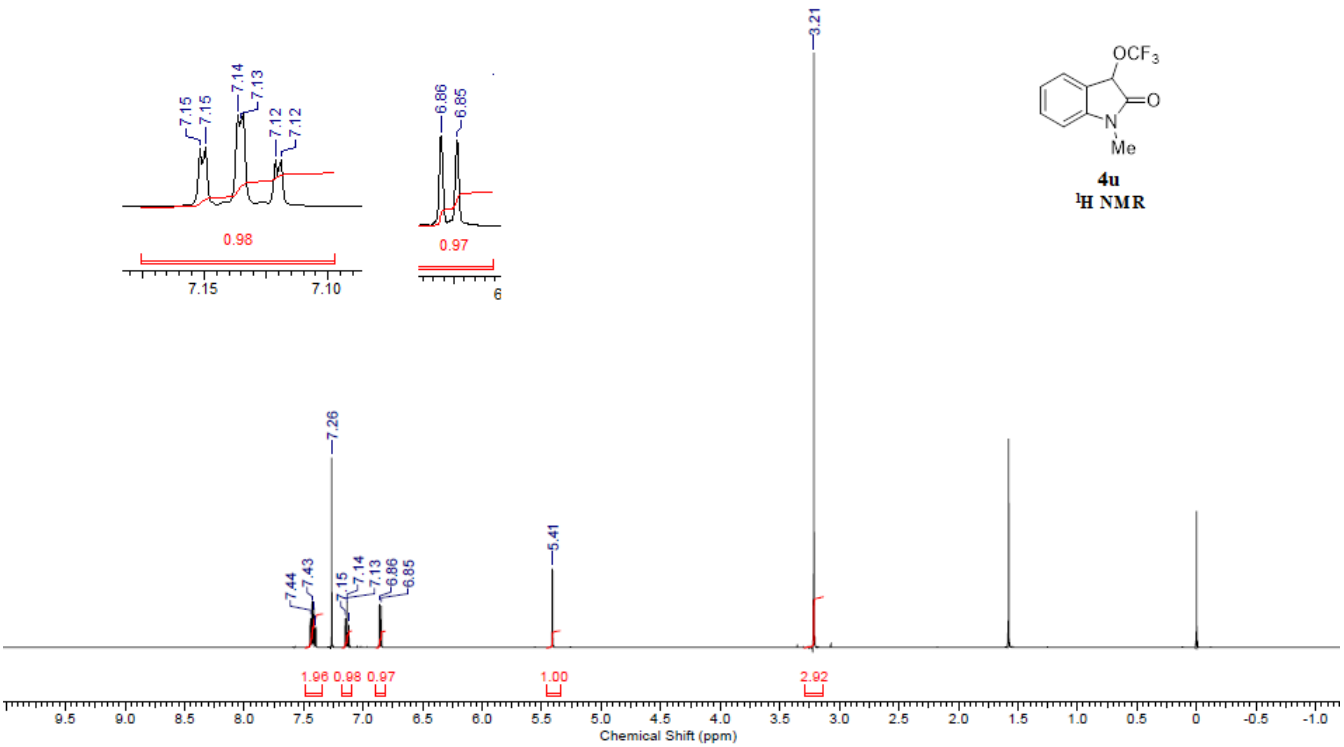
4s

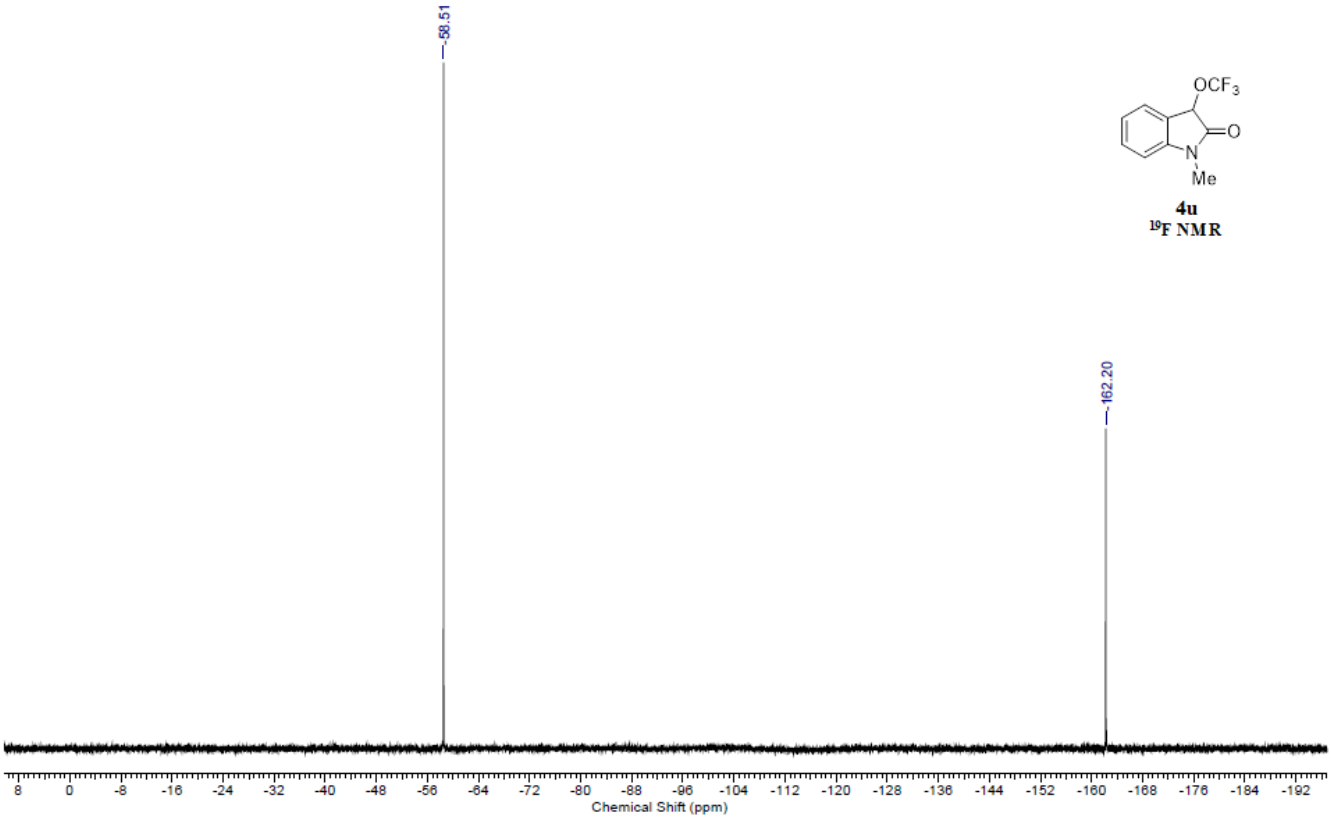
^{13}C NMR


4t
1H NMR
Chemical Shift (ppm)

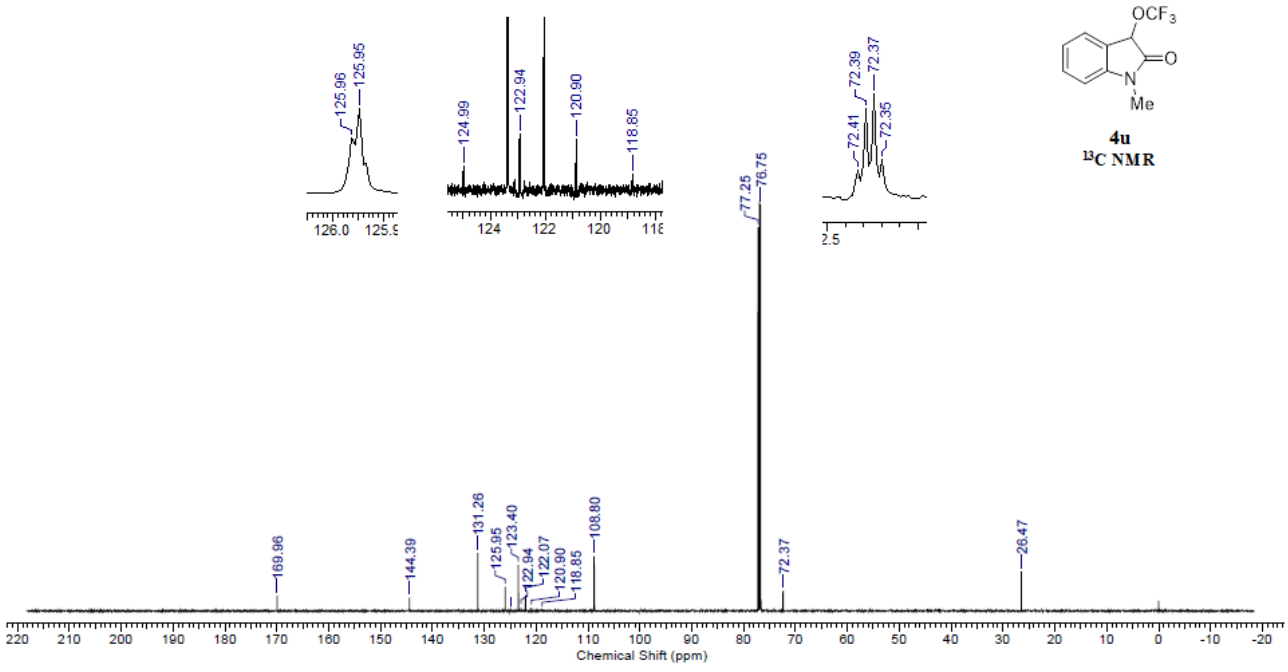

4t
19F NMR
Chemical Shift (ppm)


124.56
122.51
120.46
119.40
118.41
77.00
76.75
77.25
72.43
72.41
72.4
O
OCF3
O
4t
13C NMR
136.89
122.44
68.60
127.88
117.85
160.99
119.40
185.37
124.56
Chemical Shift (ppm)

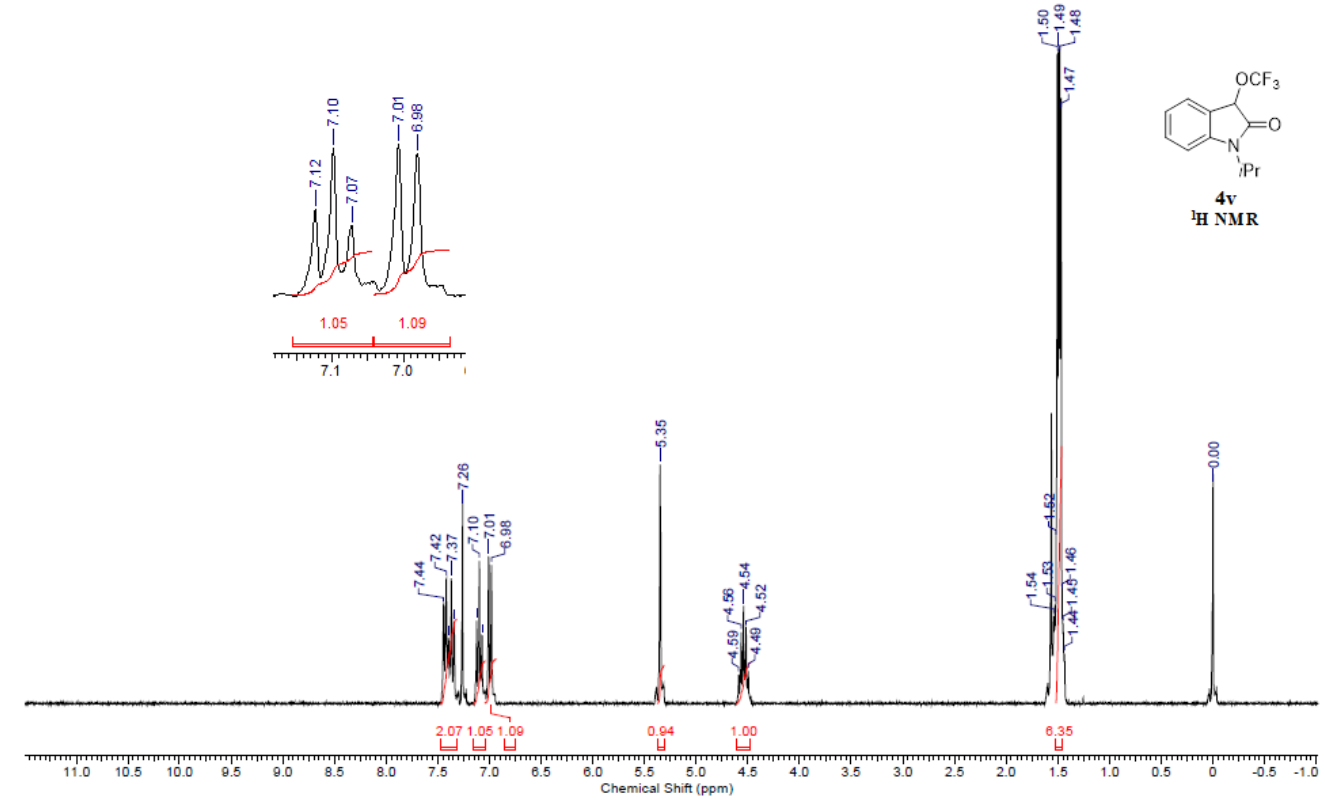

7.15
7.15
7.14
7.13
7.12
7.12
0.98
6.86
6.85
0.97
3.21
OCF3
O
N
Me
4u
1H NMR
7.26
7.44
7.43
7.15
7.14
7.13
6.86
6.85
5.41
1.96
0.98
0.97
1.00
2.92
Chemical Shift (ppm)

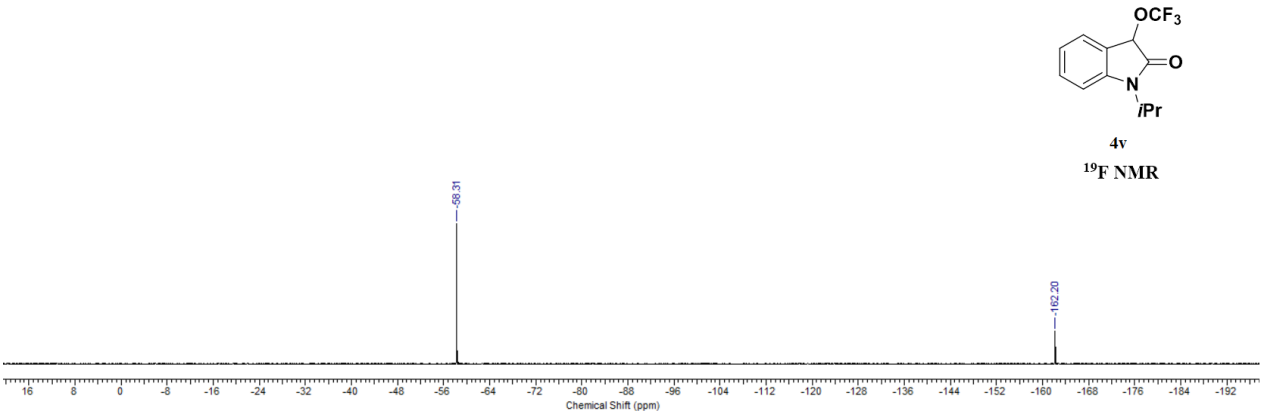


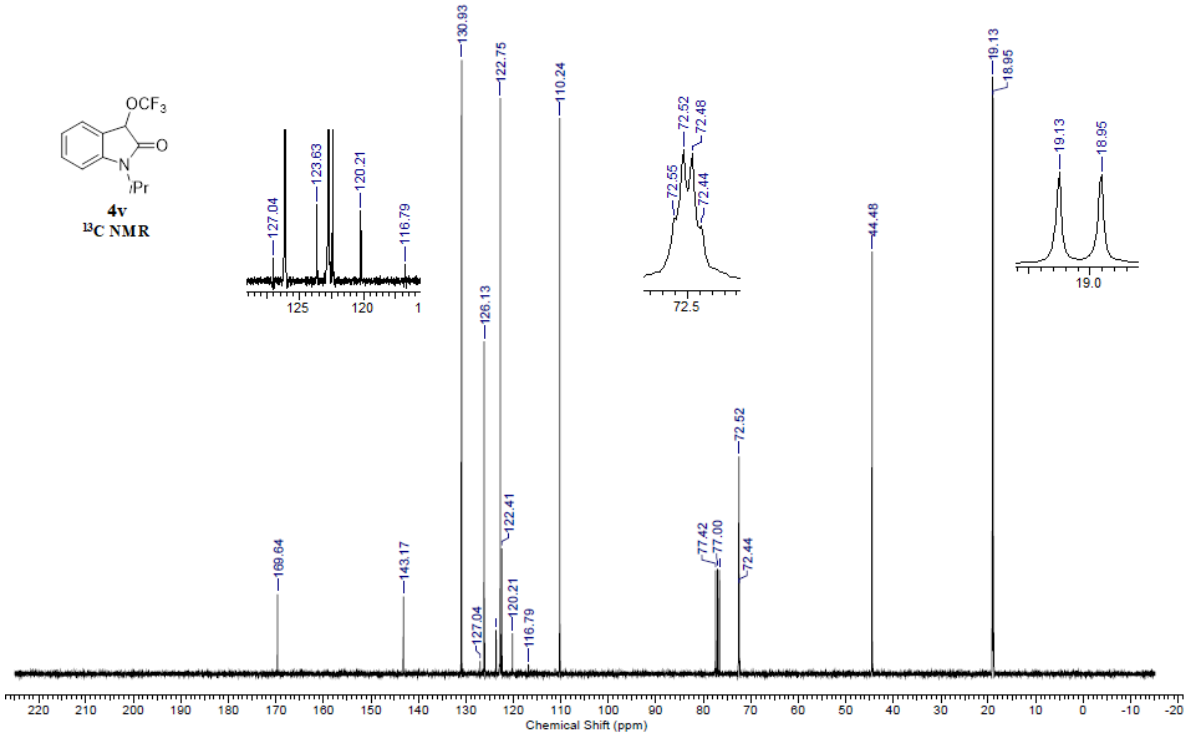
4u
^{19}F NMR

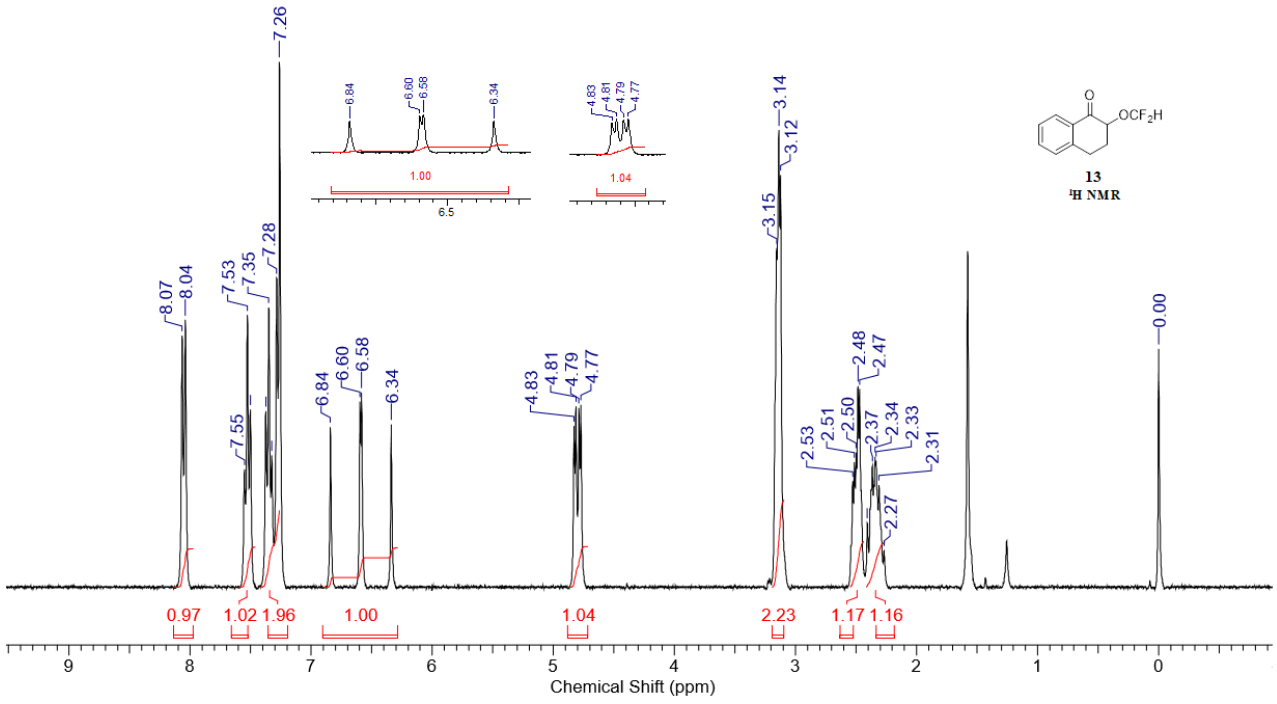


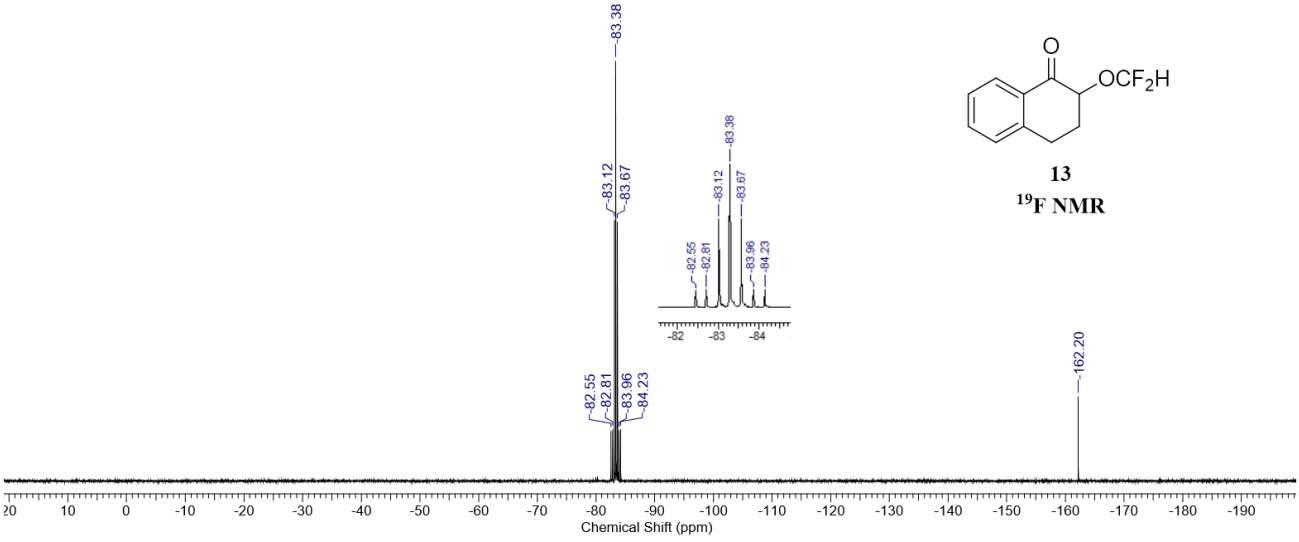
4u
^{13}C NMR


7.12
7.10
7.07
7.01
6.98
1.05
1.09
7.1
7.0
1.50
1.49
1.48
1.47
OCF3
O
N
iPr
4v
1H NMR
7.44
7.42
7.37
7.26
7.10
7.01
6.98
5.35
4.59
4.56
4.54
4.52
4.49
1.54
1.53
1.52
1.46
1.44
1.40
0.00
2.07
1.05
1.09
0.94
1.00
6.35
Chemical Shift (ppm)


OCF3
O
N
iPr
4v
19F NMR
-58.31
-162.20
Chemical Shift (ppm)


OCF3
O
N
iPr
4v
13C NMR
130.93
126.13
122.75
122.41
120.21
116.79
110.24
72.52
72.48
72.55
72.44
44.48
19.13
18.95
169.64
143.17
127.04
123.63
120.21
116.79
77.42
77.00
72.44
Chemical Shift (ppm)


7.26
6.84
6.60
6.58
6.34
4.83
4.81
4.79
4.77
3.14
3.12
3.15
OCF2H
13
1H NMR
8.07
8.04
7.53
7.35
7.28
7.55
2.48
2.47
2.53
2.51
2.50
2.37
2.34
2.33
2.31
2.27
0.00
0.97
1.02
1.96
1.00
1.04
2.23
1.17
1.16
Chemical Shift (ppm)

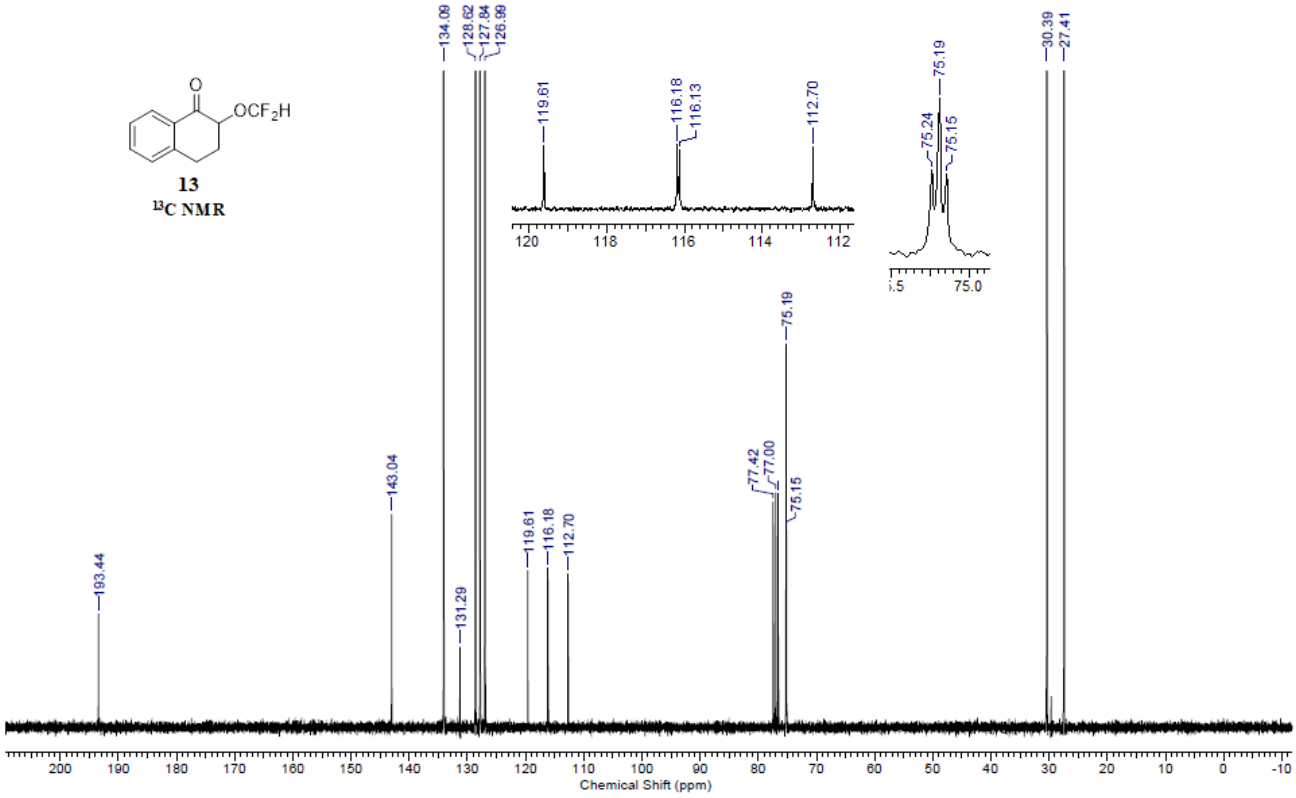


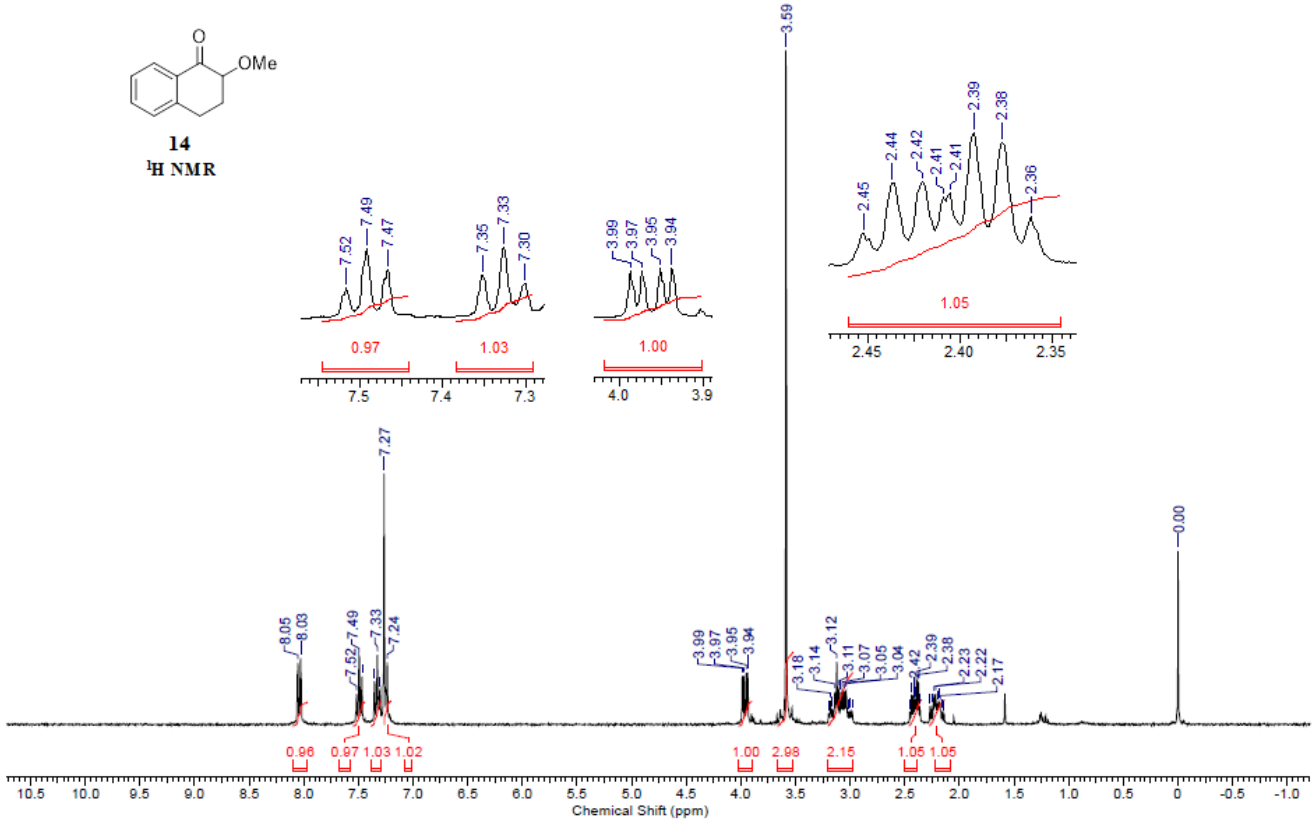
13

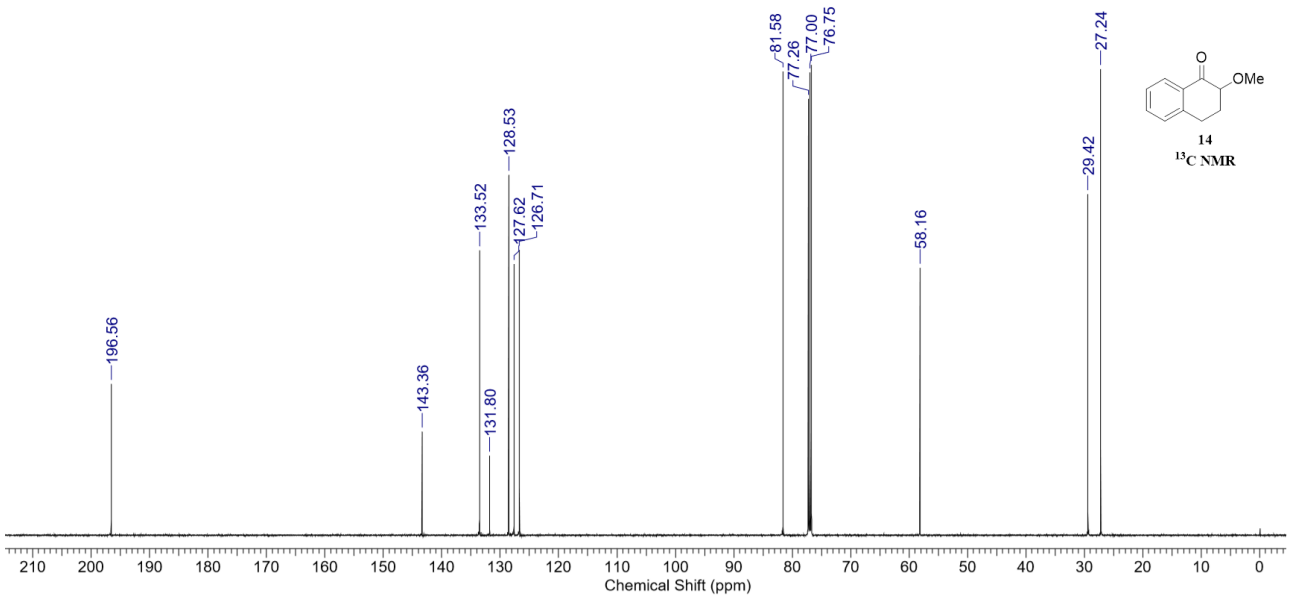
^{19}F NMR

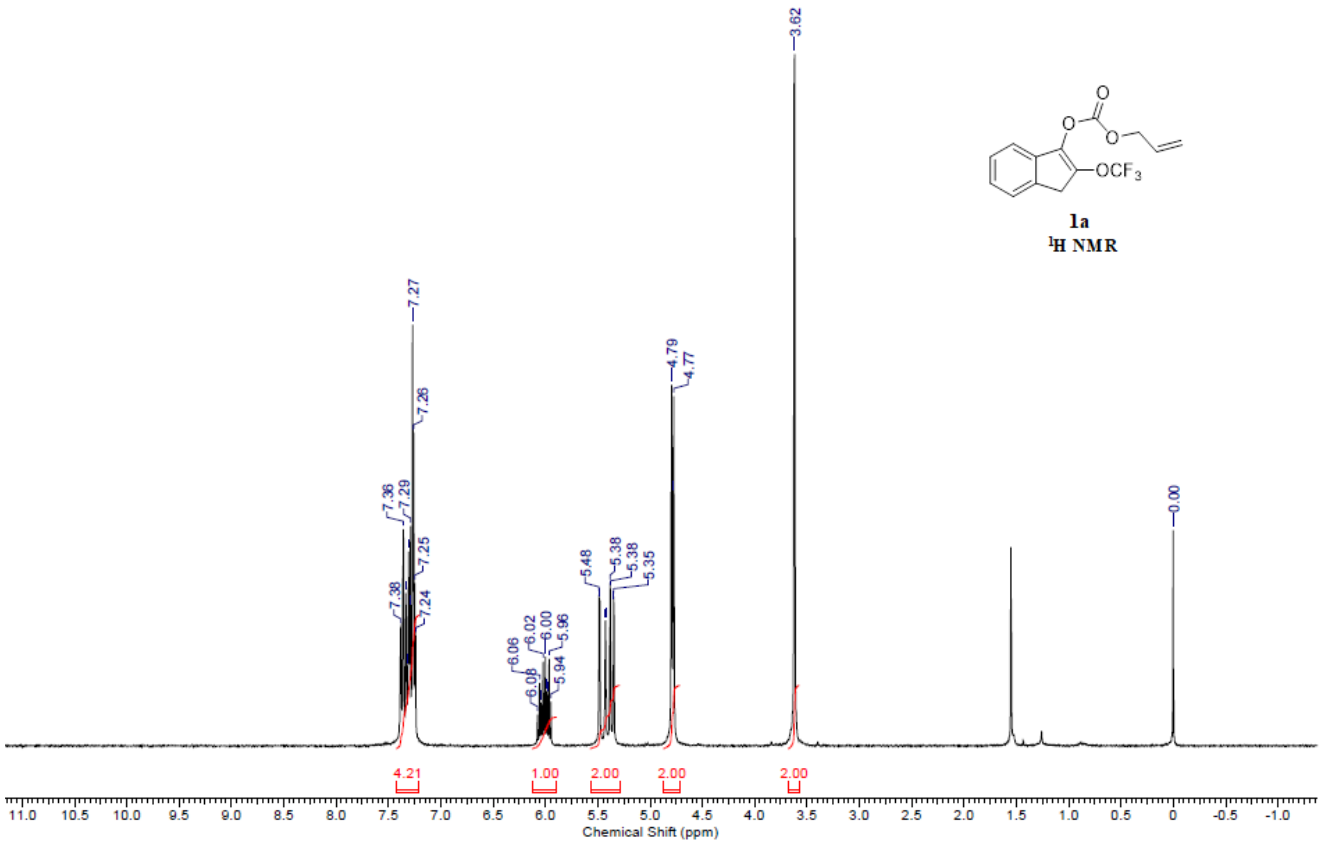
13

^{13}C NMR

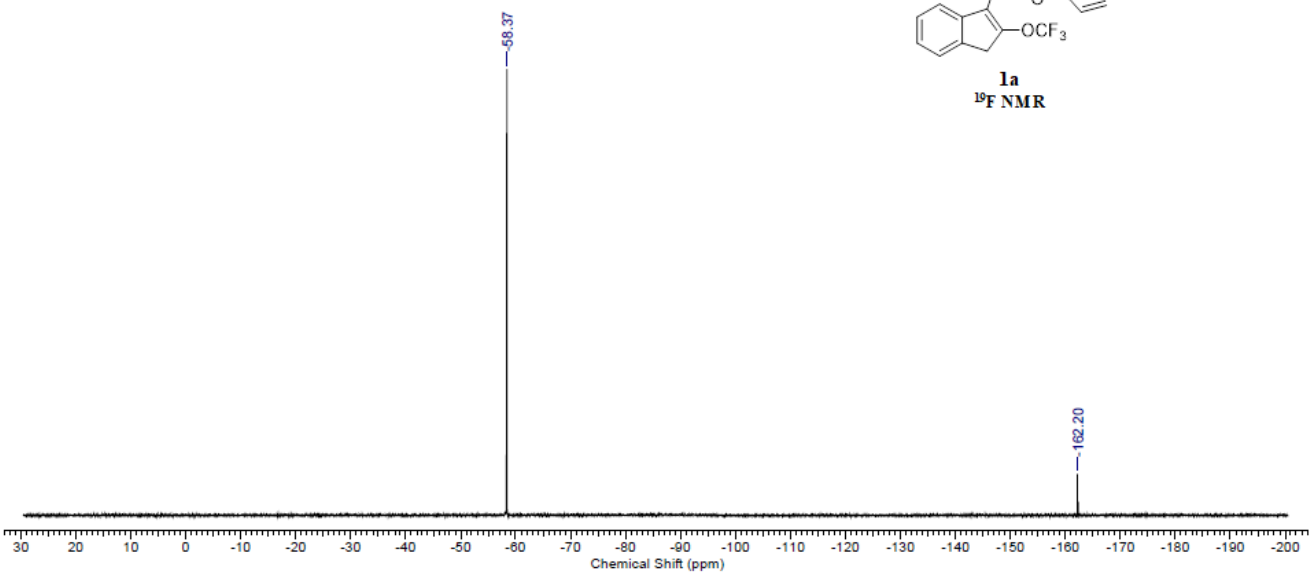



O
OMe
14
1H NMR
Chemical Shift (ppm)

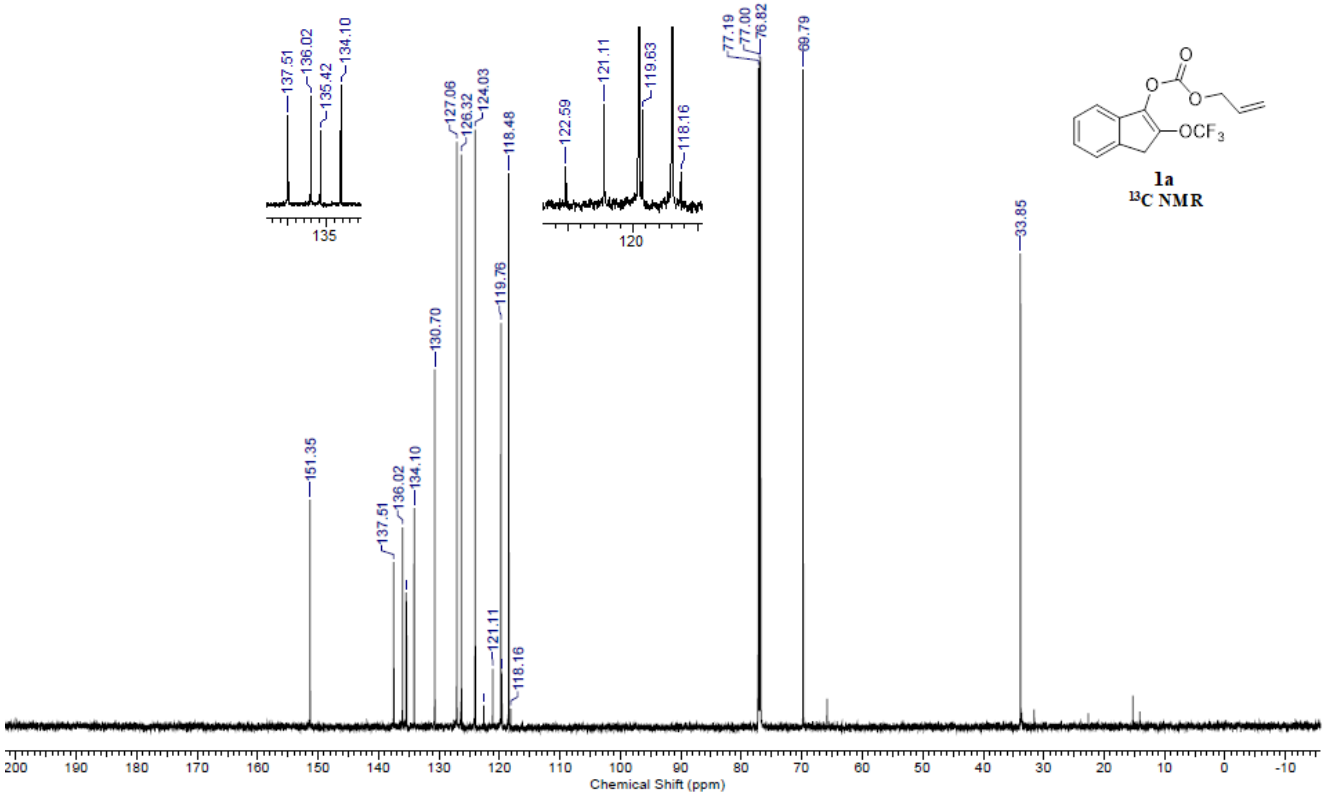

O
OMe
14
13C NMR
Chemical Shift (ppm)

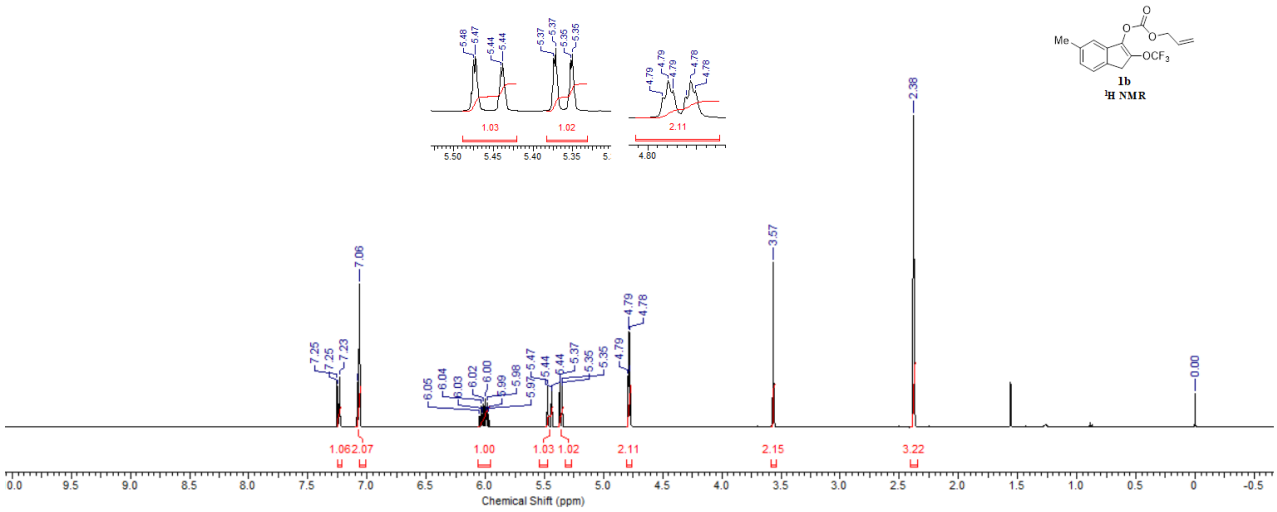


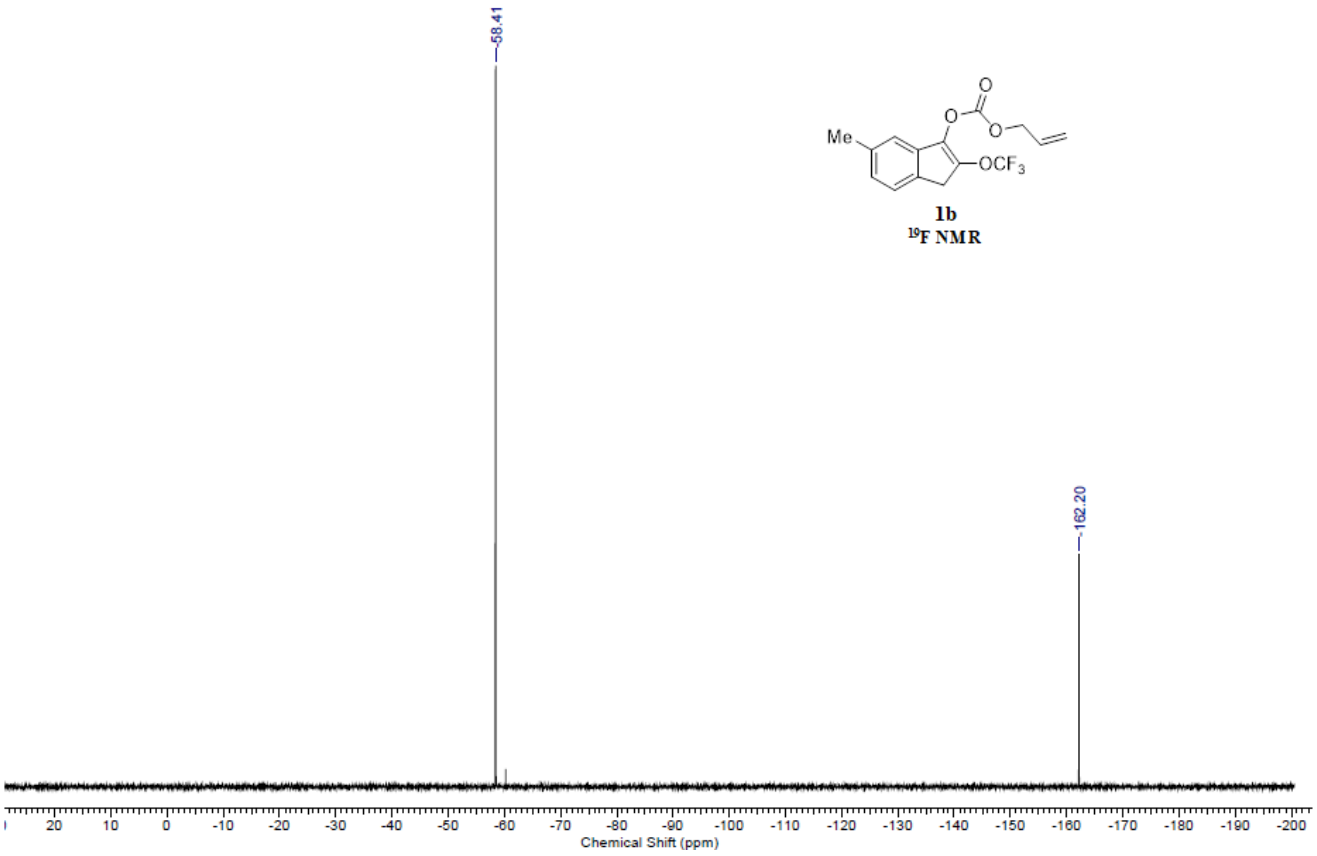
1a
^{1}H NMR

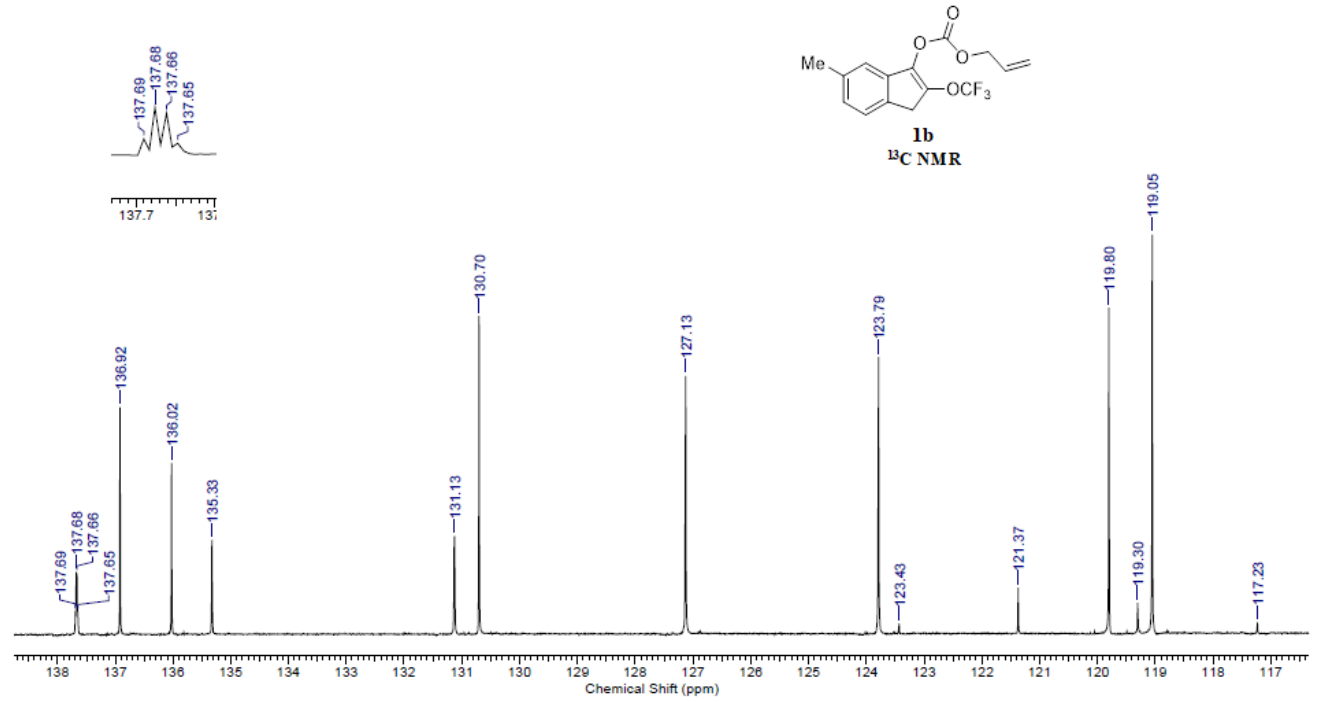


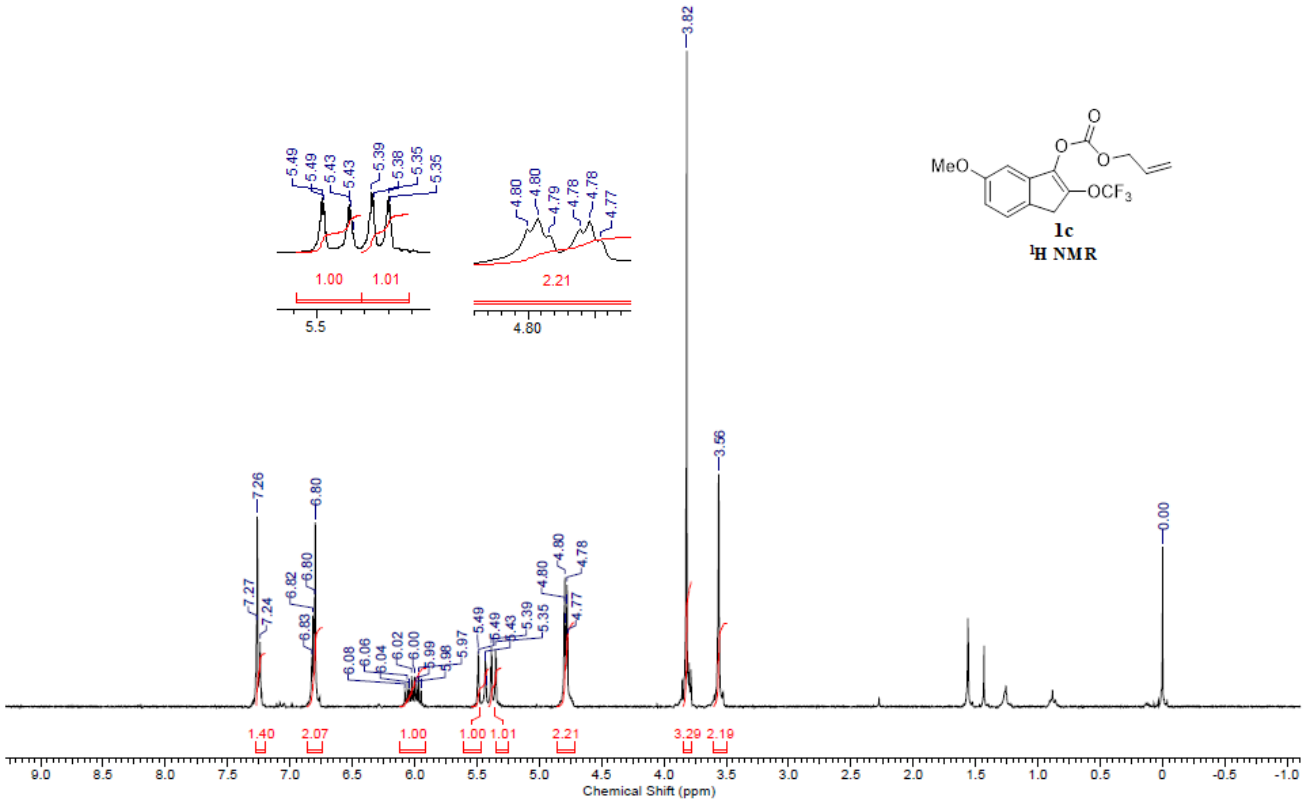
1a
^{19}F NMR

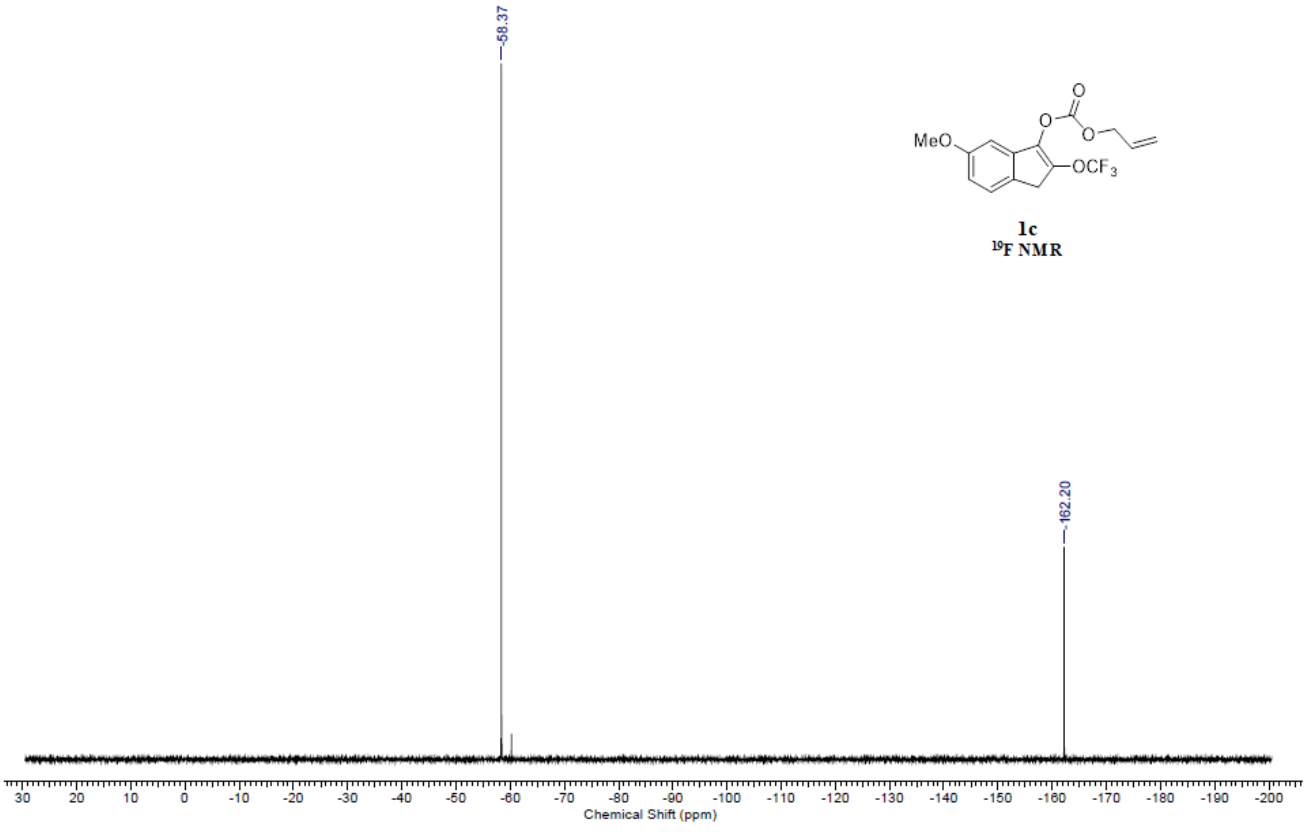

137.51
136.02
135.42
134.10
127.06
126.32
124.03
118.48
130.70
119.76
121.11
118.16
151.35
137.51
136.02
134.10
77.19
77.00
76.82
69.79
33.85
122.59
121.11
119.63
118.16
135
120
OCF3
1a
13C NMR
Chemical Shift (ppm)

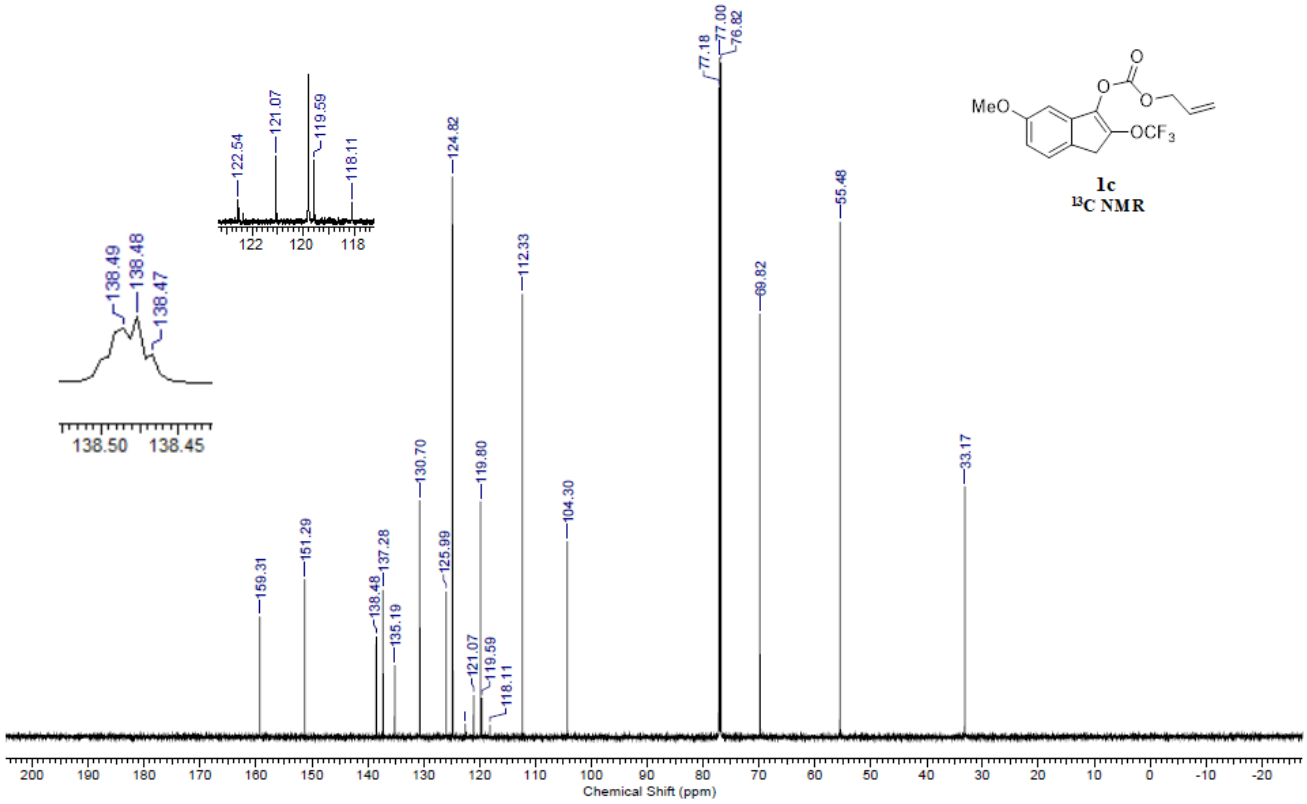

5.48
5.47
5.44
5.44
5.37
5.37
5.35
5.35
4.79
4.79
4.78
4.78
1.03
1.02
2.11
Me
OCF3
1b
1H NMR
7.25
7.25
7.23
7.06
6.05
6.04
6.03
6.02
6.00
5.99
5.98
5.97
5.47
5.44
5.37
5.35
5.35
4.79
4.79
4.78
3.57
2.38
0.00
1.06
2.07
1.00
1.03
1.02
2.11
2.15
3.22
Chemical Shift (ppm)

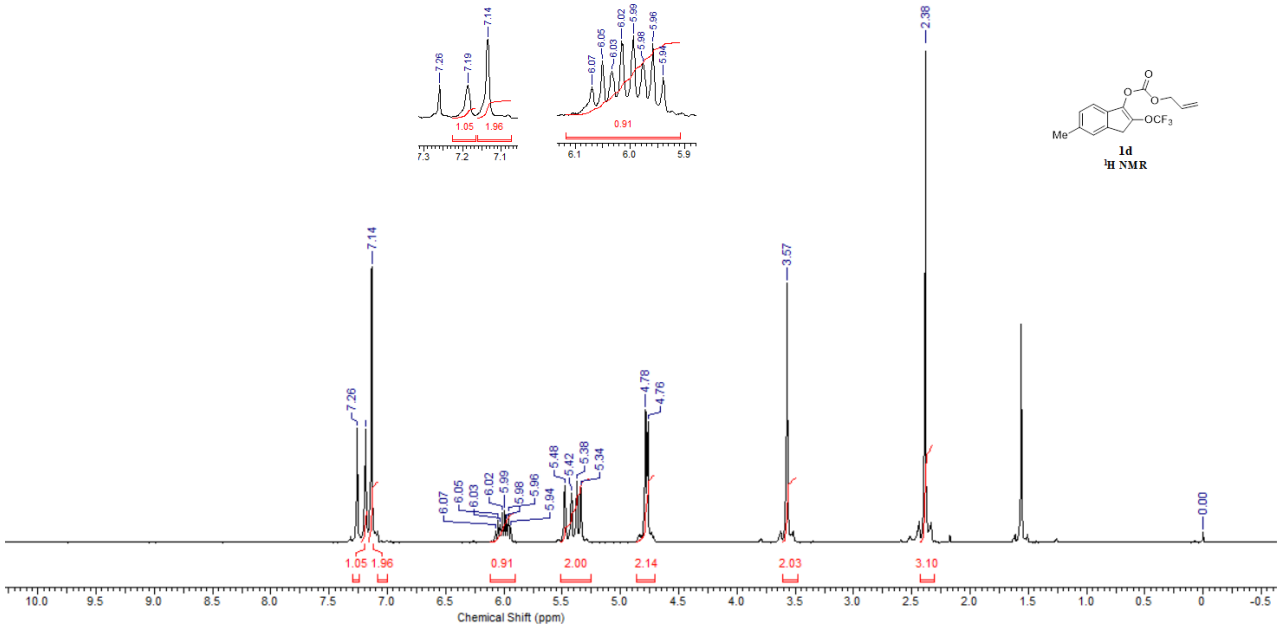

58.41
162.20
Me
O
O
O
OCF3
1b
19F NMR
Chemical Shift (ppm)

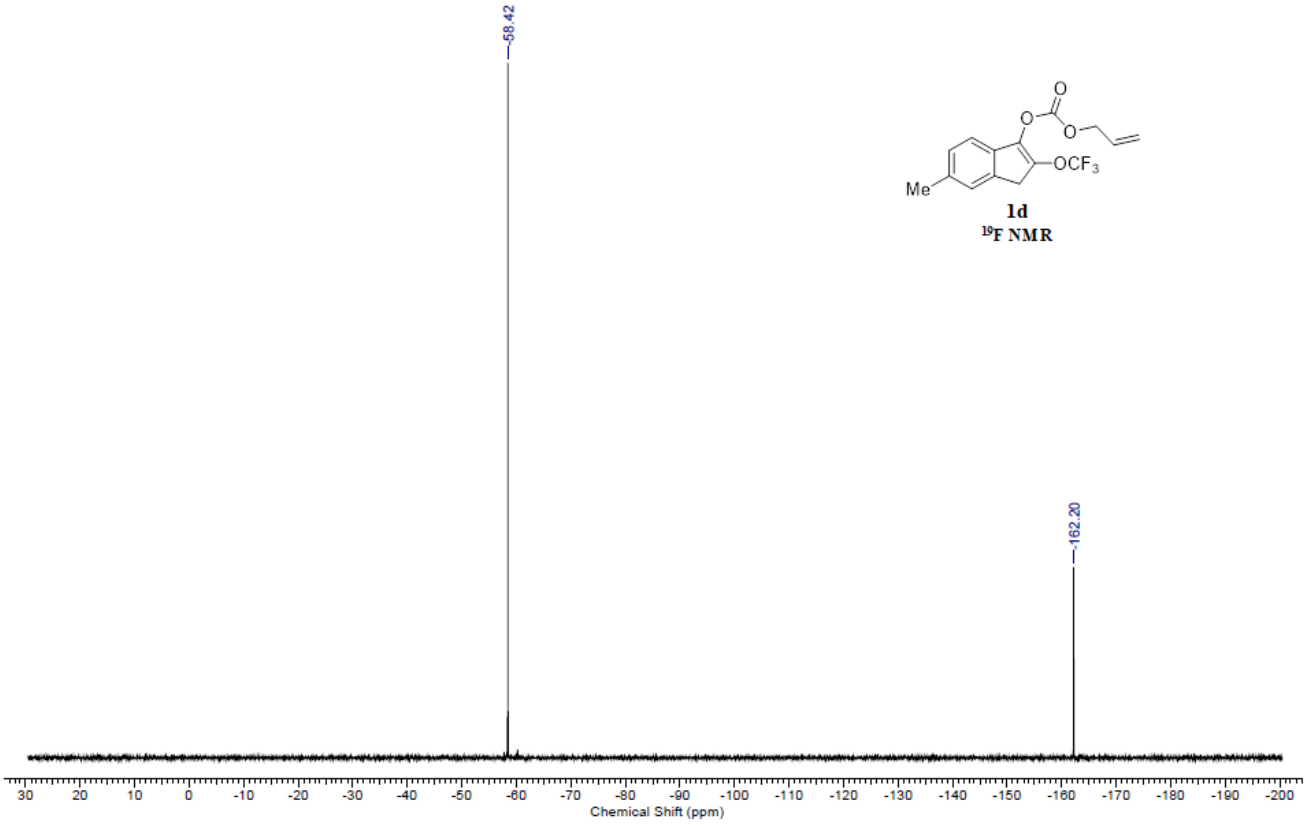

137.69
137.68
137.66
137.65
136.92
136.02
135.33
131.13
130.70
127.13
123.79
123.43
121.37
119.80
119.30
119.05
117.23
Me
O
O
O
OCF3
1b
13C NMR
Chemical Shift (ppm)


MeO
OCF3
1c
1H NMR
Chemical Shift (ppm)

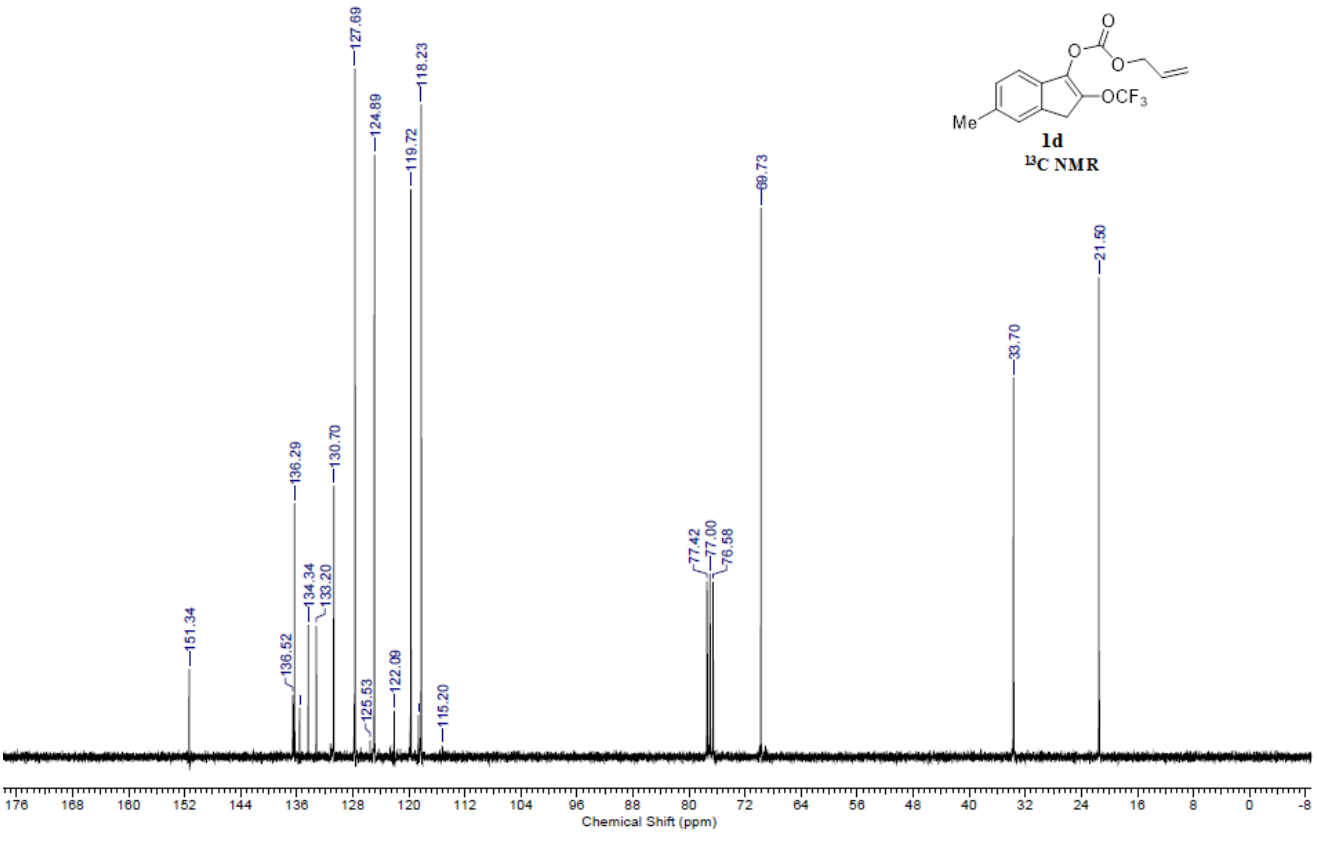

MeO
OCF3
1c
19F NMR
Chemical Shift (ppm)


MeO
OCF3
1c
13C NMR
Chemical Shift (ppm)

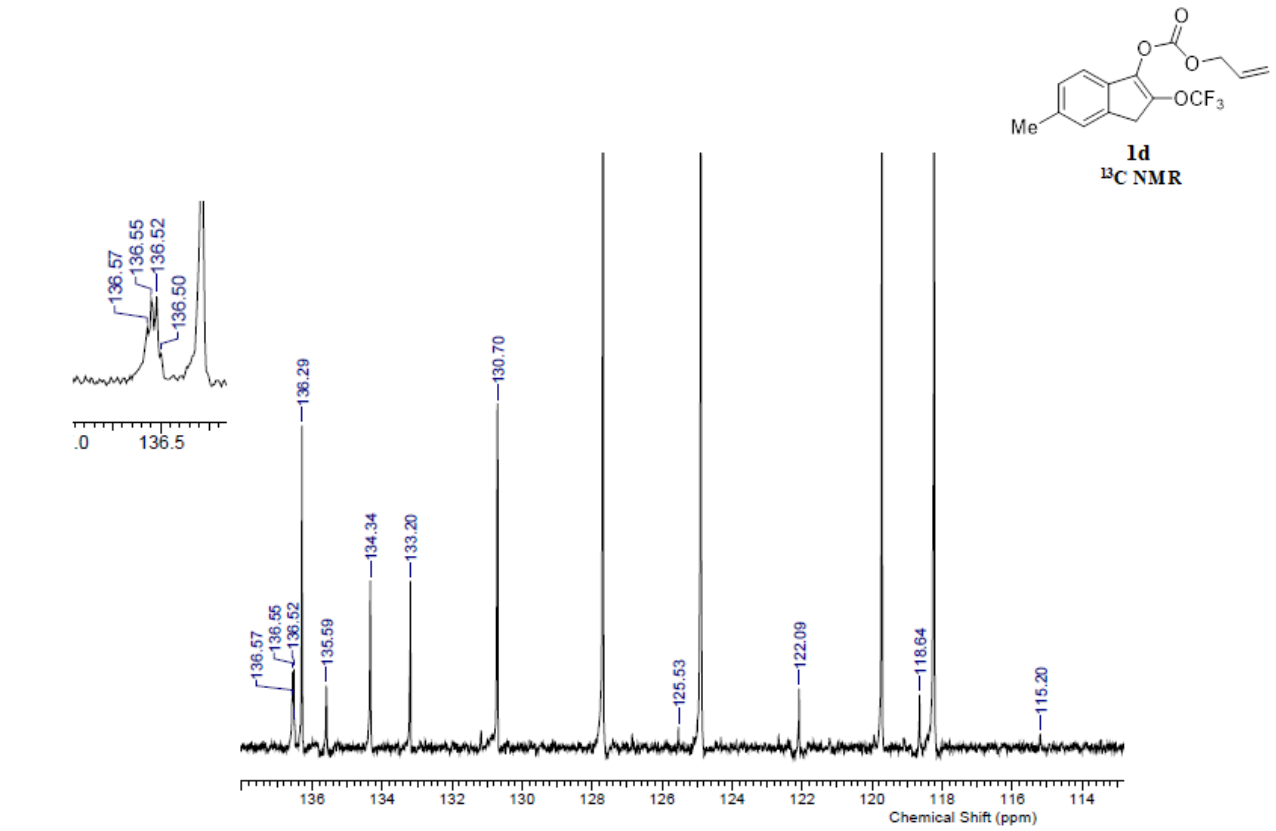

Me
OCF3
1d
1H NMR
Chemical Shift (ppm)

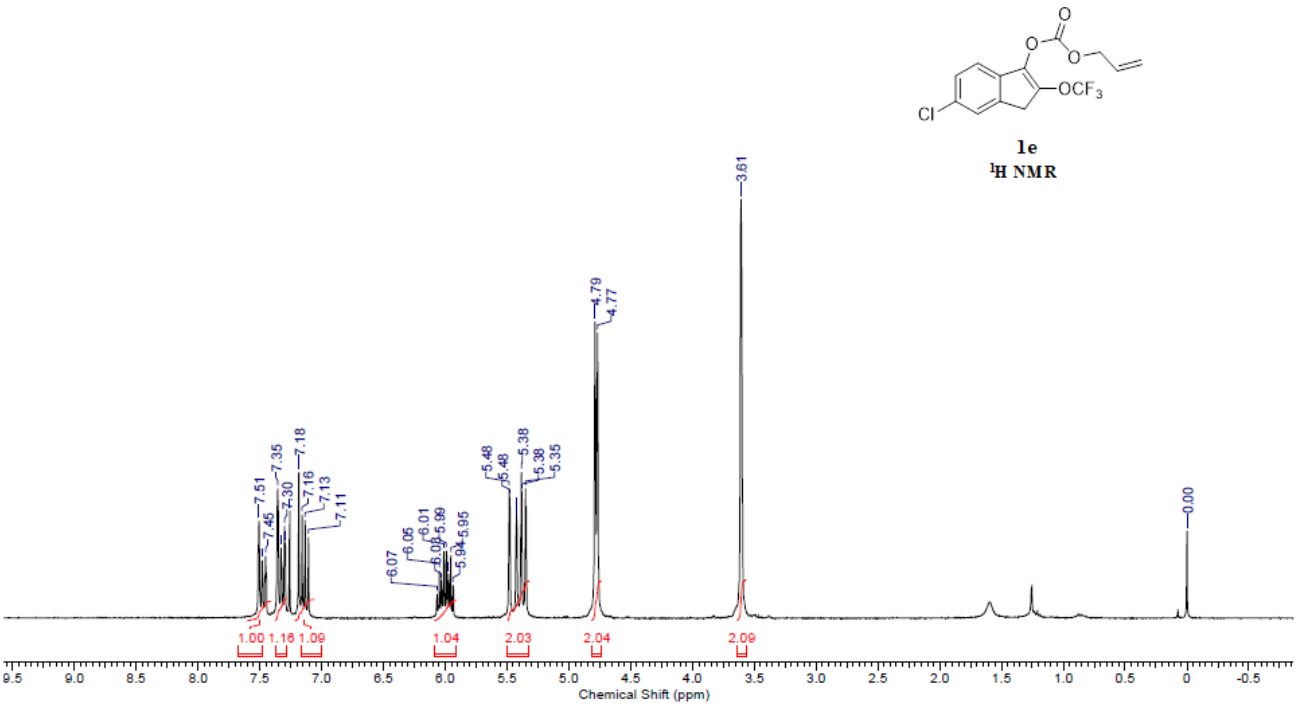


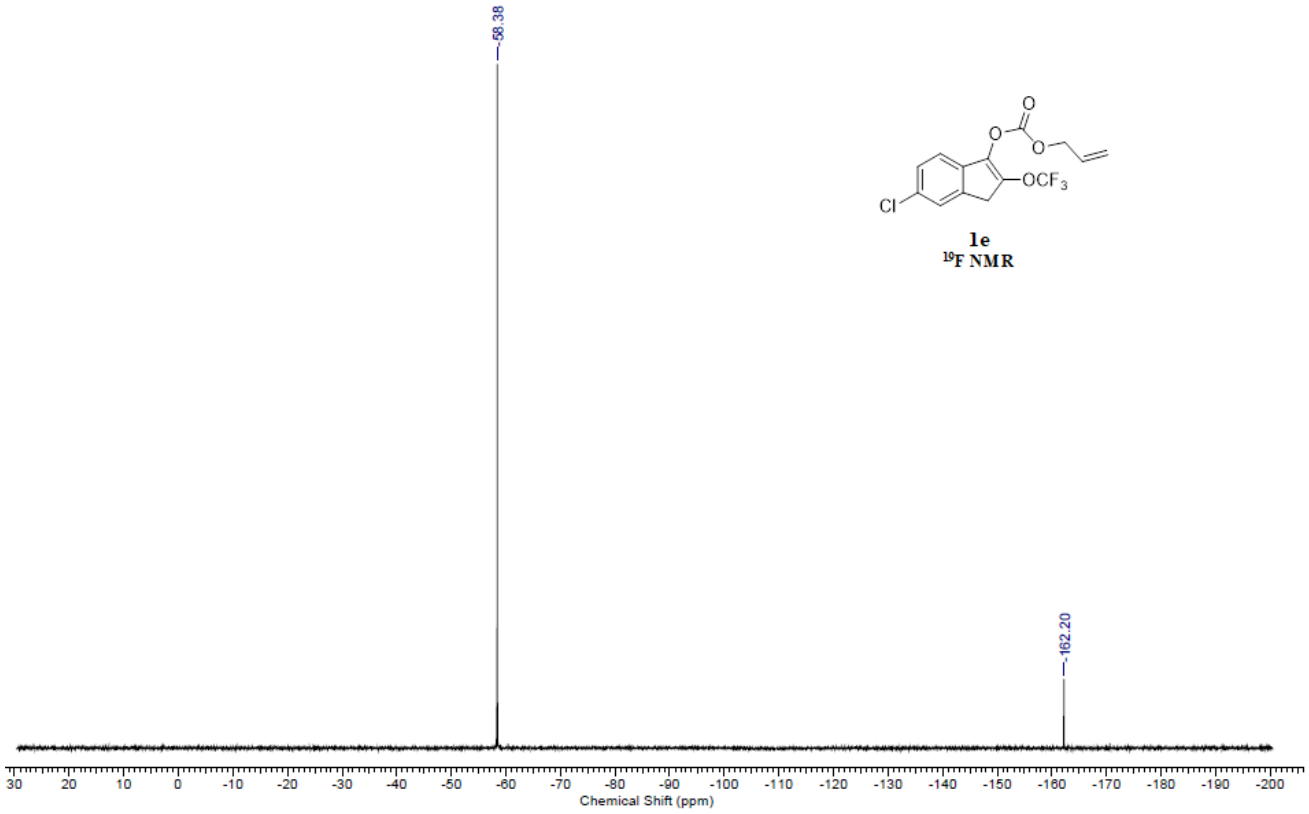
1d
^{19}F NMR



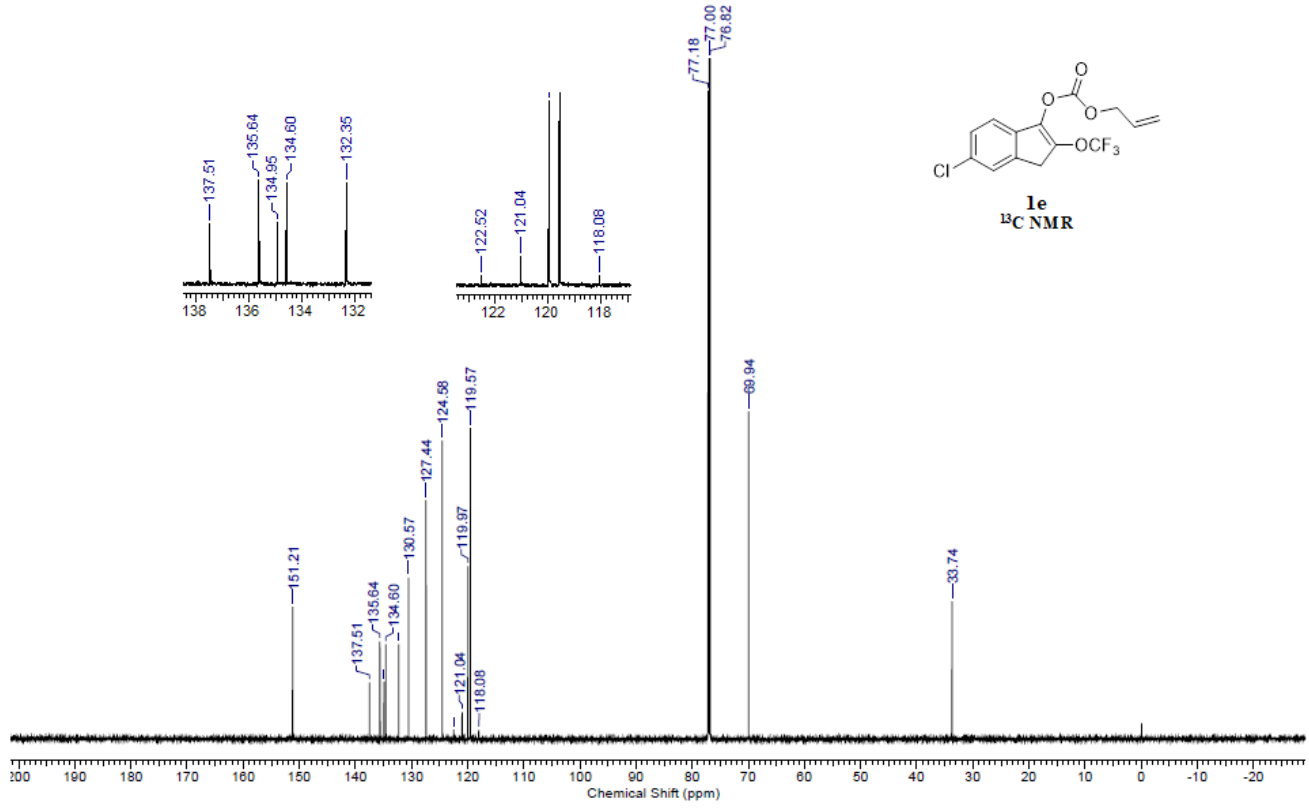
1d
^{13}C NMR


Me
OCF3
1d
13C NMR
136.57
136.55
136.52
136.50
136.5
136.29
130.70
134.34
133.20
135.59
125.53
122.09
118.64
115.20
Chemical Shift (ppm)

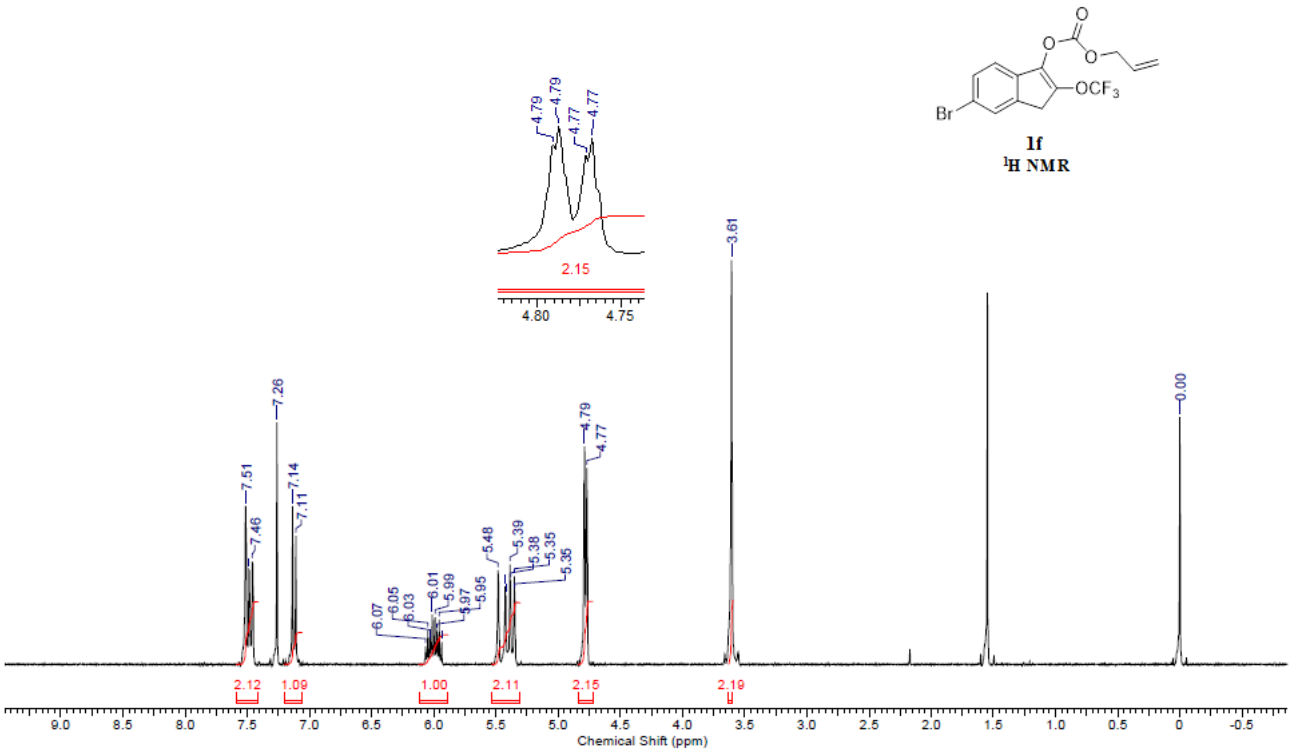

Cl
OCF3
1e
1H NMR
3.61
4.79
4.77
7.51
7.45
7.35
7.30
7.18
7.16
7.13
7.11
6.07
6.05
6.01
5.99
5.95
5.48
5.38
5.35
0.00
1.00
1.16
1.09
1.04
2.03
2.04
2.09
Chemical Shift (ppm)

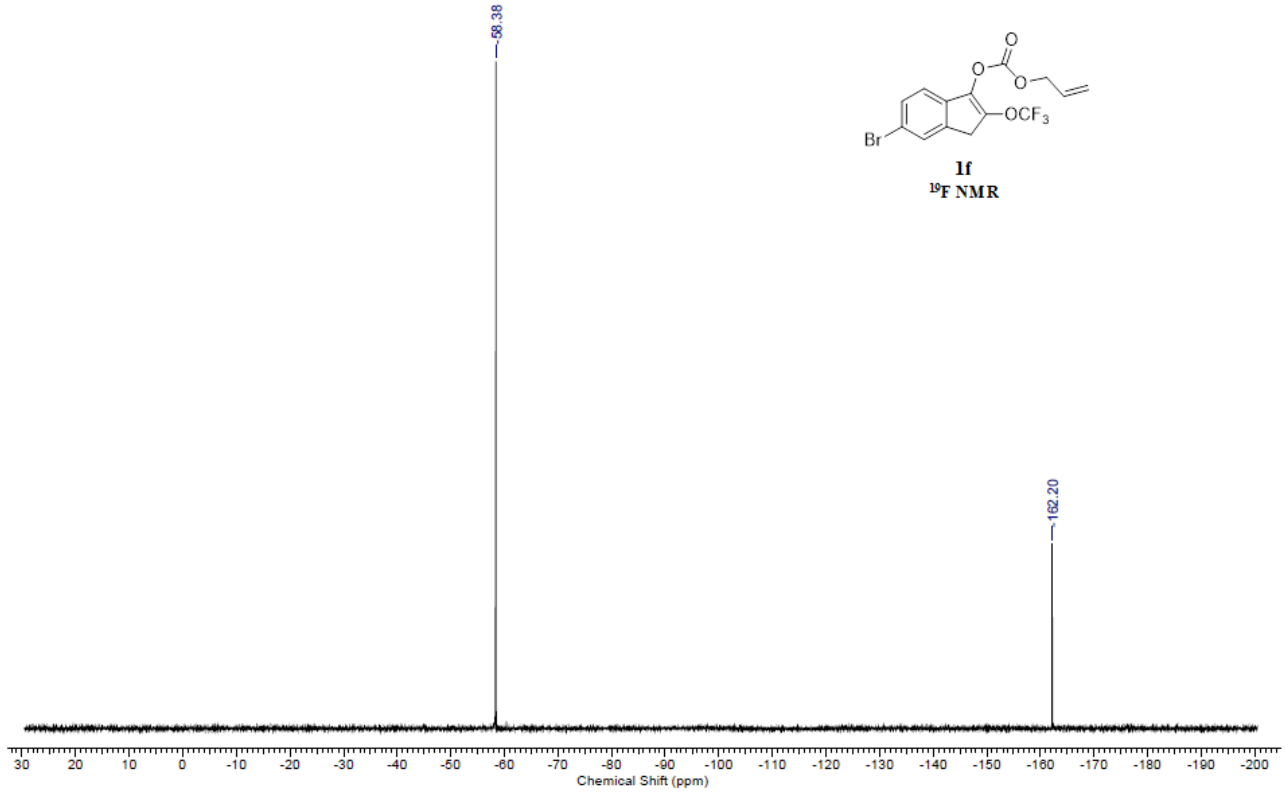


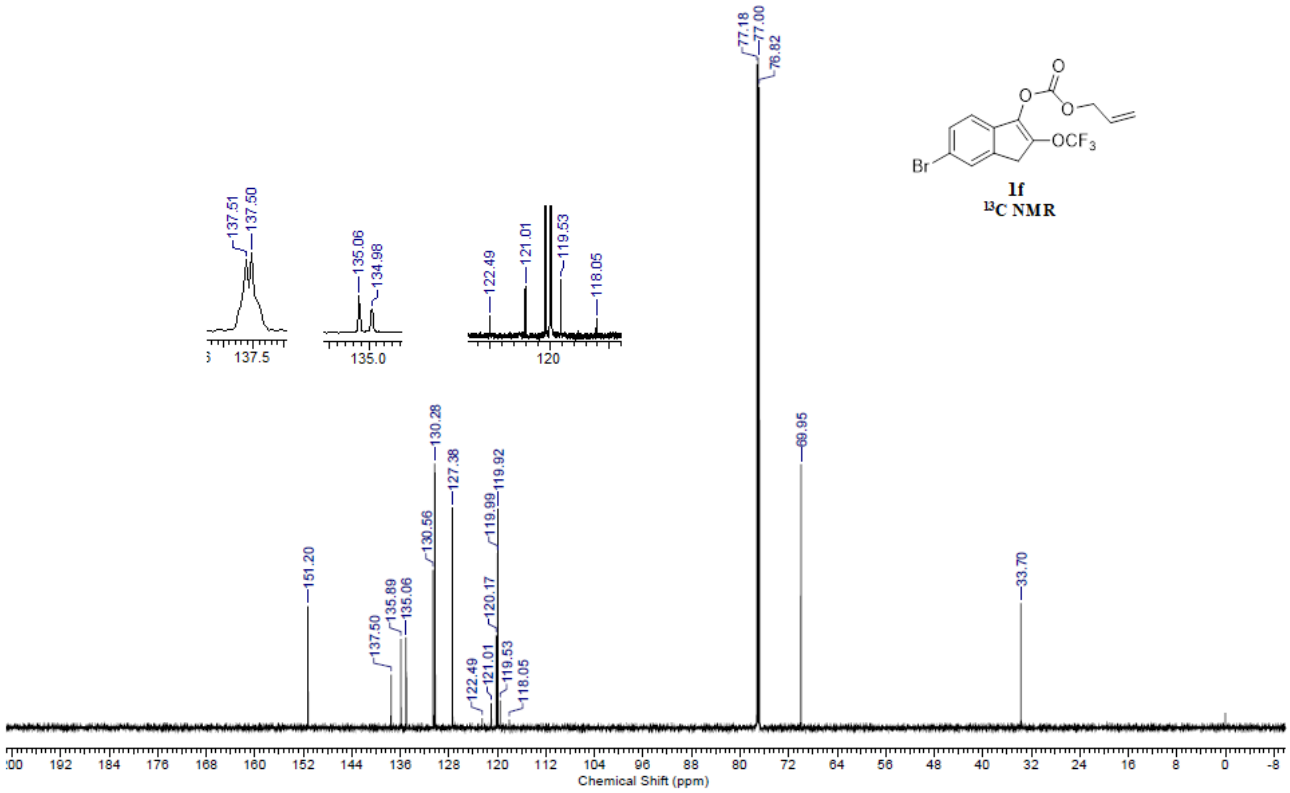
1e
^{19}F NMR



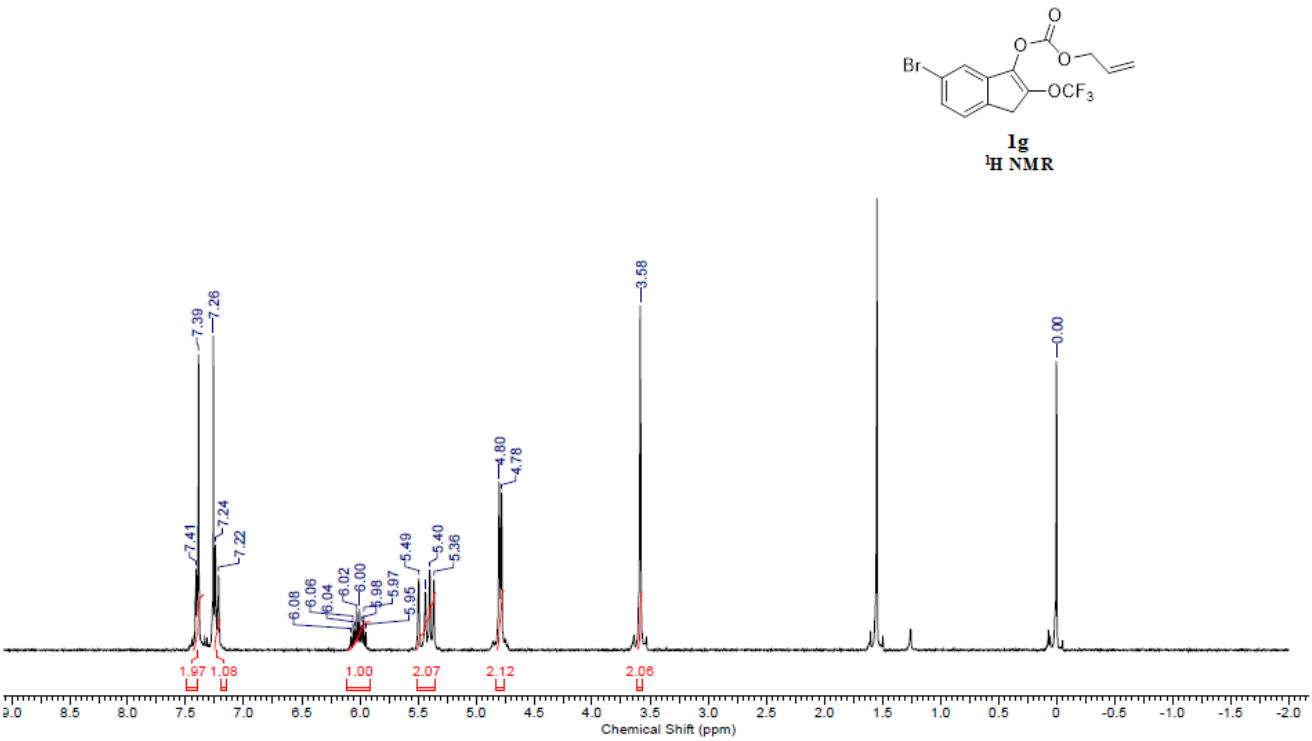
1e
^{13}C NMR


Br
OCF3
1f
1H NMR
4.79
4.79
4.77
4.77
2.15
4.80
4.75
3.61
7.26
0.00
7.51
7.46
7.14
7.11
6.07
6.05
6.03
6.01
5.99
5.97
5.95
5.48
5.39
5.38
5.35
5.36
4.79
4.77
2.12
1.09
1.00
2.11
2.15
2.19
Chemical Shift (ppm)

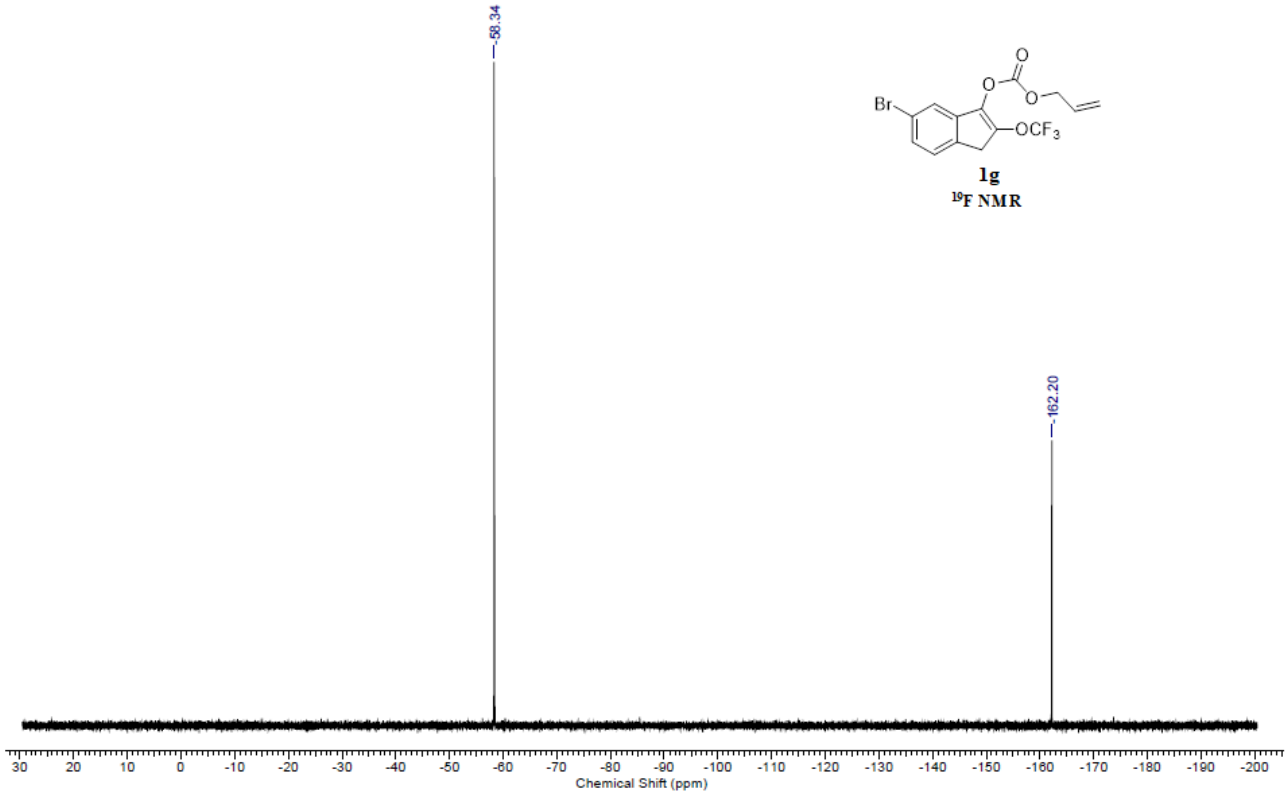

Br
OCF3
1f
19F NMR
-58.38
-162.20
Chemical Shift (ppm)



1f
^{13}C NMR

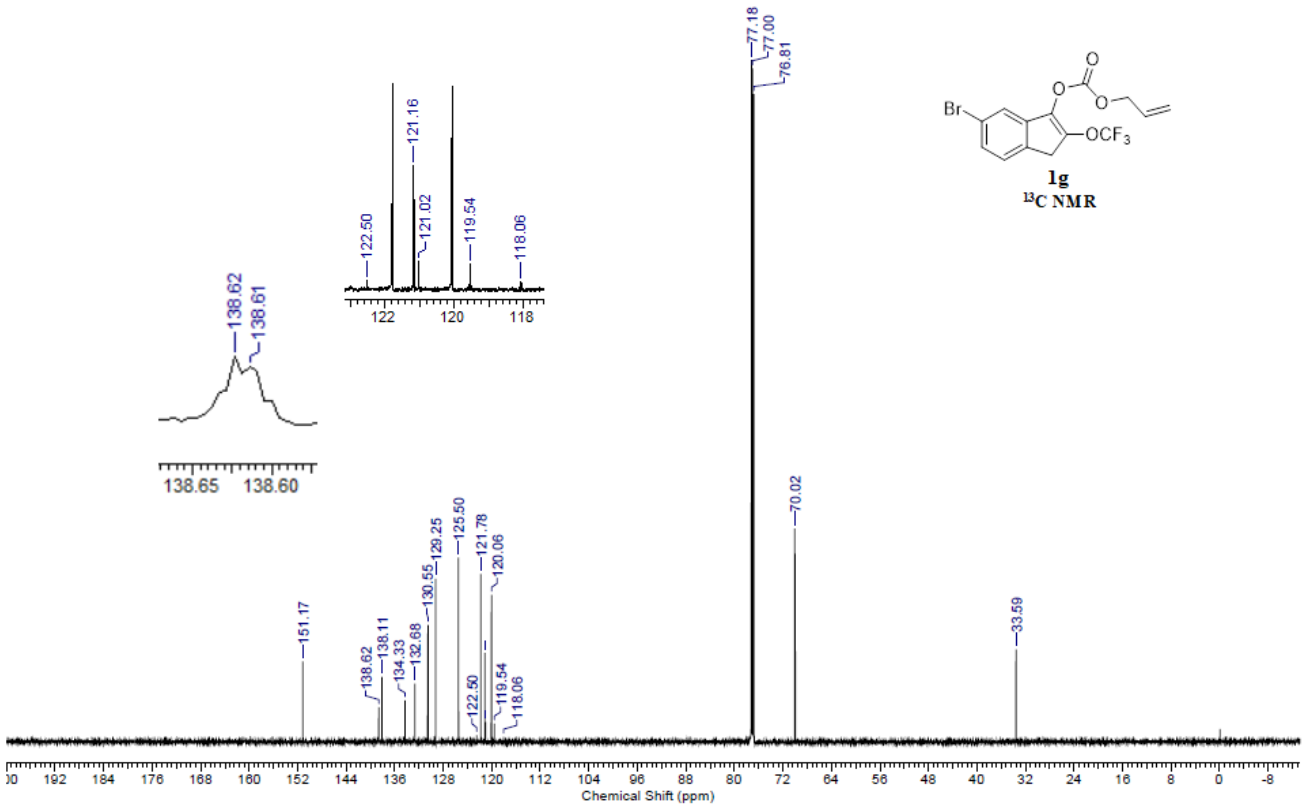


1g
^{1}H NMR



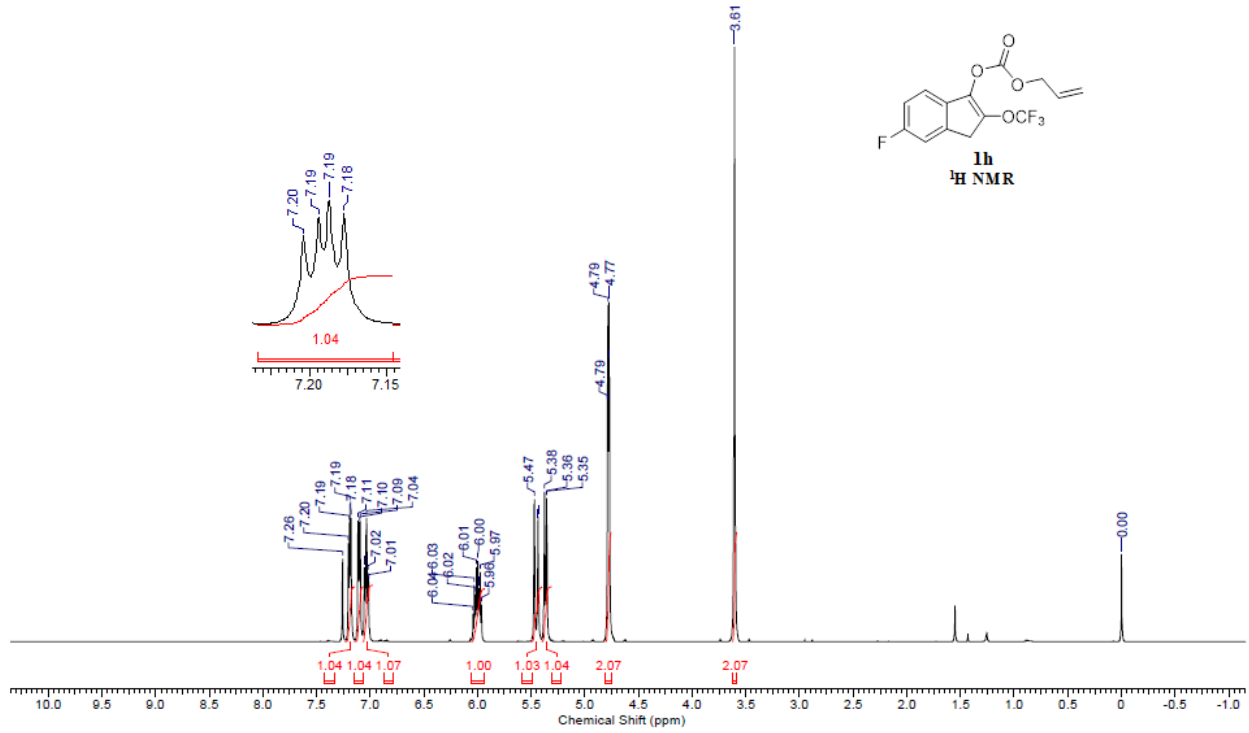
1g

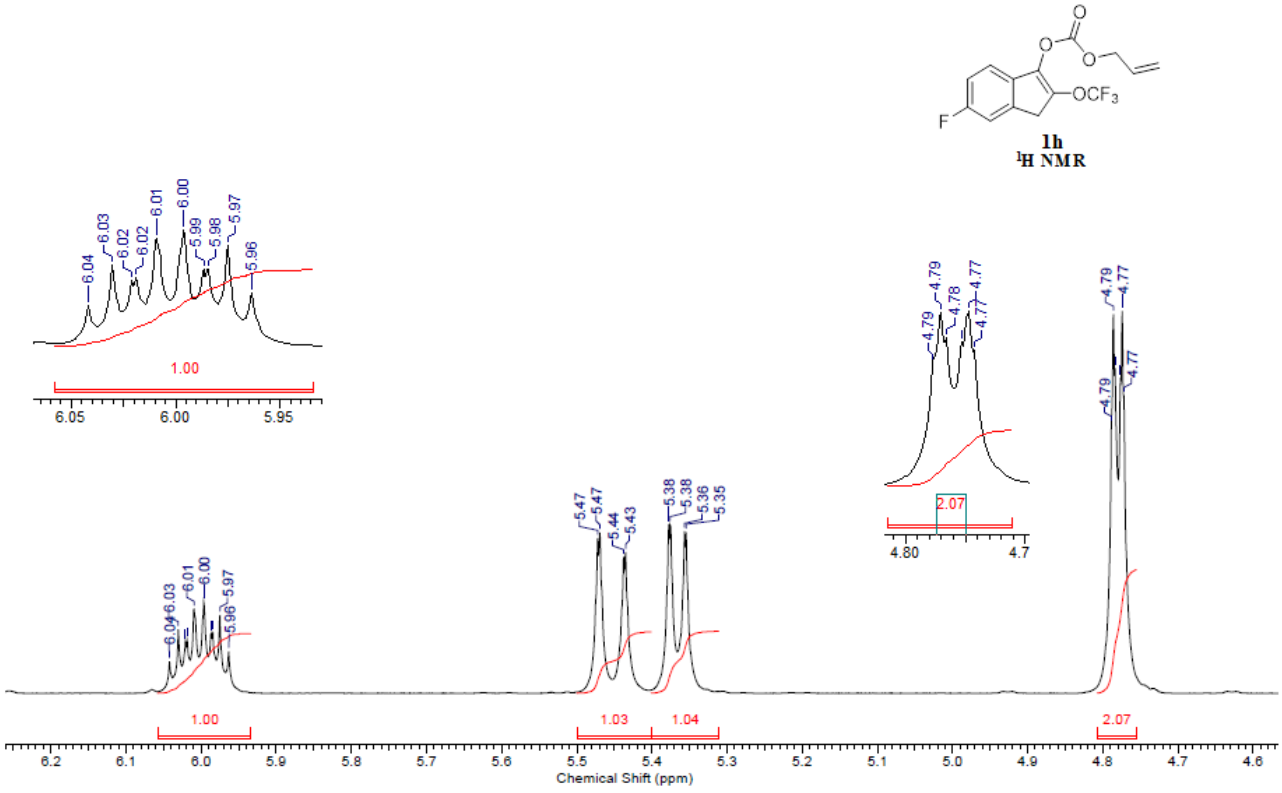
^{19}F NMR

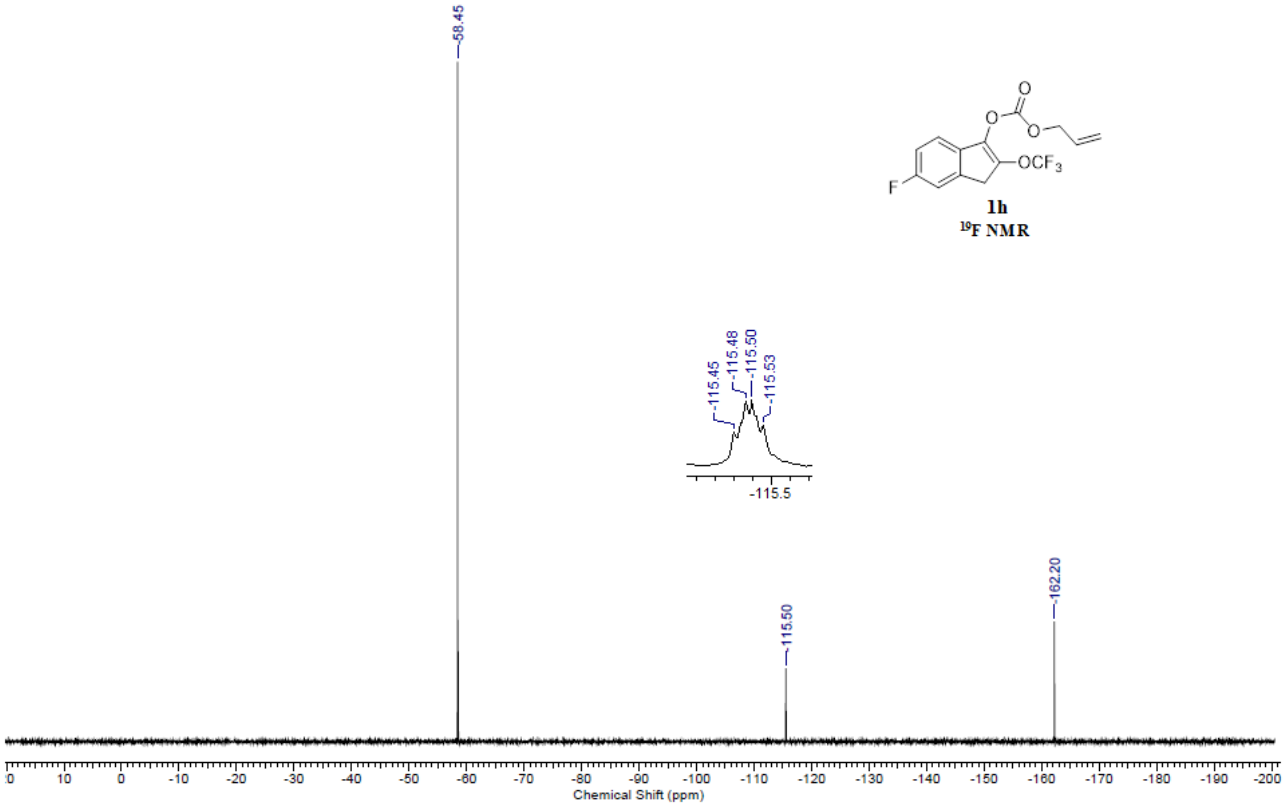


1g

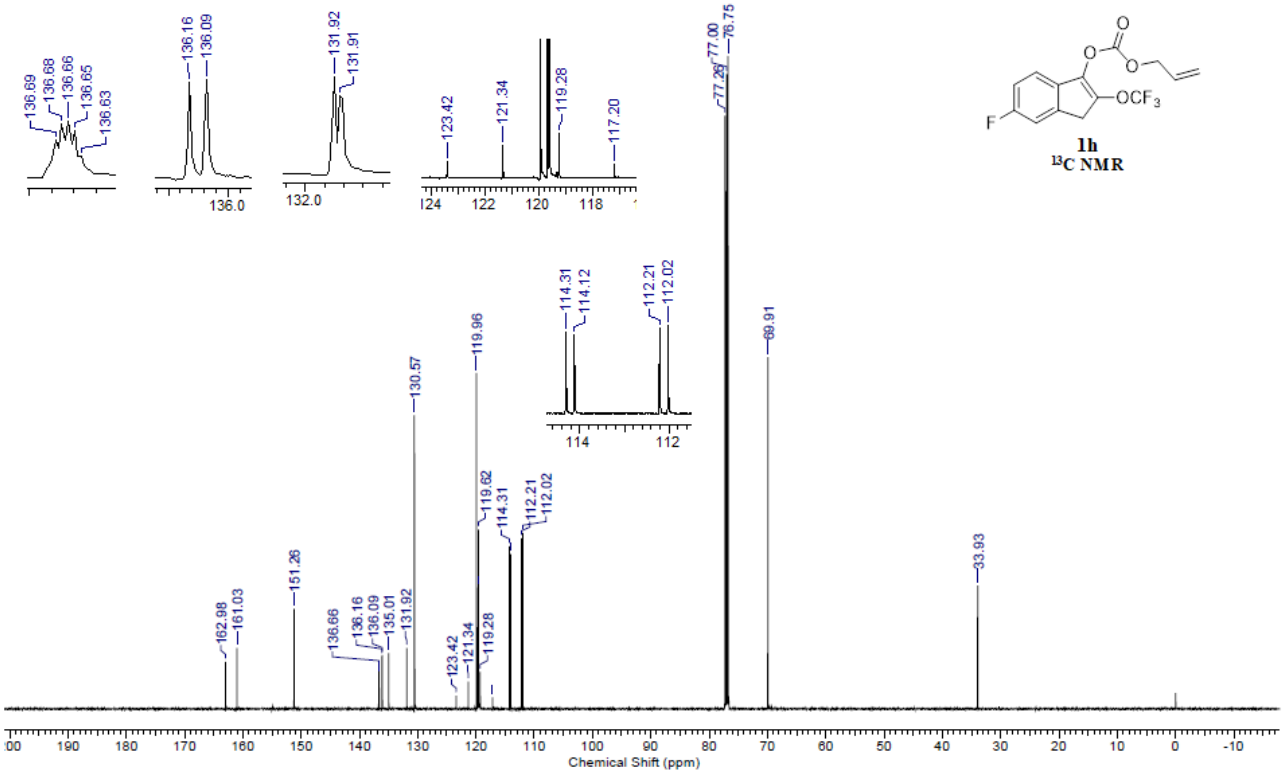
^{13}C NMR


1h
1H NMR
Chemical Shift (ppm)

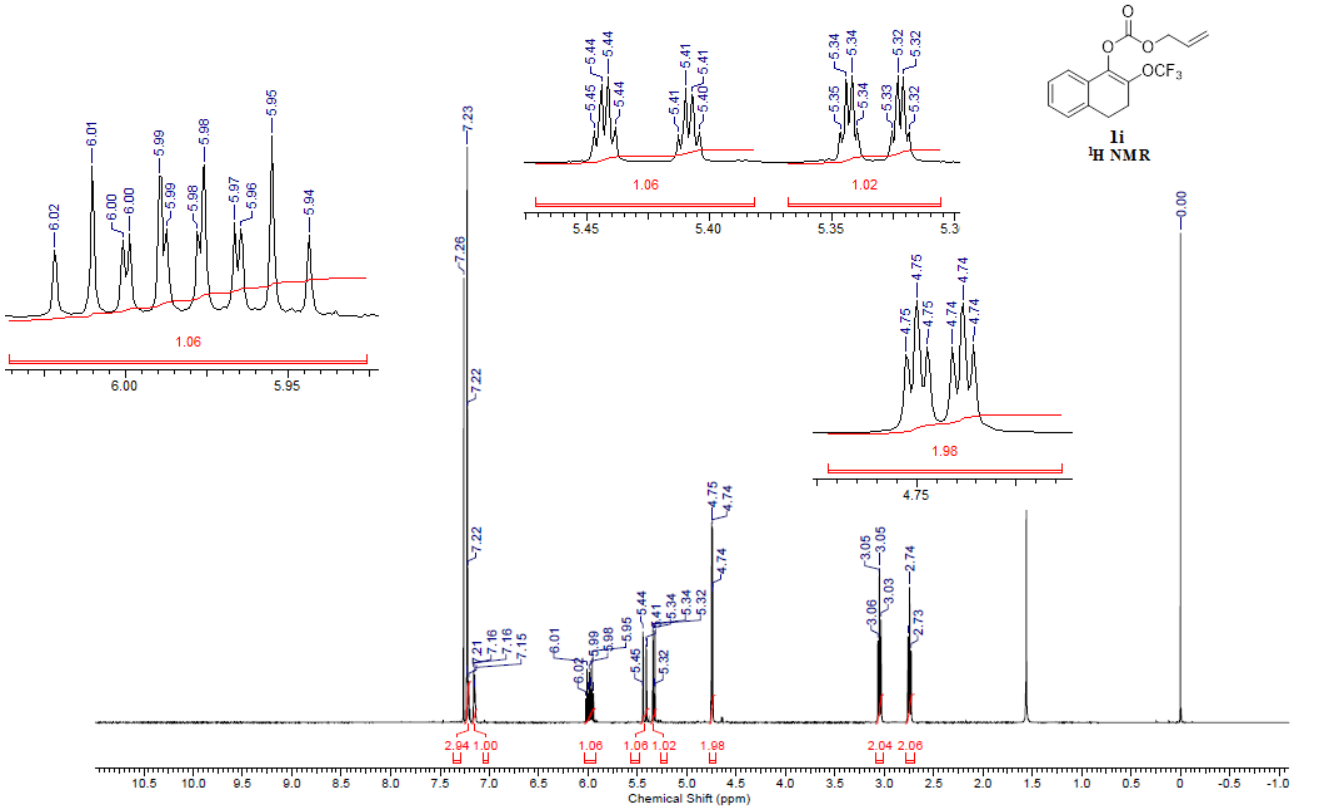

1h
1H NMR
Chemical Shift (ppm)

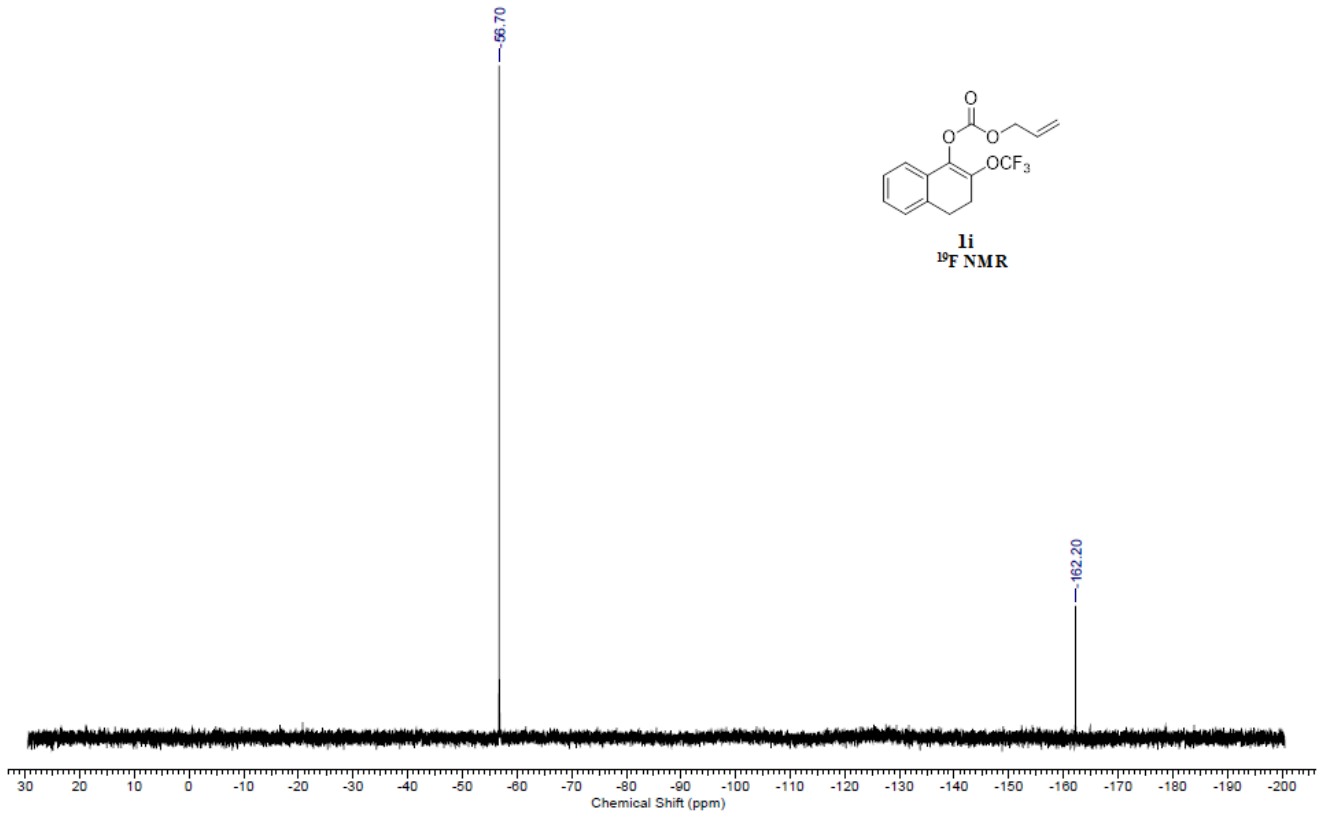


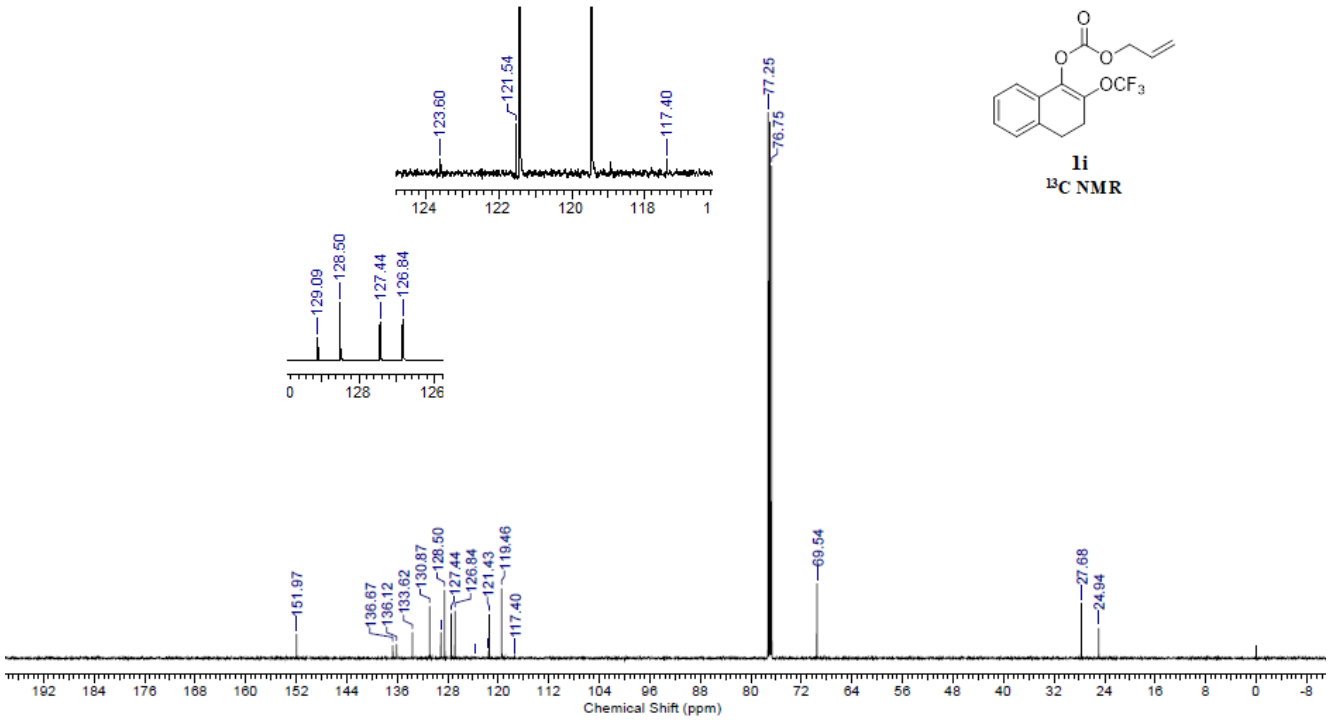
1h
^{19}F NMR

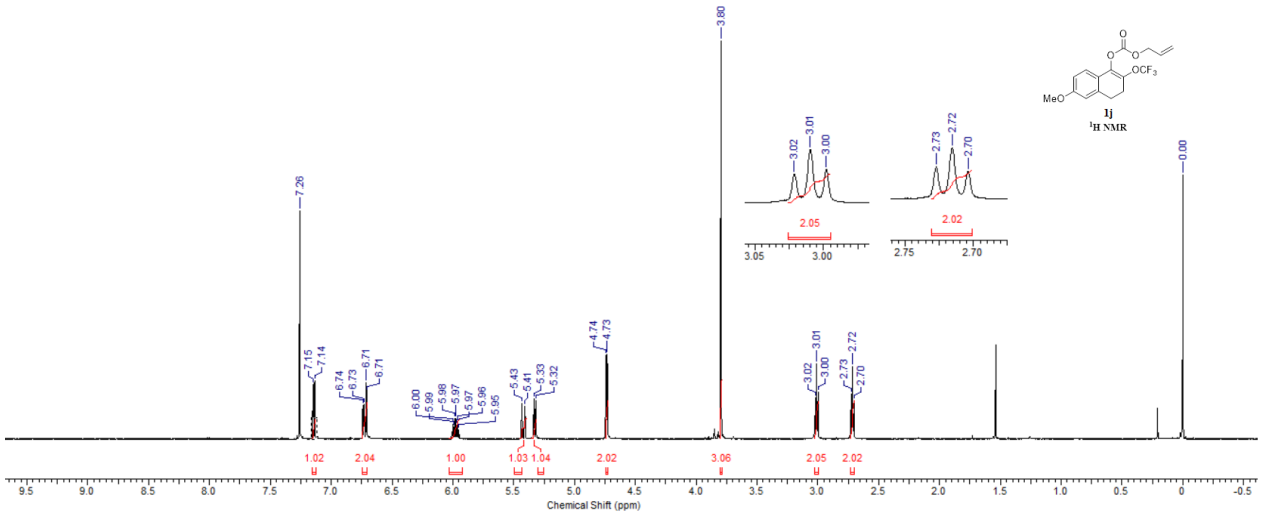


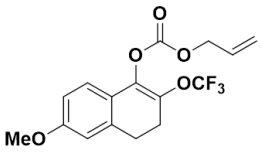
1h
^{13}C NMR


1i
1H NMR
Chemical Shift (ppm)


1i
19F NMR
Chemical Shift (ppm)

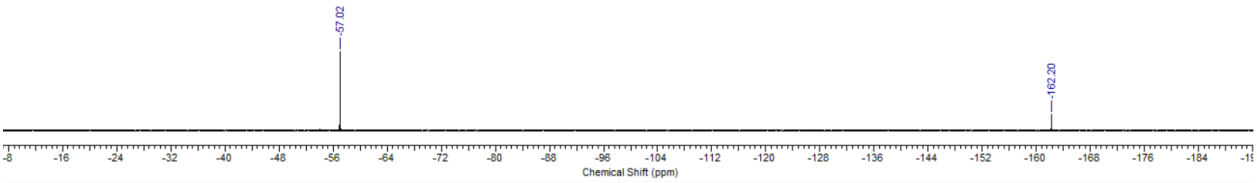

1i
13C NMR
Chemical Shift (ppm)

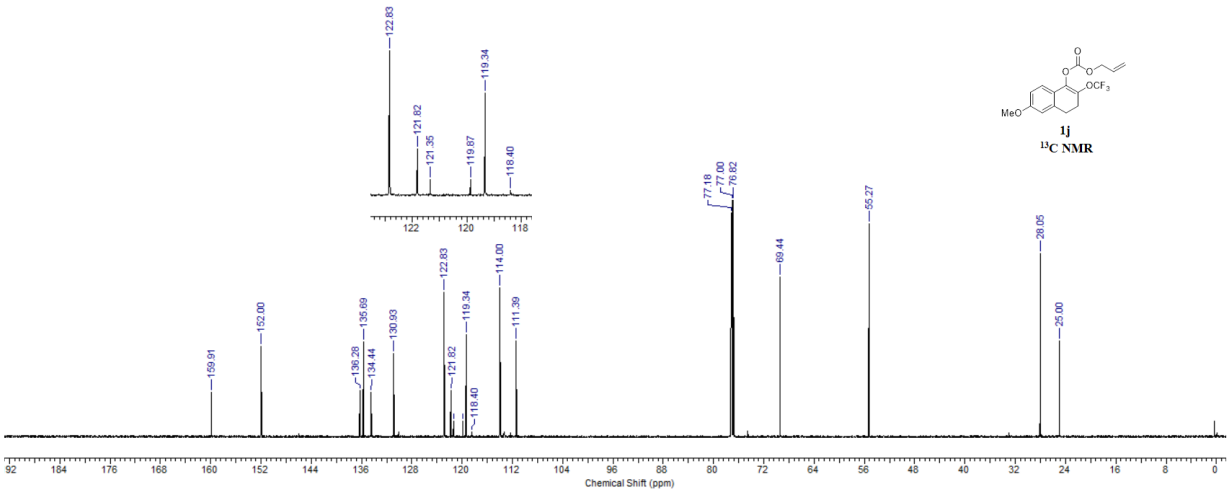

1j
1H NMR
Chemical Shift (ppm)



1j

^{19}F NMR



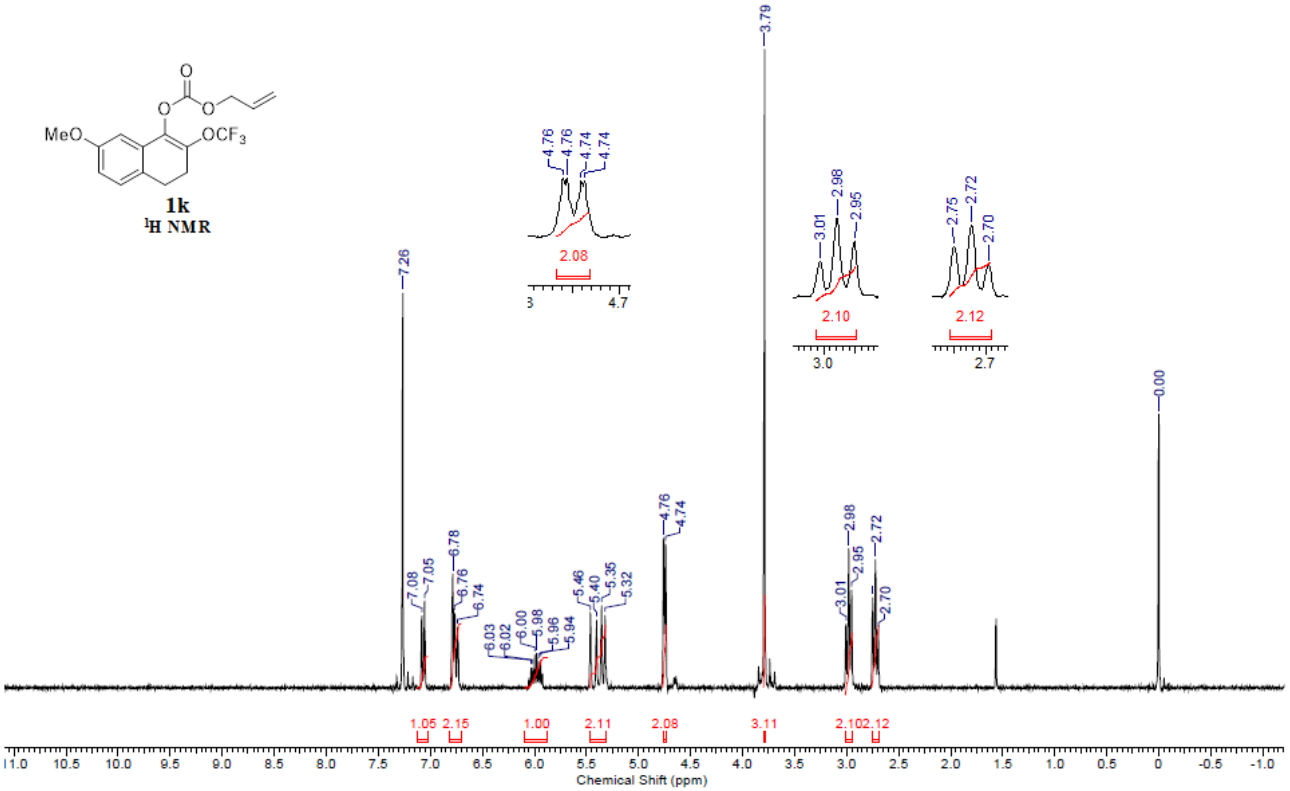


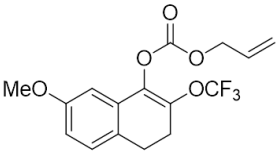
1j

^{13}C NMR

1k

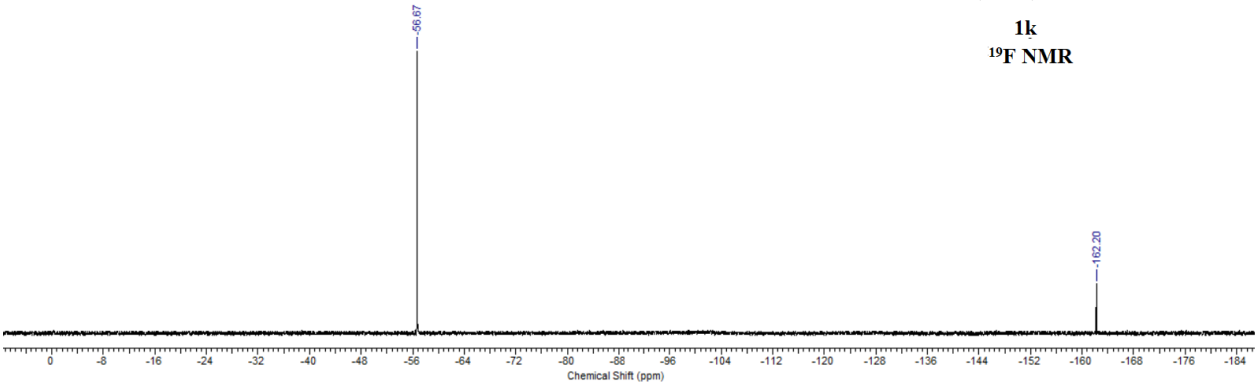
^{1}H NMR

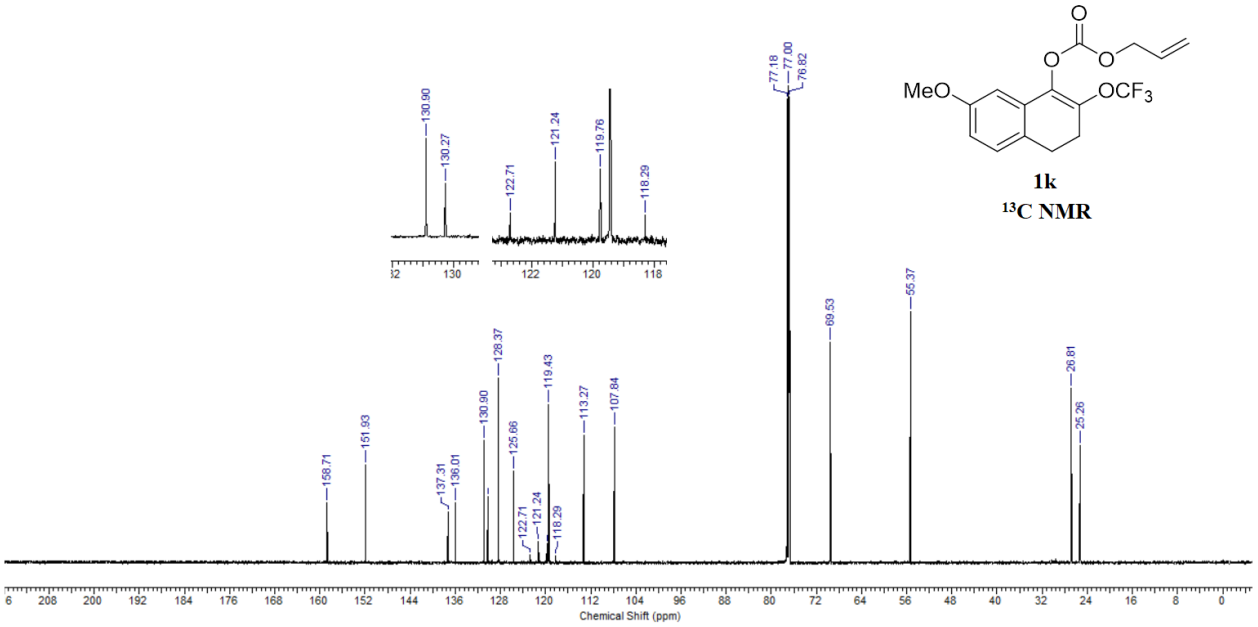


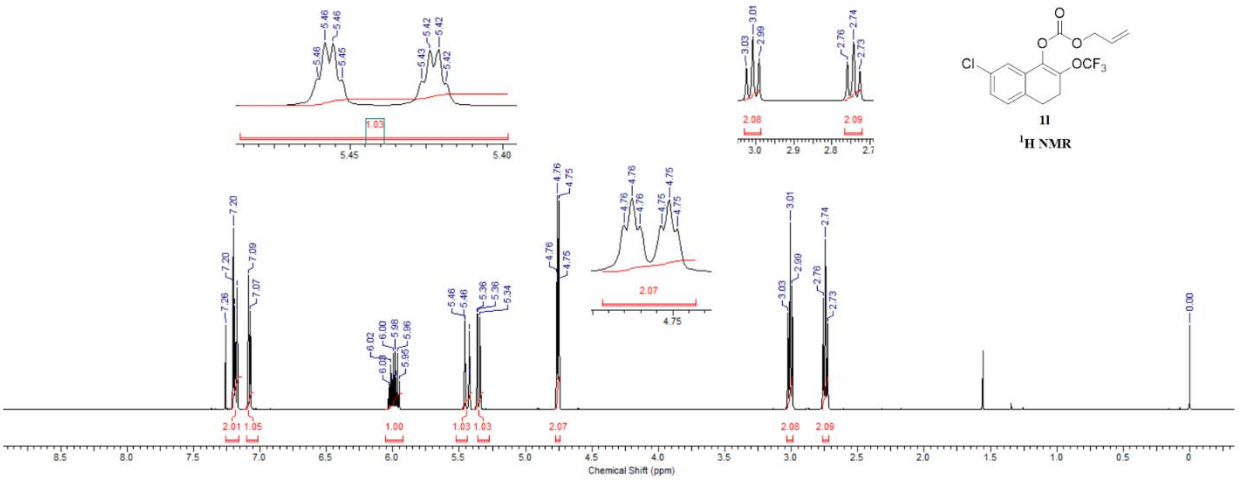


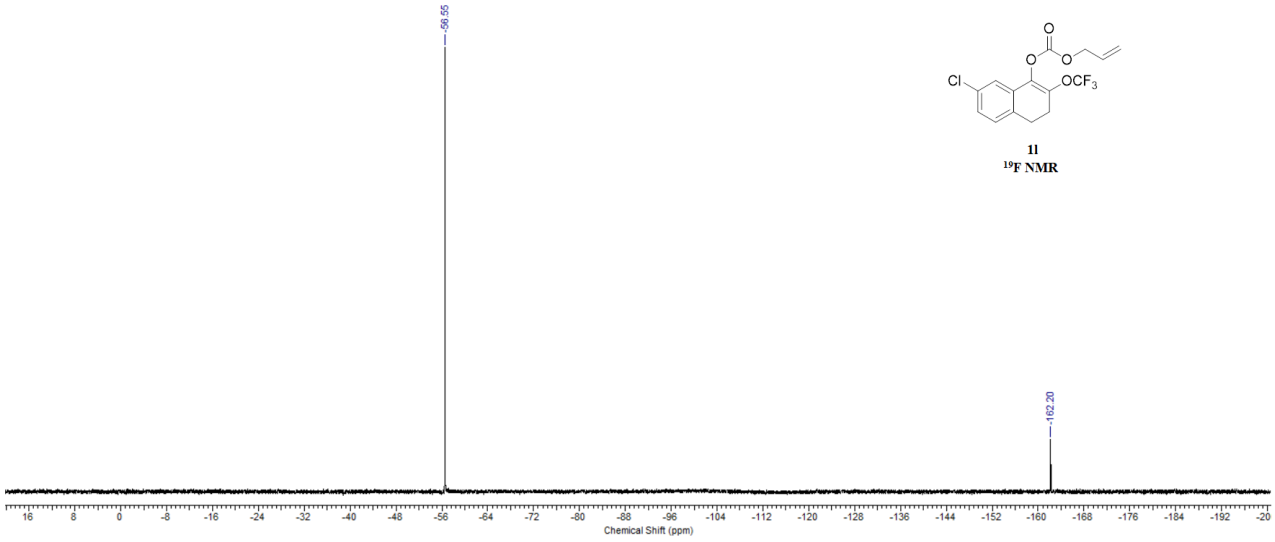
1k

^{19}F NMR



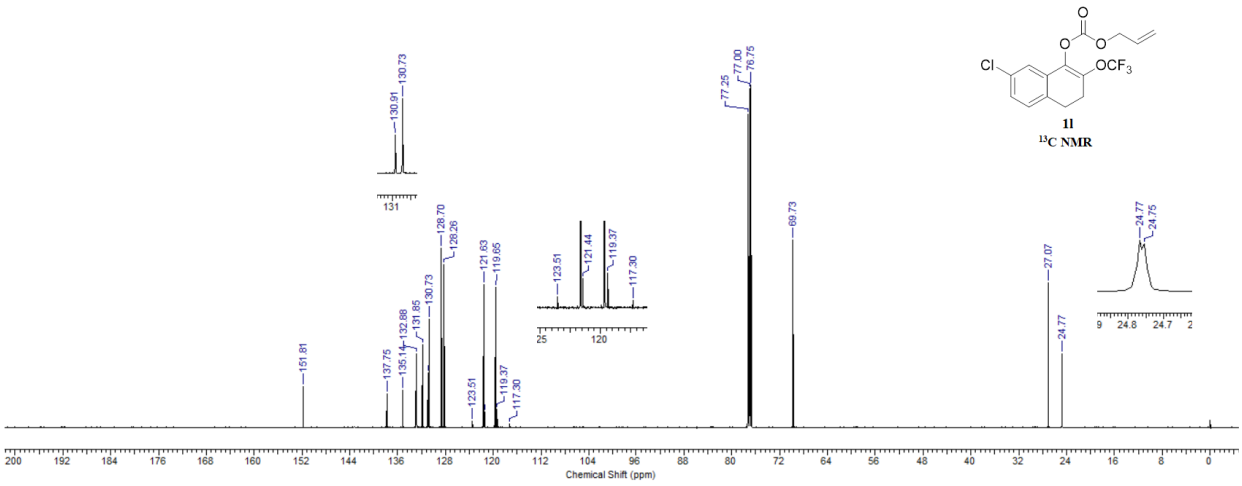

MeO
OCF3
1k
13C NMR
Chemical Shift (ppm)


Cl
OCF3
1l
1H NMR
Chemical Shift (ppm)



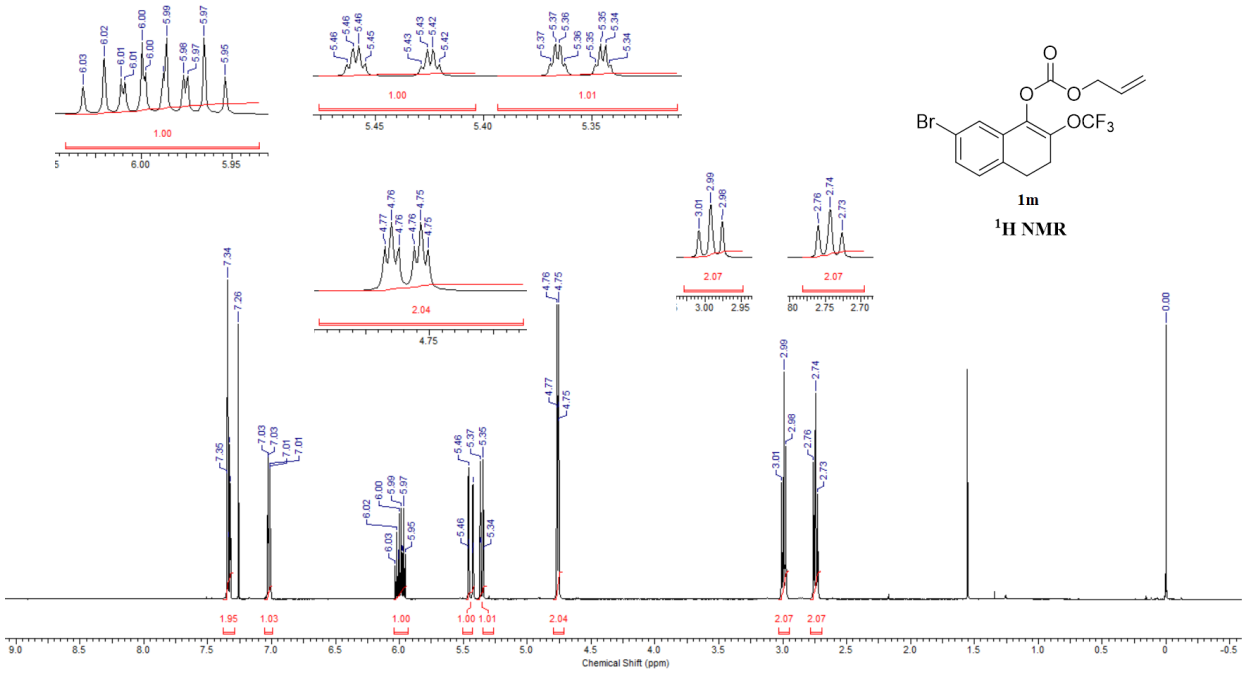
1l

^{19}F NMR



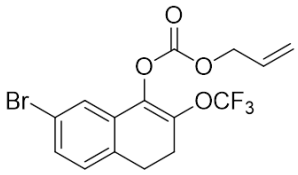
1l

^{13}C NMR



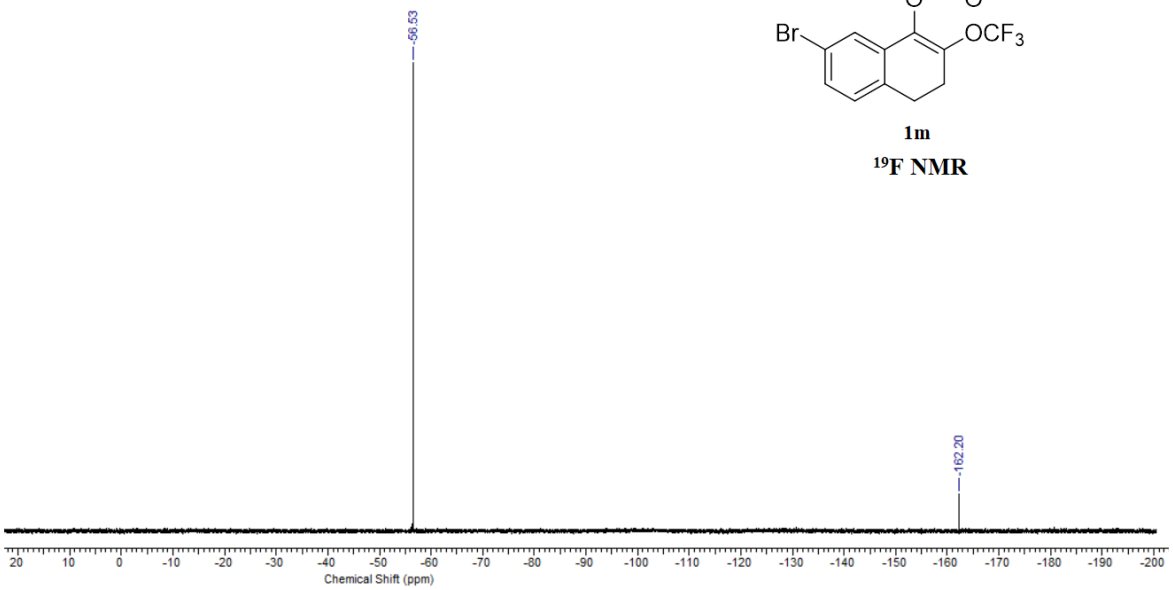
1m

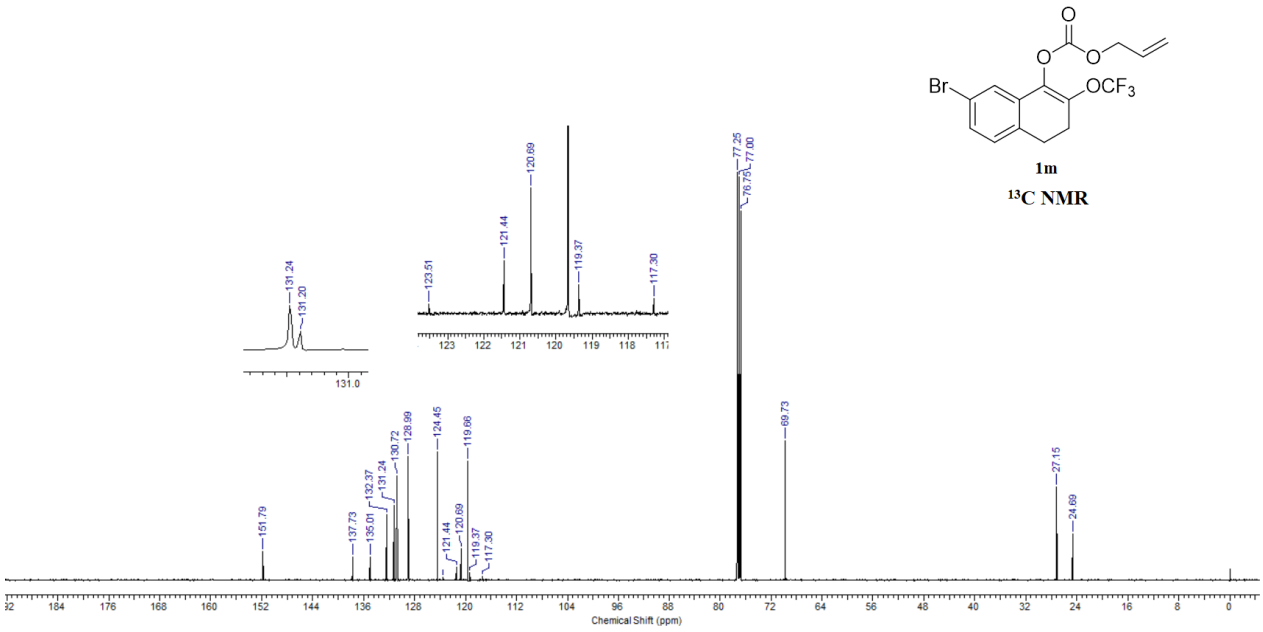
^{1}H NMR

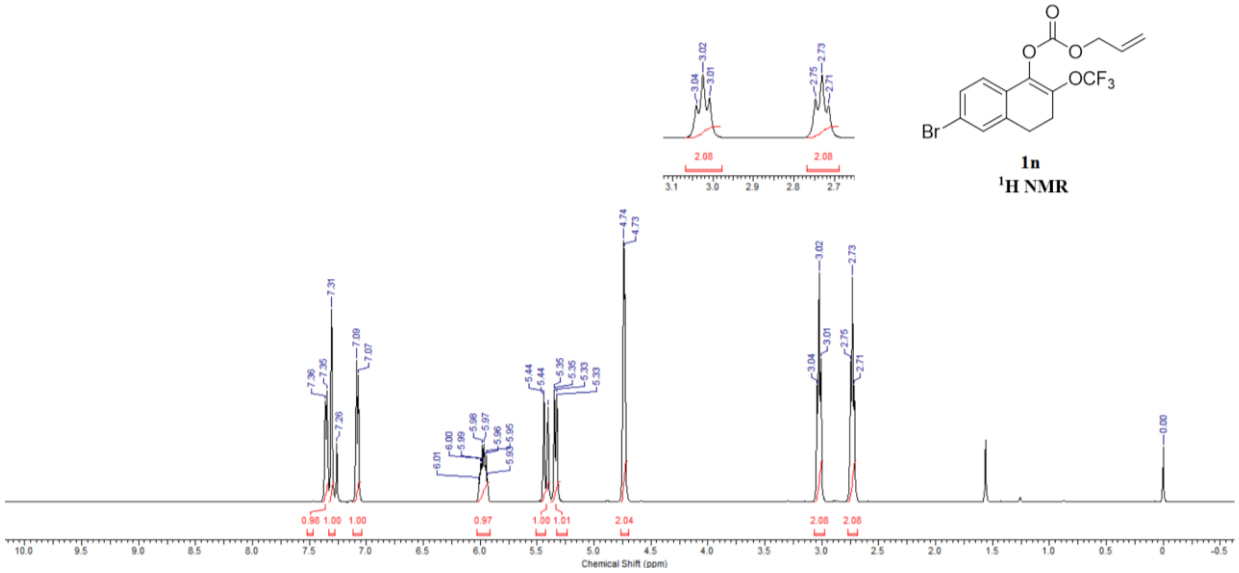


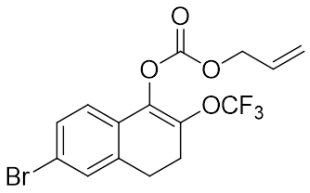
1m

^{19}F NMR



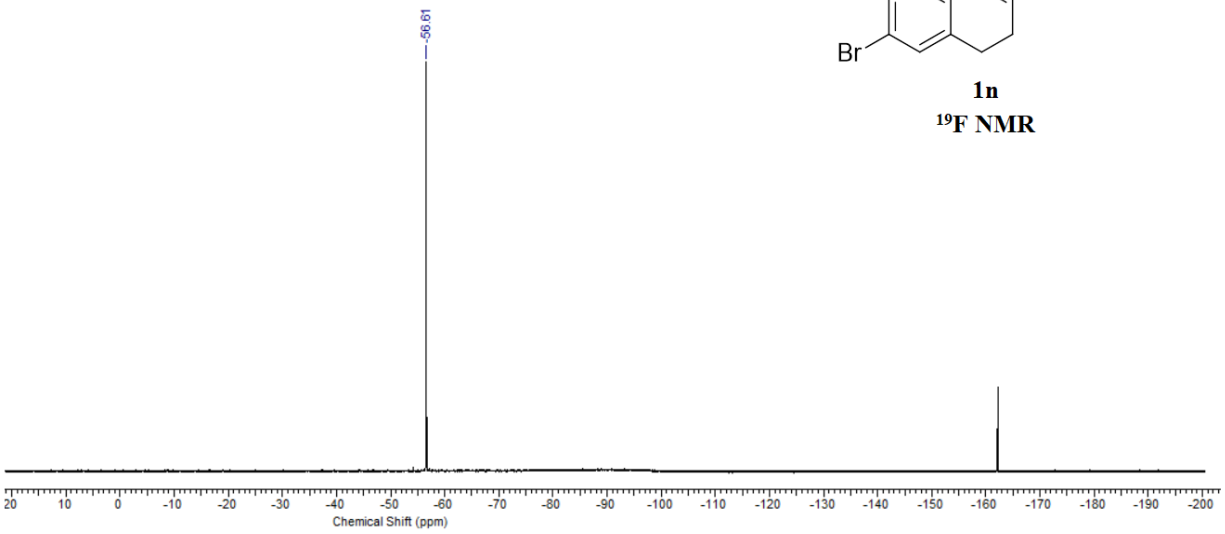

Br
OCF3
1m
13C NMR
Chemical Shift (ppm)

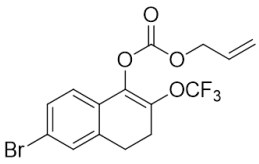

Br
OCF3
1n
1H NMR
Chemical Shift (ppm)



1n

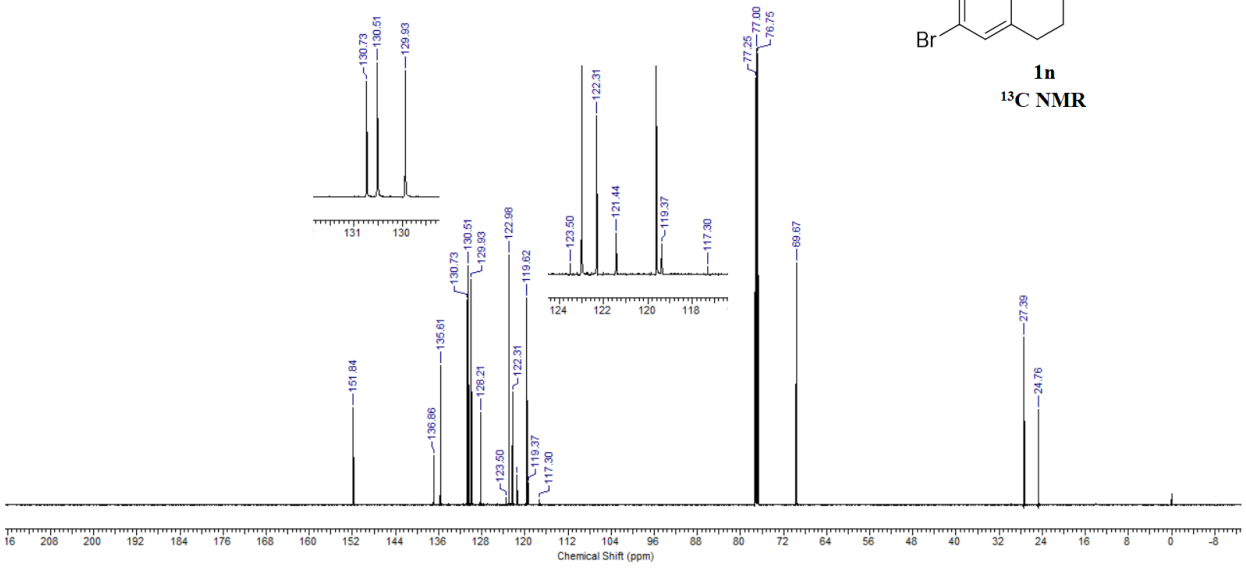
^{19}F NMR

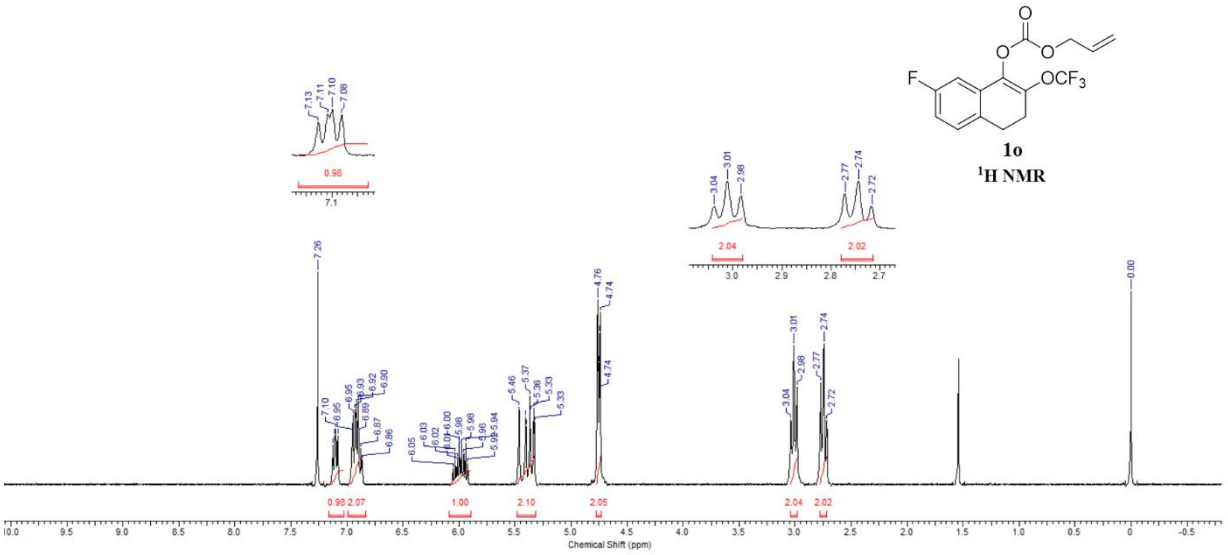


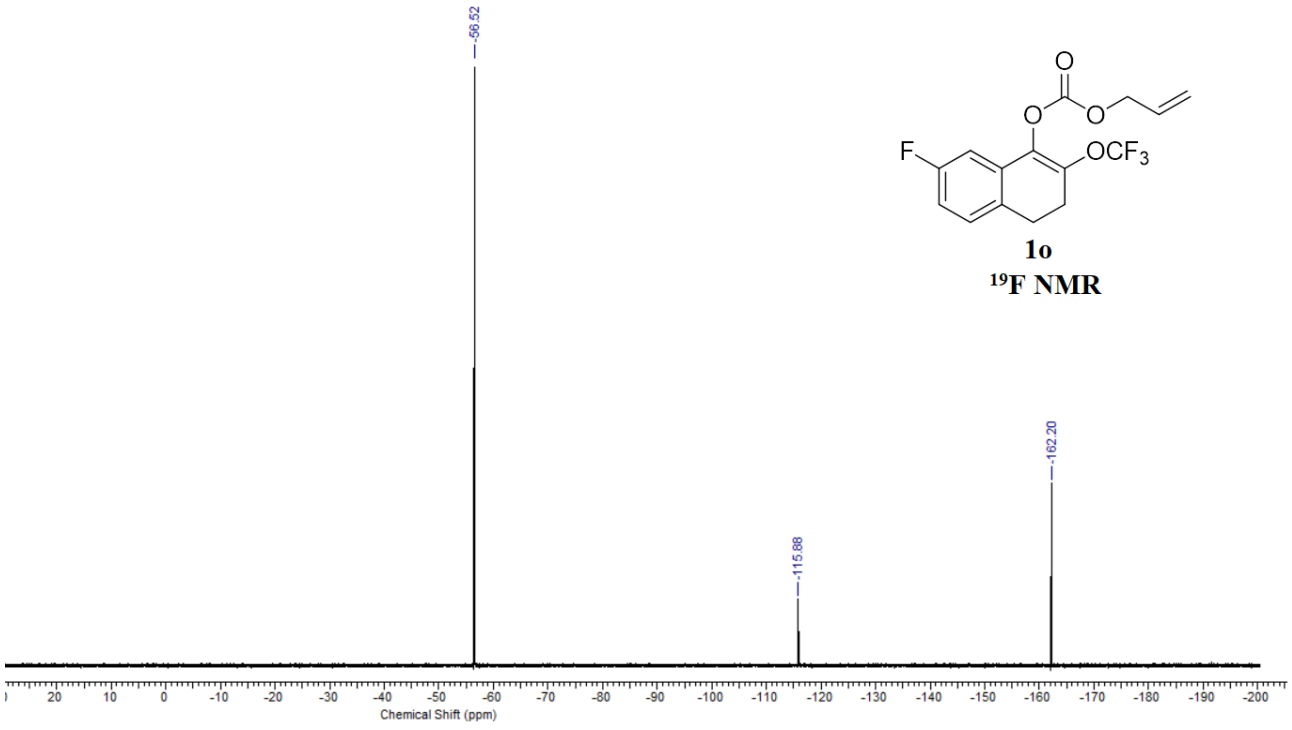


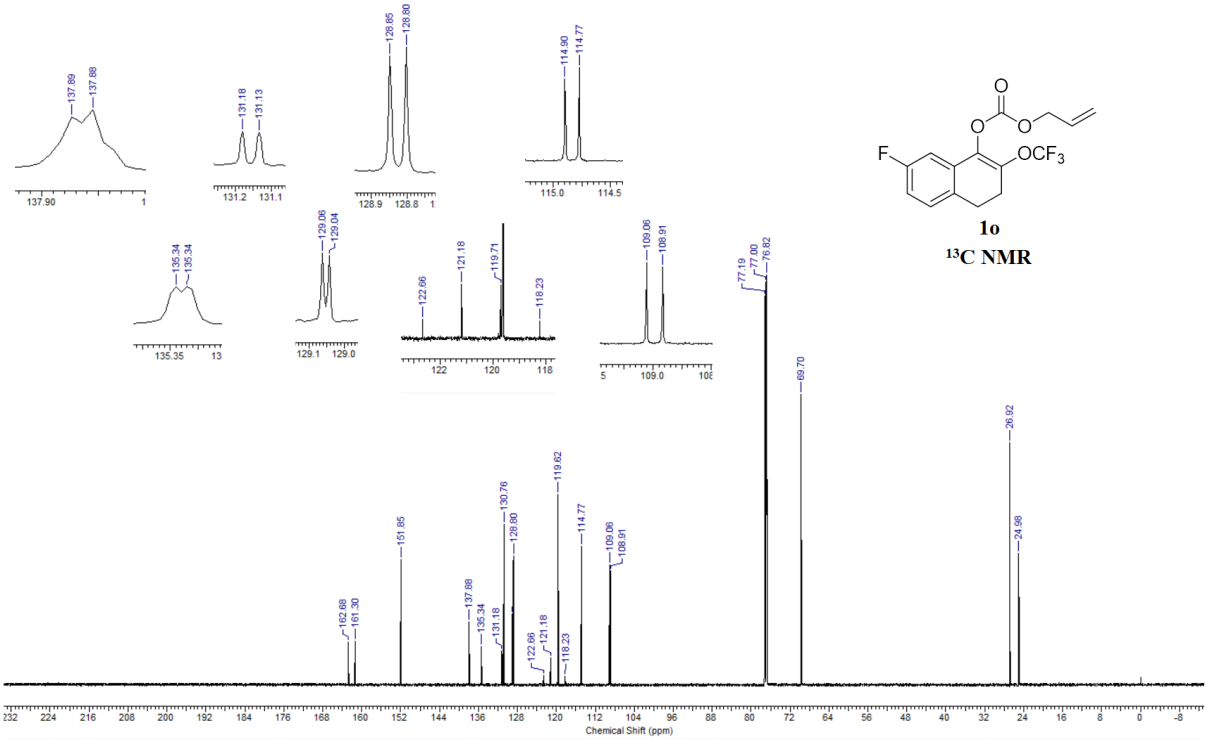
1n

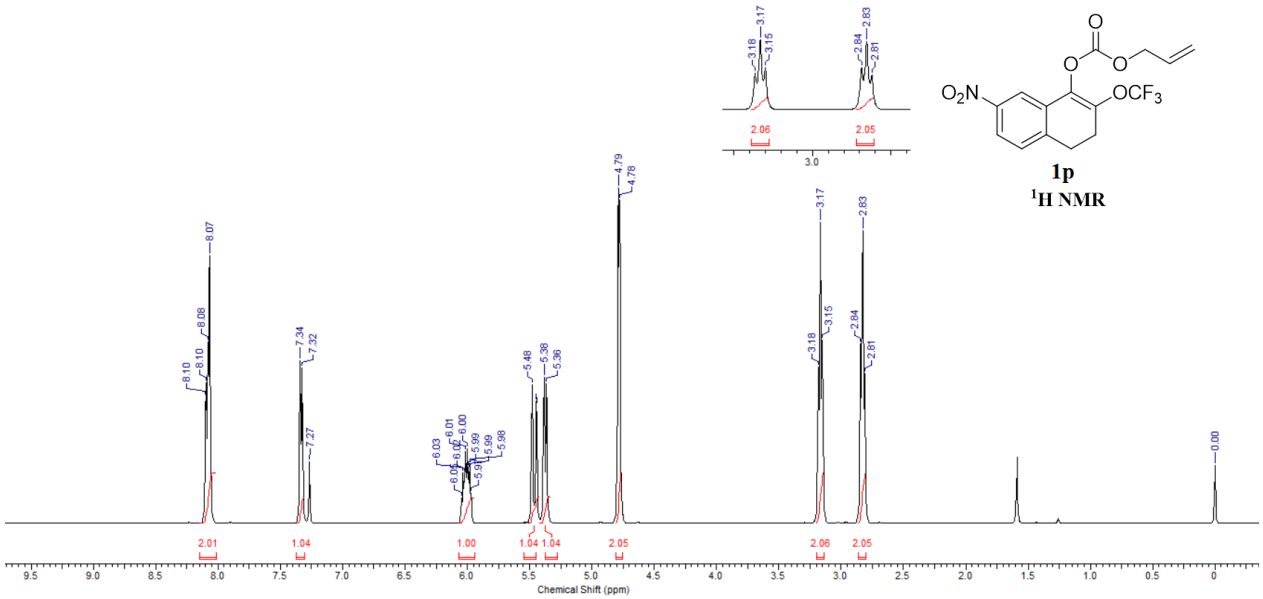
^{13}C NMR

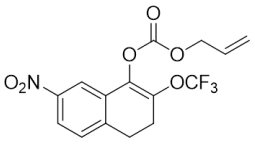



1o
1H NMR
Chemical Shift (ppm)


1o
19F NMR
Chemical Shift (ppm)

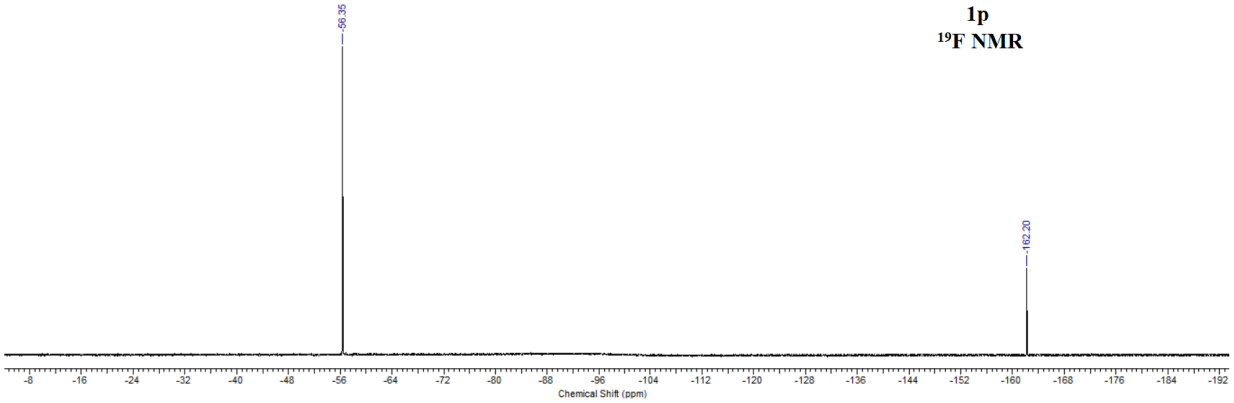

F
O
O
O
OCF3
1o
13C NMR
Chemical Shift (ppm)


O2N
O
O
O
OCF3
1p
1H NMR
Chemical Shift (ppm)



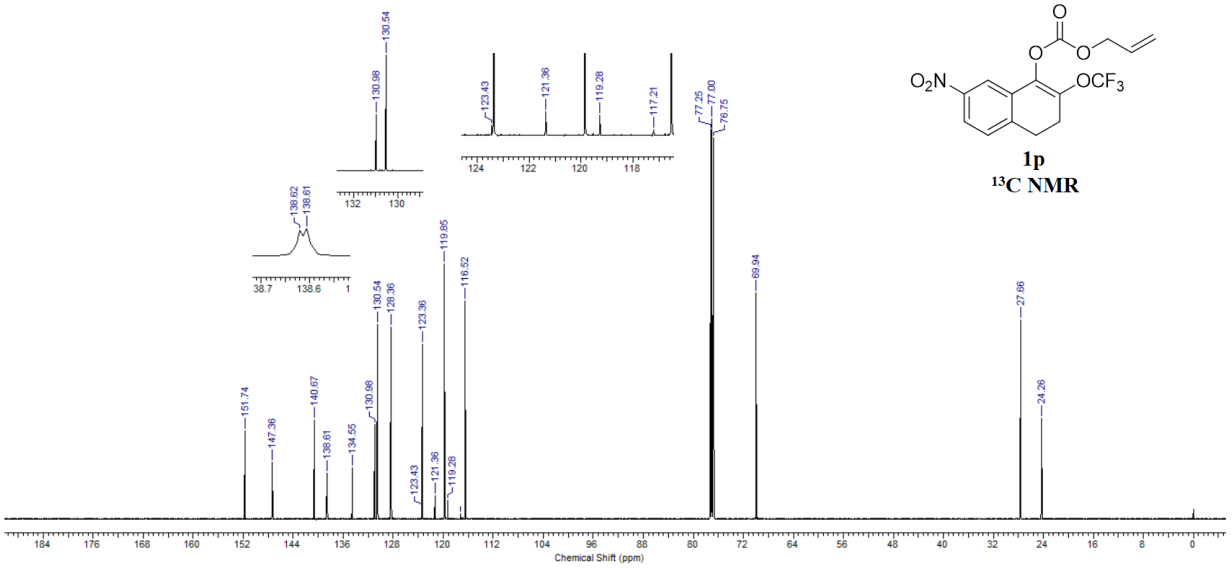
1p

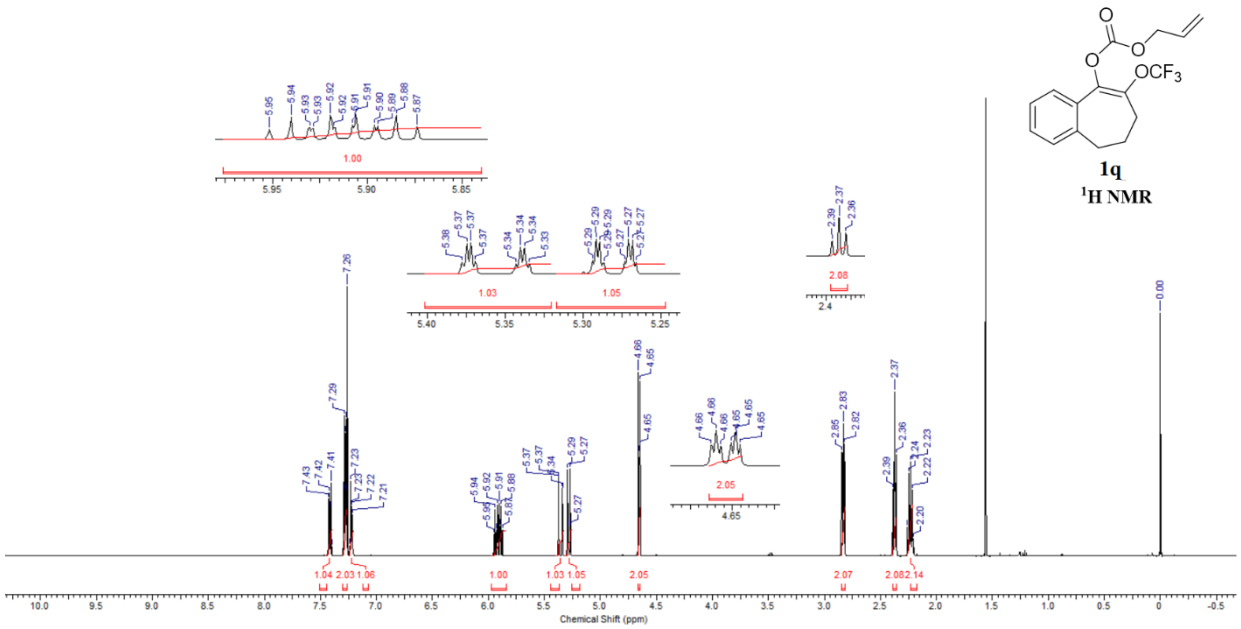
^{19}F NMR



1p

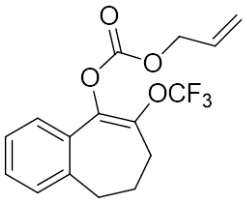
^{13}C NMR





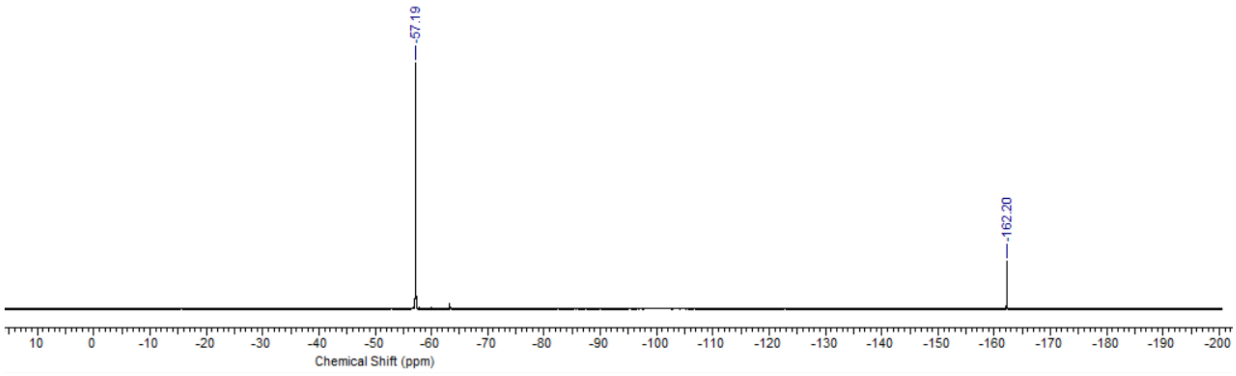
1q

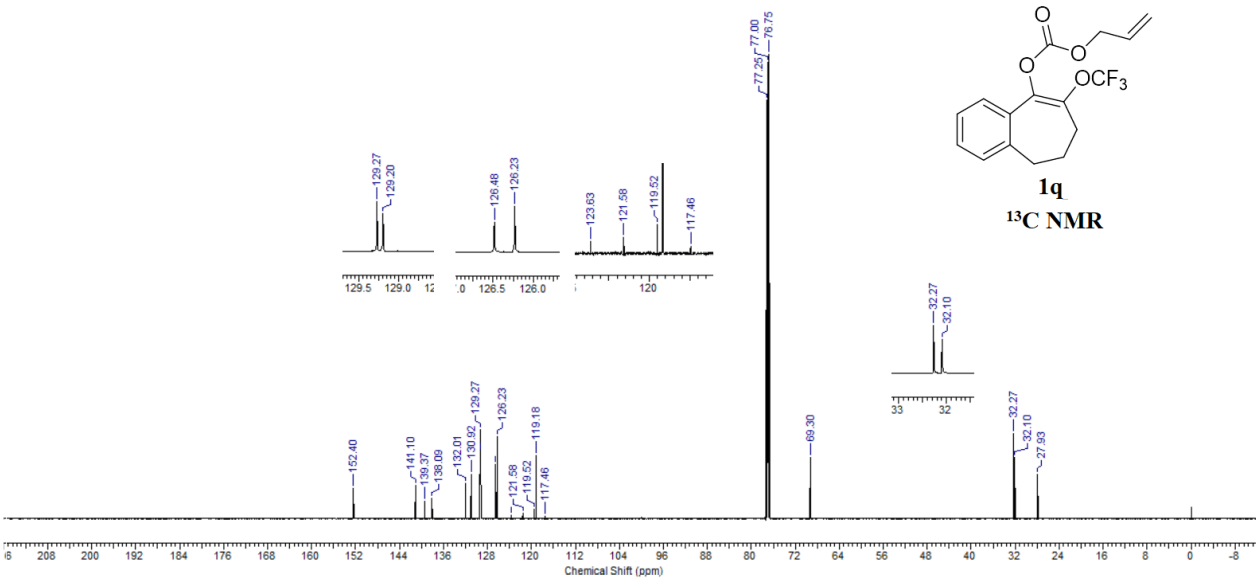
^{1}H NMR

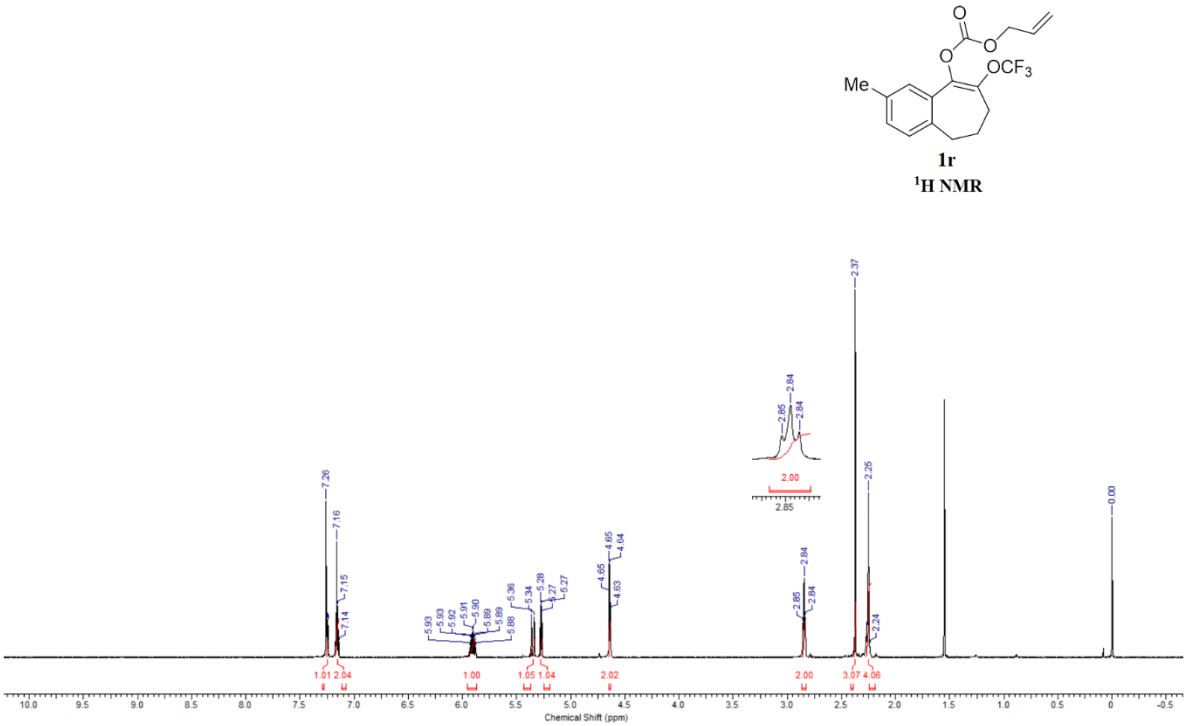


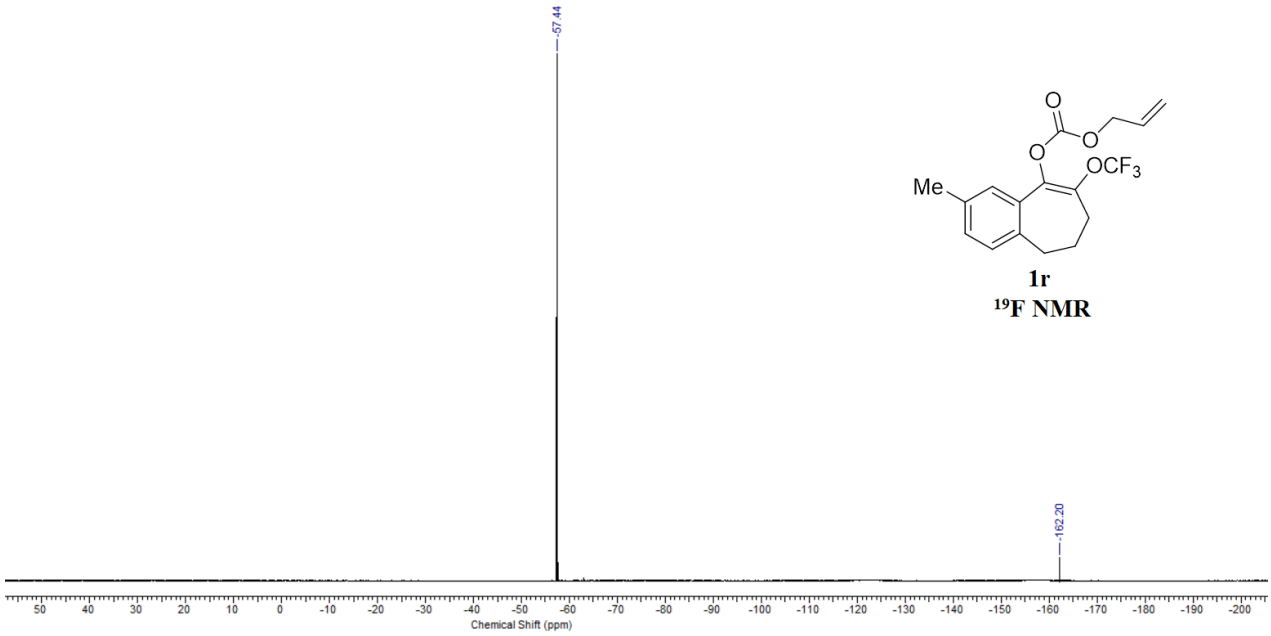
1q

^{19}F NMR



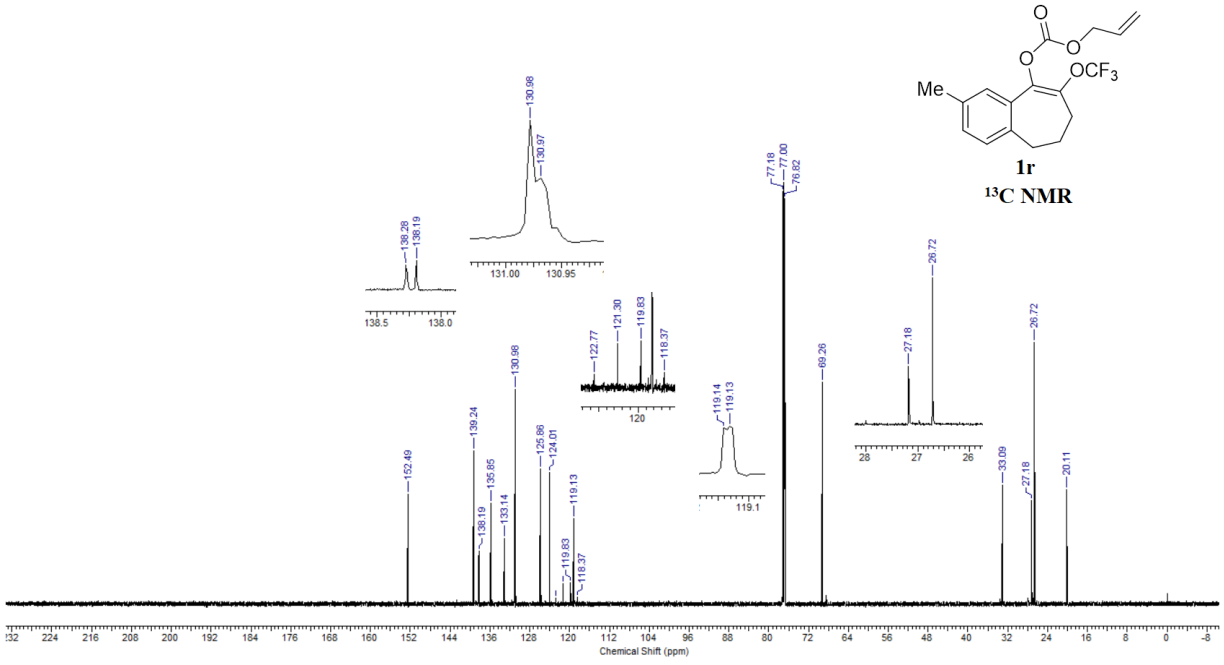

1q
13C NMR
Chemical Shift (ppm)


1r
1H NMR
Chemical Shift (ppm)



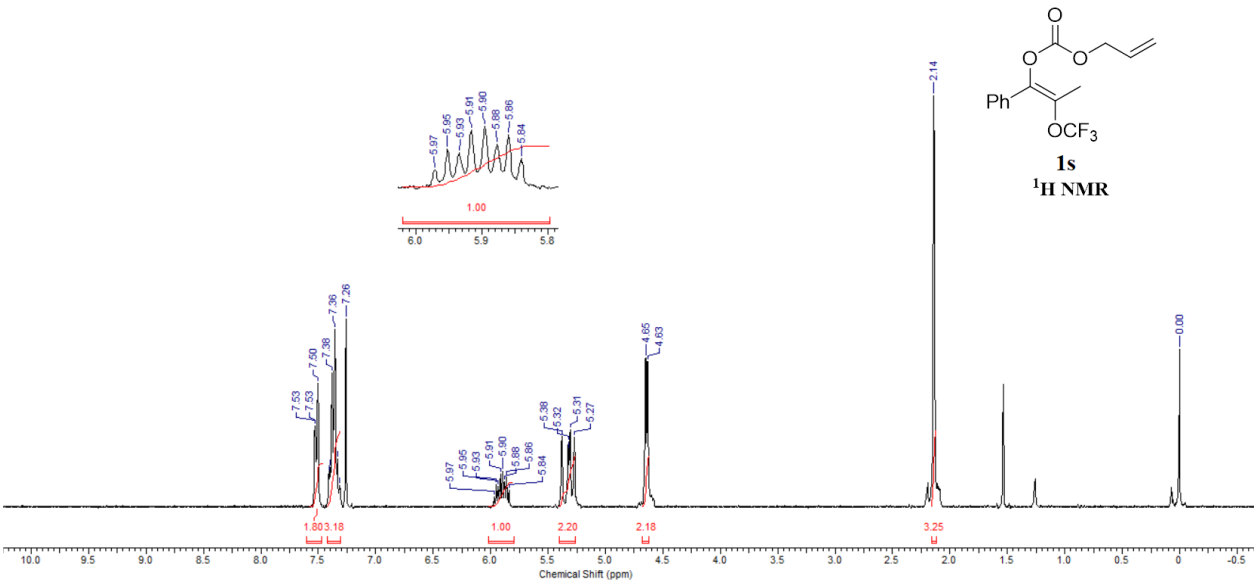
1r

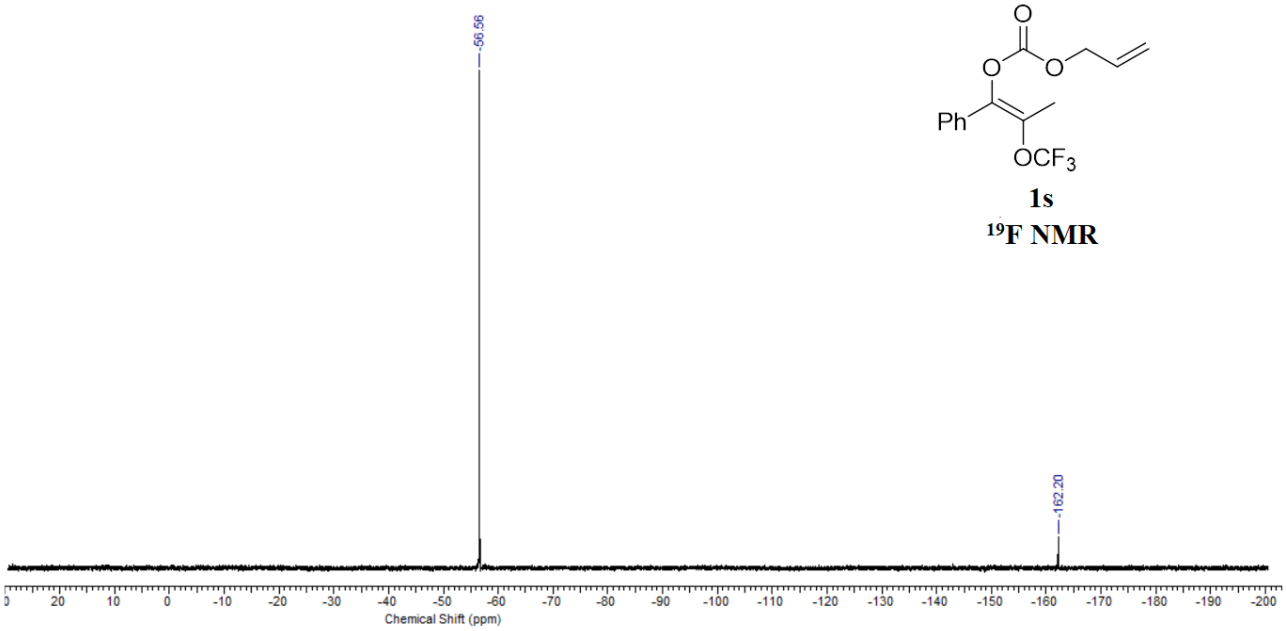
^{19}F NMR

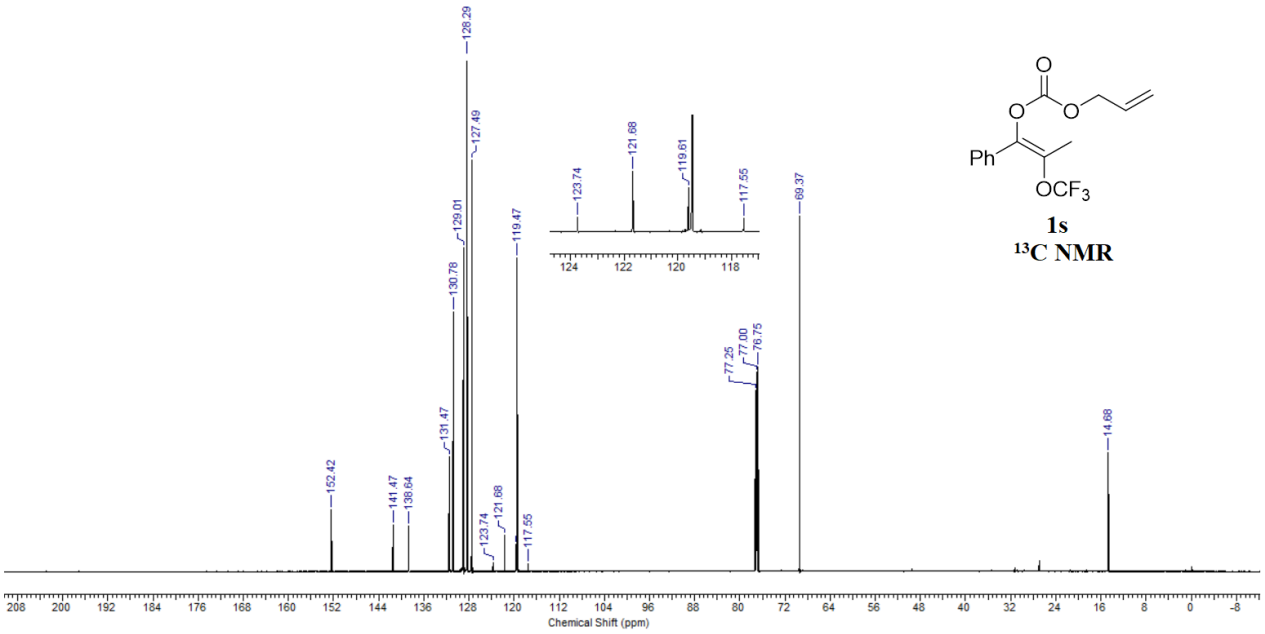


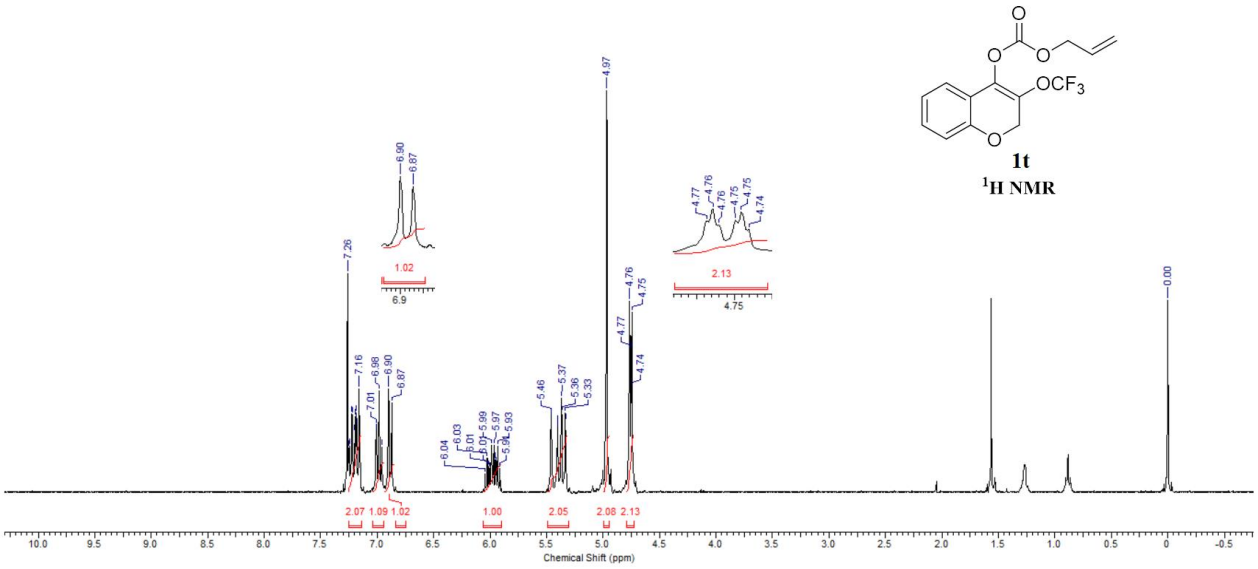
1r

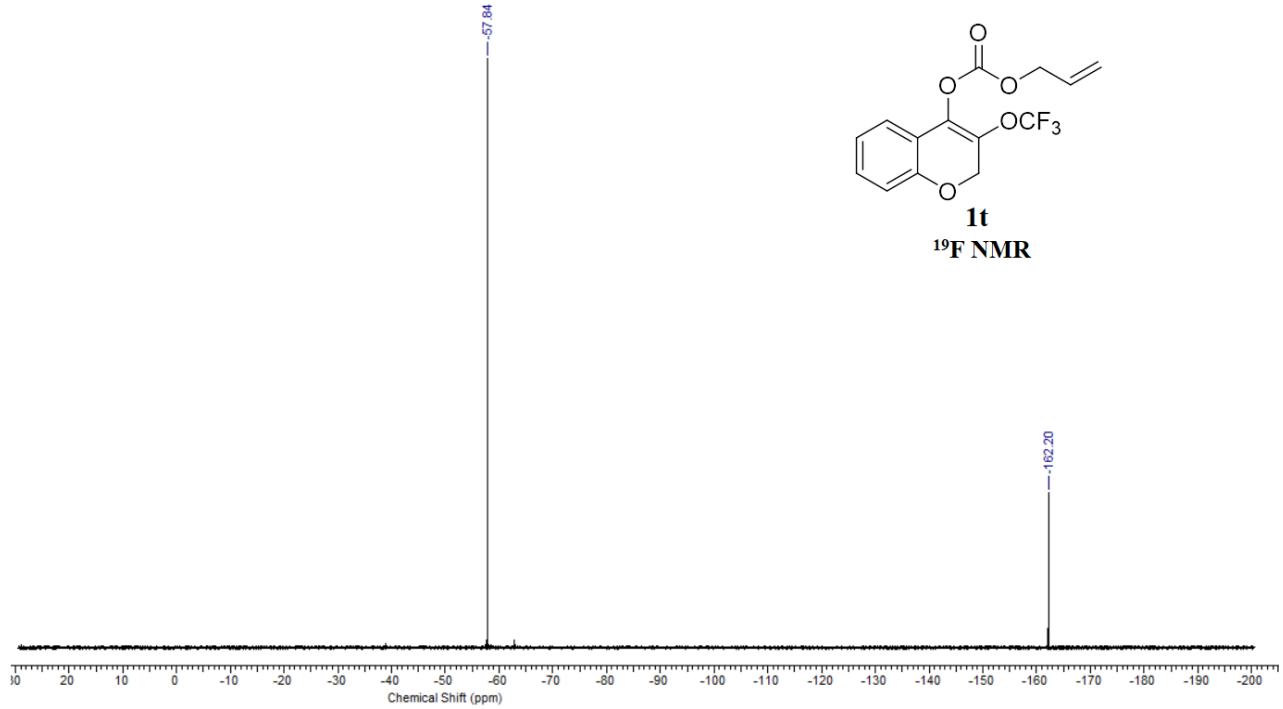
^{13}C NMR


Ph
OCF3
1s
1H NMR
Chemical Shift (ppm)


Ph
OCF3
1s
19F NMR
Chemical Shift (ppm)

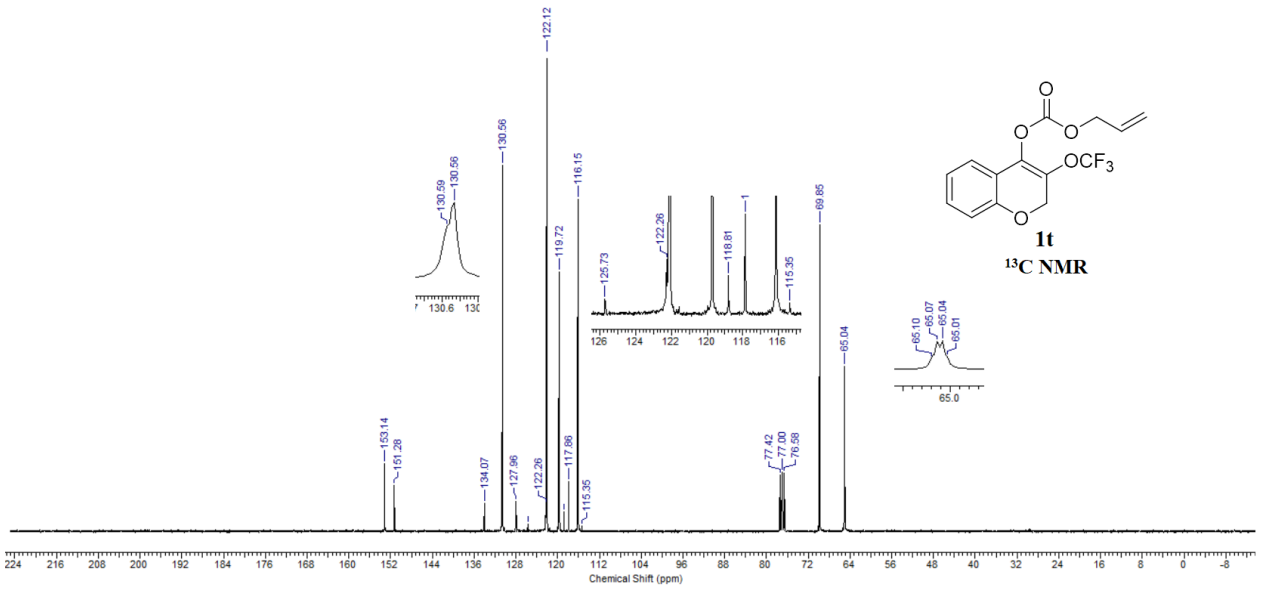

Ph
OCF3
1s
13C NMR
Chemical Shift (ppm)


OCF3
1t
1H NMR
Chemical Shift (ppm)



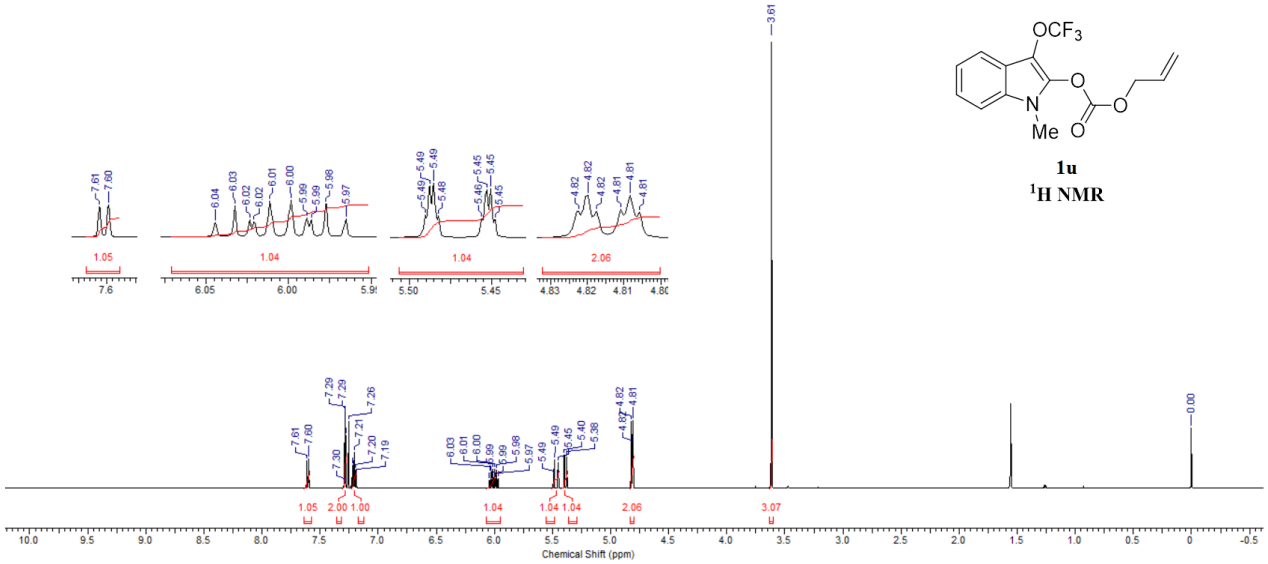
1t

^{19}F NMR



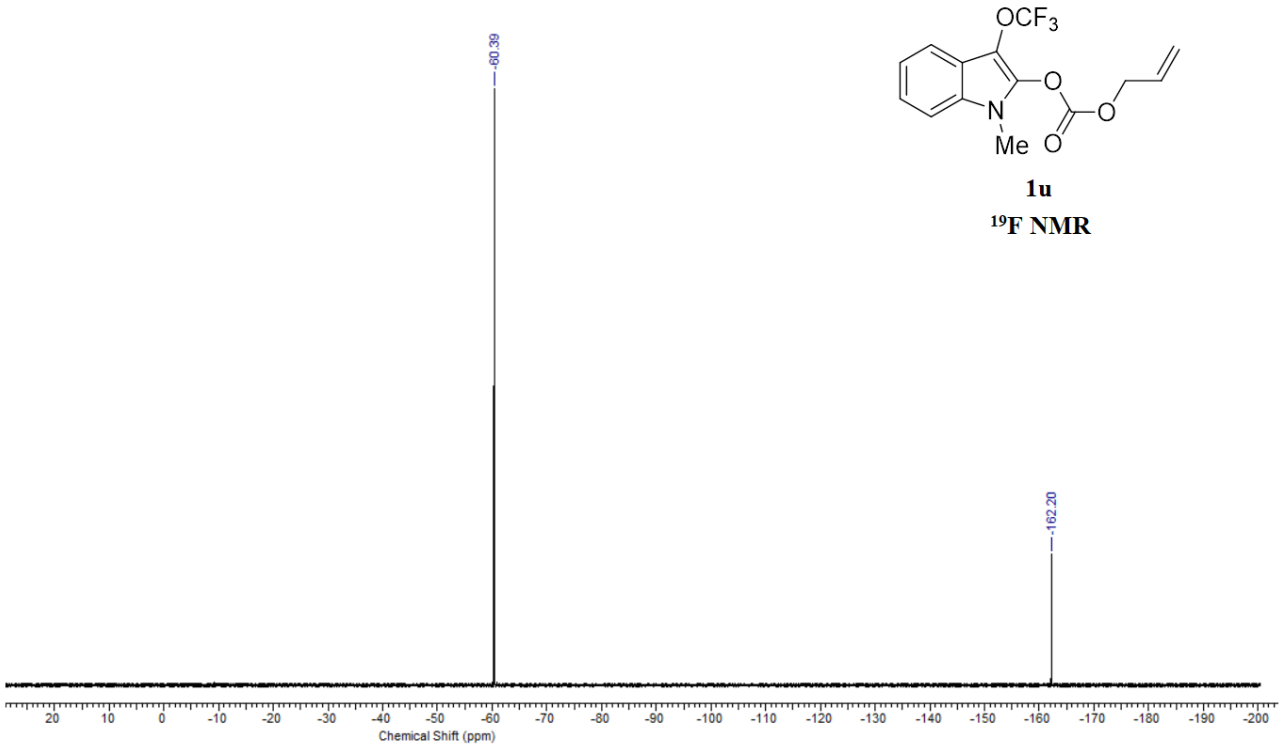
1t

^{13}C NMR



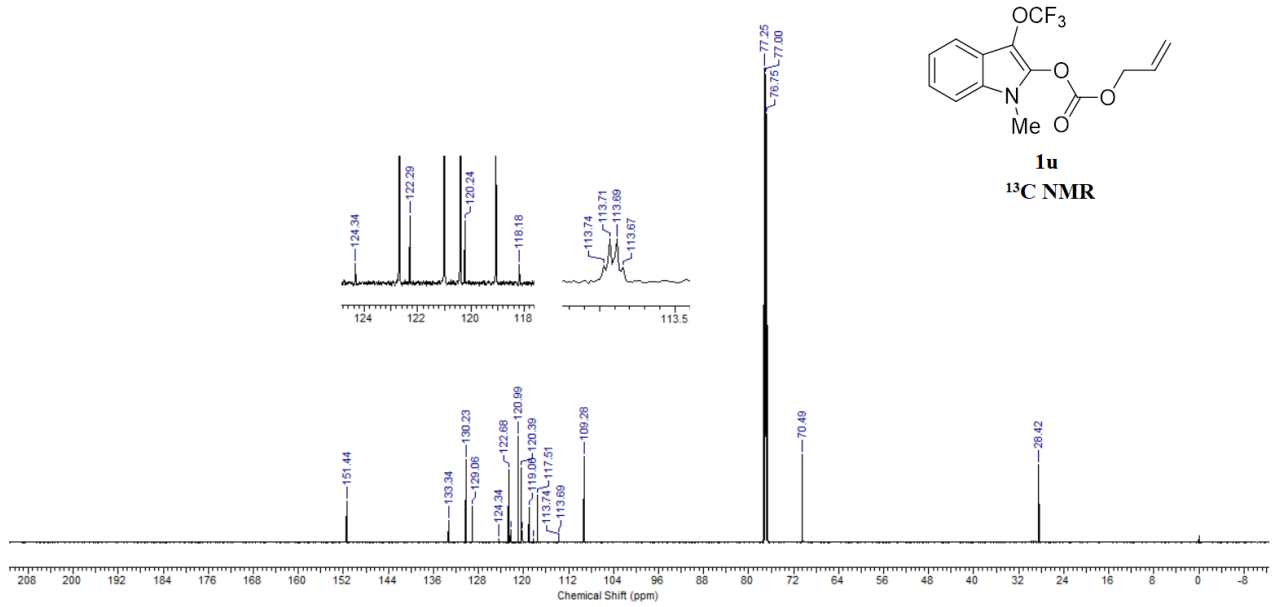
1u

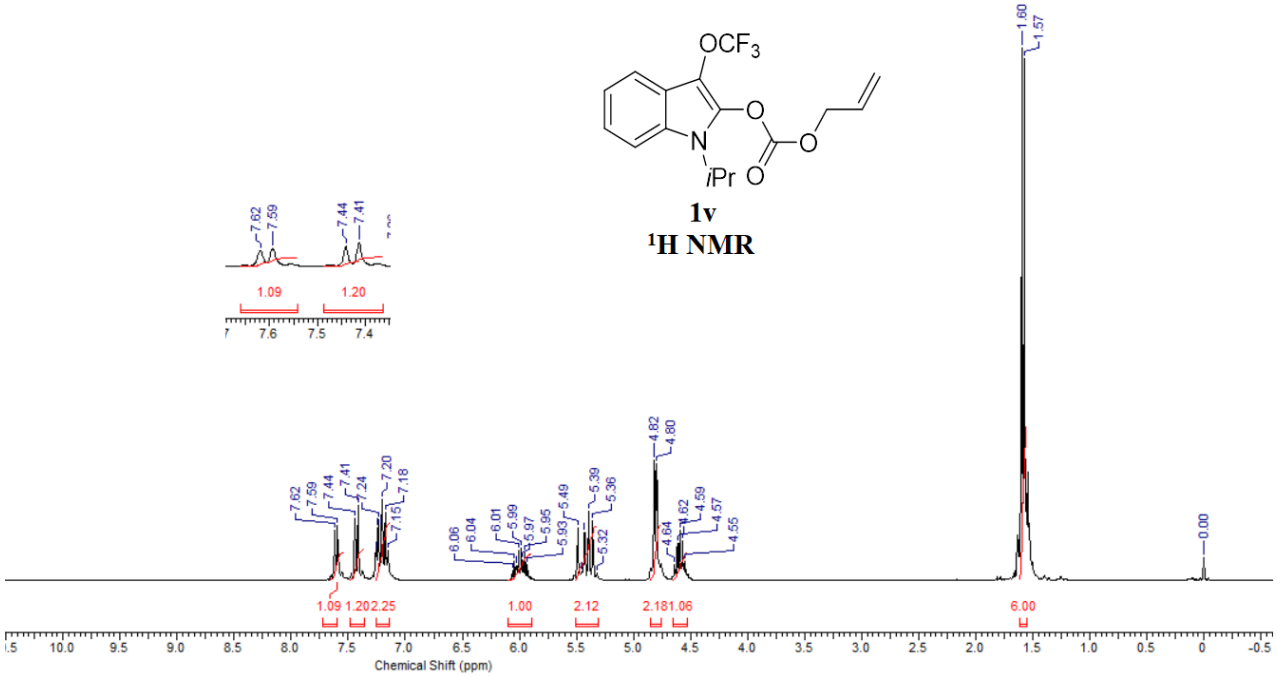
^{1}H NMR

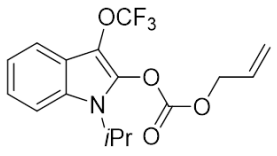


1u

^{19}F NMR

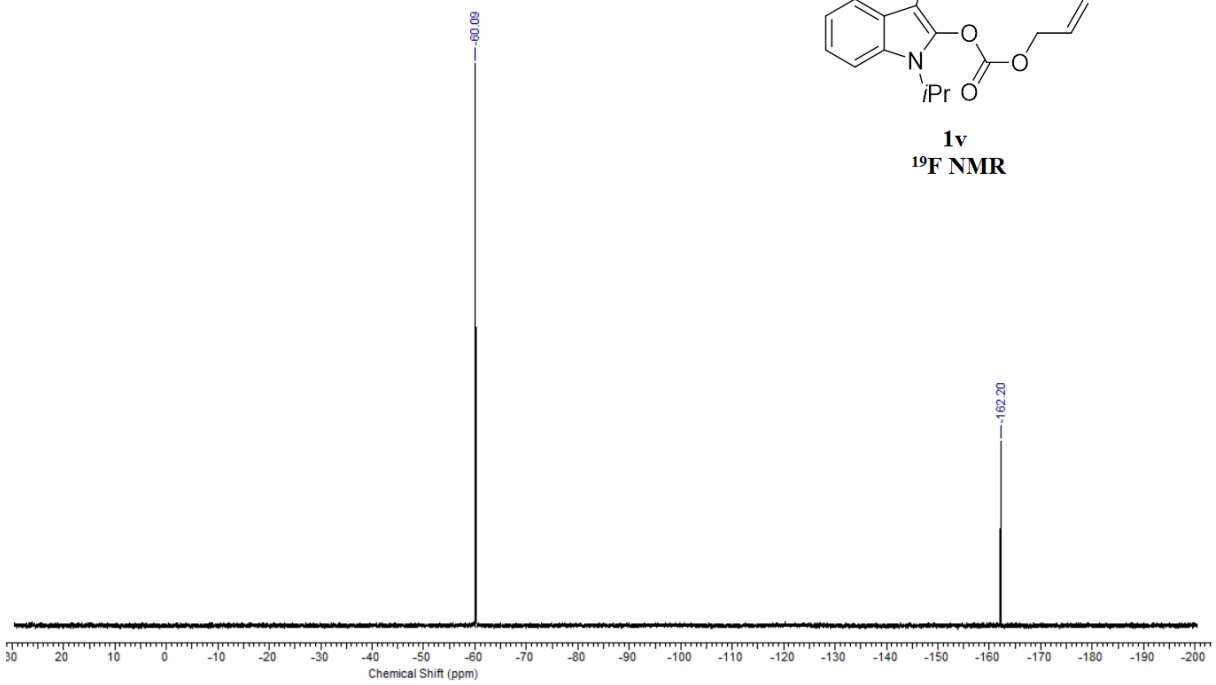

OCF3
O
O
N
Me
O
1u
13C NMR
77.25
77.00
76.75
124.34
122.29
120.24
118.18
113.74
113.71
113.69
113.67
151.44
133.34
130.23
129.06
124.34
122.68
120.99
120.39
119.09
117.51
113.74
113.69
109.28
70.49
28.42
Chemical Shift (ppm)

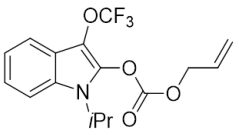

OCF3
O
O
N
iPr
O
1v
1H NMR
7.62
7.59
7.44
7.41
1.09
1.20
1.60
1.57
7.62
7.59
7.44
7.41
7.24
7.20
7.18
7.15
6.06
6.04
6.01
5.99
5.97
5.95
5.93
5.49
5.39
5.36
5.32
4.82
4.80
4.84
4.62
4.59
4.57
4.55
0.00
1.09
1.20
2.25
1.00
2.12
2.18
1.06
6.00
Chemical Shift (ppm)



1v

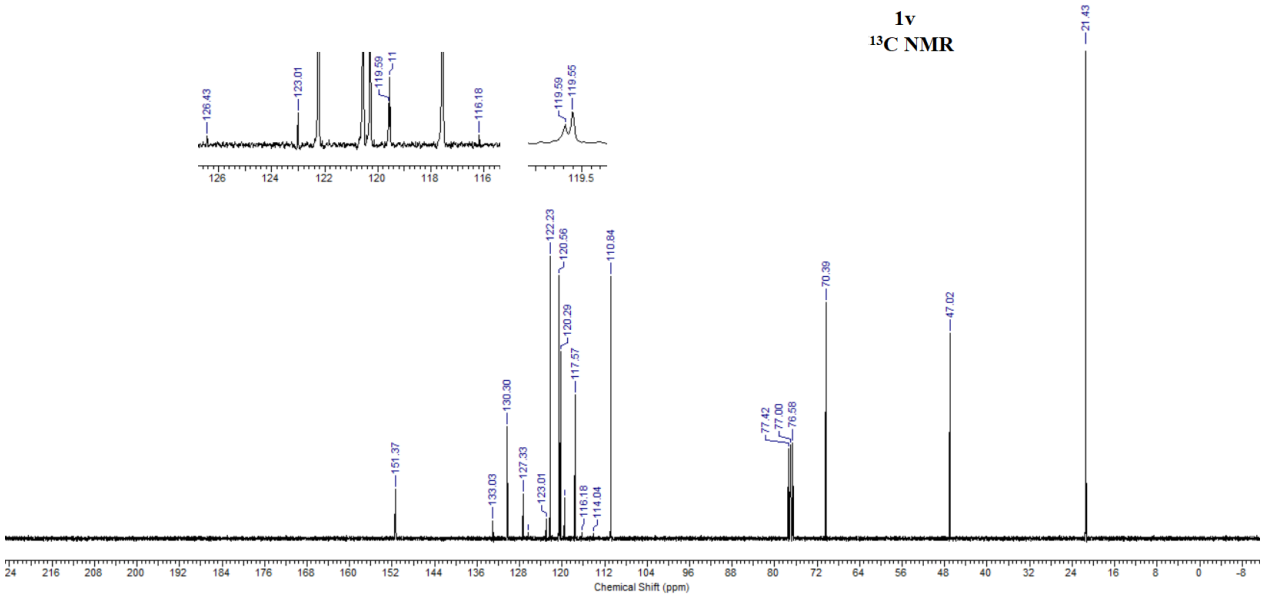
^{19}F NMR

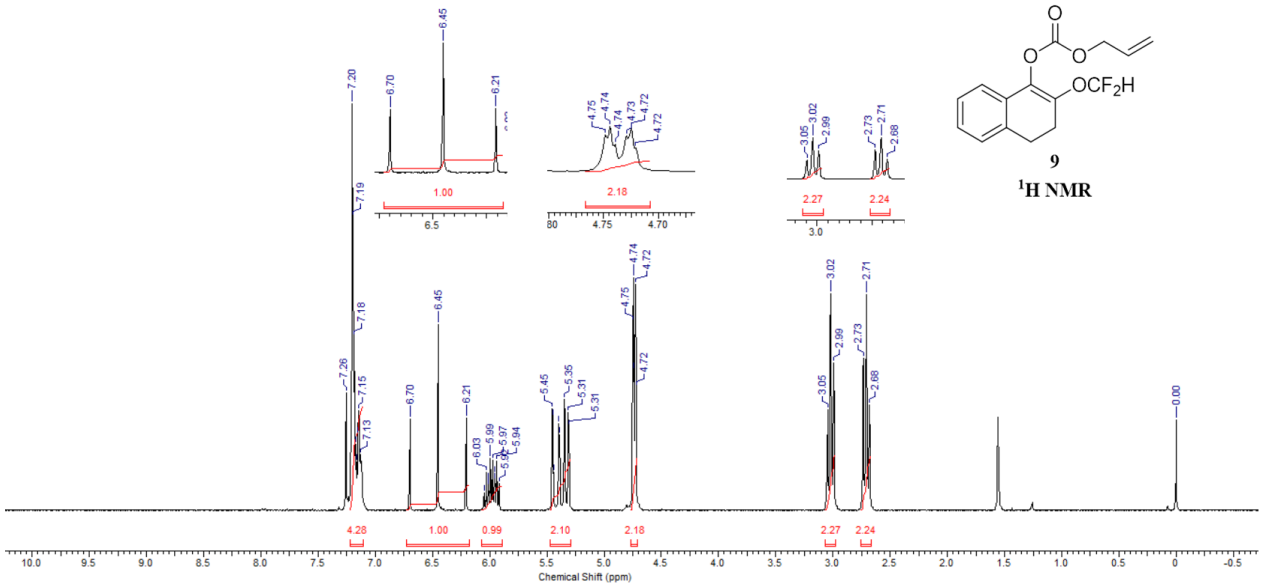


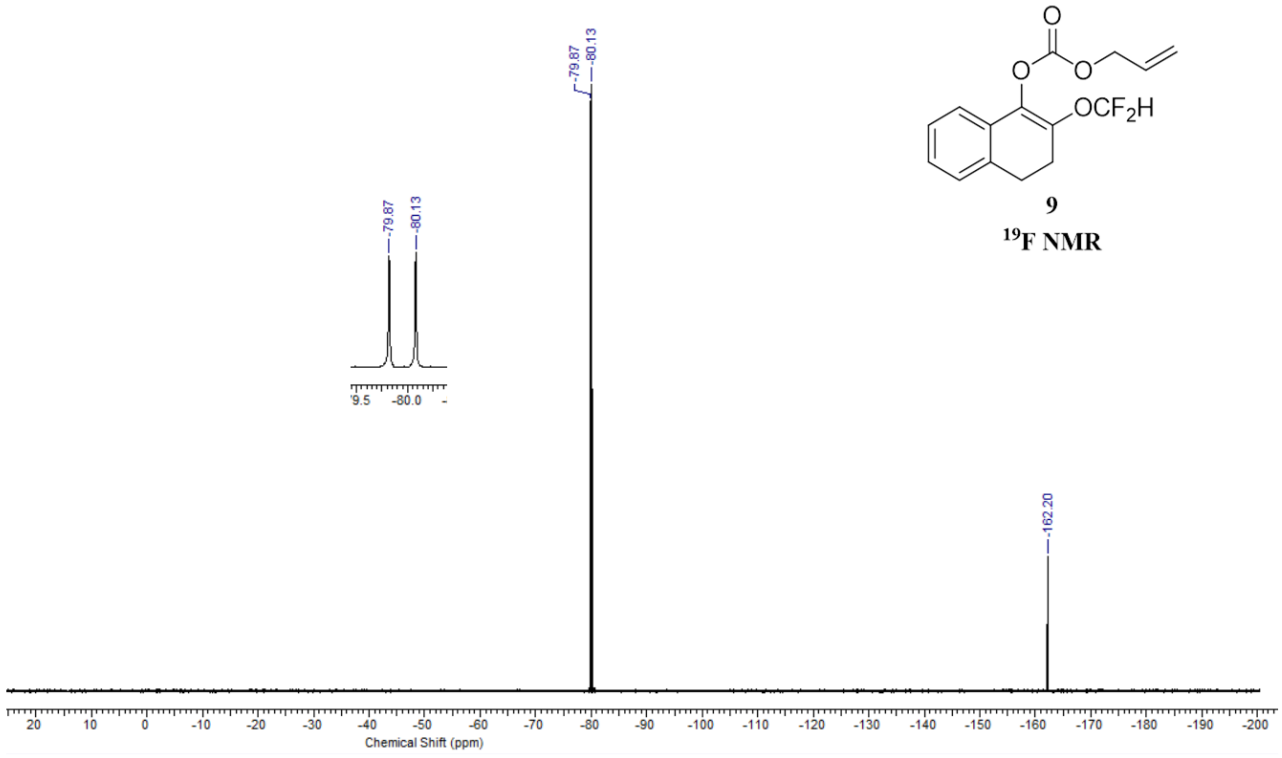


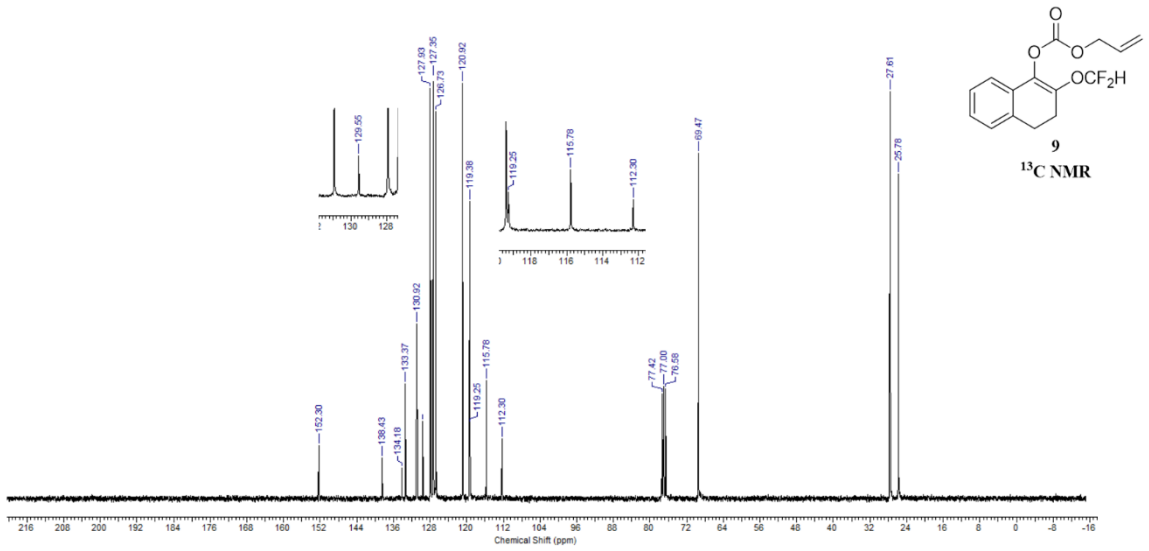
1v

^{13}C NMR



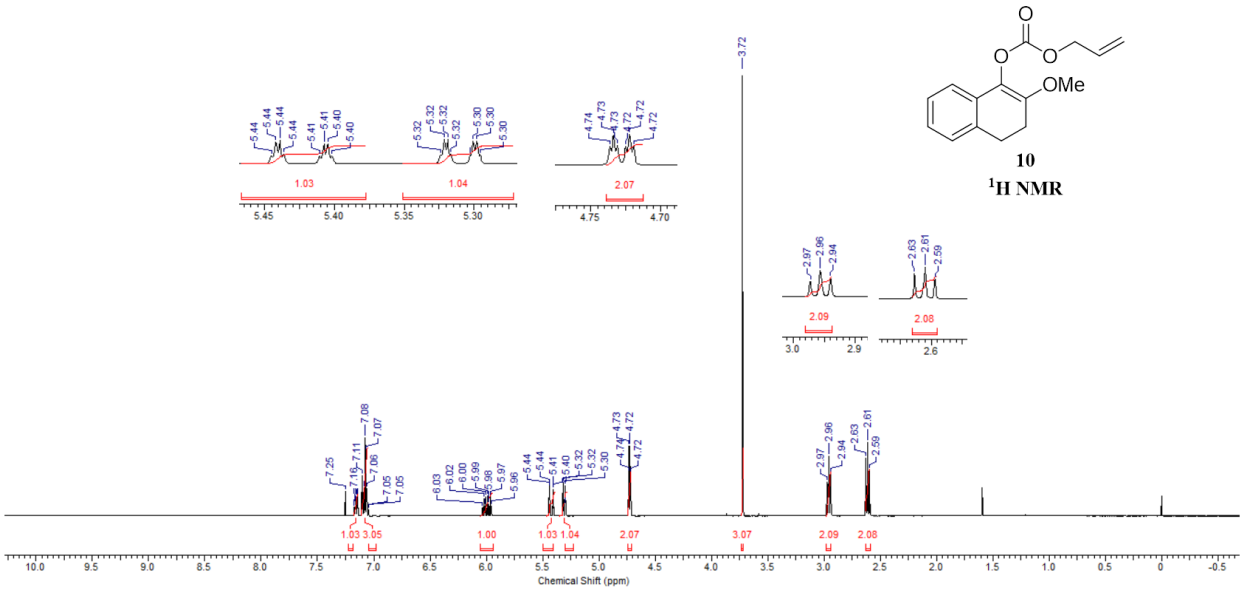

9
1H NMR
Chemical Shift (ppm)


9
19F NMR
Chemical Shift (ppm)



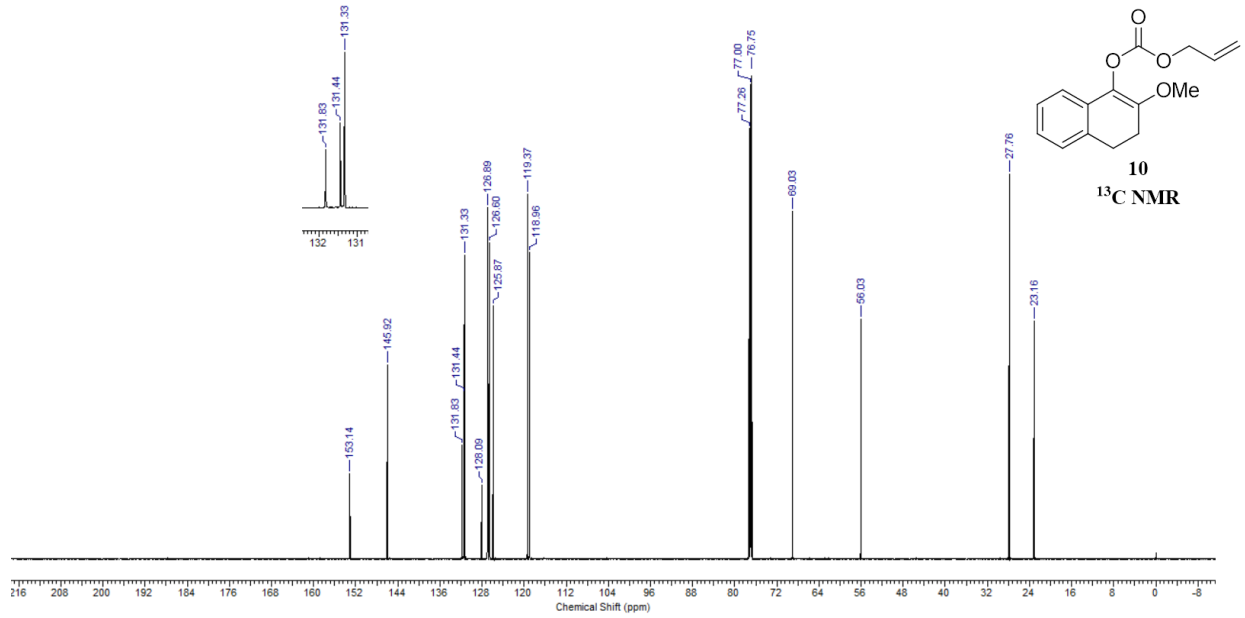
9

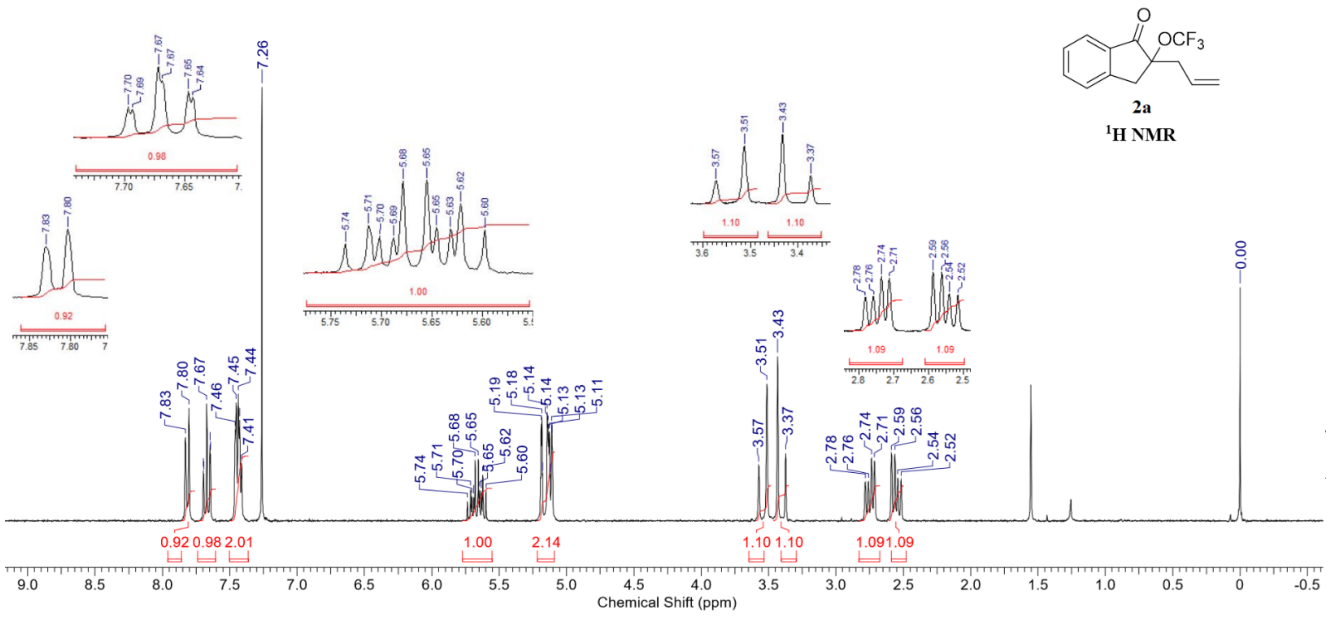
^{13}C NMR

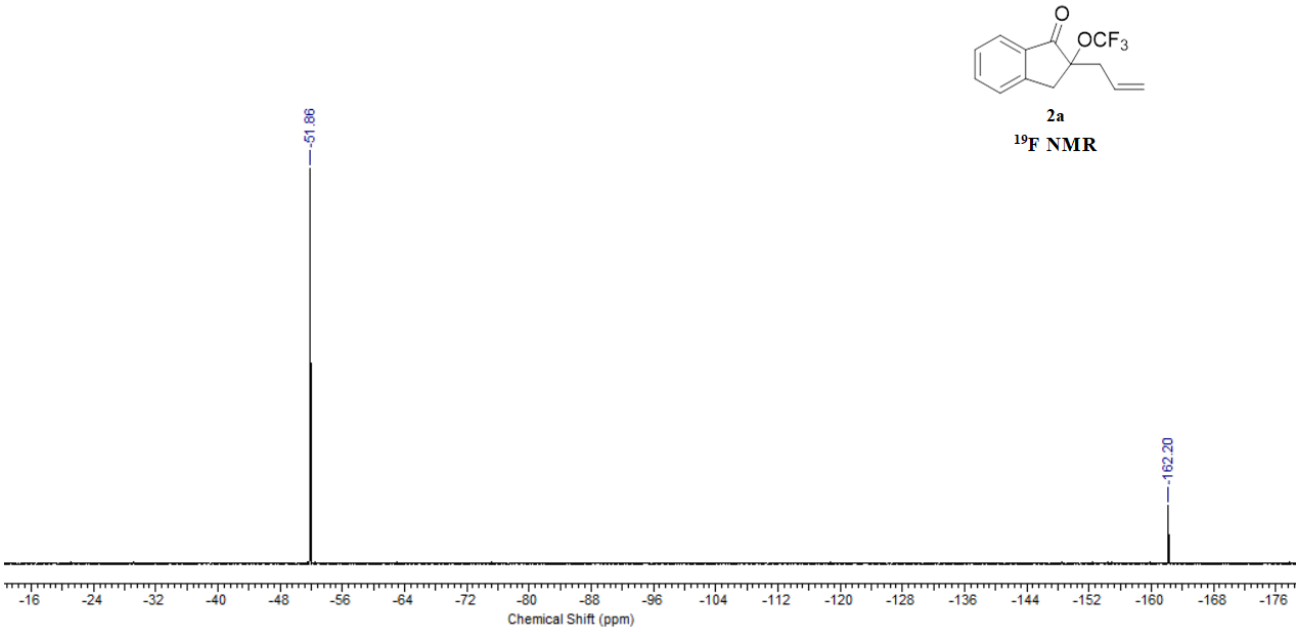


10

^{1}H NMR

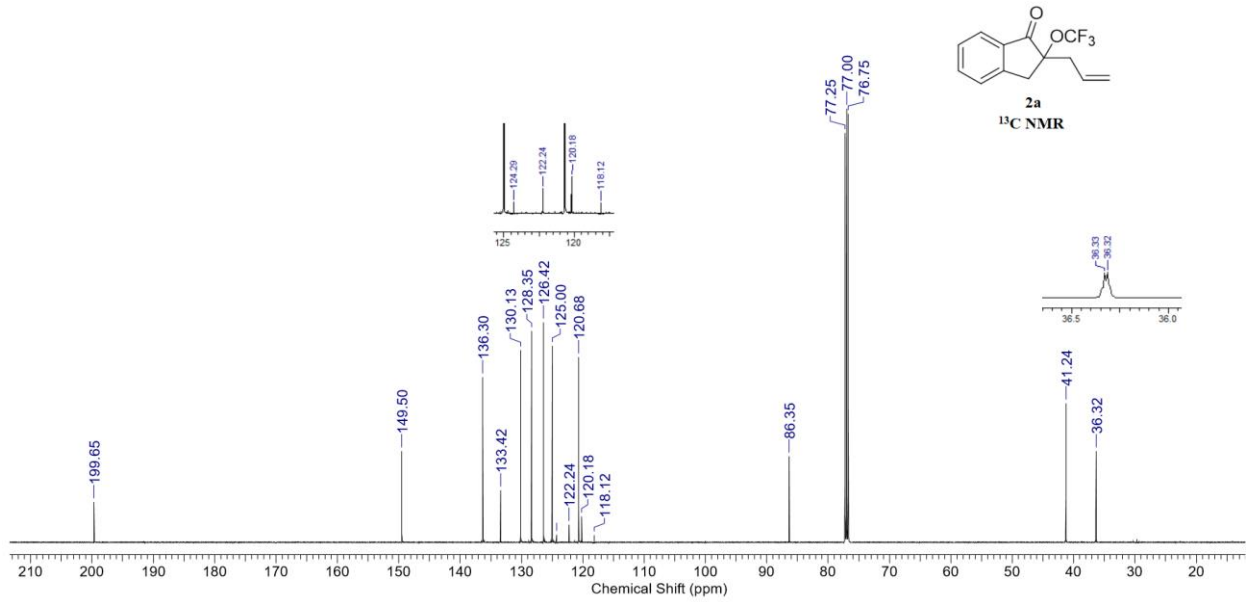

10
13C NMR
Chemical Shift (ppm)


2a
1H NMR
Chemical Shift (ppm)



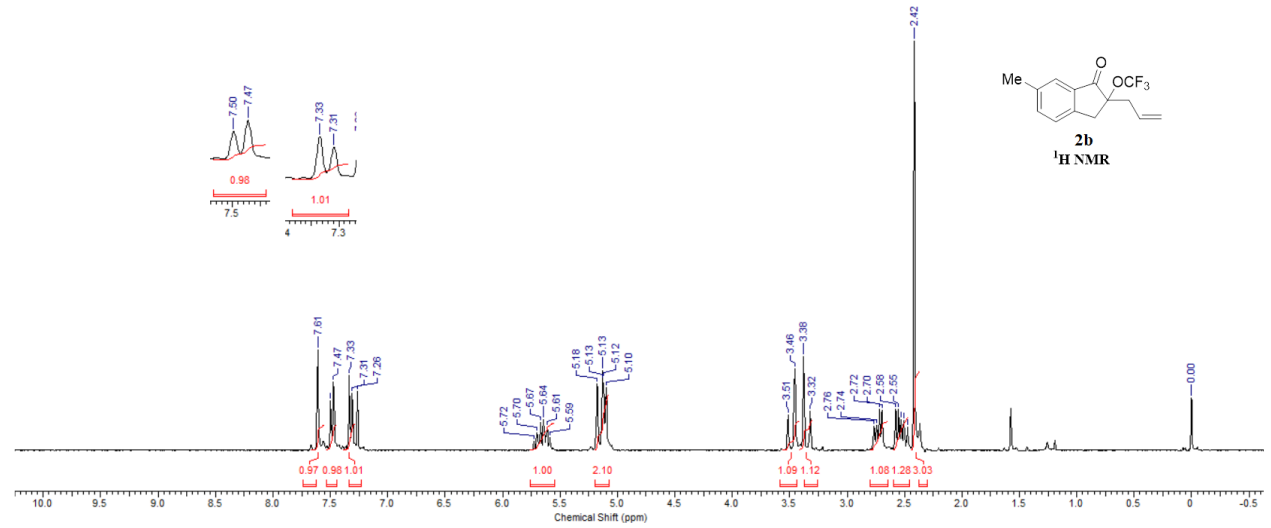
2a

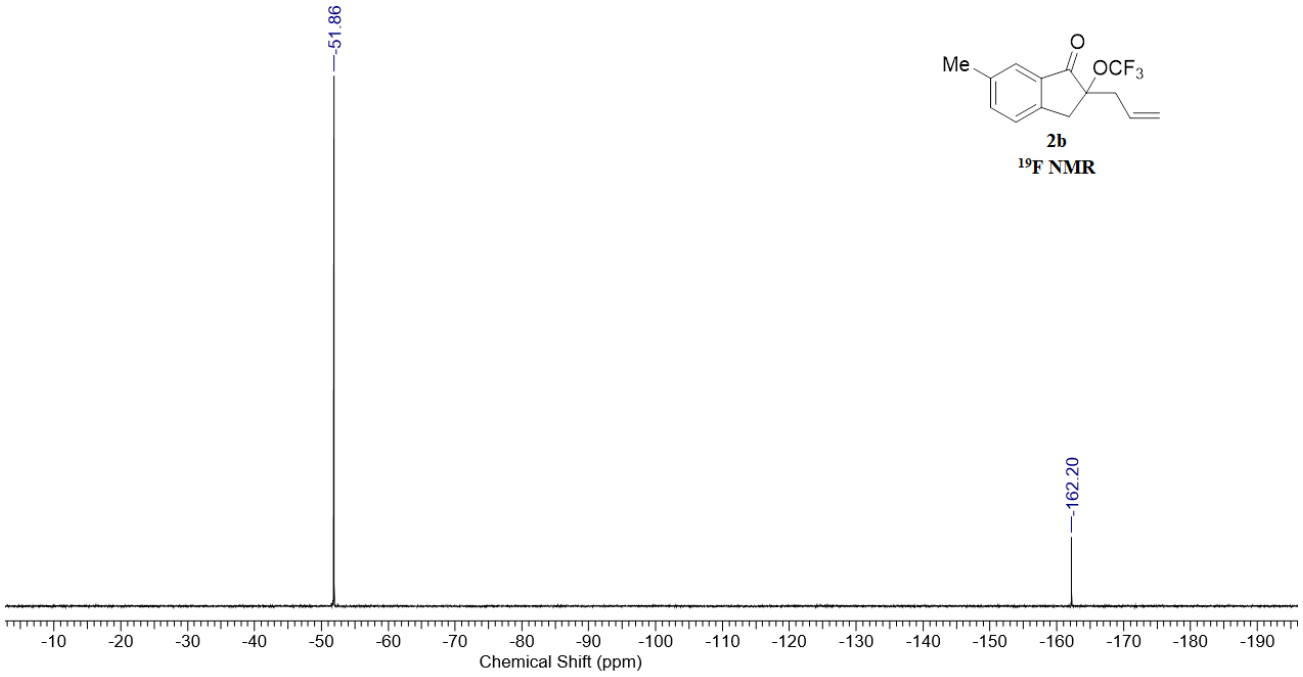
^{19}F NMR

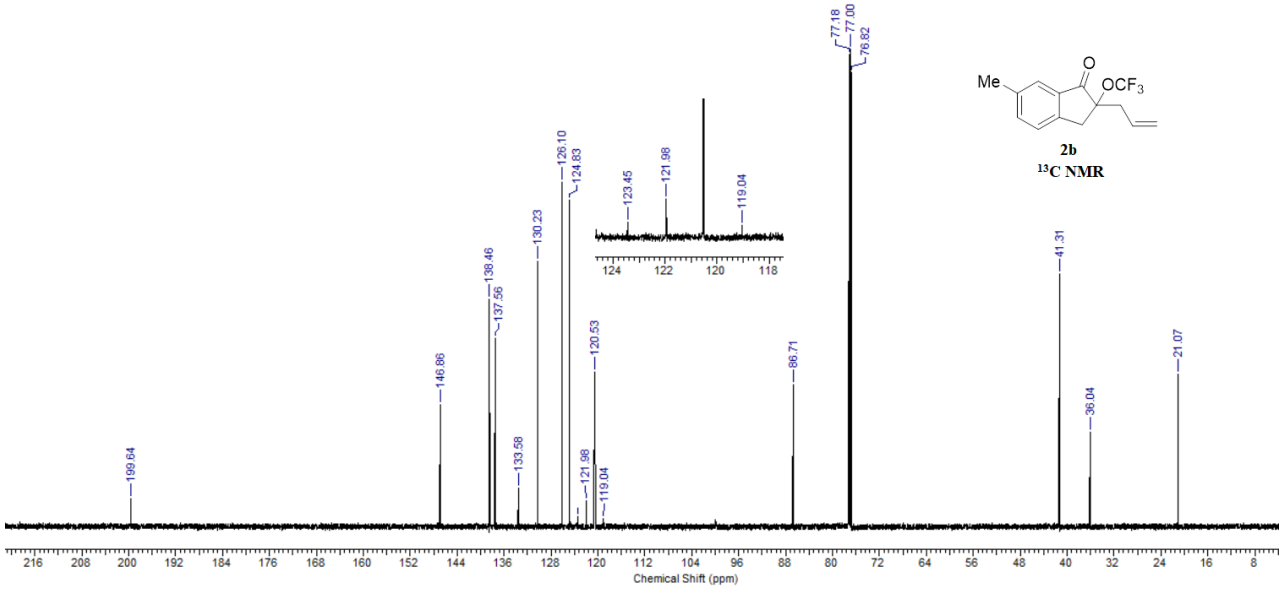


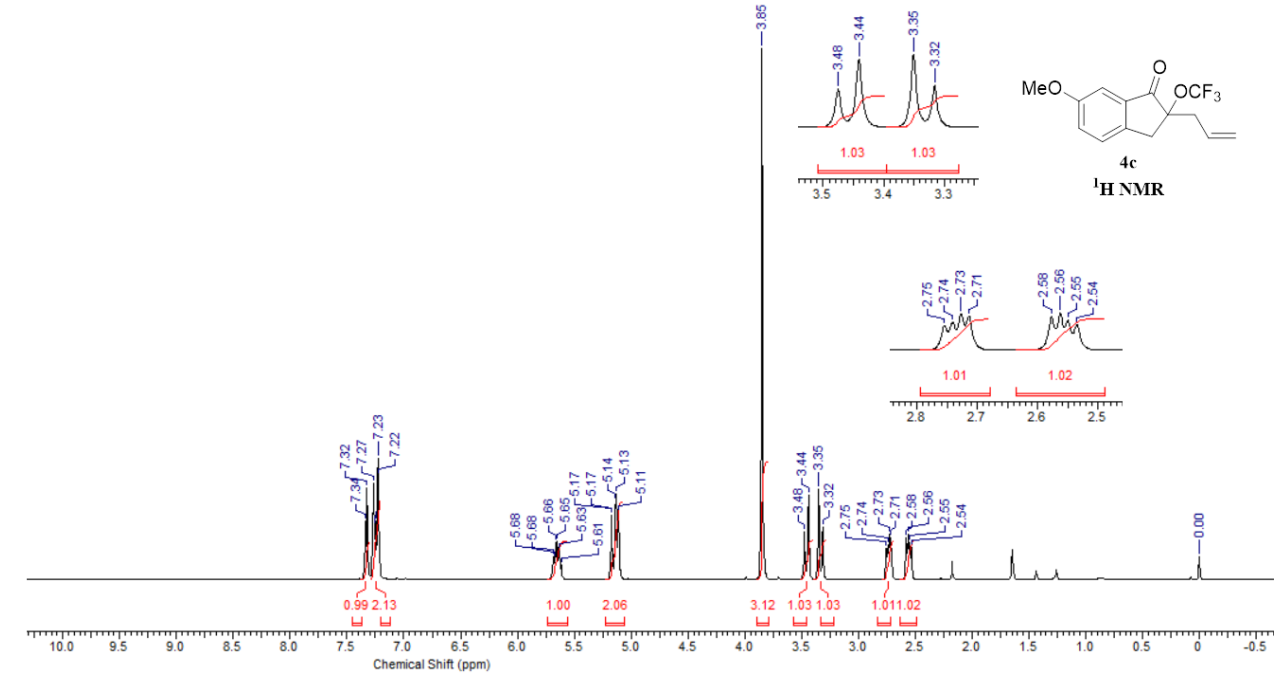
2a

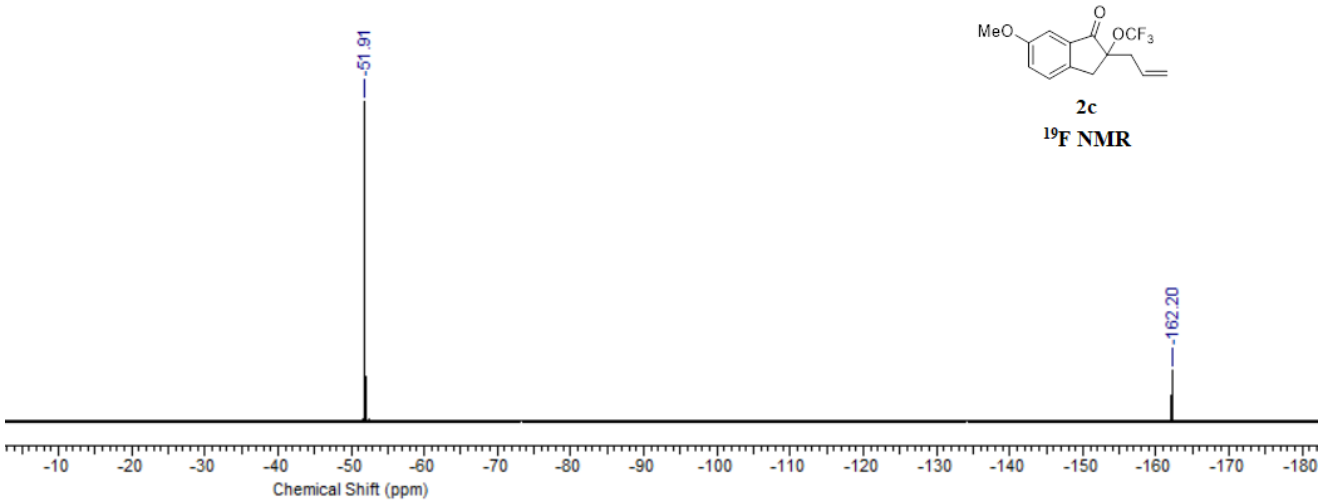
^{13}C NMR

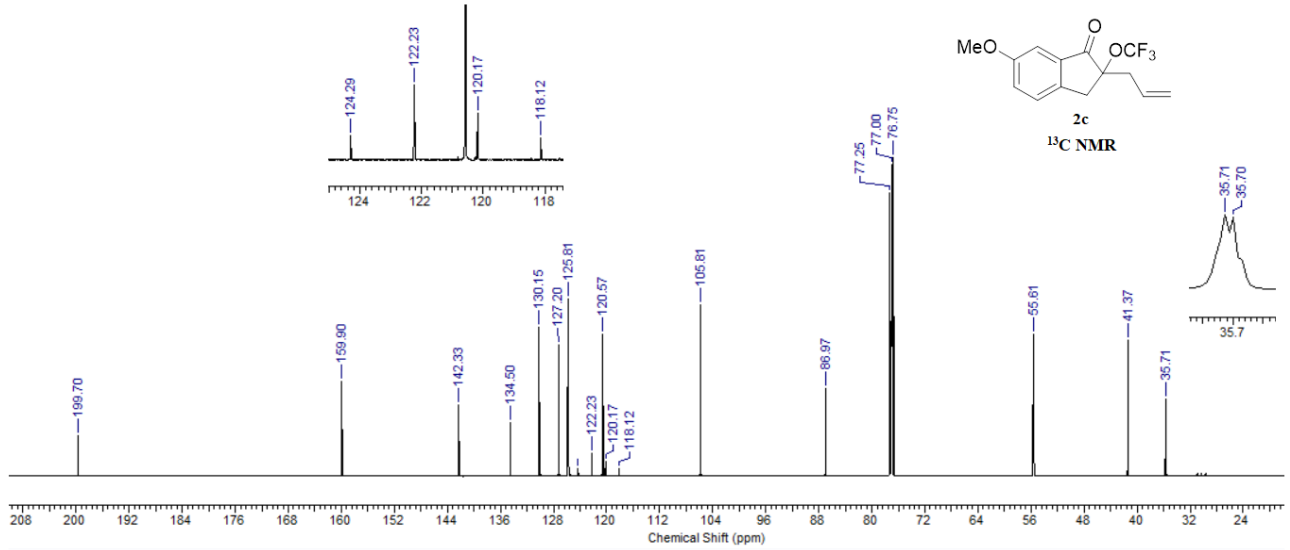

Me
O
OCF3
2b
1H NMR
Chemical Shift (ppm)

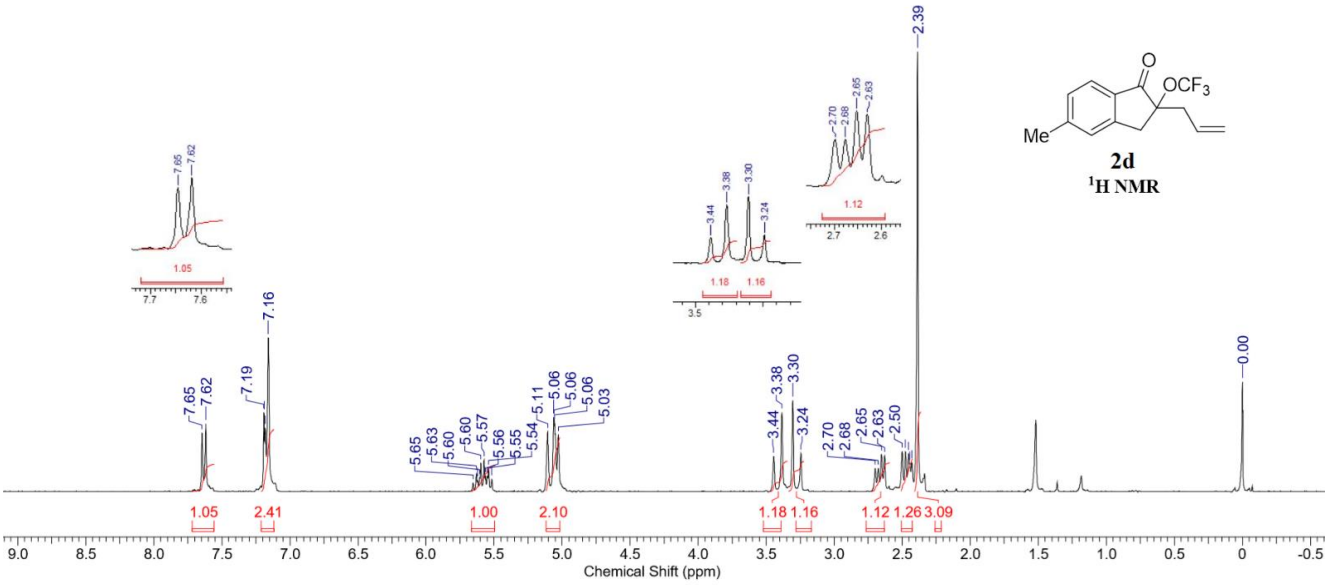

Me
O
OCF3
2b
19F NMR
Chemical Shift (ppm)


Me
O
OCF3
2b
13C NMR
Chemical Shift (ppm)


MeO
O
OCF3
4c
1H NMR
Chemical Shift (ppm)

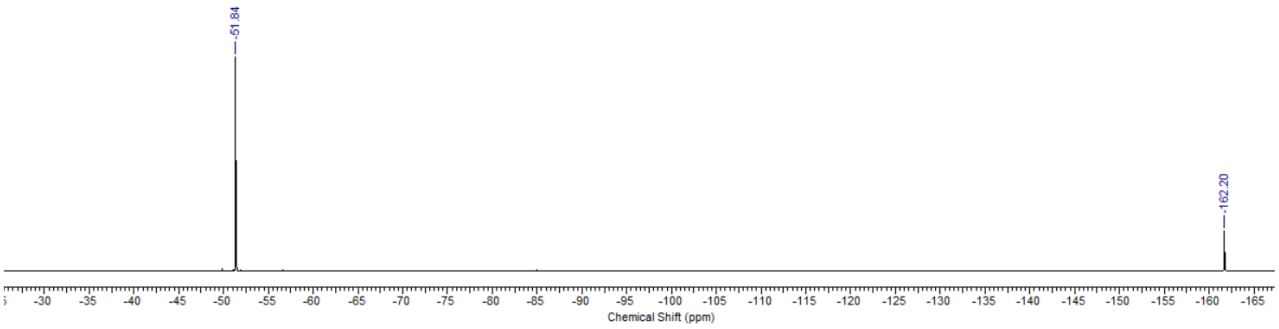

-51.91
-162.20
MeO
O
OCF3
2c
19F NMR
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
Chemical Shift (ppm)


124.29
122.23
120.17
118.12
124 122 120 118
MeO
O
OCF3
2c
13C NMR
77.25
77.00
76.75
35.71
35.70
35.7
199.70
159.90
142.33
134.50
130.15
127.20
125.81
120.57
122.23
120.17
118.12
105.81
86.97
55.61
41.37
35.71
208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24
Chemical Shift (ppm)



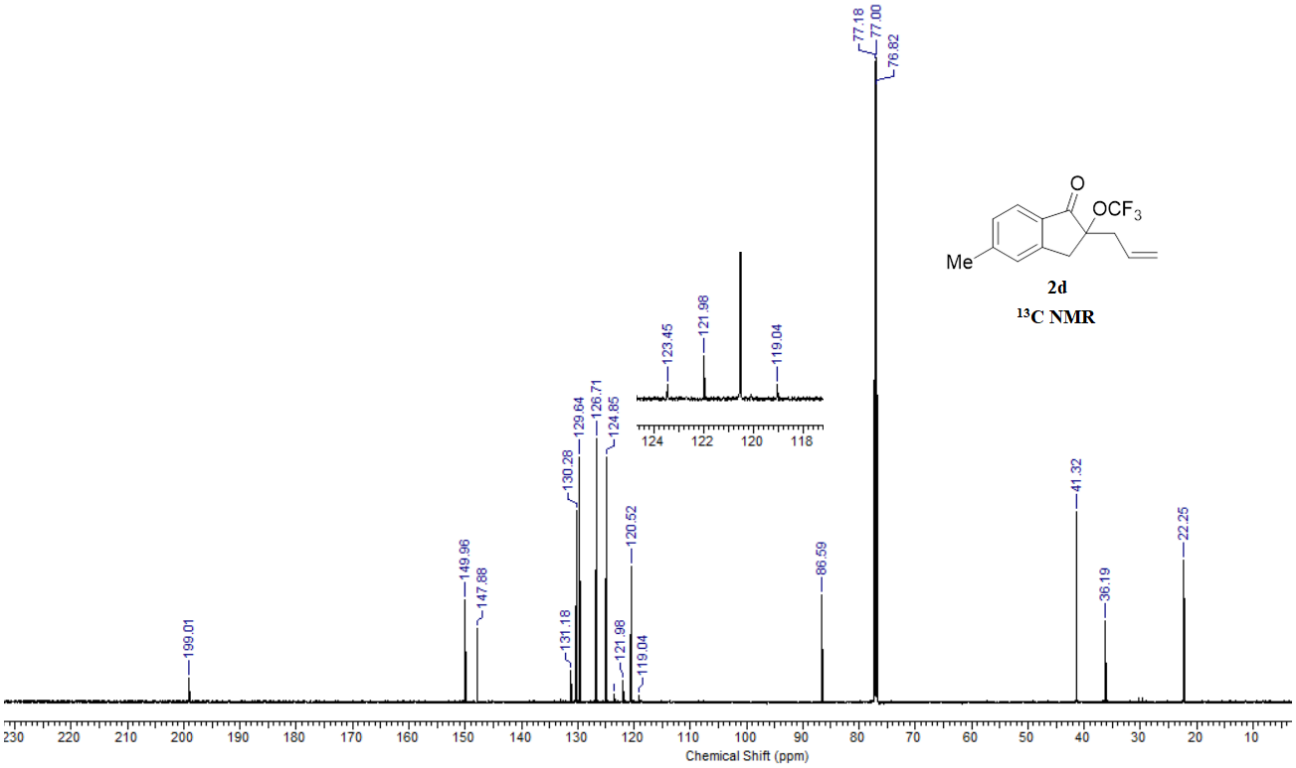
2d

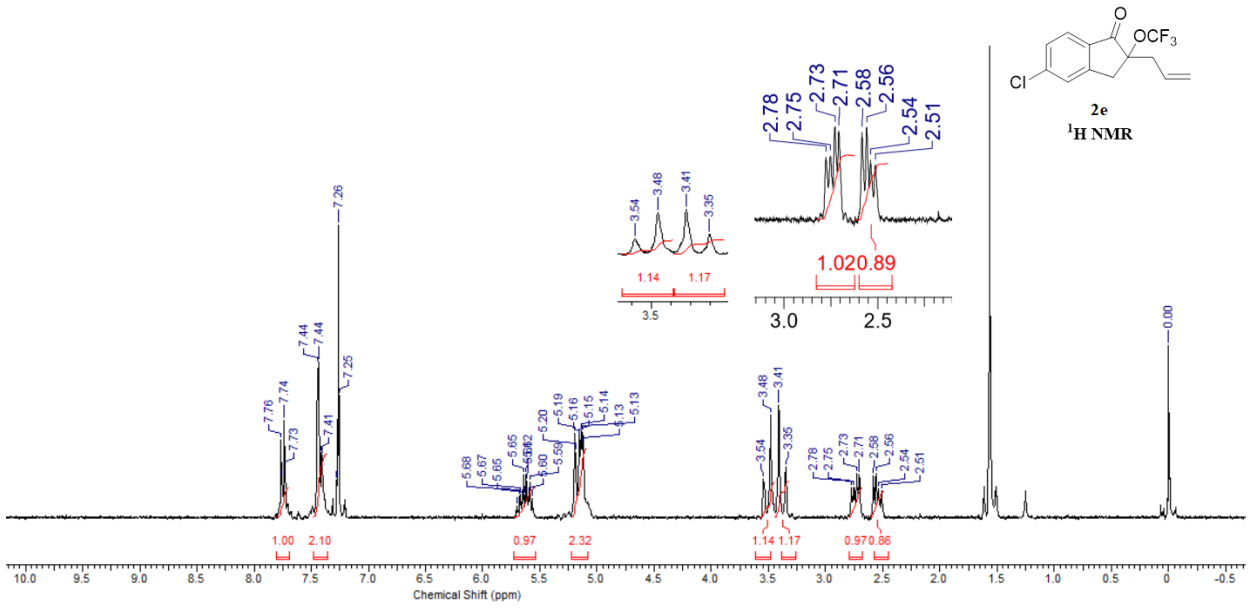
^{1}H NMR

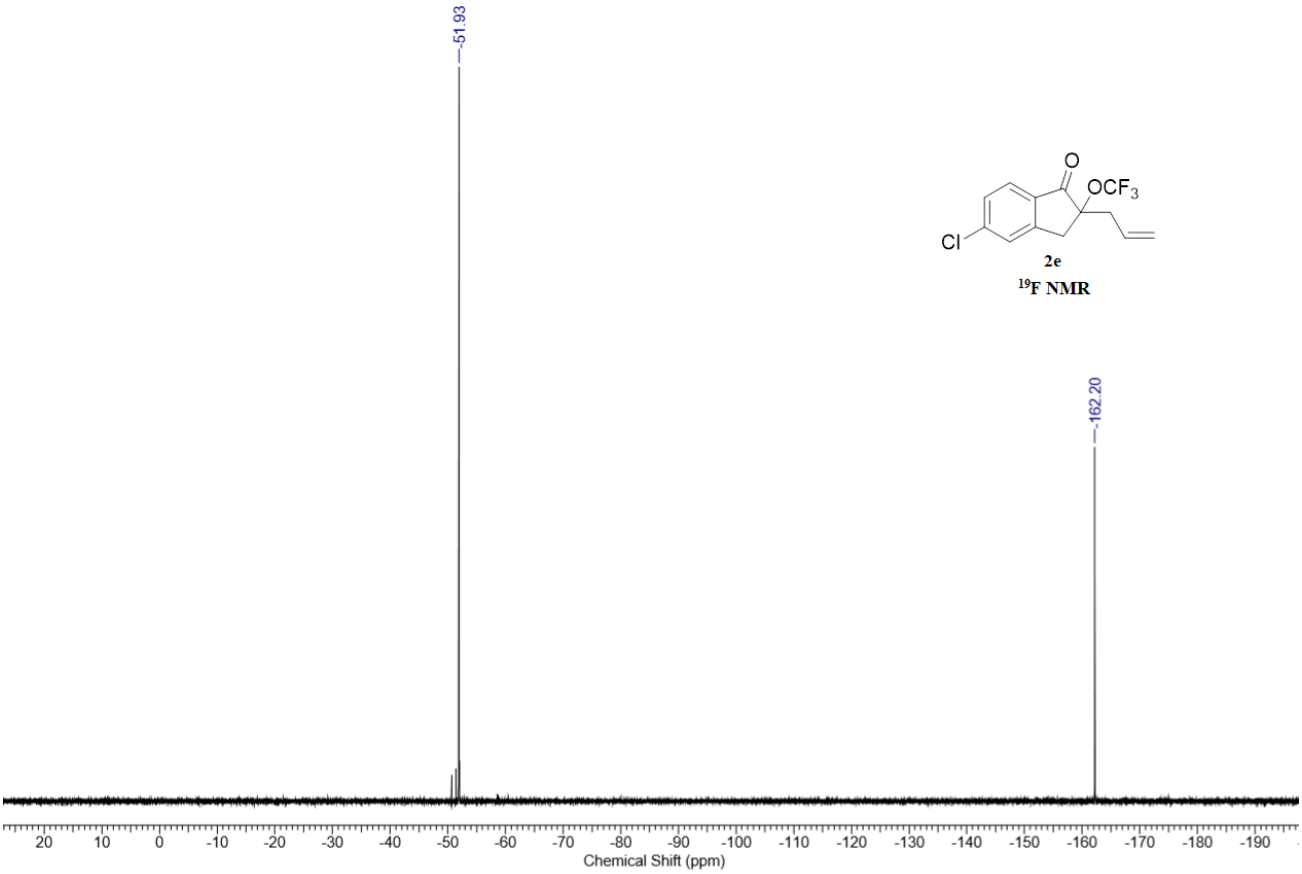


2d

^{19}F NMR

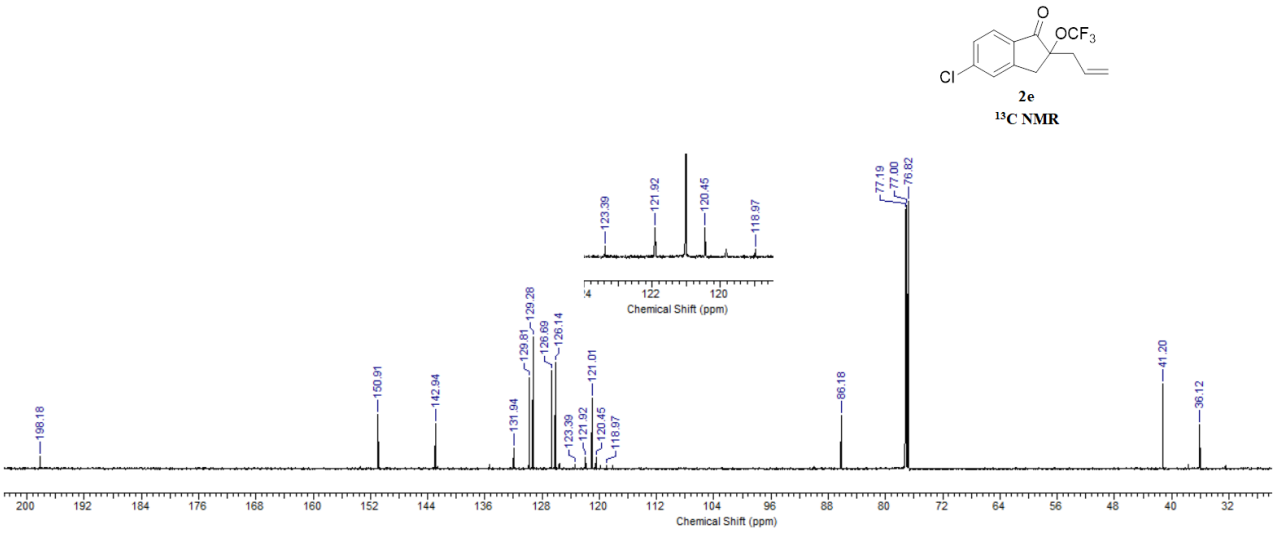

77.18
77.00
76.82
O
OCF3
Me
2d
13C NMR
123.45
121.98
119.04
124 122 120 118
130.28
129.64
126.71
124.85
120.52
149.96
147.88
131.18
121.98
119.04
86.59
41.32
36.19
22.25
199.01
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)


O
OCF3
Cl
2e
1H NMR
2.78
2.75
2.73
2.71
2.58
2.56
2.54
2.51
1.020.89
3.0 2.5
3.54
3.48
3.41
3.35
1.14 1.17
3.5
7.26
7.76
7.74
7.73
7.44
7.44
7.41
7.25
5.68
5.67
5.65
5.65
5.62
5.60
5.59
5.20
5.19
5.16
5.15
5.14
5.13
5.13
0.00
1.00 2.10 0.97 2.32 1.14 1.17 0.97 0.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)



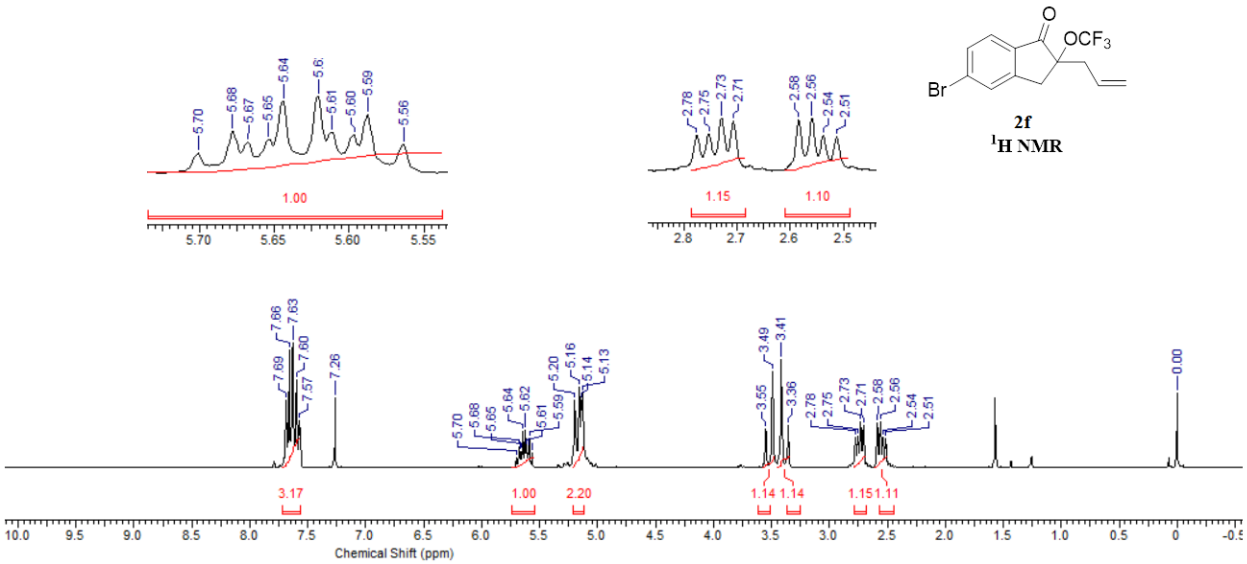
2e

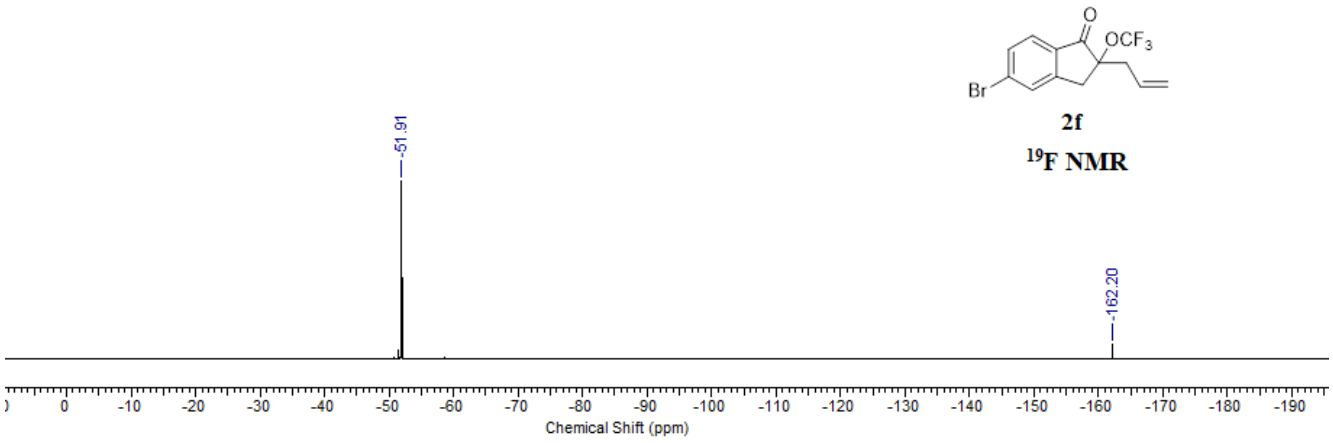
^{19}F NMR

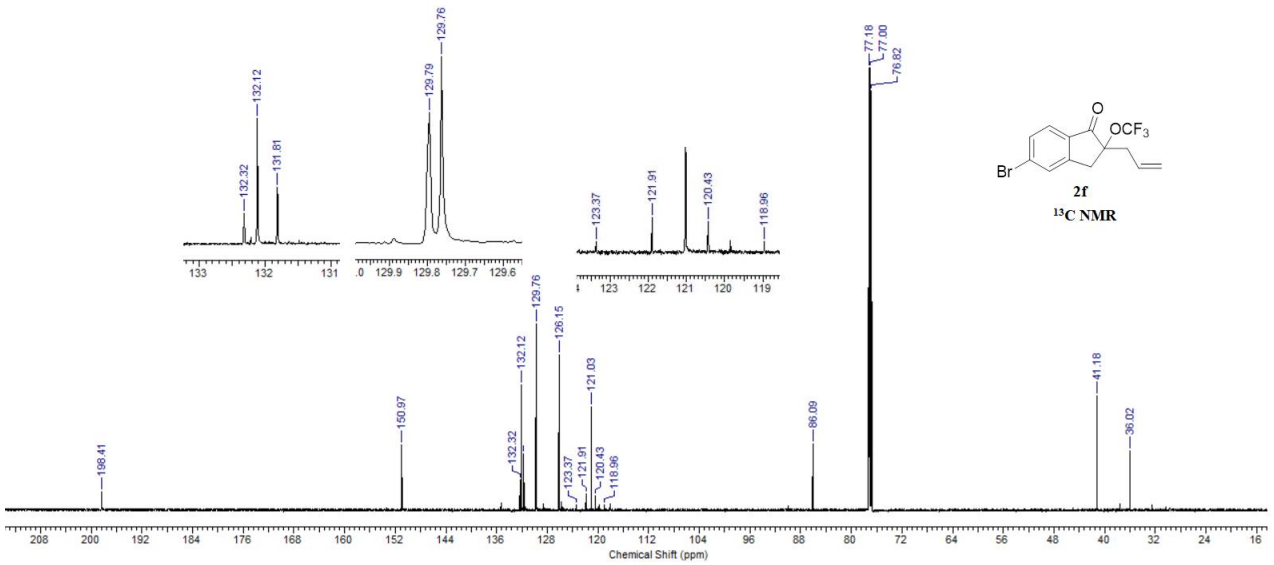


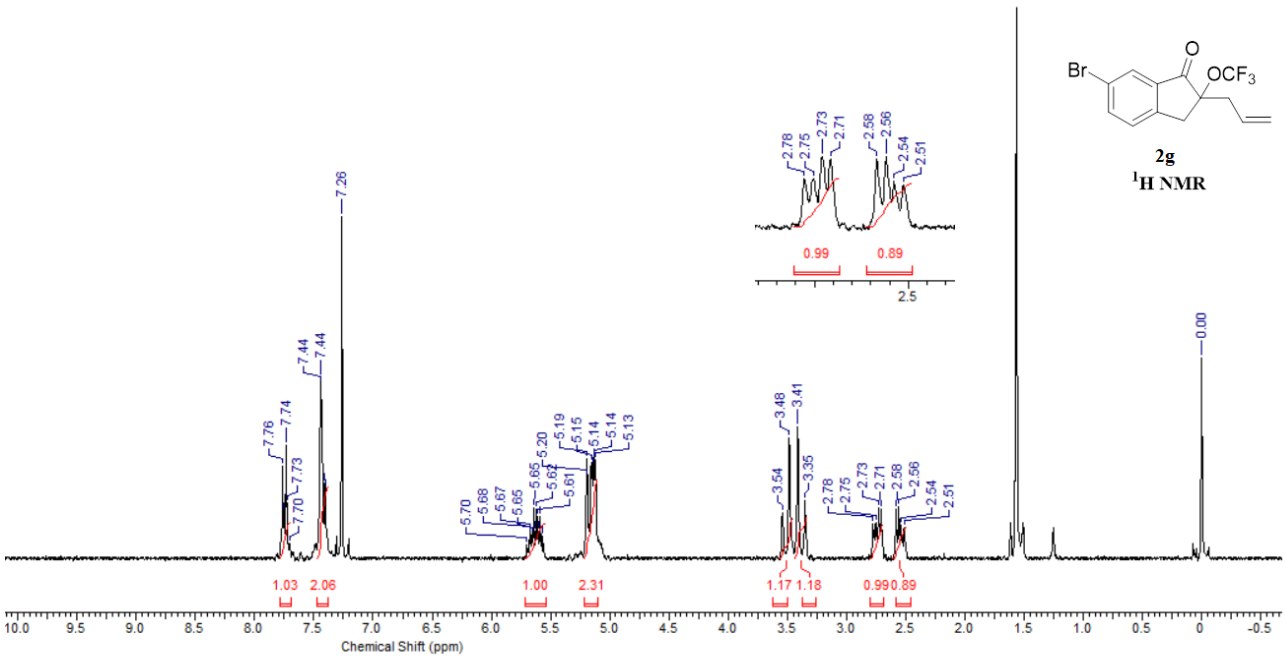
2e

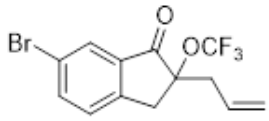
^{13}C NMR


O
OCF3
Br
2f
1H NMR
Chemical Shift (ppm)


O
OCF3
Br
2f
19F NMR
-51.91
-162.20
Chemical Shift (ppm)

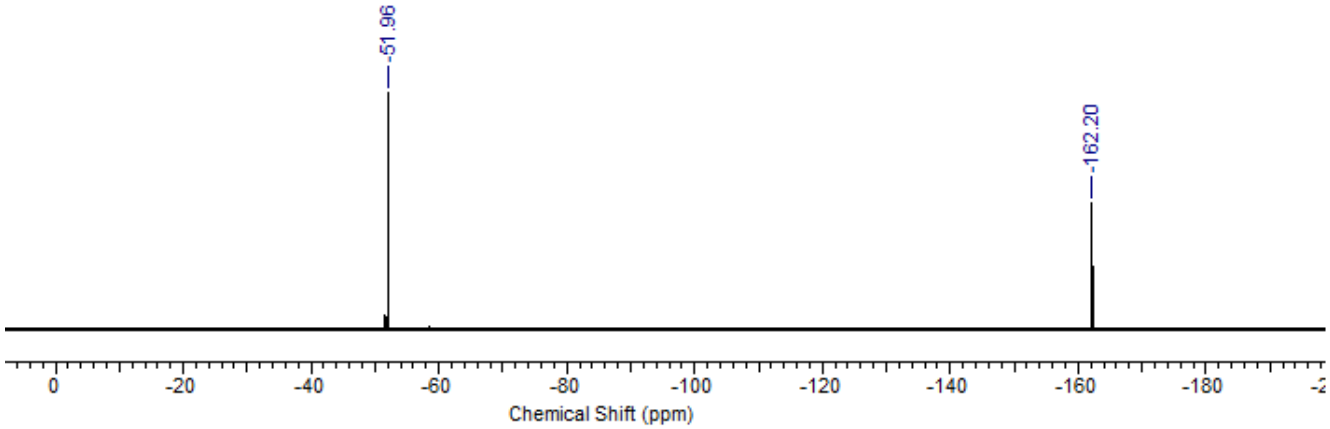

2f
13C NMR
Chemical Shift (ppm)

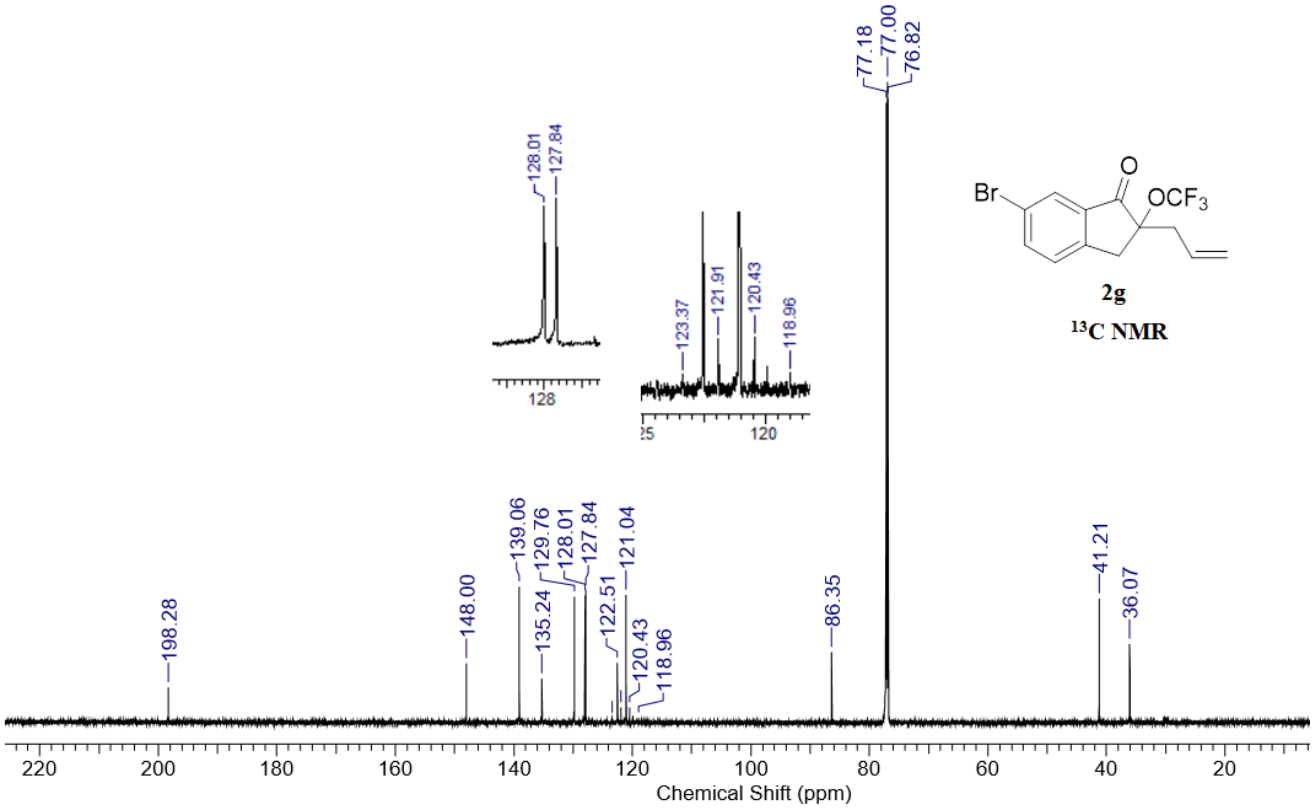

2g
1H NMR
Chemical Shift (ppm)



2g

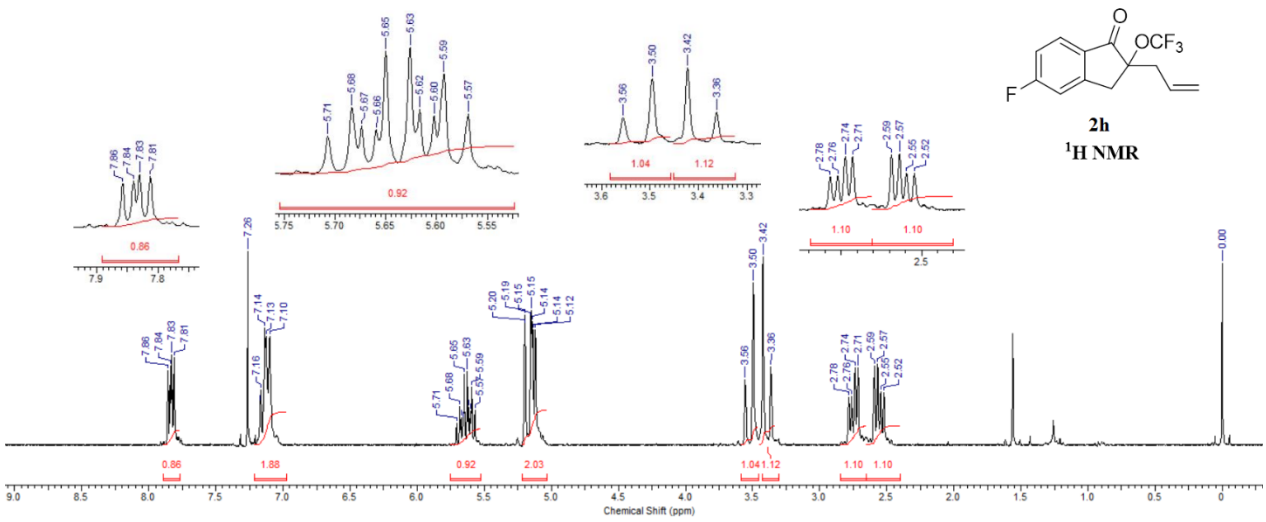
^{19}F NMR

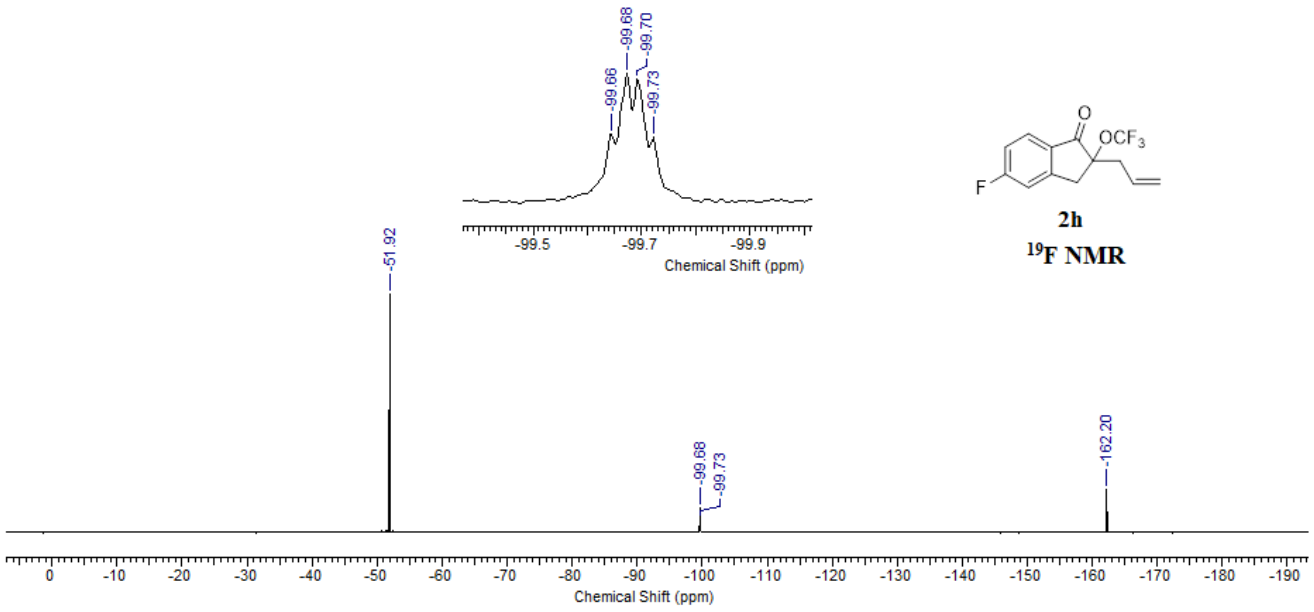


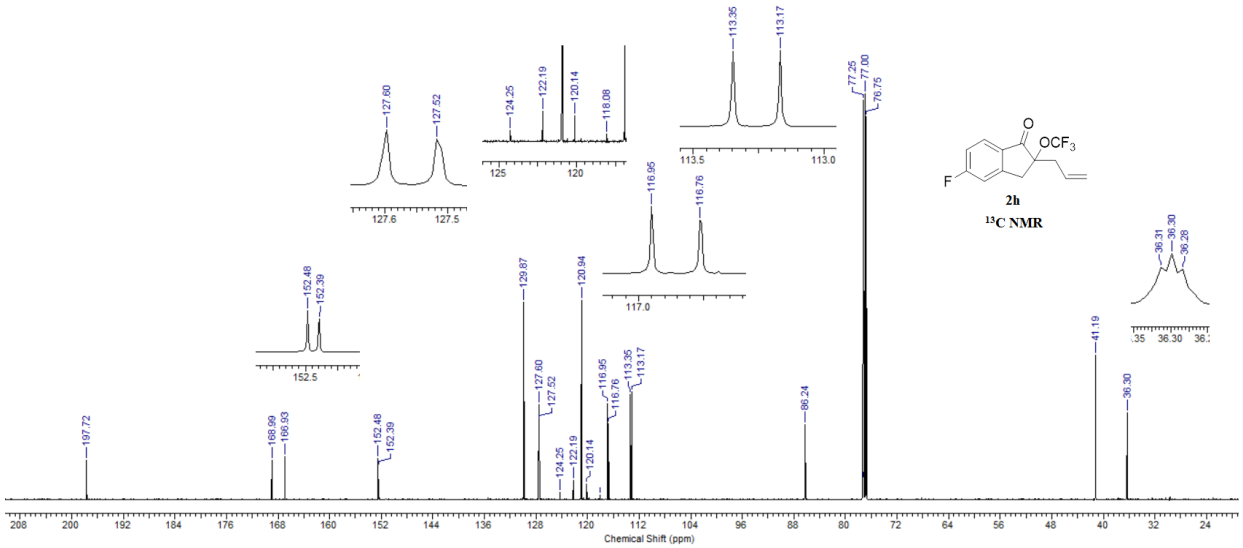


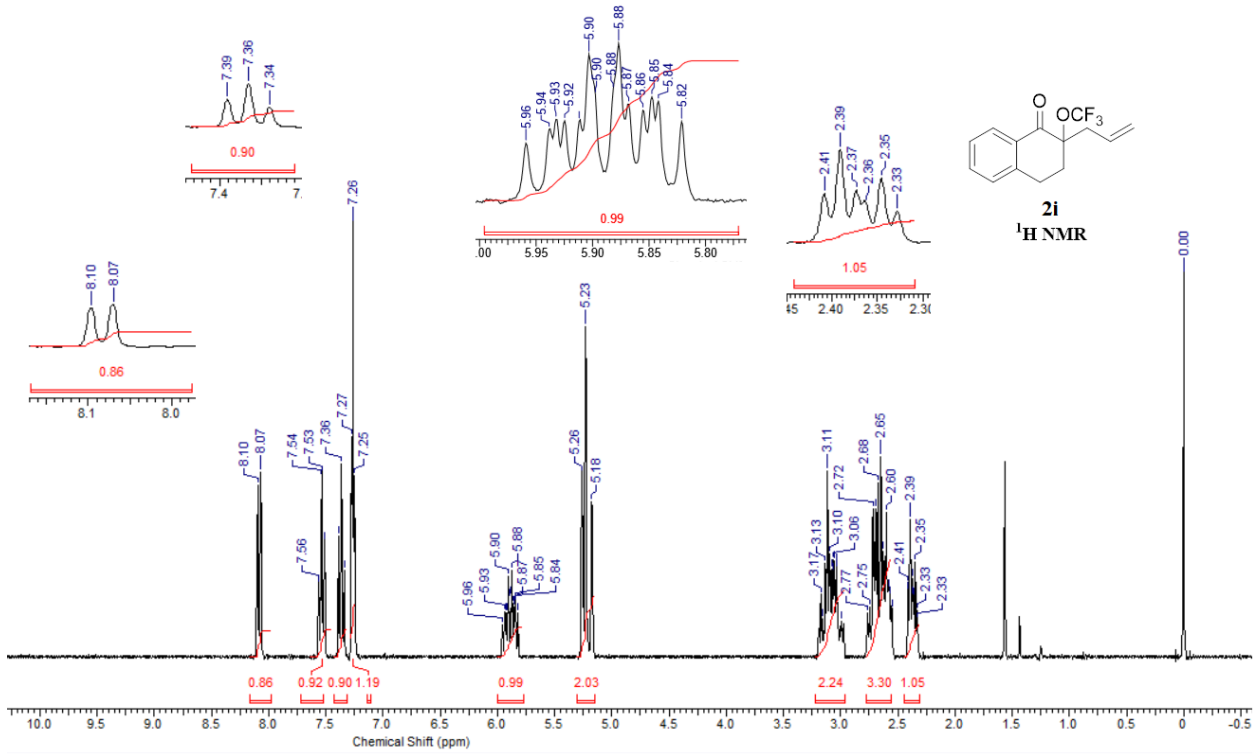
2g

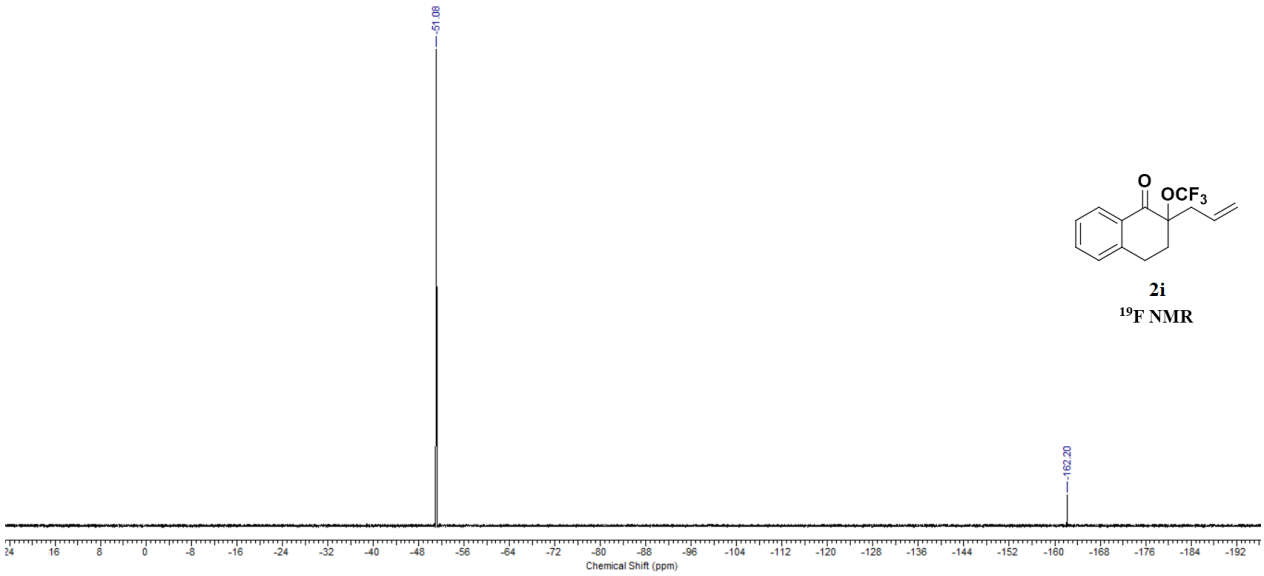
^{13}C NMR


O
OCF3
F
2h
1H NMR
Chemical Shift (ppm)


-99.66
-99.68
-99.70
-99.73
-99.5
-99.7
-99.9
Chemical Shift (ppm)
O
OCF3
F
2h
19F NMR
-51.92
-99.68
-99.73
-162.20
Chemical Shift (ppm)

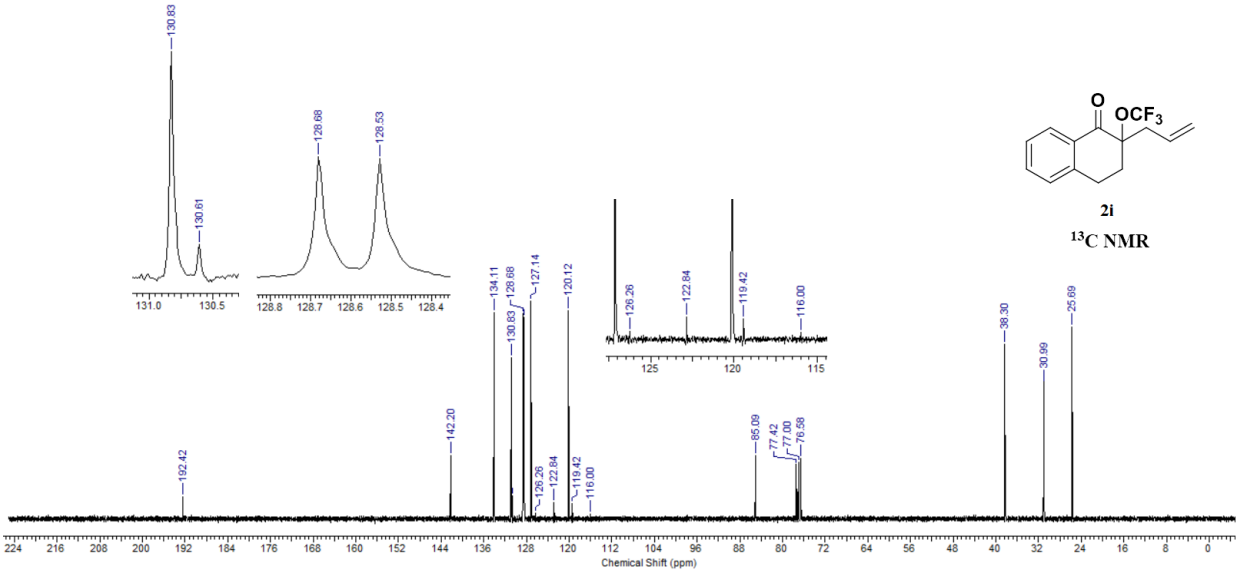

2h
13C NMR
Chemical Shift (ppm)


2i
1H NMR
Chemical Shift (ppm)



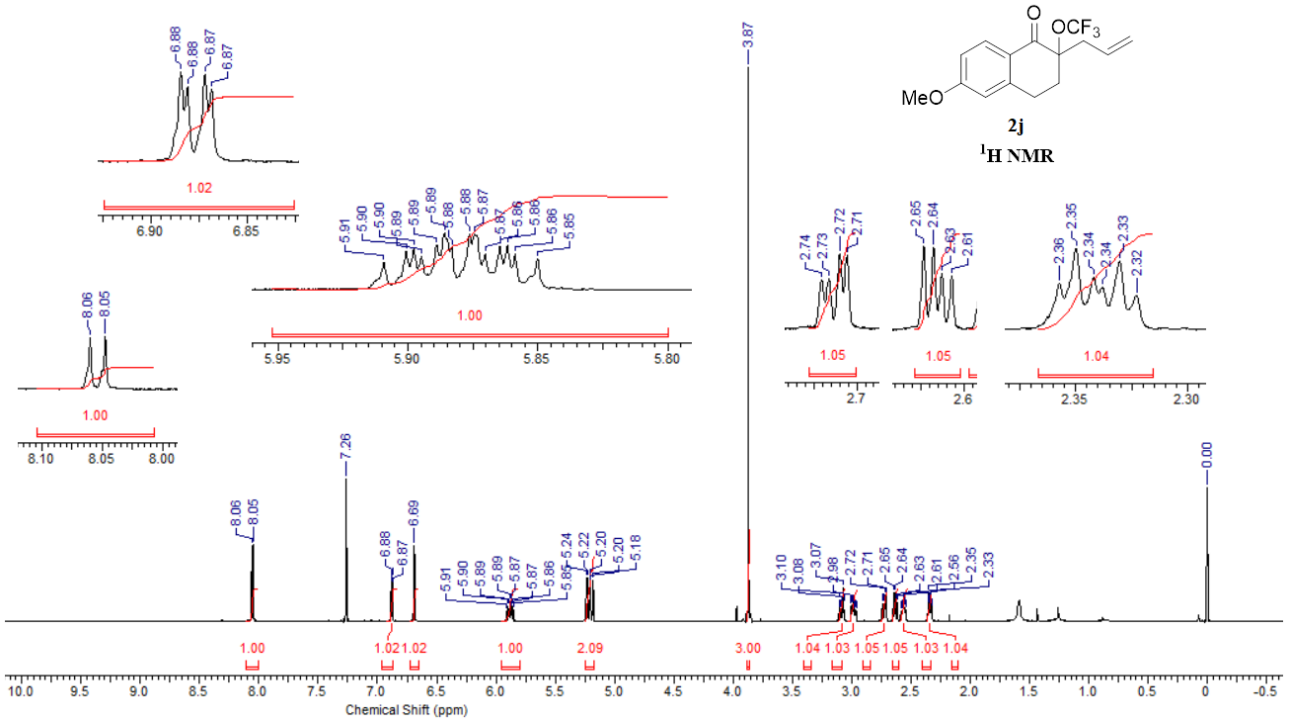
2i

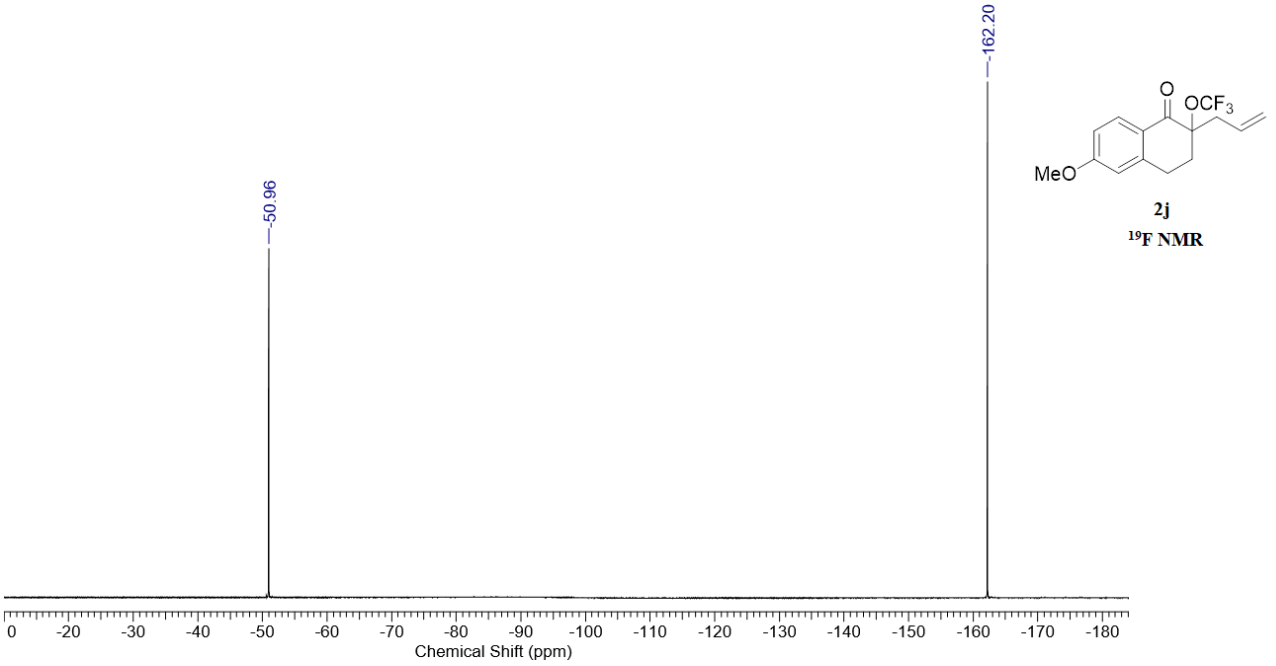
^{19}F NMR

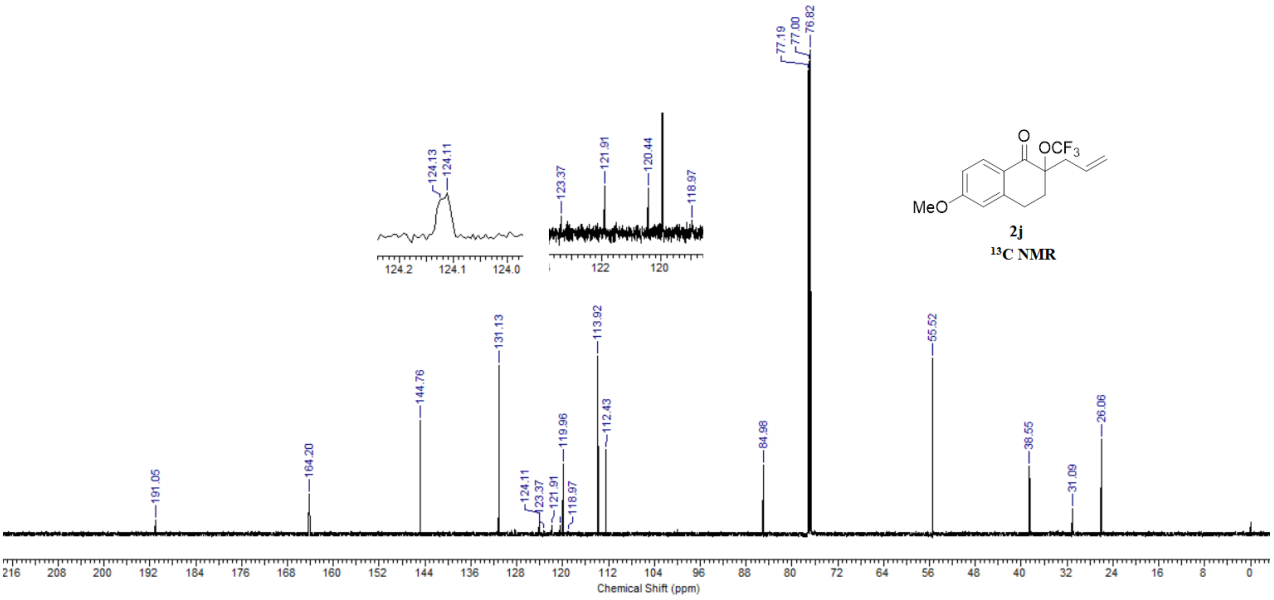


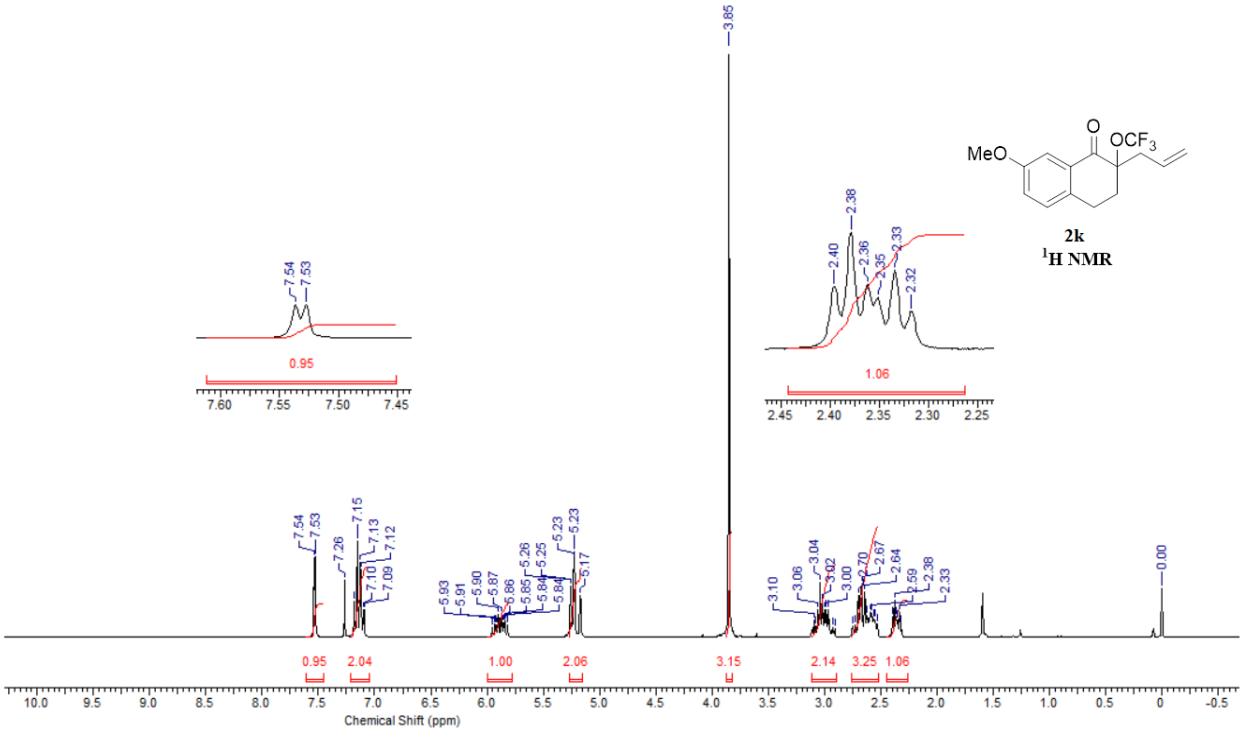
2i

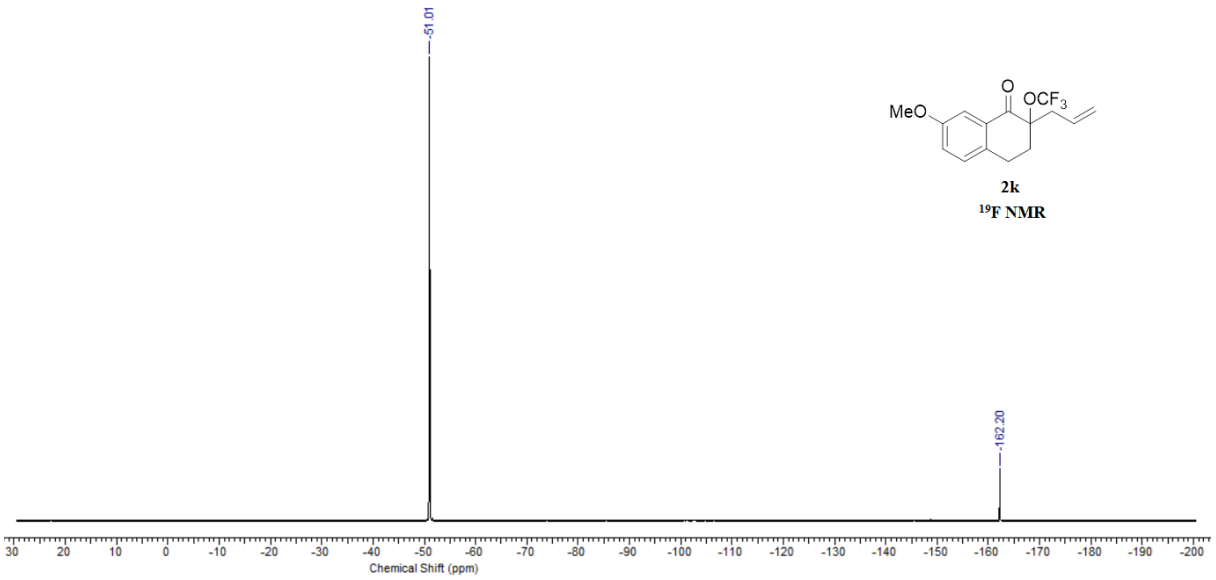
^{13}C NMR


O
OCF3
MeO
2j
1H NMR
Chemical Shift (ppm)


O
OCF3
MeO
2j
19F NMR
Chemical Shift (ppm)

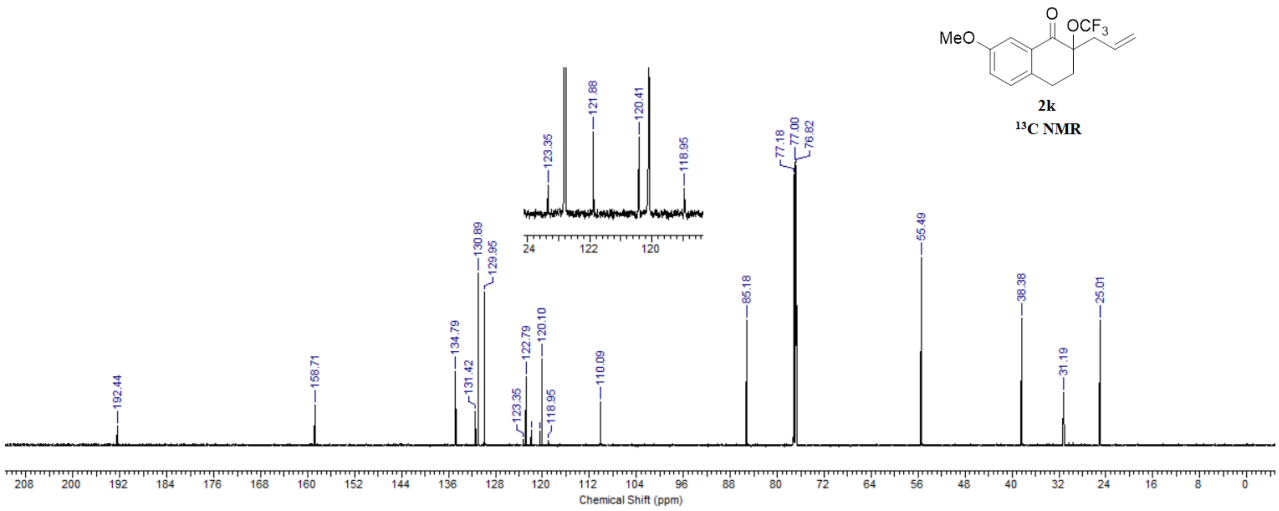

77.19
77.00
76.82
124.13
124.11
123.37
121.91
120.44
118.97
O
OCF3
MeO
2j
13C NMR
131.13
113.92
55.52
144.76
119.96
112.43
84.98
38.55
26.06
164.20
124.11
123.37
121.91
118.97
31.09
191.05
Chemical Shift (ppm)


3.85
O
OCF3
MeO
2k
1H NMR
2.38
2.40
2.36
2.35
2.33
2.32
7.54
7.53
0.95
1.06
7.26
7.15
7.13
7.12
7.10
7.09
5.93
5.91
5.90
5.87
5.86
5.26
5.25
5.23
5.17
3.10
3.06
3.04
3.02
3.00
2.70
2.67
2.64
2.59
2.38
2.33
0.00
0.95
2.04
1.00
2.06
3.15
2.14
3.25
1.06
Chemical Shift (ppm)



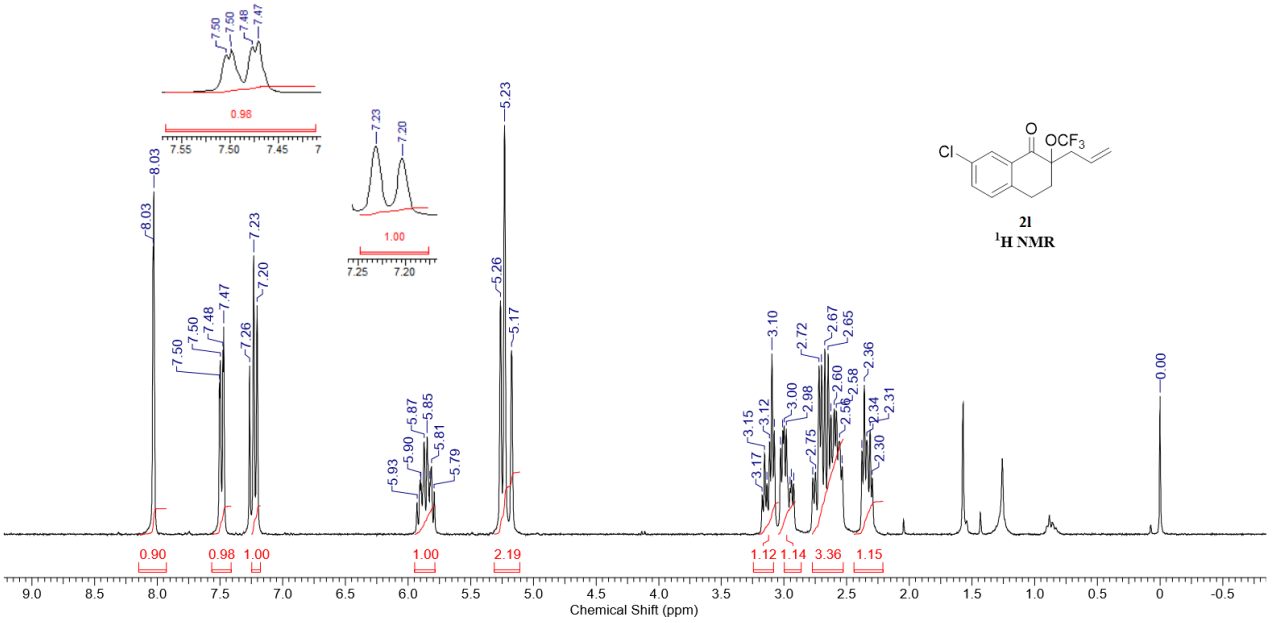
2k

^{19}F NMR



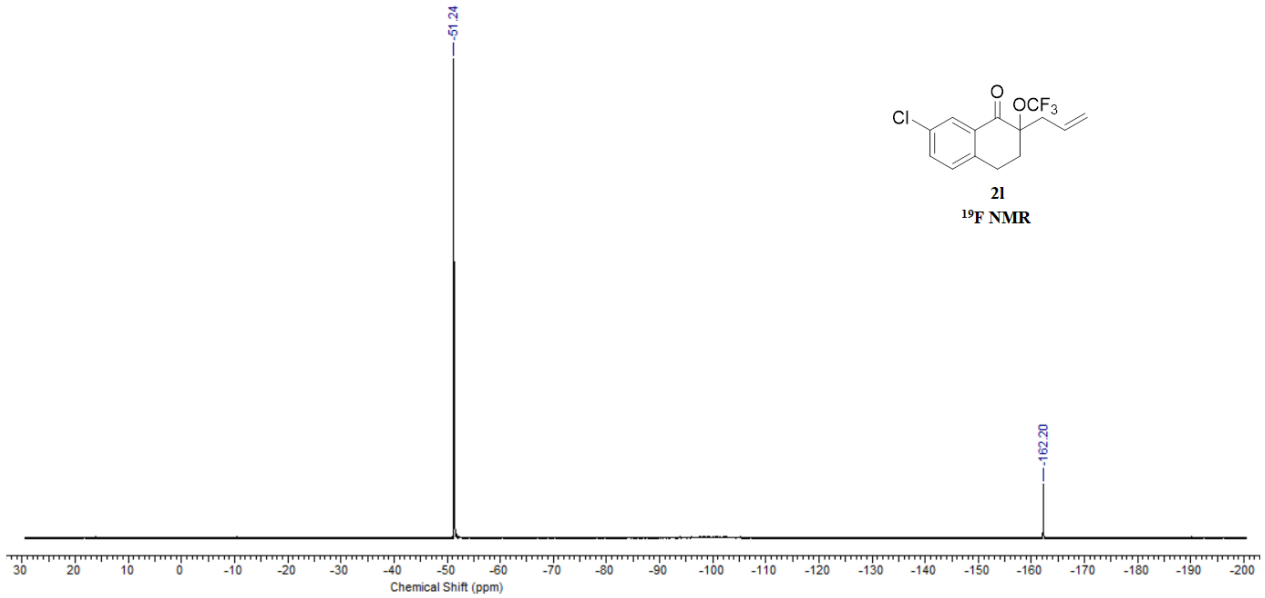
2k

^{13}C NMR



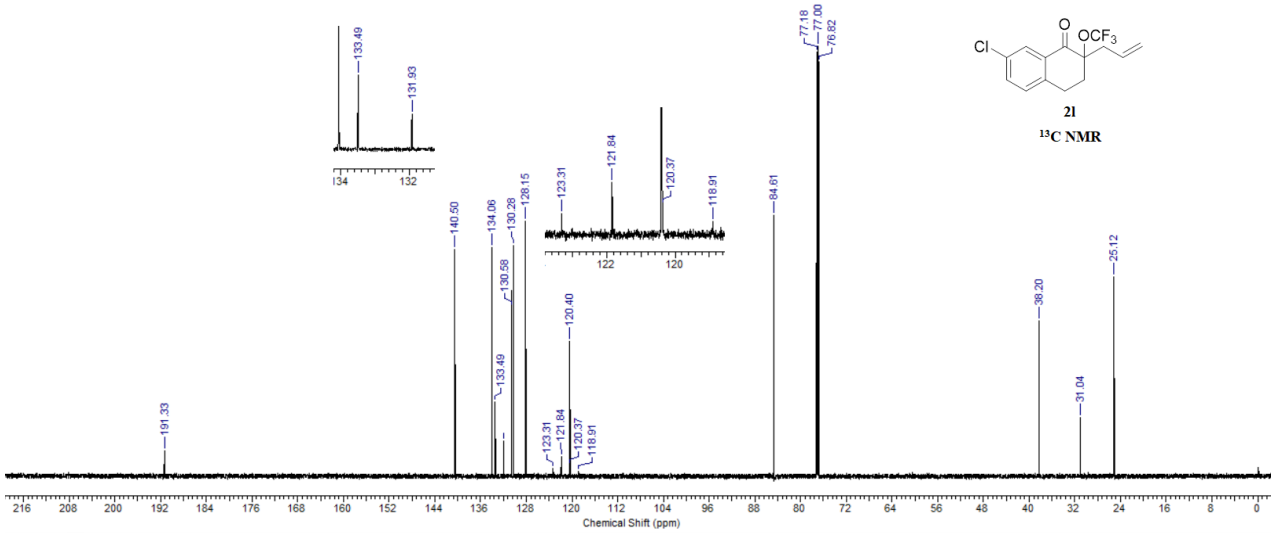
2l

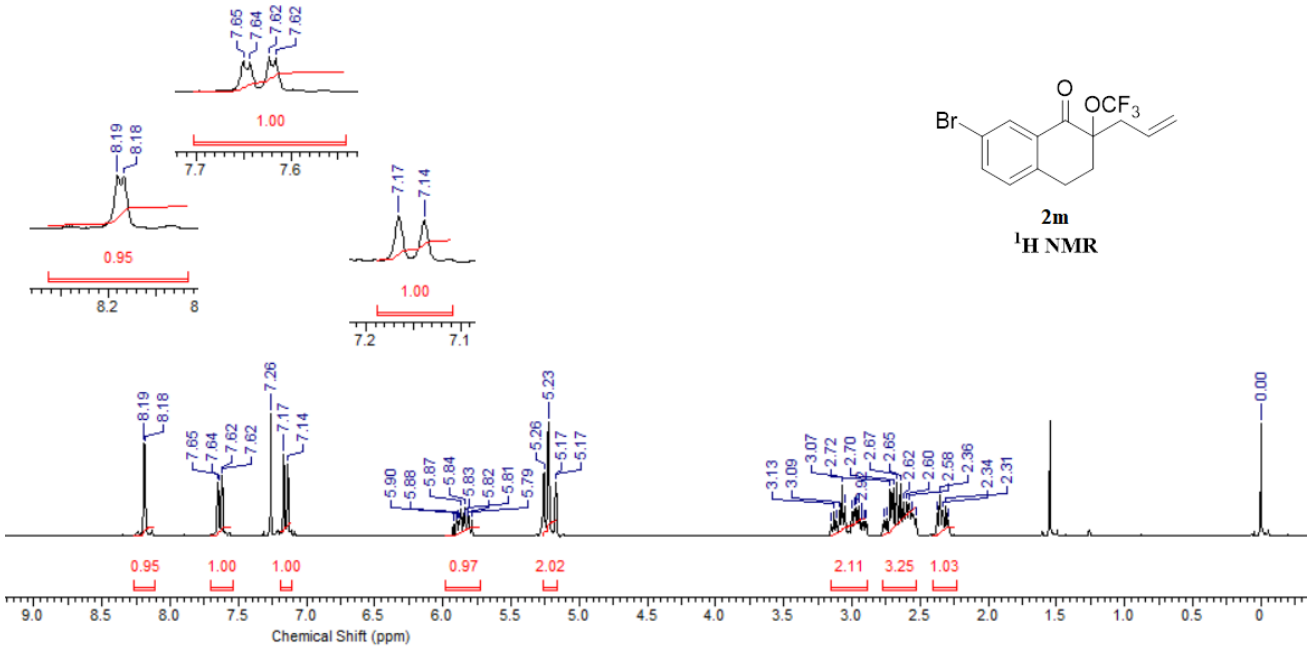
^{1}H NMR

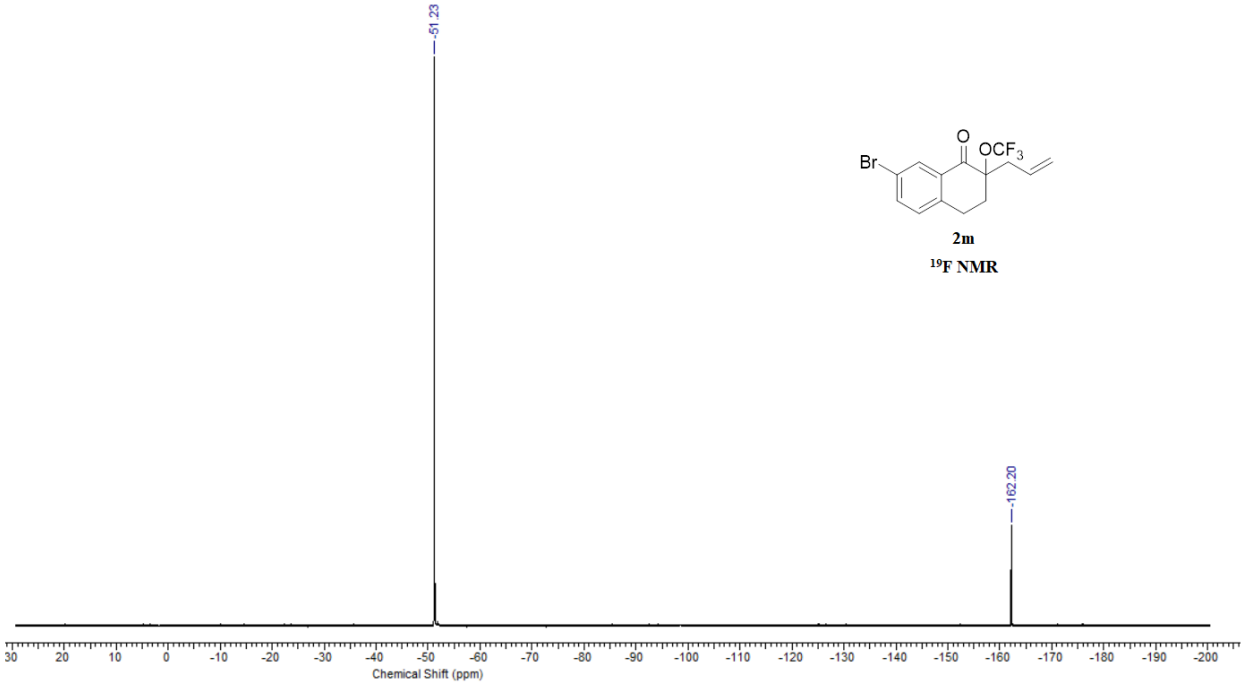


2l

^{19}F NMR

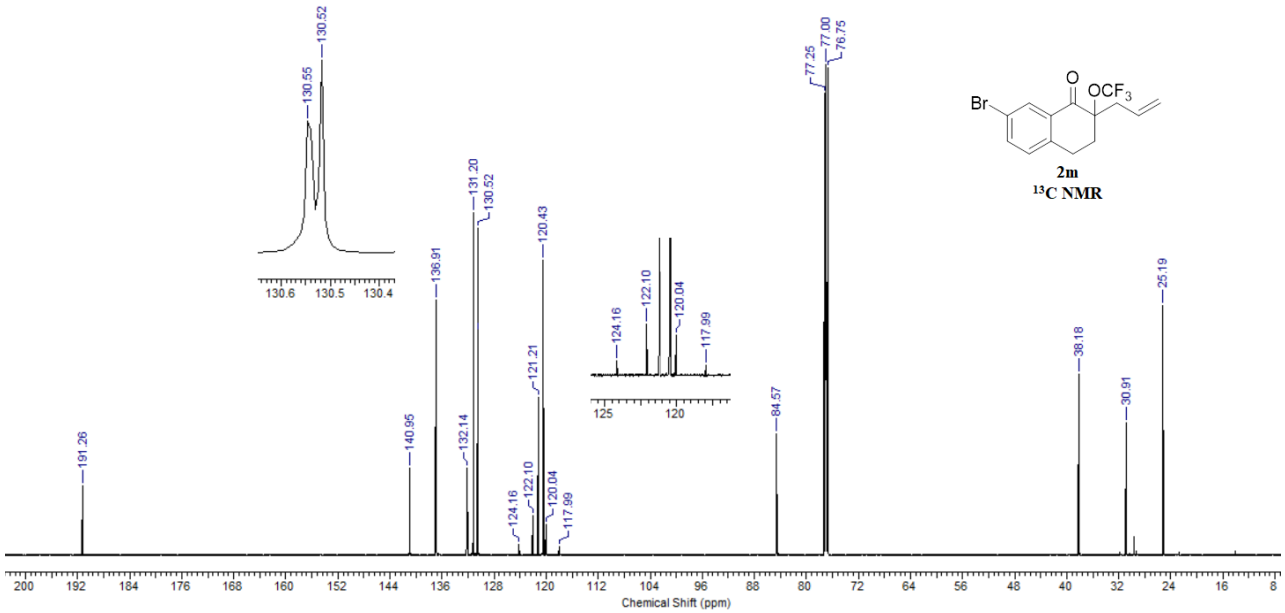

Cl
O
OCF3
2l
13C NMR
Chemical Shift (ppm)


Br
O
OCF3
2m
1H NMR
Chemical Shift (ppm)



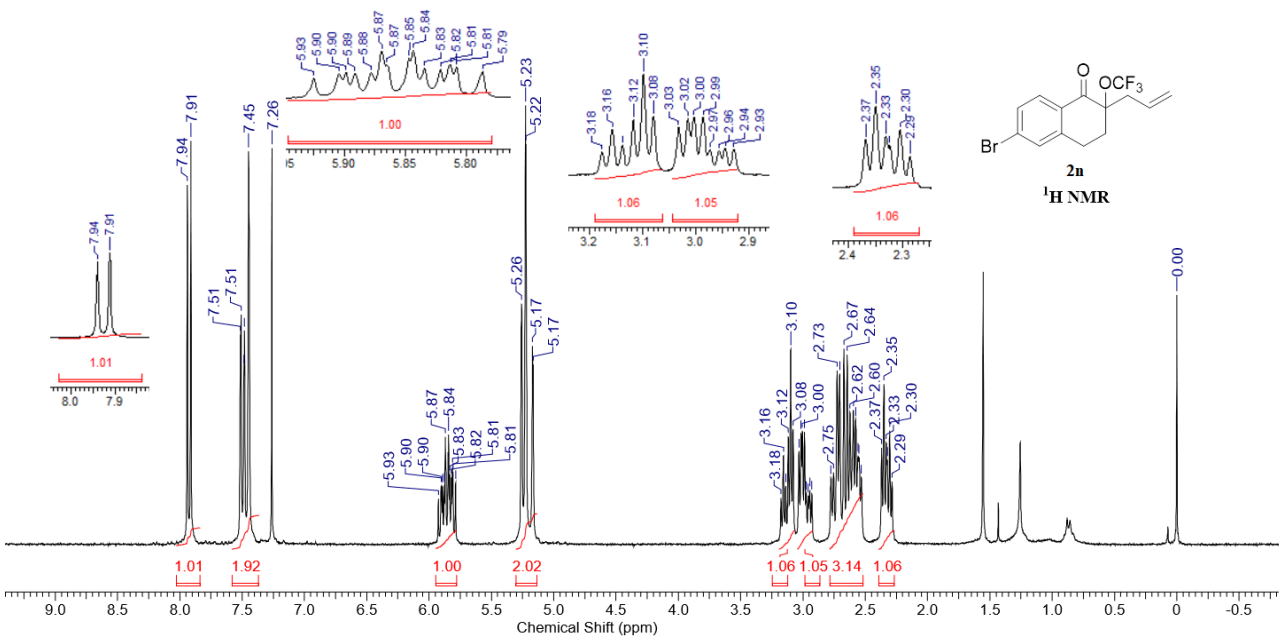
2m

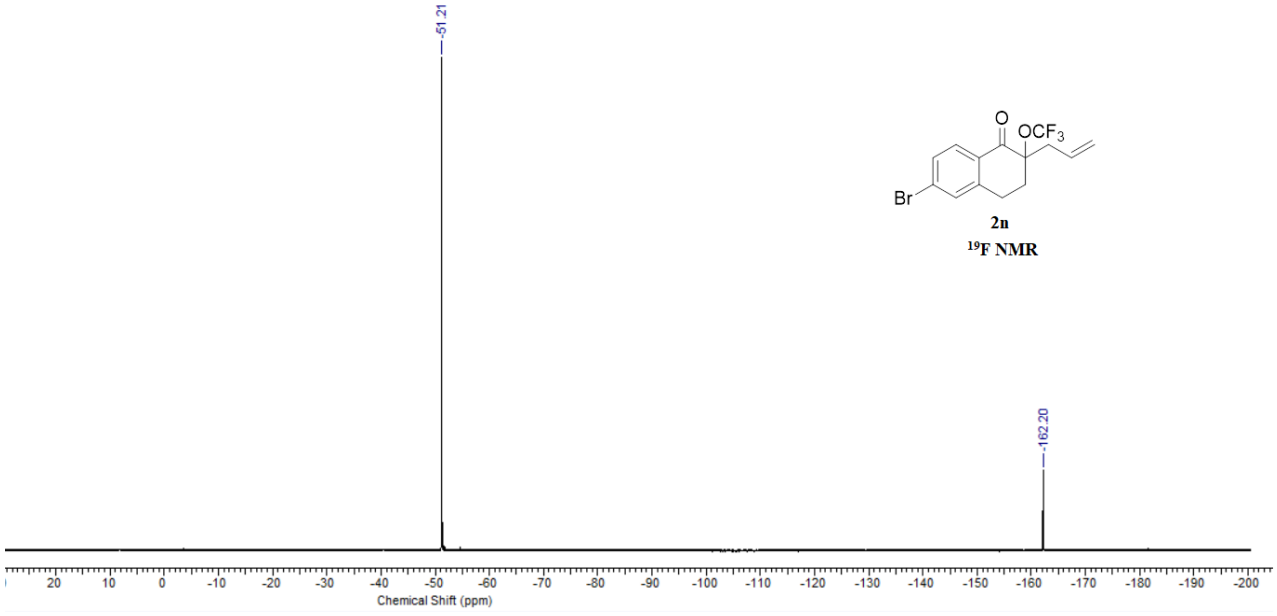
^{19}F NMR

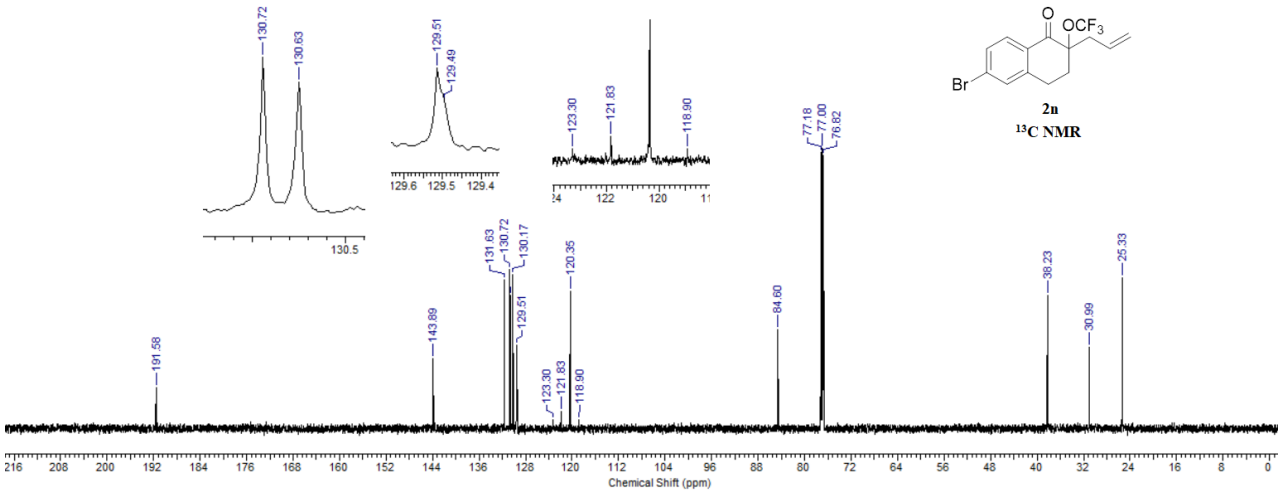


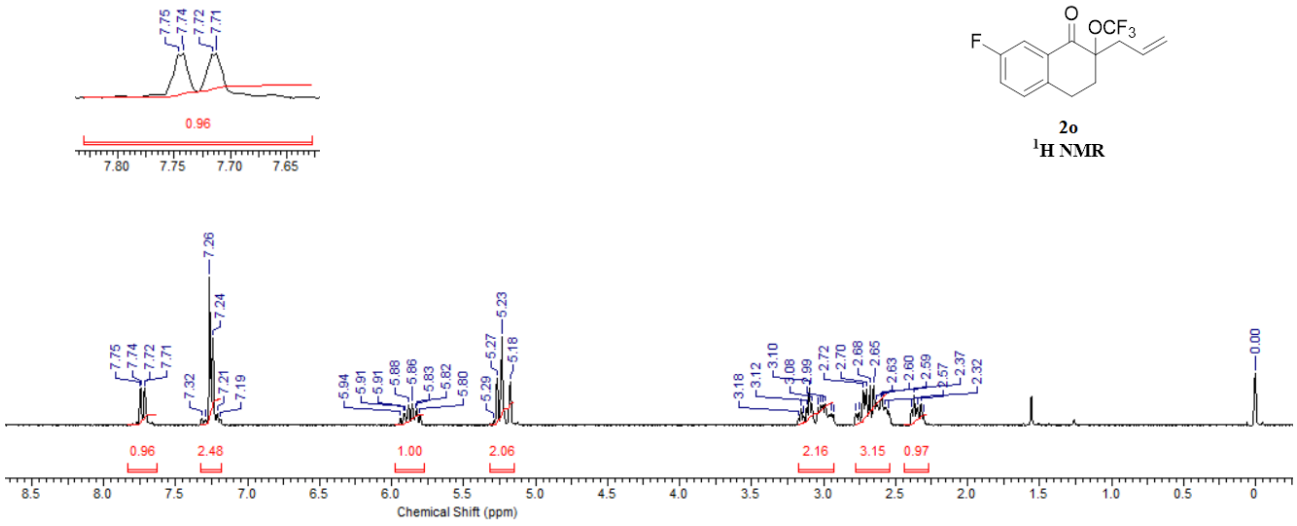
2m

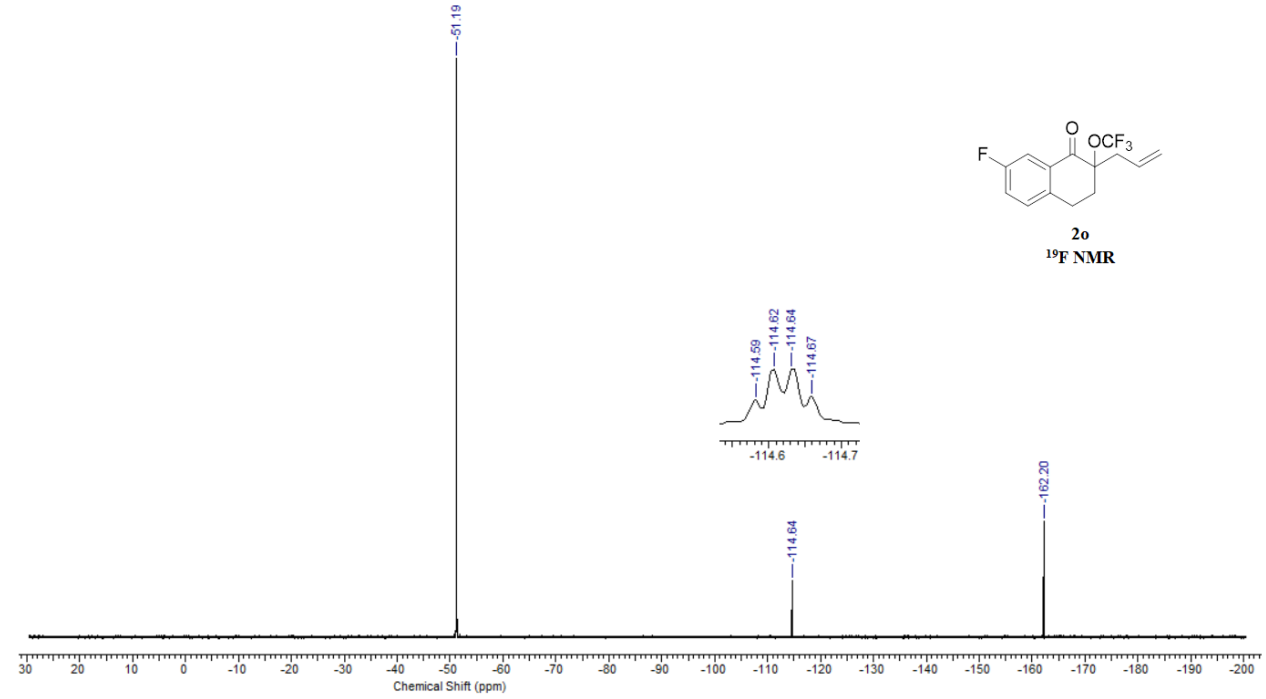
^{13}C NMR


Br
O
OCF3
2n
1H NMR
Chemical Shift (ppm)


Br
O
OCF3
2n
19F NMR
-51.21
-162.20
Chemical Shift (ppm)

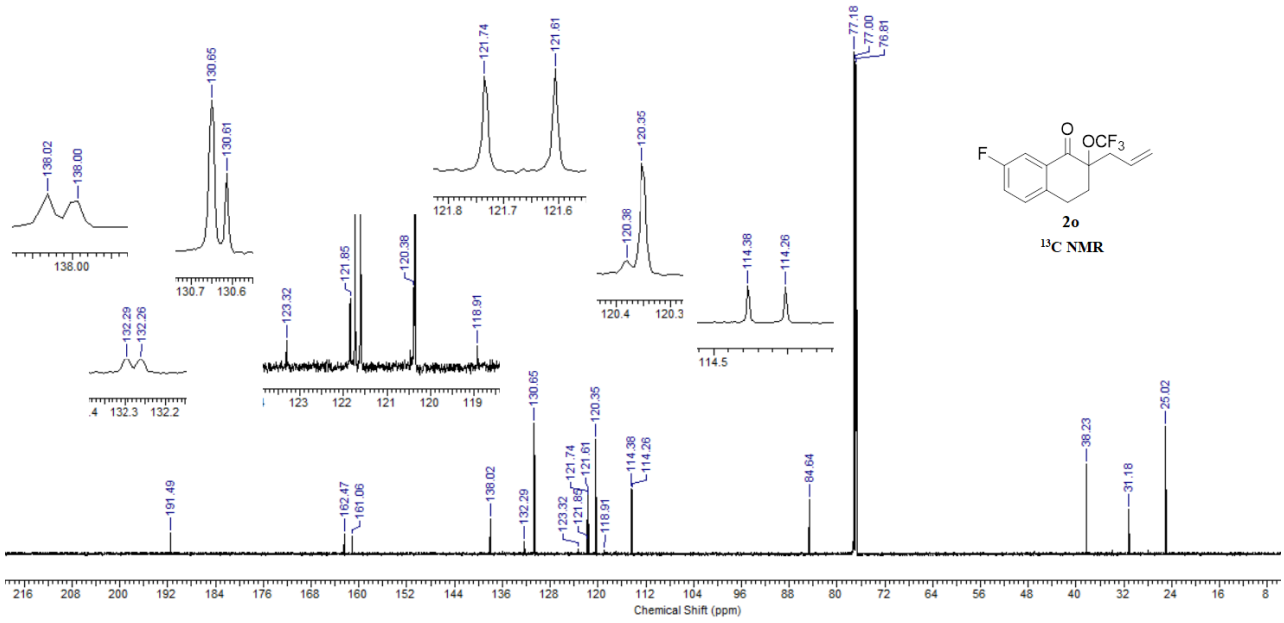

O
OCF3
Br
2n
13C NMR
Chemical Shift (ppm)


O
OCF3
F
2o
1H NMR
0.96
2.48
1.00
2.06
2.16
3.15
0.97
Chemical Shift (ppm)



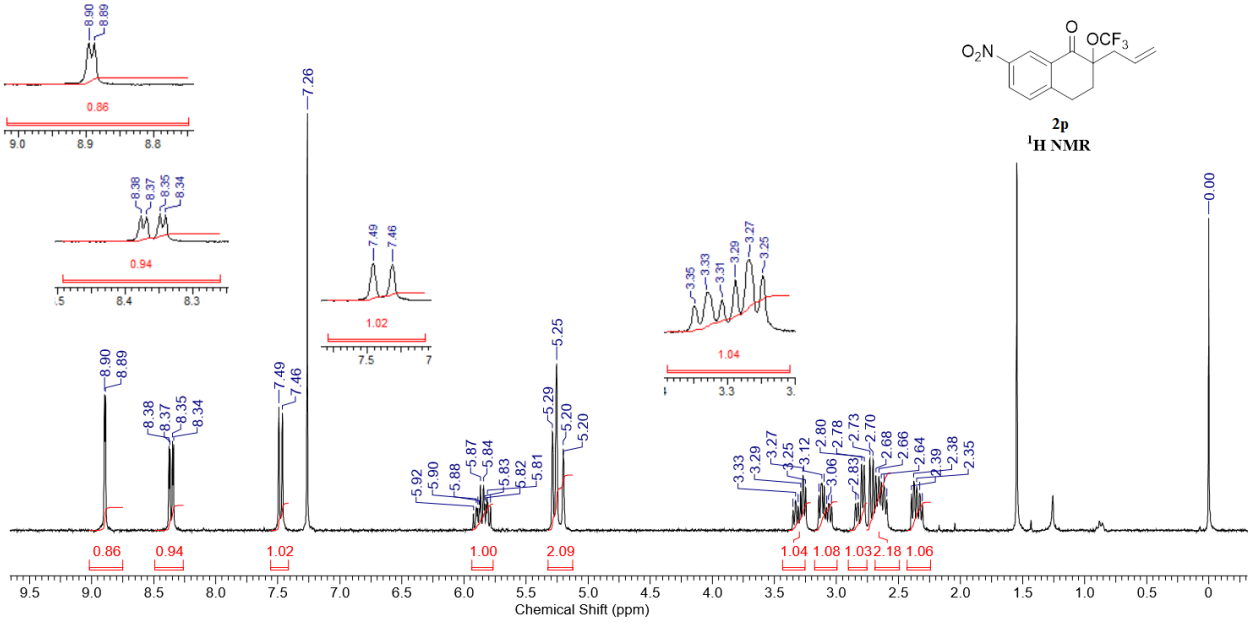
2o

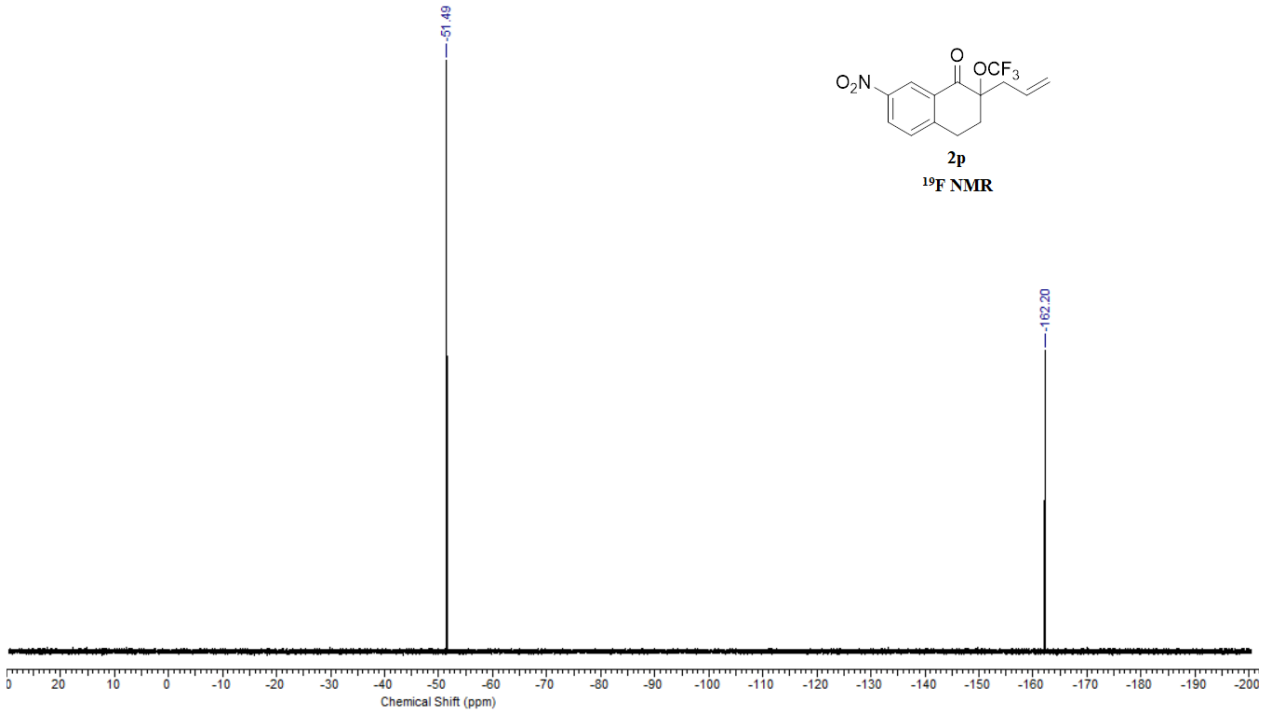
^{19}F NMR

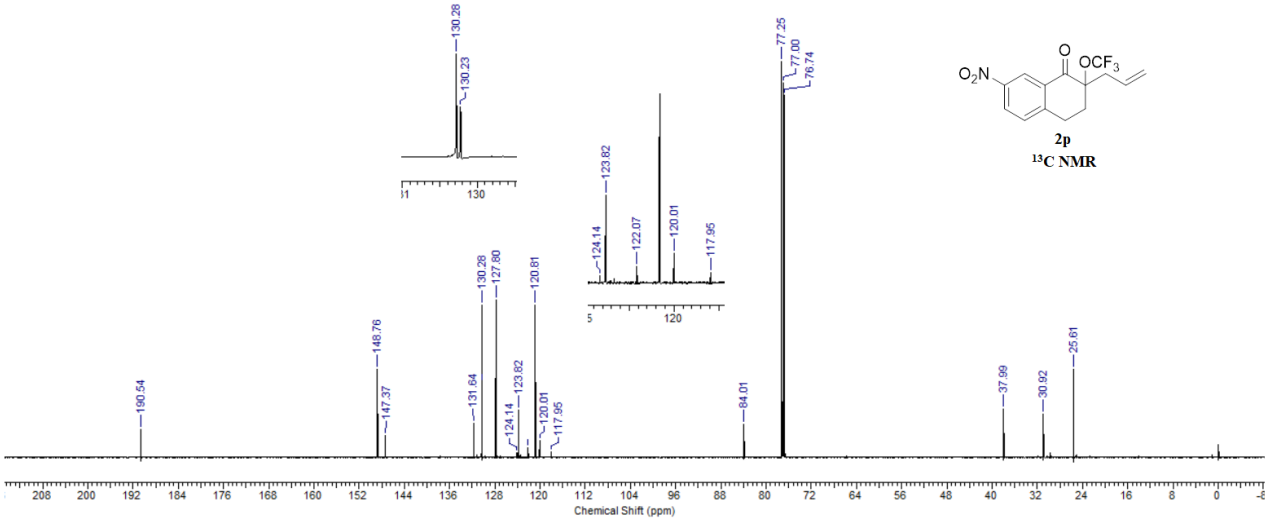


2o

^{13}C NMR

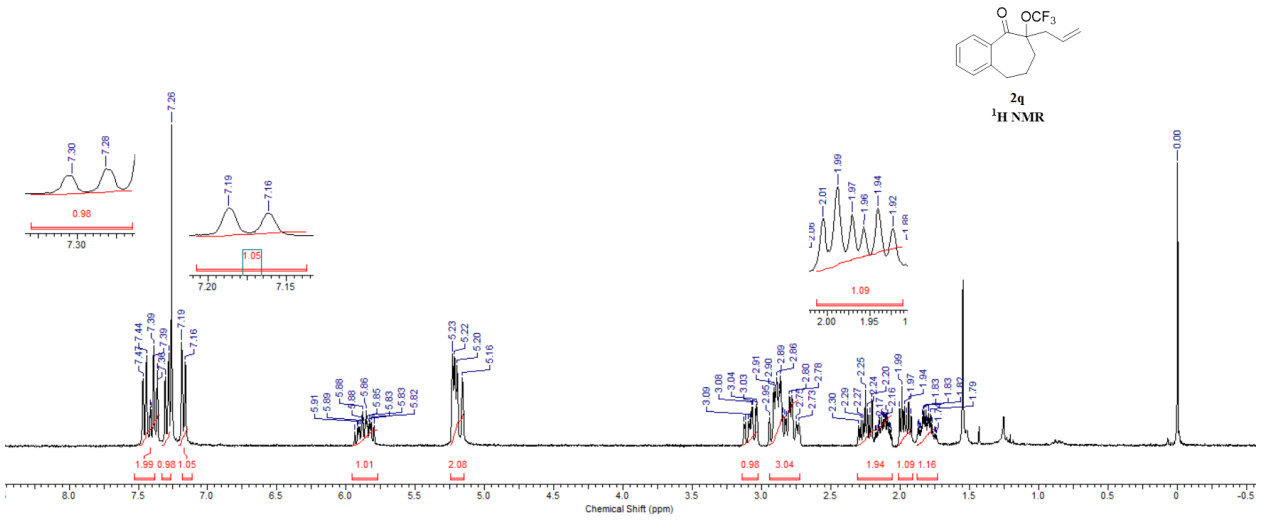

O2N
O
OCF3
2p
1H NMR
Chemical Shift (ppm)


O2N
O
OCF3
2p
19F NMR
Chemical Shift (ppm)



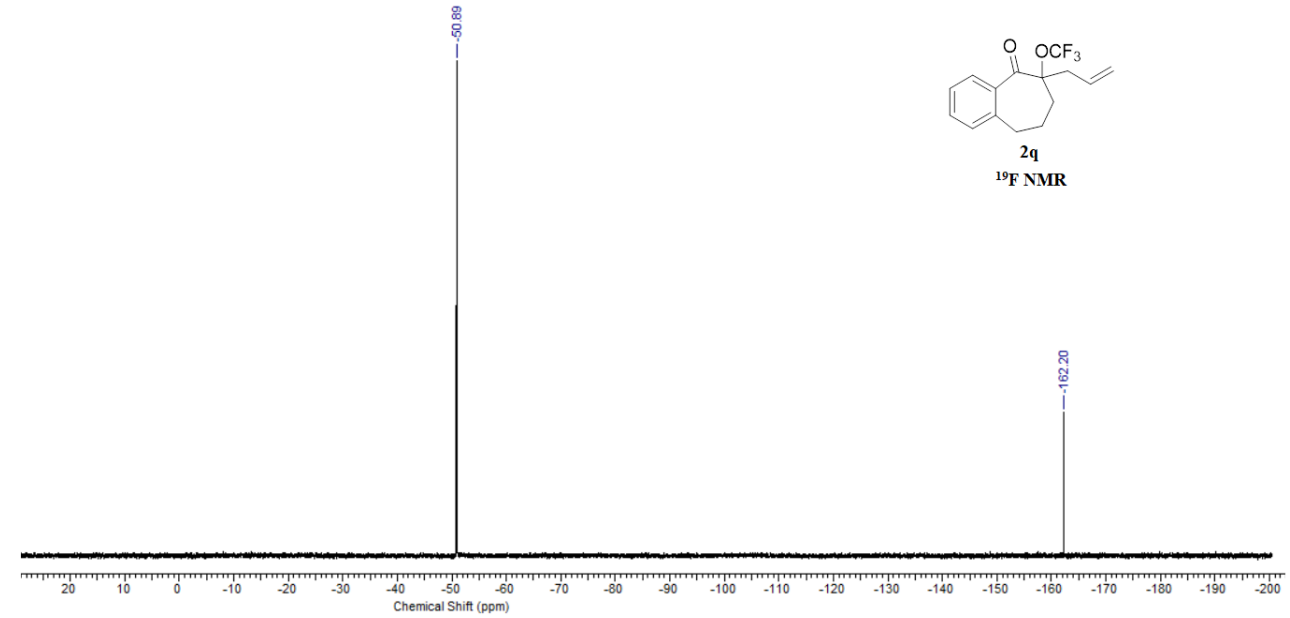
2p

^{13}C NMR



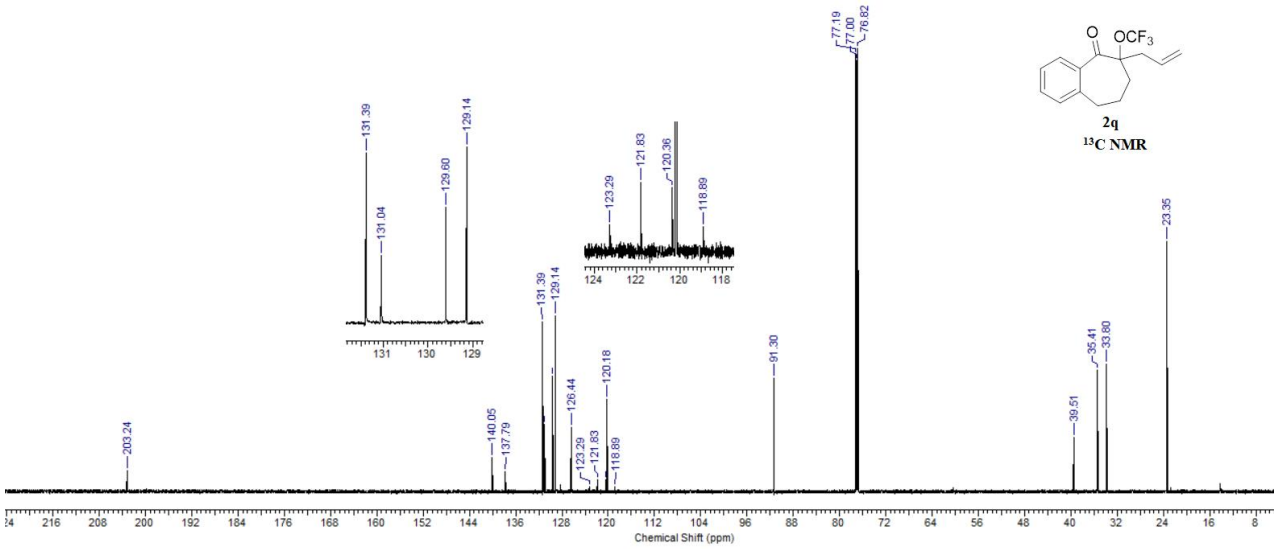
2q

^{1}H NMR



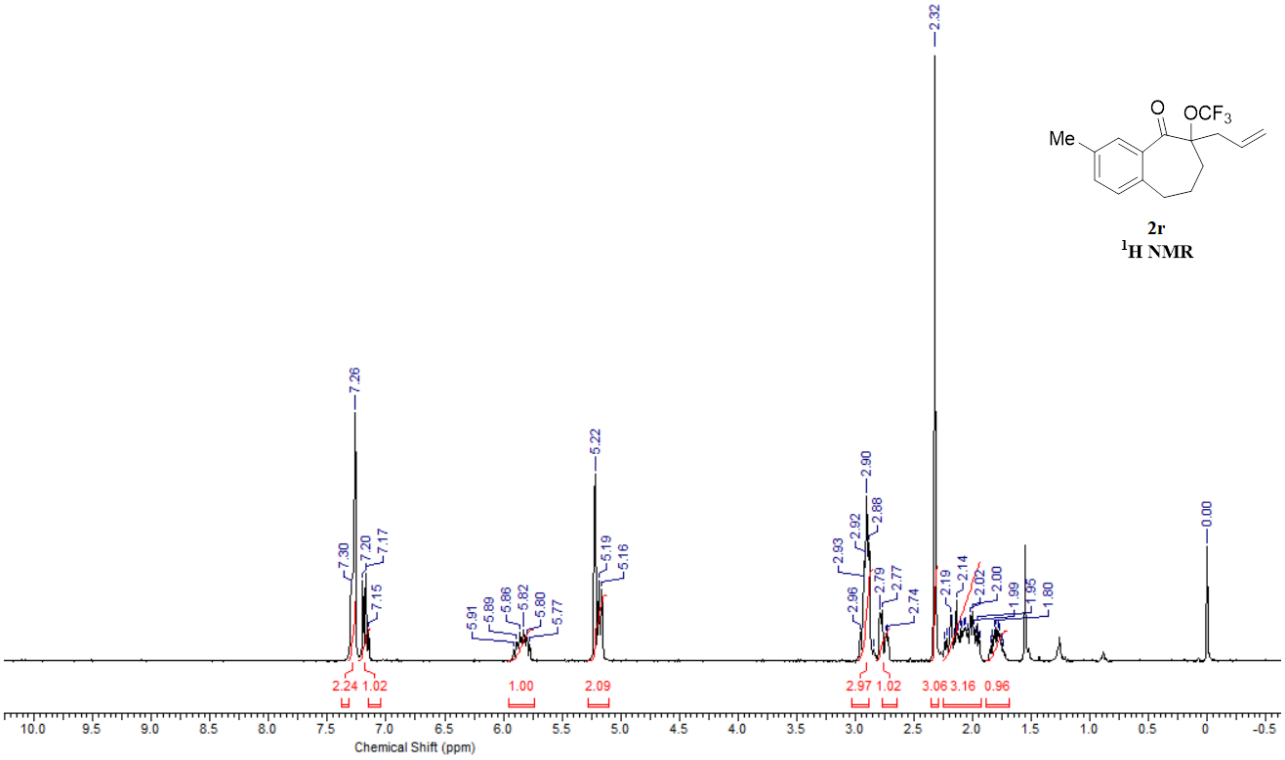
2q

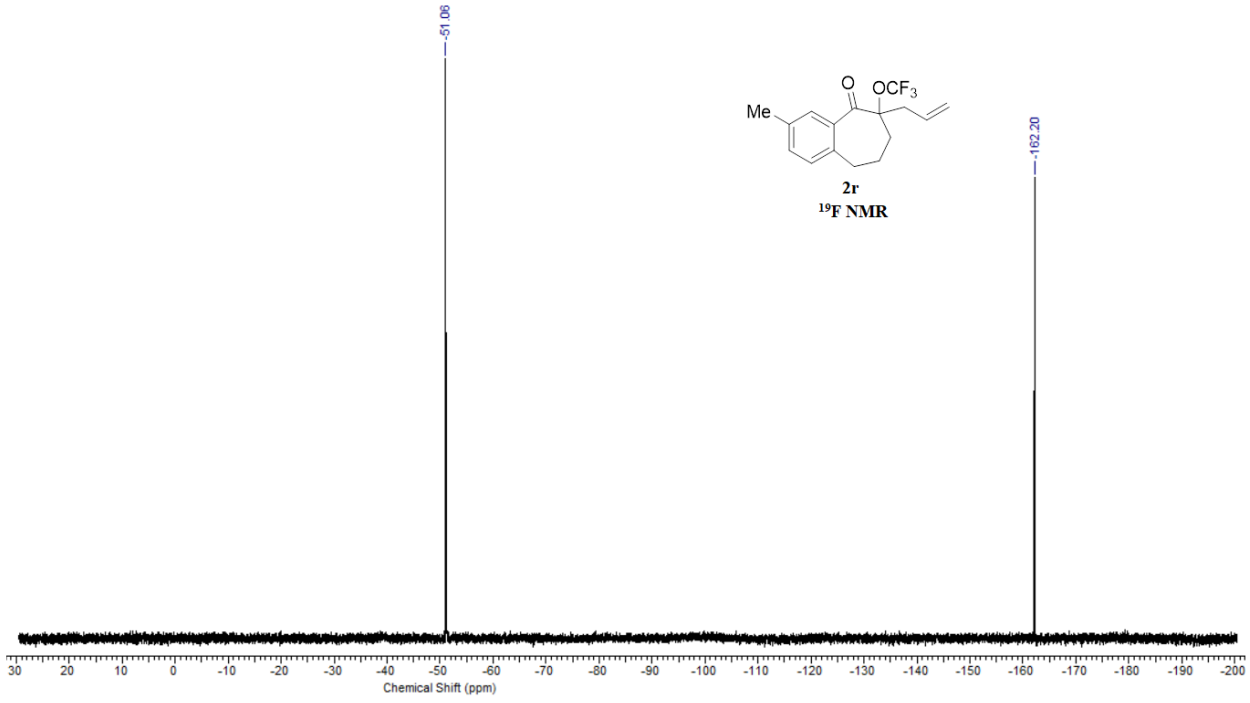
^{19}F NMR

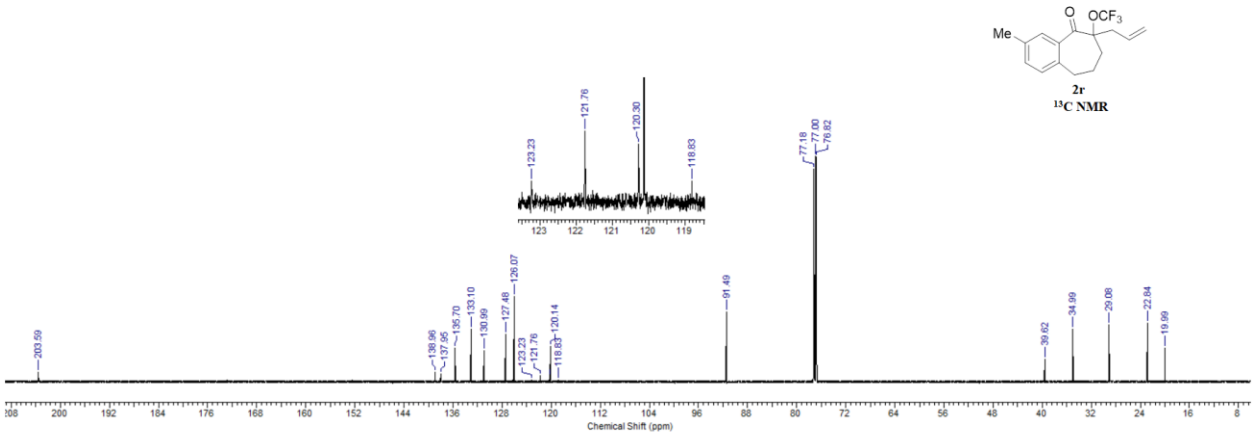


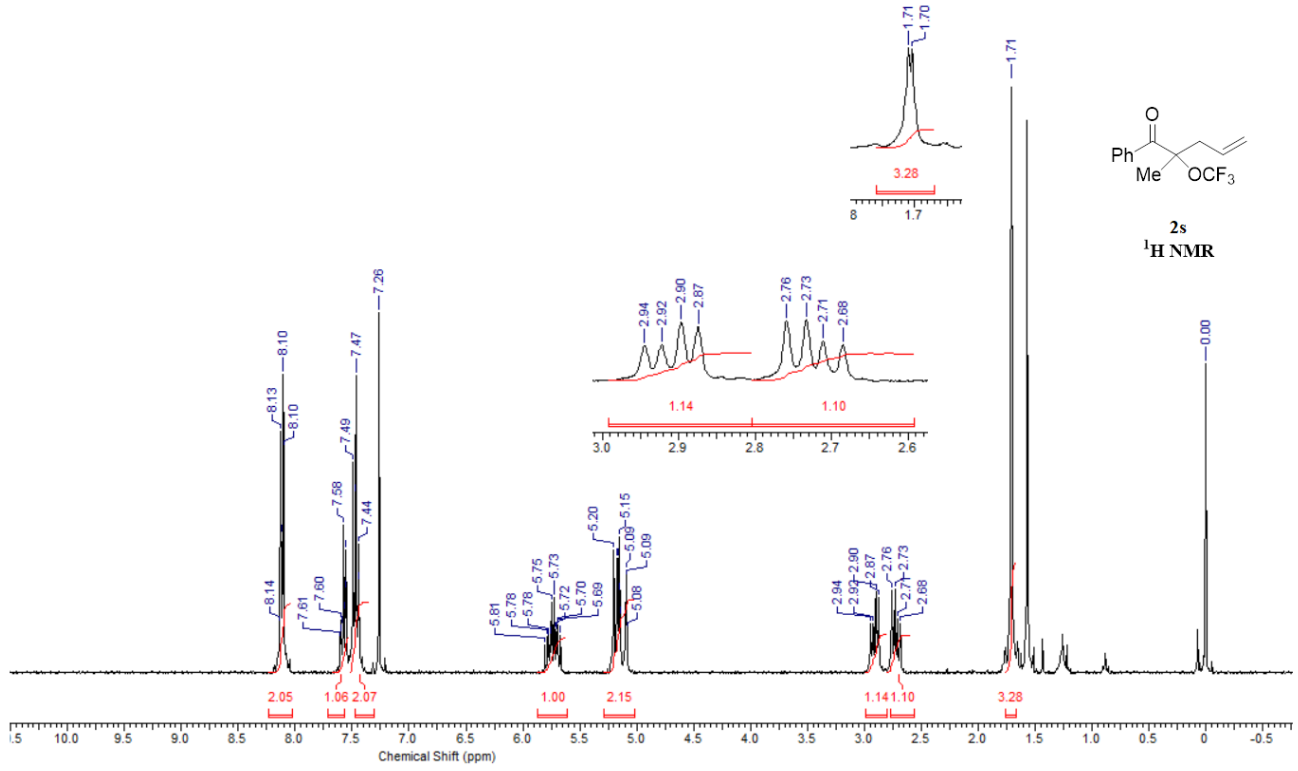
2q

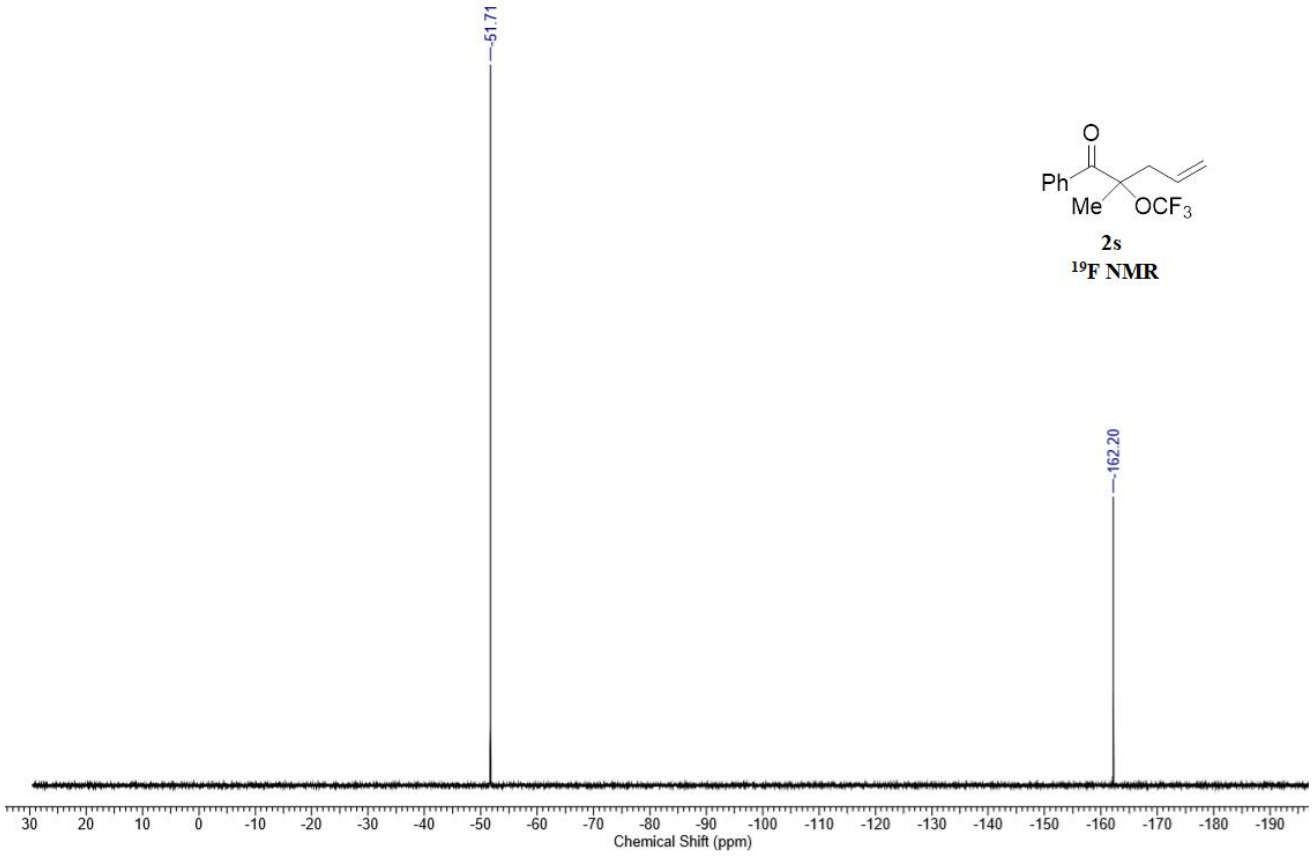
^{13}C NMR


Me
O
OCF3
2r
1H NMR
Chemical Shift (ppm)


Me
O
OCF3
2r
19F NMR
Chemical Shift (ppm)

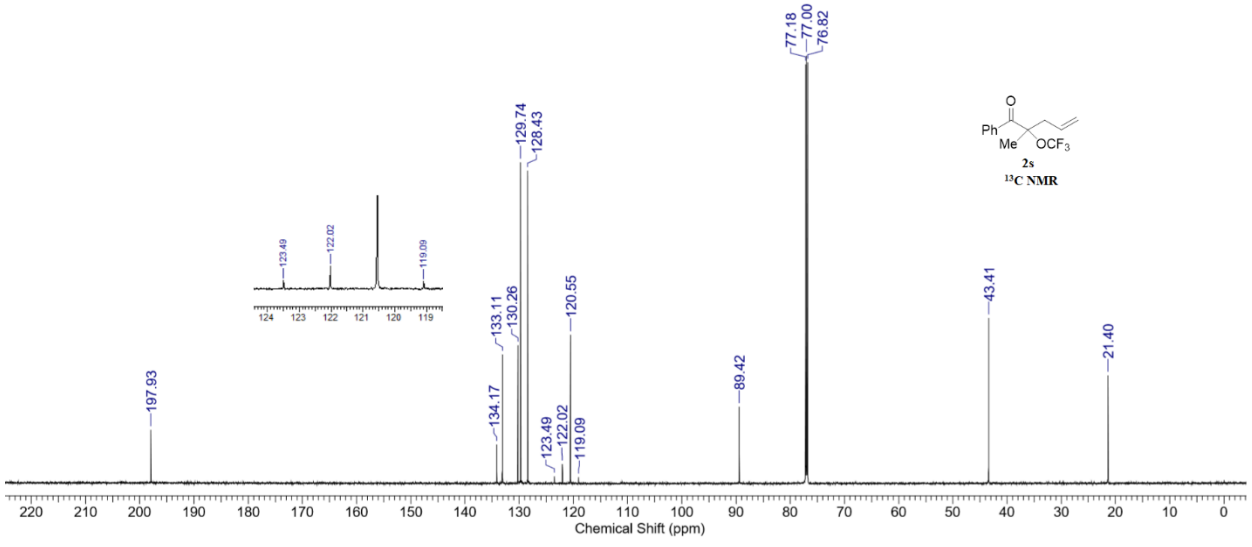

Me
O
OCF3
2r
13C NMR
Chemical Shift (ppm)


Ph
Me
O
OCF3
2s
1H NMR
Chemical Shift (ppm)



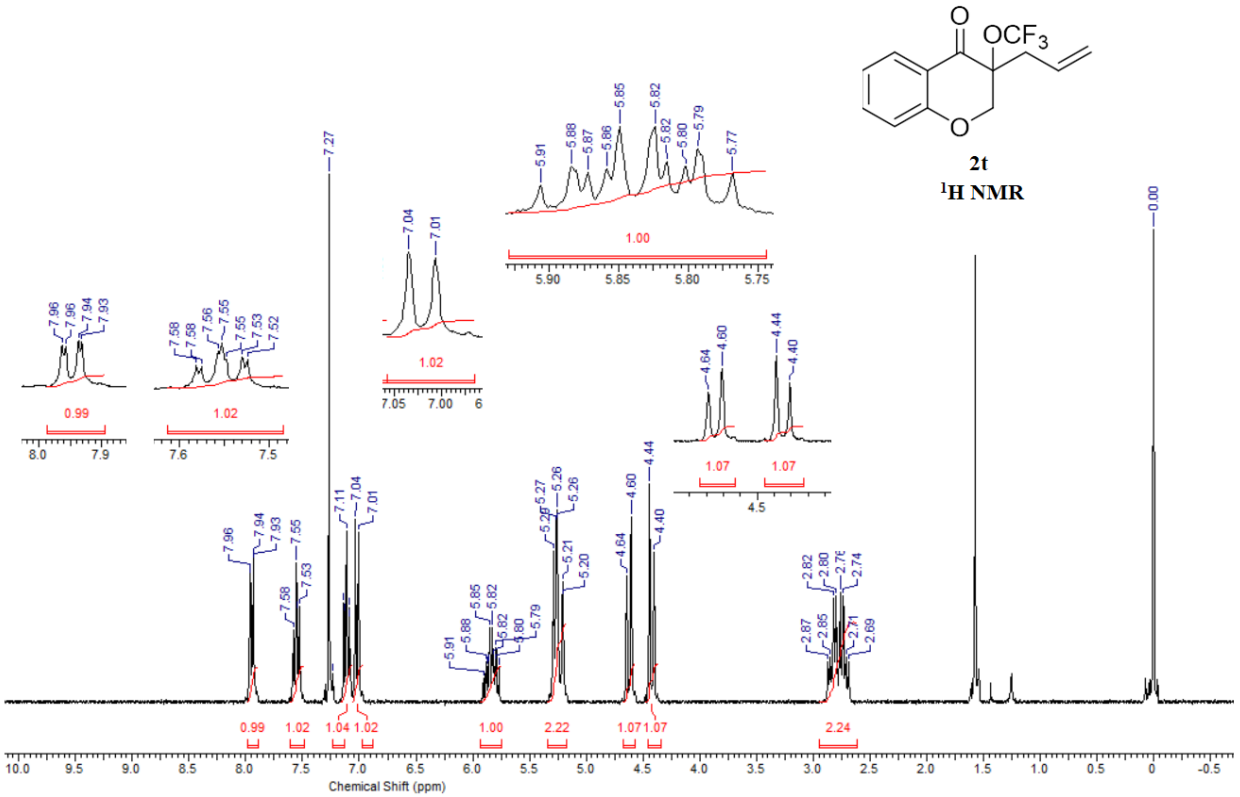
2s

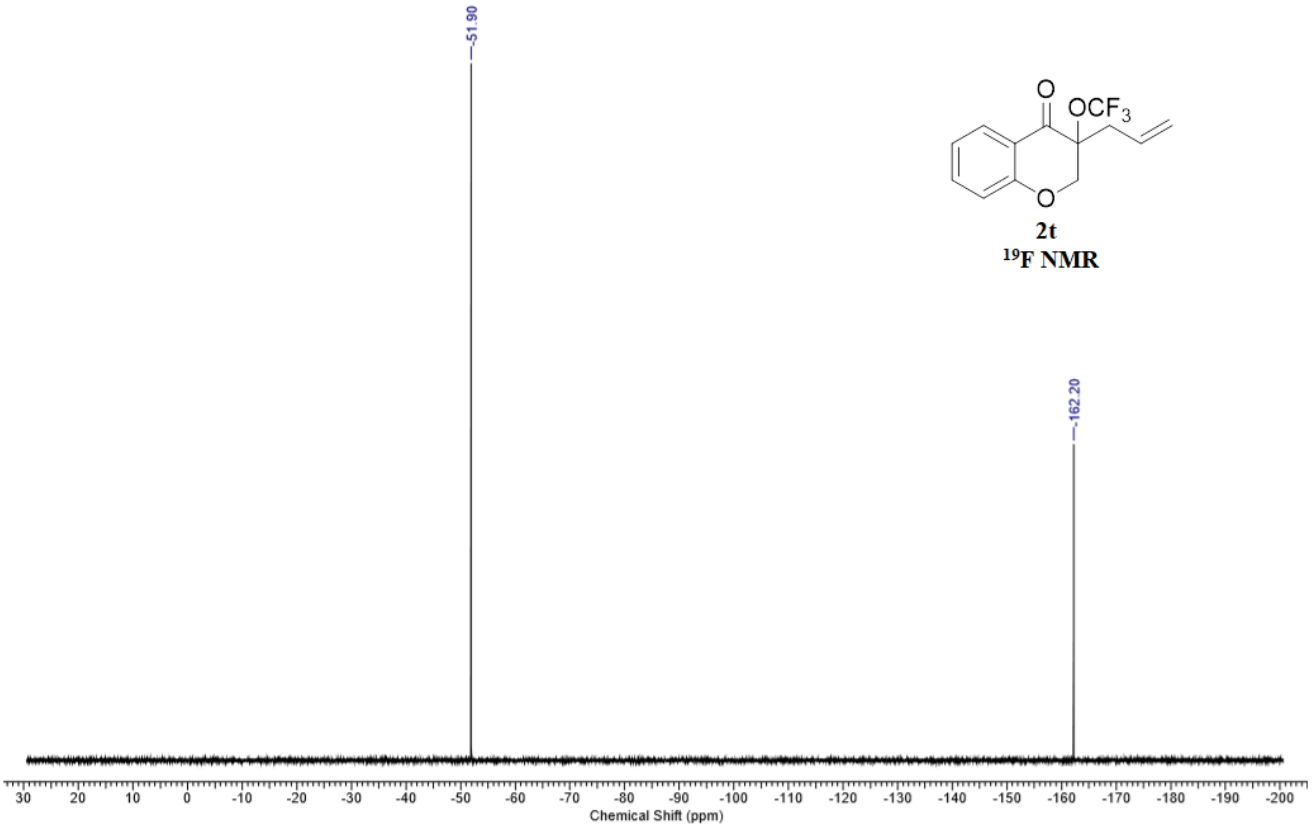
^{19}F NMR

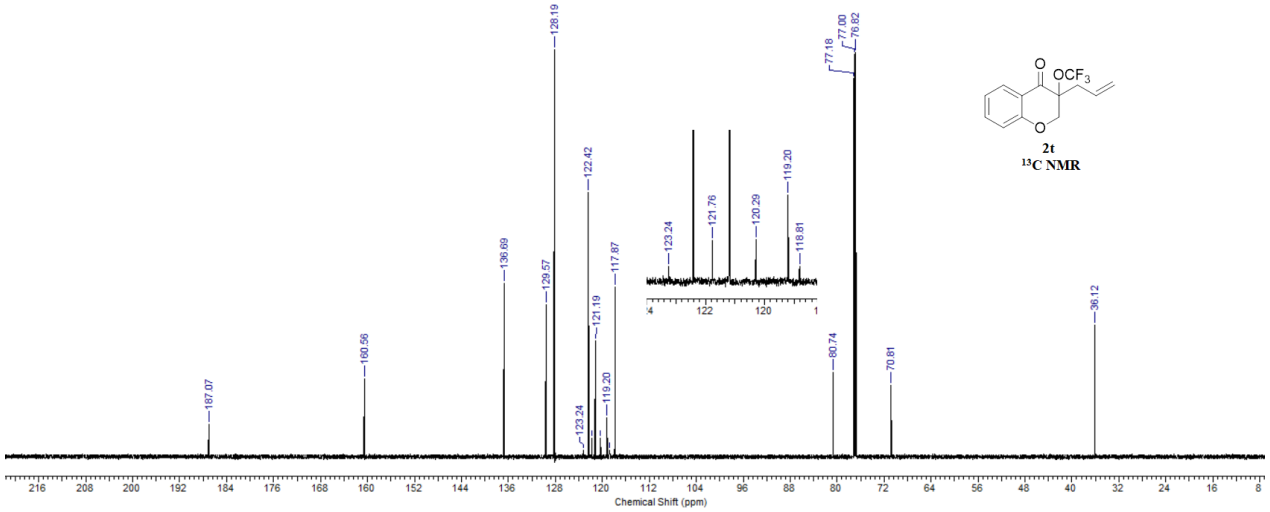


2s

^{13}C NMR

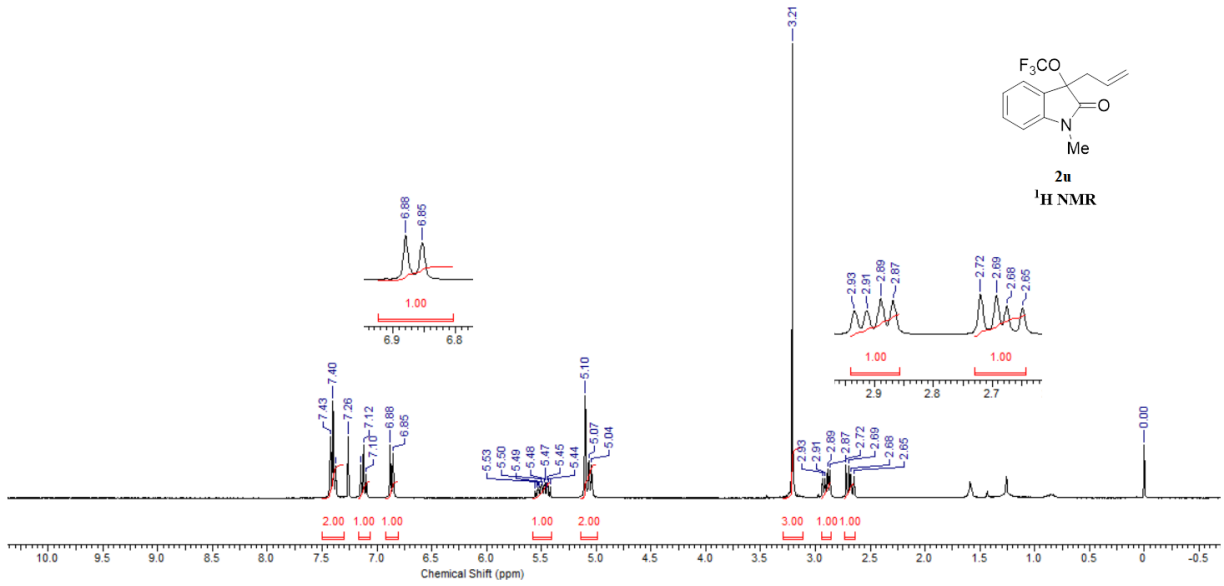

O
OCF3
2t
1H NMR
Chemical Shift (ppm)


O
OCF3
2t
19F NMR
Chemical Shift (ppm)



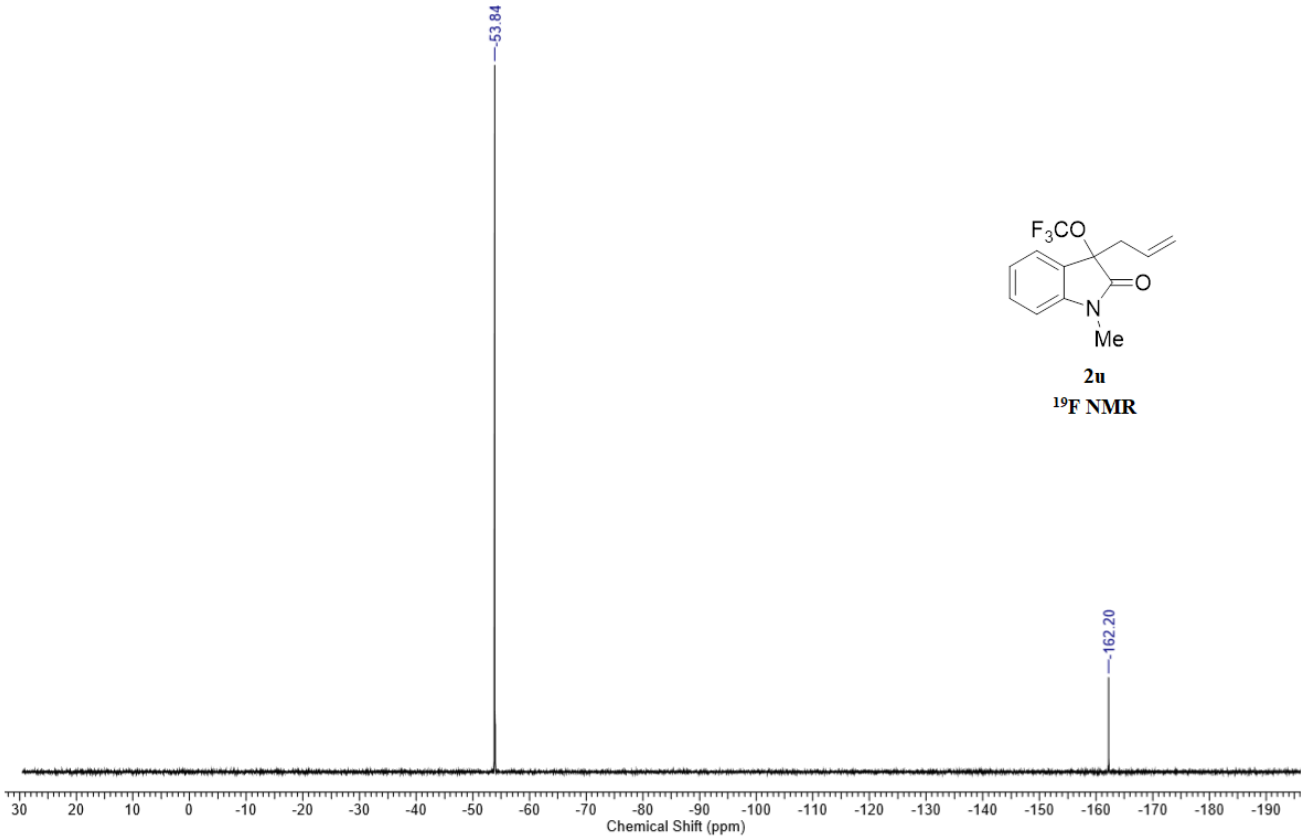
2t

^{13}C NMR



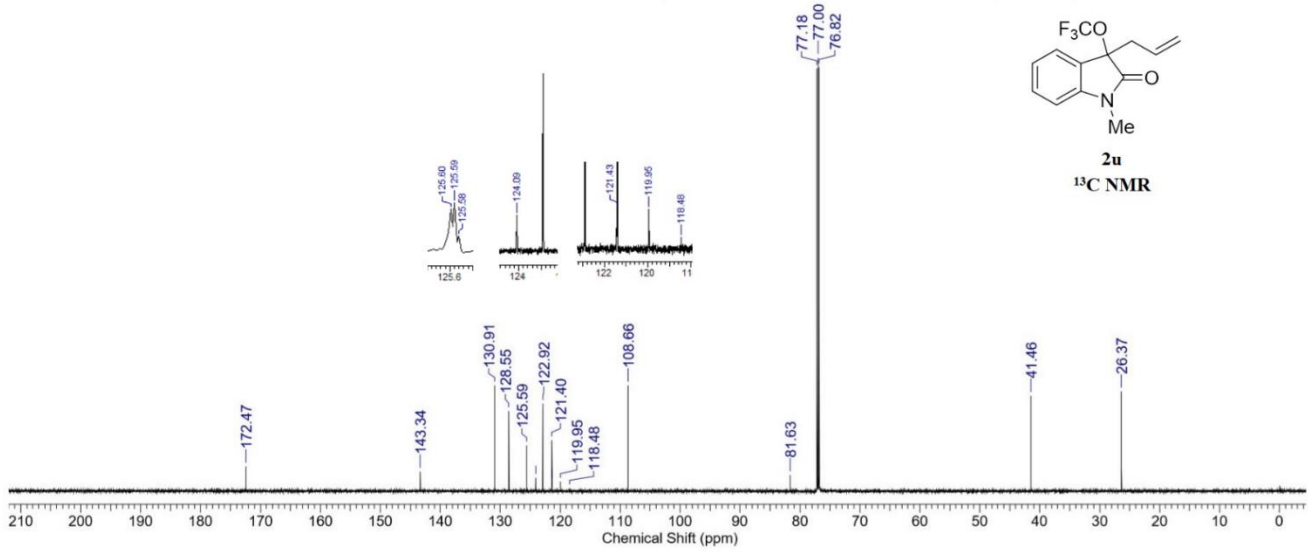
2u

^{1}H NMR



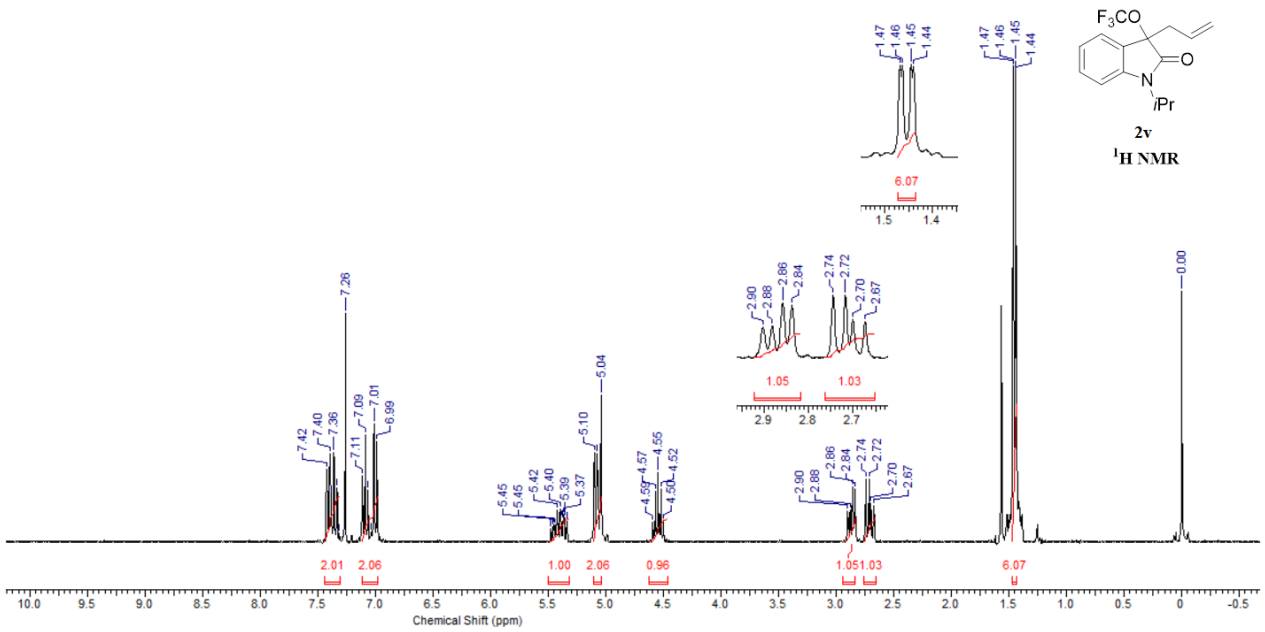
2u

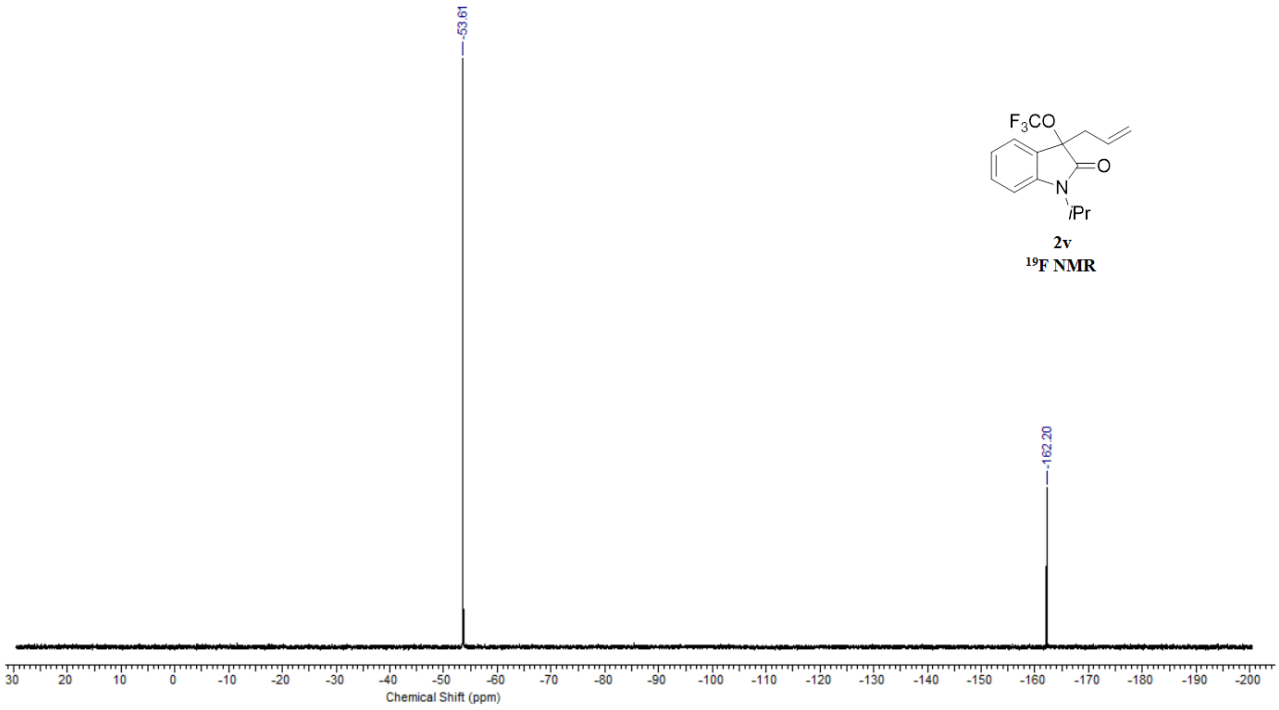
^{19}F NMR

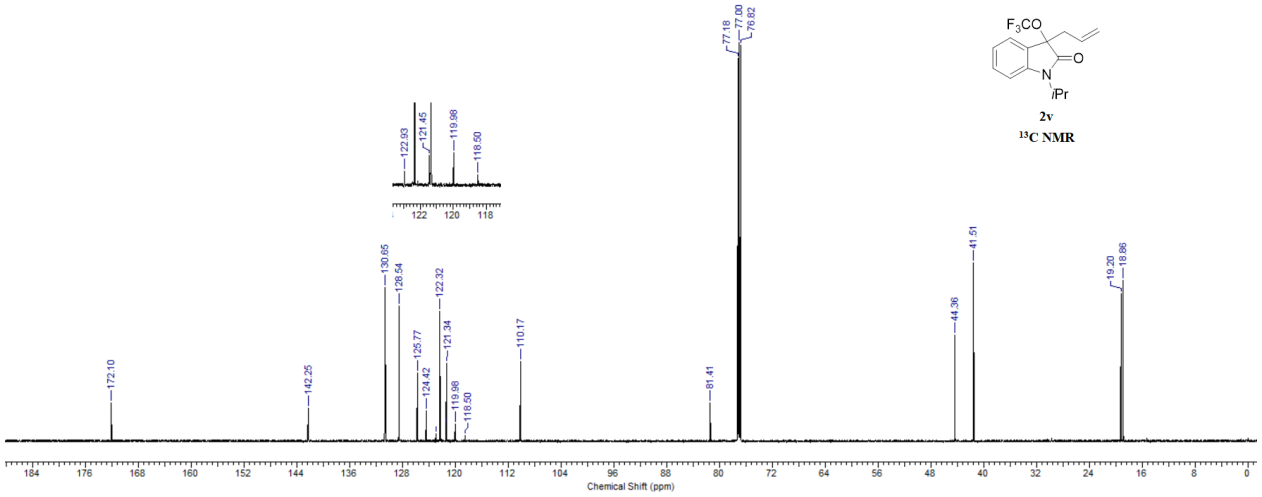


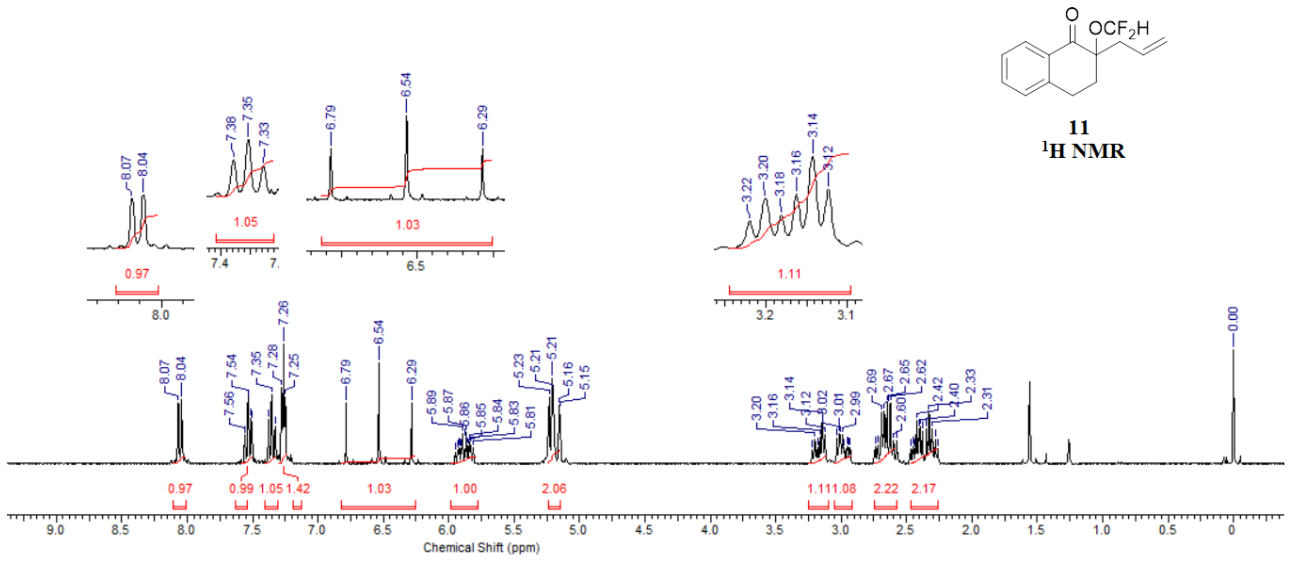
2u

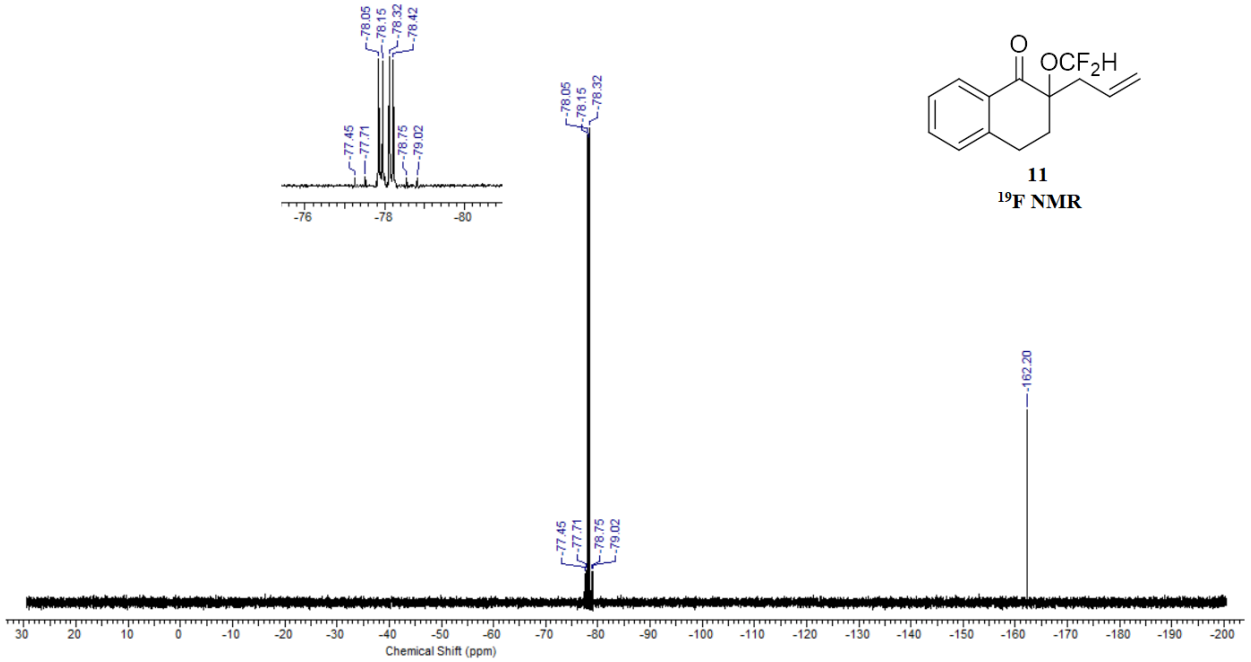
^{13}C NMR


F3CO
O
N
iPr
2v
1H NMR
Chemical Shift (ppm)


F3CO
O
N
iPr
2v
19F NMR
-53.61
-162.20
Chemical Shift (ppm)

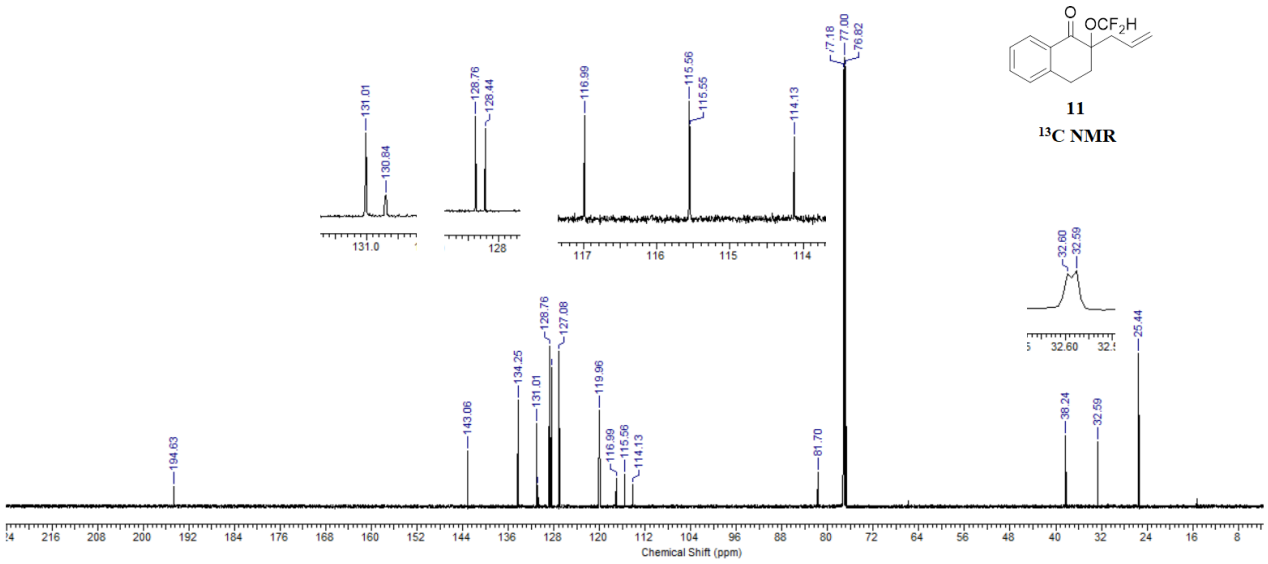

F3CO
O
N
iPr
2v
13C NMR
Chemical Shift (ppm)


O
OCF2H
11
1H NMR
Chemical Shift (ppm)



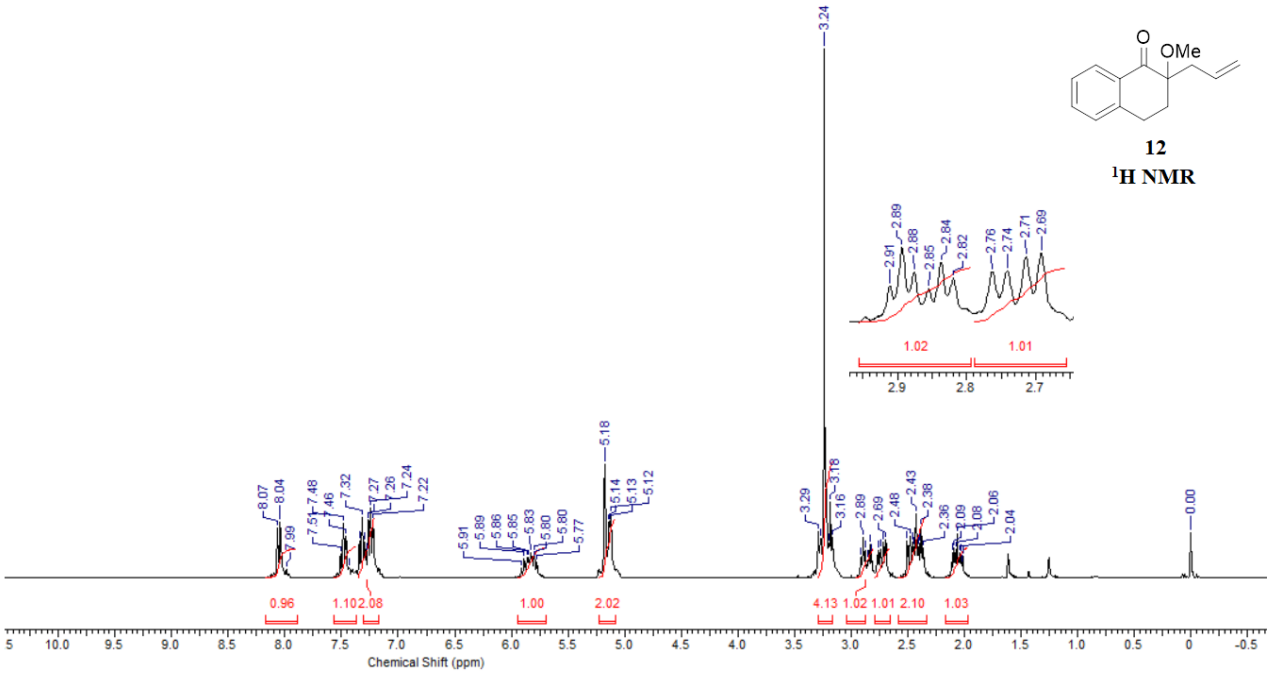
11

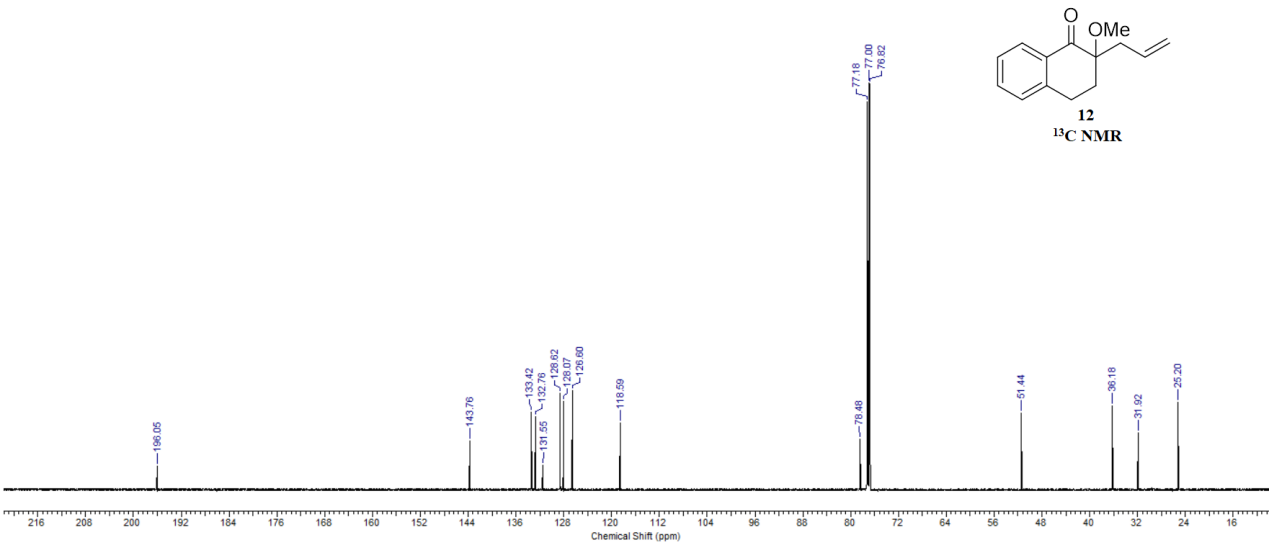
^{19}F NMR

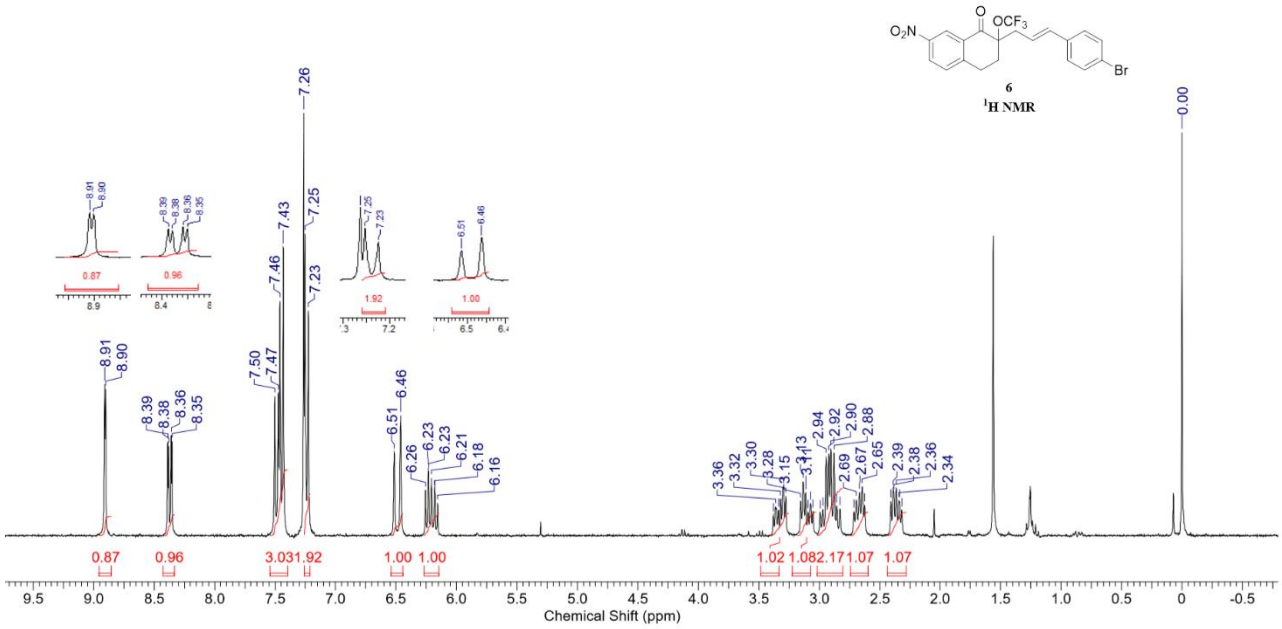


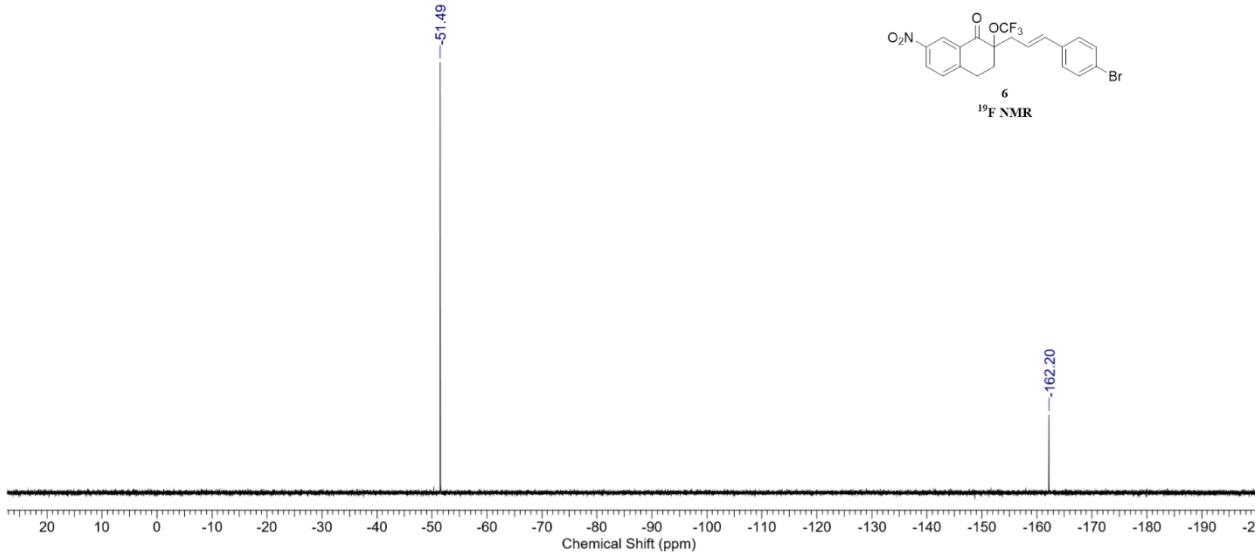
11

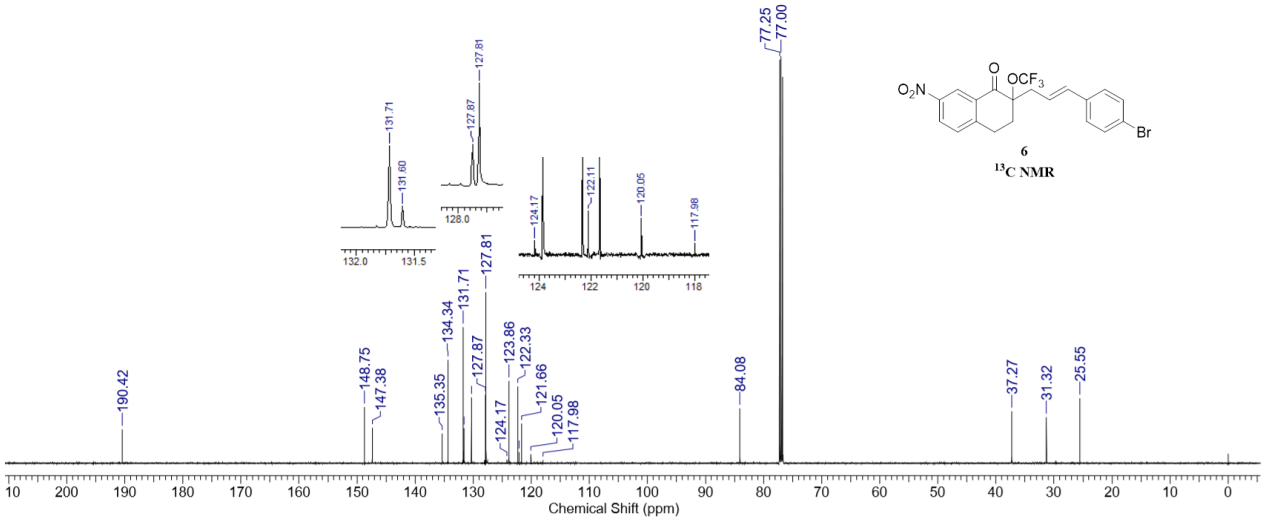
^{13}C NMR

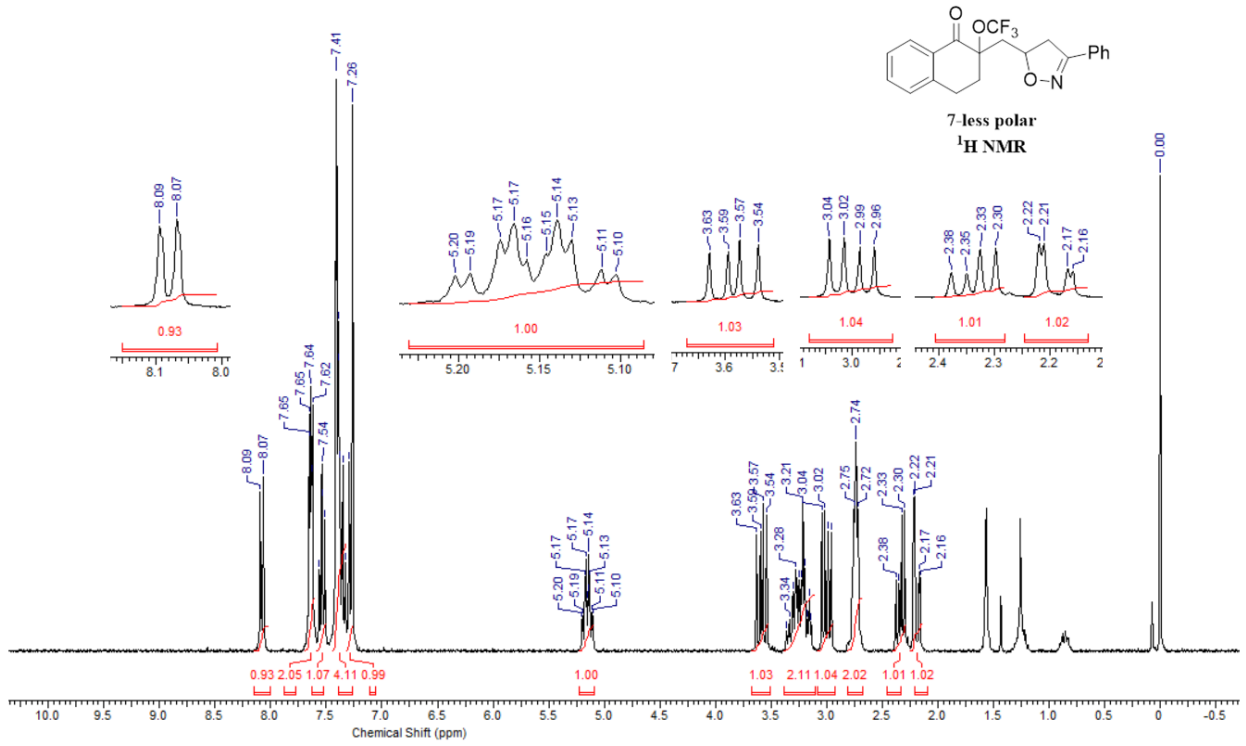

O
OMe
12
1H NMR
Chemical Shift (ppm)

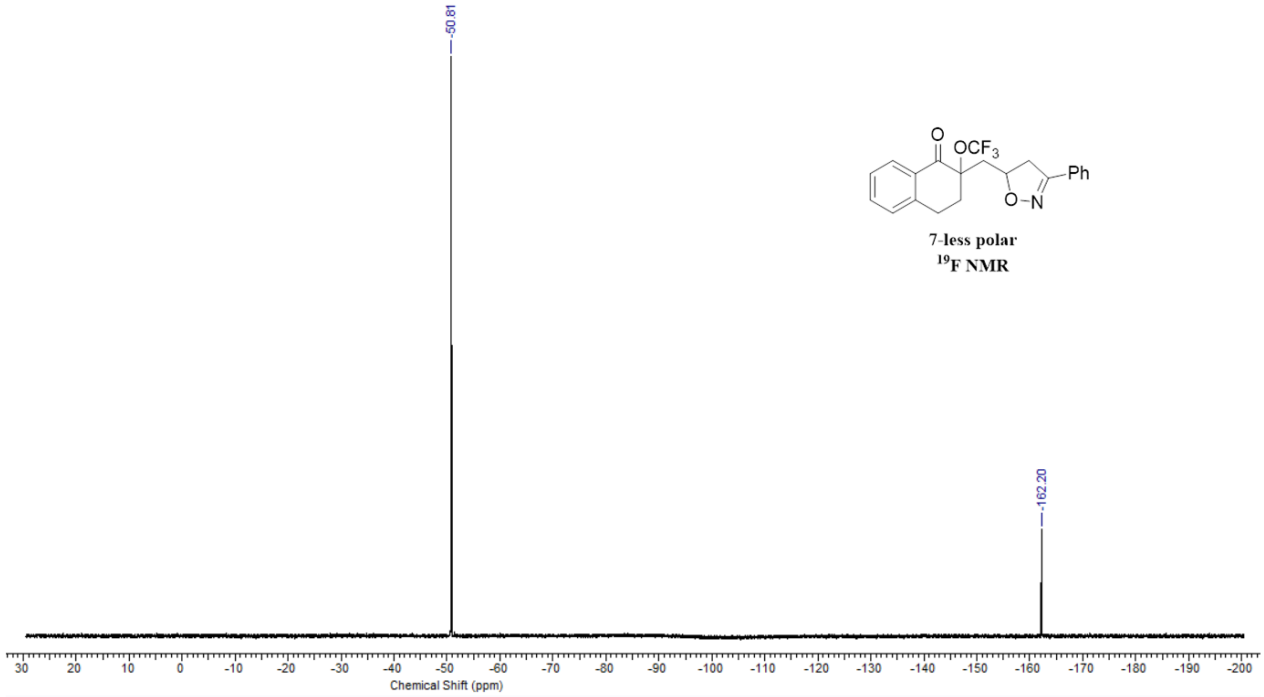

O
OMe
12
13C NMR
Chemical Shift (ppm)


O2N
O
OCF3
Br
6
1H NMR
Chemical Shift (ppm)

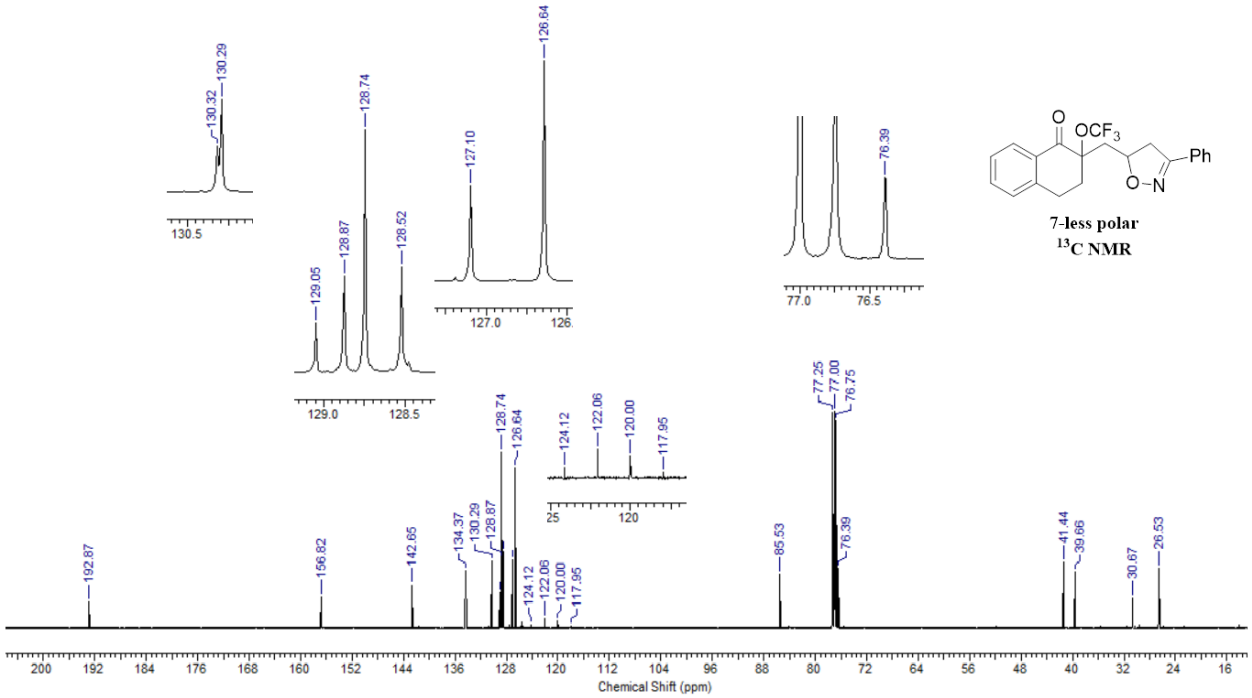

O2N
O
OCF3
Br
6
19F NMR
Chemical Shift (ppm)


O
OCF3
O2N
Br
6
13C NMR
Chemical Shift (ppm)

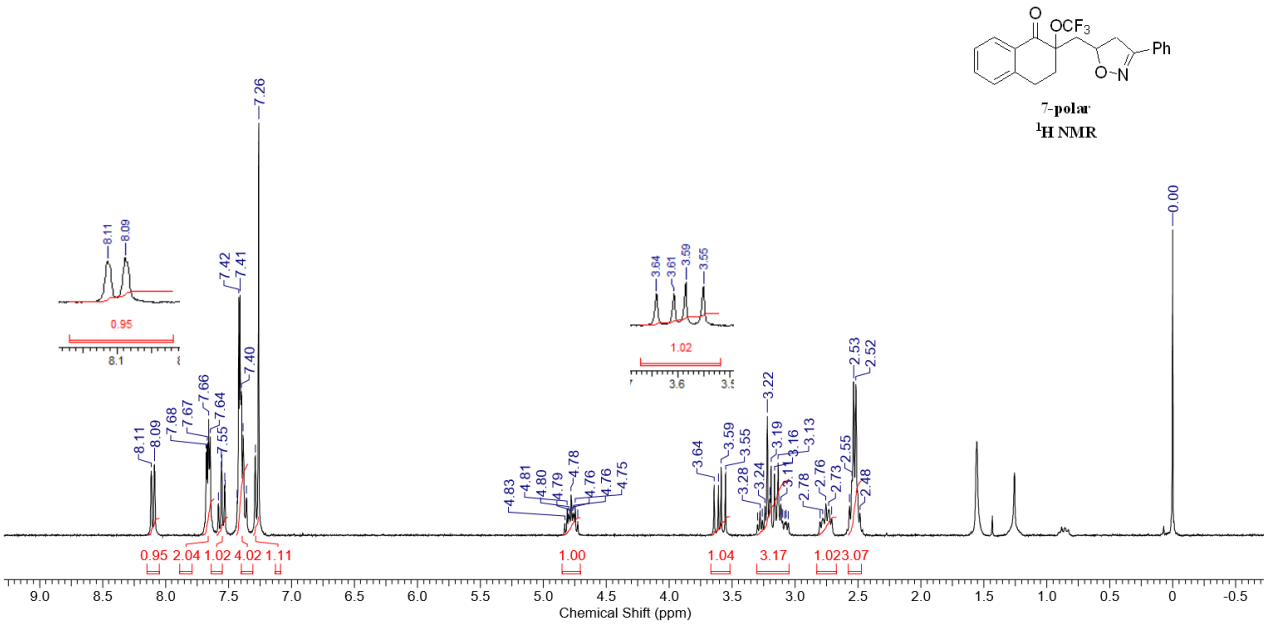

O
OCF3
Ph
O
N
7-less polar
1H NMR
Chemical Shift (ppm)

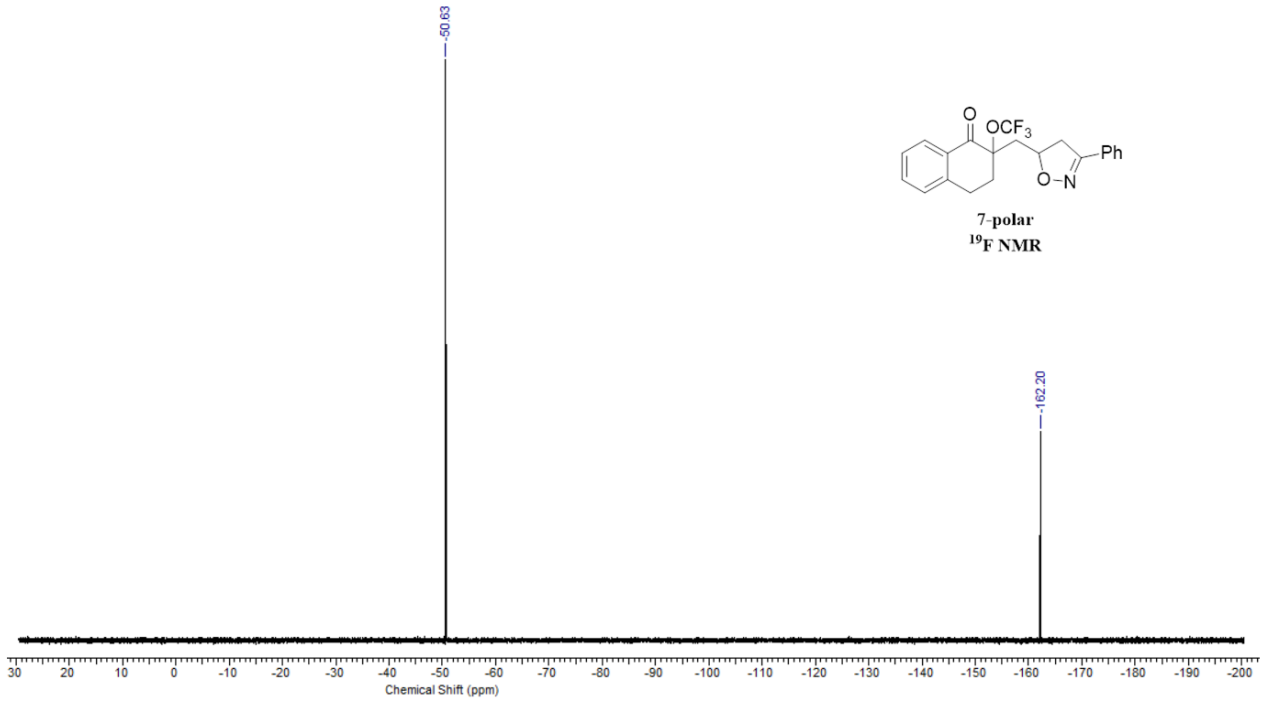


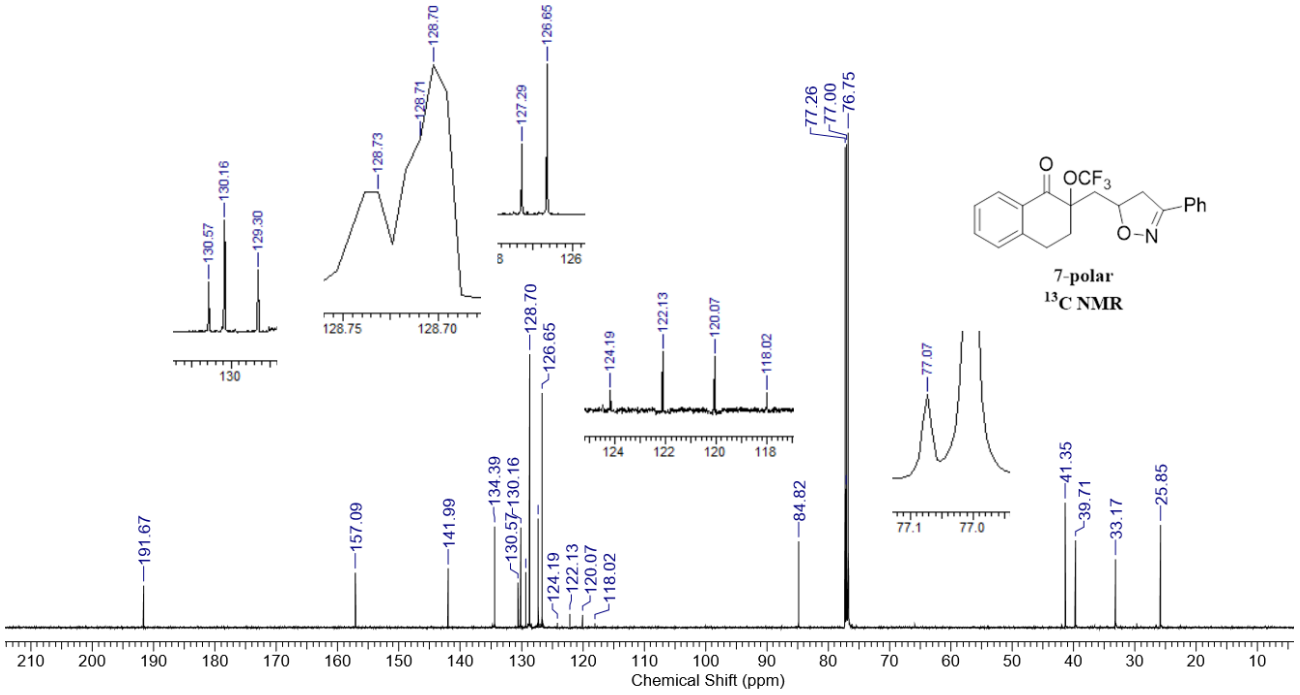
7-less polar
^{19}F NMR

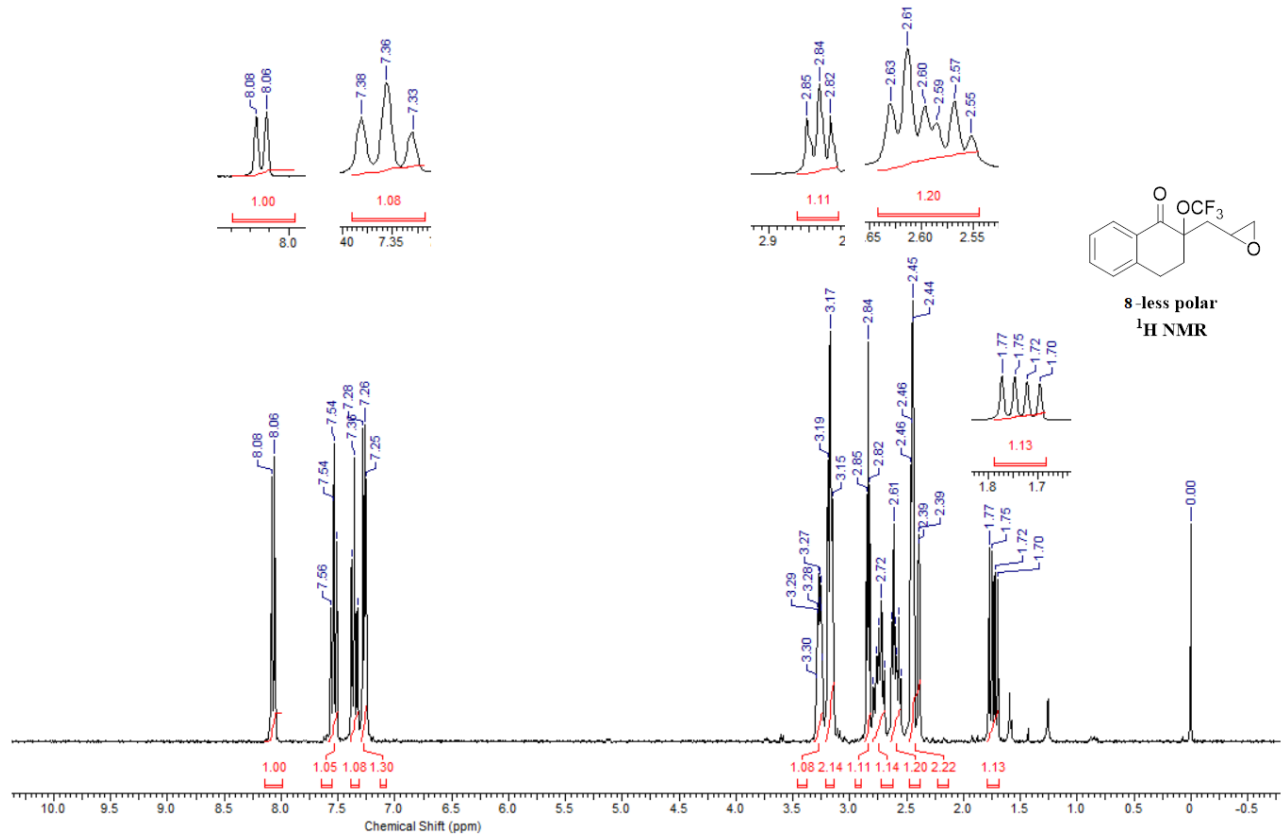


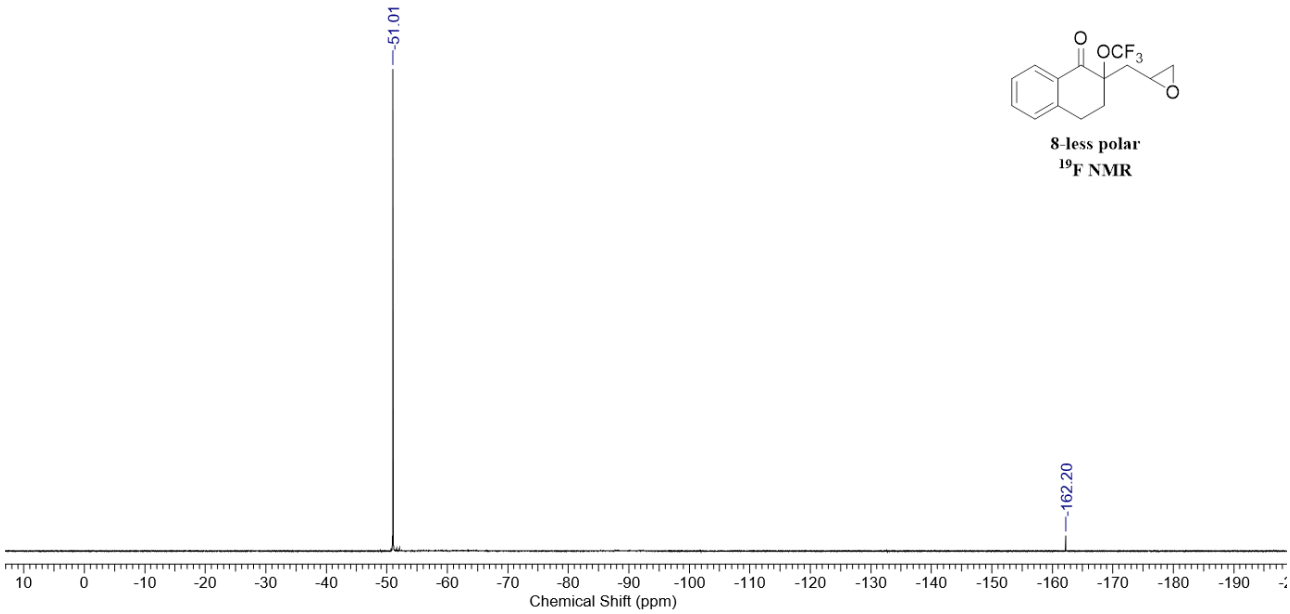
7-less polar
^{13}C NMR


O
OCF3
Ph
O
N
7-polar
1H NMR
8.11
8.09
7.68
7.67
7.66
7.64
7.55
7.42
7.41
7.40
7.26
4.83
4.81
4.80
4.79
4.78
4.76
4.76
4.75
3.64
3.61
3.59
3.55
3.28
3.24
3.22
3.19
3.16
3.13
3.11
2.78
2.76
2.73
2.55
2.53
2.52
2.48
0.00
0.95
2.04
1.02
4.02
1.11
1.00
1.04
3.17
1.02
3.07
Chemical Shift (ppm)

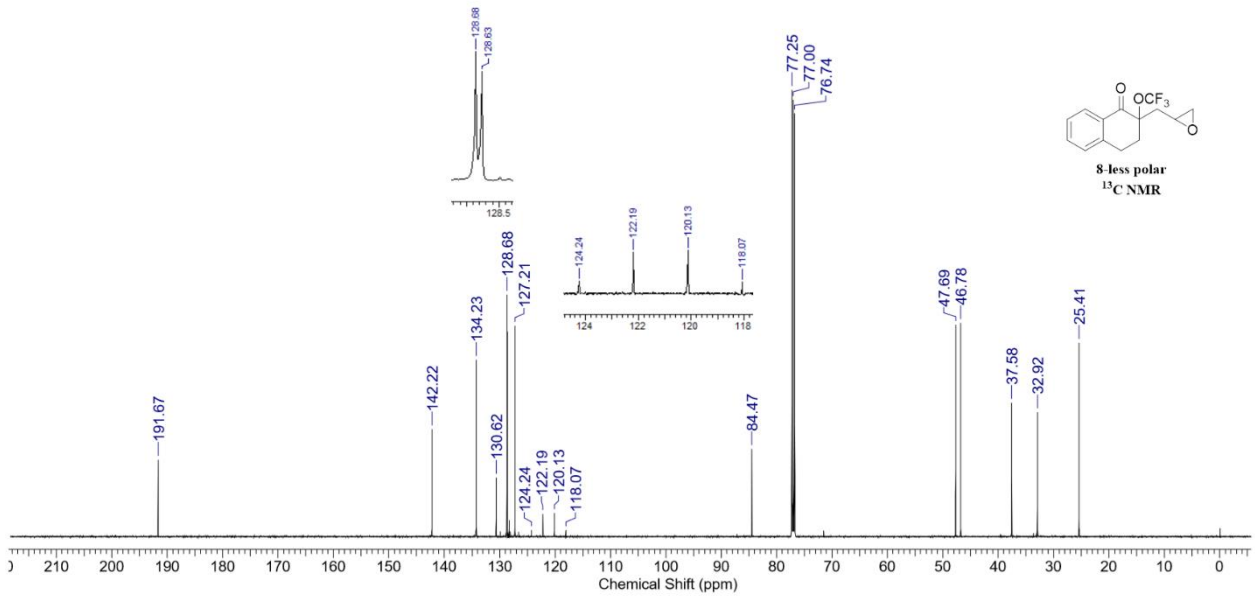

-50.63
-162.20
O
OCF3
Ph
O
N
7-polar
19F NMR
Chemical Shift (ppm)


7-polar
13C NMR
Chemical Shift (ppm)

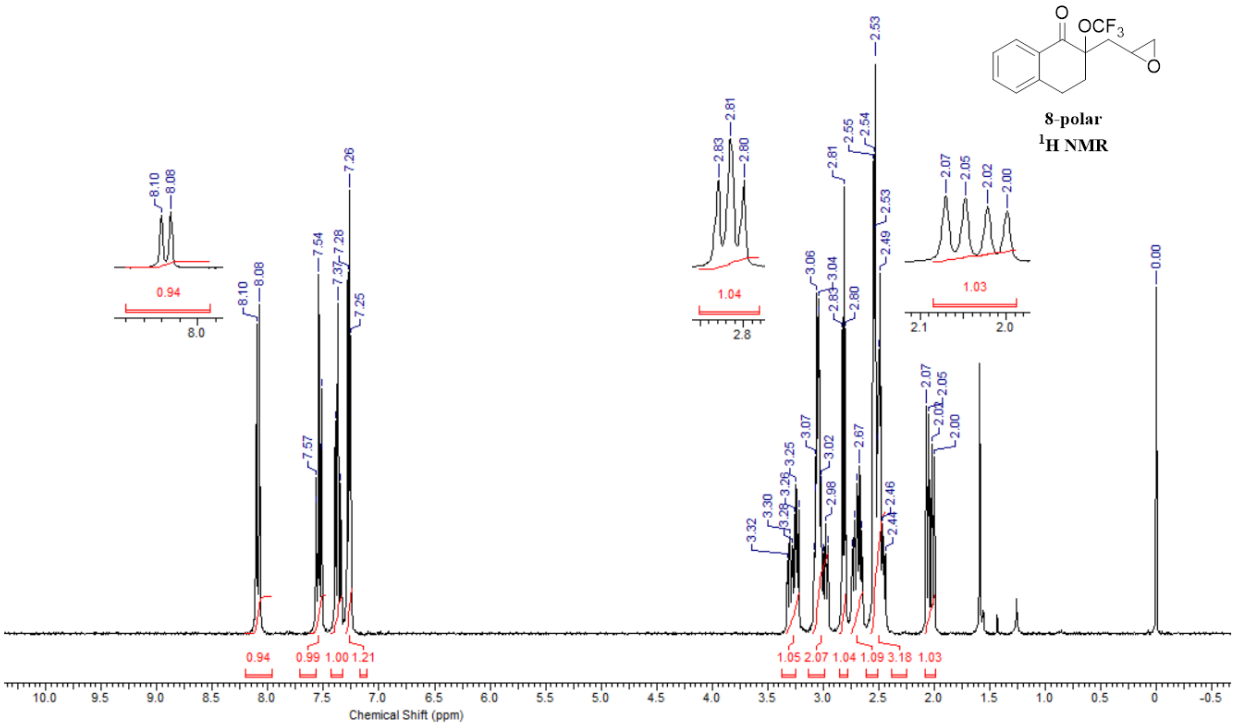

8-less polar
1H NMR
Chemical Shift (ppm)



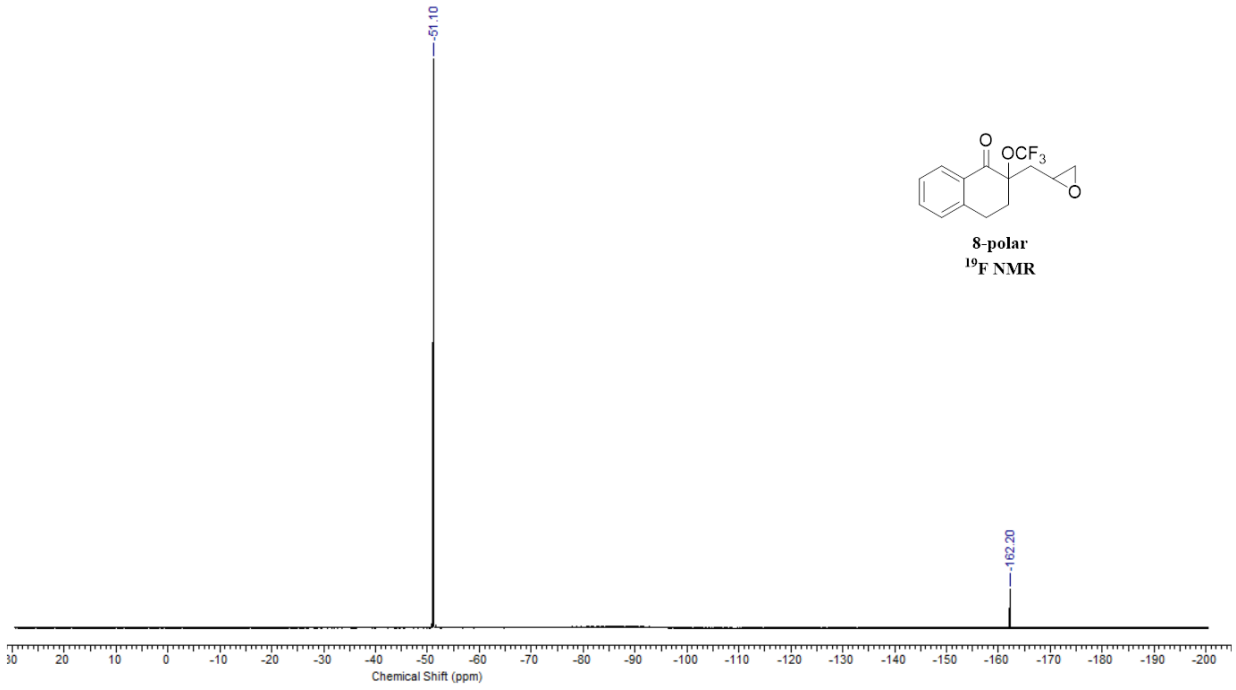
8-less polar
^{19}F NMR



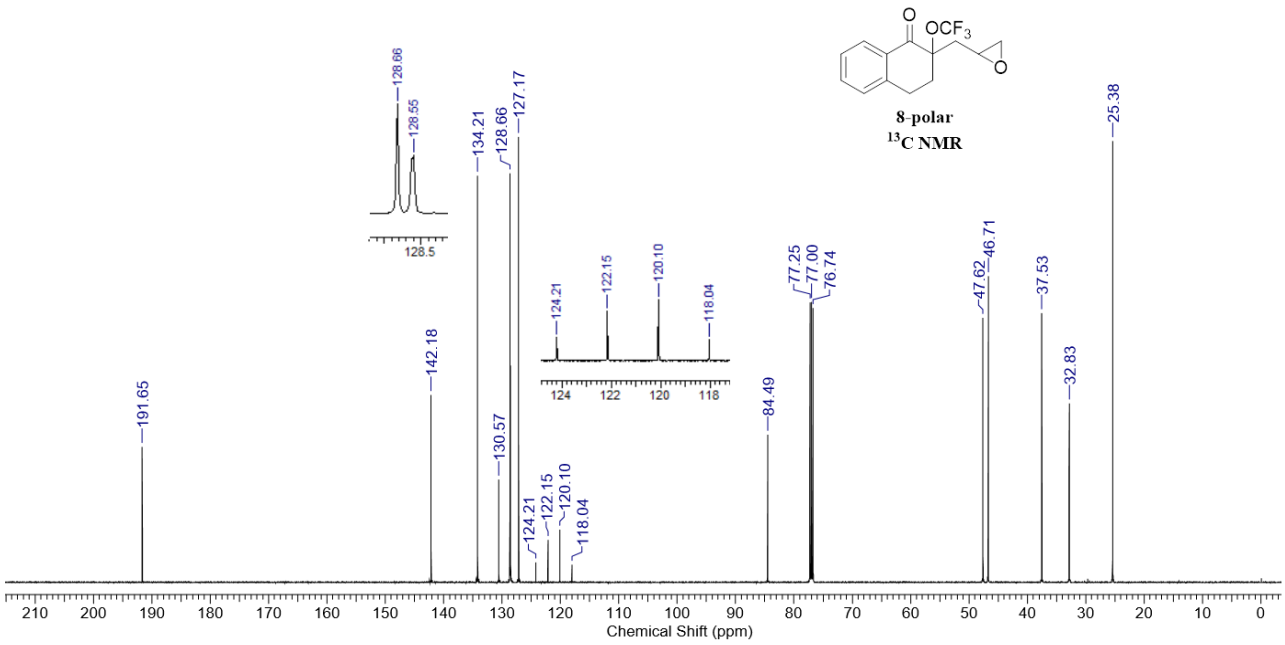
8-less polar
^{13}C NMR

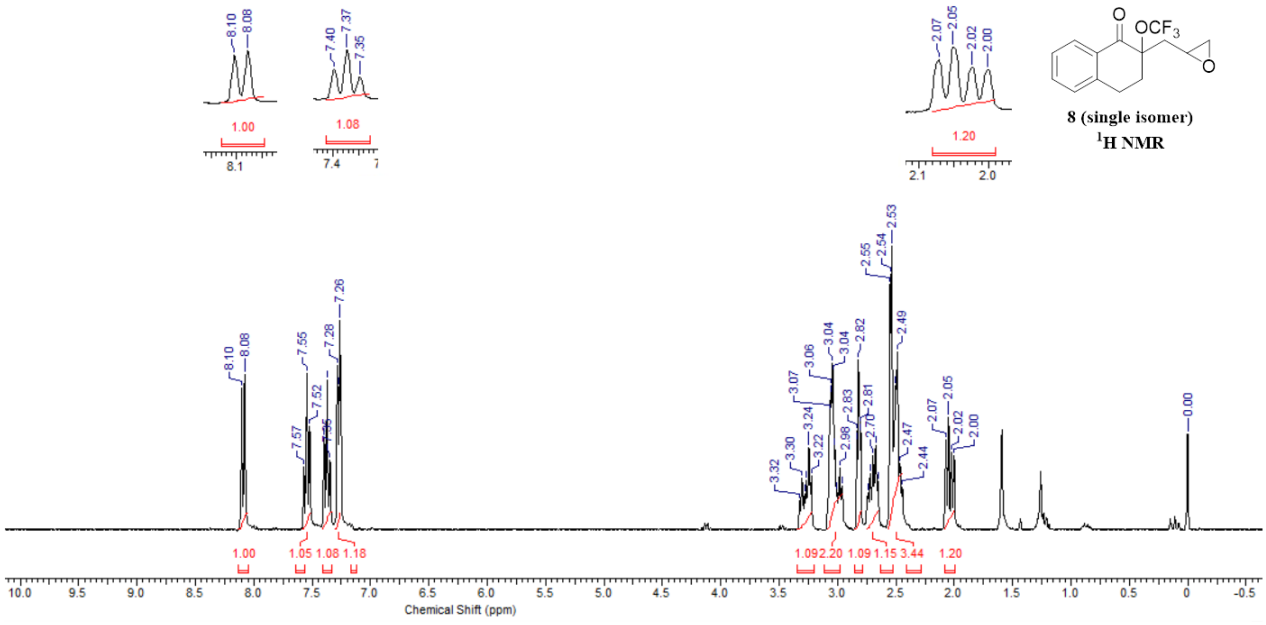


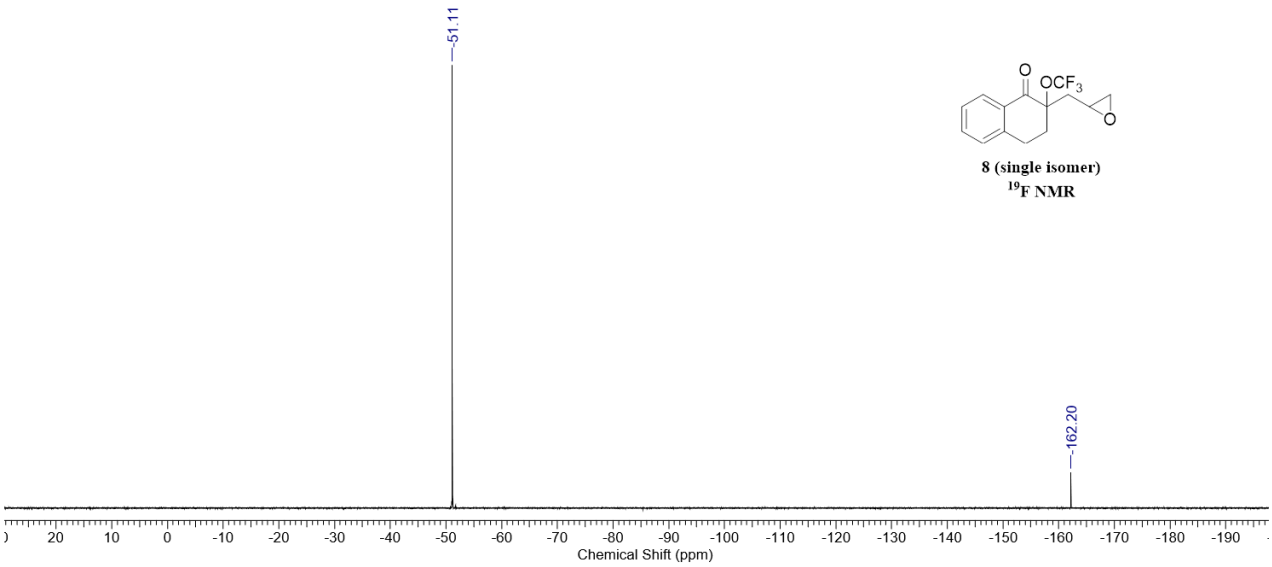
8-polar
^{1}H NMR



8-polar
^{19}F NMR


8-polar
13C NMR
Chemical Shift (ppm)


8 (single isomer)
1H NMR
Chemical Shift (ppm)



8 (single isomer)
^{19}F NMR