Electronic Supplementary Material (ESI) for Dalton Transactions.

Brønsted acid-catalyzed 1,2-fluorine migration with fluoroepoxides

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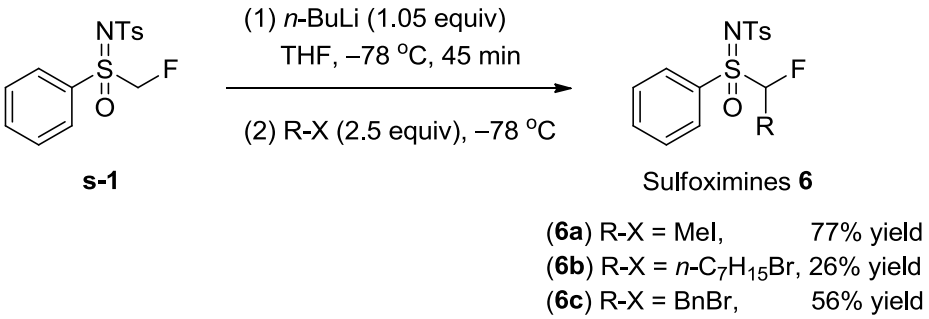
Supporting Information

1. General Information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The THF was distilled over sodium. The dichloromethane and CH_3CN were distilled over CaH_2. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ (external standard) at δ 0.0. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. Melting points are reported without correction. The *ee* values determination was carried out using chiral high performance liquid chromatography (HPLC) with Phenomenex Lux Cellulose column or Daicle Chiralpak AD-H column on Dionex Utimate 3000.

2. Typical Procedures for the Synthesis of Sulfoximines 6[1]

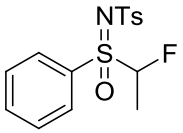


s-1

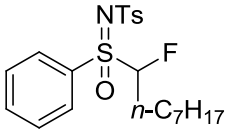
Sulfoximines **6**

(**6a**) R-X = MeI, 77% yield
(**6b**) R-X = *n*-$C_7H_{15}Br$, 26% yield
(**6c**) R-X = BnBr, 56% yield

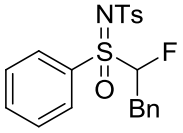
Under N_2 atmosphere, to a solution of compound (**s-1**) (500 mg, 1.53 mmol) in THF (10 mL), was added *n*-BuLi (1.6 M in THF, 1 mL, 1.6 mmol) slowly at −78 °C. After 45 min, MeI (0.24 mL, 3.8 mmol) was added. After one hour, the solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding water (20 mL), followed by extraction with ethyl ether (30 mL*3). The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in EtOH to give product sulfoximine **6a** (400 mg, 76 % yield).



Sulfoximine 6a:[1] White solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.78–7.74 (m, 1H), 7.65–7.60 (m, 2H), 7.27–7.26 (m, 2H), 5.98 (dq, *J* = 46.8 Hz, *J* = 5.9 Hz, 1H), 2.40 (s, 3H), 1.63 (dd, *J* = 22.8 Hz, *J* = 6 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −169.4 (m, 1F). MS (ESI) *m/z* 364.0 ($M+Na^+$). HRMS (ESI): Calcd. for $C_{15}H_{16}NO_3FS_2Na$: 364.0448; Found: 364.0448.

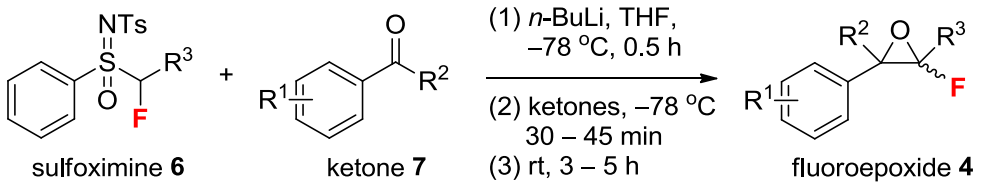


Sulfoximine 6b: White solid. Mp: 129–130 ^{o}C. IR (film): 2954, 2926, 2856, 1450, 1320, 1306, 1252, 1236, 1150, 1093, 1062, 770, 747, 686, 654, 618, 568, 545 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77–7.72 (m, 1H), 7.64–7.59 (m, 2H), 7.28–7.25 (m, 2H), 5.89–5.69 (m, 1H), 2.40 (s, 3H), 2.21–1.98 (m, 1H), 1.67–1.45 (m, 3H), 1.24 (s, 8H), 0.88–0.84 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −175.8 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.0, 140.6, 135.0, 132.3, 129.8, 129.5, 129.3, 126.7, 103.8 (d, *J* = 224.8 Hz), 31.5, 28.86, 28.82, 28.2 (d, *J* = 18.9 Hz), 24.5, 22.5, 21.5, 14.0. MS (ESI): *m/z* 448.1 ($M+Na^+$). HRMS (ESI): Calcd. for $C_{21}H_{28}NO_3FS_2Na$: 448.1387; Found: 448.1392.



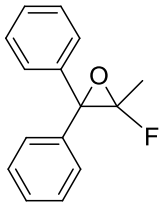
Sulfoximine 6c: White solid. Mp: 135-136 ^{o}C. IR (film): 2969, 1448, 1327, 1246, 1223, 1153, 1088, 1059, 815, 764, 732, 653, 623, 577, 556, 545, 508 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.79–7.74 (m, 1H), 7.66–7.61 (m, 2H), 7.29–7.17 (m, 7H), 5.99–5.79 (m, 1H), 3.57–3.39 (m, 1H), 2.96–2.82 (m, 1H), 2.41 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −176.3 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 140.5, 135.2, 132.8, 132.4, 129.8, 129.7, 129.5, 129.4, 128.9, 127.8, 126.7, 103.5 (d, *J* = 229.7 Hz), 34.5 (d, *J* = 19 Hz), 21.6. MS (ESI): *m/z* 440.0 ($M+Na^+$). HRMS (ESI): Calcd. for $C_{21}H_{20}NO_3FS_2Na$: 440.0761; Found: 440.0759.

3. Typical Procedures for Synthesis of Fluoroepoxides 4[2]

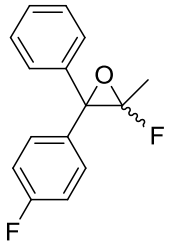


Under N_2 atmosphere, to a solution of sulfoximine **6** (R^3 = Me) (512 mg, 1.5 mmol, 1.5 equiv.) in 10 mL THF, was added *n*-BuLi (2.5 M in THF, 0.6 mL, 1.5 mmol, 1.5 equiv.) slowly at –78 °C. After 30 min, a solution of (4-fluorophenyl)(phenyl)methanone **7** (R^1 = 4-F, R^2 = Ph) (200 mg, 1.0 mmol, 1.0 equiv.) in THF (1 mL) was added into the reaction system. After 45 min, the reaction system was allowed to warm to room temperature and stirred for another 5 h. The reaction was quenched by adding water (20 mL), followed by extraction with ethyl ether (30 mL*3). The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to TLC preparative plate (pre-treated with triethylamine in PE, 2% v/v) by using PE : EA = 40 : 1 (PE: petroleum ether; EA: ethyl acetate) as eluent to get fluoroepoxides **4b** (195 mg, 79% yield).

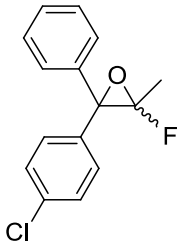
(**NOTE**: The relative configuration of the isolated fluoroepoxides **4o-s** were determined by comparing the ^{1}H NMR signals of the methyl groups with those of the known fluoroepoxides.[2])



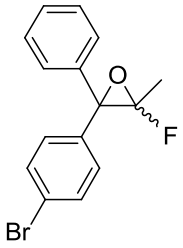
2-fluoro-2-methyl-3,3-diphenyloxirane (**4a**): 72% yield. Colorless oil. IR (film): 3063, 3032, 2939, 1603, 1496, 1449, 1417, 1377, 1196, 1178, 1109, 1078, 888, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48–7.33 (m, 10H), 1.64 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –121.8 (q, *J* = 15.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.0, 136.4 (d, *J* = 3.2 Hz), 128.5, 128.2, 128.1, 127.9, 127.1, 127.0, 99.5 (d, *J* = 264.6 Hz), 70.4 (d, *J* = 18.9 Hz), 17.1 (d, *J* = 32.6 Hz). MS (EI, *m/z*, %): 228 (M^+, 0.12), 166 ([M-MeCOF]$^+$, 70.53), 165 (100). HRMS (EI): Calcd. for $C_{13}H_{10}$ (M-MeCOF): 166.0783; Found: 166.0780.



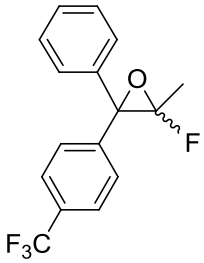
(*cis*)&(*trans*)-2-fluoro-3-(4-fluorophenyl)-2-methyl-3-phenyloxirane (4b): 79% yield. Colorless oil. IR (film): 3064, 1608, 1510, 1225, 1176, 1159, 907, 892, 835, 698, 575 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44–7.41 (m, 2H), 7.37–7.32 (m, 5H), 7.07–7.00 (m, 2H), 1.66–1.61 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –113.4 (m), –113.8 (m), –121.2 (q, *J* = 16.5 Hz), –121.8 (q, *J* = 15.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (d, *J* = 247.4 Hz), 162.5 (d, *J* = 247.3 Hz), 136.8 (d, *J* = 3.3 Hz), 136.2 (d, *J* = 4.7 Hz), 132.9 (t, *J* = 3 Hz), 132.3 (t, *J* = 4 Hz), 129.9 (dd, J_1 = 1.6 Hz, J_2 = 8.3 Hz), 129.0 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz), 128.6, 128.33, 128.31, 128.29, 127.9, 127.0 (d, *J* = 1.5 Hz), 115.5 (d, *J* = 38.2 Hz), 115.2 (d, *J* = 39 Hz), 99.5 (d, *J* = 267.4 Hz), 99.4 (d, *J* = 267.3 Hz), 69.86 (d, *J* = 20.0 Hz), 69.85 (d, *J* = 20.0 Hz), 17.1 (d, *J* = 32.9 Hz), 17.0 (d, *J* = 32.7 Hz). MS (EI, *m/z*, %): 184 ($[M\text{-}MeCOF]^+$, 55.22). HRMS (EI): Calcd. for $C_{13}H_9F$ (M-MeCOF): 184.0688; Found: 184.0686.



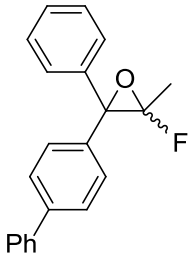
(*cis*)&(*trans*)-2-(4-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4c): 80% yield. Colorless oil. IR (film): 3063, 1597, 1496, 1463, 1376, 1172, 1111, 1011, 922, 908, 827, 774, 727, 718, 695, 609 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44–7.30 (m, 9H), 1.66–1.61 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –120.9 (q, *J* = 15.4 Hz), –121.9 (q, *J* = 16.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4 (d, *J* = 3.0 Hz), 135.8 (d, *J* = 3.9 Hz), 135.5 (d, *J* = 3.0 Hz), 134.9 (d, *J* = 3.8 Hz), 134.2, 129.4 (d, *J* = 1.3 Hz), 128.8, 128.63, 128.62, 128.5 (d, *J* = 1.6 Hz), 128.41, 128.40, 128.3, 127.85, 127.84, 127.0 (d, *J* = 1.6 Hz), 99.4 (d, *J* = 267.1 Hz), 99.3 (d, *J* = 267.1 Hz), 69.80 (d, *J* = 19.7 Hz), 69.78 (d, *J* = 20.0 Hz), 17.1 (d, *J* = 32.3 Hz), 16.9 (d, *J* = 32.7 Hz). MS (EI, *m/z*, %): 262 (M^+, 0.07), 200 ($[M\text{-}MeCOF]^+$, 35.30). HRMS (EI): Calcd. for $C_{15}H_{12}OFCl$: 262.0561; Found: 262.0564.



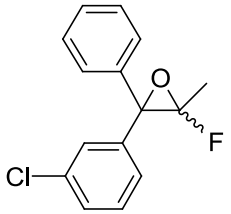
(*cis*)&(*trans*)-2-(4-bromophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4d): 81% yield.Colorless oil. IR (film): 3062, 3031, 2986, 2939, 1592, 1488, 1395, 1195, 1173, 1112, 1071, 1033, 918, 891, 820, 762, 698, 610 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51–7.24 (m, 9H), 1.66–1.61 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ–121.3 (m), –122.3 (m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4 (d, *J* = 2.8 Hz), 136.1 (d, *J* = 2.8 Hz), 135.8 (d, *J* = 4.2 Hz), 135.4 (d, *J* = 4.2 Hz), 131.7, 131.3, 129.6, 128.76, 128.6, 128.4, 128.3, 127.8, 127.04, 127.02, 122.44, 122.37, 99.3 (d, *J* = 265.8 Hz), 99.2 (d, *J* = 266.0 Hz), 69.84 (d, *J* = 19.4 Hz), 69.81 (d, *J* = 20.0 Hz), 17.1 (d, *J* = 33.1 Hz), 16.9 (d, *J* = 32.1 Hz). MS (EI, *m/z*, %): 306 (M^+, 0.06), 244 ([M-MeCOF]$^+$, 24.46). HRMS (EI): Calcd. for $C_{15}H_{12}OFBr$: 306.0056; Found: 306.0053.



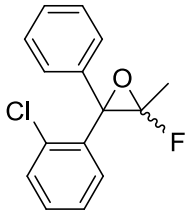
(*cis*)&(*trans*)-2-fluoro-2-methyl-3-phenyl-3-(4-(trifluoromethyl)phenyl)oxirane (4e): 76% yield. Colorless oil. IR (film): 3065, 3033, 2942, 1621, 1497, 1448, 1408, 1378, 1327, 1170, 1128, 1105, 1068, 921, 895, 837, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.58 (m, 3H), 7.52–7.45 (m, 2H), 7.37–7.31 (m, 4H), 1.66–1.56 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –62.28 (s), –62.31 (s), –120.0 (q, *J* = 15.7 Hz), –121.5 (q, *J* = 16.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 140.5 (d, *J* = 4.2 Hz), 136.1 (d, *J* = 3.0 Hz), 135.6 (d, *J* = 4.9 Hz), 130.5 (q, *J* = 33.0 Hz), 130.4 (q, *J* = 32.5 Hz), 128.8, 128.63, 128.60, 128.5, 128.4, 128.0, 127.5, 127.1, 125.6 (q, *J* = 38.3 Hz), 125.2 (q, *J* = 39.7 Hz), 124.2 (q, *J* = 270.3 Hz), 124.0 (q, *J* = 270.6 Hz), 99.4 (d, *J* = 265.5 Hz), 99.2 (d, *J* = 265.9 Hz), 69.87 (d, *J* = 19.4 Hz), 69.86 (d, *J* = 19.4 Hz), 17.1 (d, *J* = 32.1 Hz), 16.8 (d, *J* = 33 Hz). MS (EI, *m/z*, %): 234 ([M-MeCOF]$^+$, 62.46). HRMS (EI): Calcd. for $C_{14}H_9F_3$ (M-MeCOF): 234.0656; Found: 234.0654.



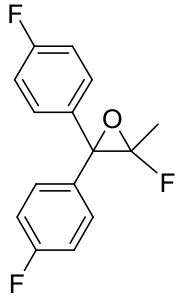
(*cis*)&(*trans*)-2-(biphenyl-4-yl)-3-fluoro-3-methyl-2-phenyloxirane (4f): 70% yield. Colorless oil. IR (film): 3060, 3030, 2992, 1598, 1496, 1488, 1462, 1416, 1378, 1172, 1106, 1076, 1007, 934, 912, 891, 833, 762, 724, 609 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60–7.34 (m, 14H), 1.72–1.64 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –121.3 (q, *J* = 16.4 Hz), –122.1 (q, *J* = 15.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 140.7, 140.4, 136.9 (d, *J* = 3.3 Hz), 136.4 (d, *J* = 4.8 Hz), 136.0 (d, *J* = 2.9 Hz), 135.3 (d, *J* = 4.5 Hz), 128.9, 128.8, 128.5, 128.3, 128.24, 128.22, 127.9, 127.6, 127.5, 127.4, 127.3, 127.20, 127.17, 127.1, 127.0, 99.6 (d, *J* = 264.3 Hz), 99.5 (d, *J* = 265.1 Hz), 70.31 (d, *J* = 19.4 Hz), 70.30 (d, *J* = 19.4 Hz), 17.2 (d, *J* = 33.0 Hz), 17.1 (d, *J* = 32.3 Hz). MS (EI, *m/z*, %): 304 (M^+, 0.63), 242 ([M-MeCOF]$^+$, 100.00). HRMS (EI): Calcd. for $C_{19}H_{14}$ (M-MeCOF): 242.1096; Found: 242.1100.



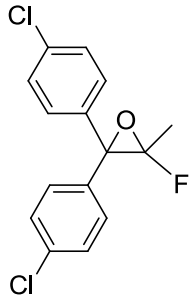
(*cis*)&(*trans*)-2-(3-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4g): 81% yield. Colorless oil. IR (film): 3064, 3031, 2938, 2856, 1598, 1572, 1497, 1474, 1448, 1415, 1377, 1180, 1112, 1079, 931, 897, 879, 789, 734, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.26 (m, 9H), 1.66–1.61 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –120.4 (q, *J* = 16.0 Hz), –121.4 (q, *J* = 16.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0 (d, *J* = 3.2 Hz), 138.4 (d, *J* = 4.6 Hz), 136.3 (d, *J* = 2.8 Hz), 135.7 (d, *J* = 4.0 Hz), 134.6, 134.2, 129.9, 129.5, 128.7, 128.5, 128.41, 128.38, 128.1, 127.9, 127.22, 127.20, 127.05, 127.04, 126.1, 125.2, 99.3 (d, *J* = 266.0 Hz), 99.2 (d, *J* = 265.9 Hz), 69.72 (d, *J* = 19.3 Hz), 69.68 (d, *J* = 20.6 Hz), 17.1 (d, *J* = 32.8 Hz), 17.0 (d, *J* = 32.5 Hz). MS (EI, *m/z*, %): 262 (M^+, 0.1), 200 ([M-MeCOF]$^+$, 32.51). HRMS (EI): Calcd. for $C_{13}H_9Cl$ (M-MeCOF): 200.0393; Found: 200.0391.



(*cis*)&(*trans*)-2-(2-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4h): 76% yield. Colorless oil. IR (film): 3063, 3030, 2990, 2930, 1596, 1572, 1497, 1478, 1447, 1438, 1416, 1377, 1182, 1062, 987, 921, 909, 893, 697, 670, 612 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–7.27 (m, 9H), 1.74–1.67 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –115.2 (s), –125.8 (s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.9, 135.7, 134.7, 133.1, 130.5, 129.83, 129.78, 129.67, 128.4, 128.3, 128.0, 127.1, 126.9, 99.30 (d, *J* = 266.6 Hz), 99.29 (d, *J* = 266.6 Hz), 68.91 (d, *J* = 19.4 Hz), 68.90 (d, *J* = 19.4 Hz), 15.59 (d, *J* = 31.7 Hz) , 15.58 (d, *J* = 31.7 Hz). MS (EI, *m/z*, %): 200 ($[M\text{-}MeCOF]^+$, 22.14). HRMS (EI): Calcd. for $C_{13}H_9Cl$ (M-MeCOF): 200.0393; Found: 200.0391.

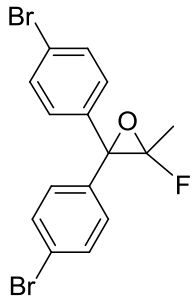


2-fluoro-3,3-bis(4-fluorophenyl)-2-methyloxirane (4i): 76% yield. Colorless oil. IR (film): 3078, 2942, 1607, 1510, 1234, 1177, 1159, 933, 917, 896, 837, 562 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41–7.31 (m, 4H), 7.08–7.01 (m, 4H), 1.63 (d, *J* = 16.0 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –112.7 (m), –133.1 (m), –121.2 (q, *J* = 16.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (d, *J* = 245.1 Hz), 162.5 (d, *J* = 246.7 Hz), 132.7, 132.0, 129.8 (d, *J* = 8.3 Hz), 128.9 (d, *J* = 7.8 Hz), 115.6 (d, *J* = 20.9 Hz), 115.2 (d, *J* = 21.4 Hz), 99.3 (d, *J* = 265.2 Hz), 89.3 (d, *J* = 19.9 Hz), 17.0 (d, *J* = 32.8 Hz). MS (EI, *m/z*, %): 264 (M^+, 0.33), 202 ($[M\text{-}MeCOF]^+$, 64.83). HRMS (EI): Calcd. for $C_{15}H_{11}OF_3$: 264.0762; Found: 264.0763.

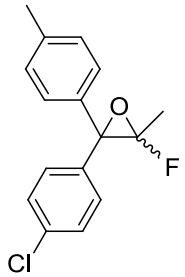


2,2-bis(4-chlorophenyl)-3-fluoro-3-methyloxirane (4j): 71% yield. Colorless oil. IR (film): 2940, 1598, 1492, 1418, 1402, 1376, 1196, 1182, 1092, 1016, 934, 917, 895, 826, 615 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.27 (m, 8H), 1.63 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –121.8 (q, *J* = 15.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.0 (d, *J* = 3.1 Hz), 134.51, 134.49, 134.4 (d, *J* = 4.4 Hz), 129.3, 128.9, 128.54, 128.46, 99.2 (d, *J* = 265.4 Hz), 69.2 (d, *J* = 20.4 Hz), 17.0 (d, *J* = 32.6 Hz). MS (EI,

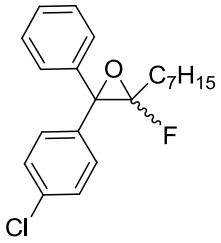
m/z, %): 234 ([M-MeCOF]$^+$, 38.10). HRMS (EI): Calcd. for $C_{13}H_8Cl_2$ (M-MeCOF): 234.0003; Found: 234.0001.



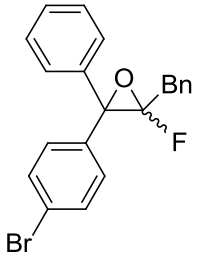
2,2-bis(4-bromophenyl)-3-fluoro-3-methyloxirane (4k): 71% yield. Colorless oil. IR (film): 2938, 1593, 1489, 1418, 1396, 1195, 1099, 1072, 1012, 916, 895, 821, 613, 550 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52–7.47 (m, 4H), 7.30–7.21 (m, 4H), 1.62 (d, *J* = 16.1 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –121.3 (q, *J* = 16.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.4 (d, *J* = 3.1 Hz), 134.9 (d, *J* = 3.8 Hz), 131.9, 131.5, 129.7, 128.8, 122.8, 122.7, 99.1 (d, *J* = 266.2 Hz), 69.3 (d, *J* = 19.7 Hz), 17.0 (d, *J* = 32.1 Hz). MS (EI, *m/z*, %): 322 ([M-MeCOF]$^+$, 48). HRMS (EI): Calcd. for $C_{13}H_{18}Br_2$ (M-MeCOF): 321.8993; Found: 321.8989.



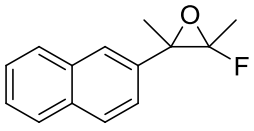
(*cis*)&(*trans*)-2-(4-chlorophenyl)-3-fluoro-3-methyl-2-p-tolyloxirane (4l): 77% yield. Colorless oil. IR (film): 3029, 2924, 2867, 1598, 1514, 1491, 1196, 1173, 1093, 1012, 934, 917, 893, 814 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39–7.14 (m, 8H), 2.34–2.33 (m, 3H), 1.66–1.59 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –121.3 (q, *J* = 16.2 Hz), –122.3 (q, *J* = 16.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.3, 135.8, 135.2, 134.1, 133.5, 132.9, 129.34, 129.27, 129.2, 129.0, 128.7, 128.4, 128.3, 127.8, 127.0, 99.5 (d, *J* = 264.6 Hz), 99. 3 (d, *J* = 265.2 Hz), 69.8 (d, *J* = 23.3 Hz), 69.7 (d, *J* = 22.3 Hz), 21.2, 17.1 (d, *J* = 33.2 Hz), 17.0 (d, *J* = 33.0 Hz). MS (EI, *m/z*, %): 276 (M$^+$, 0.12), 214 ([M-MeCOF]$^+$, 43.26). HRMS (EI): Calcd. for $C_{14}H_{11}Cl$ (M-MeCOF): 214.0549; Found: 214.0550.



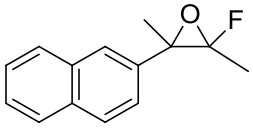
(*cis*)&(*trans*)-2-(4-chlorophenyl)-3-fluoro-3-heptyl-2-phenyloxirane (4m): 64% yield. Colorless oil. IR (film): 2957, 2929, 2857, 1492, 1448, 1195, 1092, 1016, 976, 932, 824, 760, 699, 650 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45–7.32 (m, 9H), 1.83–1.73 (m, 2H), 1.63–1.54 (m, 2H), 1.26–1.22 (m, 8H), 0.89–0.84 (M, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –128.7 (t, *J* = 19 Hz), –129.8 (t, *J* = 19 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4 (d, *J* = 2.9 Hz), 136.1 (d, *J* = 3.8 Hz), 135.5 (d, *J* = 3.8 Hz), 135.1 (d, *J* = 4.7 Hz), 134.1, 134.0, 129.4 (d, *J* = 1.4 Hz), 128.6, 128.5, 128.4, 128.33, 128.31, 128.29, 128.23, 127.9, 126.8 (d, *J* = 1.4 Hz), 101.3 (d, *J* = 271 Hz), 101.2 (d, *J* = 271.9 Hz), 69.87 (d, *J* = 19.8 Hz), 69.86 (d, *J* = 19.8 Hz), 31.6, 30.3, 30.1, 30.0, 29.8, 29.1, 28.92, 28.90, 23.32, 23.27, 22.6, 14.0. MS (EI, *m/z*, %): 346 (M^+, 0.14), 200 ([M-$C_7H_{15}COF$]$^+$, 100). HRMS (EI): Calcd. for $C_{21}H_{24}OFCl$: 346.1500; Found: 346.1499.



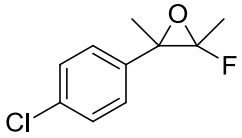
(*cis*)&(*trans*)-2-benzyl-3-(4-bromophenyl)-2-fluoro-3-phenyloxirane (4n): 60% yield. Colorless oil. IR (film): 3088, 3063, 3031, 2928, 1604, 1591, 1496, 1456, 1448, 1432, 1394, 1220, 1188, 1124, 1072, 1012, 941, 906, 887, 820, 759, 726, 699, 593 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52–7.44 (m, 2H), 7.37–7.25 (m, 10H), 7.16–7.14 (m, 2H), 3.23–3.01 (m, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –126.4 (t, *J* = 20.2 Hz), –127.5 (t, *J* = 19.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.1 (d, *J* = 3.1 Hz), 135.8 (d, *J* = 2.8 Hz), 135.7 (d, *J* = 3.7 Hz), 135.3 (d, *J* = 3.4 Hz), 133.8, 133.7, 131.7, 131.4, 129.8, 129.6, 129.5, 128.8, 128.6, 128.54, 128.49, 128.4, 127.9, 127.23, 127.20, 127.1, 122.54, 122.50, 100.8 (d, *J* = 270.6 Hz), 100.7 (d, *J* = 271.2 Hz), 70.31 (d, *J* = 19.5 Hz), 70.30 (d, *J* = 19.5 Hz), 36.7 (d, *J* = 29.5 Hz), 36.6 (d, *J* = 28.9 Hz). MS (EI, *m/z*, %): 244 ([M-BnCOF]$^+$, 26.61). HRMS (EI): Calcd. for $C_{13}H_9Br$ (M-BnCOF): 243.9888; Found: 243.9886.



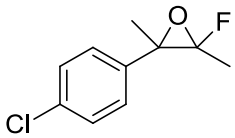
(*cis*)-2-fluoro-2,3-dimethyl-3-(naphthalen-2-yl)oxirane (***cis*-4o**): The less polar component, 33% yield. Colorless oil. IR (film): 3508, 3010, 2938, 1603, 1507, 1467, 1376, 1186, 1110, 967, 887, 798, 749, 479 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.86–7.83 (m, 3H), 7.76 (s, 1H), 7.52–7.48 (m, 2H), 7.43–7.40 (m, 1H), 1.87 (s, 3 H), 1.46 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –125.0 (q, *J* = 16.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.7, 133.0, 132.8, 128.3, 128.0, 127.7, 126.5, 126.3, 124.7 (d, *J* = 1.4 Hz), 123.4, 100.0 (d, *J* = 264.1 Hz), 64.4 (d, *J* = 20.2 Hz), 19.1, 16.0 (d, *J* = 33.2 Hz). MS (EI, *m/z*, %): 216 (M^+, 8.47). HRMS (EI): Calcd. for $C_{14}H_{13}OF$: 216.0950; Found: 216.0947.



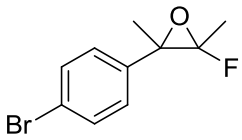
(*trans*)-2-fluoro-2,3-dimethyl-3-(naphthalen-2-yl)oxirane (***trans*-4o**): The more polar component, 37% yield. Colorless oil. The isolated compound is not stable enough for further characterization.



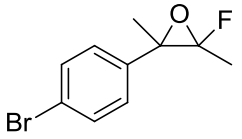
(*cis*)-2-(4-chlorophenyl)-3-fluoro-2,3-dimethyloxirane (*cis*-4p): The less polar component, 21% yield. Colorless oil. IR (film): 3011, 2974, 2938, 1908, 1601, 1494, 1475, 1377, 1286, 1189, 1115, 1093, 1074, 1015, 961, 895, 855, 831, 570, 531 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 1.76 (s, 3H), 1.42 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –124.2 (q, *J* = 16.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.0 (d, *J* = 2.8 Hz), 133.8, 128.3, 127.9, 98.8 (d, *J* = 259.1 Hz), 66.1 (d, *J* = 20.1 Hz), 19.8 (d, *J* = 2.4 Hz), 16.3 (d, *J* = 34.2 Hz). MS (EI, *m/z*, %): 200 (M^+, 2.86). HRMS (EI): Calcd. for $C_{10}H_{10}OFCl$: 200.0404; Found: 200.0403.



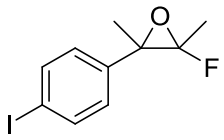
(*trans*)-2-(4-chlorophenyl)-3-fluoro-2,3-dimethyloxirane (*trans*-4p): The more polar component, 38% yield. Colorless oil. IR (film): 2997, 2939, 1600, 1495, 1386, 1187, 1116, 1092, 1046, 963, 893, 847, 832, 733, 579, 547 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (s, 4H), 1.81 (d, *J* = 16.2 Hz, 3H), 1.64 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –124.6 (q, *J* = 16.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 133.8, 128.7, 127.1 (d, *J* = 1.7 Hz), 99.6 (d, *J* = 264.4 Hz), 66.6 (d, *J* = 20 Hz), 18.9 (d, *J* = 0.9 Hz), 15.9 (d, *J* = 34.1 Hz). MS (EI, *m/z*, %): 200 (M^+, 2.79). HRMS (EI): Calcd. for $C_{10}H_{10}OFCl$: 200.0404; Found: 200.0402.



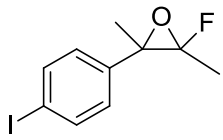
(*cis*)-2-(4-bromophenyl)-3-fluoro-2,3-dimethyloxirane (*cis*-4q): The less polar component, 16% yield. Colorless oil. IR (film): 3010, 2932, 2855, 1594, 1490, 1396, 1189, 1115, 1078, 1011, 960, 895, 853, 825, 530 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 1.75 (d, *J* = 0.9 Hz, 3H), 1.42 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –122.5 (q, *J* = 16.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3 (d, *J* = 2.8 Hz), 131.6, 127.5 (d, *J* = 1.4 Hz), 121.9, 99.5 (d, *J* = 264.1 Hz), 66.6 (d, *J* = 19.3 Hz), 18.8 (d, *J* = 1.3 Hz), 15.9 (d, *J* = 33.4 Hz). MS (EI, *m/z*, %): 244 ([^{78}Br]M^+, 2.32), 246 ([^{80}Br]M^+, 2.04). HRMS (EI): Calcd. for $C_{10}H_{10}OFBr$: 243.9899; Found: 243.9902.



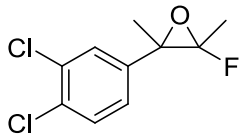
(*trans*)-2-(4-bromophenyl)-3-fluoro-2,3-dimethyloxirane (*trans*-4q): The more polar component, 30% yield. Colorless oil. IR (film): 2996, 2938, 1593, 1490, 1386, 1186, 1118, 1098, 1011, 962, 894, 846, 827, 721, 593, 570, 547 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 1.81 (d, *J* = 16.5 Hz, 3H), 1.63 (d, *J* = 1.8 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –125.2 (q, *J* = 16.8 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.6 (d, *J* = 3.0 Hz), 131.3, 128.3, 122.0, 98.7 (d, *J* = 259.9 Hz), 66.2, 19.8 (d, *J* = 2.4 Hz), 16.3 (d, *J* = 34.7 Hz). MS (EI, *m/z*, %): 246 ([^{80}Br]M^+, 2.17), 244 ([^{78}Br]M^+, 3.61). HRMS (EI): Calcd. for $C_{10}H_{10}OFBr$: 243.9899; Found: 243.9904.



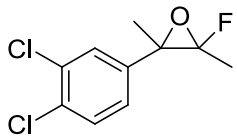
(*cis*)-2-fluoro-3-(4-iodophenyl)-2,3-dimethyloxirane (*cis*-4r): The less polar component, 30% yield. Colorless oil. IR (film): 3009, 2973, 2937, 1908, 1652, 1590, 1488, 1389, 1189, 1114, 1076, 1040, 1007, 960, 894, 851, 821, 529 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 1.75 (s, 3H), 1.42 (d, *J* = 16.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –125.0 (q, *J* = 16.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.0, 137.6, 127.7, 99.5 (d, *J* = 265.1 Hz), 93.5, 66.7 (d, *J* = 19.2 Hz), 18.8 (d, *J* = 1.9 Hz), 15.9 (d, *J* = 33.3 Hz). MS (EI, *m/z*, %): 292 (M^+, 5.93). HRMS (EI): Calcd. for $C_{10}H_{10}OFI$: 291.9760; Found: 291.9764.



(*trans*)-2-fluoro-3-(4-iodophenyl)-2,3-dimethyloxirane (***trans*-4r**): The more polar component, 38% yield. Colorless oil. The isolated compound is not stable enough for further characterization.

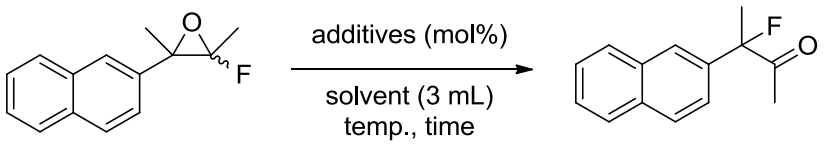


(*cis*)-2-(3,4-dichlorophenyl)-3-fluoro-2,3-dimethyloxirane (*cis*-4s): The less polar component, 24% yield. Colorless oil. IR (film): 3010, 2938, 1558, 1472, 1382, 1190, 1114, 1082, 1031, 964, 895, 835, 771 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.39 (m, 2H), 7.16–7.13 (m, 1H), 1.75 (s, 3H), 1.44 (d, *J* = 15.9 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –124.7 (q, *J* = 15.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5 (d, *J* = 2.7 Hz), 132.9, 132.2, 130.6, 127.9 (d, *J* = 1.0 Hz), 125.1, 99.3 (d, *J* = 265.5 Hz), 65.9 (d, *J* = 19.7 Hz), 18.7 (d, *J* = 1.6 Hz), 15.8 (d, *J* = 32.6 Hz). MS (EI, *m/z*, %): 234 (M^+, 2.57). HRMS (EI): Calcd. for $C_{10}H_9OFCl_2$: 234.0014; Found: 234.0015.



(*trans*)-2-(3,4-dichlorophenyl)-3-fluoro-2,3-dimethyloxirane (*trans*-4s): The more polar component, 29% yield. Colorless oil. IR (film): 3074, 2998, 2940, 1560, 1473, 1388, 1286, 1187, 1121, 1107, 1031, 967, 892, 878, 773, 673, 617 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50–7.49 (m, 1H), 7.44–7.42 (m, 1H), 7.25–7.22 (m, 1H), 1.82 (d, *J* = 16.5 Hz, 3H), 1.64–1.63 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –125.3 (q, *J* = 15.9 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8 (d, *J* = 3.8 Hz), 132.4, 132.1, 130.1, 128.7, 125.9, 98.7 (d, *J* = 260.6 Hz), 65.5 (d, *J* = 20.4 Hz), 19.6 (d, *J* = 2.4 Hz), 16.3 (d, *J* = 33.4 Hz). MS (EI, *m/z*, %): 234 (M^+, 3.78). HRMS (EI): Calcd. for $C_{10}H_9OFCl_2$: 234.0014; Found: 234.0020.

4. Initial Optimization Studies Using *Crude* Fluoroepoxide 4o as Model Substrate



crude

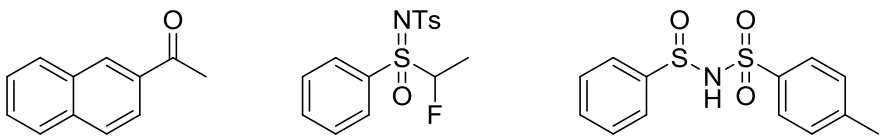
entry	additives (mol%)	solvent (3 mL)	temp. (°C)	time (h)	yield
1[a]	Null	DCM	60	10	N.R.
2[a]	AgF (20)	dioxane	60	40	N.R.
3[a]	FeF_3 (20)	dioxane	60	24	N.R.
4[a]	$AgSbF_6$ (20)	dioxane	60	24	mess
5[a]	$MgSO_4$ (60)	dioxane	60	24	N.R.
6[a]	Al_2O_3 (50)	DCM	60	16	N.R.
7[a]	$Ti(O\text{-}iPr)_4$ (20)	DCM	60	8	N.R.
8[a]	$P(n\text{-}Bu)_4$ (20)	*t*-BuOH	80	22	N.R.
9[a]	NEt_3 (20)	*t*-BuOH	80	22	N.R.
10[a]	NEt_3 (100)	dioxane	60	24	N.R.
11[a]	CH_3COOH (100)	DCM	60	5	N.R.
12[a]	H_2O (20)	neat	50	6	21[b]
13[c]	TiF_4 (10)	THF	60	48	33
14[c]	TiF_4 (20)	THF	60	18	67
15[c]	TiF_4 (30)	THF	60	18	77
16[c]	TiF_4 (40)	THF	60	24	90

[a]General conditions: Crude fluoroepoxides (0.2 mmol) were dissolved in solvent (3 mL) and stirred with additives in sealed tube. The yield was ditected by ^{19}F-NMR using $PhCF_3$ as internal standard. N.R. = No Reaction. [b]The fluoroepoxides were completely comsupted. [c]The data were from our previous work.[2]

Summary of results:

From data of the table we found that: 1) The 1,2-fluorine migration reaction did not occur in the presence of different kinds of additives (entries 1-3, 5-11). 2) An efficient 1,2-fluorine migration reaction could be obtained by adding a large amount of external fluorination reagents (entries 4, 12-16).

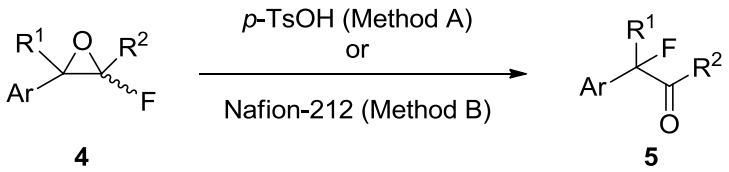
NoTE: Possible impurities in crude fluoroepoxide 4o



ketone fluorosulfoximines sulfinamide

These possible impurities can influence the 1,2-fluorine migration reaction in two ways: 1) forming complexes with the acid catalyst, thus inhibiting the to activation of fluoroepoxides; 2) competing with fluoride to capture the reactive intermediate.

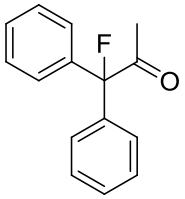
5. Typical Procedures for 1,2-Fluorine Migration Reactions



4 **5**

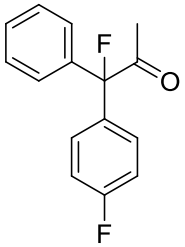
Method A: Under N_2 atmosphere, the fluoroepoxide **4b** (74 mg, 0.3 mmol) were dissolved in dichloromethane (3 mL) and stirred with *p*-TsOH (1.0 mg, 2 mol%) in sealed tube at room temperature. The reaction progress was detected by ^{19}F-NMR. When the reaction was finished (generally, the color of the reaction system turned to be light yellow from colorless), after removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to obtain α-fluoroketone **5b** (65 mg, 88% yield).

Method B: Under N_2 atmosphere, the fluoroepoxide **4b** (100 mg, 0.4 mmol) were dissolved in dichloromethane (3 mL) and stirred with Nafion-212 (1.1 mg, 0.001 mmol H^+, 0.25 mol%) in sealed tube at room temperature. The reaction progress was detected by ^{19}F-NMR. When the reaction was finished (generally, the color of the reaction system turned to be light yellow from colorless), after filtering and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to obtain 1,2-F migration product **5b** (88 mg, 88% yield).

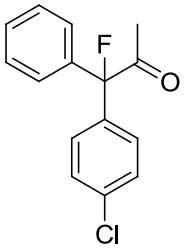


Fluoro-1,1-diphenylpropan-2-one (**5a**): Colorless oil. IR (film): 3427, 3060, 3008, 2920, 1724, 1494, 1448, 1414, 1353, 1219, 1279, 1016, 894, 761, 703, 593 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37 (s, 10H), 2.42 (d, *J* = 6 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –142.9 (q, *J* = 6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5 (d, *J* = 31.8 Hz), 138.2 (d, *J* = 23.1 Hz), 128.8 (d, *J* = 1.8 Hz), 128.4, 126.7 (d, *J* = 6.5

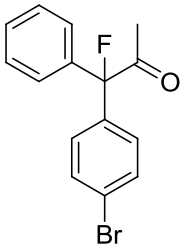
Hz), 102.2 (d, *J* = 184.5 Hz), 26.7. MS (EI, *m/z*, %): 228 (M^+, 0.33), 185 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{13}OF$: 228.0950; Found: 228.0951.



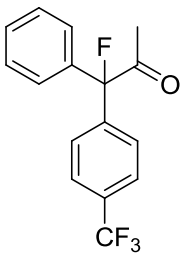
1-fluoro-1-(4-fluorophenyl)-1-phenylpropan-2-one (**5b**): IR (film): 3064, 2926, 2854, 1727, 1603, 1508, 1356, 1236, 1178, 1163, 1023, 896, 832, 812, 755, 699, 592 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36–7.33 (m, 7H), 7.03 (t, *J* = 8.6 Hz, 2H), 2.40 (d, *J* = 5.7 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –112.5 (m, 1F), -141.7 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.4 (d, *J* = 32.7 Hz), 163.0 (dd, *J* = 246.8 Hz, *J* = 2.1 Hz), 137.9 (d, *J* = 21.7 Hz), 134.2 (dd, *J* = 22.7 Hz, *J* = 3.1 Hz), 128.9 (d, *J* = 18.6 Hz), 128.9 (d, *J* = 9.5 Hz), 128.5, 126.5 (d, *J* = 7.3 Hz), 115.4 (d, *J* = 21.1 Hz), 101.8 (d, *J* = 184.5 Hz), 26.2. MS (EI, *m/z*, %): 246 (M^+, 0.29), 203 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{12}OF_2$: 246.0856; Found: 246.0859.



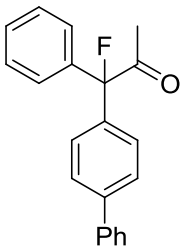
1-(4-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (**5c**): IR (film): 3063, 3037, 2925, 2853, 1728, 1491, 1449, 1356, 1179, 1094, 1014, 925, 894, 821, 758, 698, 592 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.33 (m, 9H), 2.41 (d, *J* = 5.7 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –143.2 (q, *J* = 5.7 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.1 (d, *J* = 32.3 Hz), 137.7 (d, *J* = 22.6 Hz), 136.8 (d, *J* = 23.4 Hz), 135.0 (d, *J* = 2.4 Hz), 129.1 (d, *J* = 1.8 Hz), 128.60, 128.59, 128.2 (d, *J* = 6.7 Hz), 126.5 (d, *J* = 7.2 Hz), 101.7 (d, *J* = 185.6 Hz), 26.7. MS (EI, *m/z*, %): 262 (M^+, 0.59), 219 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{12}OFCl$: 262.0561; Found: 262.0564.



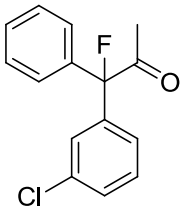
1-(4-bromophenyl)-1-fluoro-1-phenylpropan-2-one (**5d**): IR (film): 3062, 3032, 2924, 2852, 1728, 1590, 1288, 1449, 1355, 1178, 1010, 893, 817, 757, 698, 592 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52–7.27 (m, 9H), 2.42 (d, *J* = 6 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –143.8 (q, *J* = 5.9 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.0 (d, *J* = 32.4 Hz), 137.6 (d, *J* = 22.6 Hz), 137.3 (d, *J* = 22.6 Hz), 131.6, 129.1 (d, *J* = 1.4 Hz), 128.6, 128.5 (d, *J* = 8.5 Hz), 126.5 (d, *J* = 6.6 Hz), 123.3 (d, *J* = 2.4 Hz), 101.8 (d, *J* = 185.8 Hz), 26.7. MS (EI, *m/z*, %): 263 ($[M–MeCO]^+$, 100). HRMS (EI): Calcd. for $C_{13}H_9FBr$ (M–MeCO): 262.9872; Found: 262.9871.



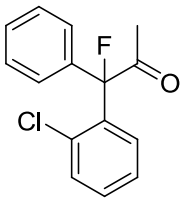
Fluoro-1-phenyl-1-(4-(trifluoromethyl)phenyl)propan-2-one (**5e**): Colorless oil. IR (film): 3065, 3033, 2928, 2856, 1728, 1619, 1495, 1449, 1412, 1357, 1328, 1170, 1129, 1070, 896, 834, 755, 697, 611, 593 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.38 (s, 5H), 2.42 (d, *J* = 6 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –62.5 (s, 3F), –145.2 (q, *J* = 5.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.7 (d, *J* = 31.4 Hz), 142.0 (d, *J* = 23.4 Hz), 137.5 (d, *J* = 21.2 Hz), 130.9 (q, *J* = 33.4 Hz), 129.2, 128.7, 127.0 (d, *J* = 7.8 Hz), 126.4 (d, *J* = 6.6 Hz), 125.3 (q, *J* = 3.1 Hz), 123.9 (q, *J* = 270.6 Hz), 101.6 (d, *J* = 185.6 Hz), 26.6. MS (EI, *m/z*, %): 296 (M^+, 1.16), 253 ($[M-MeCO]^+$,100.00). HRMS (EI): Calcd. for $C_{16}H_{12}OF_4$: 296.0824; Found: 296.0827.



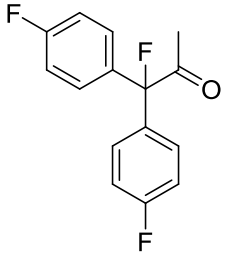
1-(biphenyl-4-yl)-1-fluoro-1-phenylpropan-2-one (**5f**): Colorless oil. IR (film): 3060, 3031, 2924, 2852, 1725, 1600, 1488, 1448, 1355, 1178, 1008, 896, 835, 763, 746, 730, 698, 596 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60–7.55 (m, 4H), 7.46–7.31 (m, 10H), 2.43 (d, *J* = 5.7 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –143.3 (q, *J* = 5.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5 (d, *J* = 31.7 Hz), 141.8 (d, *J* = 1.5 Hz), 140.4, 138.1 (d, *J* = 22.5 Hz), 137.2 (d, *J* = 22.2 Hz), 128.9, 128.5, 127.7, 127.3, 127.2, 127.1, 126.73, 126.66, 102.2 (d, *J* = 184.8 Hz), 26.7. MS (EI, *m/z*, %): 304 (M^+, 0.86), 261 ($[M–MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{19}H_{14}F$ (M–MeCO): 261.1080; Found: 261.1079.



1-(3-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (**5g**): Colorless oil. IR (film): 3065, 3030, 2925, 1728, 1595, 1574, 1421, 1212, 1186, 1103, 1026, 877, 786, 765, 738, 696, 599 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41–7.28 (m, 9H), 2.42 (d, *J* = 6 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –144.0 (q, *J* = 5.8 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.8 (d, *J* = 32.0 Hz), 140.1 (d, *J* = 23.4 Hz), 137.5 (d, *J* = 22.6 Hz), 134.5, 129.6, 129.1 (d, *J* = 1.6 Hz), 129.0 (d, *J* = 2.0 Hz), 128.6, 126.8 (d, *J* = 8.6 Hz), 126.4 (d, *J* = 7.2 Hz), 124.9 (d, *J* = 7.8 Hz), 101.5 (d, *J* = 187.3 Hz), 26.6. MS (EI, *m/z*, %): 262 (M^+, 1.16), 219 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{12}OFCl$: 262.0561; Found: 262.0560.

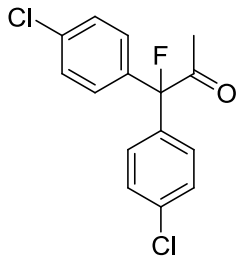


1-(2-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (**5h**): Colorless oil. IR (film): 3064, 2926, 1726, 1592, 1448, 1355, 1179, 1066, 1038, 1021, 899, 757, 700, 596 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.49–7.44 (m, 6H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 2.44 (d, *J* = 4.8 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –145.9 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.7 (d, *J* = 31.7 Hz), 137.6 (d, *J* = 20.9 Hz), 134.7 (d, *J* = 23.6 Hz), 134.5, 131.7 (d, *J* = 3.5 Hz), 130.8 (d, *J* = 2.1 Hz), 129.1, 128.8, 126.6, 126.5, 126.3, 101.9 (d, *J* = 188.2 Hz), 25.8. MS (EI, *m/z*, %): 262 (M^+, 0.43), 219 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{12}OFCl$: 262.0561; Found: 262.0557.

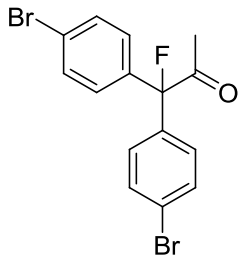


1-fluoro-1,1-bis(4-fluorophenyl)propan-2-one (**5i**): Colorless oil. IR (film): 3080, 3011, 2927, 1728, 1603, 1508, 1412, 1356, 1238, 1177, 1162, 1027, 1016, 900, 835, 591, 565 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (t, *J* = 6.6 Hz, 4H), 7.05 (t, *J* = 8.7 Hz, 4H), 2.41 (d, *J* = 6.3 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –112.4 (m, 1F), –140.8 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.3 (d, *J* = 32.4 Hz), 163.0 (dd,

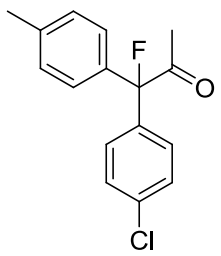
J = 248 Hz, *J* = 1.7 Hz), 133.9 (dd, *J* = 22.6 Hz, *J* = 3.3 Hz), 128.7 (t, *J* = 8.1 Hz), 115.5 (d, *J* = 21.7 Hz), 101.4 (d, *J* = 185.2 Hz), 26.5. MS (EI, *m/z*, %): 264 (M^+, 0.24), 221 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{11}OF_3$: 264.0762; Found: 264.0766.



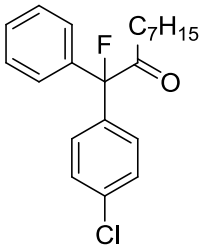
1,1-bis(4-chlorophenyl)-1-fluoropropan-2-one (**5j**): Colorless oil. IR (film): 3073, 2925, 2853, 1731, 1594, 1491, 1417, 1402, 1356, 1210, 1178, 1095, 1031, 1014, 895, 818, 593 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (d, *J* = 9 Hz, 4H), 7.30 (d, *J* = 8.7 Hz, 4H), 2.41 (d, *J* = 6.3 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –143.4 (q, *J* = 6.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.8 (d, *J* = 32.7 Hz), 136.3 (d, *J* = 22.8 Hz), 135.2 (d, *J* = 2.4 Hz), 128.8, 128.0 (d, *J* = 6.5 Hz), 101.2 (d, *J* = 186.3 Hz), 26.6. MS (EI, *m/z*, %): 296 (M^+, 0.51), 253 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{15}H_{11}OFCl_2$: 296.0171; Found: 296.0168.



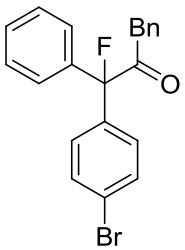
1,1-bis(4-bromophenyl)-1-fluoropropan-2-one (**5k**): Colorless oil. IR (film): 3070, 2924, 1728, 1559, 1485, 1416, 1397, 1355, 1212, 1177, 1074, 1030, 1010, 894, 812, 591, 488 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52–7.47 (m, 4H), 7.24–7.22 (m, 4H), 2.42–2.37 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –144.4 (m, *J* = 6.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.6 (d, *J* = 32.3 Hz), 136.7 (d, *J* = 22.9 Hz), 131.7, 128.2 (d, *J* = 8.2 Hz), 123.5 (d, *J* = 2.4 Hz), 101.3 (d, *J* = 187.1 Hz), 26.6. MS (EI, *m/z*, %): 341 ([M–MeCO]$^+$, 43.86). HRMS (EI): Calcd. for $C_{13}H_8FBr_2$: 340.8977; Found: 340.8980.



1-(4-chlorophenyl)-1-fluoro-1-p-tolylpropan-2-one (**5l**): Colorless oil. IR (film): 3031, 2923, 1728, 1511, 1490, 1418, 1355, 1215, 1175, 1094, 1031, 1014, 897, 811, 591 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32 (s, 4H), 7.20 (q, *J* = 8.2 Hz, 4H), 2.40 (d, *J* = 5.7 Hz, 3H), 2.35 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –143.1 (q, *J* = 5.6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.2 (d, *J* = 32.6 Hz), 139.0 (d, *J* = 1.5 Hz), 136.9 (d, *J* = 23.6 Hz), 134.9 (d, *J* = 2.5 Hz), 134.8 (d, *J* = 23.0 Hz), 129.2, 128.5, 128.2 (d, *J* = 6.5 Hz), 126.5 (d, *J* = 7.0 Hz), 101.8 (d, *J* = 184.7 Hz), 26.6, 21.1. MS (EI, *m/z*, %): 276 (M^+, 0.31), 233 ($[M\text{-}MeCO]^+$, 100.00). HRMS (EI): Calcd. for $C_{16}H_{14}OFCl$: 276.0717; Found: 276.0714.

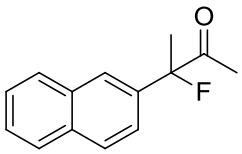


1-(4-chlorophenyl)-1-fluoro-1-phenylnonan-2-one (**5m**): Colorless oil. IR (film): 2928, 2856, 1727, 1491, 1449, 1400, 1093, 1015, 821, 755, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (s, 5H), 7.32 (s, 4H), 2.81–2.75 (m, 2H), 1.60–1.55 (m, 2H), 1.24 (s, 8H), 0.86 (t, *J* = 6.4 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –146.4 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.2 (d, *J* = 30.9 Hz), 138.0 (d, *J* = 22.0 Hz), 137.1 (d, *J* = 23.3 Hz), 134.9 (d, *J* = 2.3 Hz), 128.9 (d, *J* = 2.0 Hz), 128.51, 128.50, 128.1 (d, *J* = 8.3 Hz), 126.4 (d, *J* = 7.9 Hz), 101.8 (d, *J* = 185.4 Hz), 38.6, 31.6, 29.0, 23.05, 23.03, 22.6, 14.0. MS (EI, *m/z*, %): 346 (M^+, 0.89), 219 ($[M–C_7H_{15}CO]^+$, 78.75). HRMS (EI): Calcd. for $C_{13}H_9FCl$ ($M–C_7H_{15}CO$): 219.0377; Found: 219.0376.

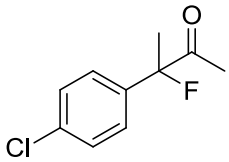


1-(4-bromophenyl)-1-fluoro-1,3-diphenylpropan-2-one (**5n**): Colorless oil. IR (film): 3088, 3062, 3030, 2925, 1732, 1588, 1488, 1449, 1396, 1318, 1185, 1122, 1073, 1028, 1010, 896, 819, 752, 724, 697, 588 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.49–7.46 (m, 10H), 7.15–7.11 (m, 2H), 4.08 (d, *J* = 3.3 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –146.6 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.0 (d, *J* = 31.7 Hz), 137.6 (d, *J* = 22.2 Hz), 137.3 (d, *J* = 23.0 Hz), 132.8, 131.5, 129.9, 129.0, 128.6, 128.5, 128.4 (d, *J* = 8.1 Hz), 127.1, 126.5 (d, *J* = 7.6 Hz), 123.2 (d, *J* = 3.3 Hz), 102.2 (d, *J* = 186.7 Hz),

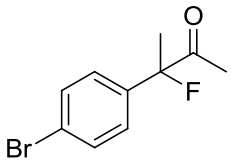
45.2. MS (EI, *m/z*, %): 263 ([M–BnCO]$^+$, 81.90). HRMS (EI): Calcd. for $C_{13}H_9FBr$ (M–BnCO): 262.9872; Found: 262.9868.



3-fluoro-3-(naphthalen-2-yl)butan-2-one (**5o**): Colorless oil. IR (film): 3060, 2988, 2936, 1725, 1600, 1507, 1373, 1355, 1126, 1108, 907, 858, 820, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93–7.82 (m, 4H), 7.53–7.48 (m, 3H), 2.26 (d, *J* = 5.1 Hz, 3H), 1.87 (d, *J* = 23.1 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –154.7 (qq, *J* = 22.8 Hz, *J* = 4.9 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.1 (d, *J* = 30.8 Hz), 136.3 (d, *J* = 21.8 Hz), 133.0 (d, *J* = 2.4 Hz), 128.6, 128.6, 128.3, 127.7, 126.6, 126.6, 123.3 (d, *J* = 9.9 Hz), 121.9 (d, *J* = 7.6 Hz), 100.7 (d, *J* = 182.7 Hz), 24.6, 24.2 (d, *J* = 23.6 Hz). MS (EI, *m/z*, %): 216 (M$^+$, 10.44), 173 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{14}H_{13}OF$: 216.0950; Found: 216.0948.

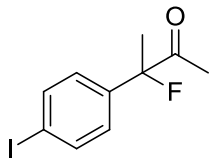


3-(4-chlorophenyl)-3-fluorobutan-2-one (**5p**): Colorless oil. IR (film): 2989, 2928, 2855, 1729, 1598, 1491, 11356, 1246, 1096, 1014, 904, 842, 819, 582 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (s, 4H), 2.22 (d, *J* = 5.1 Hz, 3H), 1.76 (d, *J* = 23.1 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –154.4 (qq, *J* = 22.3 Hz, *J* = 5.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.9 (d, *J* = 30.1 Hz), 137.3 (d, *J* = 22.5 Hz), 134.5, 128.8 (d, *J* = 1.4 Hz), 125.7 (d, *J* = 9.4 Hz), 100.2 (d, *J* = 184.5 Hz), 24.5, 24.2 (d, *J* = 23.7 Hz). MS (EI, *m/z*, %): 200 (M$^+$, 5.94), 157 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{10}H_{10}OFCl$: 200.0404; Found: 200.0400.

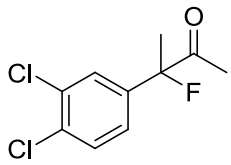


3-(4-bromophenyl)-3-fluorobutan-2-one (5q): Colorless oil. IR (film): 2989, 2936, 2854, 1728, 1592, 1488, 1396, 1356, 1235, 1010, 904, 840, 814, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.22 (d, *J* = 5.1 Hz, 3H), 1.75 (d, *J* = 22.5 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ –154.9 (qq, *J* = 22.8 Hz, *J* = 5.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8 (d, *J* = 31.0 Hz), 138.8 (d, *J* = 22.7 Hz), 131.8, 126.0 (d, *J* = 9.6 Hz), 122.7, 100.2 (d, *J* = 183.8 Hz), 22.5, 24.2 (d, *J* =

23.8 Hz). MS (EI, *m/z*, %): 246 ([^{80}Br]M^+, 2.55), 244 ([^{48}Br]M^+, 2.64), 201([M-MeCO]$^+$, 100). HRMS (EI): Calcd. for $C_{10}H_{10}OFBr$: 243.9899; Found: 243.9896.

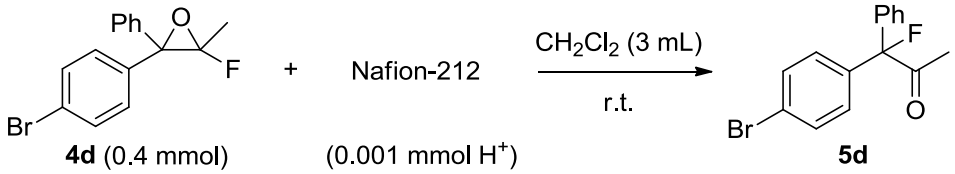


3-fluoro-3-(4-iodophenyl)butan-2-one (**5r**): Colorless oil. IR (film): 2988, 2936, 2853, 1728, 1587, 1484, 1392, 1355, 1232, 1109, 1006, 904, 838, 809, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.22 (d, *J* = 5.1 Hz, 3H), 1.74 (d, *J* = 22.8 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −155.0 (qq, *J* = 22.3 Hz, *J* = 5.6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8 (d, *J* = 31.1 Hz), 138.7 (d, *J* = 22.7 Hz), 137.8, 126.2 (d, *J* = 9.5 Hz), 100.2 (d, *J* = 184.4 Hz), 94.4, 24.5, 24.1 (d, *J* = 23.0 Hz). MS (EI, *m/z*, %): 292 (M^+, 9.18), 249 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{10}H_{10}OFI$: 291.9760; Found: 291.9762.



3-(3,4-dichlorophenyl)-3-fluorobutan-2-one (**5s)**: Colorless oil. IR (film): 3096, 2991, 2939, 1728, 1472, 1382, 1356, 1238, 1140, 1126, 1031, 912, 832, 678, 606 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.28–7.25 (m, 1H), 2.25 (d, *J* = 5.1 Hz, 3H), 1.75 (d, *J* = 23.1 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −155.3 (qq, *J* = 23.1 Hz, *J* = 4.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5 (d, *J* = 30.6 Hz), 139.1 (d, *J* = 22.9 Hz), 133.0 (d, *J* = 1.4 Hz), 132.8, 130.6 (d, *J* = 1.5 Hz), 126.4 (d, *J* = 9.9 Hz), 123.7 (d, *J* = 9.9 Hz), 99.6 (d, *J* = 185.7 Hz), 24.6, 24.2 (d, *J* = 23.1 Hz). MS (EI, *m/z*, %): 234 (M^+, 11.00), 191 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{10}H_9OFCl_2$: 234.0014; Found: 234.0013.

6. The Reuse of Nafion-212 as Catalyst



4d (0.4 mmol) (0.001 mmol H^+) **5d**

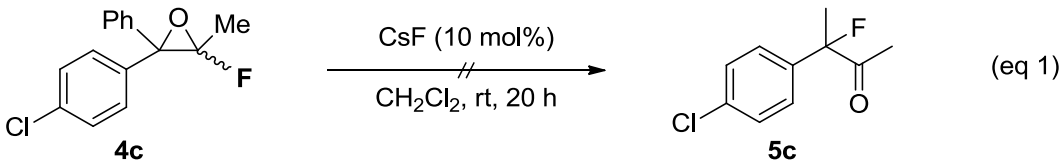
entry[a]	run	yield[b]
1	1st	83%
2	2nd	76%
3	3rd	84%
4	4th	72%
5	5th	77%
6	6th	84%
7	7th	78%
8	8th	85%

[a] Conditions: fluoroepoxide **4d** (0.4 mmol) was dissolved in CH_2Cl_2 (3 mL) and stirred with Nafion-212 (1.1 mg, 0.001 mmol H^+, 0.25 mol%) in sealed tube. The reaction progress was determined by ^{19}F NMR. [b] Yields given refer to the isolated yields of analytically pure products **5d**.

Under N_2 atmosphere, fluoroepoxide **4d** (123 mg, 0.4 mmol) was dissolved in dichloromethane (3 mL), and stirred with recovered Nafion-212 (1.1 mg, 0.001 mmol H^+, 0.25 mol%) in sealed tube at room temperature. The reaction progress was detected by ^{19}F NMR. After filtering to recover the Nafion-212 and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to get the product **5d**. The recycled Nafion-212 could be reused after soaking in HCl (1 M, aq.) for 6 hours and drying under an infrared lamp.

7. Mechanism Studies

7.1 CsF-Promoted Rearrangement of Fluoroepoxide 1c

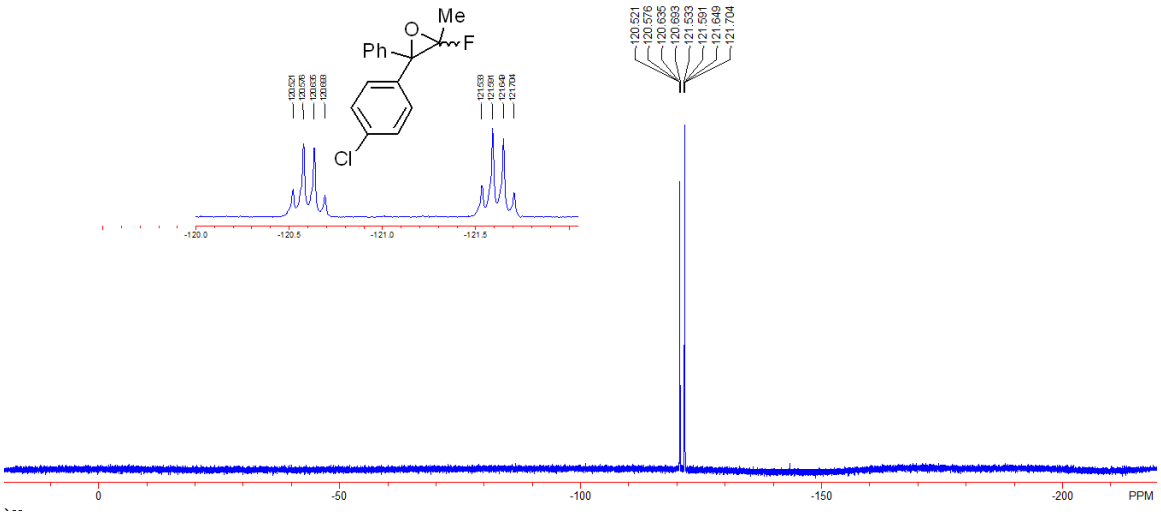


4c **5c** (eq 1)

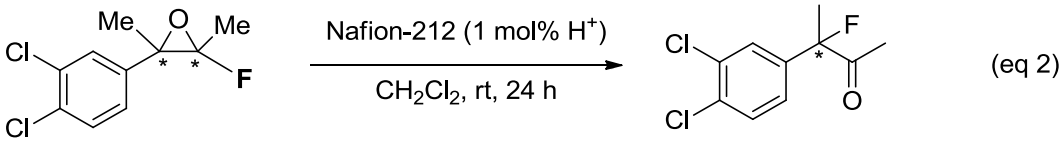
Under N_2 atmosphere, fluoroepoxide **4c** (52 mg, 0.2 mmol) was dissolved in dichloromethane (2 mL), and stirred with CsF (3 mg, 10 mol%) in sealed tube at room temperature for 20 h. The reaction system

was detected by ^{19}F NMR. From the spectra we can see there are only the signals of unreacted fluoroepoxide **4c**.

The ^{19}F NMR spectra of the reaction system:



7.2 The Rearrangement of Enantiomerically Enriched Fluoroepoxide 4s

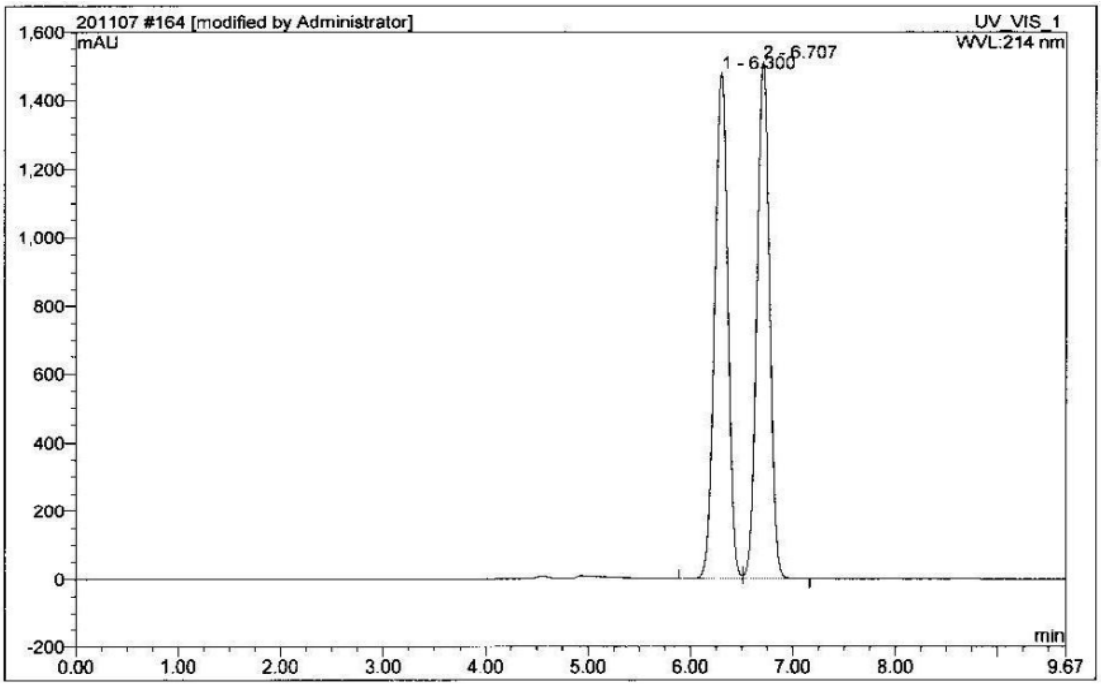


cis-**4s** (82% *ee*) **5s**, 65% yield (53% *ee*)

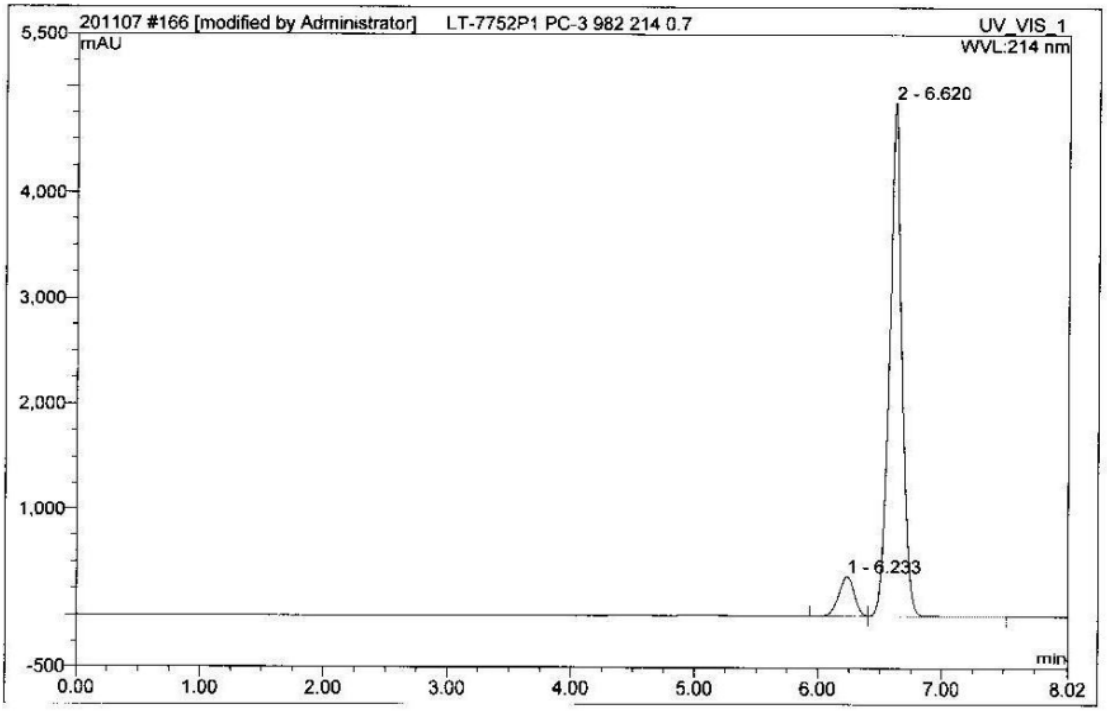
Under N_2 atmosphere, fluoroepoxide *cis*-**4s** (24 mg, 0.1 mmol, *ee* = 82%) was dissolved in dichloromethane (1 mL), and stirred with Nafion-212 (1.1 mg, 0.001 mmol H^+, 1 mol%) in sealed tube at room temperature for 1 day. After filtering and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to get the product **5s** (16 mg, 65%, *ee* = 53%).

The Enantiomerically enriched fluoroepoxide *cis*-**4s** (*ee* = 82%) was prepared from optically pure sulfoximine **6a** [1]. For ***cis*-4s**, the enantiomeric excess was determined by Lux 5u Cellulose-2 (4.6 mm × 250 mm), Hexane / IPA= 98 / 2, 0.7 mL/min, λ = 214 nm, t_R (minor) = 6.23 min, t_R (major) = 6.62 min on DIOMEX Ultimate 3000; 82% *ee*.

HPLC chart of ***cis*-4s**



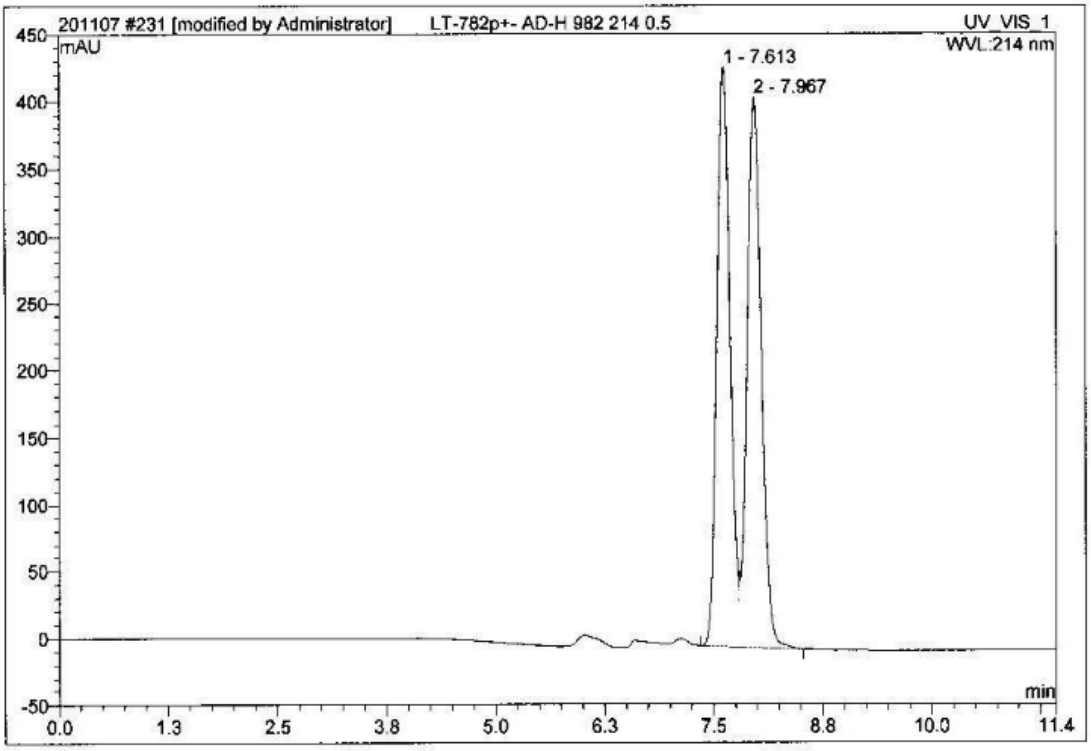
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.30	n.a.	1479.443	220.252	49.99	n.a.	BM
2	6.71	n.a.	1510.935	220.326	50.01	n.a.	MB*
Total:			2990.378	440.578	100.00	0.000	



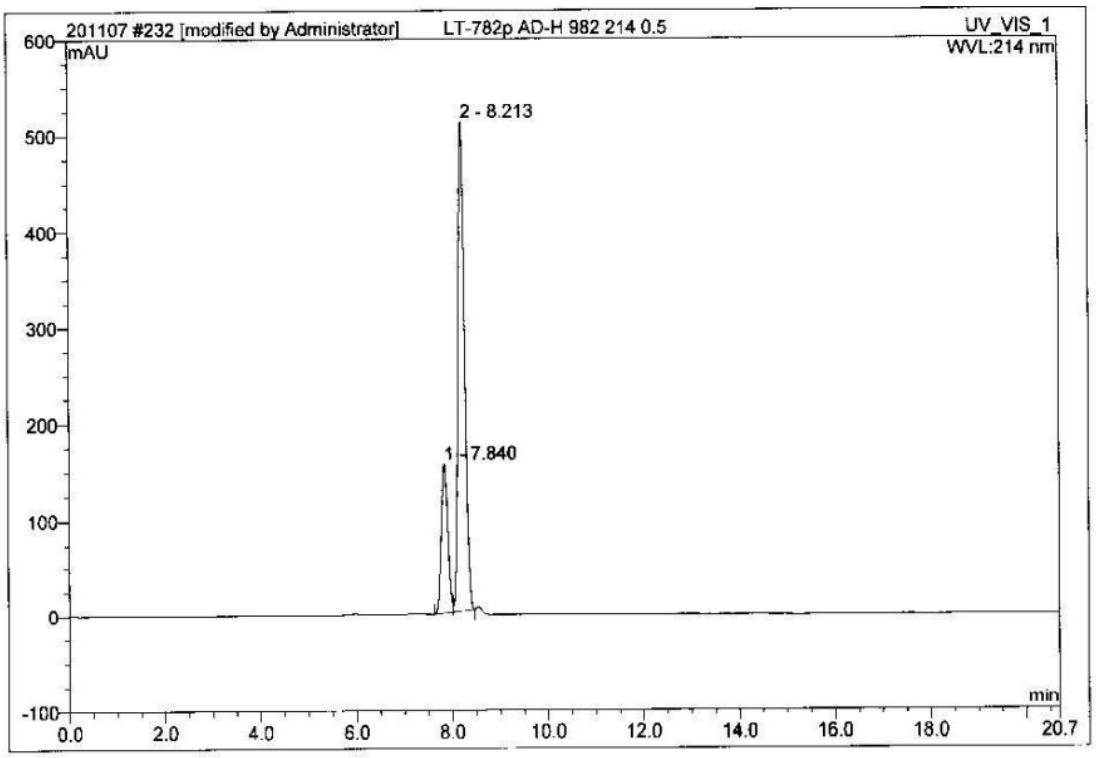
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.23	n.a.	372.643	54.892	8.81	n.a.	BM *
2	6.62	n.a.	4855.666	567.960	91.19	n.a.	MB*
Total:			5228.309	622.852	100.00	0.000	

For 1,2-fluorine migration products **5s**, the enantionmetric excess was determined by CHIRAPAK AD-H (4.6 mm × 250 mm, 5 um), Hexane / IPA= 98 / 2, 0.5 mL/min, λ = 214 nm, t_R (minor) = 7.84 min, t_R (major) = 8.21 min on DIOMEX Ultimate 3000s; 53% *ee*.

HPLC chart of **5s**

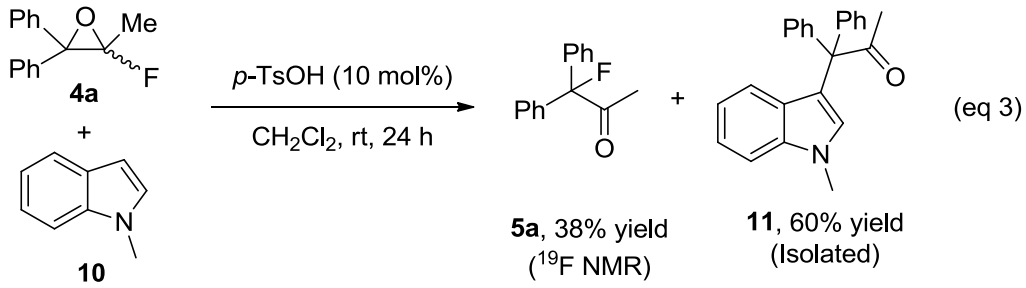


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.61	n.a.	431.232	75.781	49.17	n.a.	BM *
2	7.97	n.a.	409.645	78.353	50.83	n.a.	MB*
Total:			840.877	154.134	100.00	0.000	



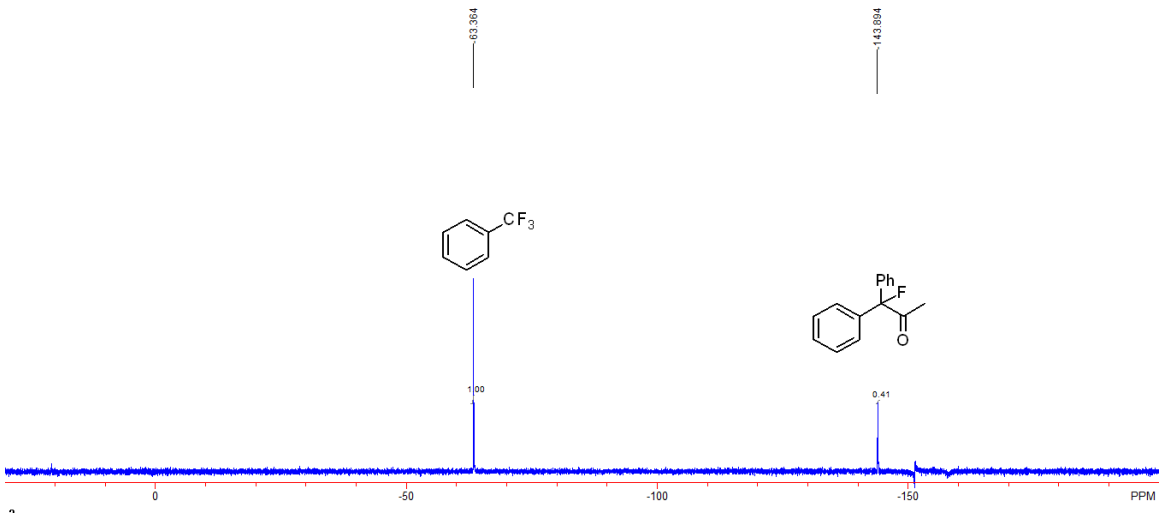
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.84	n.a.	155.264	24.721	23.53	n.a.	BM *
2	8.21	n.a.	509.102	80.362	76.47	n.a.	MB*
Total:			664.366	105.083	100.00	0.000	

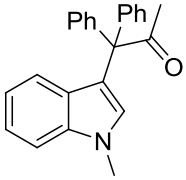
7.3 The Reaction of Fluoroepoxide 4a with *N*-methyl Indole 10



Under N_2 atmosphere, monofluorinated epoxide **4a** (46 mg, 0.2 mmol) and N-methyl indole **10** (26 mg, 0.2 mmol, 1.0 equiv.) were dissolved in dichloromethane (2 mL), and stirred with *p*-TsOH (3.6 mg, 10 mol%) in sealed tube at room temperature for 20 h. The reaction system was detected by ^{19}F-NMR using $PhCF_3$ as internal standard. After removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 30 : 1 as eluent to get the major product **11** (41 mg, 60%).

The ^{19}F NMR spectra of the reaction system





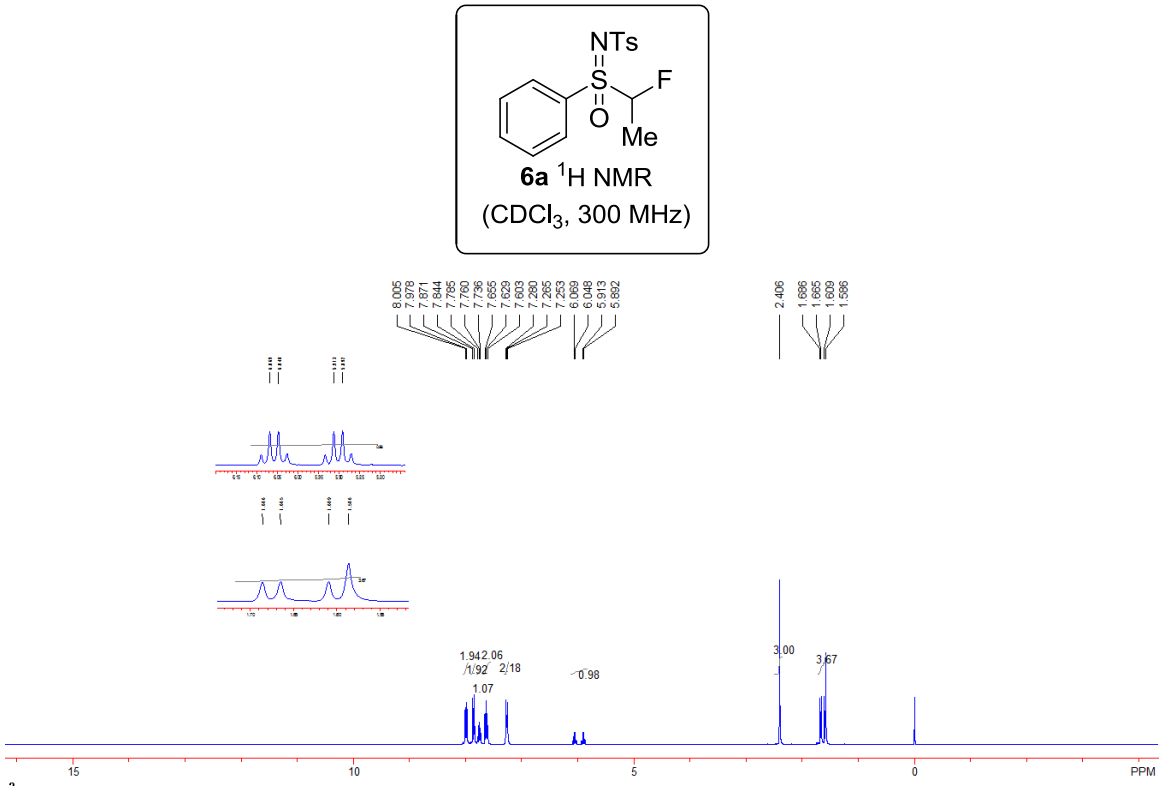
1-(1-methyl-1H-indol-3-yl)-1,1-diphenylpropan-2-one (11): Brown solid. Mp: 183-185 ^{o}C. IR (film): 3055, 2926, 1708, 1532, 1485, 1446, 1350, 1154, 771, 745, 734, 704, 696, 579 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32–7.17 (m, 12H), 6.94–6.93 (m, 3H), 3.78 (s, 3H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 142.6, 137.5, 130.1, 129.7, 127.9, 127.2, 126.6, 121.9, 121.8, 119.4, 115.2, 109.3, 67.6, 32.9, 29.5. MS (EI, *m/z*, %): 339 (M^+, 0.35), 296 ([M–MeCO]$^+$, 100.00). HRMS (EI): Calcd. for $C_{24}H_{21}NO$: 339.1623; Found: 339.1628.

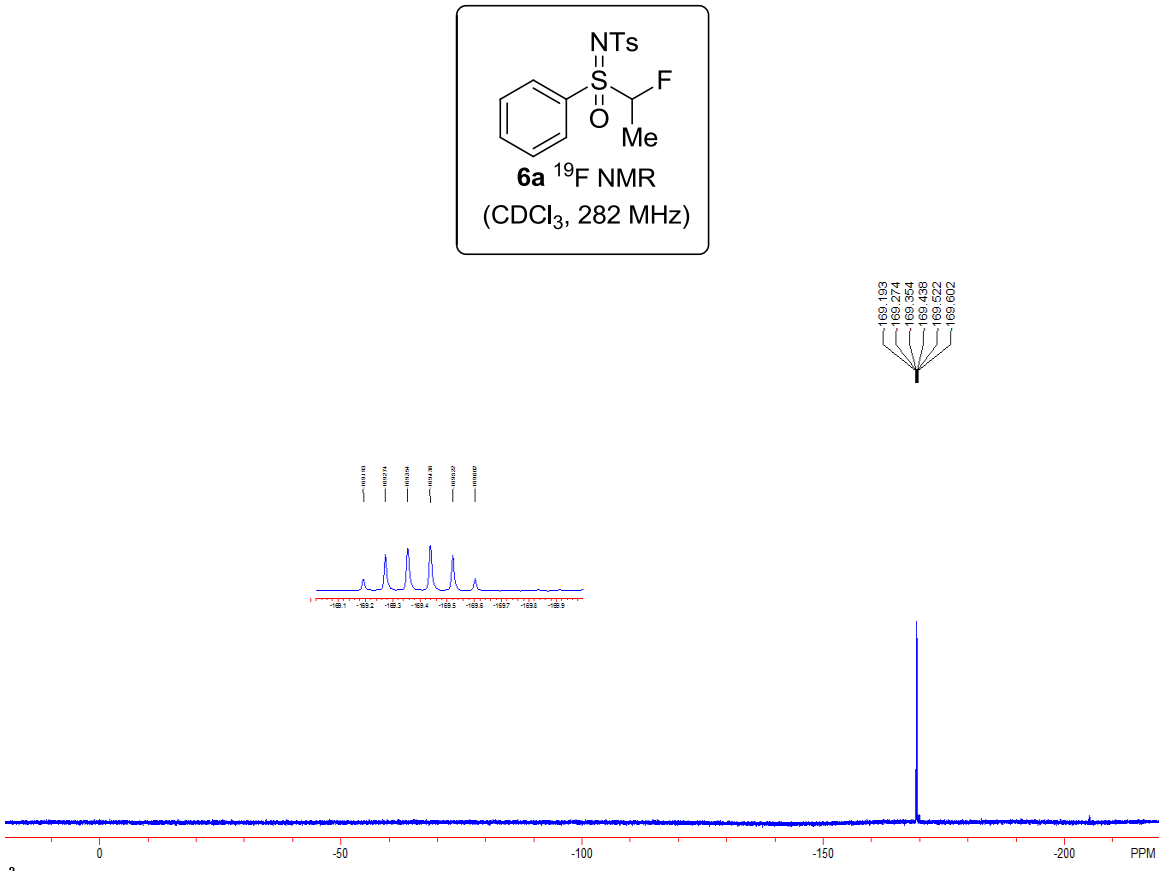
8. References

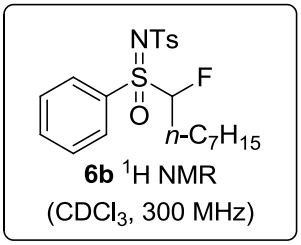
(1) X. Shen, W. Zhang, L. Zhang, T. Luo, X. Wan, Y. Gu, J. Hu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6966.

(2) W. Zhang, J. Hu, *Adv. Synth.Catal.* **2010**, *352*, 2799.

9. NMR Spectra of Isolated Products

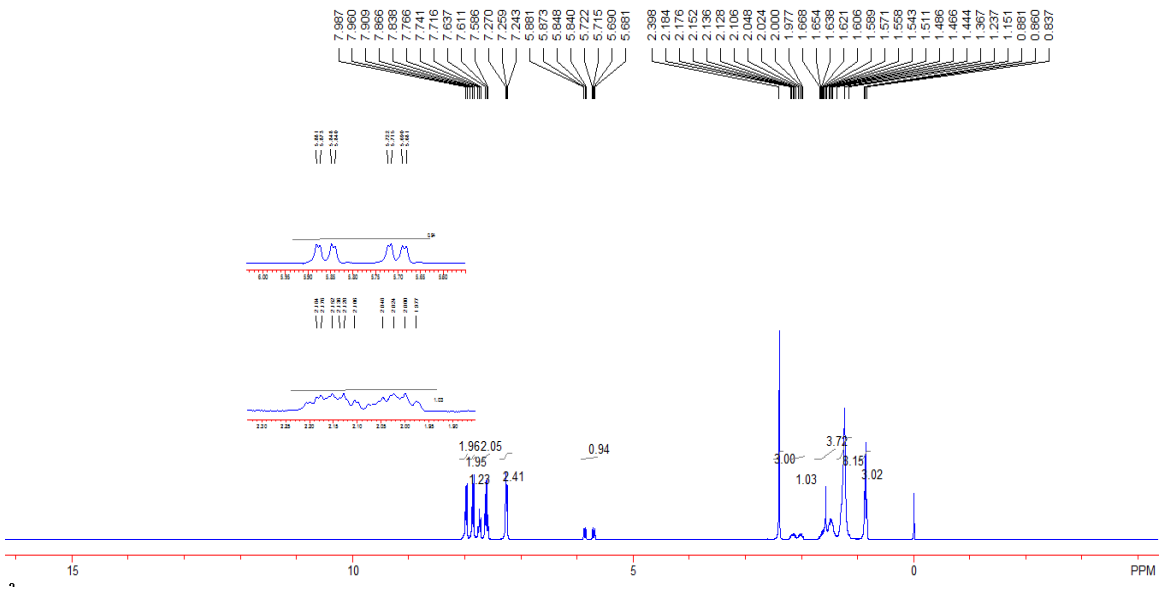


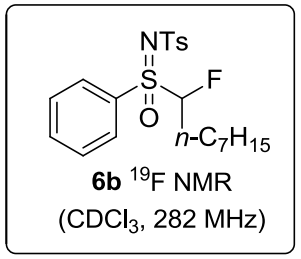




6b ^{1}H NMR

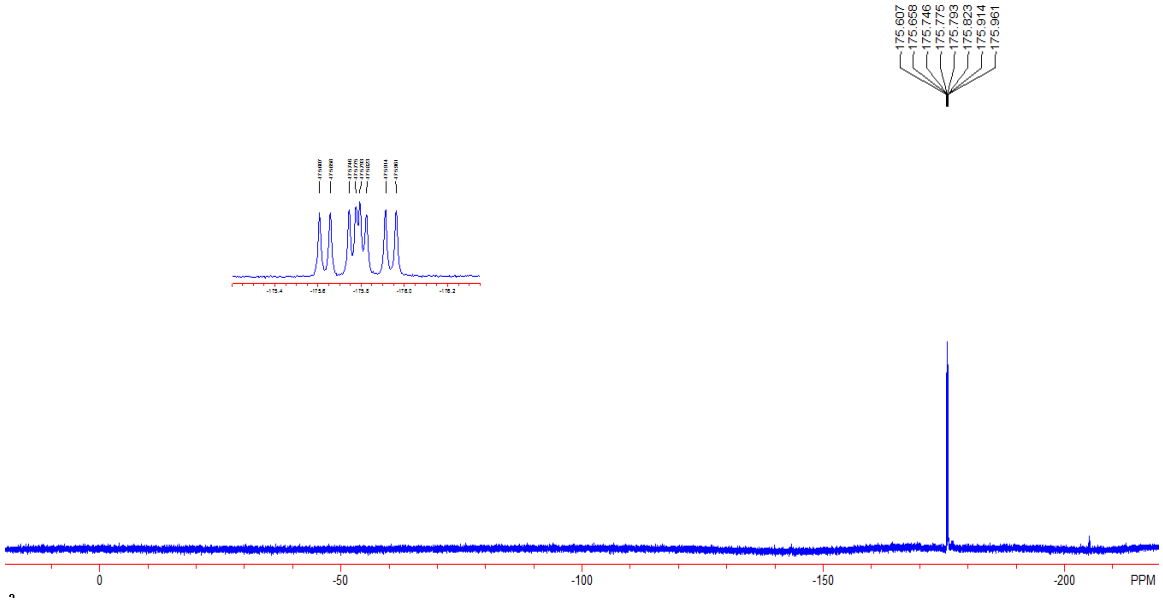
($CDCl_3$, 300 MHz)

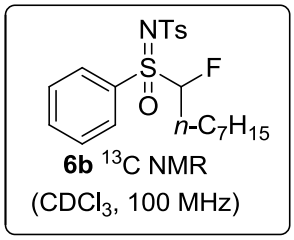




6b ^{19}F NMR

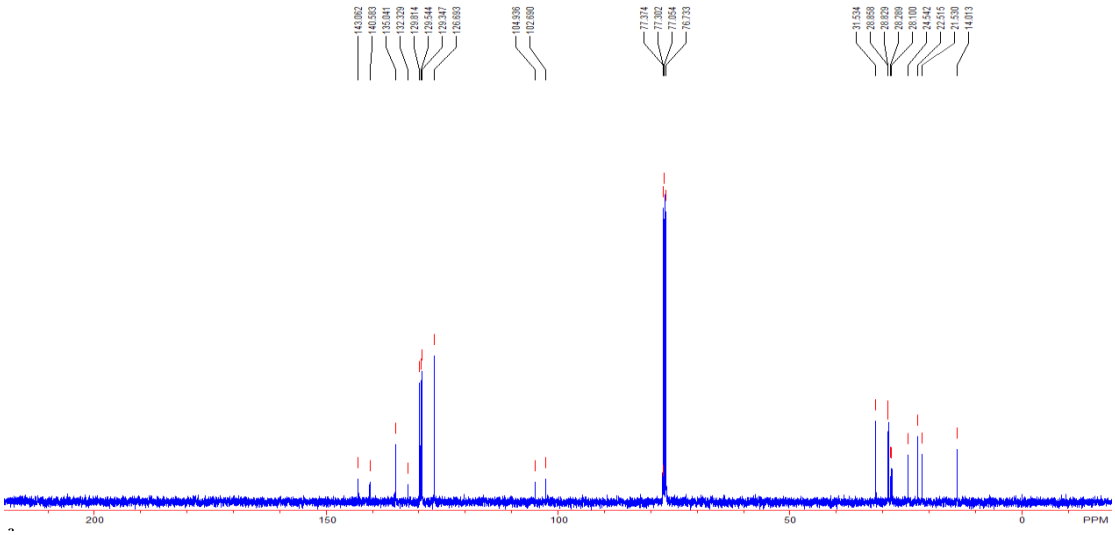
($CDCl_3$, 282 MHz)

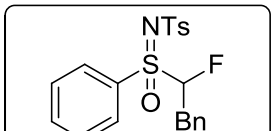




6b ^{13}C NMR

($CDCl_3$, 100 MHz)





6c ^{1}H NMR

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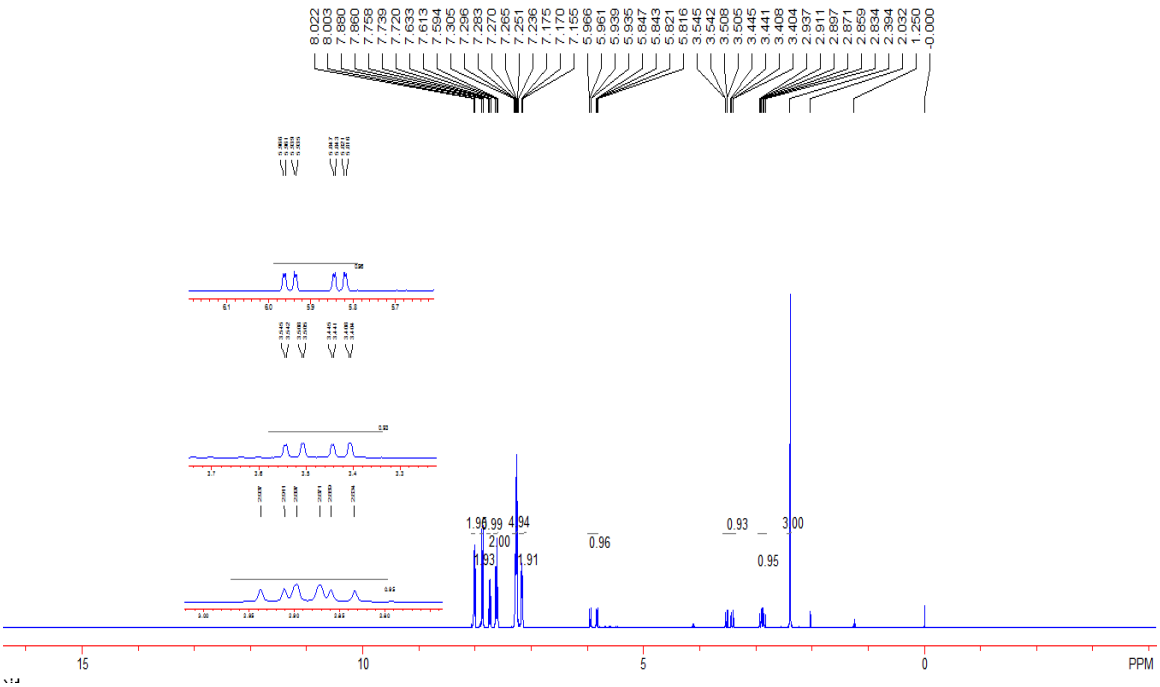
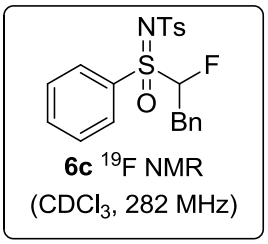
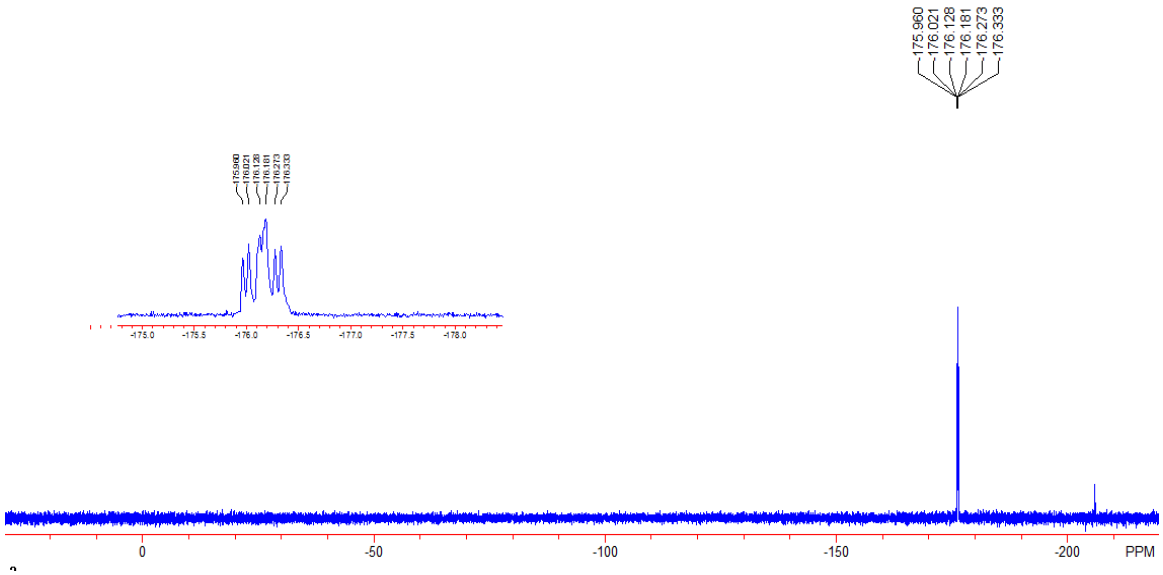
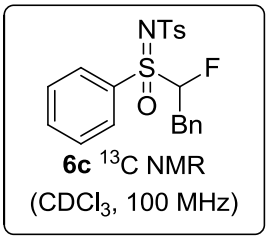




6c ^{19}F NMR
($CDCl_3$, 282 MHz)





6c ^{13}C NMR
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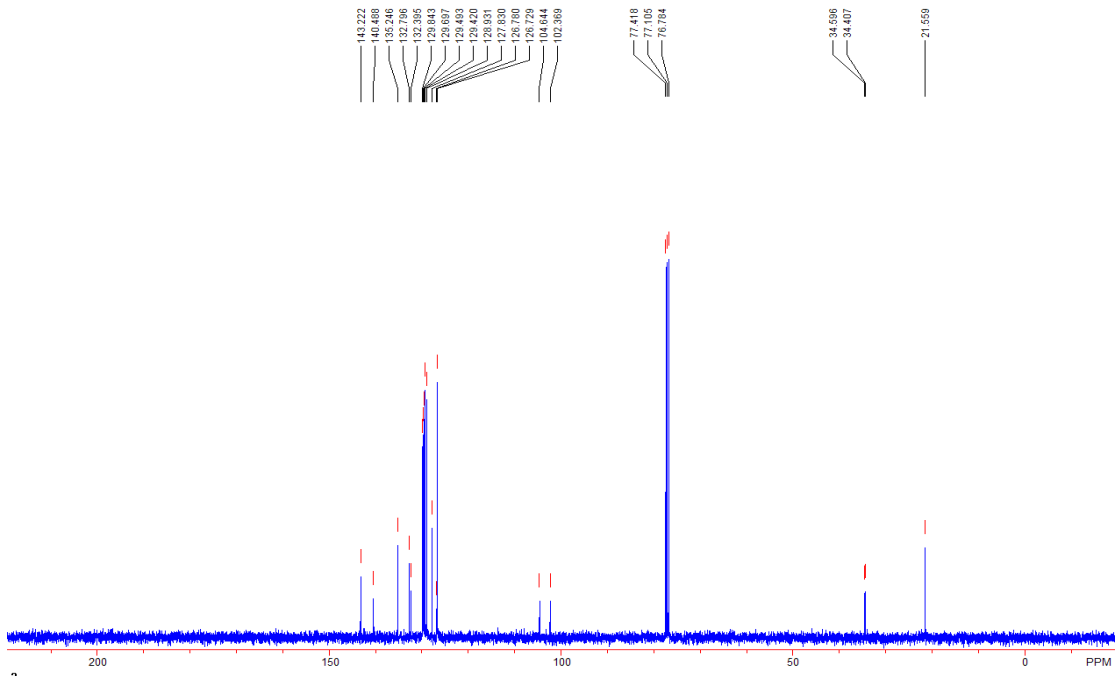
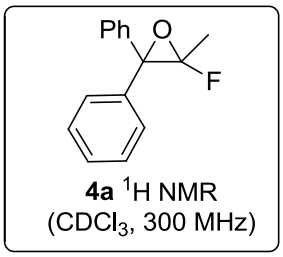
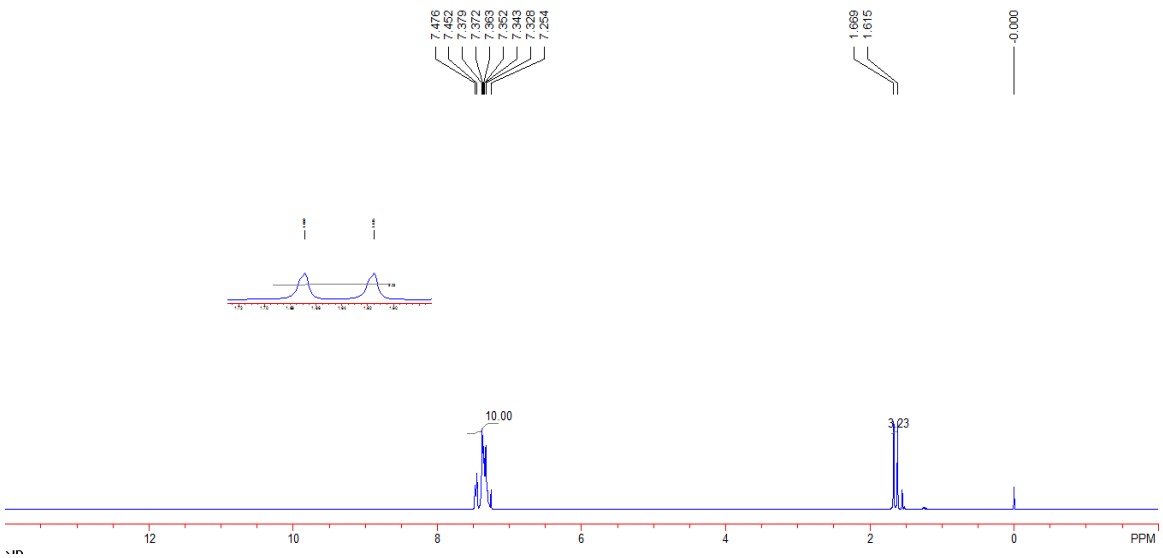
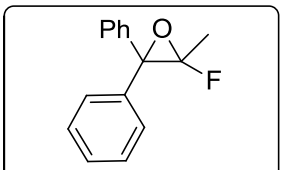


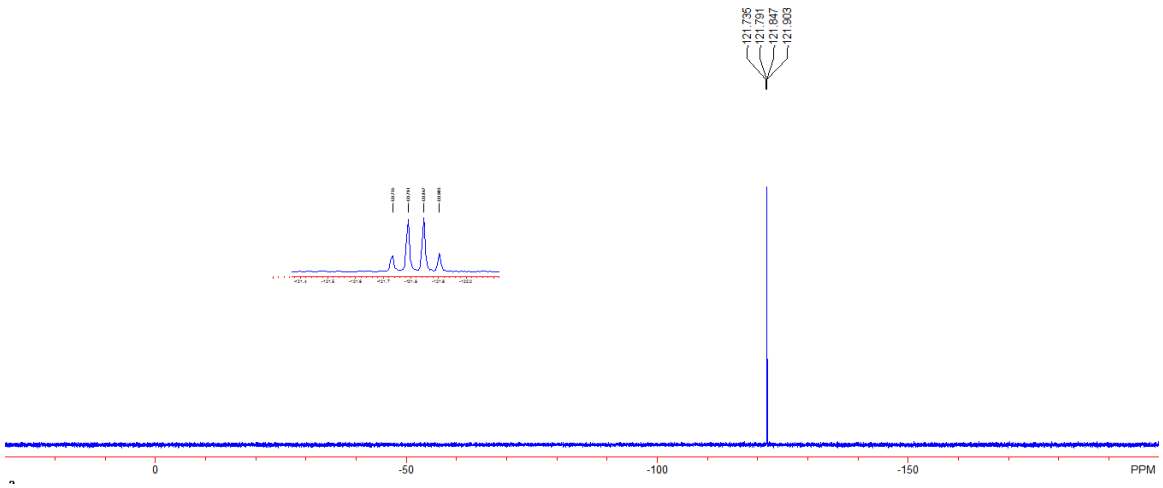


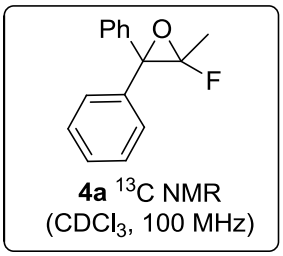
4a ^{1}H NMR
($CDCl_3$, 300 MHz)





4a ^{19}F NMR
($CDCl_3$, 282 MHz)





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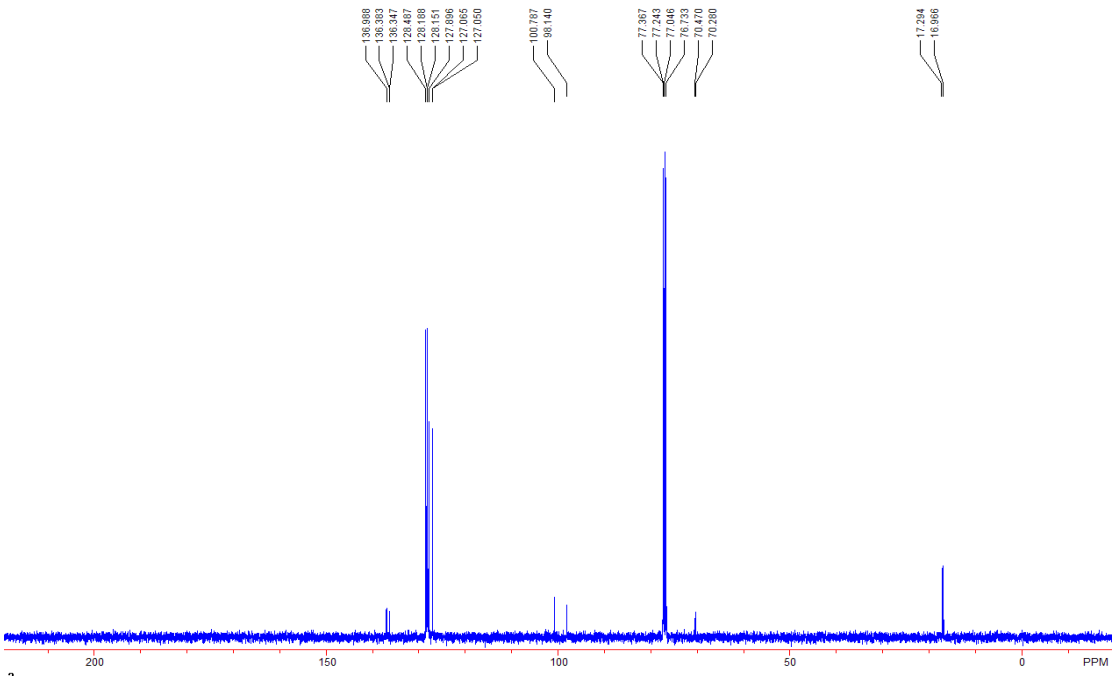

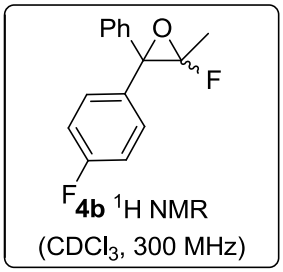

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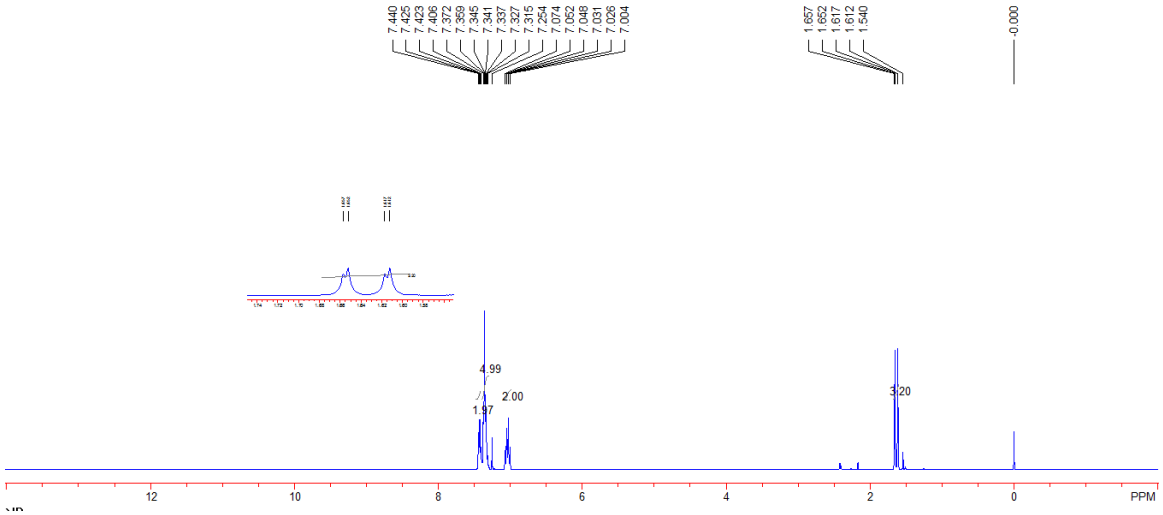

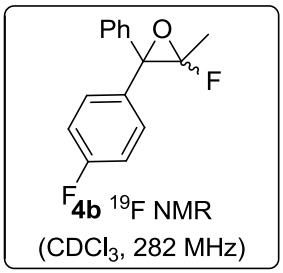

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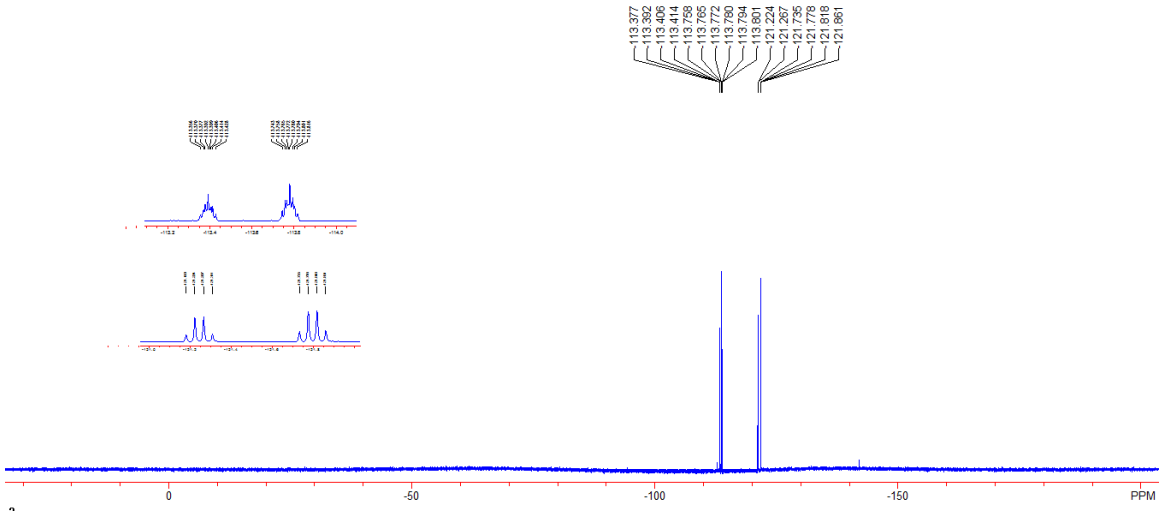

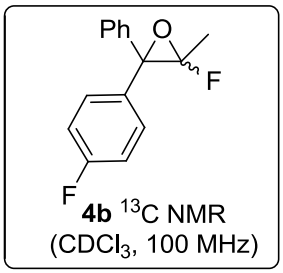

4b ^{13}C NMR
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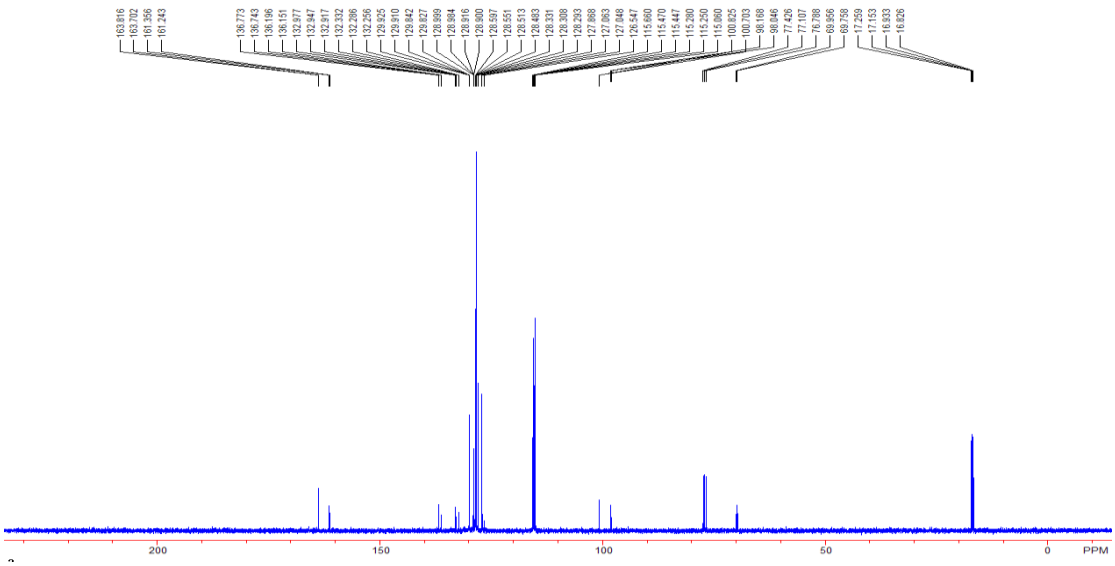

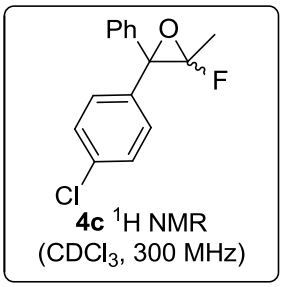

4c ^{1}H NMR
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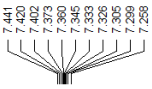

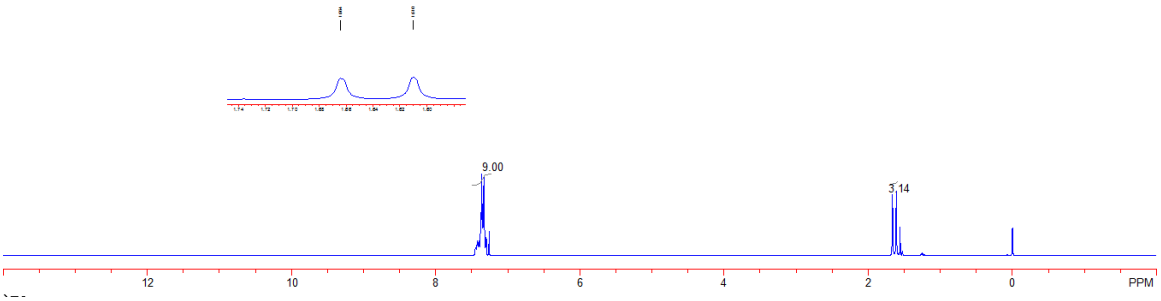

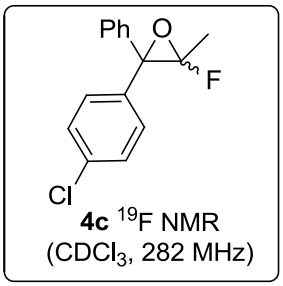

4c ^{19}F NMR
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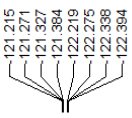

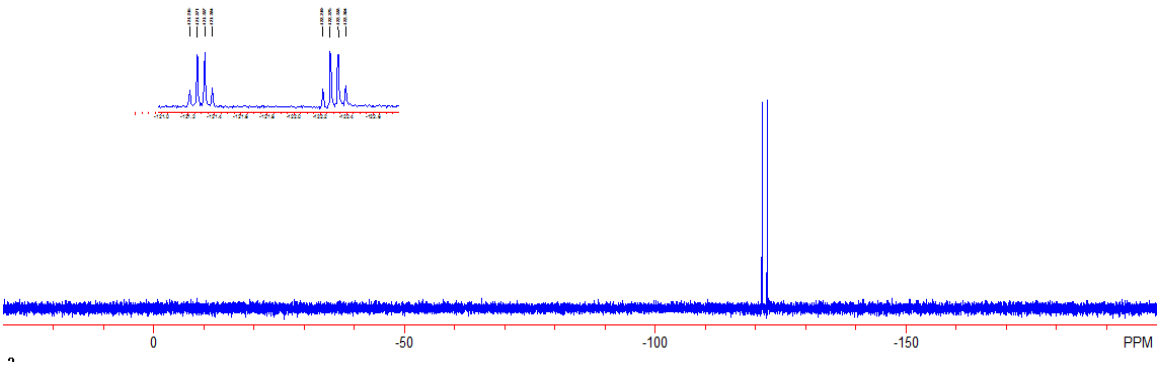

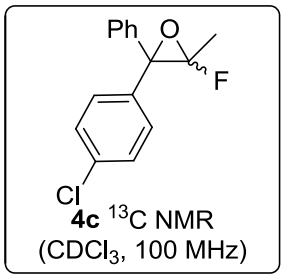

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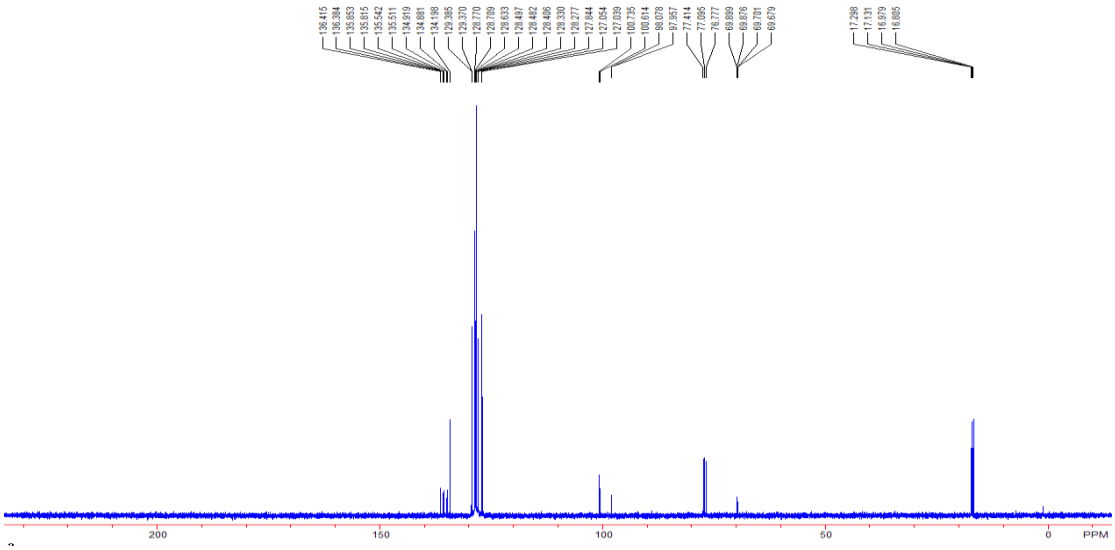

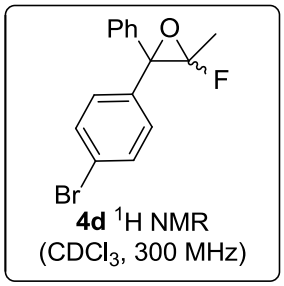

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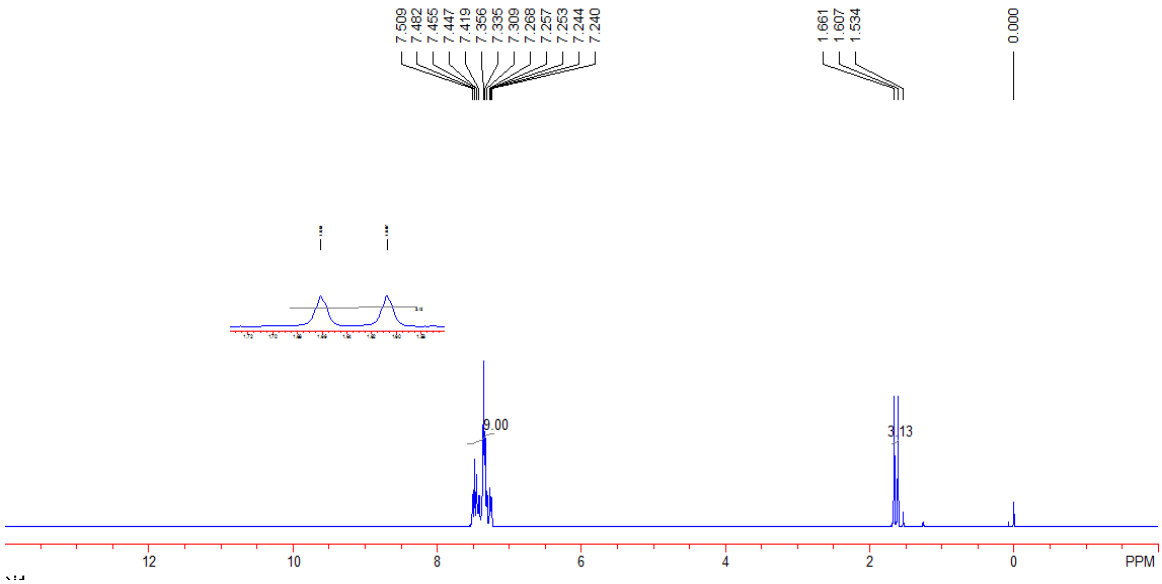

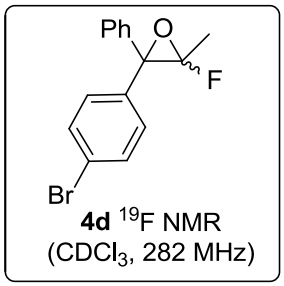

4d ^{19}F NMR
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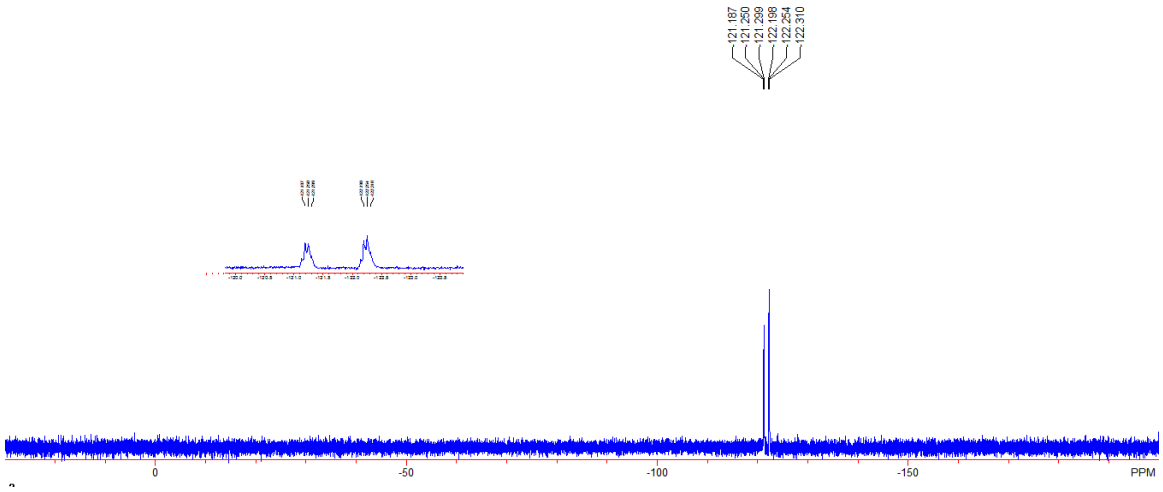

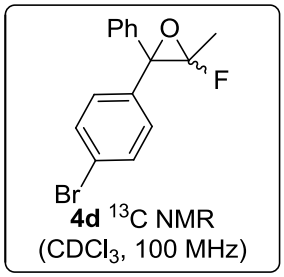

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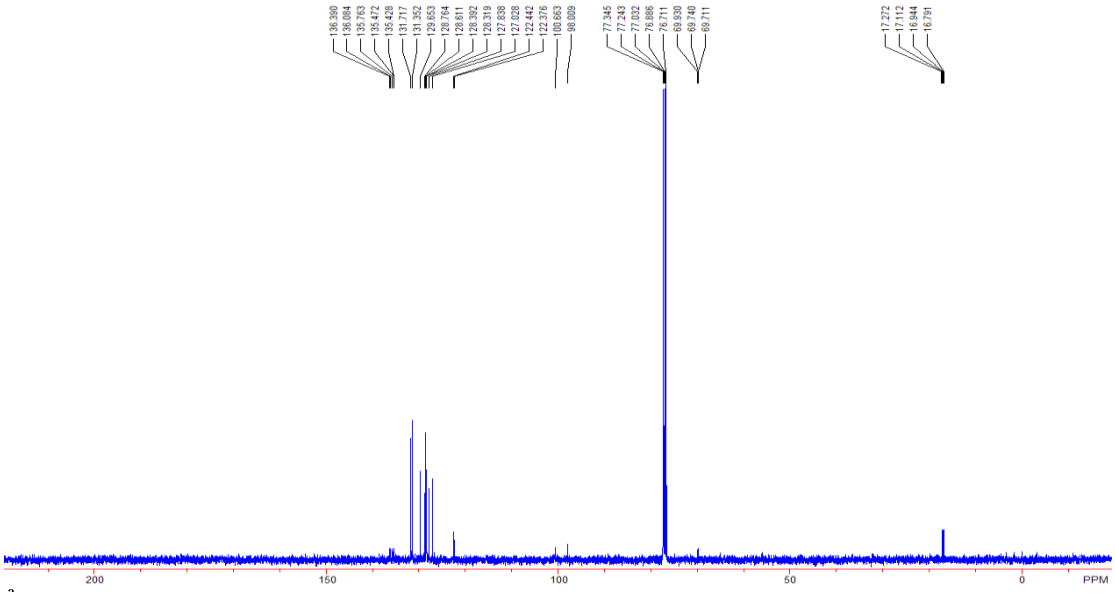

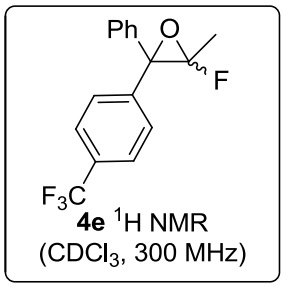

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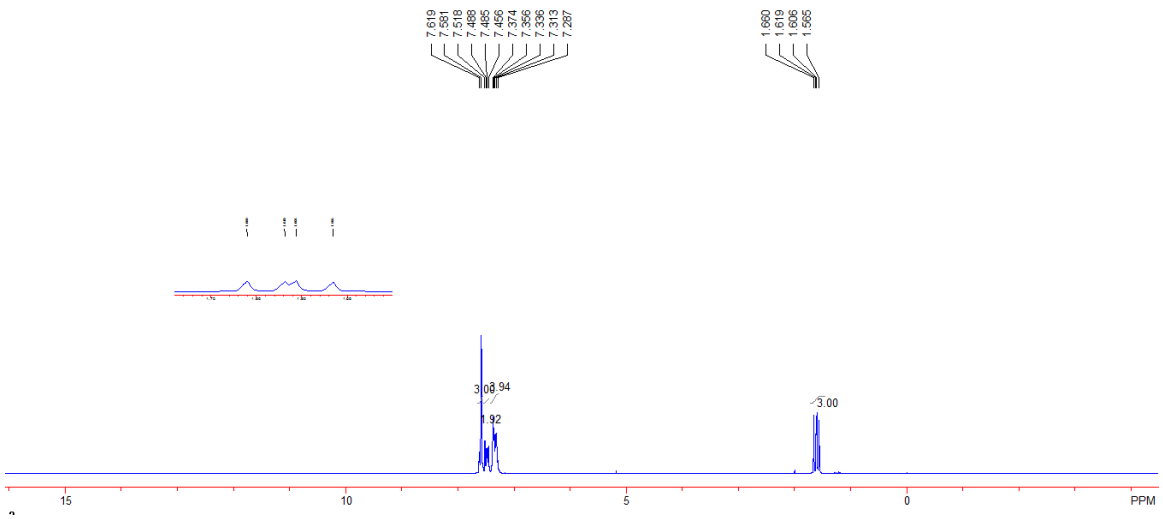

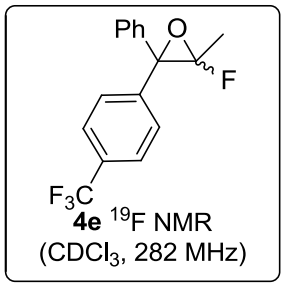

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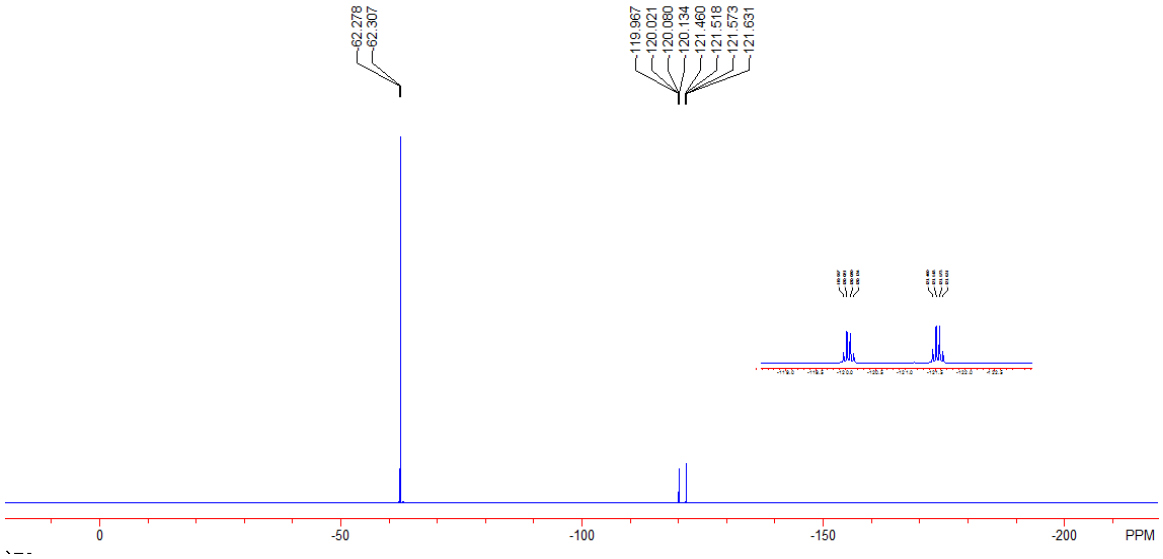

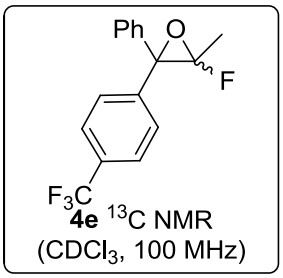

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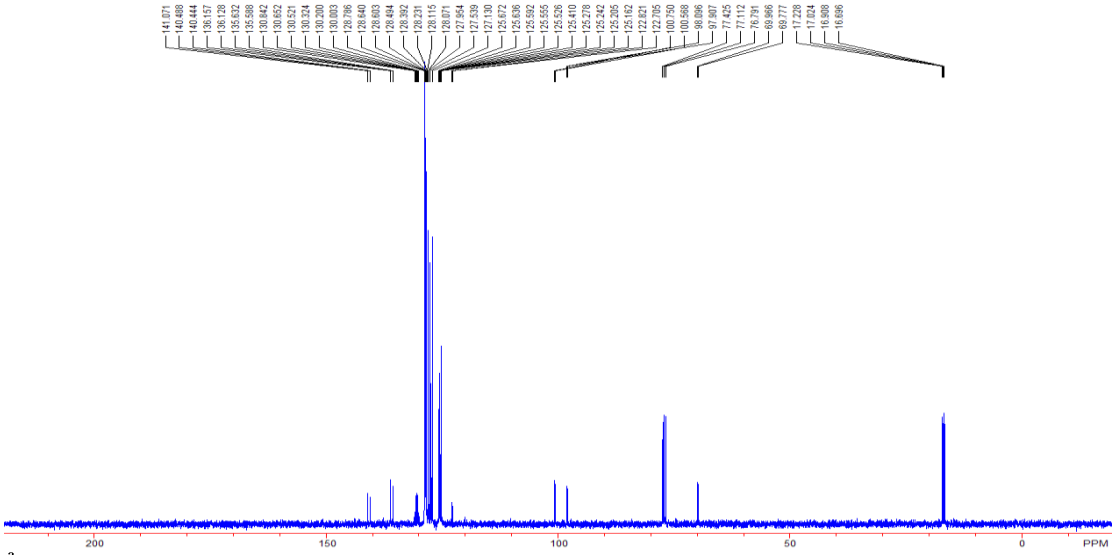

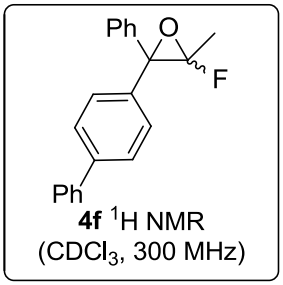

4f ^{1}H NMR
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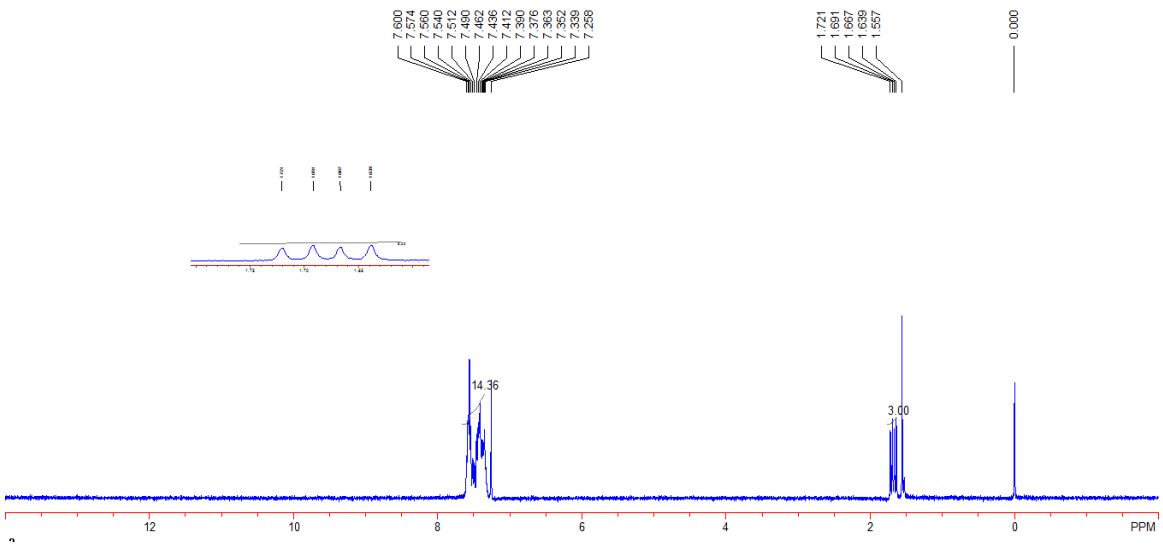

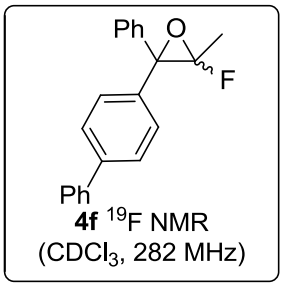

4f ^{19}F NMR
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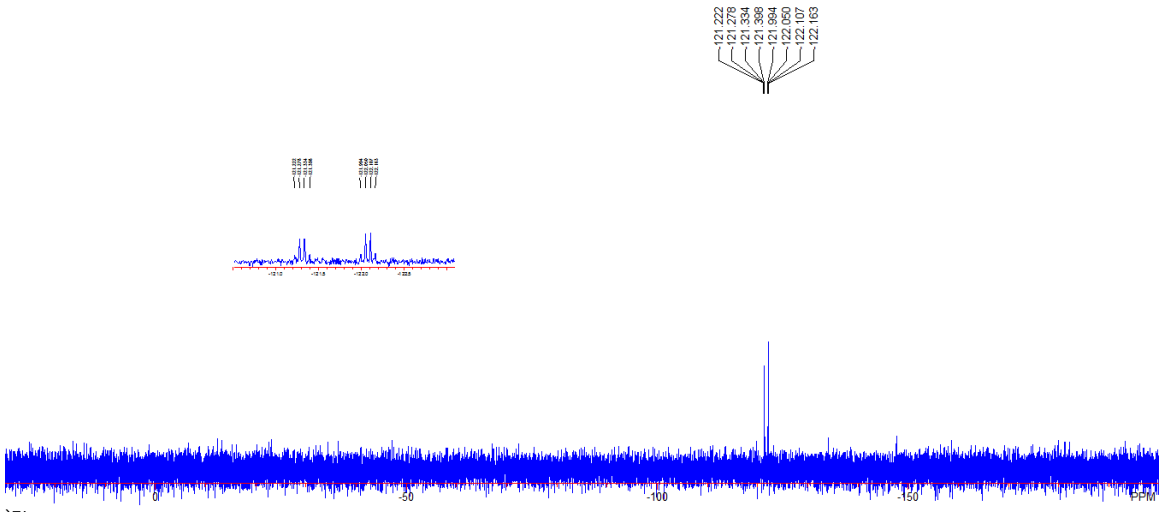

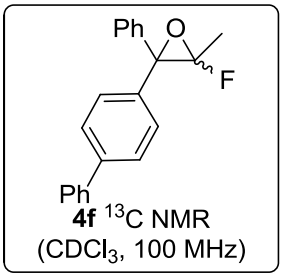

4f ^{13}C NMR
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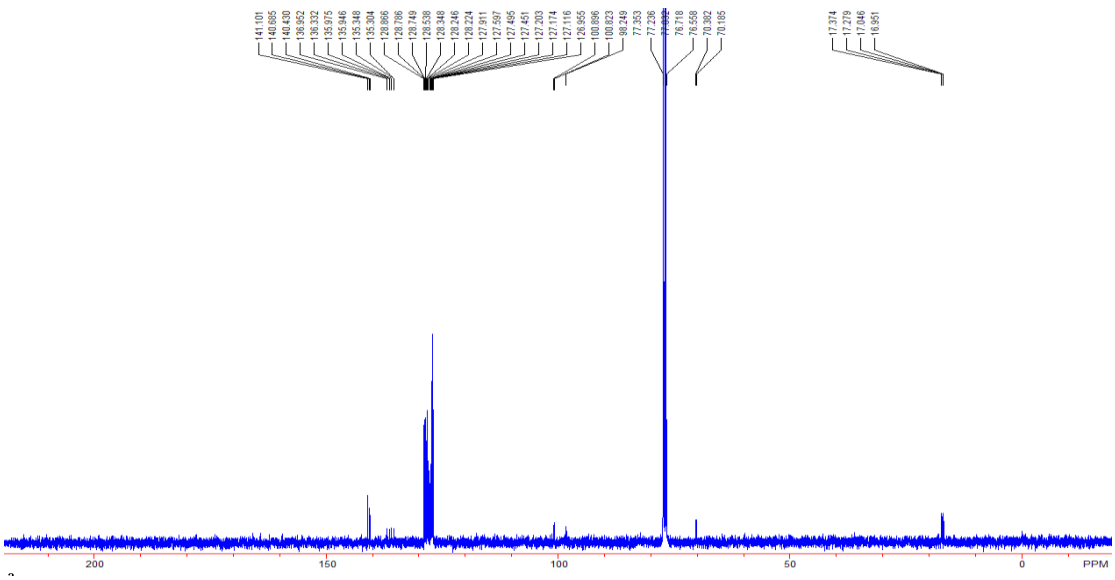

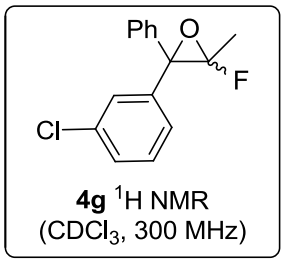

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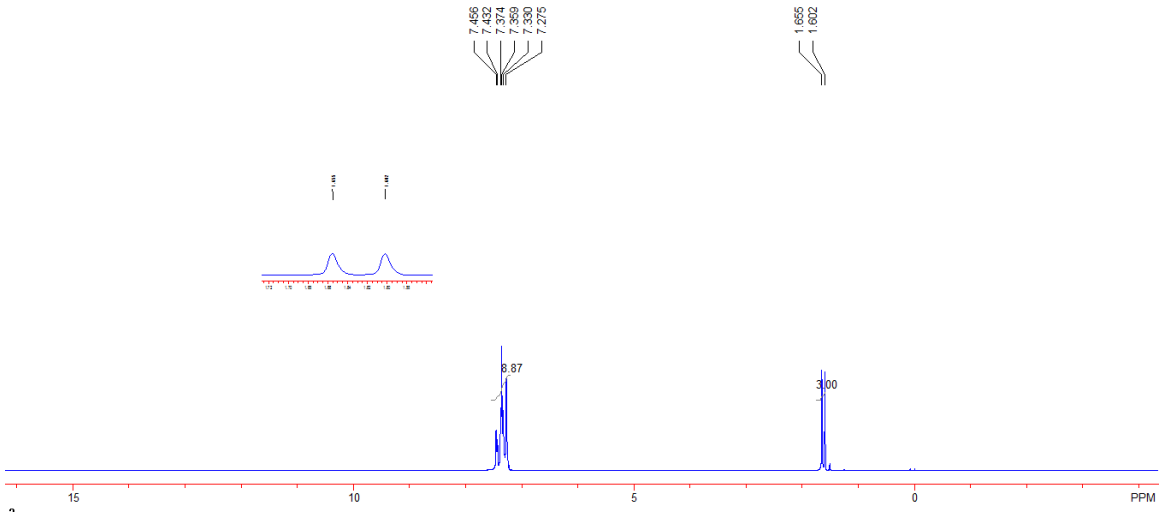
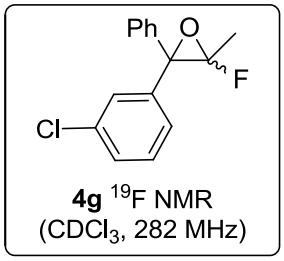
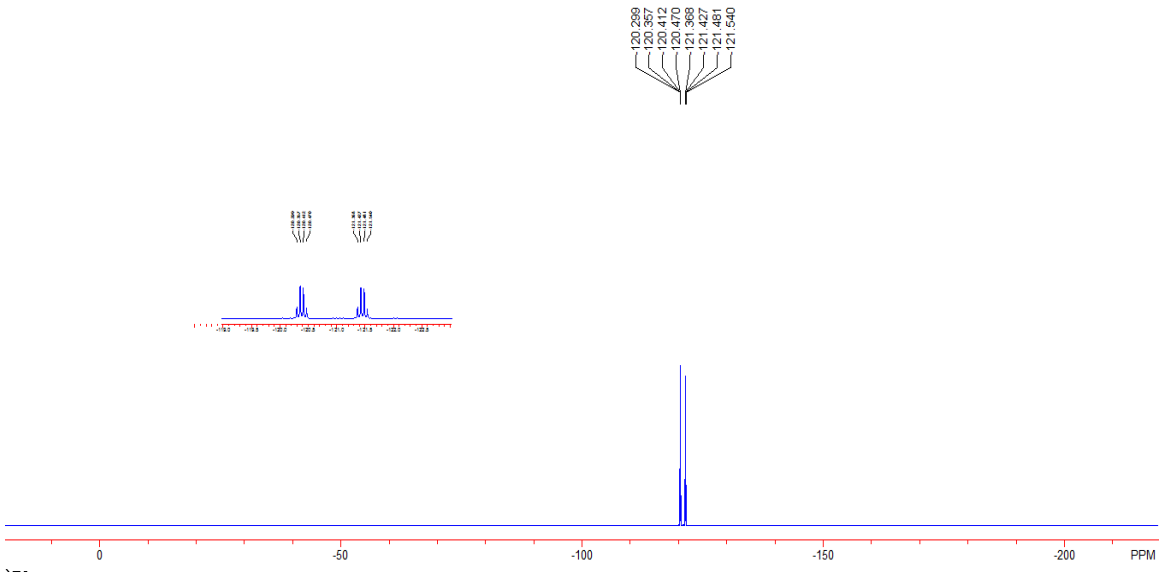
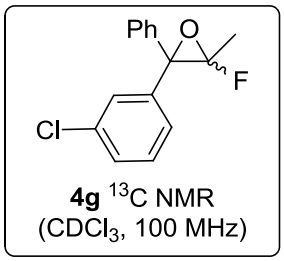


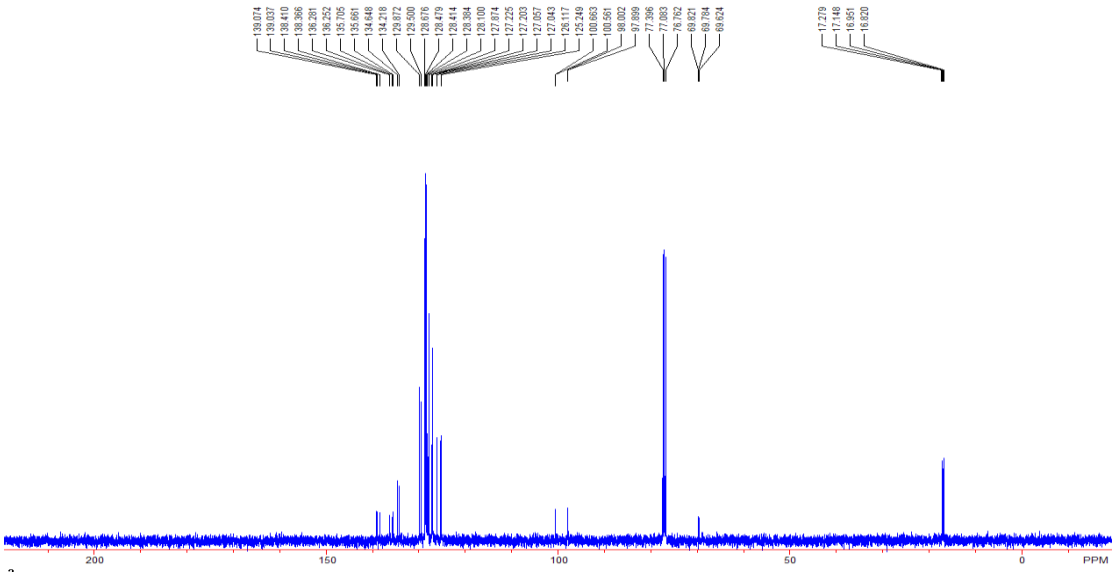


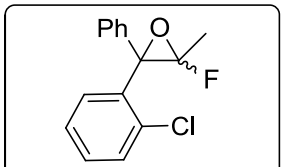
4g ^{19}F NMR
($CDCl_3$, 282 MHz)



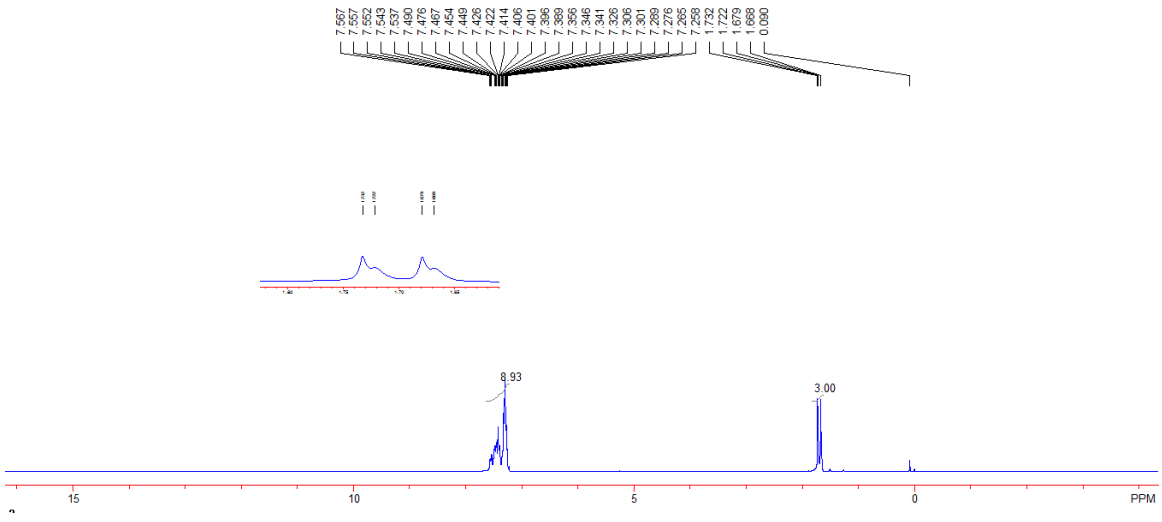


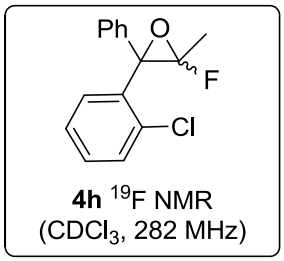
4g ^{13}C NMR
($CDCl_3$, 100 MHz)



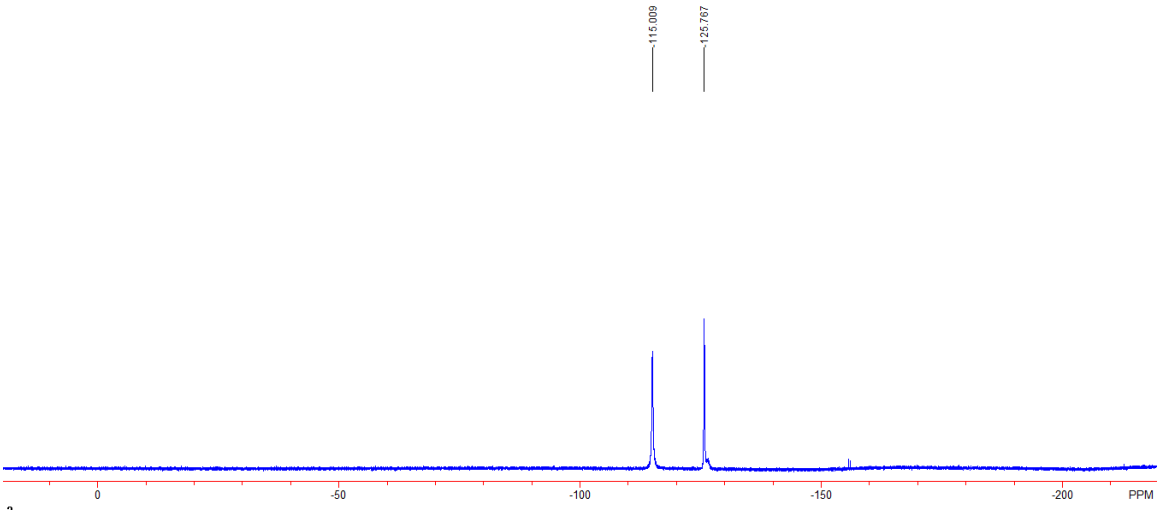


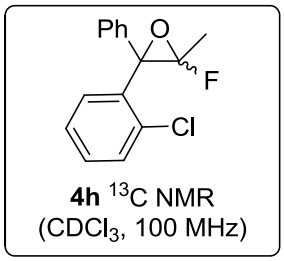
4h ^{1}H NMR
($CDCl_3$, 300 MHz)



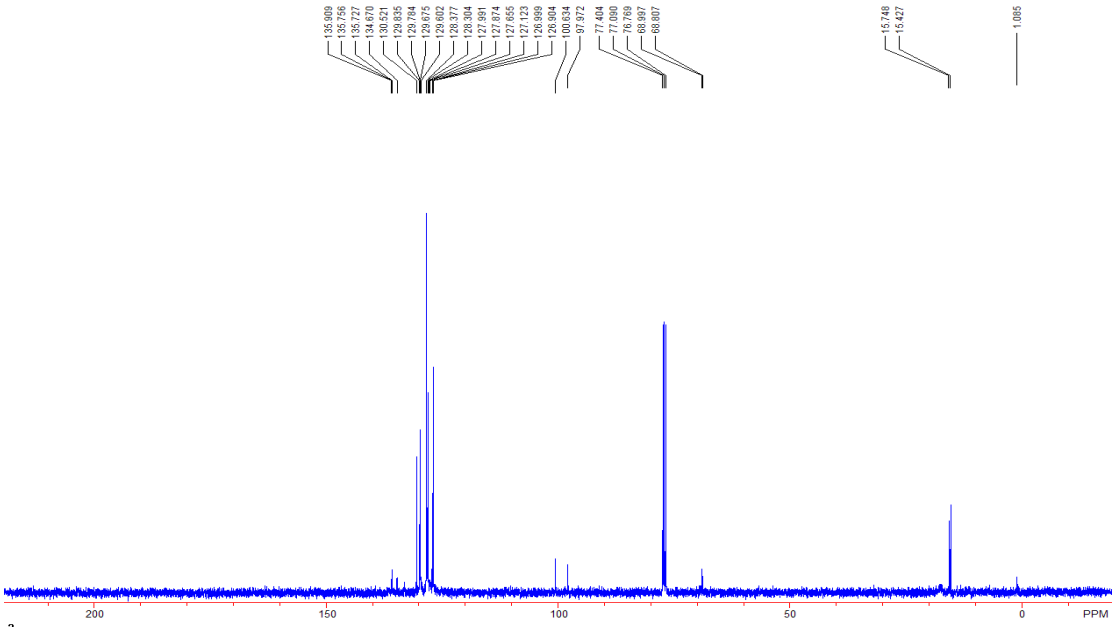


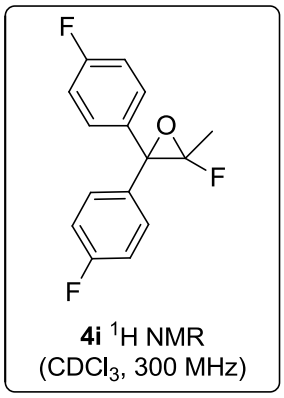
4h ^{19}F NMR
($CDCl_3$, 282 MHz)



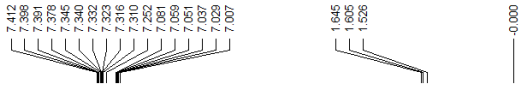


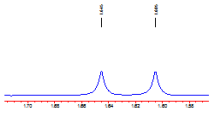
4h ^{13}C NMR
($CDCl_3$, 100 MHz)

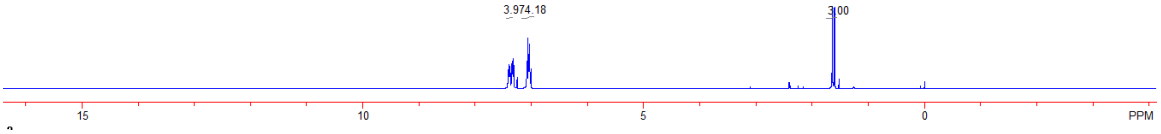


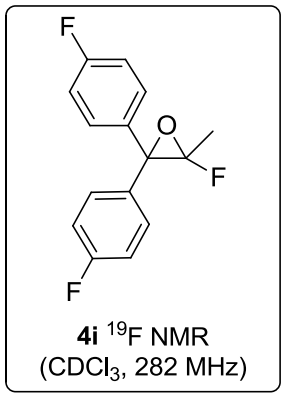


4i ^{1}H NMR
($CDCl_3$, 300 MHz)

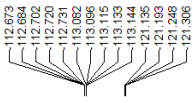


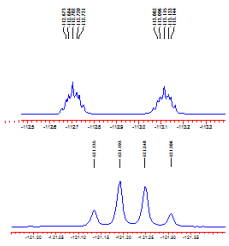


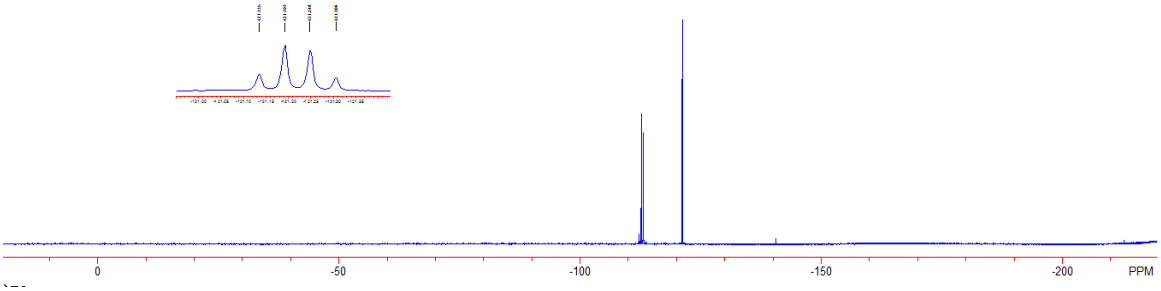


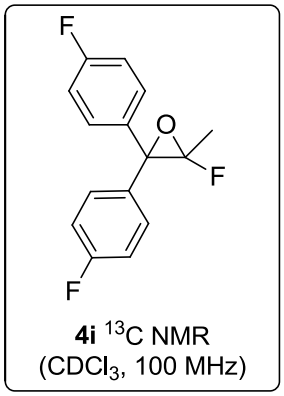


4i ^{19}F NMR
($CDCl_3$, 282 MHz)

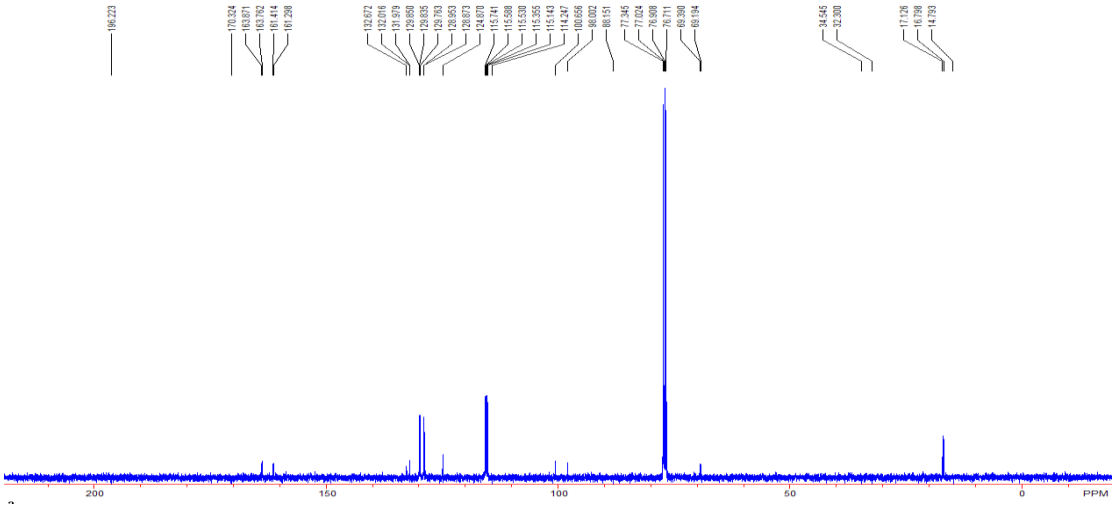


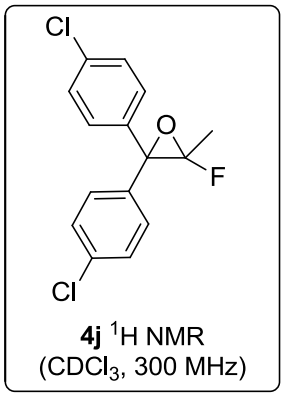




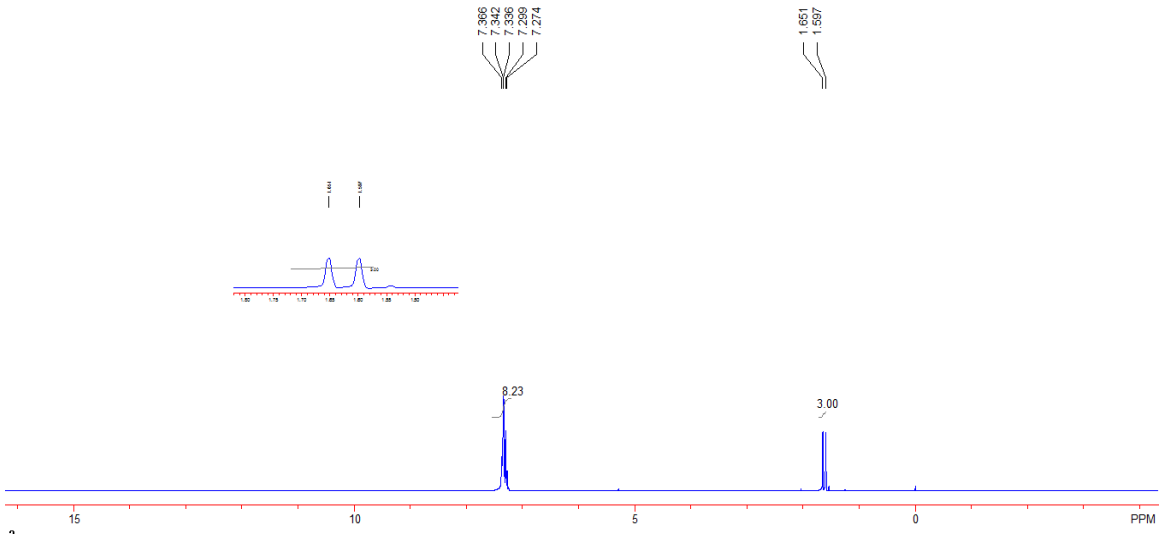


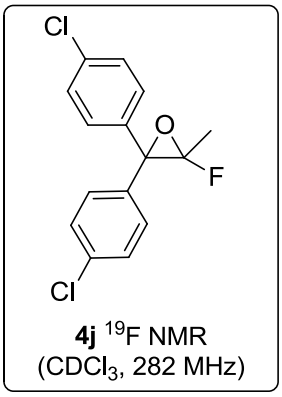
4i ^{13}C NMR
($CDCl_3$, 100 MHz)



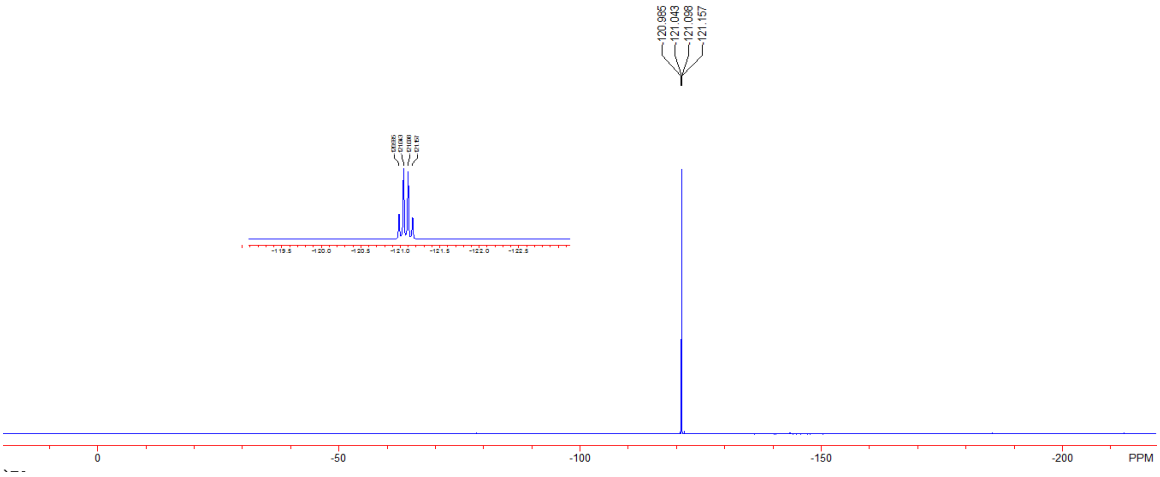


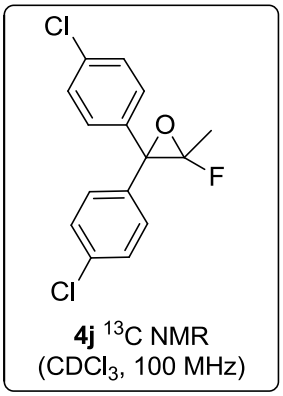
4j ^{1}H NMR
($CDCl_3$, 300 MHz)



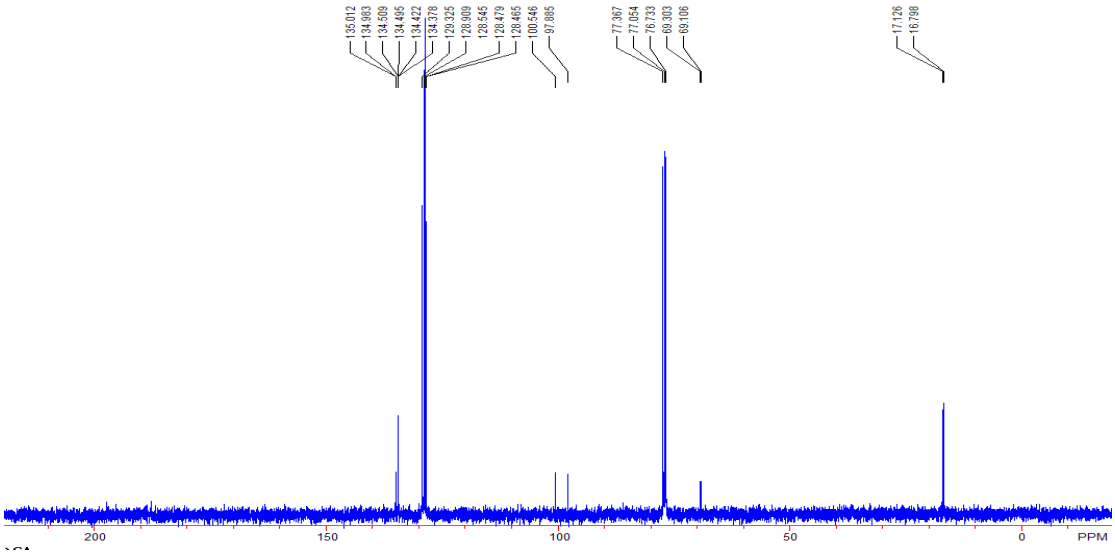


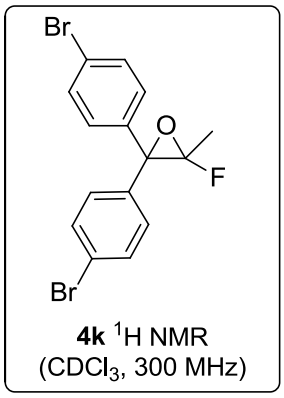
4j ^{19}F NMR
($CDCl_3$, 282 MHz)



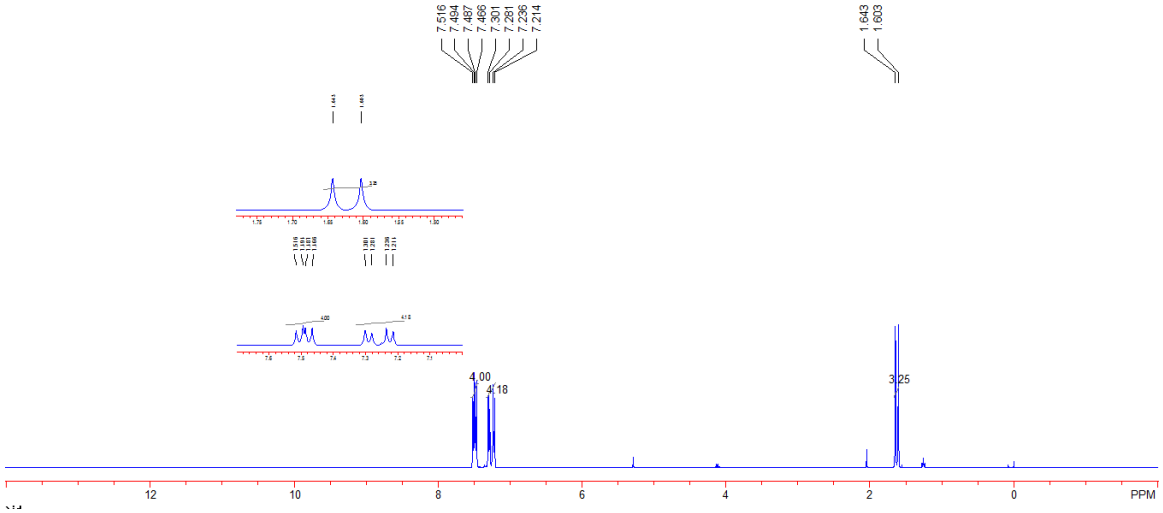


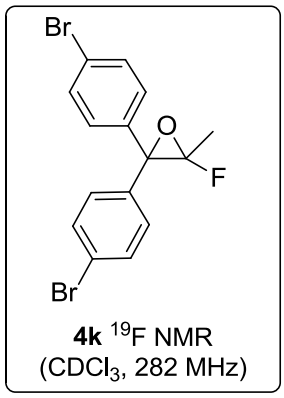
4j ^{13}C NMR
($CDCl_3$, 100 MHz)



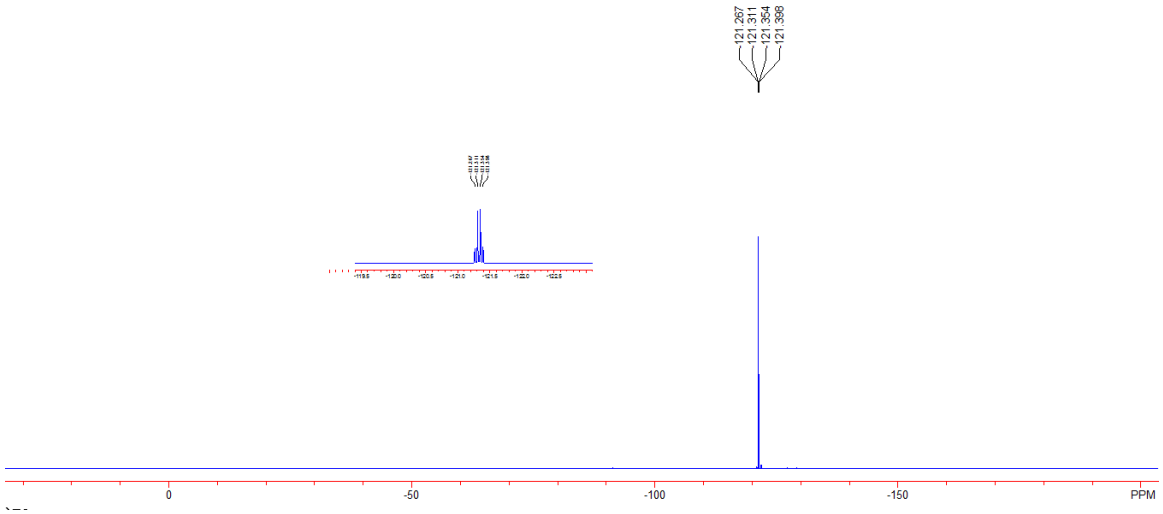


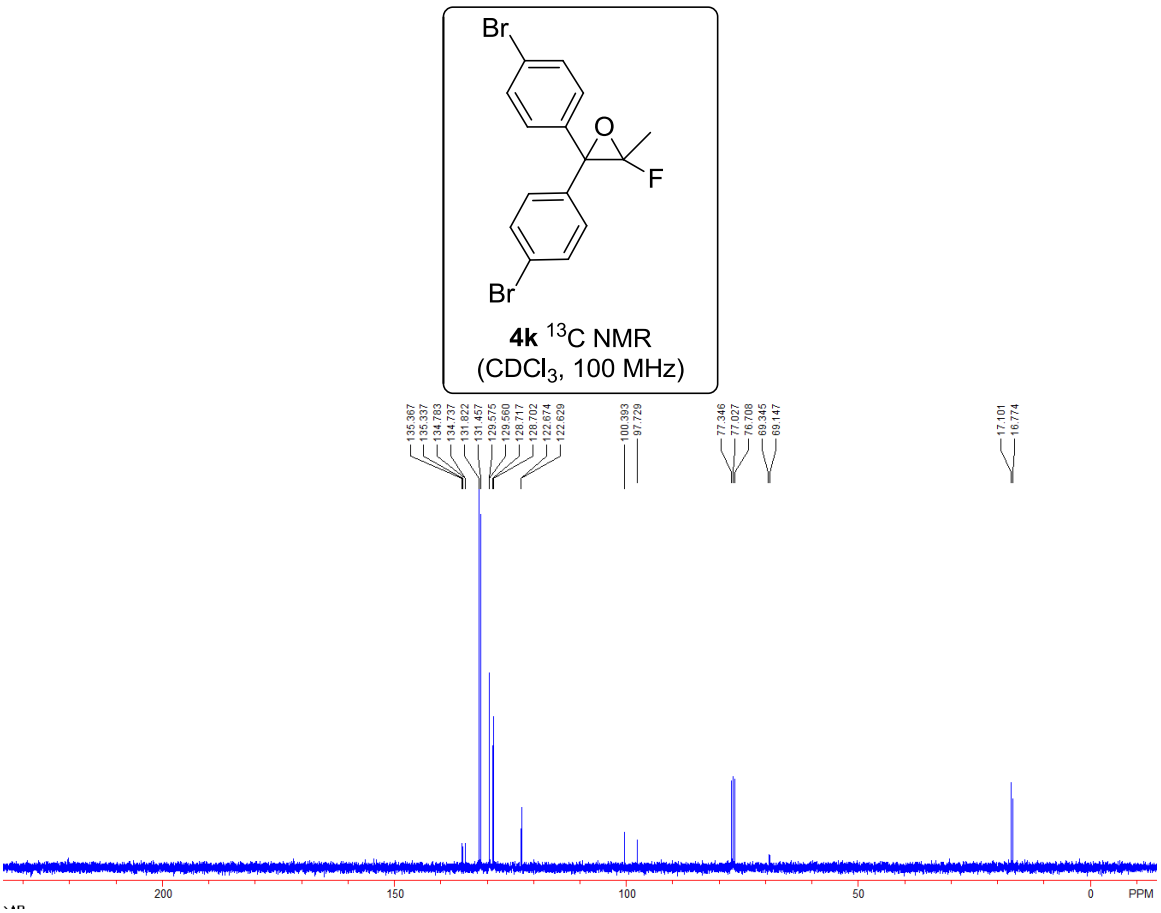
4k ^{1}H NMR
($CDCl_3$, 300 MHz)

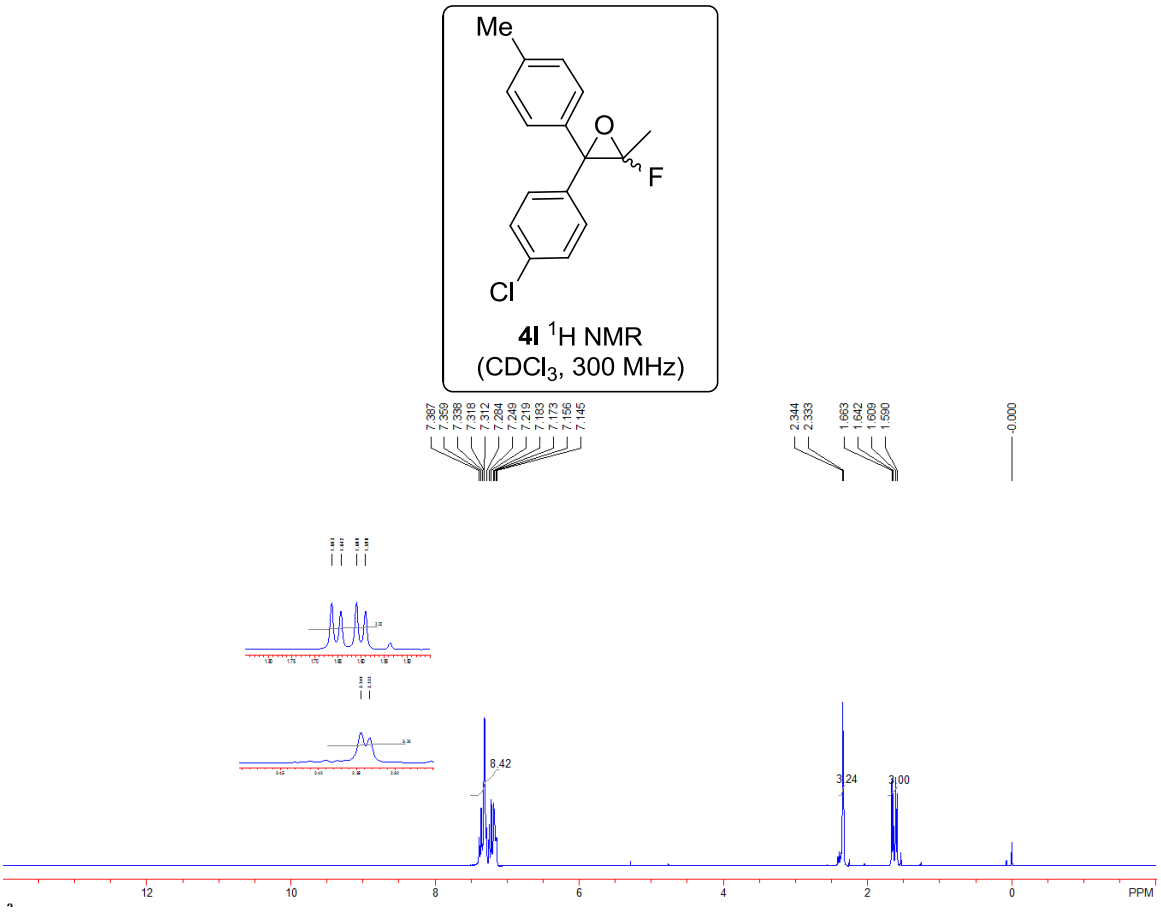


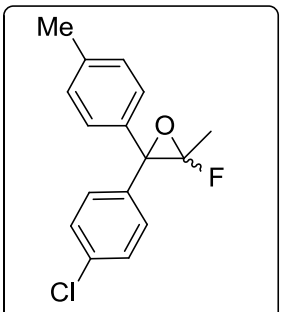


4k ^{19}F NMR
($CDCl_3$, 282 MHz)

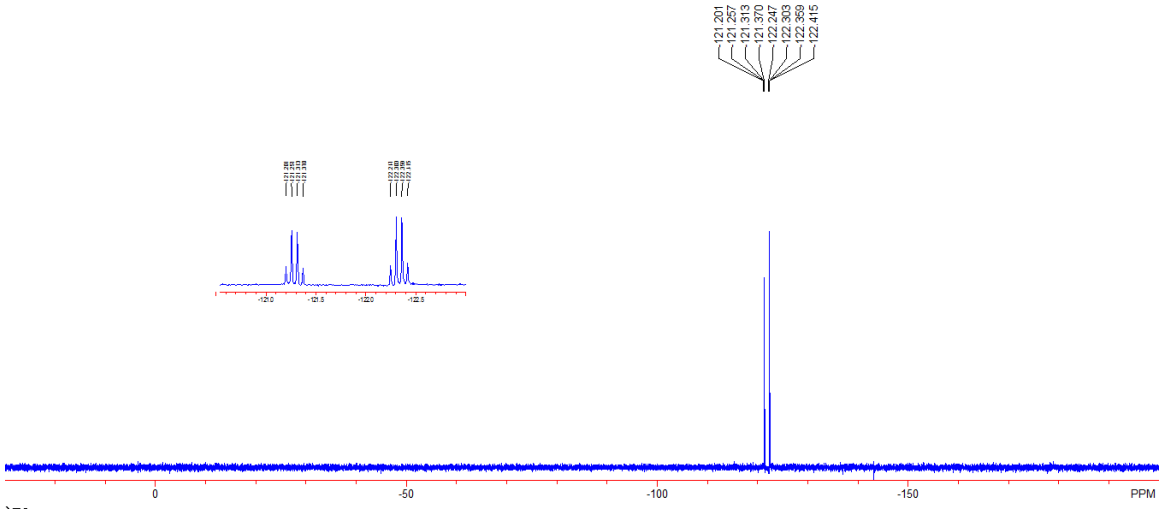


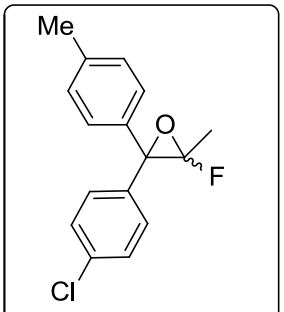

Br
O
F
Br
4k 13C NMR
(CDCl3, 100 MHz)
135.367
135.337
134.783
134.737
131.822
131.457
129.575
129.560
128.717
128.702
122.674
122.629
100.393
97.729
77.346
77.027
76.708
69.345
69.147
17.101
16.774
200
150
100
50
0
PPM


Me
O
F
Cl
4l 1H NMR
(CDCl3, 300 MHz)
7.397
7.389
7.338
7.318
7.312
7.284
7.249
7.219
7.183
7.173
7.156
7.145
2.344
2.333
1.663
1.642
1.609
1.590
-0.000
8.42
3.24
3.00
12
10
8
6
4
2
0
PPM

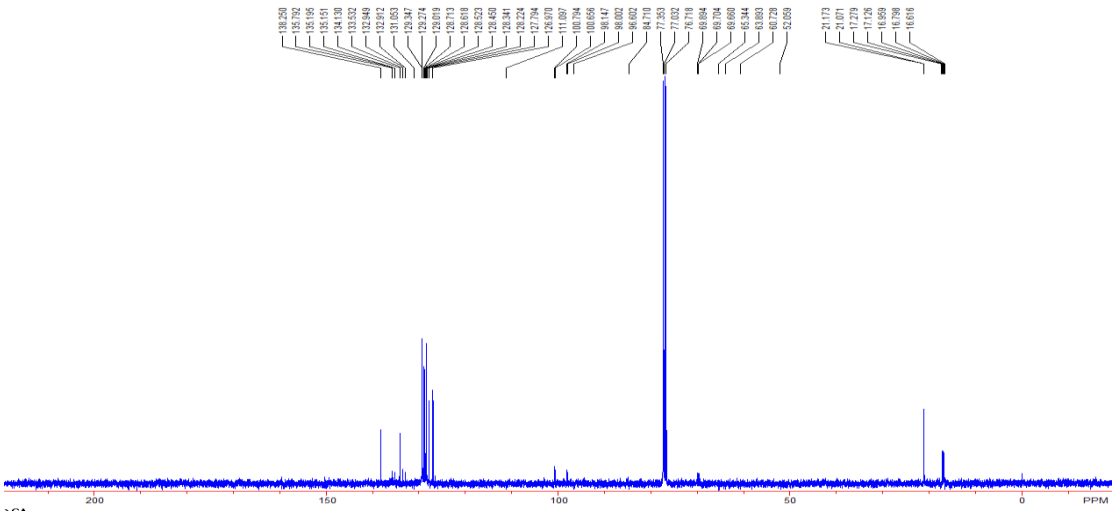


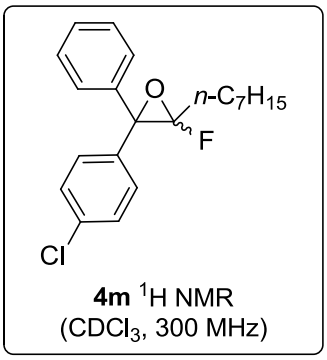
4l ^{19}F NMR
($CDCl_3$, 282 MHz)



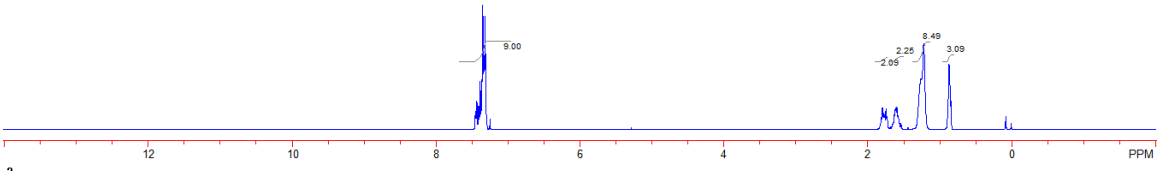


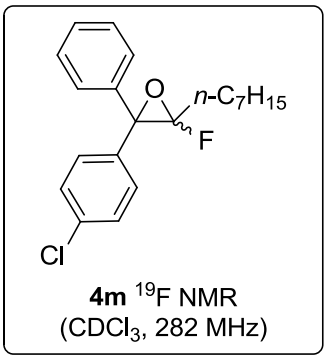
4l ^{13}C NMR
($CDCl_3$, 100 MHz)



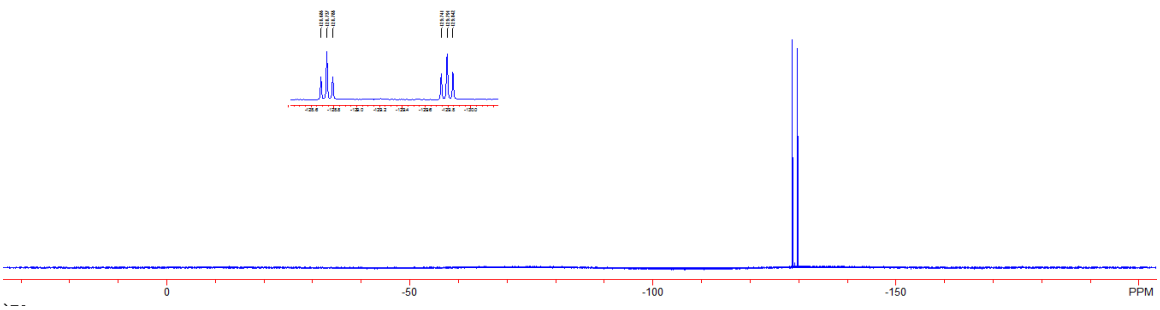


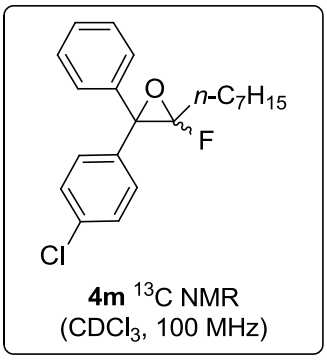
4m ^{1}H NMR
($CDCl_3$, 300 MHz)



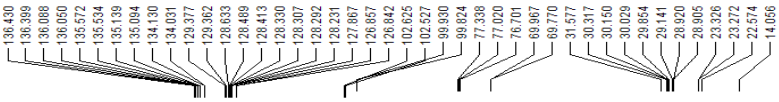


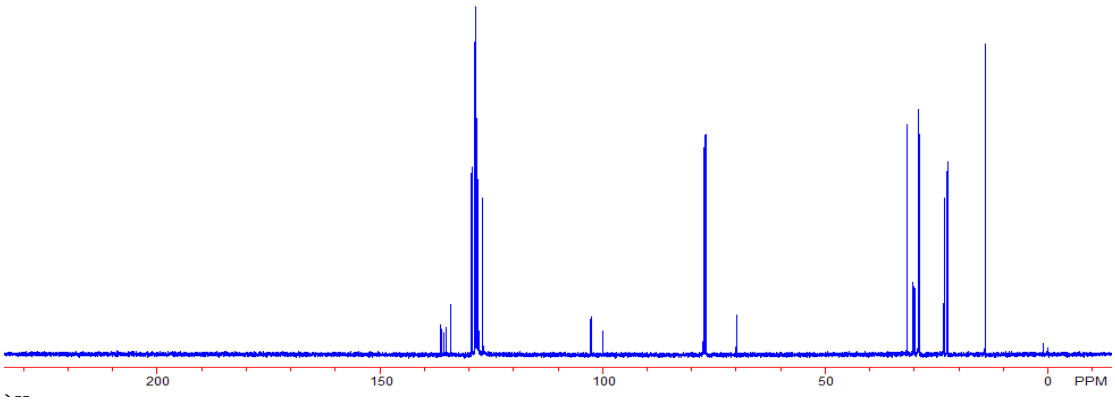
4m ^{19}F NMR
($CDCl_3$, 282 MHz)

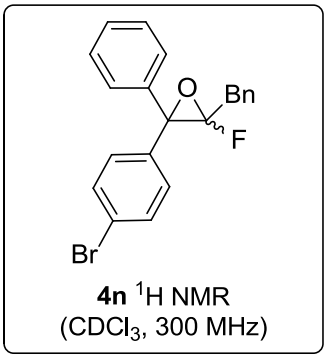




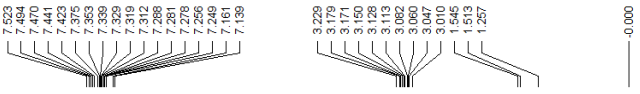
4m ^{13}C NMR
($CDCl_3$, 100 MHz)

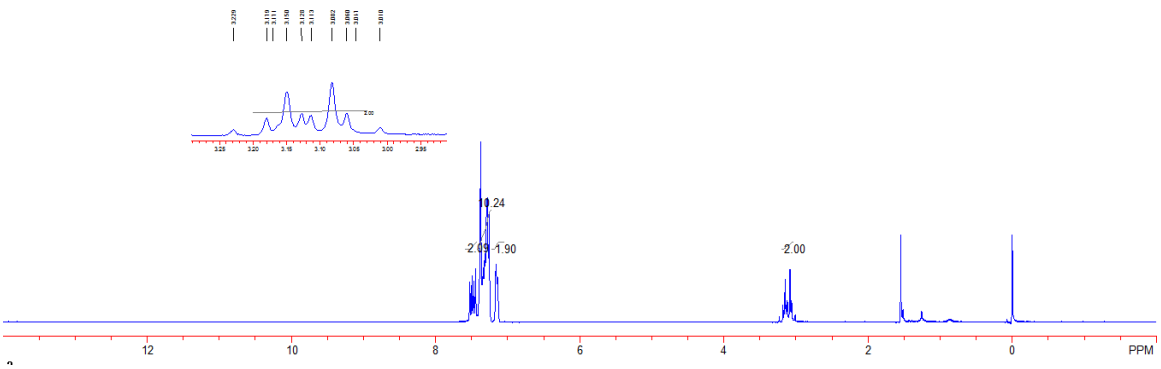


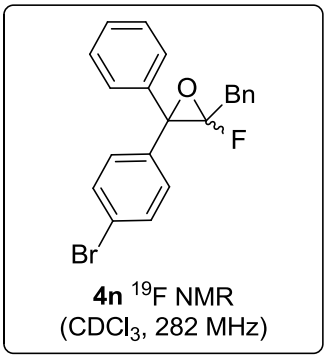




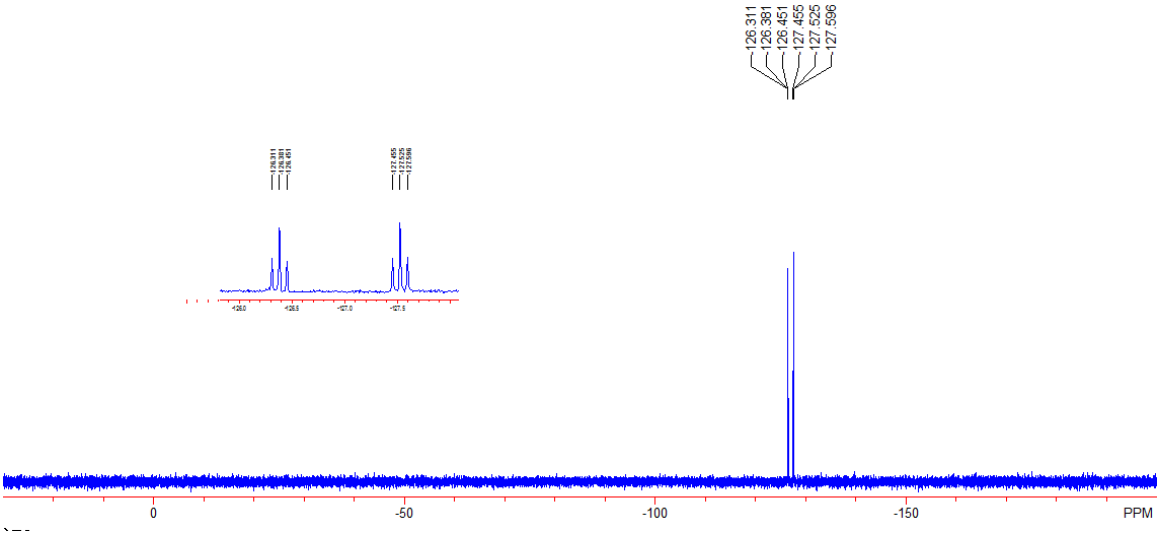
4n ^{1}H NMR
($CDCl_3$, 300 MHz)

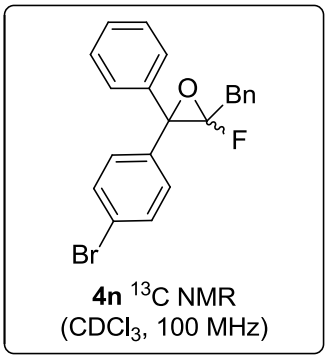




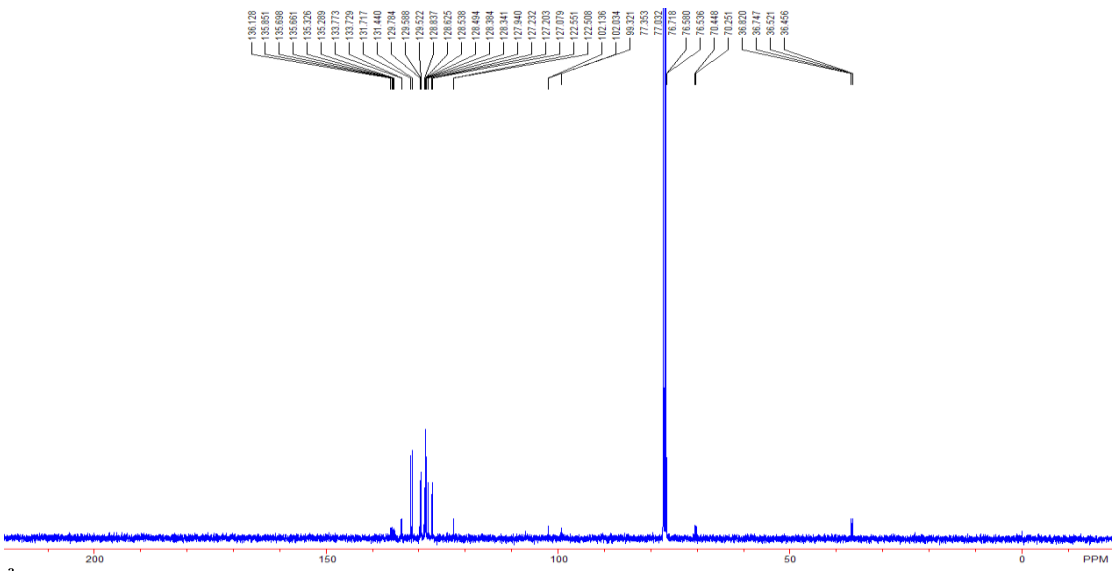


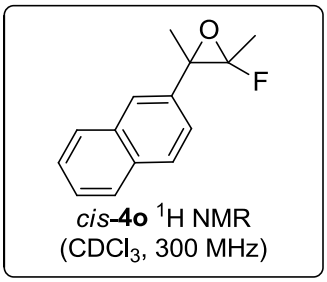
4n ^{19}F NMR
($CDCl_3$, 282 MHz)



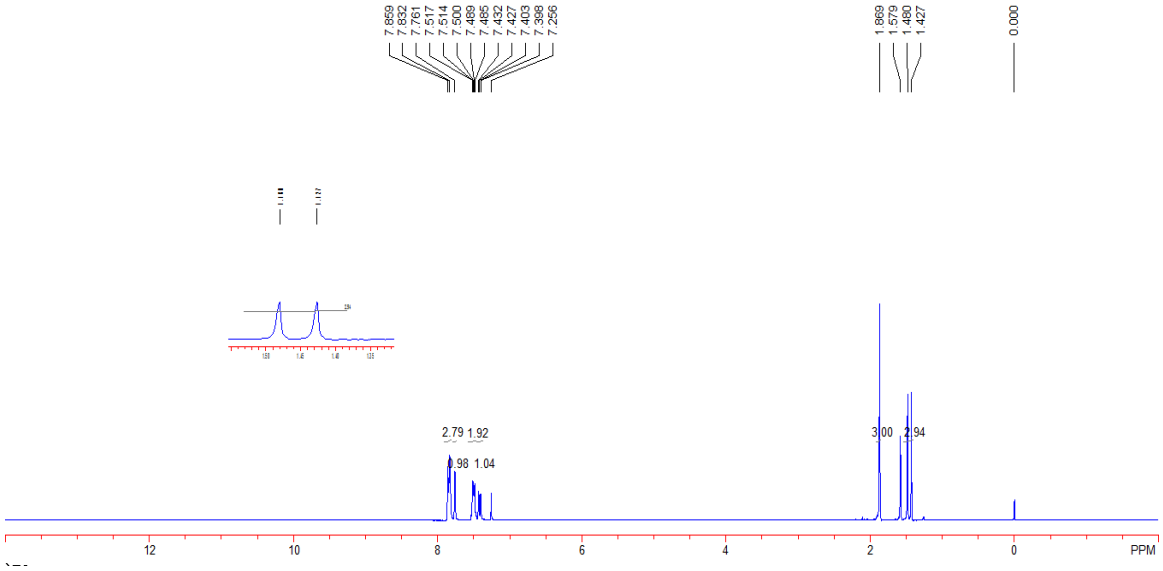


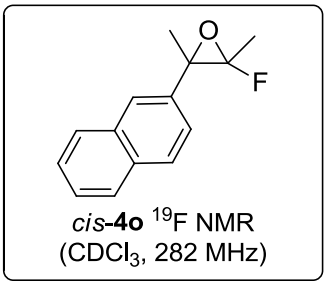
4n ^{13}C NMR
($CDCl_3$, 100 MHz)



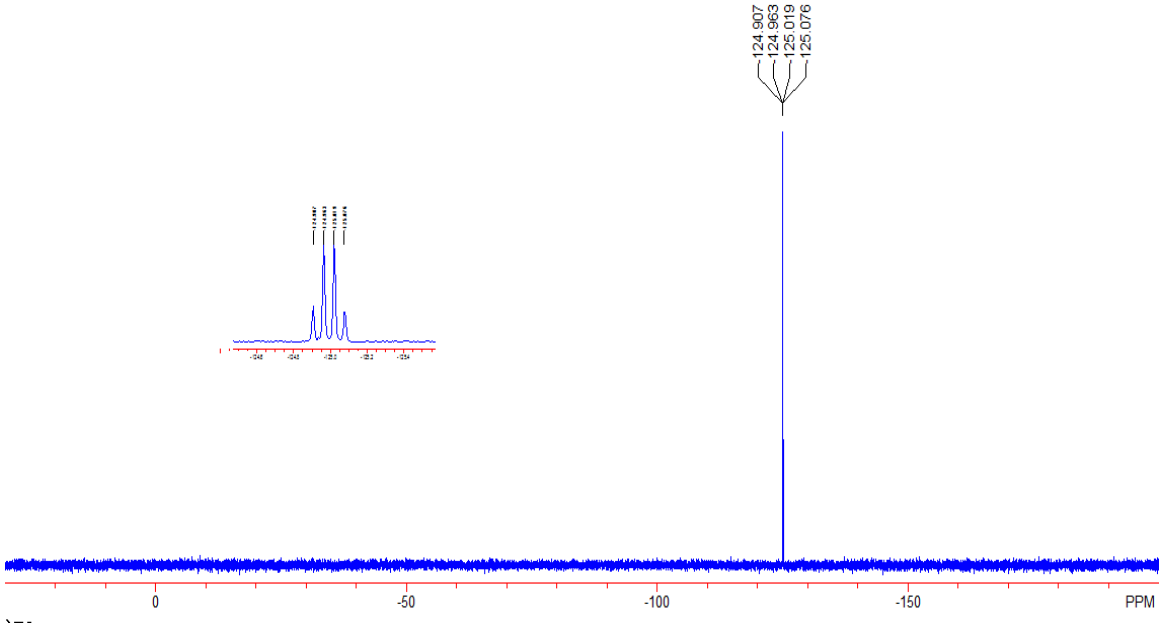


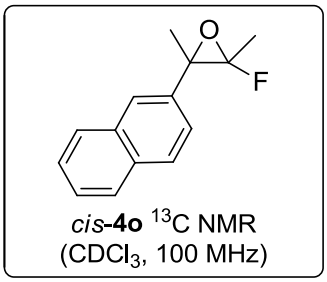
cis-**4o** ^{1}H NMR
($CDCl_3$, 300 MHz)



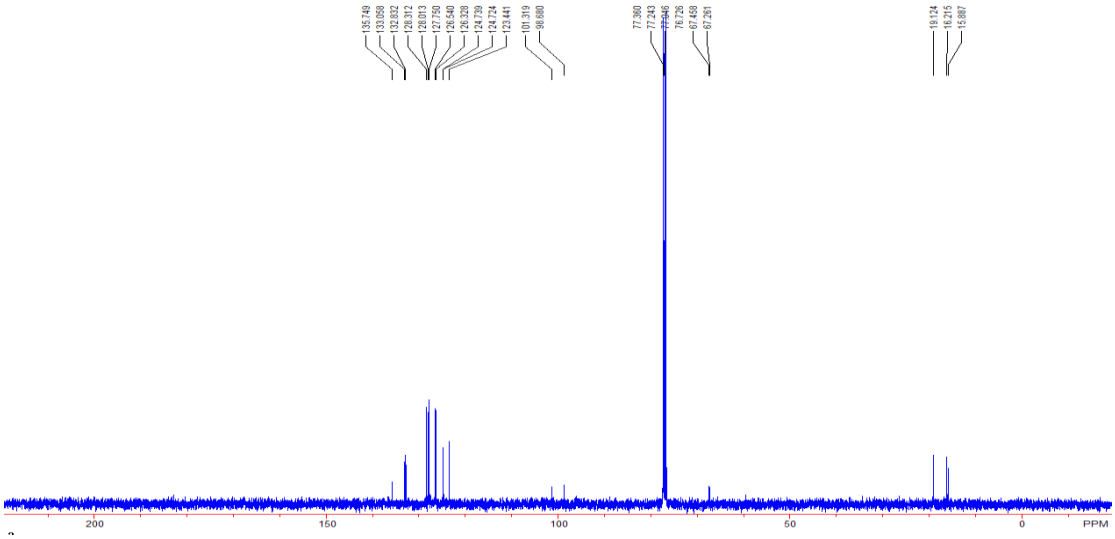


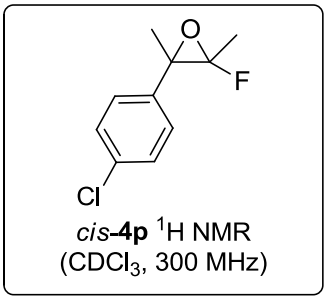
cis-**4o** ^{19}F NMR
($CDCl_3$, 282 MHz)



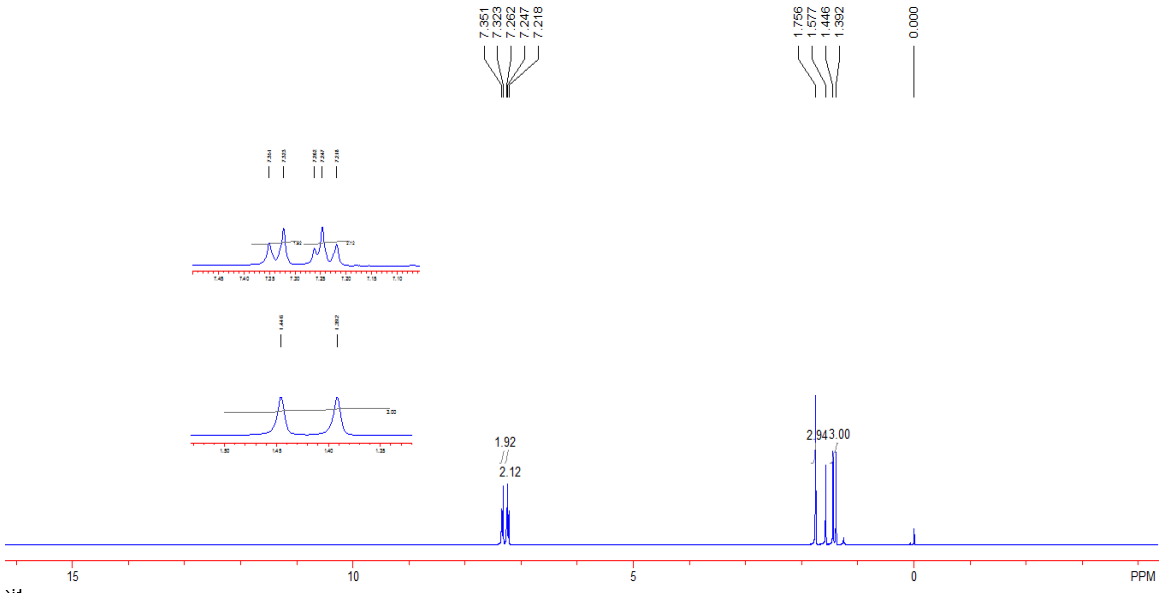


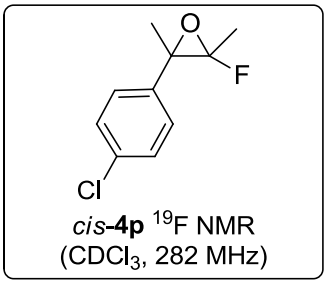
cis-**4o** ^{13}C NMR
($CDCl_3$, 100 MHz)



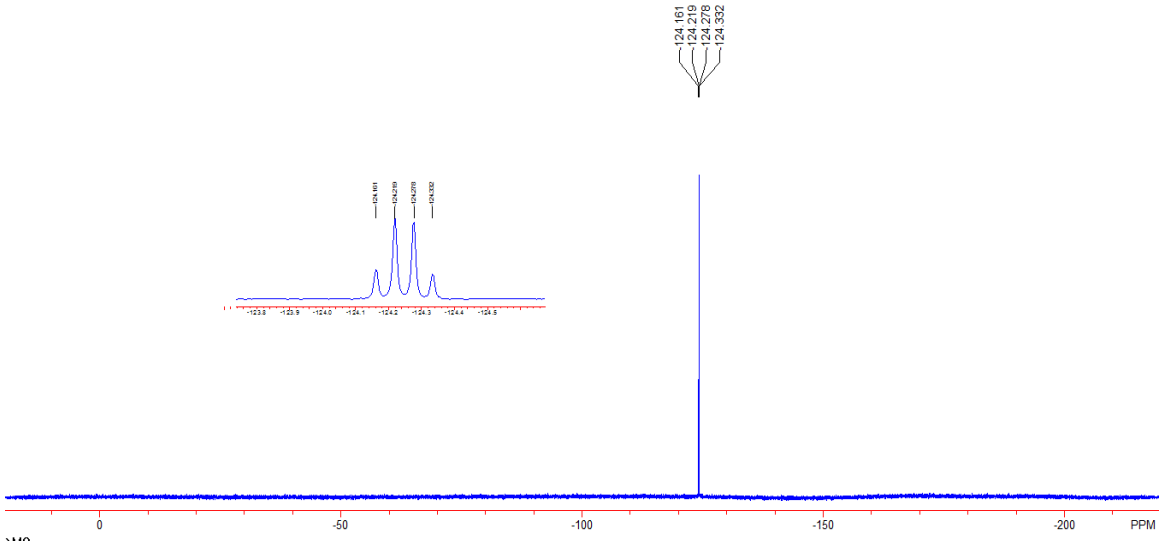


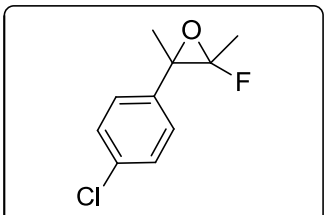
cis-**4p** ^{1}H NMR
($CDCl_3$, 300 MHz)



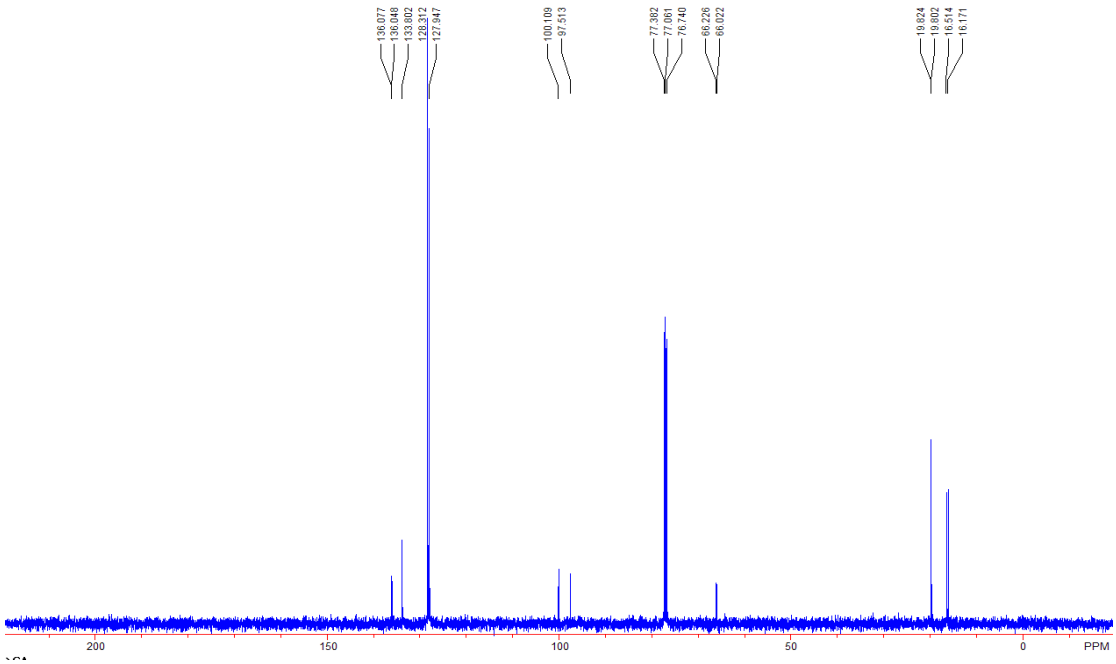


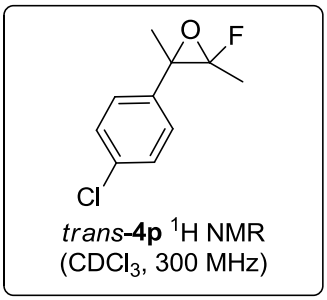
cis-**4p** ^{19}F NMR
($CDCl_3$, 282 MHz)



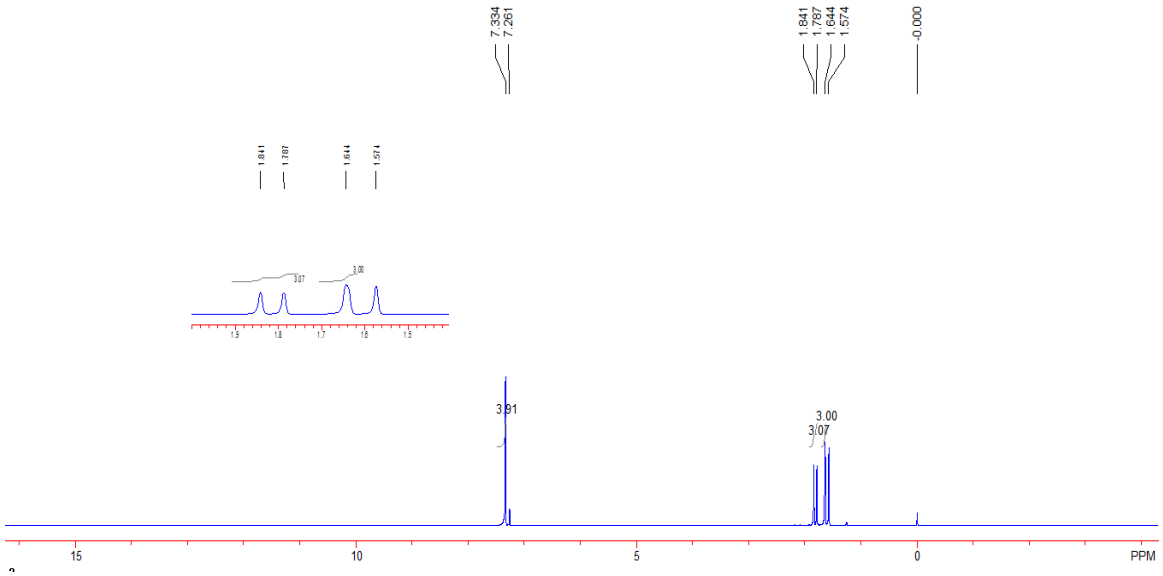


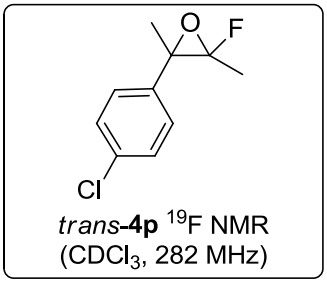
cis-**4p** ^{13}C NMR
($CDCl_3$, 100 MHz)



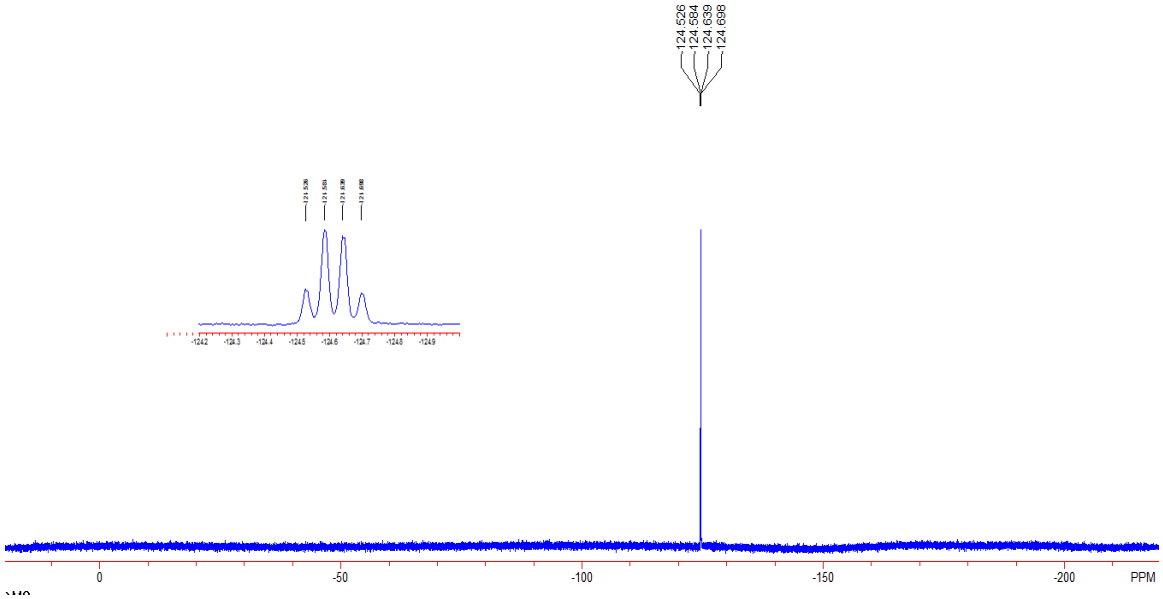


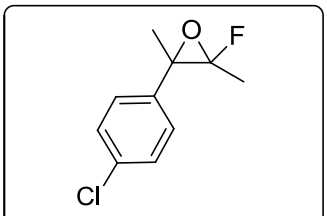
trans-**4p** ^{1}H NMR
($CDCl_3$, 300 MHz)



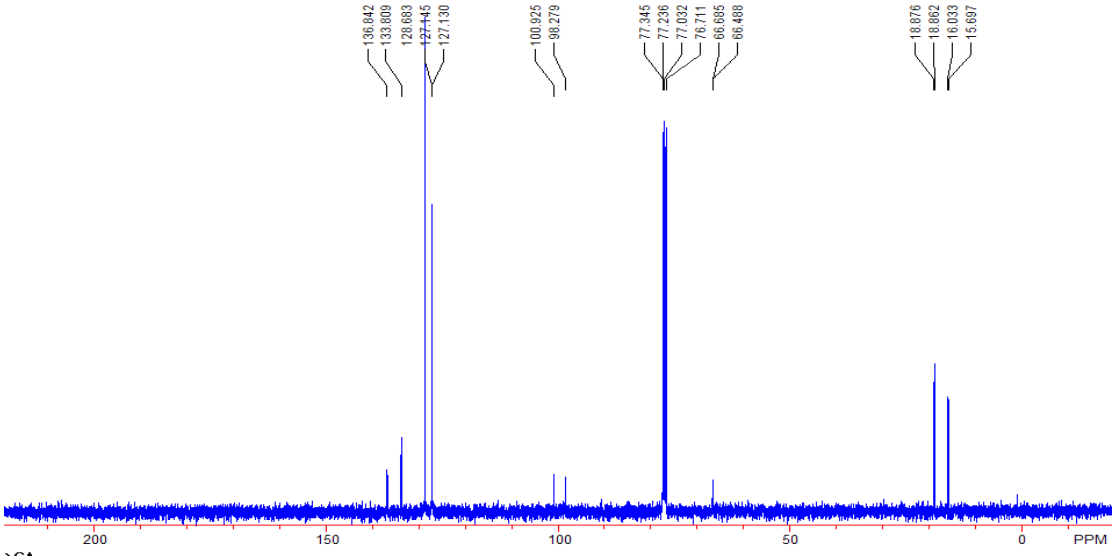


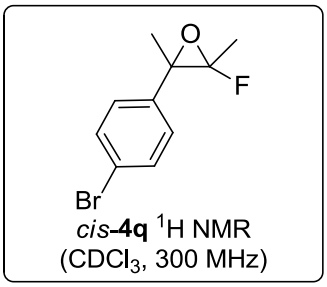
trans-**4p** ^{19}F NMR
($CDCl_3$, 282 MHz)



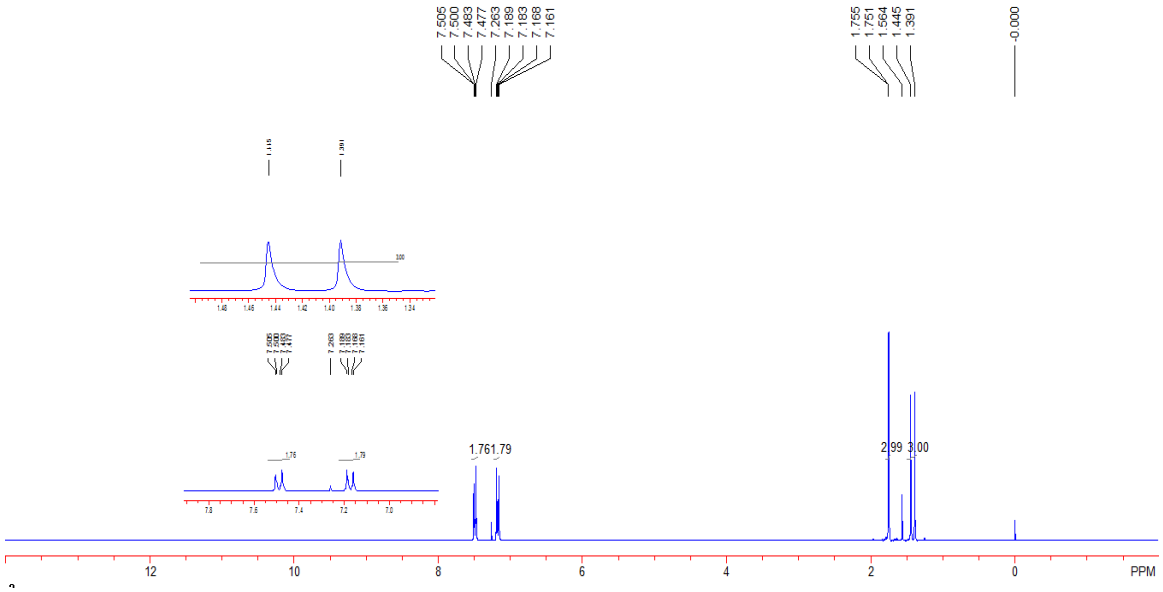


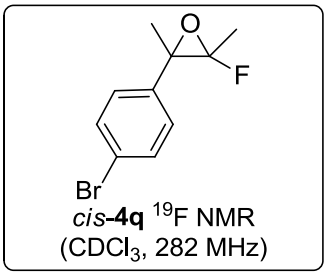
trans-**4p** ^{13}C NMR
($CDCl_3$, 100 MHz)



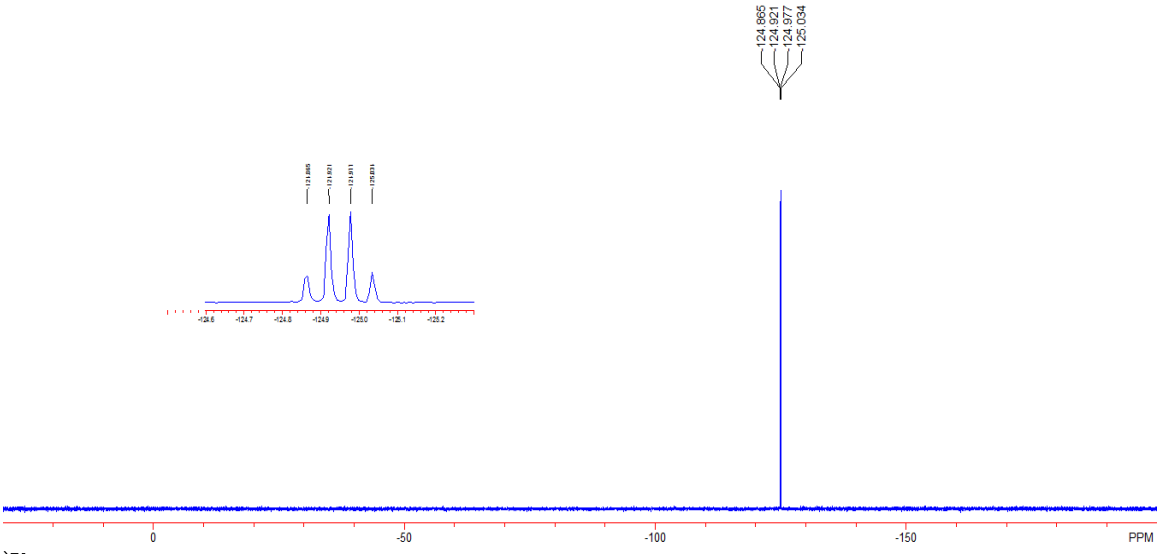


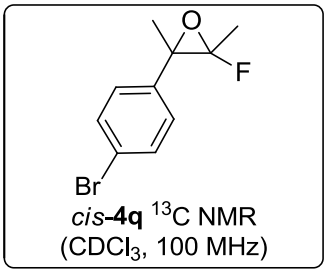
cis-**4q** ^{1}H NMR
($CDCl_3$, 300 MHz)



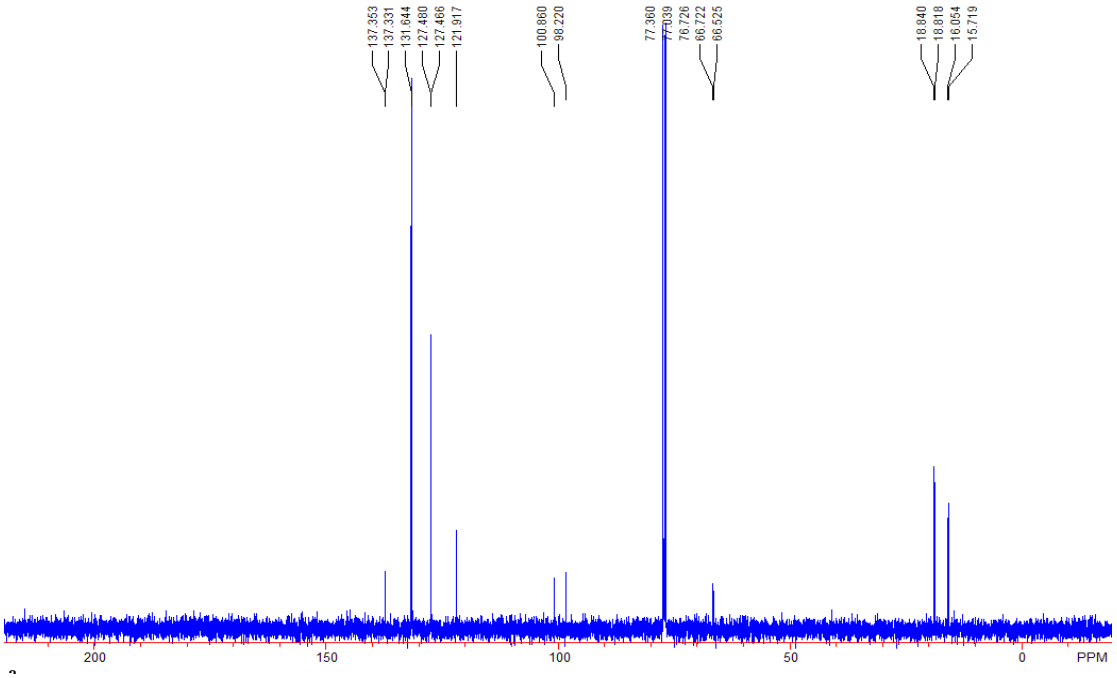


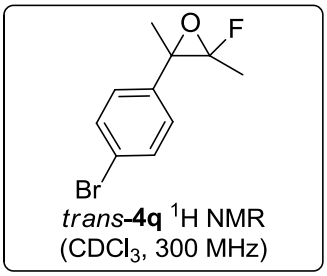
cis-**4q** ^{19}F NMR
($CDCl_3$, 282 MHz)



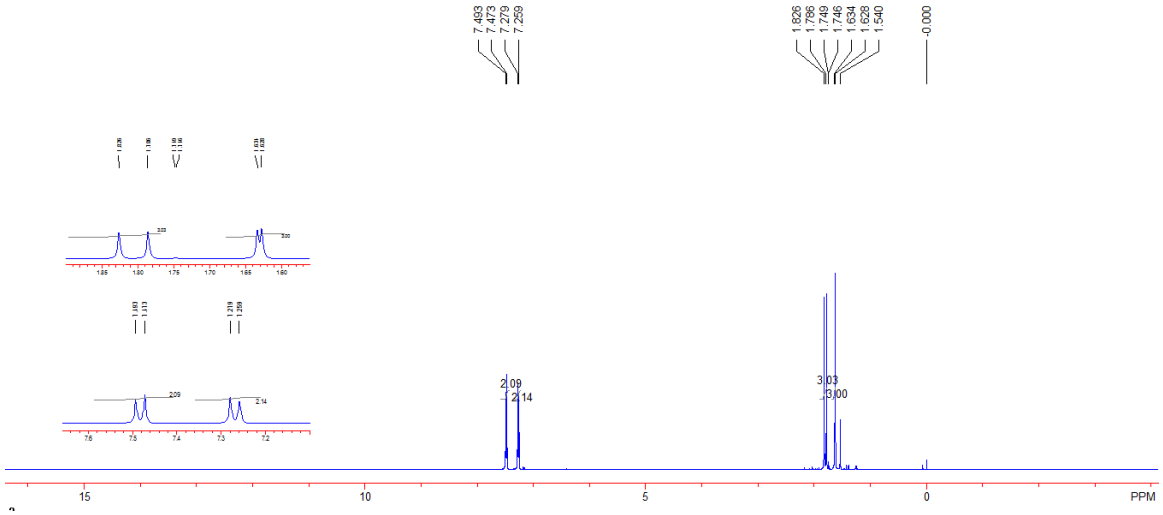


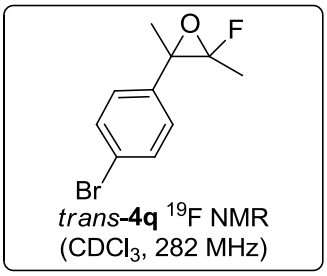
cis-**4q** ^{13}C NMR
($CDCl_3$, 100 MHz)



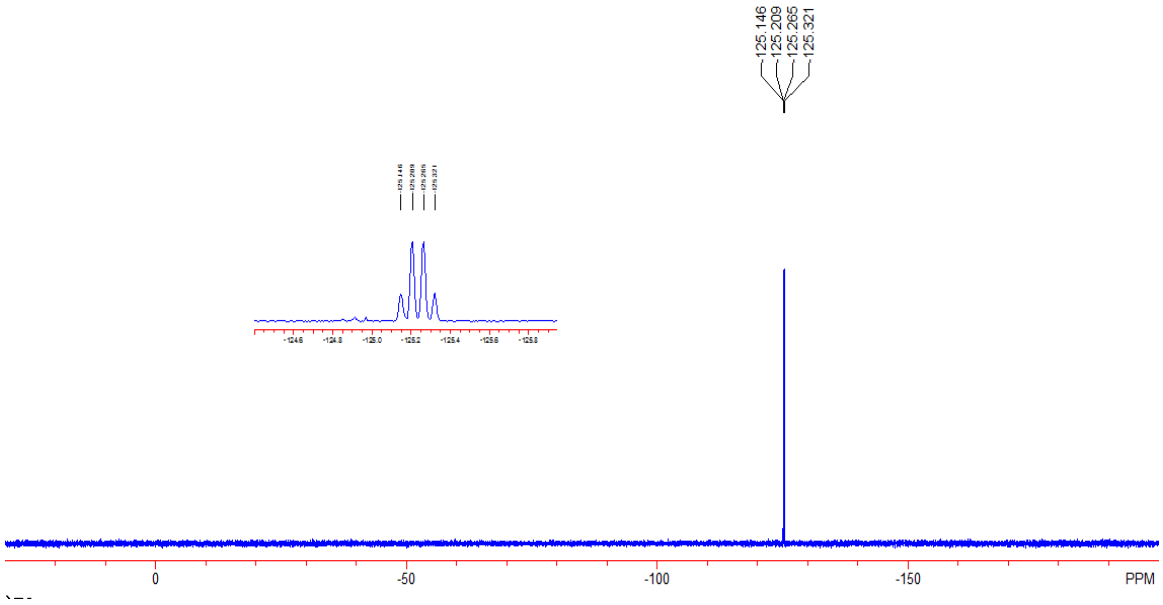


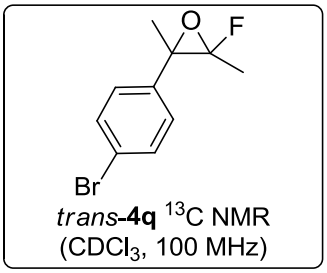
trans-**4q** ^{1}H NMR
($CDCl_3$, 300 MHz)



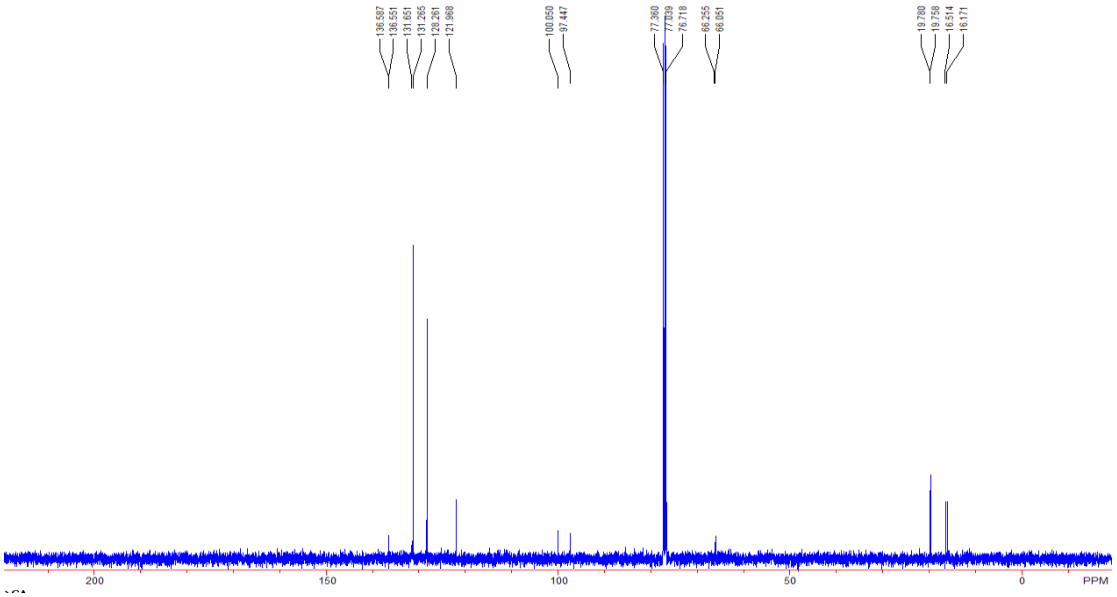


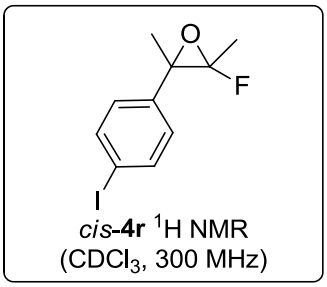
trans-**4q** ^{19}F NMR
($CDCl_3$, 282 MHz)



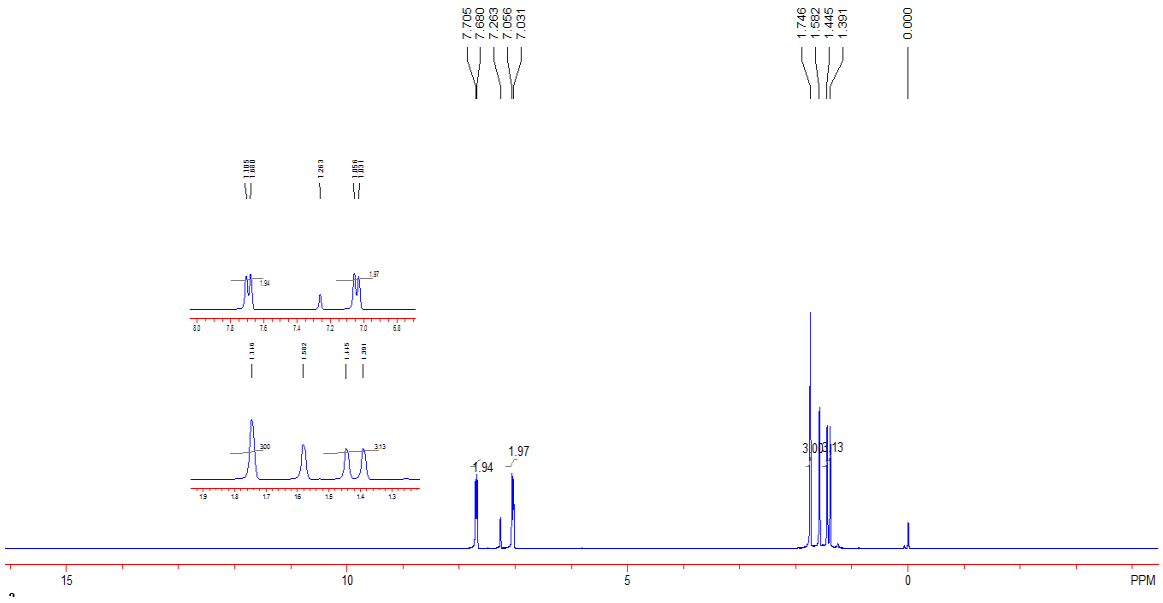


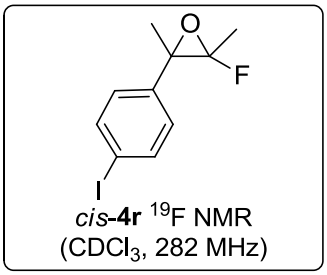
trans-**4q** ^{13}C NMR
($CDCl_3$, 100 MHz)



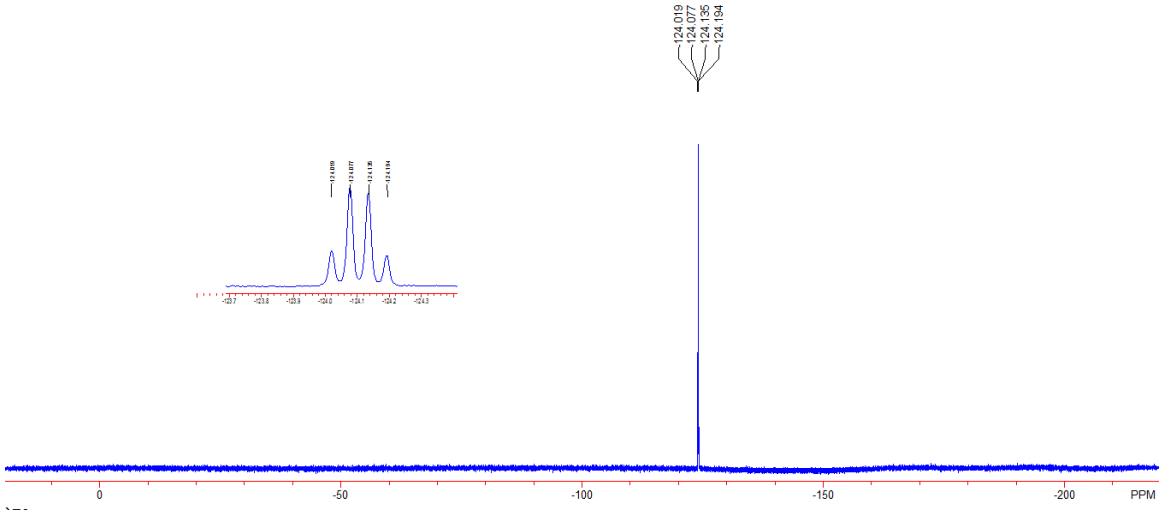


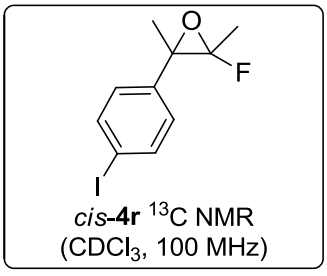
cis-**4r** ^{1}H NMR
($CDCl_3$, 300 MHz)



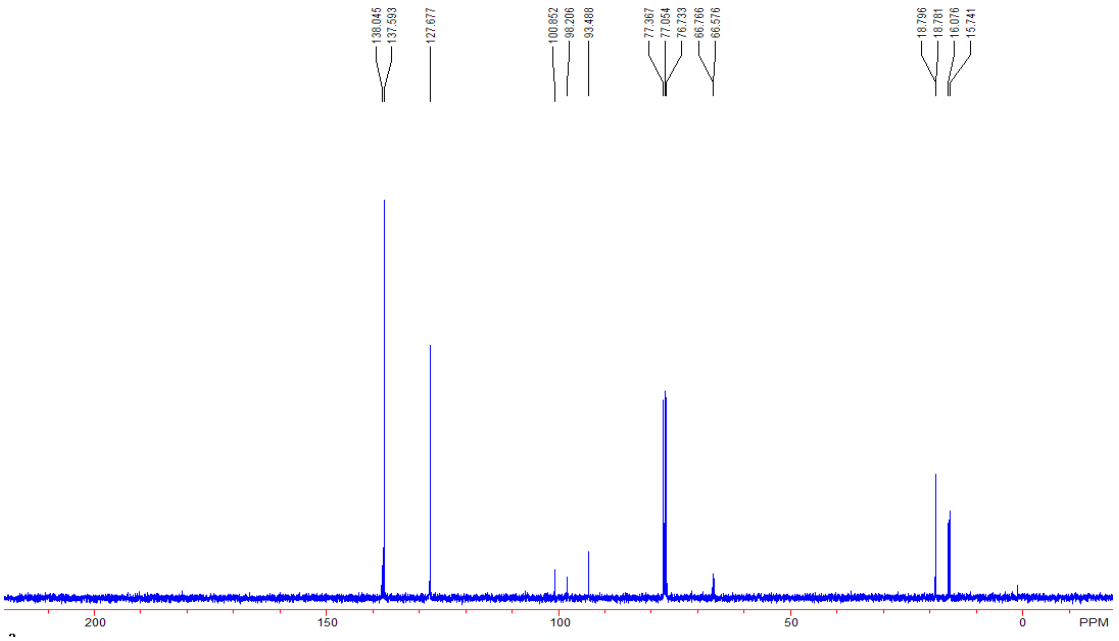


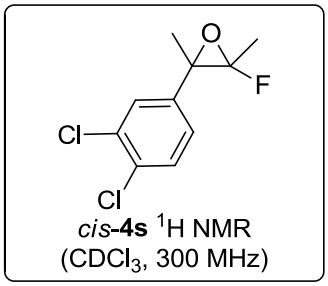
cis-**4r** ^{19}F NMR
($CDCl_3$, 282 MHz)



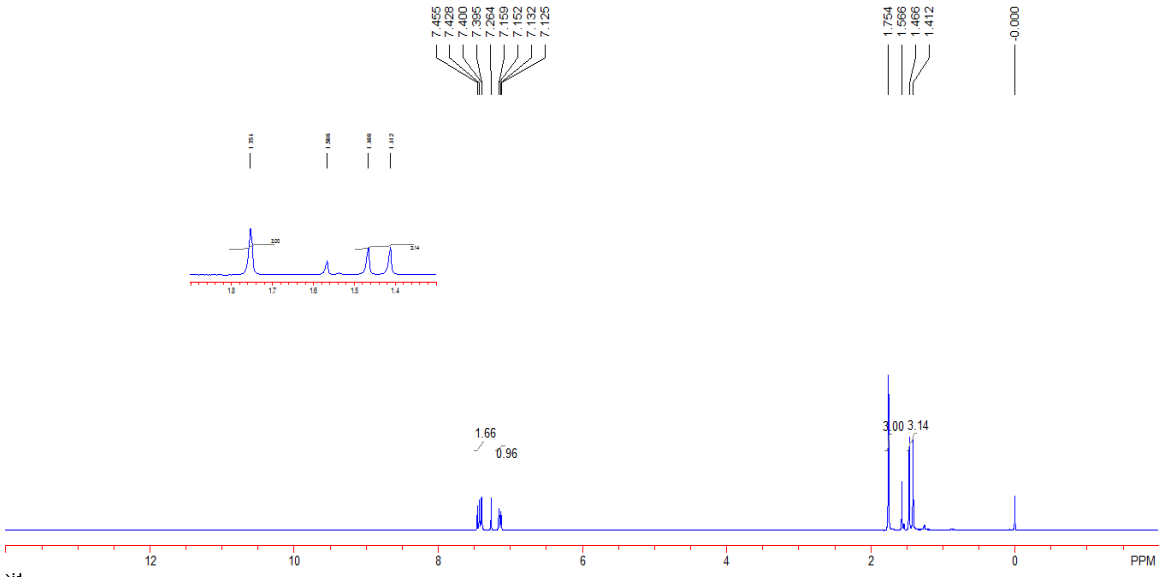


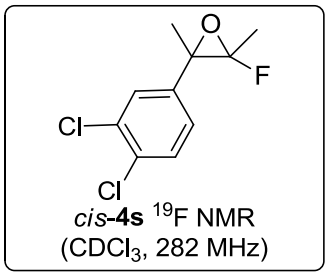
cis-**4r** ^{13}C NMR
($CDCl_3$, 100 MHz)



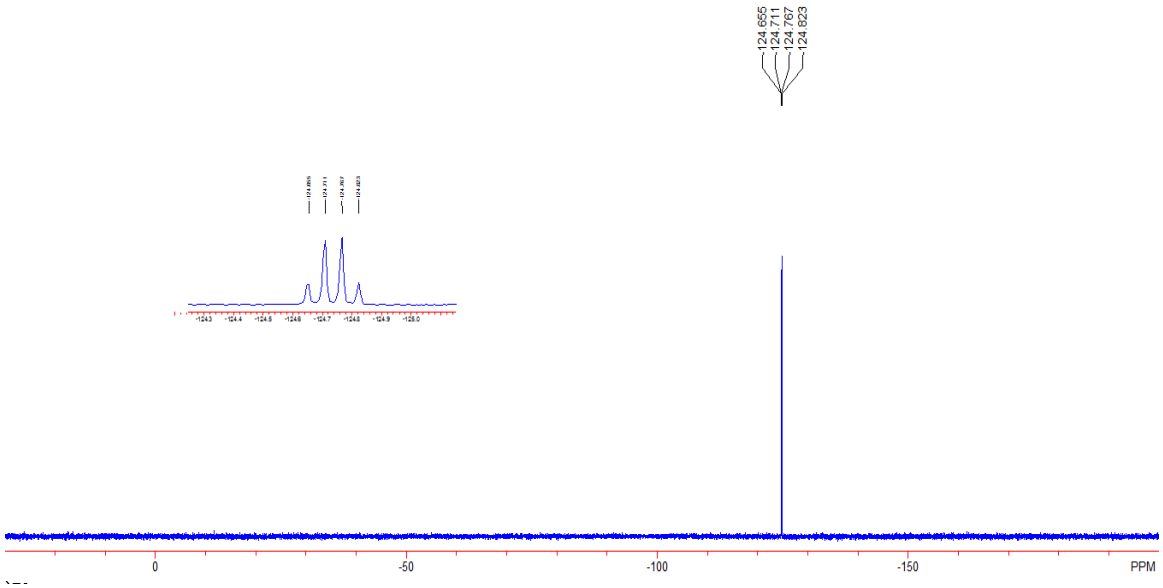


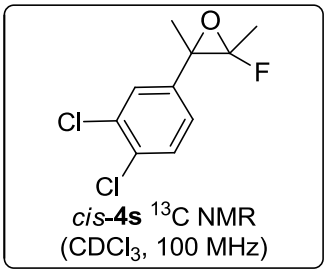
cis-**4s** ^{1}H NMR
($CDCl_3$, 300 MHz)



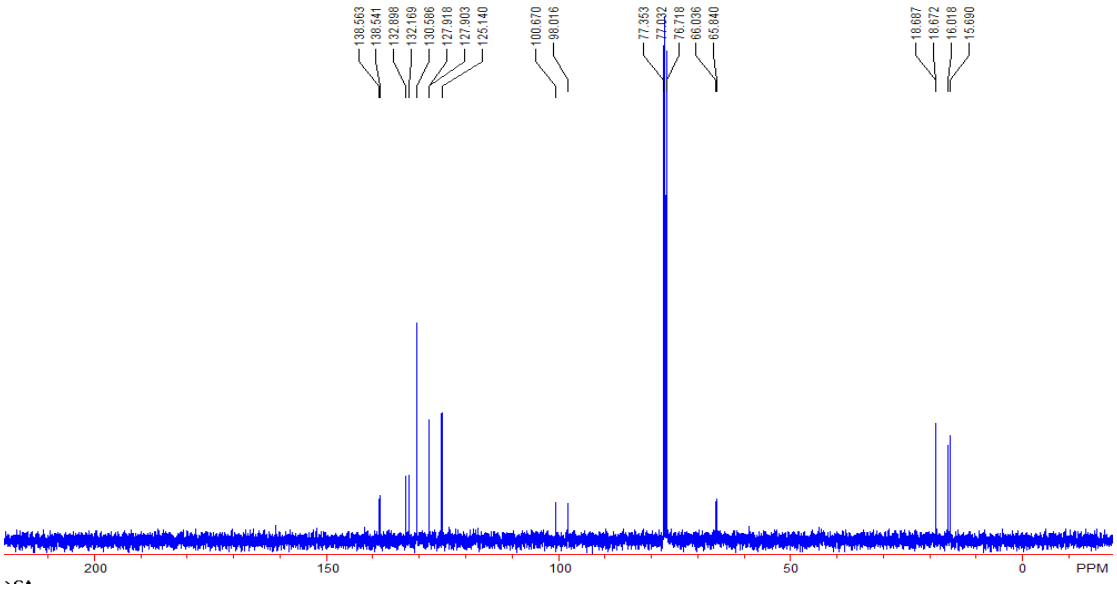


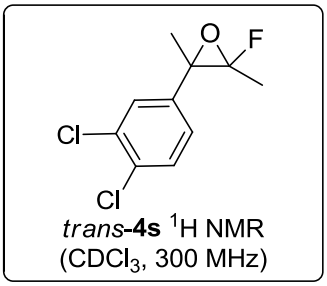
cis-**4s** ^{19}F NMR
($CDCl_3$, 282 MHz)



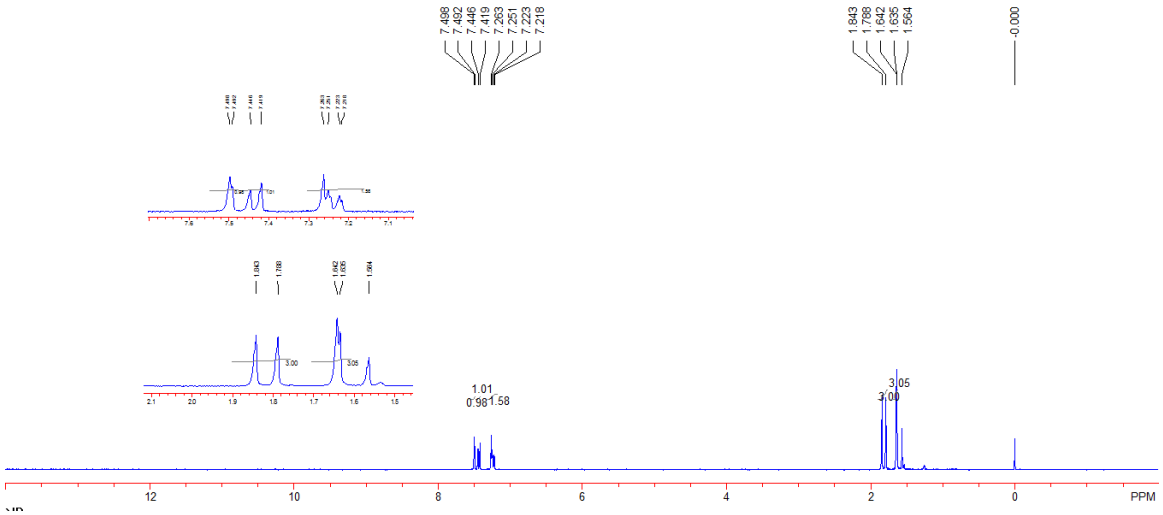


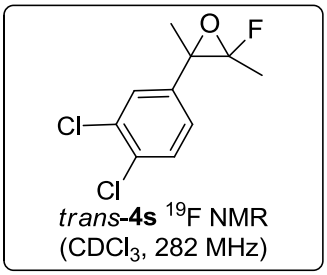
cis-**4s** ^{13}C NMR
($CDCl_3$, 100 MHz)



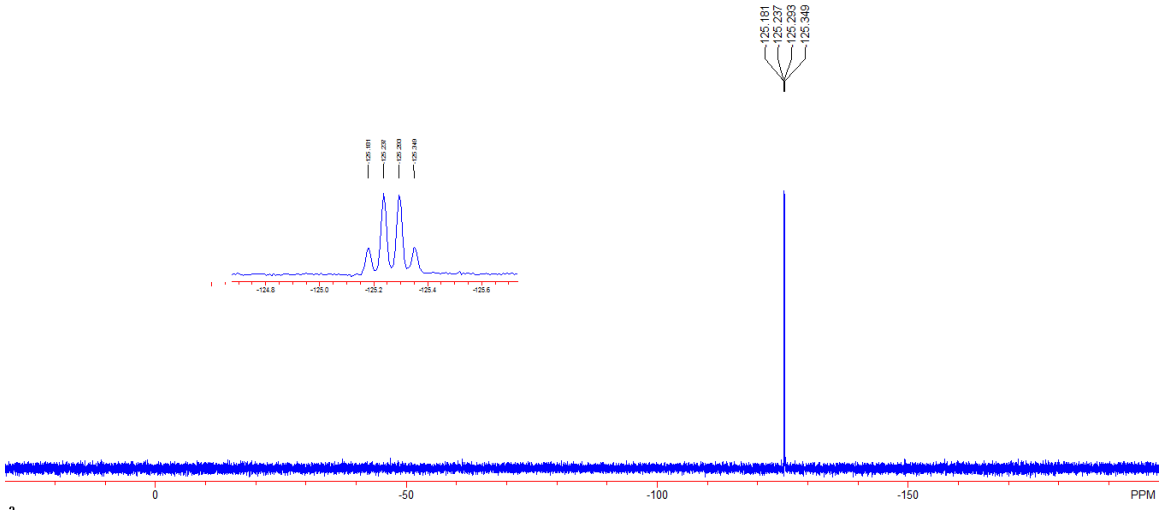


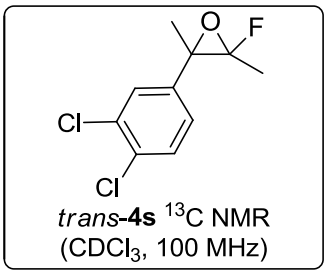
trans-**4s** ^{1}H NMR
($CDCl_3$, 300 MHz)



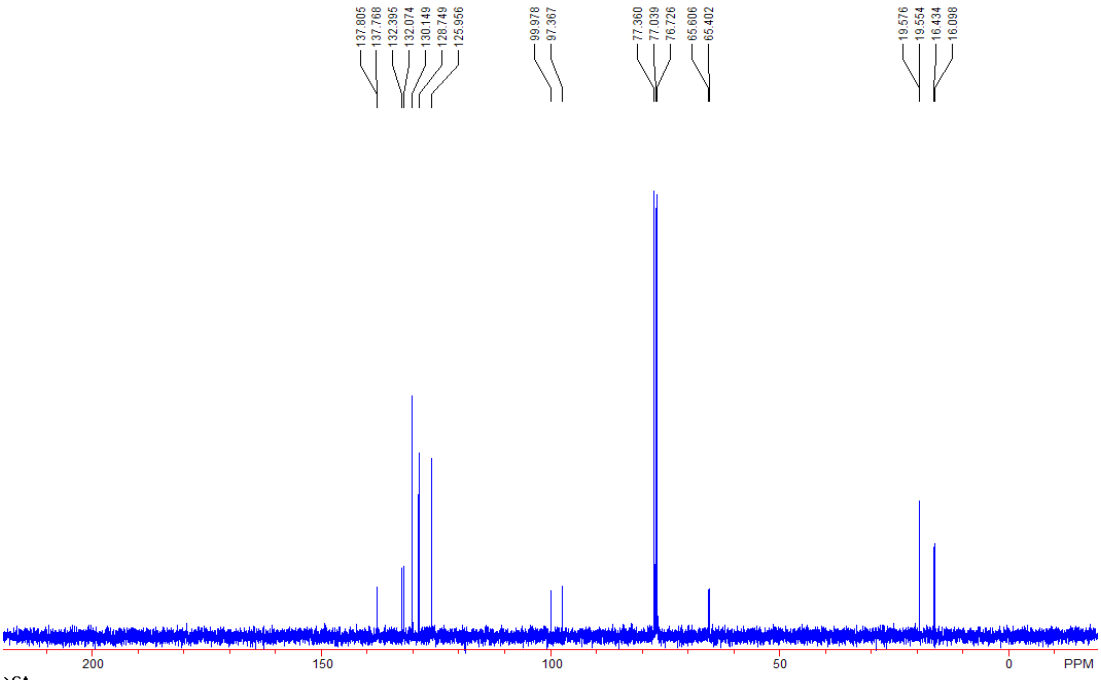


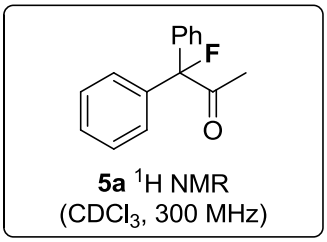
trans-**4s** ^{19}F NMR
($CDCl_3$, 282 MHz)



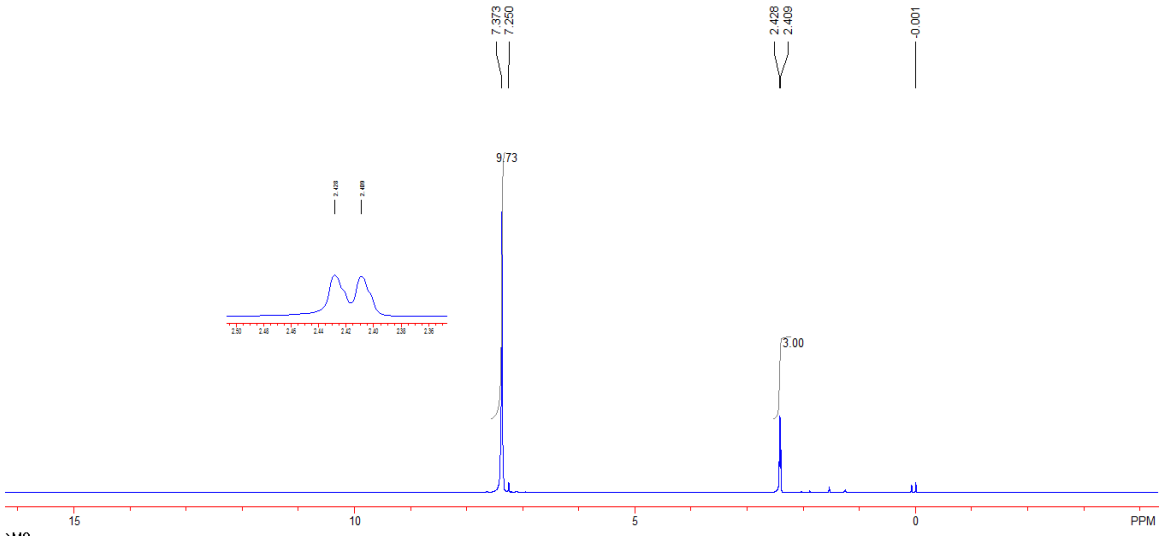


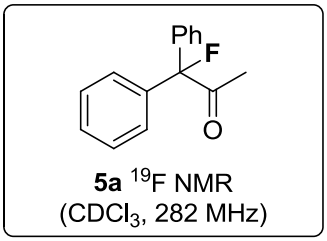
trans-**4s** ^{13}C NMR
($CDCl_3$, 100 MHz)



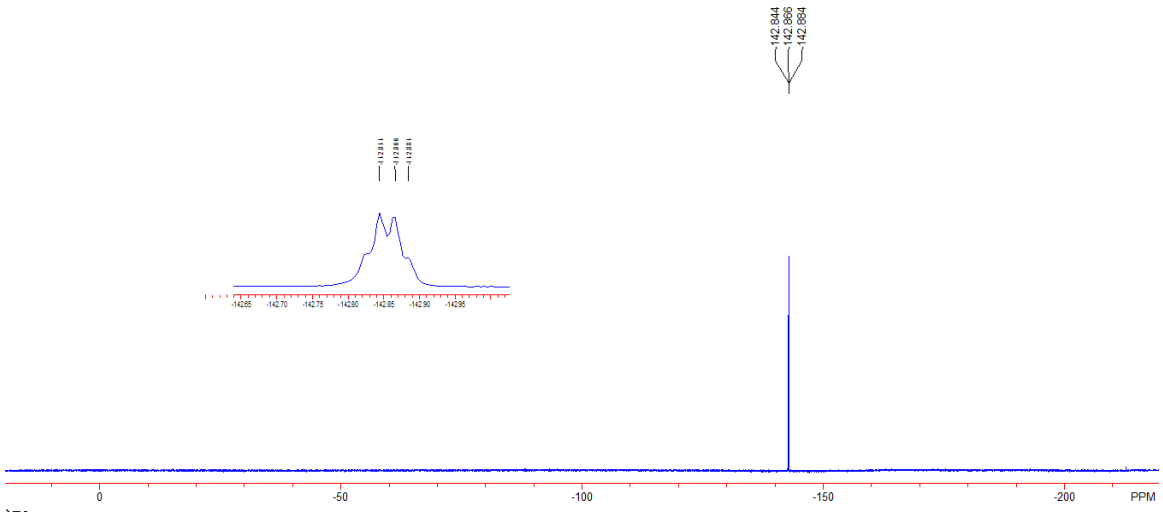


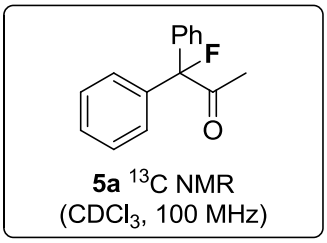
5a ^{1}H NMR
($CDCl_3$, 300 MHz)



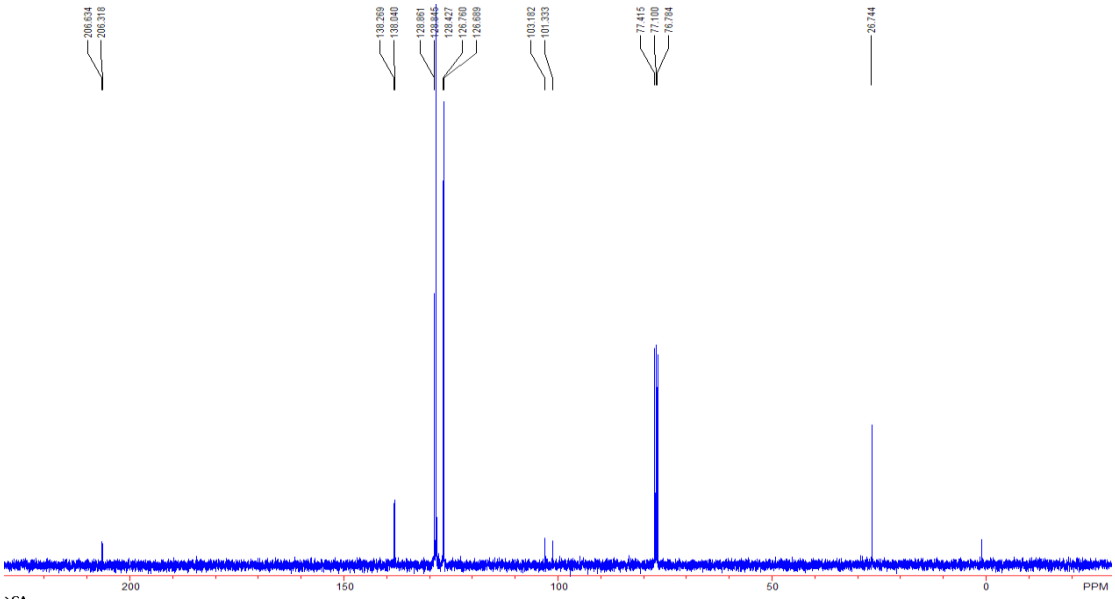


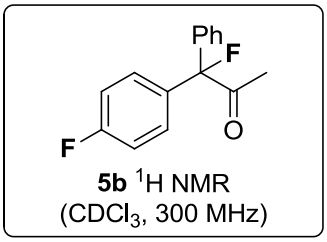
5a ^{19}F NMR
($CDCl_3$, 282 MHz)



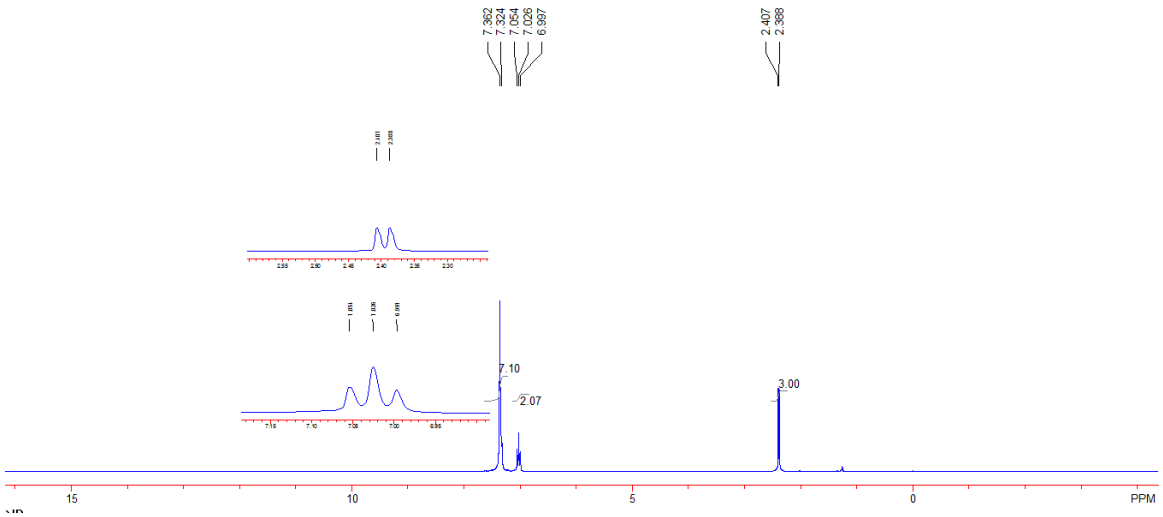


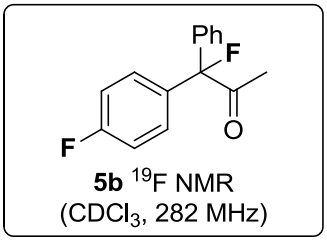
5a ^{13}C NMR
($CDCl_3$, 100 MHz)



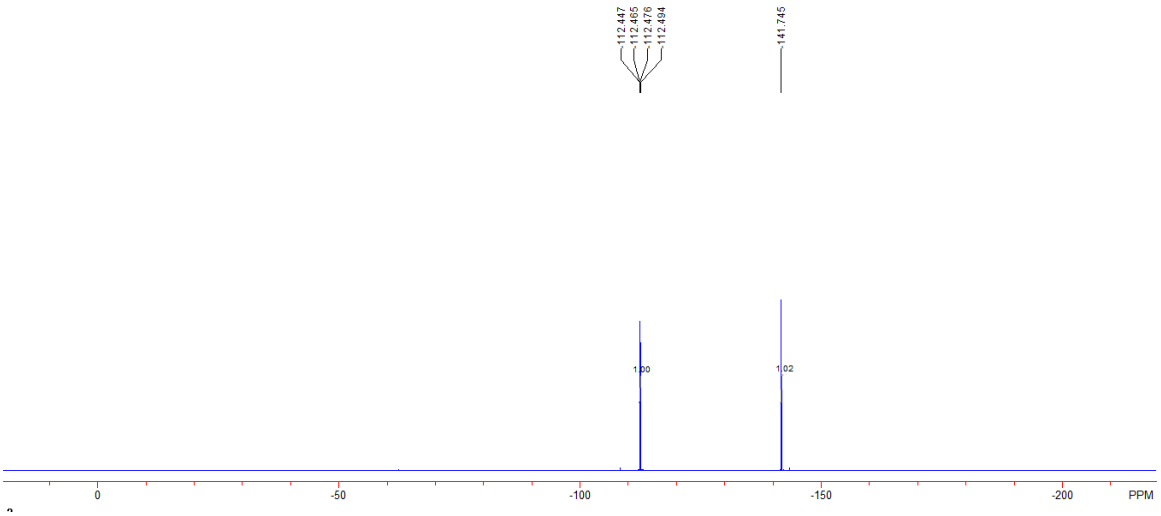


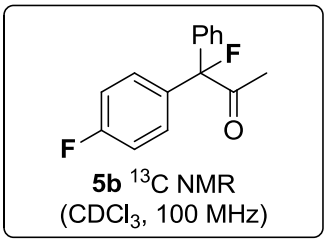
5b ^{1}H NMR
($CDCl_3$, 300 MHz)



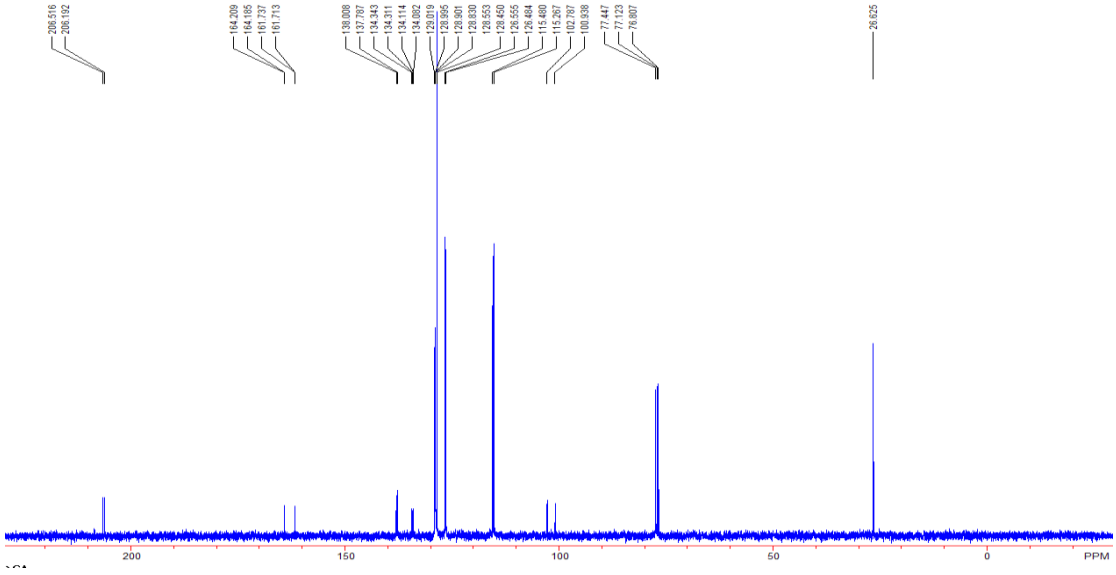


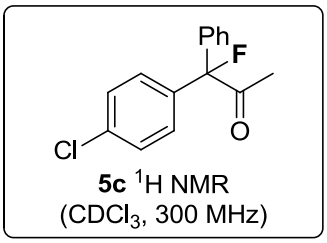
5b ^{19}F NMR
($CDCl_3$, 282 MHz)



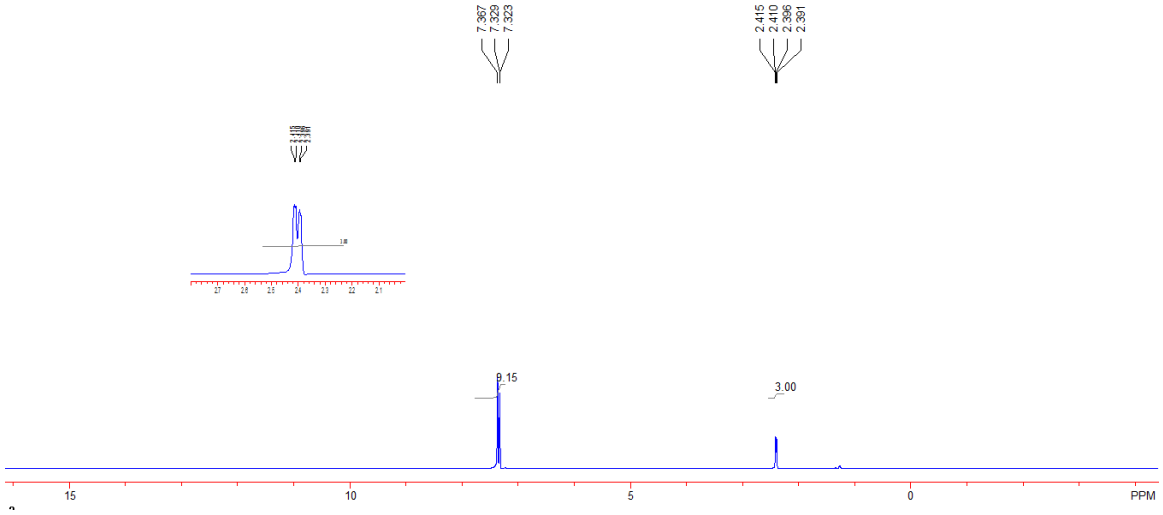


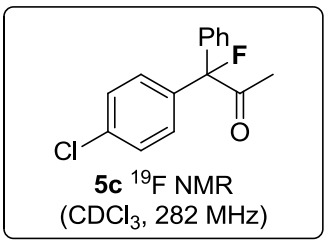
5b ^{13}C NMR
($CDCl_3$, 100 MHz)



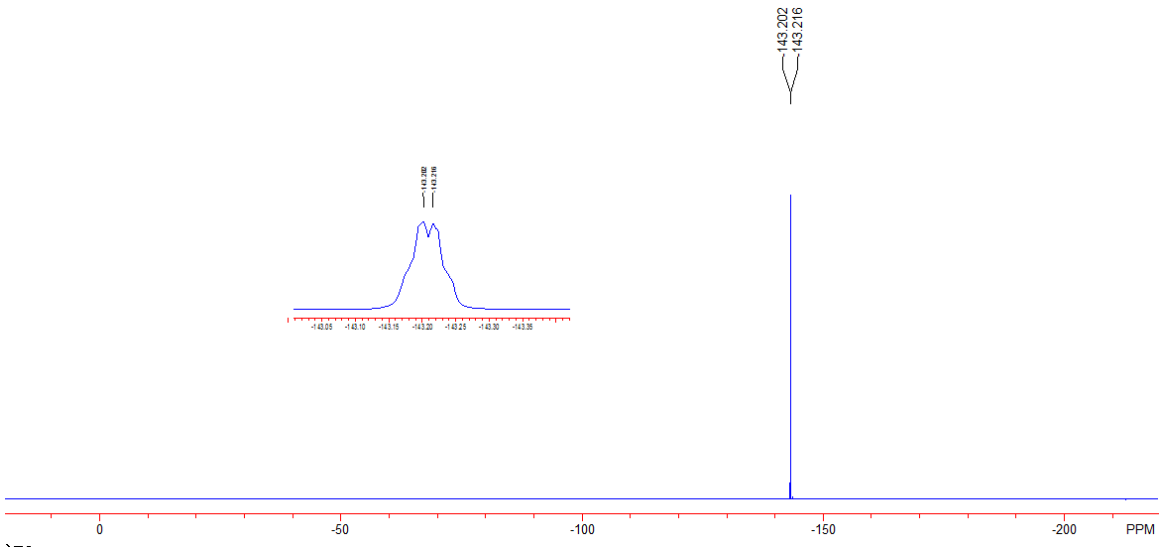


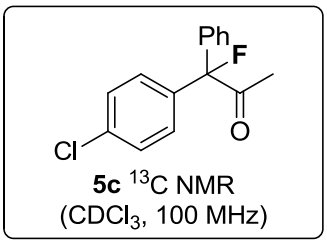
5c ^{1}H NMR
($CDCl_3$, 300 MHz)



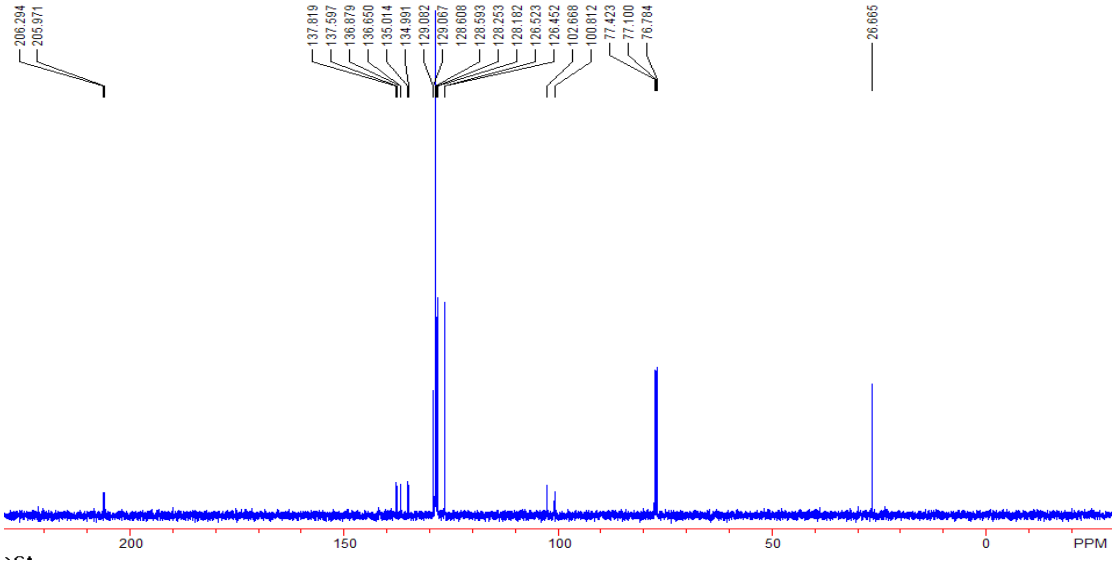


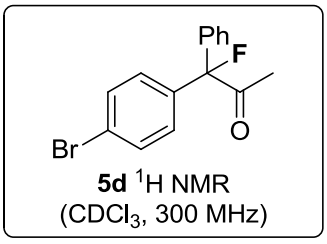
5c ^{19}F NMR
($CDCl_3$, 282 MHz)



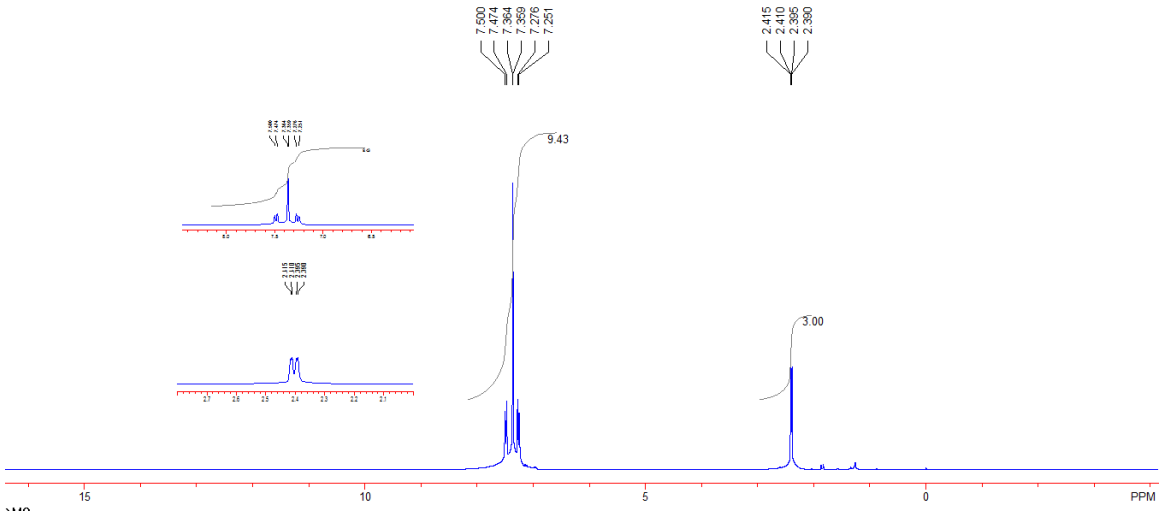


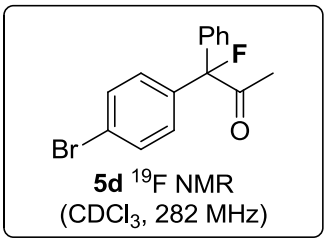
5c ^{13}C NMR
($CDCl_3$, 100 MHz)



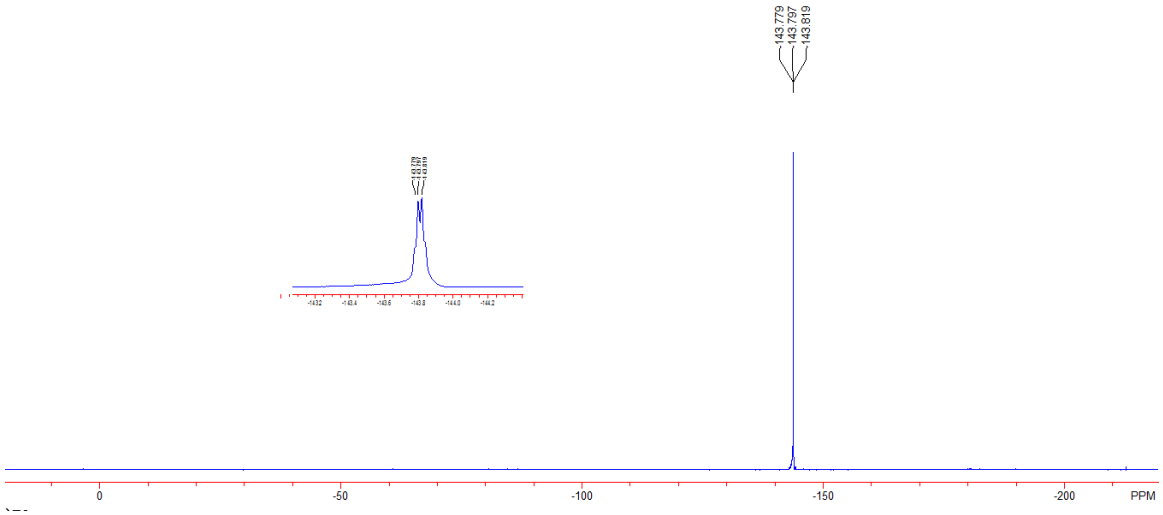


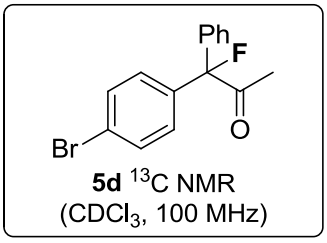
5d ^{1}H NMR
($CDCl_3$, 300 MHz)



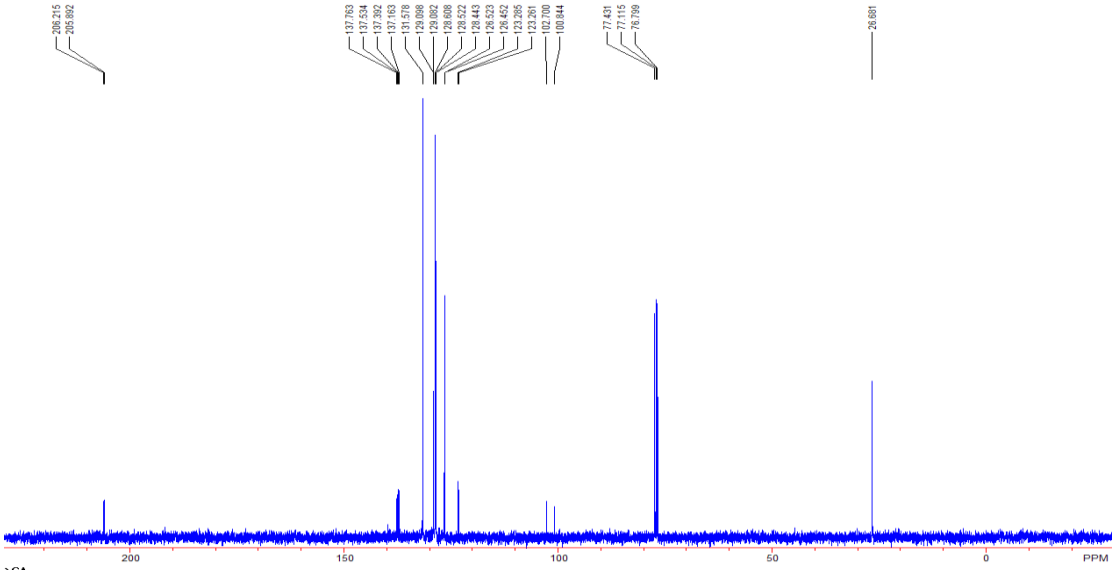


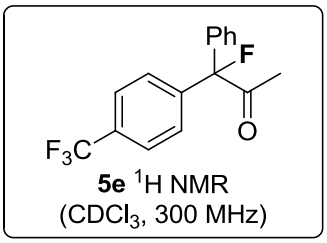
5d ^{19}F NMR
($CDCl_3$, 282 MHz)



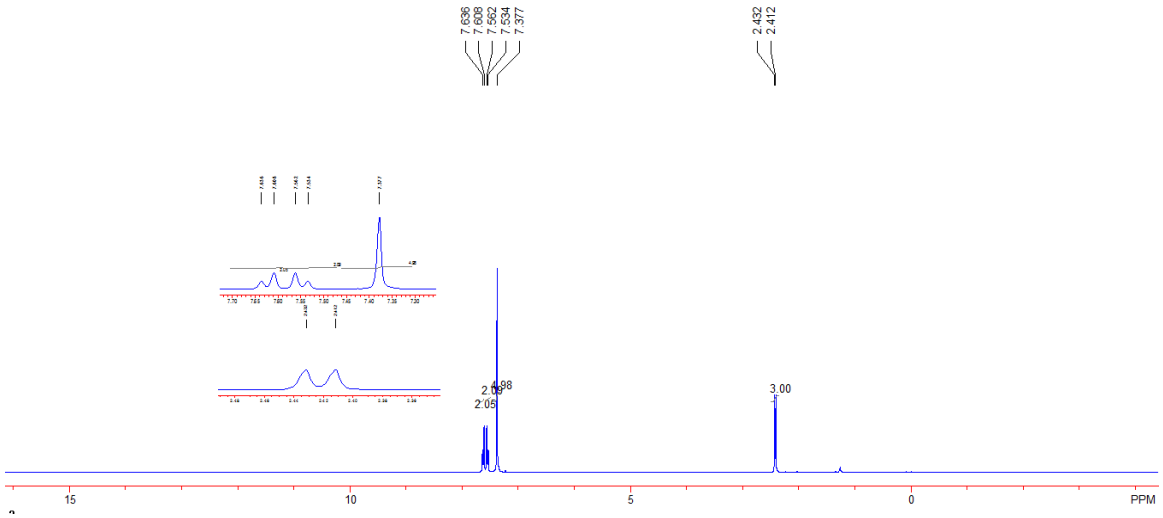


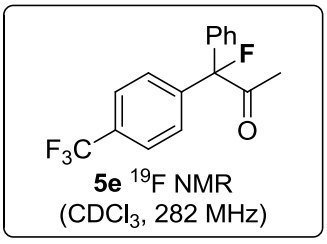
5d ^{13}C NMR
($CDCl_3$, 100 MHz)



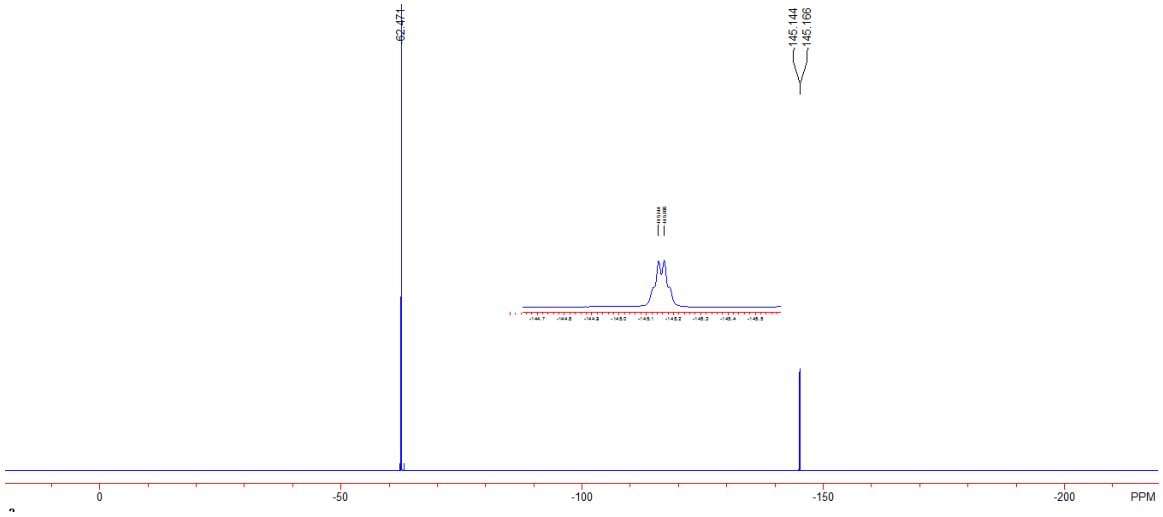


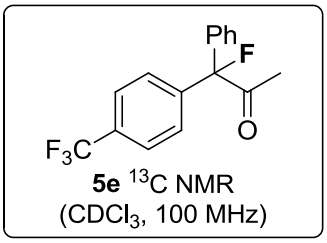
5e ^{1}H NMR
($CDCl_3$, 300 MHz)



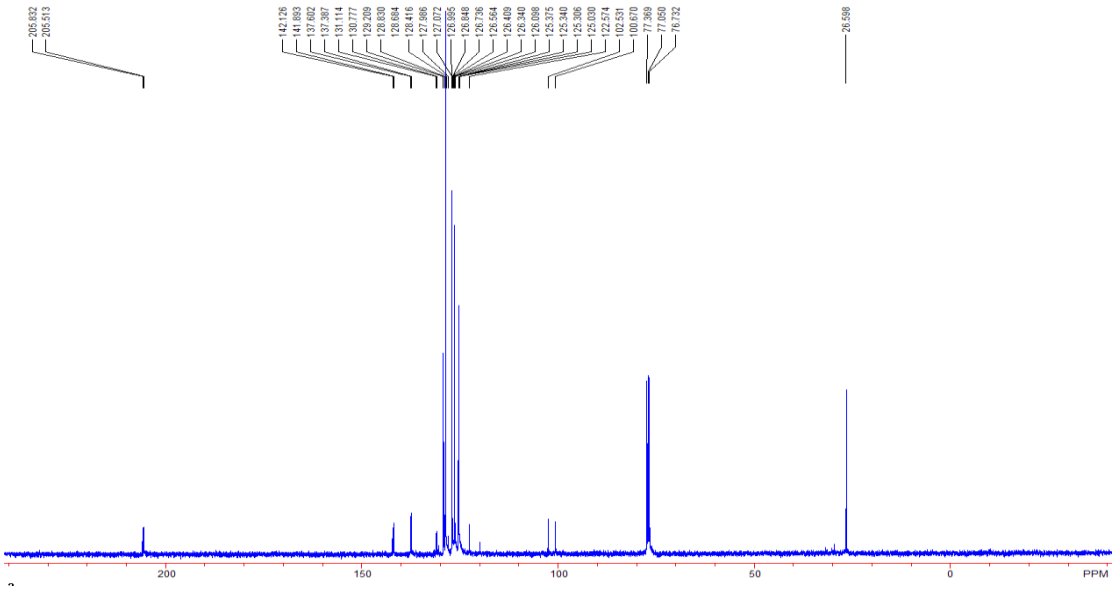


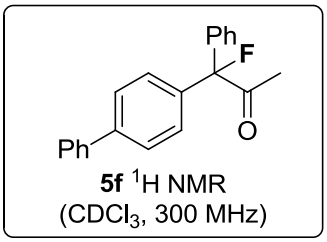
5e ^{19}F NMR
($CDCl_3$, 282 MHz)



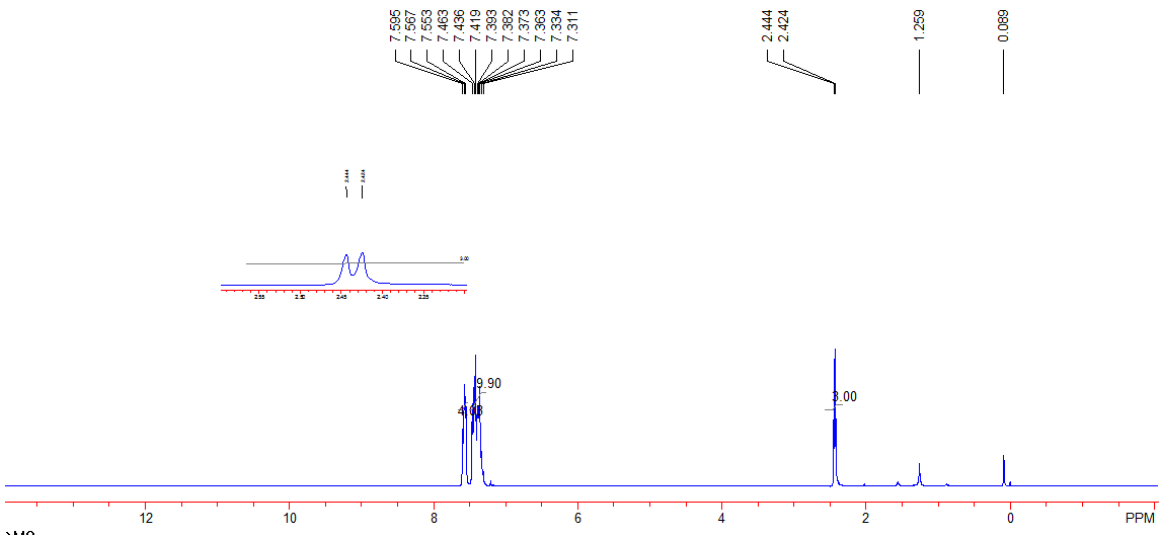


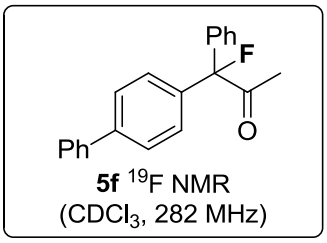
5e ^{13}C NMR
($CDCl_3$, 100 MHz)



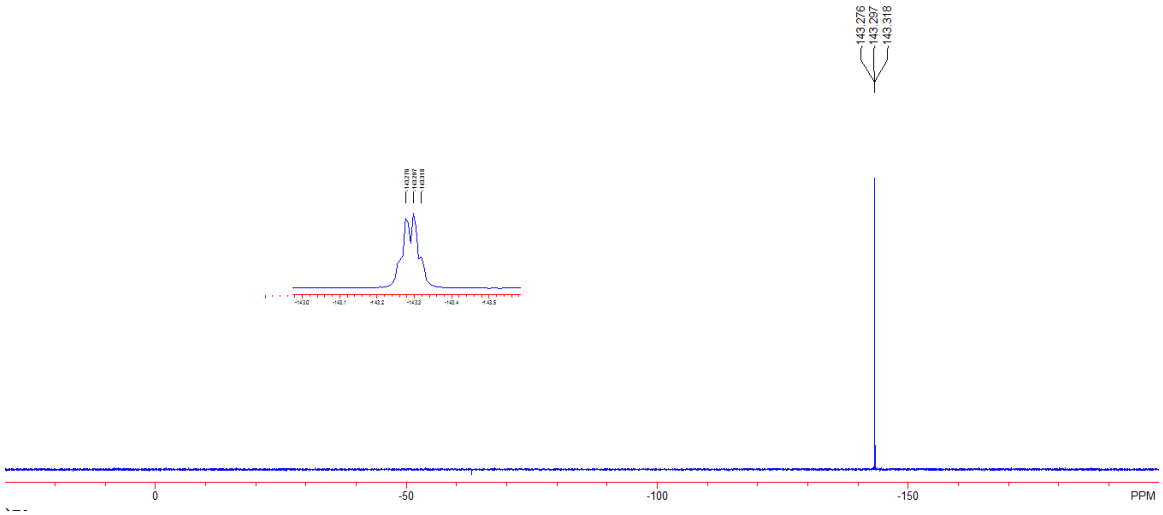


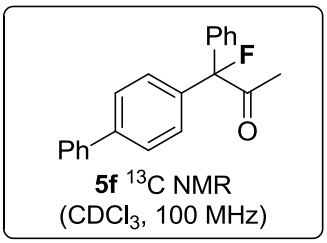
5f ^{1}H NMR
($CDCl_3$, 300 MHz)



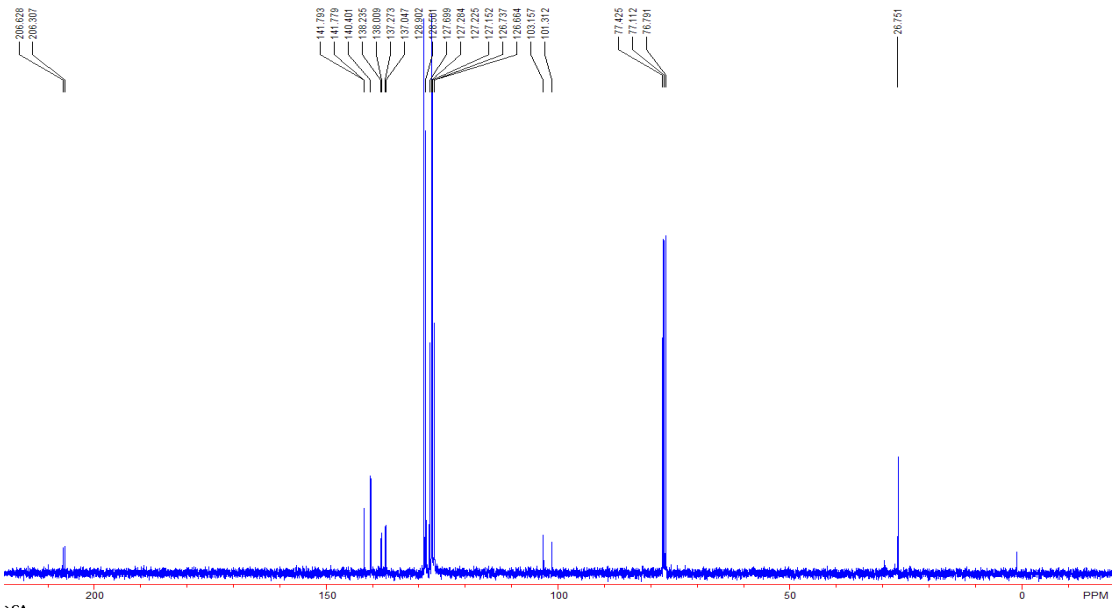


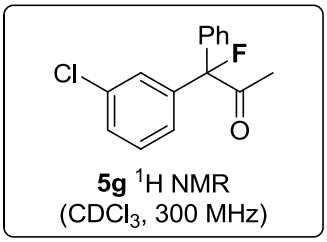
5f ^{19}F NMR
($CDCl_3$, 282 MHz)



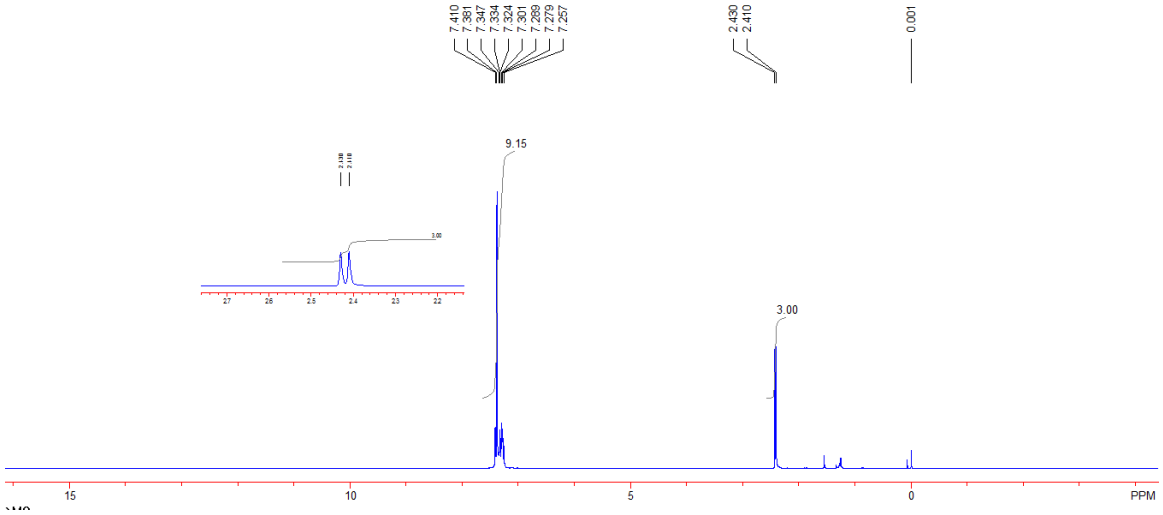


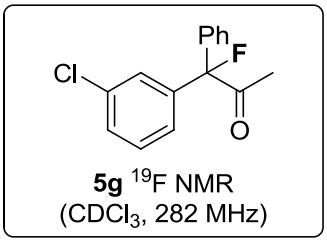
5f ^{13}C NMR
($CDCl_3$, 100 MHz)



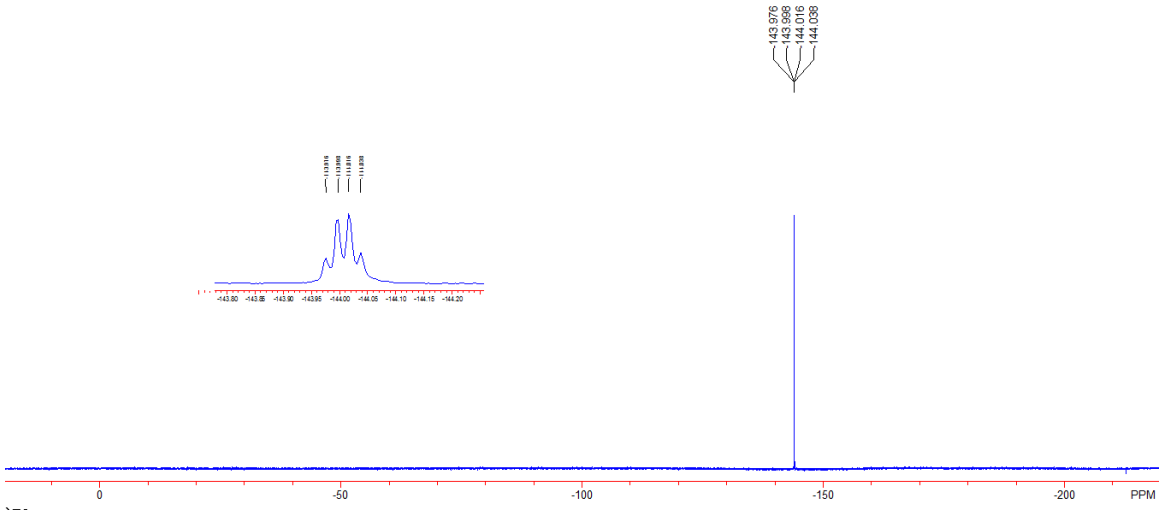


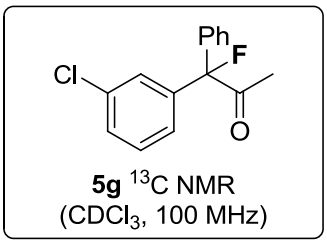
5g ^{1}H NMR
($CDCl_3$, 300 MHz)



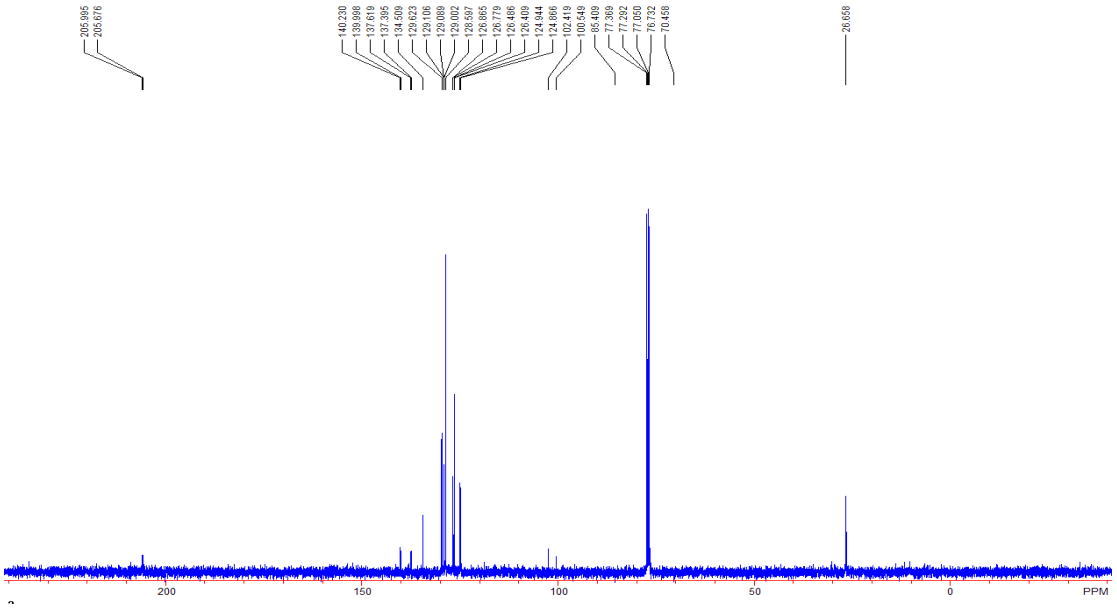


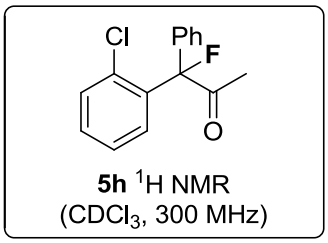
5g ^{19}F NMR
($CDCl_3$, 282 MHz)



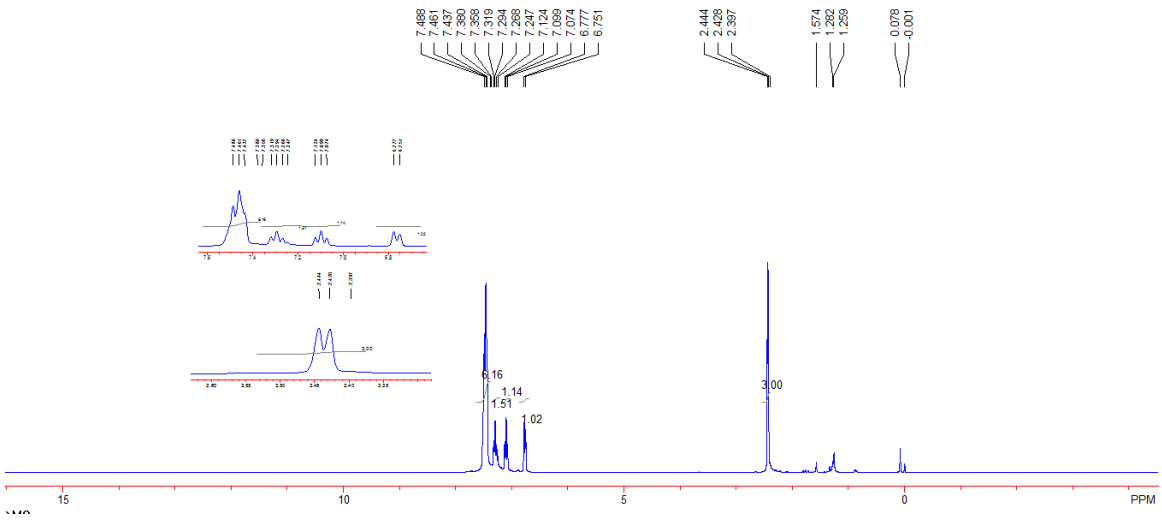


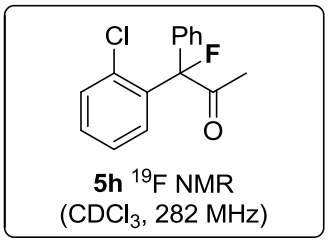
5g ^{13}C NMR
($CDCl_3$, 100 MHz)



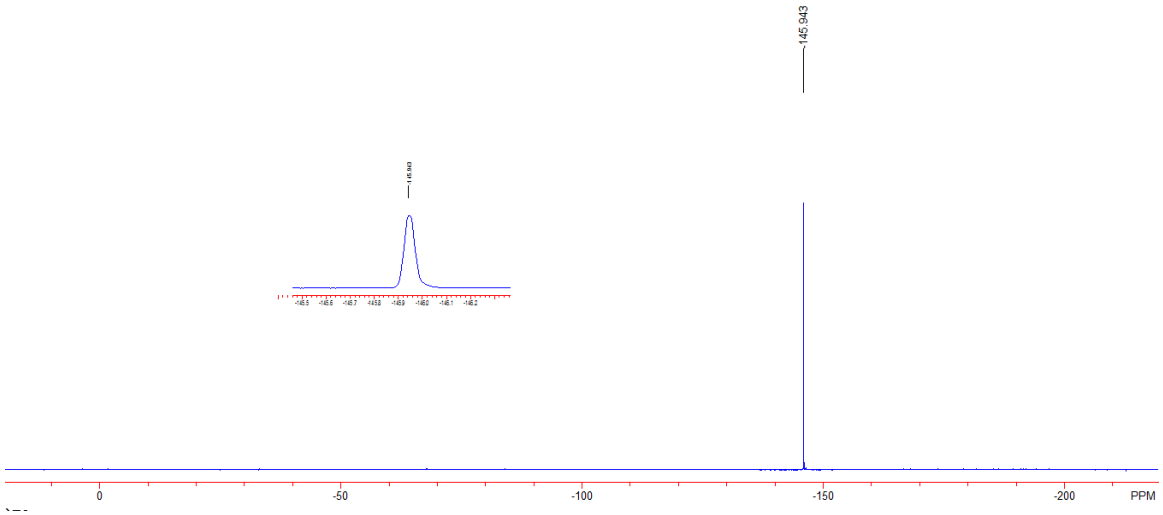


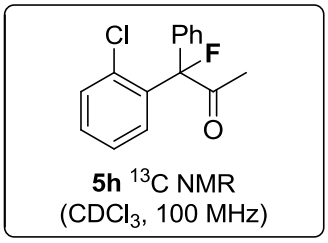
5h ^{1}H NMR
($CDCl_3$, 300 MHz)



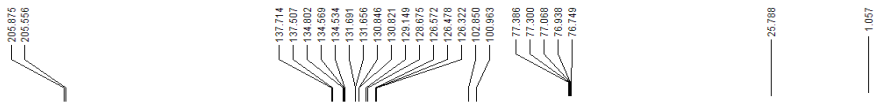


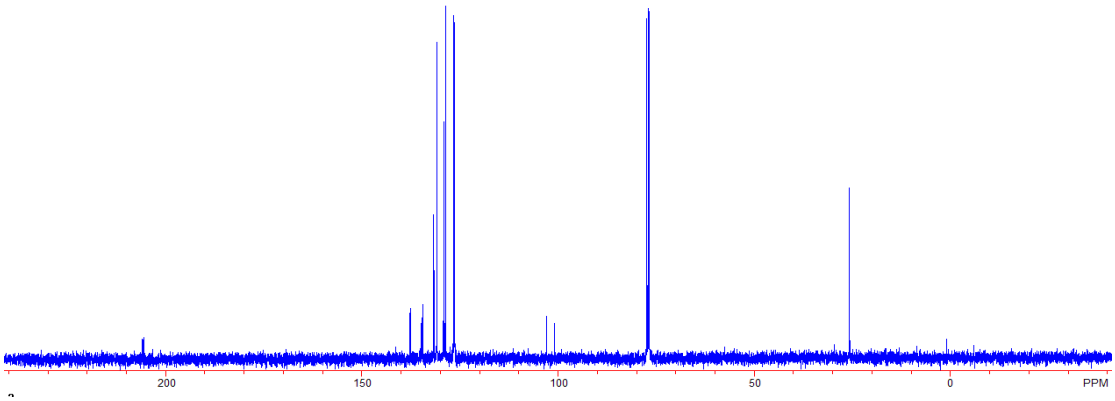
5h ^{19}F NMR
($CDCl_3$, 282 MHz)

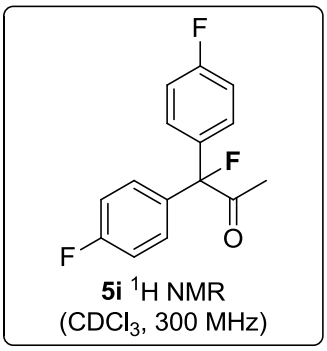




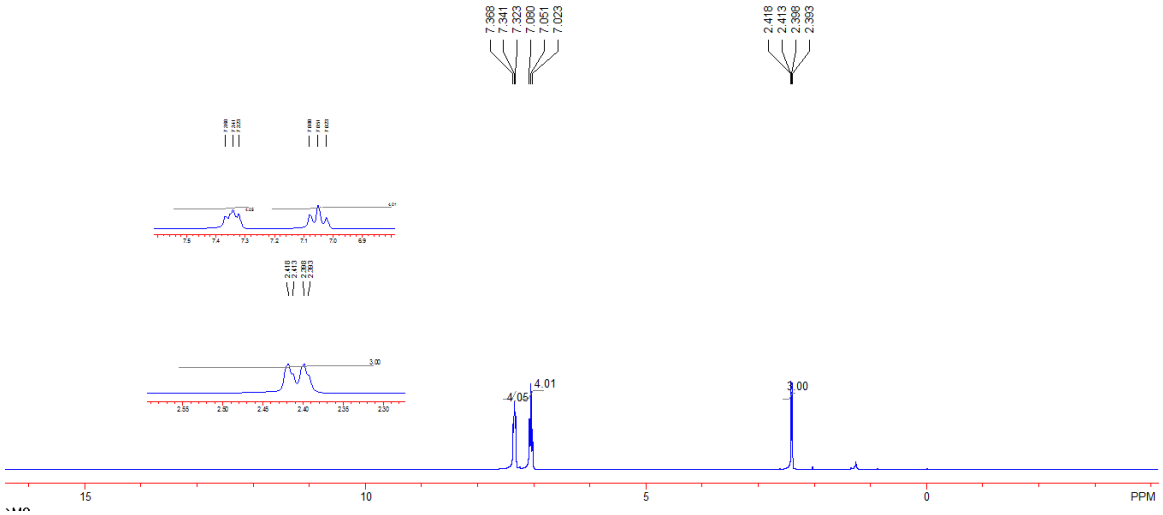
5h ^{13}C NMR
($CDCl_3$, 100 MHz)

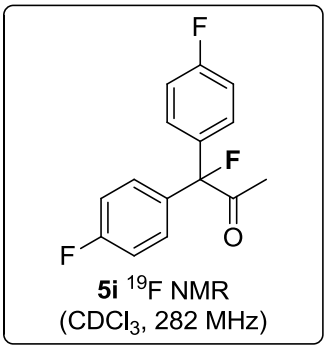




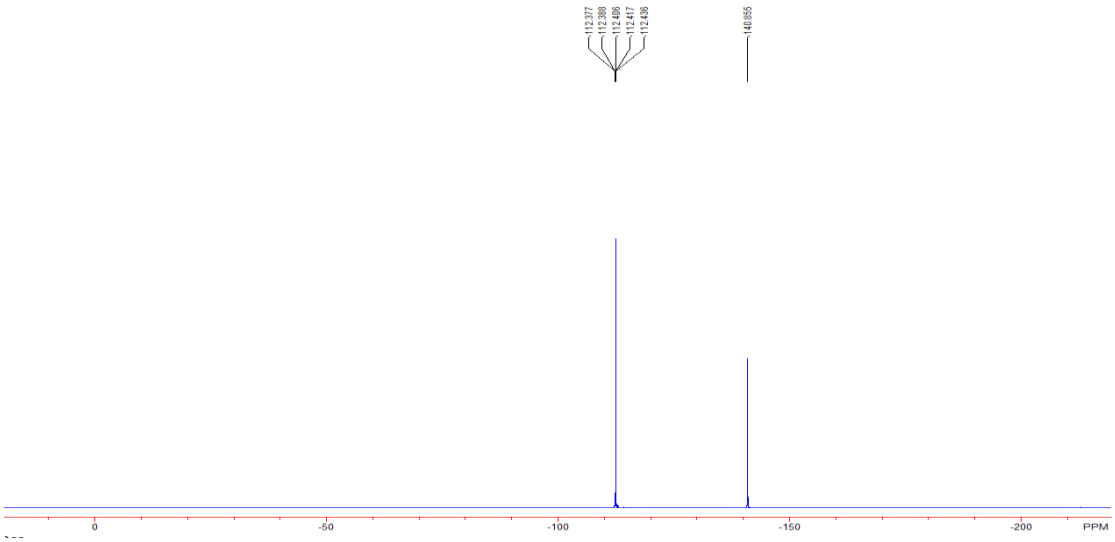


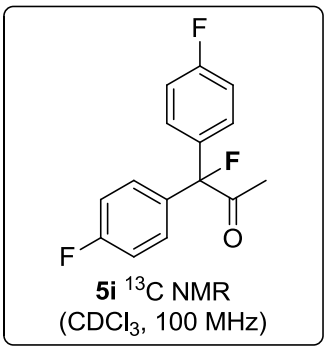
5i ^{1}H NMR
($CDCl_3$, 300 MHz)



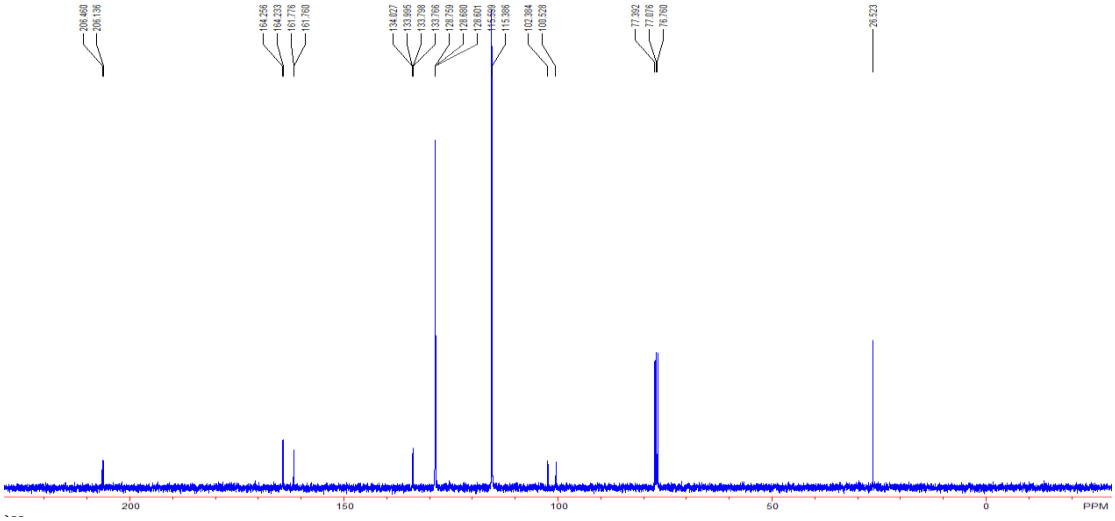


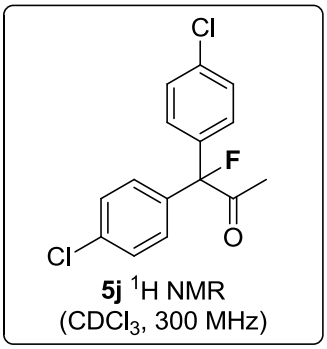
5i ^{19}F NMR
($CDCl_3$, 282 MHz)



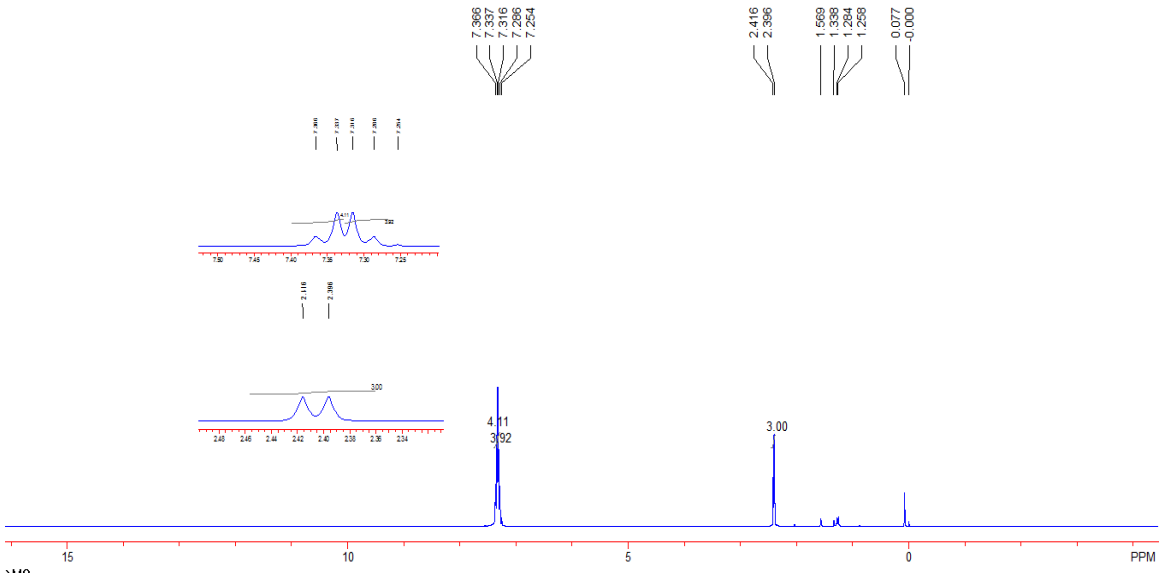


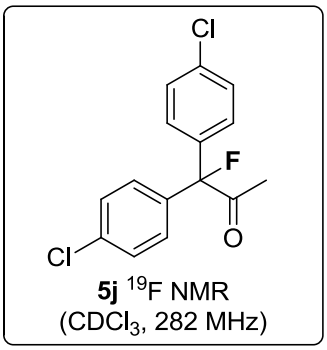
5i ^{13}C NMR
($CDCl_3$, 100 MHz)



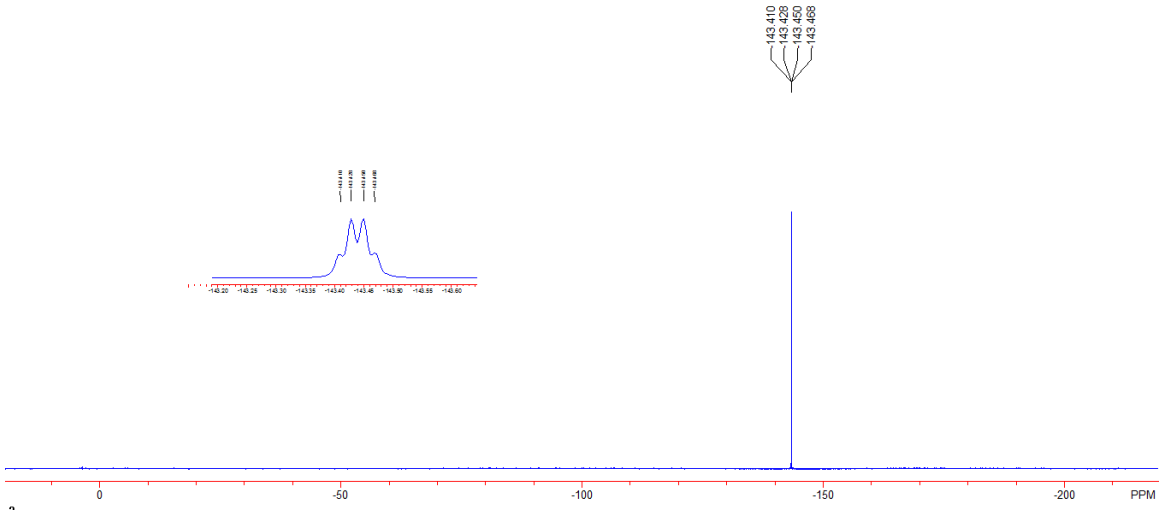


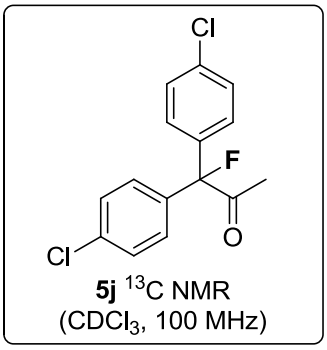
5j ^{1}H NMR
($CDCl_3$, 300 MHz)



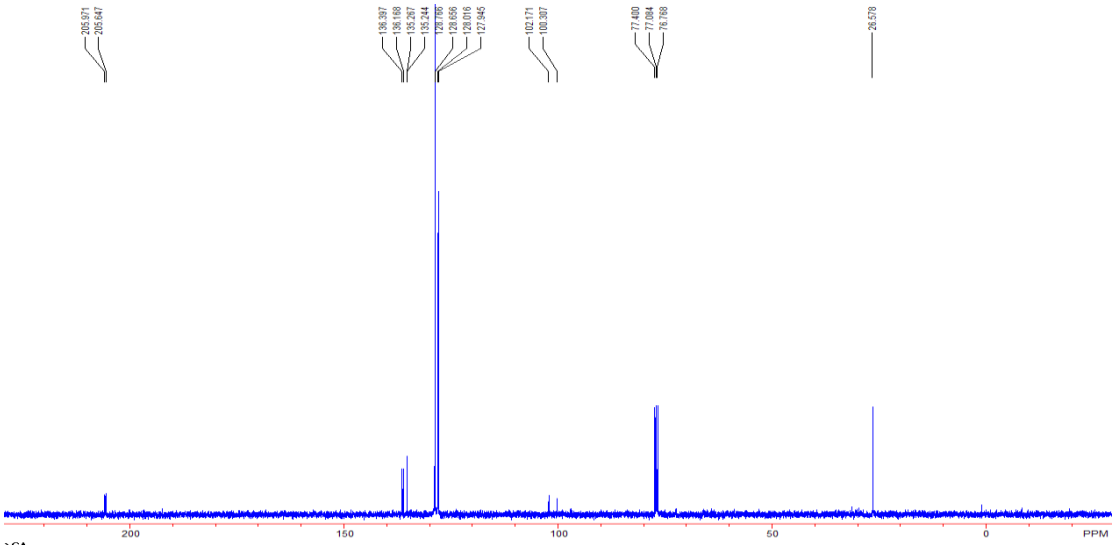


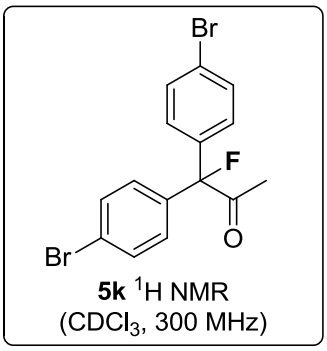
5j ^{19}F NMR
($CDCl_3$, 282 MHz)



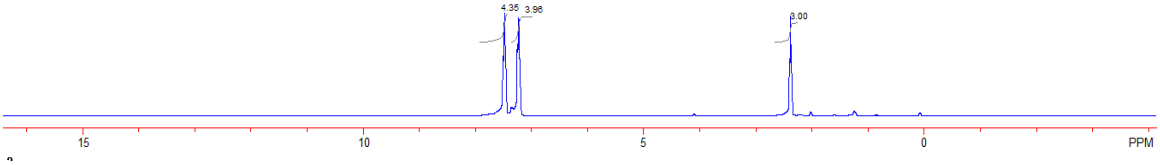


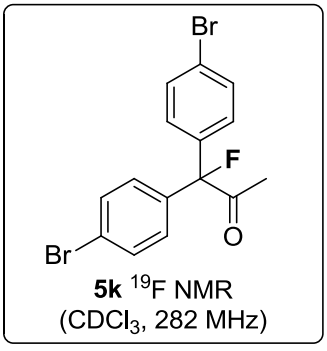
5j ^{13}C NMR
($CDCl_3$, 100 MHz)



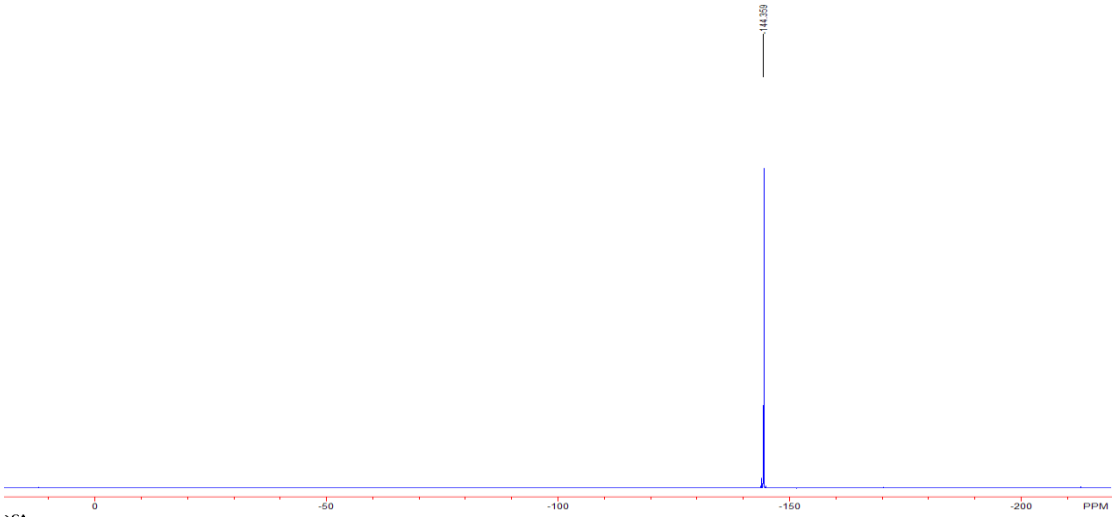


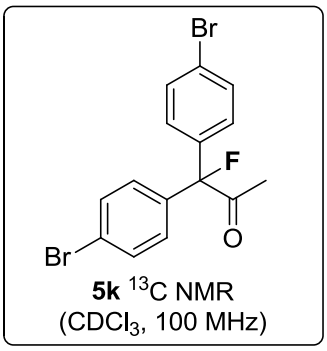
5k ^{1}H NMR
($CDCl_3$, 300 MHz)



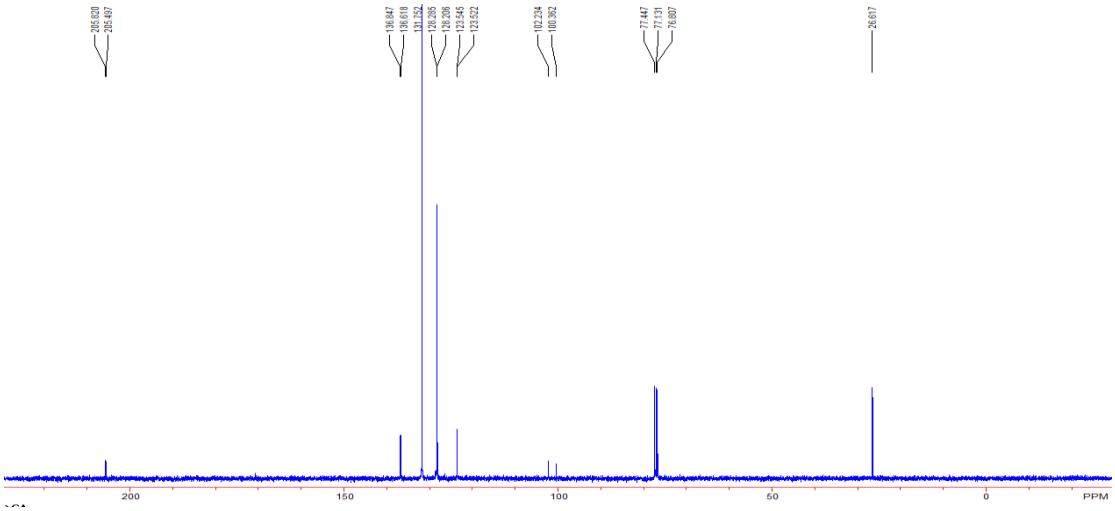


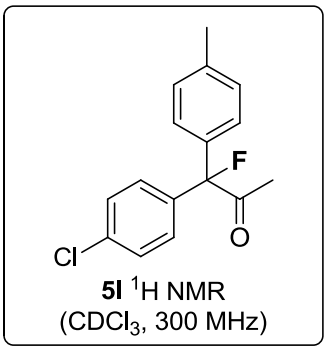
5k ^{19}F NMR
($CDCl_3$, 282 MHz)



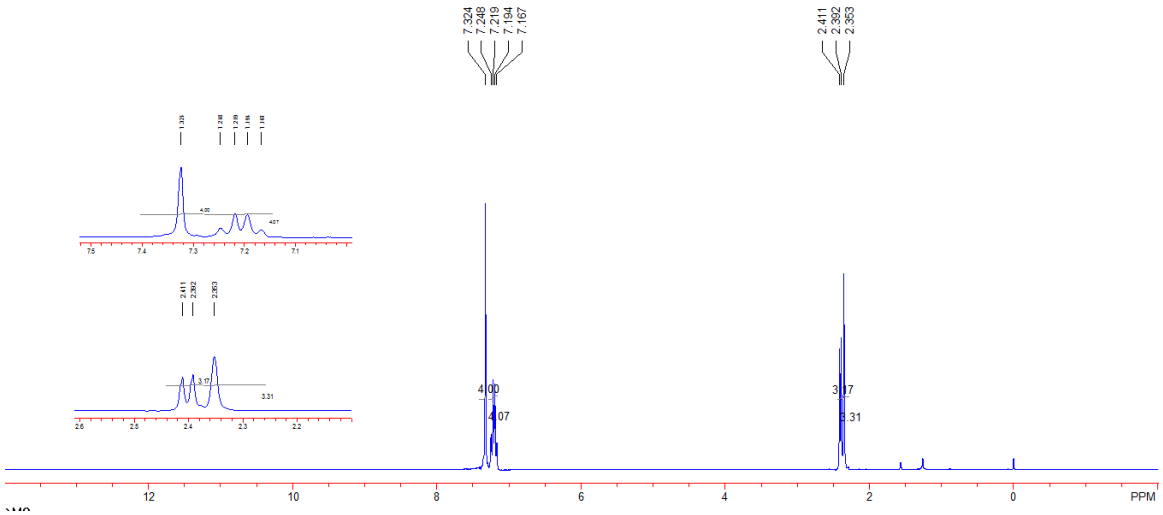


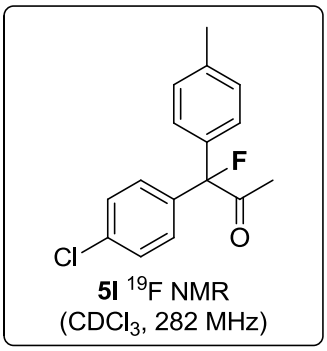
5k ^{13}C NMR
($CDCl_3$, 100 MHz)



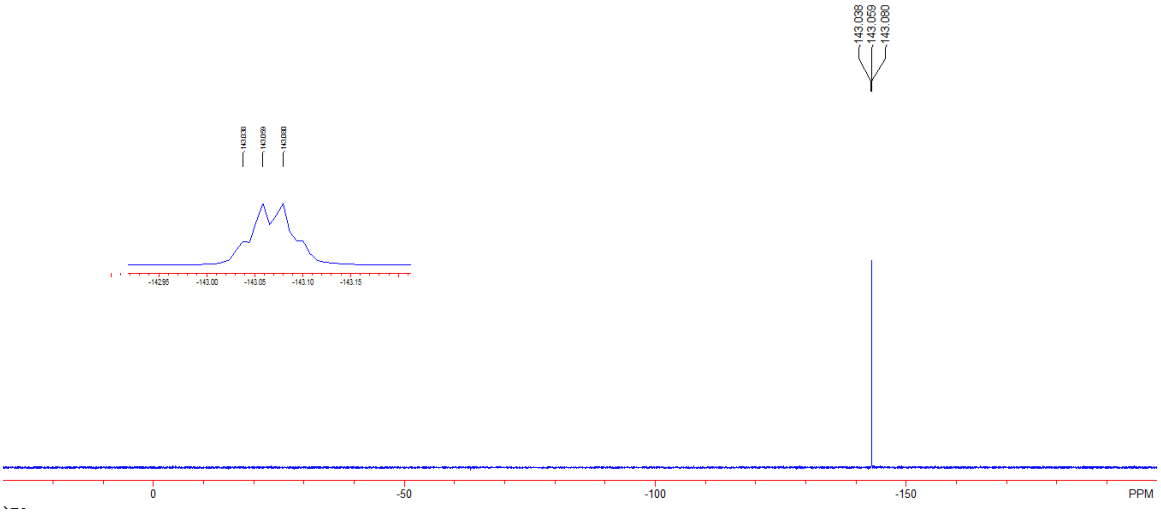


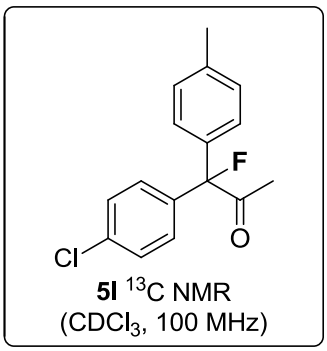
5l ^{1}H NMR
($CDCl_3$, 300 MHz)



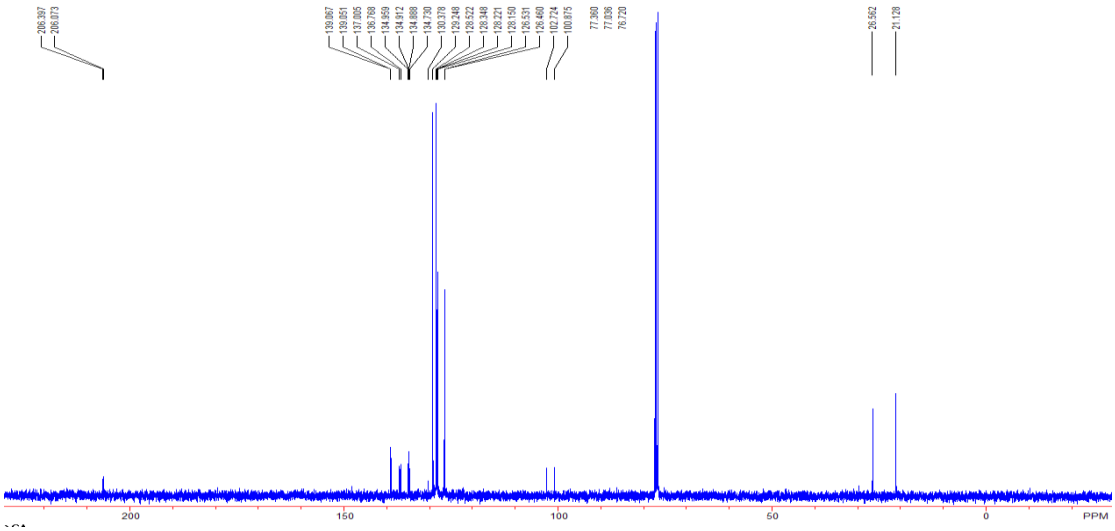


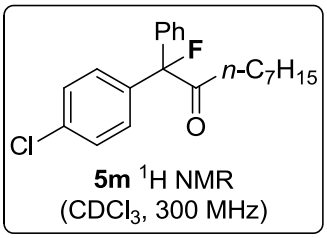
5l ^{19}F NMR
($CDCl_3$, 282 MHz)



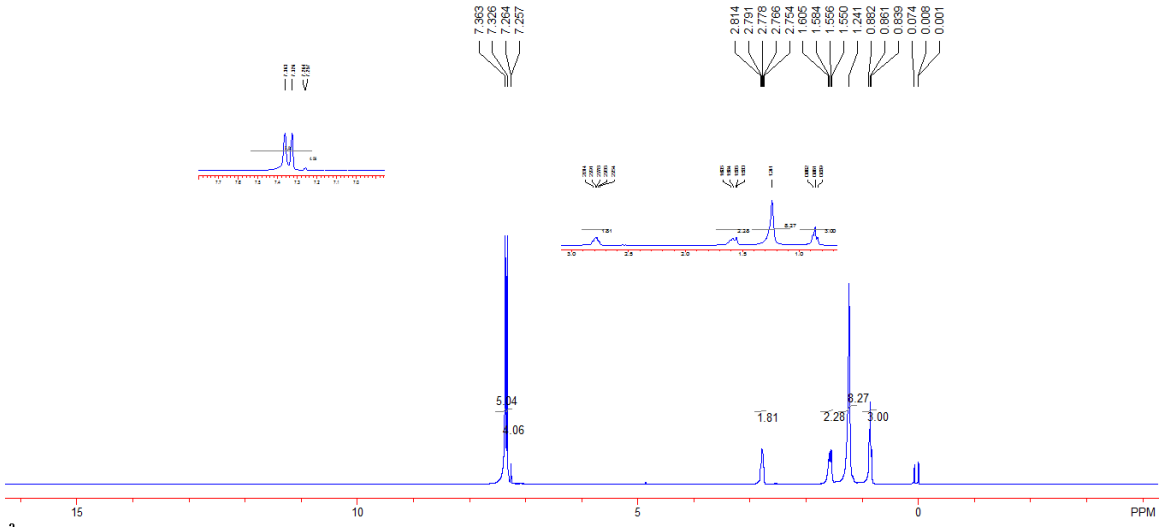


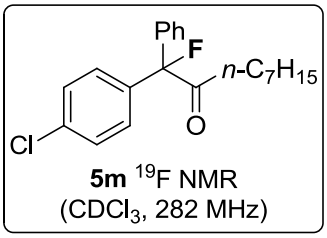
5l ^{13}C NMR
($CDCl_3$, 100 MHz)



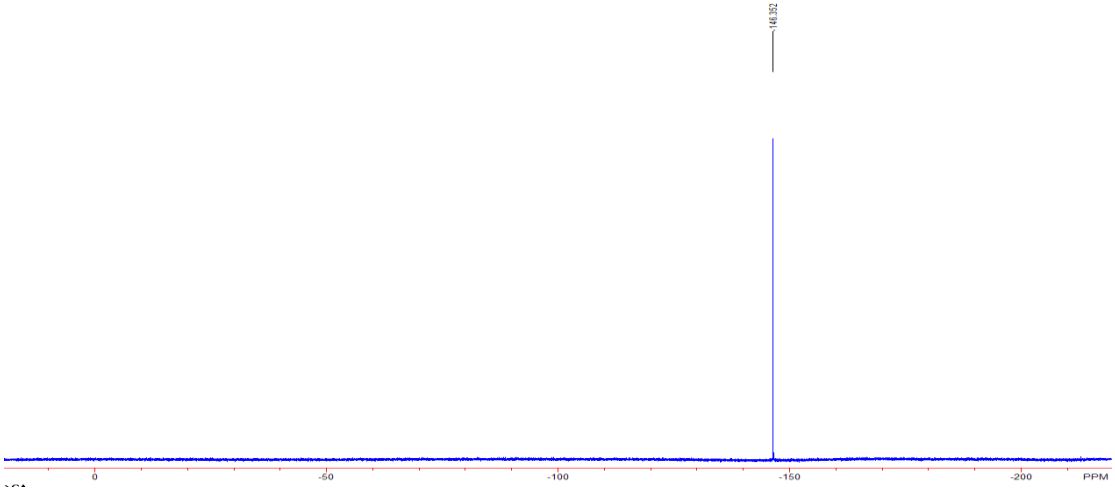


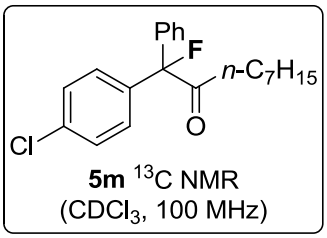
5m ^{1}H NMR
($CDCl_3$, 300 MHz)



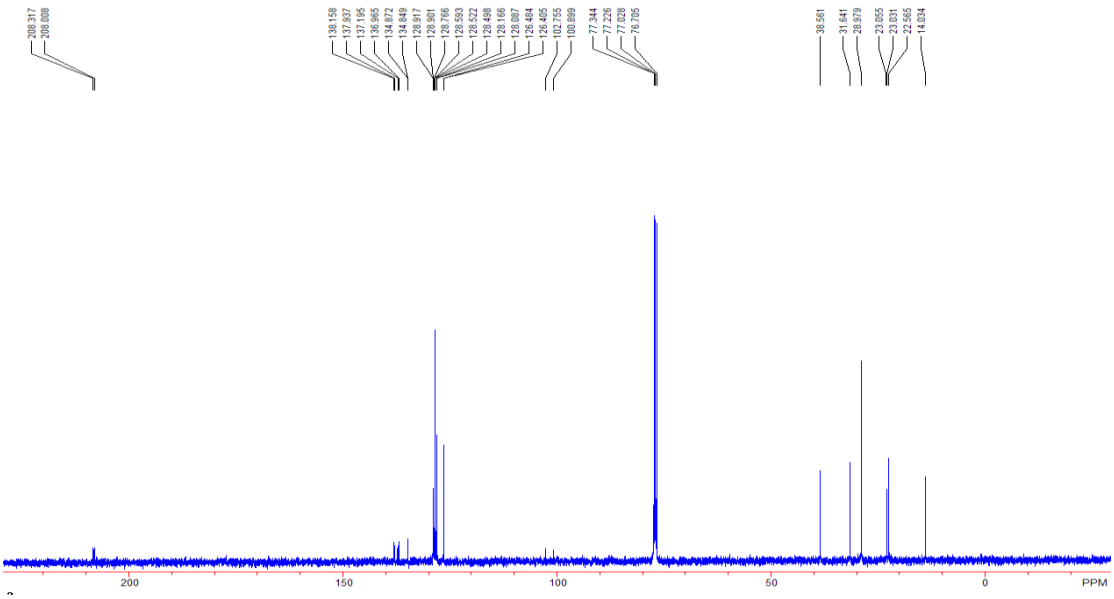


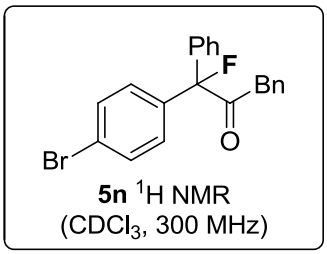
5m ^{19}F NMR
($CDCl_3$, 282 MHz)



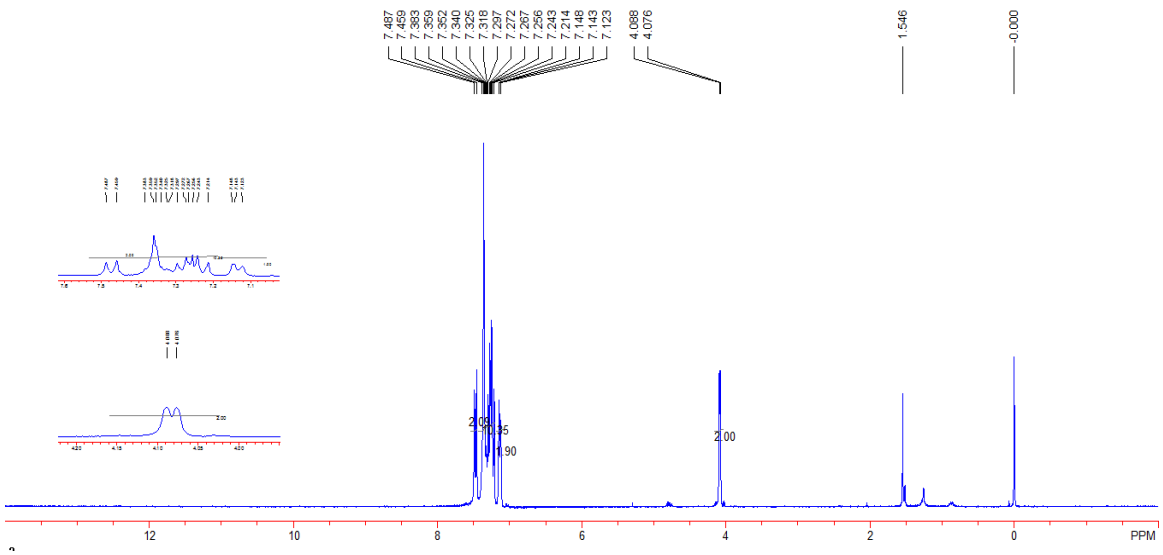


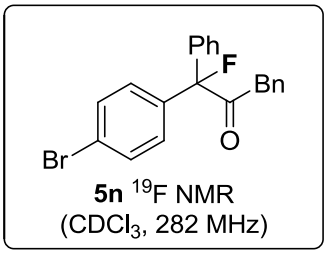
5m ^{13}C NMR
($CDCl_3$, 100 MHz)



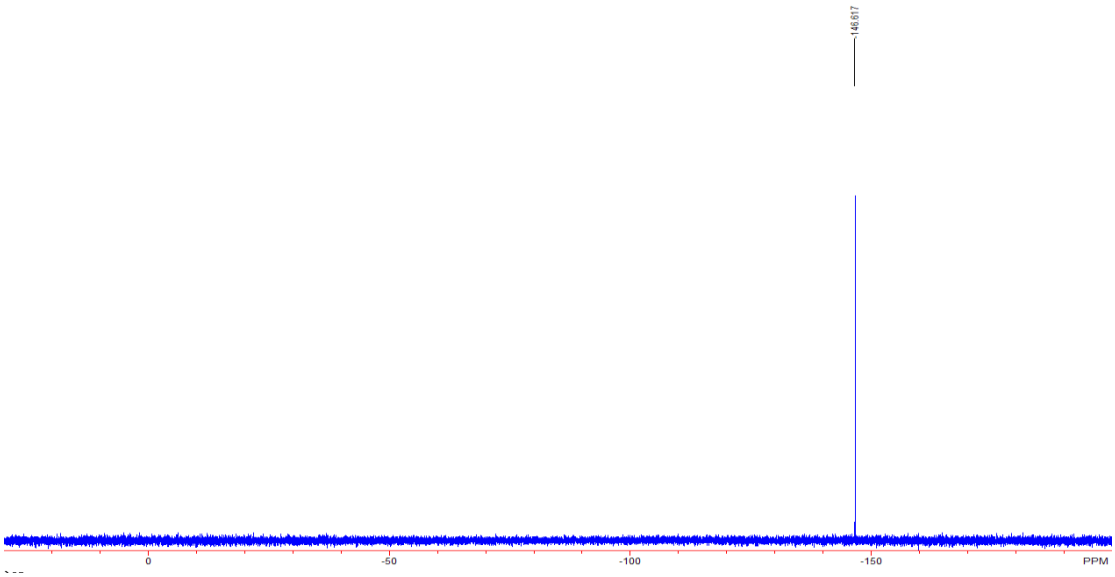


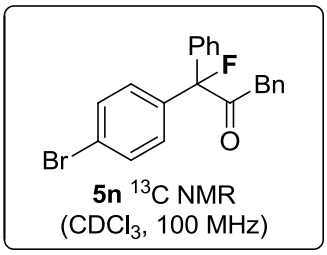
5n ^{1}H NMR
($CDCl_3$, 300 MHz)



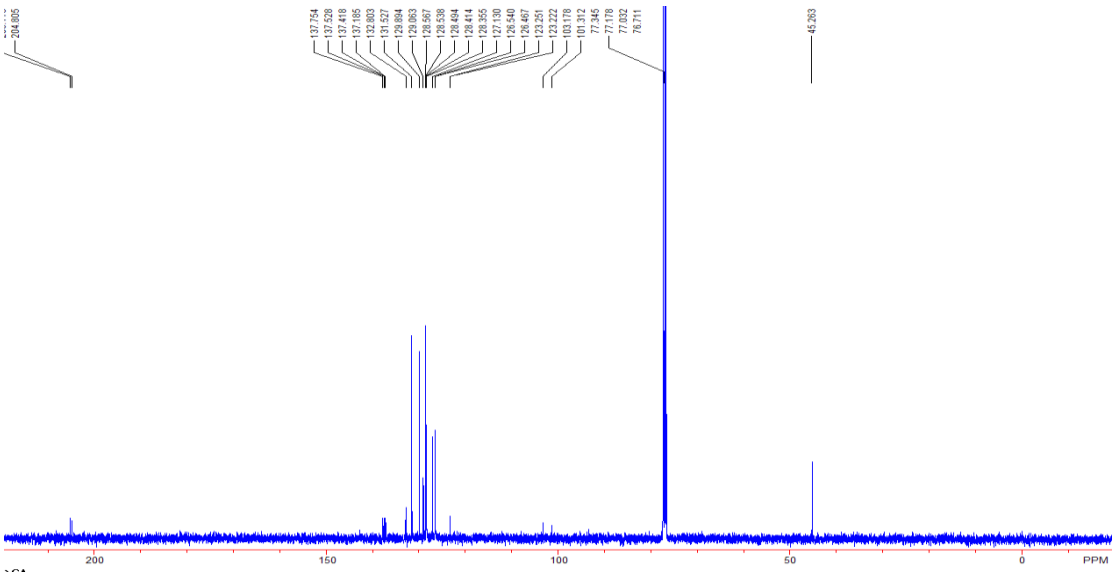


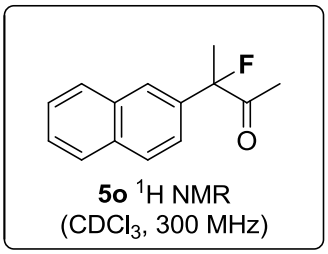
5n ^{19}F NMR
($CDCl_3$, 282 MHz)



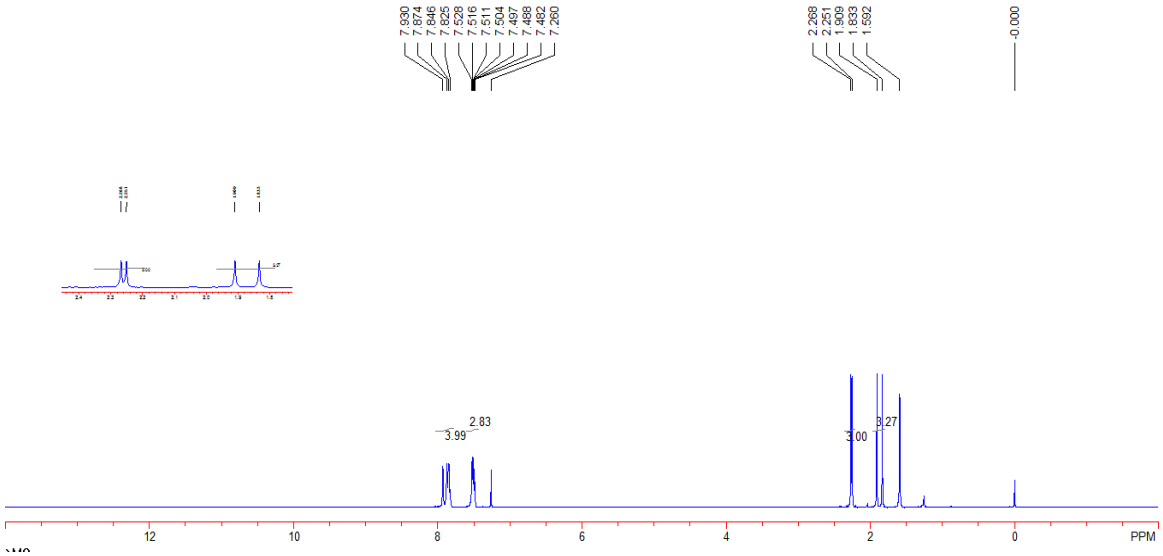


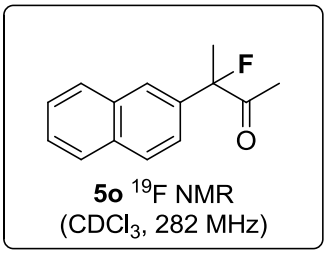
5n ^{13}C NMR
($CDCl_3$, 100 MHz)



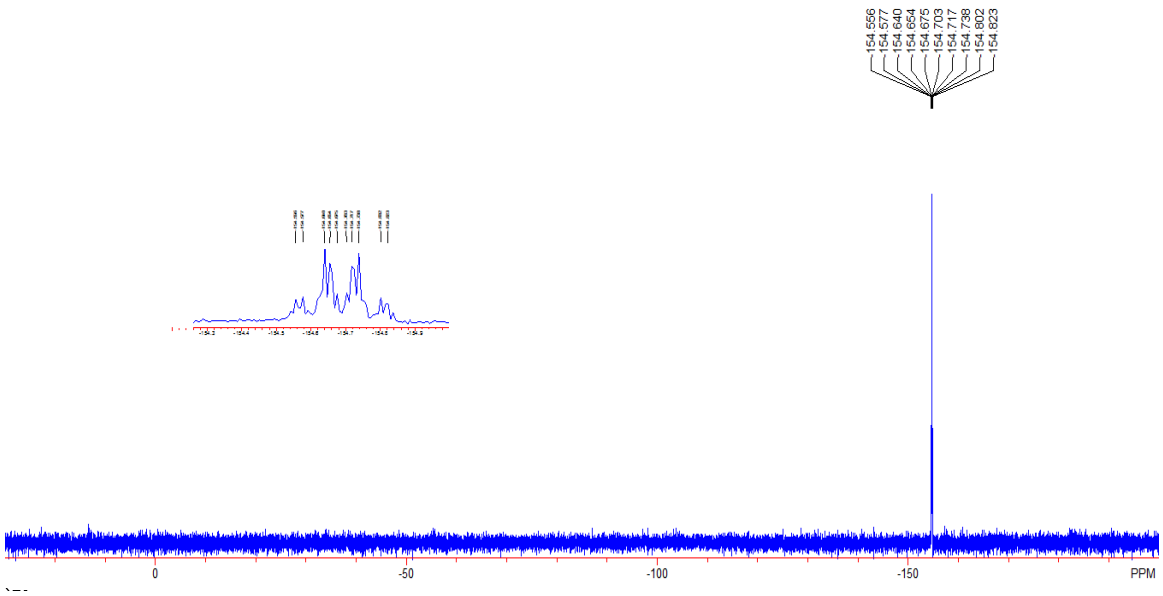


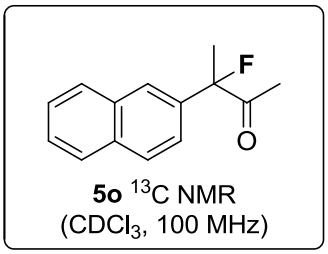
5o ^{1}H NMR
($CDCl_3$, 300 MHz)



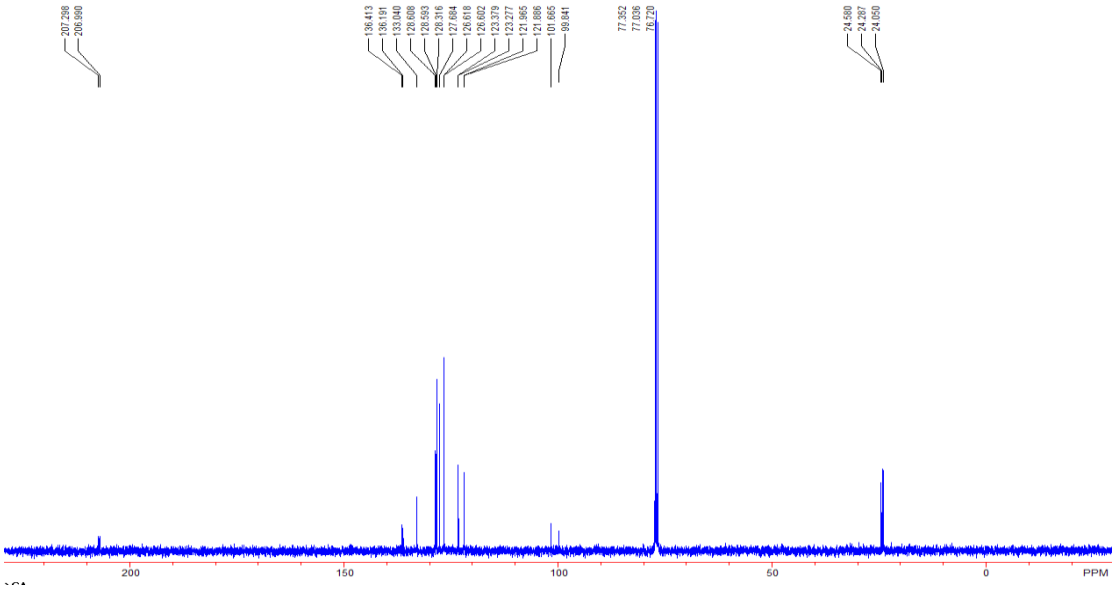


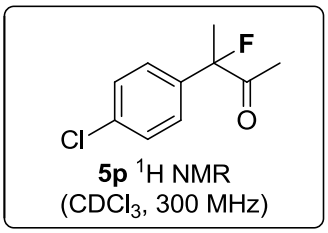
5o ^{19}F NMR
($CDCl_3$, 282 MHz)



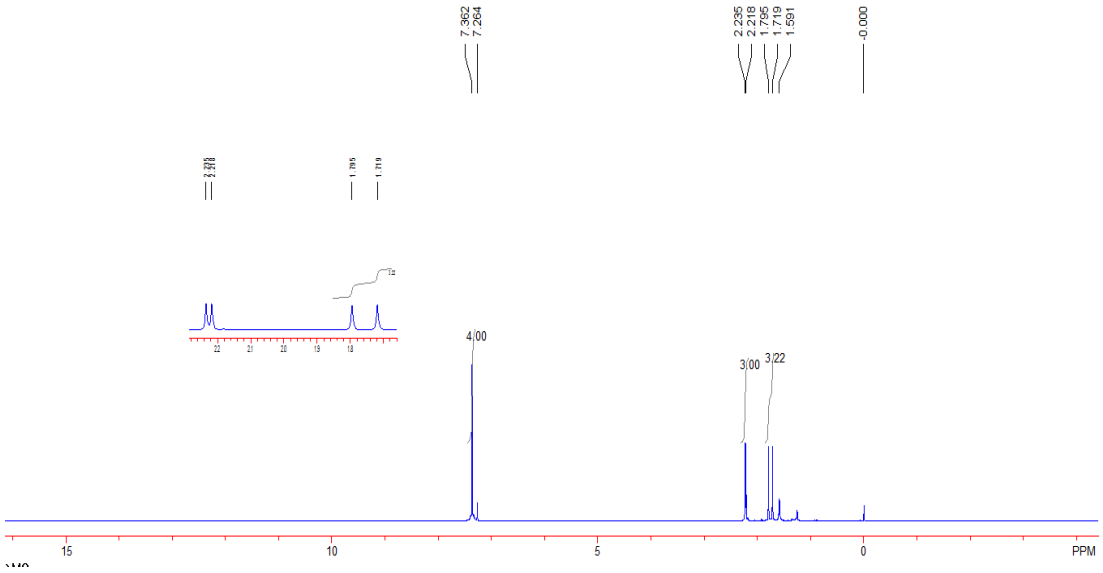


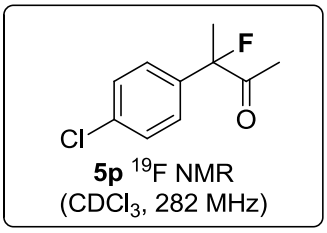
5o ^{13}C NMR
($CDCl_3$, 100 MHz)



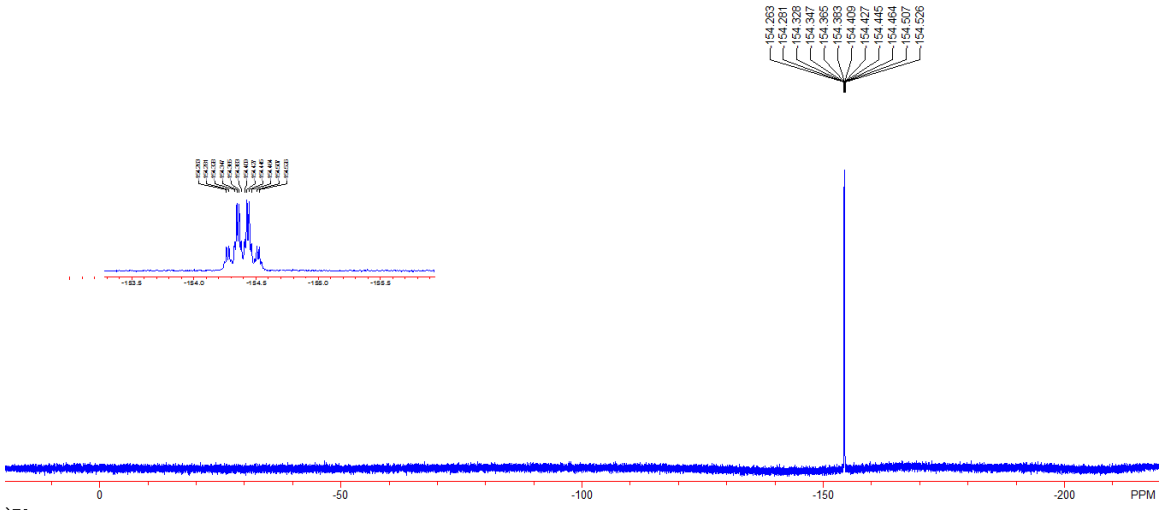


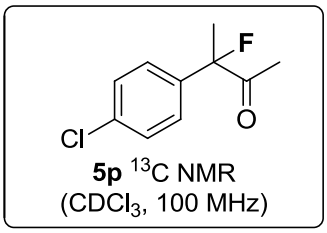
5p ^{1}H NMR
($CDCl_3$, 300 MHz)



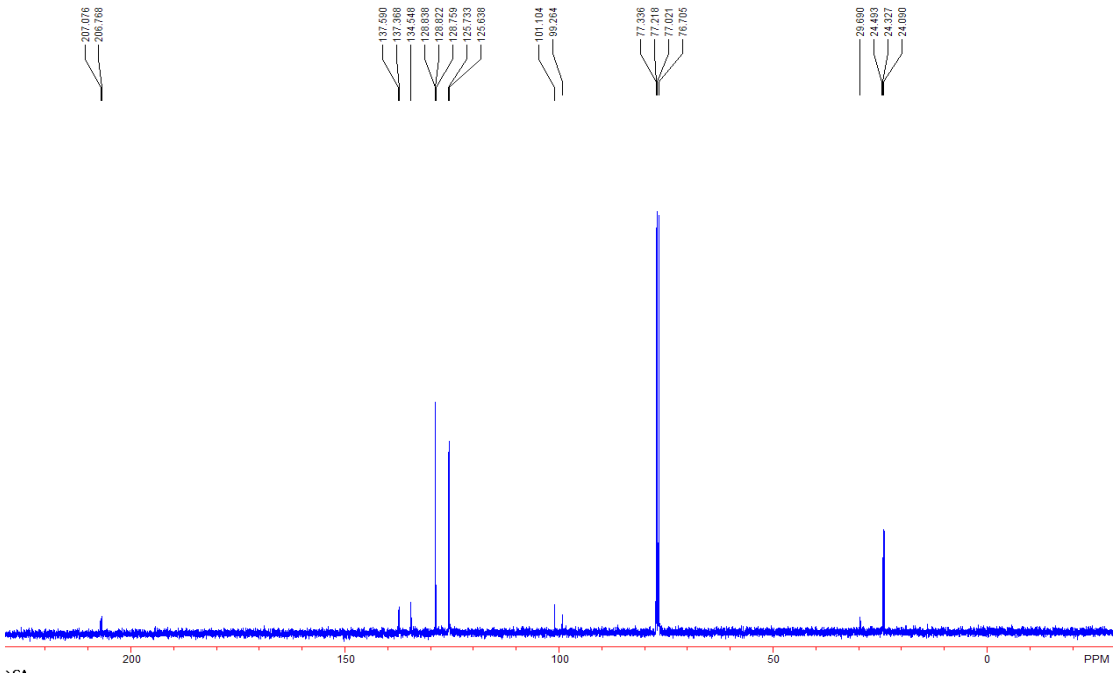


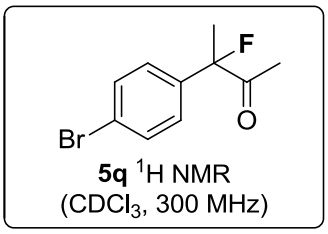
5p ^{19}F NMR
($CDCl_3$, 282 MHz)



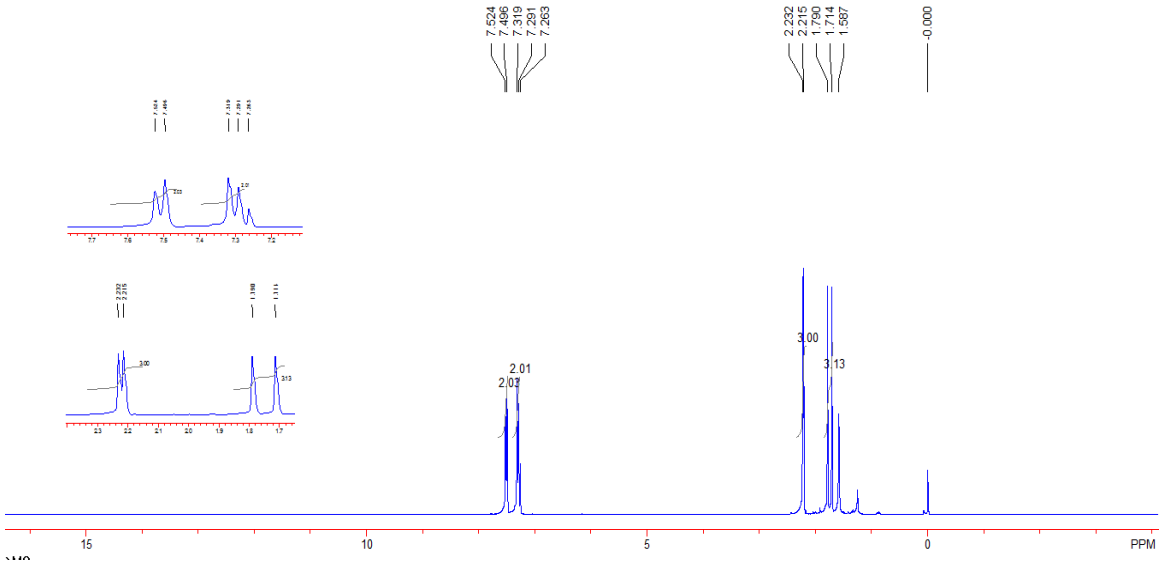


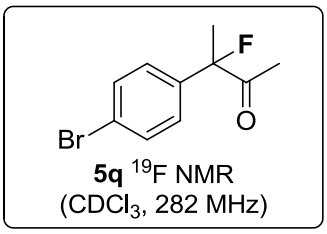
5p ^{13}C NMR
($CDCl_3$, 100 MHz)



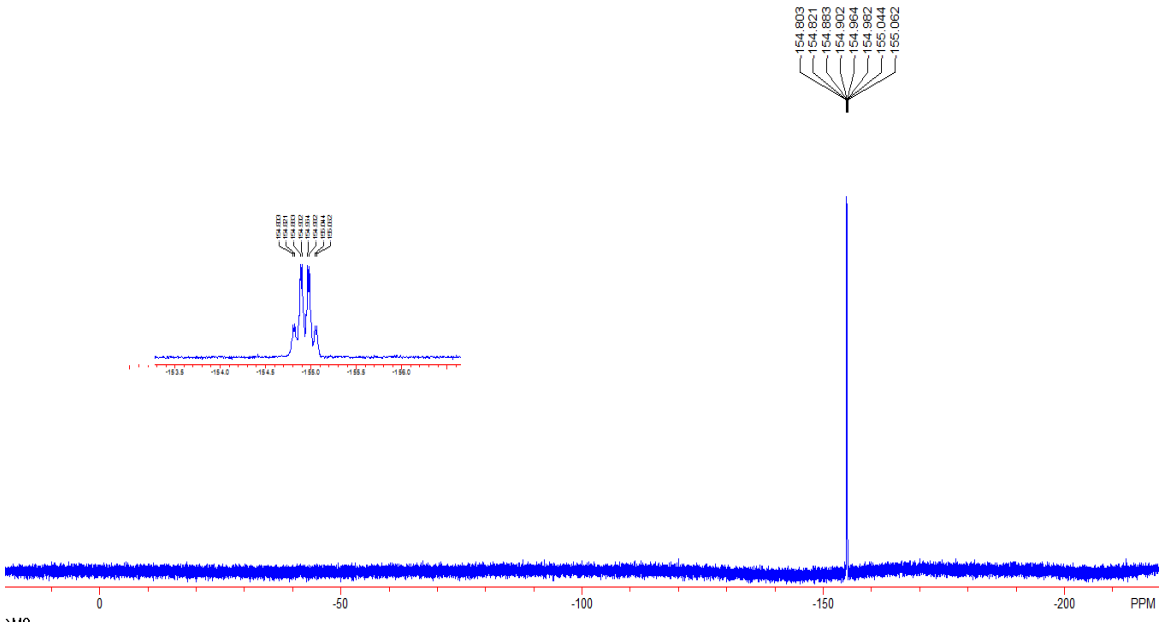


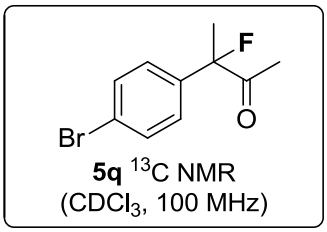
5q ^{1}H NMR
($CDCl_3$, 300 MHz)



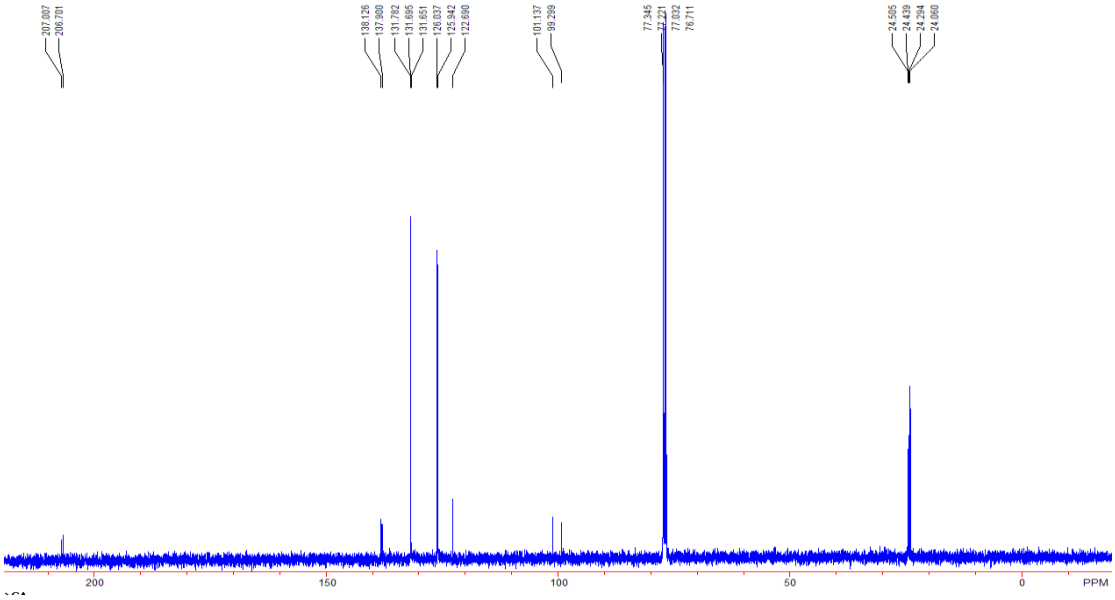


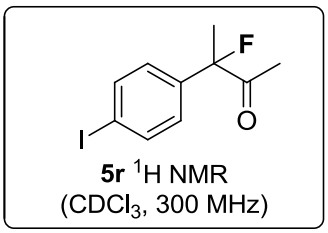
5q ^{19}F NMR
($CDCl_3$, 282 MHz)



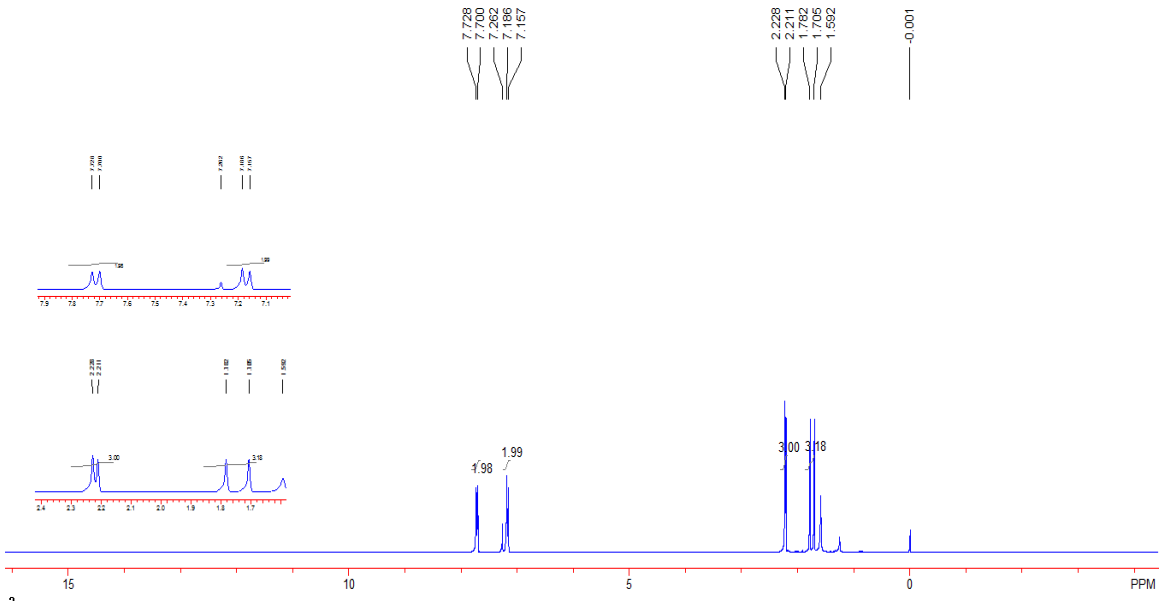


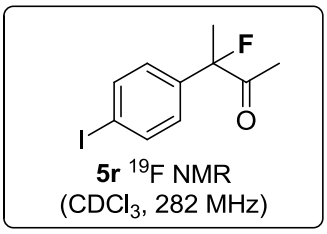
5q ^{13}C NMR
($CDCl_3$, 100 MHz)



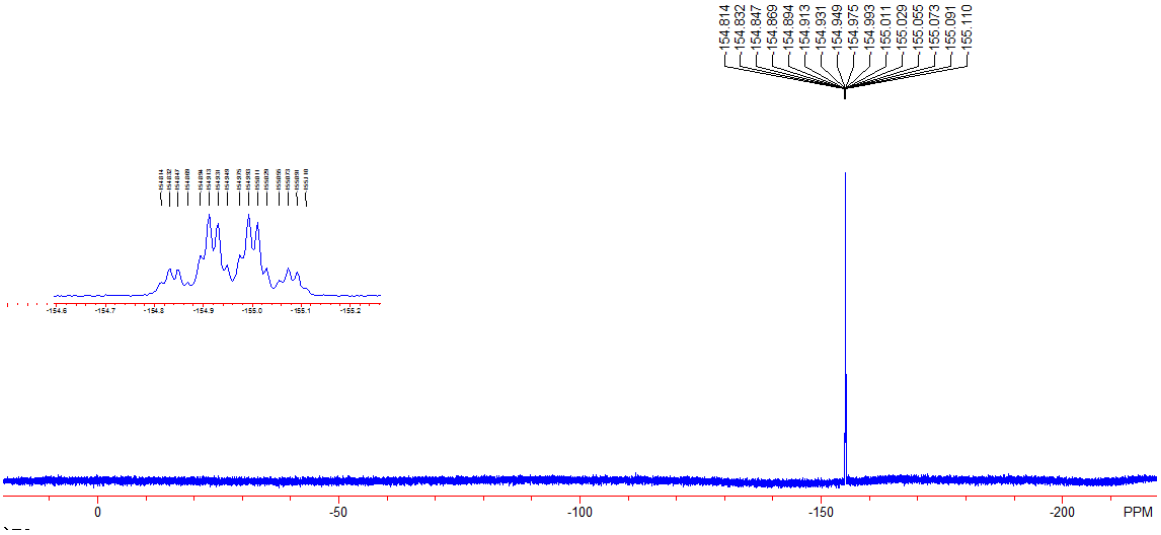


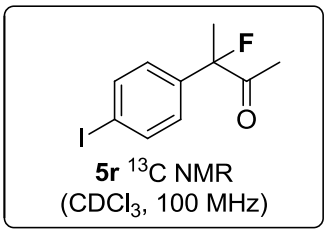
5r ^{1}H NMR
($CDCl_3$, 300 MHz)



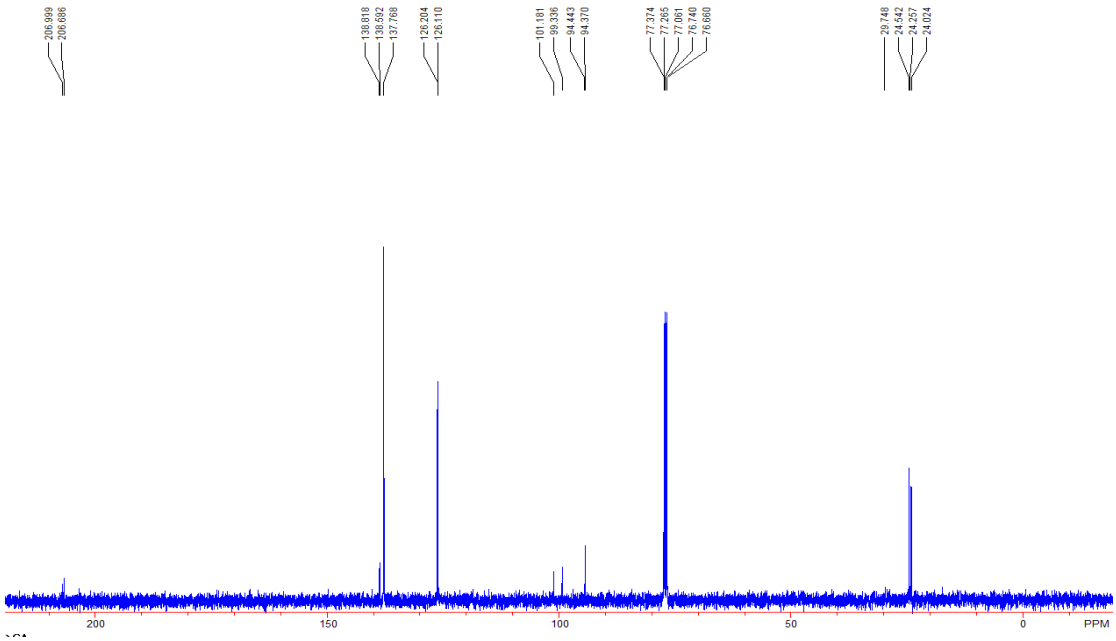


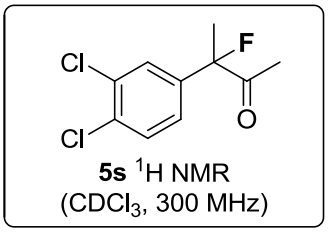
5r ^{19}F NMR
($CDCl_3$, 282 MHz)



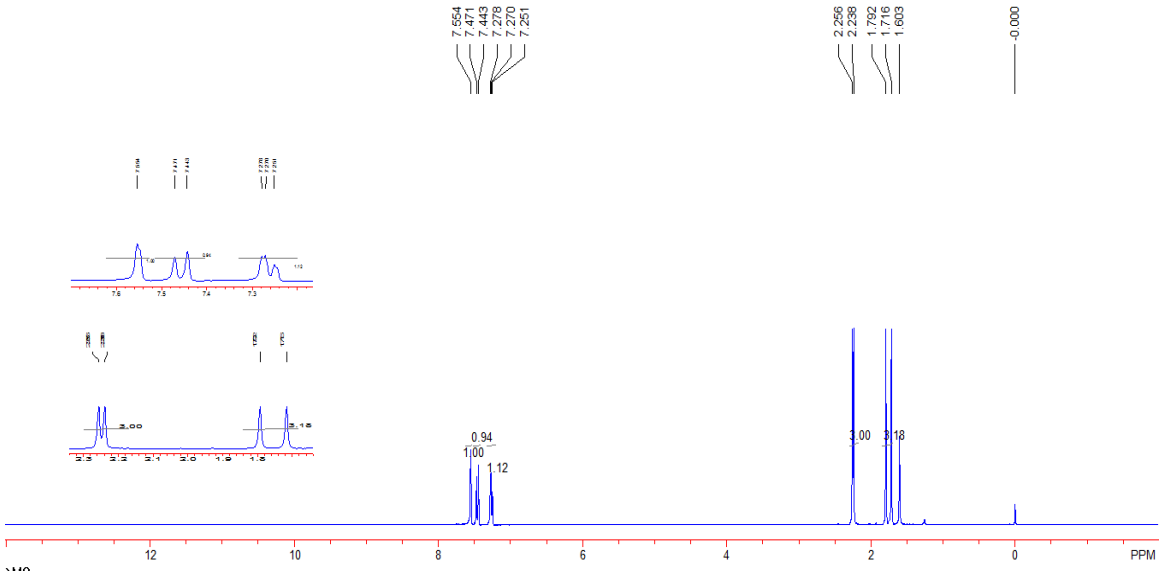


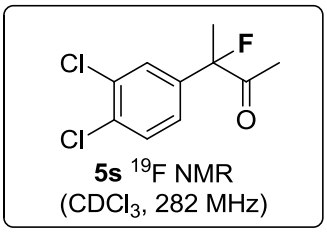
5r ^{13}C NMR
($CDCl_3$, 100 MHz)



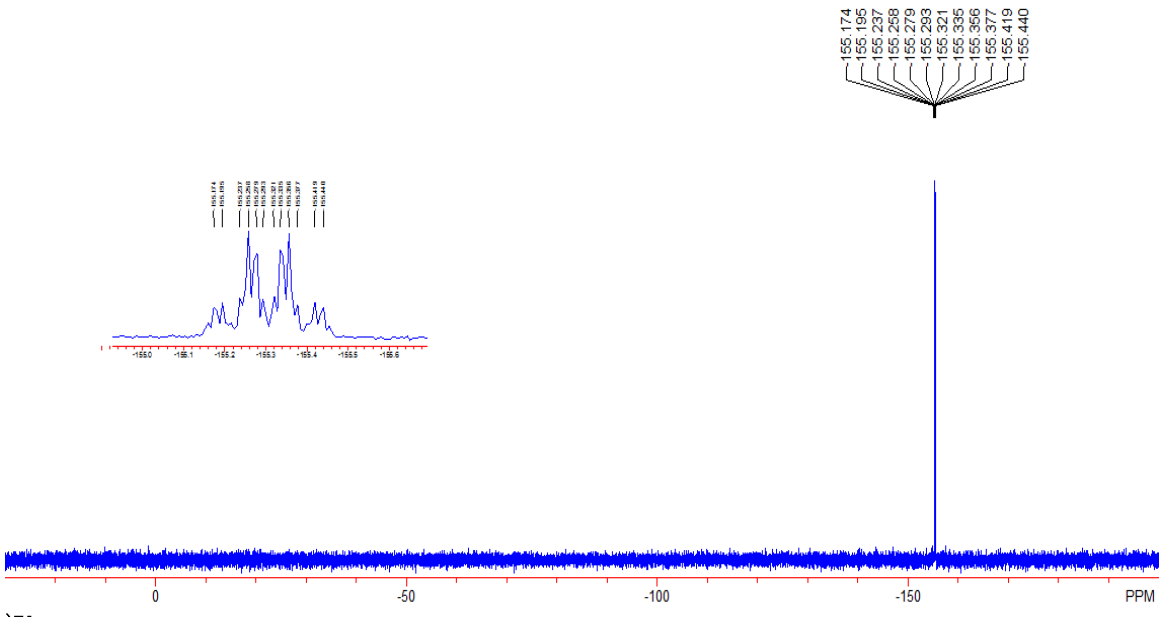


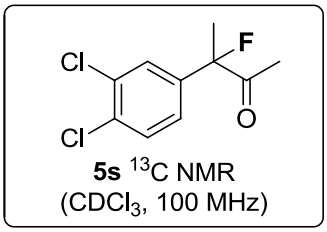
5s ^{1}H NMR
($CDCl_3$, 300 MHz)



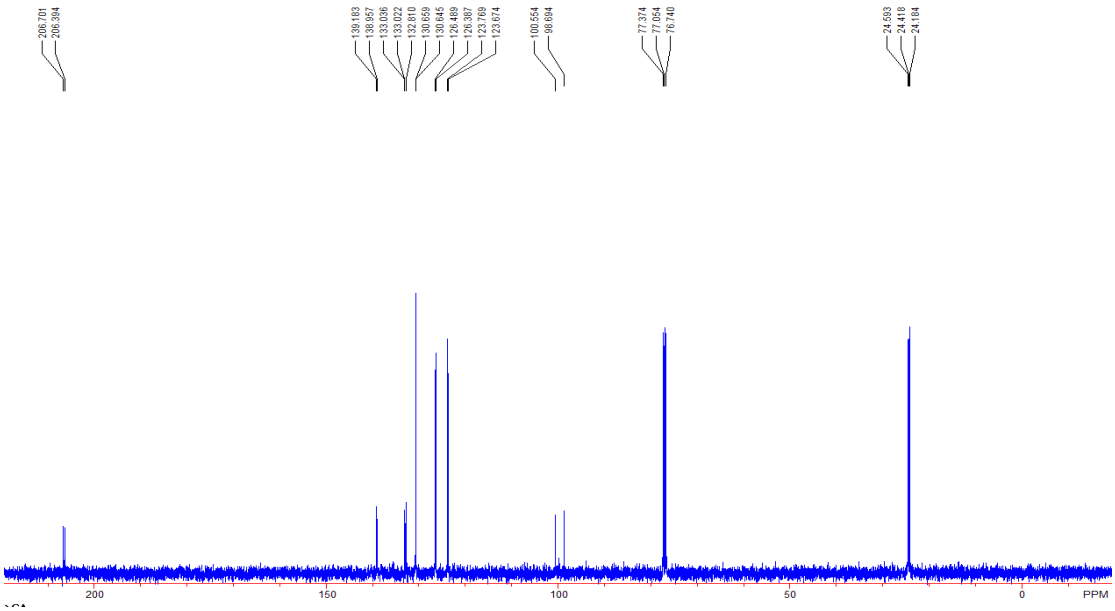


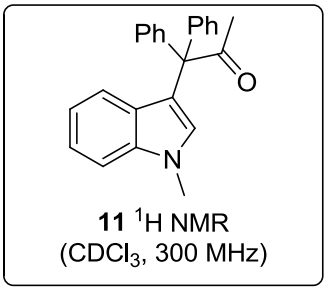
5s ^{19}F NMR
($CDCl_3$, 282 MHz)



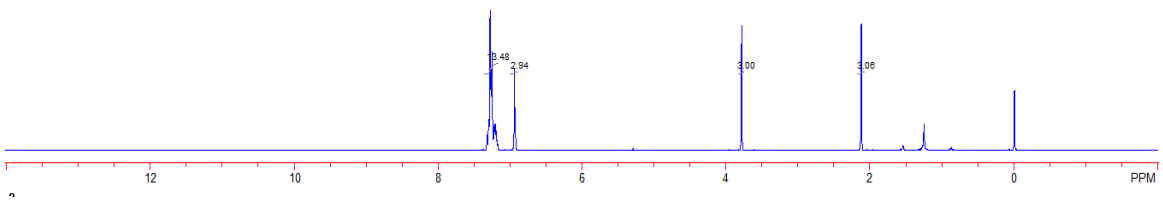


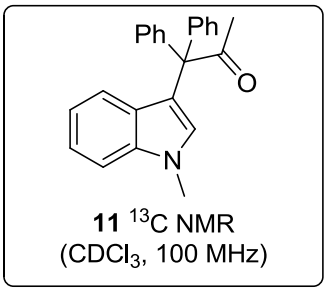
5s ^{13}C NMR
($CDCl_3$, 100 MHz)





11 ^{1}H NMR
($CDCl_3$, 300 MHz)





11 ^{13}C NMR
($CDCl_3$, 100 MHz)