Supporting information *for*

Synthesis of 2-Substituted 3-Trifluoromethylselenoindoles via a $SeCF_3$ Migration Reaction

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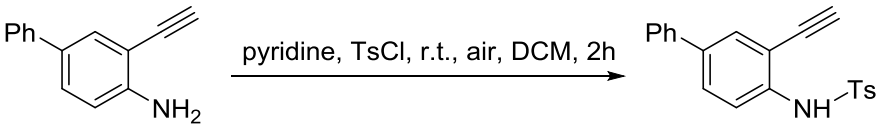
General information

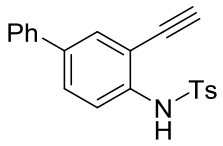
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.0), The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. $[(bpy)CuSeCF_3]_2$ (**1**)[1], *N*-Ts 2-alkynylaniline derivatives[2, 3] and 4-methyl-*N*-(2-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide[4] were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use.

Preparation of Substrates 1

Procedure for the synthesis of *N*-(3-ethynyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide



To a solution of 3-ethynyl-[1,1'-biphenyl]-4-amine (579.3 mg, 3.0 mmol) and pyridine (0.48 mL, 6.0 mmol, 2.0 equiv) in 10 mL of dichloromethane was added 4-methylbenzene-1-sulfonyl chloride (743.5 mg, 3.9 mmol, 1.3 equiv), then the reaction mixture was stirred at room temperature. After the reaction was complete (about 1 h) as monitored by TLC, 15 mL water and HCl (1.0 M, 3 mL) was added, and the mixture was extracted with dichloromethane (3 × 15 mL). The combined organic phase was washed with brine, dried with Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding *N*-(3-ethynyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide.



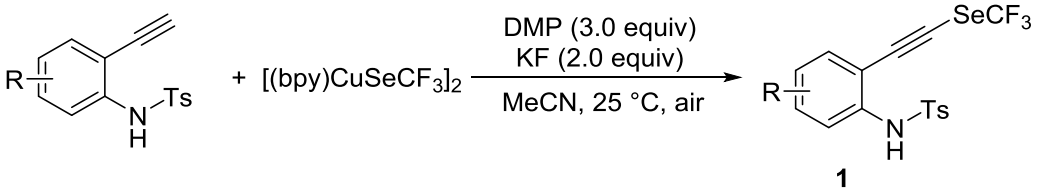
***N*-(3-ethynyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide**

Obtained as a white solid in 62% yield (645.6 mg). Mp: 148.1 – 149.2 ℃. R_f (petroleum ether/ethyl acetate = 4:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.57 – 7.48 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.2 (s), 139.1 (s), 137.5 (s), 137.2 (s), 136.0 (s), 130.9 (s), 129.7 (s), 128.9 (s), 128.8 (s), 127.7 (s), 127.4 (s), 126.7 (s), 119.7 (s), 113.1 (s), 84.5 (s), 78.6 (s), 21.6 (s). IR (ATR): ν 3264, 1731, 1596, 1480,

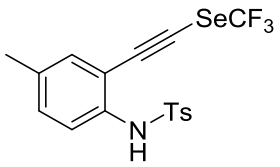
1391, 1372, 1338, 1241, 1162, 1110, 1089, 1044, 915, 864, 812, 760, 727, 696, 663, 630, 551 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{17}NNaO_2S$ $[M+Na]^+$: 370.0872; found: 370.0859.

4-Methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (**1a**) was prepared according to the literature.[5]

General procedure for the synthesis of 4-methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide 1

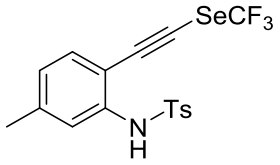


N-Ts 2-alkynylaniline (2.0 mmol), $[(bpy)Cu(SeCF_3)]_2$ (1.03 g, 2.8 mmol based on Cu, 1.4 equiv), DMP (2.54 g, 6.0 mmol, 3.0 equiv), KF (0.52 g, 4.0 mmol, 2.0 equiv), and MeCN (20 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred in air at 25 ℃ and the progress of the reaction was monitored by TLC. When the 2,3-bis(trifluoromethylseleno) indole species[5] was generated, the reaction was terminated. The resulting solution was filtered through a pad of celite. The filtrate was poured into brine, the phases were separated, and then the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic extract was dried ($MgSO_4$), filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1).



4-methyl-*N*-(4-methyl-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (1b)

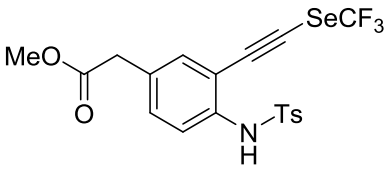
Obtained as a yellow solid in 33% yield (292.8 mg). Mp: 139.1 – 140.3 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.10 (m, 2H), 6.97 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.7 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.0 (s), 135.9 (s), 135.8 (s), 134.7 (s), 133.1 (s), 131.9 (s), 129.6 (s), 127.2 (s), 121.2 (s), 120.5 (q, *J* = 336.8 Hz), 113.6 (s), 102.1 (s), 68.4 (q, *J* = 3.1 Hz), 21.5 (s), 20.5 (s). IR (ATR): *v* 3260, 2923, 1597, 1494, 1392, 1335, 1155, 1084, 811, 662 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{14}F_3NO_2SSe^+$: 432.9857; found: 432.9860.



4-methyl-*N*-(5-methyl-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (1c)

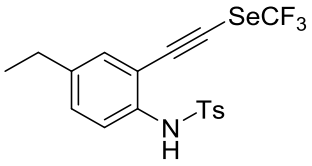
Obtained as a yellow solid in 29% yield (254.6 mg). Mp: 168.1 – 168.9 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.10 (m, 2H), 6.99 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.7. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.1 (s), 135.9 (s), 135.8 (s), 134.7 (s), 133.1 (s), 131.9 (s), 129.6 (s), 127.2 (s), 121.3 (s), 120.5 (q, *J* = 336.8 Hz), 113.6 (s), 102.1 (s), 68.5 (q, *J* = 3.0 Hz), 21.5 (s), 20.5 (s). IR (ATR): *v* 2955, 2923, 2853, 1740, 1373, 1238, 1092,

1046, 665 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{14}F_3NO_2SSe^+$: 432.9857; found: 432.9846.



methyl 2-(4-((4-methylphenyl)sulfonamido)-3-(((trifluoromethyl)selanyl)ethynyl)phenyl) acetate (1d)

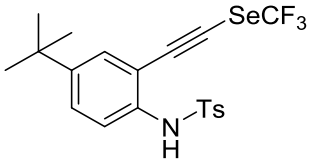
Obtained as a yellow solid in 45% yield (441.9 mg). Mp: 106.4 – 107.7 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 3.68 (s, 3H), 3.52 (s, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.6. (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.3 (s), 144.2 (s), 137.5 (s), 135.9 (s), 133.5 (s), 132.1 (s), 130.5 (s), 129.7 (s), 127.2 (s), 120.7 (s), 120.5 (q, *J* = 336.9 Hz), 113.4 (s), 101.6 (s), 69.4 (q, *J* = 3.2 Hz), 52.2 (s), 39.9 (s), 21.5 (s). IR (ATR): *v* 3250, 2953, 1732, 1597, 1494, 1338, 1264, 1156, 1086, 734, 547 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{19}H_{16}F_3NO_4SSe^+$: 490.9912; found: 490.9911.



***N*-(4-ethyl-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1e)**

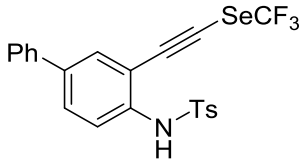
Obtained as a yellow solid in 27% yield (244.3 mg). Mp: 134.6 – 135.3 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.13 (m, 4H), 6.96 (s, 1H), 2.55 (q, *J* =

7.6 Hz, 2H), 2.36 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.7 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.0 (s), 140.9 (s), 136.1 (s), 135.9 (s), 132.0 (s), 130.8 (s), 129.6 (s), 127.2 (s), 121.2 (s), 120.5 (q, J = 336.8 Hz), 113.5 (s), 102.3 (s), 68.4 (q, J = 3.1 Hz), 27.9 (s), 21.5 (s), 15.1 (s). IR (ATR): 3263, 2966, 1598, 1492, 1394, 1336, 1156, 1084, 885, 811 cm^{-1} cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd. for $C_{18}H_{16}F_3NO_2SSe^+$: 447.0008; found: 447.0011.



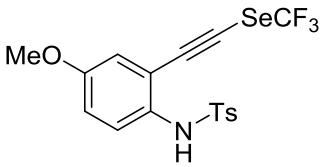
_N_-(4-(tert-butyl)-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1f)

Obtained as a yellow solid in 31% yield (297.8 mg). Mp: 122.8 – 124.1 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.03 (s, 1H), 2.37 (s, 3H), 1.25 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.7 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.8 (s), 144.0 (s), 136.1 (s), 136.0 (s), 129.7 (s), 129.6 (s), 128.5 (s), 127.2 (s), 120.6 (q, J = 336.8 Hz), 120.5 (s), 112.9 (s), 102.5 (s), 68.2 (q, J = 3.0 Hz), 34.3 (s), 31.0 (s), 21.5 (s). IR (ATR): v 3266, 2957, 2923, 1495, 1338, 1162, 1089, 891, 664, 551 cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd. for $C_{20}H_{20}F_3NO_2SSe^+$: 475.0327; found: 475.0324.



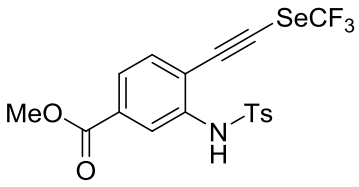
4-methyl-_N_-(3-(((trifluoromethyl)selanyl)ethynyl)-[1,1'-biphenyl]-4-yl)benzenesulfonamide (1g)

Obtained as a yellow liquid in 35% yield (348.7 mg). R_f (petroleum ether/ethyl acetate = 8:1) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 3H), 7.58 – 7.52 (m, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 – 7.17 (m, 3H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3 (s), 138.8 (s), 137.7 (s), 137.6 (s), 135.9 (s), 131.2 (s), 129.7 (s), 129.6 (s), 128.9 (s), 127.8 (s), 127.3 (s), 126.7 (s), 122.2 (q, *J* = 338.3 Hz), 121.0 (s), 113.8 (s), 101.9 (s), 69.4 (q, *J* = 3.2 Hz), 21.5 (s). IR (ATR): *v* 3032, 2918, 2850, 1481, 1163, 1089, 922, 761, 551 cm^{-1}. HRMS (EI) *m*/*z*: [M]$^+$ calcd. for $C_{22}H_{16}F_3NO_2SSe^+$: 495.0014; found: 495.0018.



_N_-(4-methoxy-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1h)

Obtained as a yellow solid in 51% yield (457.9 mg). Mp: 110.7 –112.7 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.97 – 6.88 (m, 1H), 6.84 – 6.74 (m, 2H), 3.75 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.8 (s), 144.0 (s), 135.8 (s), 131.3 (s), 127.2 (s), 124.6 (s), 120.5 (q, *J* = 336.8 Hz), 117.6 (s), 116.7 (s), 115.9 (s), 102.0 (s), 68.4 (q, *J* = 3.2 Hz), 55.5 (s), 21.5 (s). IR (ATR): *v* 3260, 2923, 1727, 1599, 1495, 1335, 1155, 1084, 811, 550 cm^{-1}. HRMS (EI) *m*/*z*: [M]$^+$ calcd. for $C_{17}H_{13}F_3NO_3SSe^+$: 448.9806; found: 448.9812.

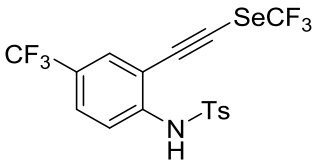


methyl

3-((4-methylphenyl)sulfonamido)-4-(((trifluoromethyl)selanyl)ethynyl)benzoate

(1i)

Obtained as a yellow solid in 45% yield (433.3 mg). Mp: 142.1 – 144.3 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.5 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.17 (s, 1H), 3.94 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.1 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7 (s), 144.5 (s), 138.4 (s), 135.6 (s), 132.5 (s), 132.1 (s), 129.7 (s), 127.3 (s), 125.4 (s), 121.2 (s), 120.5 (q, *J* = 337.0 Hz), 117.3 (s), 101.2 (s), 72.2 (q, *J* = 3.1 Hz), 52.6 (s), 21.5 (s). IR (ATR): *v* 3255, 2954, 1722, 1294, 1259, 1159, 1084, 735, 665 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{18}H_{14}F_3NO_4SSe^+$: 476.9755; found: 476.9753.

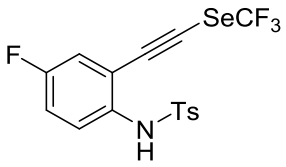


4-methyl-*N*-(4-(trifluoromethyl)-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)ben

zenesulfonamide (1j)

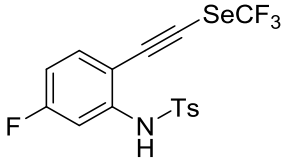
Obtained as a yellow solid in 47% yield (231.7 mg). Mp: 136.3 – 138.1 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 3H), 7.61 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.38 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F), -62.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8 (s), 141.4 (s), 135.5 (s), 130.0 (s), 129.9 (s), 127.7 (q, *J* = 3.6 Hz), 127.2 (s), 126.3 (q, *J* = 33.7 Hz), 123.2 (q, *J* = 272.1 Hz), 120.5 (q, *J* = 336.9 Hz), 118.9 (s), 112.5 (s), 100.3 (s), 71.6 (q, *J* = 3.0 Hz), 21.5 (s). IR (ATR): *v*

3387, 3041, 1597, 1503, 1331, 1264, 1164, 1088, 733, 703, 547 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{11}F_6NO_2SSe^+$: 486.9580; found: 486.9574.



_N_-(4-fluoro-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1k)

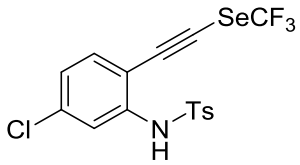
Obtained as a yellow solid in 23% yield (199.6 mg). Mp: 150.3 – 151.7 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.36. NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 9.1, 5.0 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.04 (m, 1H), 7.04 – 6.96 (m, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F), -116.1 – -116.2 (m, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 246.7 Hz), 144.3 (s), 135.6 (s), 134.5 (d, *J* = 3.0 Hz), 129.7 (s), 127.2 (s), 123.9 (d, *J* = 8.6 Hz), 120.5 (q, *J* = 336.9 Hz), 118.9 (d, *J* = 24.4 Hz), 118.3 (d, *J* = 22.7 Hz), 115.7 (d, *J* = 9.8 Hz), 100.8 (d, *J* = 2.9 Hz), 70.2 (q, *J* = 3.2 Hz), 21.5 (s). IR (ATR): *v* 3247, 2972, 1598, 1490, 1391, 1332, 1264, 1153, 1088, 734, 703, 664, 599, 550 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}F_4NO_2SSe^+$: 436.9606; found: 436.9611.



_N_-(5-fluoro-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1l)

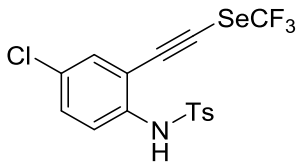
Obtained as a yellow solid in 22% yield (194.4 mg). Mp: 93.1 – 95.2 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.40 (dd, *J* = 10.3, 2.6 Hz, 1H), 7.33 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.28 –

7.20 (m, 3H), 6.75 (td, *J* = 8.2, 2.5 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.6 (s, 3F), -104.0 – -104.1 (m, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.8 (d, *J* = 252.7 Hz), 144.6 (s), 140.7 (d, *J* = 11.8 Hz), 135.6 (s), 134.7 (d, *J* = 10.0 Hz), 129.8 (s), 127.2 (s), 120.5 (q, *J* = 337.0 Hz), 111.8 (d, *J* = 22.7 Hz), 108.5 (d, *J* = 3.3 Hz), 107.3 (d, *J* = 27.5 Hz), 100.9 (s), 69.5 (q, *J* = 3.2 Hz), 21.5 (s). IR (ATR): *v* 3039, 2925, 1607, 1497, 1402, 1341, 1264, 1153, 1087, 989, 885, 812, 733, 703, 661, 590, 547 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}F_4NO_2SSe^+$: 436.9606; found: 436.9613.



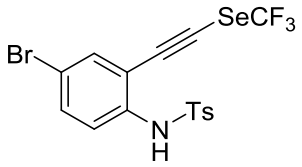
_N_-(5-chloro-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1m)

Obtained as a yellow solid in 21% yield (194.3 mg). Mp: 162.3–169.8 ℃. R_f (petroleum ether/ ethyl acetate = 8:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.63 (m, 3H), 7.32 – 7.20 (m, 3H), 7.19 (s, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.5 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.6 (s), 139.6 (s), 137.1 (s), 135.6 (s), 133.6 (s), 129.8 (s), 127.2 (s), 124.8 (s), 120.5 (q, *J* = 336.9 Hz), 120.2 (s), 111.3 (s), 100.9 (s), 70.5 (q, *J* = 3.0 Hz), 21.5 (s). IR (ATR): *v* 3242, 2925, 1592, 1558, 1483, 1390, 1336, 1160, 1136, 1083, 937, 812, 738, 663, 632, 574, 546 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}ClF_3NO_2SSe^+$: 452.9316; found: 452.9311.



_N_-(4-chloro-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1n)

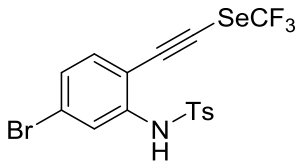
Obtained as a yellow solid in 35% yield (318.5 mg). Mp: 164.8 – 165.9 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.33 – 7.27 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.07 (s, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5 (s), 137.0 (s), 135.6 (s), 132.2 (s), 131.1 (s), 130.0 (s), 129.8 (s), 127.2 (s), 122.0 (s), 120.5 (q, *J* = 336.8 Hz), 114.9 (s), 100.6 (s), 70.7 (q, *J* = 3.1 Hz), 21.5 (s). IR (ATR): *v* 3256, 2925, 1597, 1481, 1387, 1337, 1158, 1083, 820, 875, 811, 739, 661, 593 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}ClF_3NO_2SSe^+$: 452.9311; found: 452.9313.



_N_-(4-bromo-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1o)

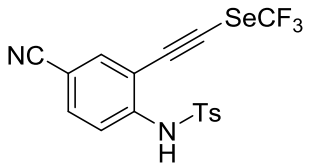
Obtained as a yellow solid in 40% yield (397.5 mg). Mp: 143.1 – 146.0 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 9.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.27 – 7.19 (m, 3H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.3 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5 (s), 137.5 (s), 135.6 (s), 135.0 (s), 133.9 (s), 129.8 (s), 127.2 (s), 122.2 (s), 120.5 (q, *J* = 338.3 Hz), 117.3 (s), 115.2 (s), 100.4 (s), 71.0 (q, *J* = 3.1 Hz), 21.5 (s). IR (ATR): *v* 3252, 2925, 1596, 1478, 1385, 1336, 1267, 1157, 1082, 913, 863,

811, 739, 663, 591 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}BrF_3NO_2SSe^+$: 496.8806; found: 496.8807.



_N_-(5-bromo-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1p)

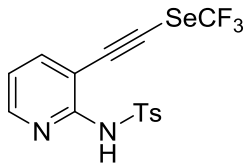
Obtained as a yellow solid in 39% yield (389.0 mg). Mp: 164.7 – 169.2 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.16 (m, 3H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.4 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.6 (s), 139.5 (s), 135.5 (s), 133.7 (s), 129.8 (s), 127.7 (s), 127.2 (s), 125.2 (s), 123.2 (s), 120.5 (q, *J* = 336.9 Hz), 111.8 (s), 100.9 (s), 70.7 (q, *J* = 3.1 Hz), 21.5 (s). IR (ATR): *v* 3254, 2916, 1586, 1555, 1479, 1388, 1332, 1159, 1134, 1086, 926, 811, 738, 664, 631, 581 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}BrF_3NO_2SSe^+$: 496.8806; found: 496.8805.



_N_-(4-cyano-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1q)

Obtained as a white solid in 15% yield (133.0 mg). Mp: 198.5 – 199.0 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4, 2H), 7.70 (s, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.44 (br s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.0

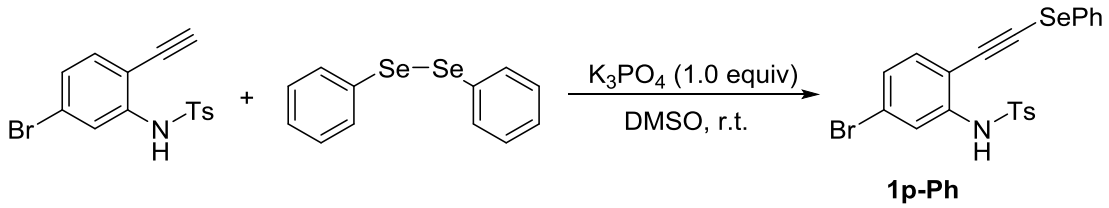
(s, 3F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 145.1 (s), 142.2 (s), 136.5 (s), 135.3 (s), 134.2 (s), 130.0 (s), 127.2 (s), 120.5 (q, *J* = 337.0 Hz), 118.5 (s), 117.3 (s), 112.8 (s), 107.6 (s), 99.4 (s), 72.8 (q, *J* = 3.0 Hz), 21.6 (s). IR (ATR): *v* 3178, 2922, 2239, 1490, 1400, 1343, 1265, 1162, 1089, 1015, 899, 850, 814, 736, 664, 562, 547 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{11}F_3N_2O_2SSe^+$: 443.9653; found: 443.9659.



4-methyl-*N*-(3-(((trifluoromethyl)selanyl)ethynyl)pyridin-2-yl)benzenesulfonamide (1r)

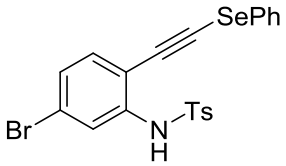
Obtained as a white solid in 26% yield (219.5 mg). Mp: 135.2 – 136.9 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 7.78 (m, 4H), 7.64 (s, 1H), 7.28 (s, 2H), 6.86 (s, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.4 (s, 3F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.7 (s), 148.6 (s), 144.1 (s), 141.4 (s), 136.9 (s), 129.3 (s), 128.3 (s), 120.6 (q, *J* = 337.0 Hz), 117.5 (s), 105.0 (m), 100.2 (s), 71.8 (s), 21.5 (s). IR (ATR): *v* 2954, 2921, 2850, 1733, 1616, 1585, 1569, 1533, 1495, 1462, 1441, 1373, 1337, 1240, 1156, 1087, 1045, 962, 913, 812, 739, 660, 578 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{15}H_{11}F_3N_2O_2SSe^+$: 419.9653; found: 419.9662.

Procedure for the synthesis of *N*-(5-bromo-2-((phenylselanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1p-Ph)



1p-Ph

N-Ts-5-Bromine-2-alkynylaniline (1.0 mmol), 1,2-diphenyldiselane (1.0 mmol, 1 equiv), K_3PO_4 (1.0 mmol, 1equiv), and DMSO (5 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred in air at 25 ℃ and monitor by TLC. After the completion of the reaction, the solution was filtered through a pad of celite. The filtrate was poured into brine, the phases were separated, and then the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic extract was dried ($MgSO_4$), filtered, and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to give product **1p-Ph** as a yellow solid in 36% yield (363.1 mg).



(1p-Ph)

Mp: 144.3 – 145.9 ℃. R_f (petroleum ether/ethyl acetate = 4:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 6.4 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.23 – 7.13 (m, 5H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ

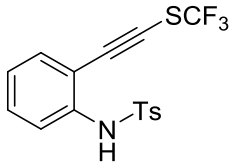
144.4 (s), 139.1 (s), 135.7 (s), 133.3 (s), 129.9 (s, 2C), 129.8 (s), 127.9 (s), 127.8 (s), 127.6 (s), 127.2 (s), 123.9 (s), 123.0 (s), 113.1 (s), 95.8 (s), 79.1 (s), 21.6 (s). IR (ATR): *v* 3057, 2921, 2852, 2153, 1586, 1556, 1476, 1438, 1387, 1335, 1259, 1161, 1089, 1019, 920, 848, 809, 733, 663, 581 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd. for $C_{21}H_{16}BrNNaO_2SSe^+$: 527.9143; found: 527.9139.

Procedure for the synthesis of

4-methyl-*N*-(2-(((trifluoromethyl)thio)ethynyl)phenyl)benzenesulfonamide (1a-S)

1a-S

4-Methyl-*N*-(2-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide (343.1 mg, 1.0 mmol), *N*-phenyl-*S*-(trifluoromethyl)thiohydroxylamine (193 mg, 1.5 mmol, 1.5 equiv), $BiCl_3$ (315.3 mg, 1.0 mmol, 1.0 equiv), and DCE (5 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred in N_2 at 80 ℃ in a metal bath for 12 h, then the filtered through a pad of celite. Water and brine were added, and the filtrate was extracted with Dichloromethane. The combined organic layers were dried by $MgSO_4$. The organic layers were concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to give product **1a-S** as a yellow solid in 33% yield (245.0 mg).

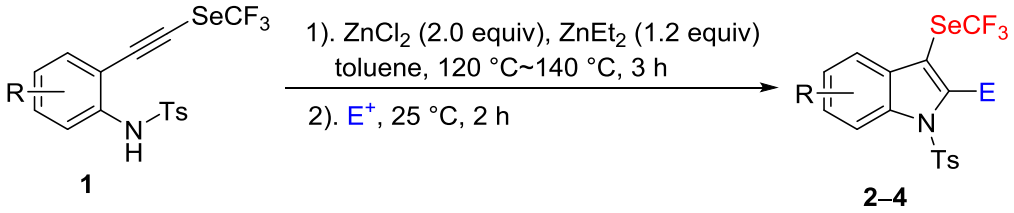


4-methyl-*N*-(2-(((trifluoromethyl)thio)ethynyl)phenyl)benzenesulfonamide (1a-S)

Mp: 166.5 – 168.3 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.56 (m, 3H), 7.41 – 7.33 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.03 (m, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.3 (s), 138.8 (s), 135.8 (s), 133.3 (s), 131.4 (s), 127.7 (q, *J* = 313.1 Hz), 127.2 (s), 124.7 (s), 120.7 (s), 112.8 (s), 96.0 (s), 73.9 (q, *J* = 4.3 Hz), 21.5 (s). IR (ATR): *v* 3251, 2922, 2177, 1600, 1574, 1486, 1450, 1394, 1333,

1279, 1153, 1090, 913, 859, 811, 760, 665, 569 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd. for $C_{16}H_{12}F_3NNaO_2S_2^+$: 394.0154; found: 394.0148.

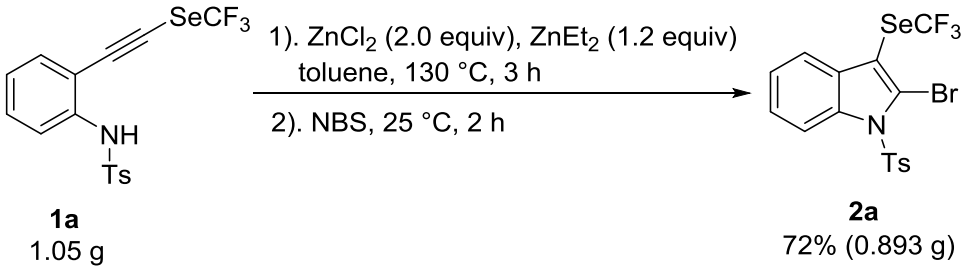
General Procedure for Zinc-Mediated Cyclization/Electrophilic Substitution



4-Methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide derivatives **1** (0.30 mmol), $ZnCl_2$ (81.7 mg, 0.60 mmol, 2.0 equiv), $ZnEt_2$ (1.0 M in toluene, 0.36 mL, 0.36 mmol, 1.2 equiv), and toluene (1.5 mL) were added to a Schlenk tube equipped with a stir bar. The mixture was stirred at 120~140 ℃ in a metal bath for 3 h. Then, the cooled reaction mixture was taken back into the box and was added electrophilic reagent (0.45 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by column chromatography on aluminum oxide eluated with petroleum ether/ethyl acetate (100:1).

Procedure for gram scale reaction for synthesis of

2-bromo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2a)



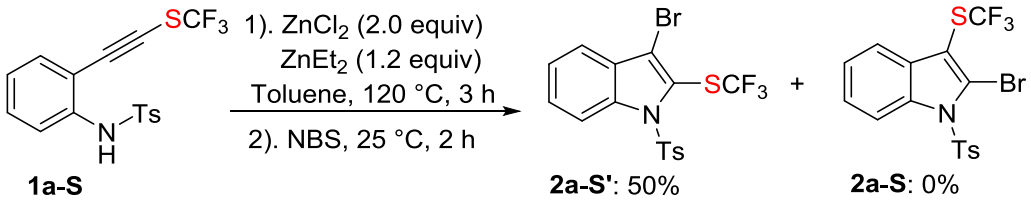
1a
1.05 g

2a
72% (0.893 g)

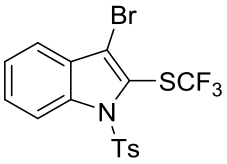
4-Methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (**1a**) (1.05 g, 2.5 mmol, 1.0 equiv), $ZnCl_2$ (680.0 mg, 5.0 mmol, 2.0 equiv), $ZnEt_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol, 1.2 equiv), and toluene (15 mL) were added to a Schlenk tube equipped with a stir bar. The mixture was stirred at 130 ℃ in a metal bath for 3 h. Then, the cooled reaction mixture was taken back into the box and was added NBS (667.5 mg, 3.75 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1) to give 0.893 g of product **2a** (72% yield).

Control Experiments

(a)



4-Methyl-*N*-(2-(((trifluoromethyl)thio)ethynyl)phenyl)benzenesulfonamide (**1a-S**) (111.3 mg, 0.30 mmol), $ZnCl_2$ (81.7 mg, 0.60 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.36 mL, 0.36 mmol, 1.2 equiv), toluene (1.5 mL) were added to a Schlenk tube equipped with a stir bar in glovebox. The mixture was stirred at 120 ℃ in a metal bath for 3 h. Then, the cooled reaction mixture was taken back into the box and was added NBS (80.1 mg, 0.45 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100:1) to furnish product **2a-S′** as a yellow solid in 50% yield (66.2 mg).

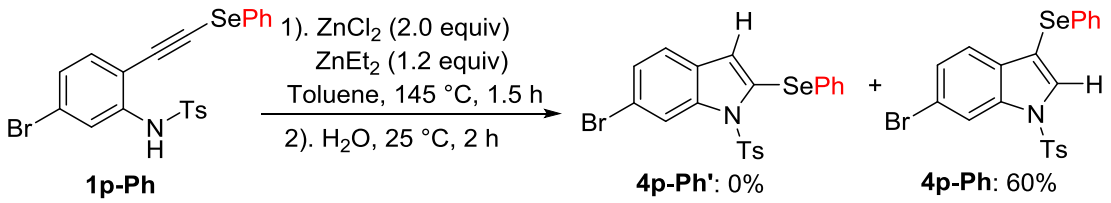


3-bromo-1-tosyl-2-((trifluoromethyl)thio)-1*H*-indole (2a-S′)

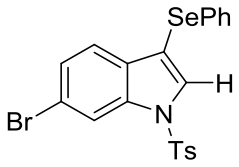
This compound was inevitably contaminated with small amount of the starting material **1a-S**. Mp: 156.9 – 158.3 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.51 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.2 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 138.4 (s), 135.5 (s), 129.9 (s), 128.6 (s), 127.1 (s), 124.6 (s), 123.0 (s), 122.7 (q, *J* = 259.1 Hz), 121.2 (s), 119.0 (s), 115.8 (s), 115.2 (s), 21.6 (s). IR (ATR): ν 2919, 2849, 1737, 1596, 1434, 1380, 1227, 1191, 1164, 1148, 1086, 1044, 811, 755, 705,

661, 568 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{11}BrF_3NNaO_2S_2^+$ $[M + Na]^+$: 471.9259; found: 471.9256.

(b)



In a nitrogen-filled glovebox, *N*-(5-bromo-2-((phenylselanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**1p-Ph**) (50.5 mg, 0.10 mmol), $ZnCl_2$ (27.2 mg, 0.20 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.12 mL, 0.12 mmol, 1.2 equiv), and toluene (1 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 145 ℃ in a metal bath for 1.5 h. Then, the cooled reaction mixture was taken back into the box and was added H_2O (2.7 mg, 0.15 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 10:1) to furnish product **4p-Ph** as a white solid in 60% yield (91.0 mg).



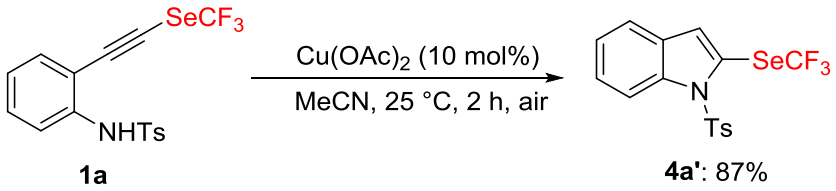
6-bromo-3-(phenylselanyl)-1-tosyl-1*H*-indole (4p-Ph)

Mp: 157.0 – 158.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.59. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.86 – 7.74 (m, 3H), 7.37 – 7.24 (m, 4H), 7.23 – 7.10 (m, 5H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 135.9 (s), 134.7 (s), 131.8 (s), 131.0 (s), 130.8 (s), 130.2 (s), 129.9 (s), 129.2 (s), 127.2 (s), 126.9 (s), 126.7 (s), 122.4 (s), 119.2 (s), 116.6 (s), 106.6 (s), 21.6 (s). IR (ATR): ν 3058, 2920,

2849, 1596, 1576, 1490, 1476, 1416, 1373, 1265, 1169, 1126, 1089, 1035, 933, 810, 730, 664, 575 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{21}H_{16}BrNO_2SSeNa^+$ $[M + Na]^+$: 527.9143; found: 527.9139.

(c)

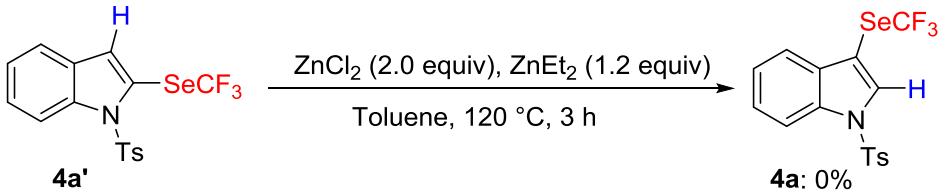
①



1a **4a'**: 87%

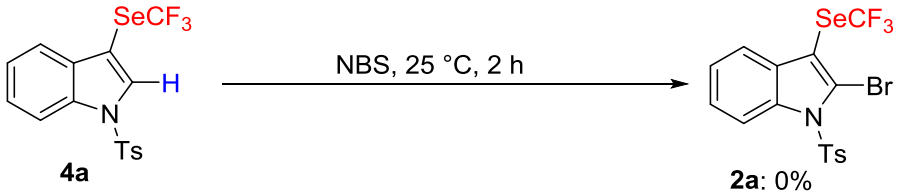
4-Methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (**1a**) (125.7 mg, 0.30 mmol), $Cu(OAc)_2$ (6.0 mg, 0.03 mmol, 10 mol%), and MeCN (3 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 25 ℃ for 2 h under benchtop air atmosphere. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to furnish product **4a′** as a white solid in 87% yield (109.4 mg). 1-Tosyl-2-((trifluoromethyl)selanyl)-1*H*-indole (**4a′**): Mp. 106.1 – 107.4 ℃. R_f (petroleum ether/CH_2Cl_2 = 8:1) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.3 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.27 – 7.20 (m, 3H), 6.98 (s, 1H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.9 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.6 (s), 138.1 (s), 135.2 (s), 130.3 (s), 130.0 (s), 128.2 (s), 127.3 (s), 125.6 (s), 124.0 (s), 122.5 (q, *J* = 334.2 Hz), 120.8 (s), 118.2 (q, *J* = 1.9 Hz), 114.5 (s), 21.6 (s). IR (ATR): *v* 2960, 1596, 1493, 1437, 1369, 1307, 1223, 1188, 1172, 1126, 1082, 1021, 1011, 896, 809, 738, 702, 672, 644, 606, 575, 566 cm^{-1}. HRMS (ESI-Orbitrap) m/z: calcd. for $C_{16}H_{13}F_3NO_2SSe$ $[M + H]^+$: 419.9779; found: 419.9775.

②



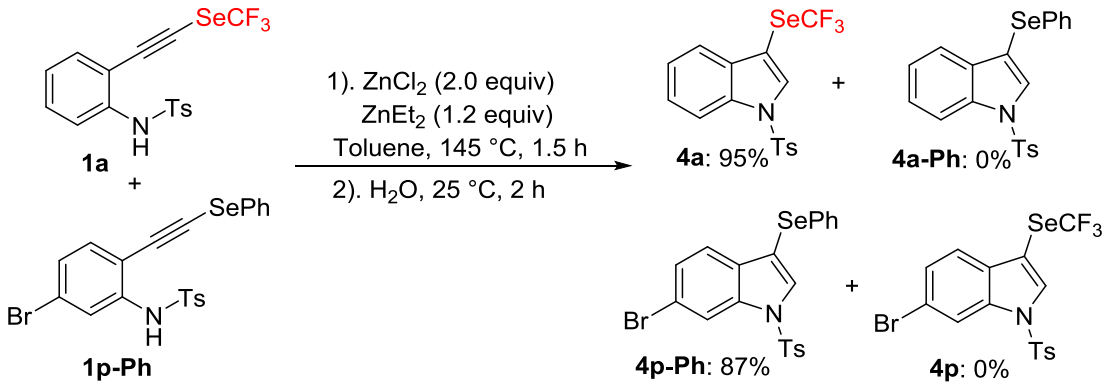
In a nitrogen-filled glovebox, 1-tosyl-2-((trifluoromethyl)selanyl)-1*H*-indole (**4a'**) (41.8 mg, 0.10 mmol), $ZnCl_2$ (27.2 mg, 0.20 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.12 mL, 0.12 mmol, 1.2 equiv), and toluene (1 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 120 ℃ in a metal bath for 3 h. A ^{19}F NMR spectrum was acquired, and no trace of the rearrangement product **4a** was detectable.

(d)



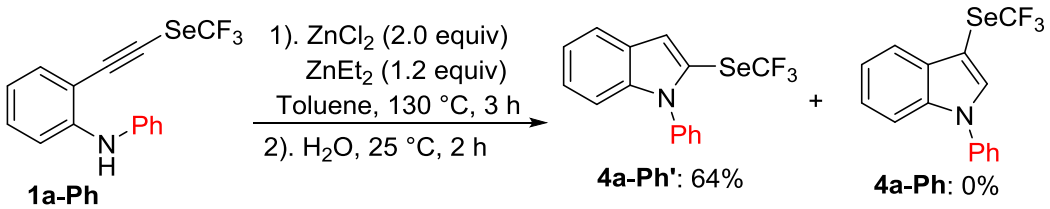
In a nitrogen-filled glovebox, 1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (**4a**) (41.8 mg, 0.10 mmol), NBS (26.7 mg, 0.15 mmol, 1.5 equiv), and toluene (1 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 25 ℃ for 2 h. A ^{19}F NMR spectrum was acquired, and no trace of the brominated product **2a** was detectable.

(e)



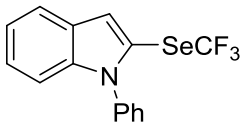
In a nitrogen-filled glovebox, 4-methyl-*N*-(2-(((trifluoromethyl)selanyl)ethynyl)phenyl)benzenesulfonamide (**1a**) (10.5 mg, 0.025 mmol), *N*-(5-bromo-2-((phenylselanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**1p-Ph**) (12.6 mg, 0.025 mmol), $ZnCl_2$ (13.6 mg, 0.10 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.06 mL, 0.06 mmol, 1.2 equiv), and toluene (0.5 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 145 ℃ for 1.5 h. Then, the cooled reaction mixture was taken back into the box and was added H_2O (2.0 μL, 0.075 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. 10 μL (trifluoromethoxy)benzene was then added as an internal standard. The reaction mixture was analyzed by ^{19}F NMR and GC-MS. The yields of **4a** and **4p-Ph** were calculated to be 95% and 87%, respectively. Formation of the crossover products (**4a-Ph** and **4p**) were not detected from ^{19}F NMR.

(f)



In a nitrogen-filled glovebox, *N*-phenyl-2-(((trifluoromethyl)selanyl)ethynyl)aniline (**1a-Ph**) (34.1mg, 0.10 mmol), $ZnCl_2$ (27.2 mg, 0.20 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.12 mL, 0.12 mmol, 1.2 equiv), and toluene (1 mL) were added to

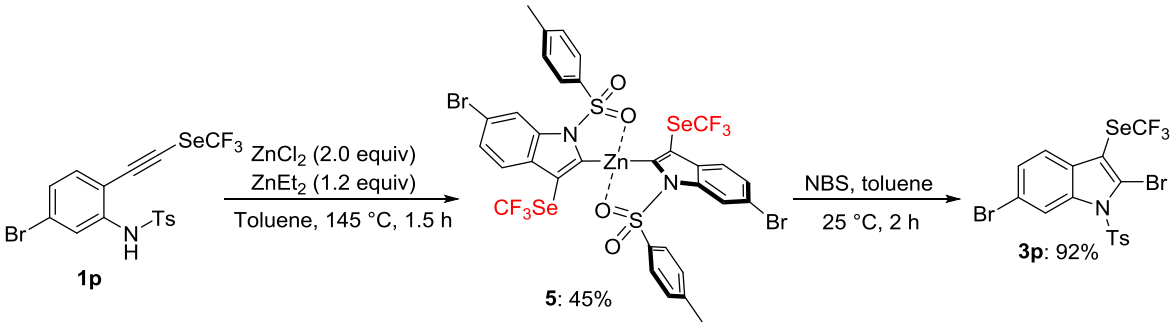
a reaction tube equipped with a stir bar. The reaction mixture was stirred at 130 ℃ in a metal bath for 3 h. Then, the cooled reaction mixture was taken back into the box and was added H_2O (3.0 μL, 0.15 mmol, 1.5 equiv), and the stirring was continued at 25 ℃ for 2 h. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue was purified by column chromatography on aluminum oxide eluated with petroleum ether to give product 1-phenyl-2-((trifluoromethyl)selanyl)-1*H*-indole (**4a-Ph′**) as a white solid in 64% yield (65.0 mg).



1-phenyl-2-((trifluoromethyl)selanyl)-1*H*-indole (4a-Ph′)

Mp: 116.5 – 117.4 ℃. R_f (petroleum) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.44 (m, 3H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.11 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.3 (s), 137.5 (s), 129.2 (s), 129.0 (s), 128.5 (s), 127.5 (s), 124.3 (s), 121.4 (q, *J* = 335.9 Hz), 121.1 (s), 120.9 (s), 118.0 (s), 117.0 (s), 111.3 (s). IR (ATR): ν 2925, 2852, 1596, 1496, 1435, 1361, 1345, 1313, 1216, 1131, 1089, 967, 812, 797, 736, 694, 603 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{11}F_3NSe$ $[M + H]^+$: 342.0003; found: 342.0002.

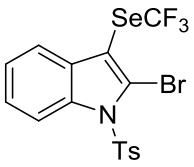
(g)



① In a nitrogen-filled glovebox, *N*-(5-bromo-2-(((trifluoromethyl)selanyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**1p**) (49.7mg, 0.10 mmol), $ZnCl_2$ (27.2 mg, 0.20 mmol, 2.0 equiv), $ZnEt_2$ (1.0 mol/L in toluene, 0.12 mL, 0.12 mmol, 1.2 equiv), and toluene (1 mL) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 145 ℃ in a metal bath for 1.5 h. Then, the cooled reaction mixture was taken back into the box and was filtered through a layer of celite. To this filtrate was carefully added *n*-hexanes (2 mL). The resulting solution was then kept at -25 ℃ for 24 h. The resulting light-yellow crystals were washed with *n*-hexanes (2 × 2 mL), and dried to give 47.0 mg of the complex **5** (45% yield). Complex **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 4H), 7.87 (s, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 4H), 2.40 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.6 (s, 6F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6 (s), 146.4 (s), 136.9 (s), 133.9 (s), 133.1 (s), 130.5 (s), 128.7 (q, *J* = 332.6 Hz), 127.5 (s), 127.3 (s), 123.7 (s), 121.8 (s), 118.4 (s), 115.4 (s), 21.7 (s).

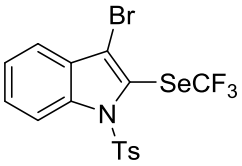
② Into a reaction tube equipped with a stir bar was placed complex **5** (21.1 mg, 0.020 mmol), NBS (5.3 mg, 0.030 mmol, 1.5 equiv), and 2 mL of toluene. The mixture was stirred at 25 ℃ for 2 h. (Trifluoromethoxy)benzene (13 μL) was then added as an internal standard. The reaction mixture was analyzed by ^{19}F NMR and GC-MS. The yield of **3p** was calculated to be 92%.

Data for Compounds 2–4



2-bromo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2a)

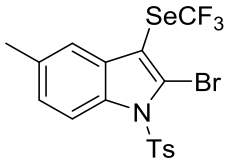
Obtained as a white solid in 91% yield (136.6 mg). Mp: 152.9 – 155.1 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.29 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.0 (s), 137.2 (s), 134.9 (s), 131.2 (s), 130.0 (s), 127.3 (s), 125.9 (s), 124.8 (s), 121.9 (s), 121.8 (q, *J* = 337.3 Hz), 120.5 (s), 115.2 (s), 107.5 (s), 21.6 (s). IR (ATR): *v* 2923, 1595, 1492, 1437, 1381, 1174, 1133, 1083, 1037, 937, 809, 738, 658, 595, 564 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{11}BrF_3NO_2SSe^+$: 496.8806; found: 496.8808.



3-bromo-1-tosyl-2-((trifluoromethyl)selanyl)-1*H*-indole (2a′)

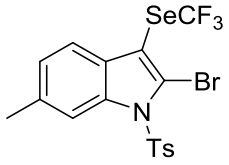
Following the reaction condition (described in Table 1, Entry 1), compound **2a′** was isolated as a white solid in 63% yield (93.9 mg). Mp: 150.3 – 151.7 ℃. R_f (petroleum ether/CH_2Cl_2 = 8:1) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.4 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 138.7 (s), 135.9 (s), 130.0 (s), 128.7 (s), 128.2 (s), 127.4 (s), 124.6 (s), 121.6 (q, *J* = 338.7 Hz), 121.4 (s), 118.8

(s), 117.1 (s), 115.7 (s), 21.7 (s). IR (ATR): *v* 2924, 1596, 1494, 1434, 1379, 1337, 1316, 1262, 1225, 1191, 1178, 1144, 1080, 1035, 939, 809, 754, 739, 704, 694, 659, 615, 594, 567 cm^{-1}. HRMS (ESI-Orbitrap) m/z: calcd. for $C_{16}H_{12}BrF_3NO_2SSe$ $[M + H]^+$: 497.8884; found: 497.8880.



2-bromo-5-methyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2b)

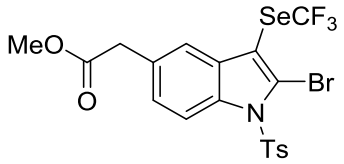
Obtained as a white solid in 88% yield (134.6 mg). Mp: 209.5 – 210.1 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 1H), 7.27 – 7.18 (m, 3H), 2.46 (s, 3H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.8 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.8 (s), 135.4 (s), 134.9 (s), 134.7 (s), 131.3 (s), 129.9 (s), 127.3 (s), 127.2 (s), 121.8 (s), 120.2 (s), 122.0 (q, *J* = 337.3 Hz), 114.9 (s), 107.3 (d, *J* = 1.7 Hz), 21.6 (s), 21.2 (s). IR (ATR): *v* 2923, 1596, 1494, 1444, 1377, 1193, 1174, 1127, 1084, 1039, 965, 804, 735, 701, 676, 657, 577 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{13}BrF_3NO_2SSe^+$: 510.8968; found: 510.8962.



2-bromo-6-methyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2c)

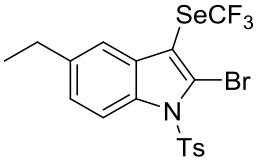
Obtained as a white solid in 95% yield (145.8 mg). Mp: 206.7 – 208.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.40 (s, 1H), 7.25 – 7.19 (m, 3H), 2.47 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.8 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.8 (s), 135.4 (s), 134.9 (s), 134.7 (s), 131.3 (s), 129.9 (s), 127.3 (s), 127.2

(s), 121.8 (s), 120.3 (q, *J* = 337.3 Hz), 120.2 (s), 114.9 (s), 107.3 (d, *J* = 1.8 Hz), 21.6 (s), 21.2 (s). IR (ATR): *v* 2926, 2854, 1716, 1595, 1493, 1445, 1377, 1174, 1127, 1083, 1039, 963, 805, 735, 701, 675, 656, 601, 578 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{13}BrF_3NO_2SSe^+$: 510.8968; found: 510.8962.



methyl 2-(2-bromo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indol-5-yl)acetate (2d)

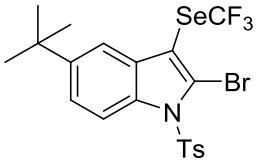
Obtained as a white solid in 33% yield (55.4 mg). Mp: 119.7 – 122.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.53 (s, 1H), 7.33 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.75 (s, 2H), 3.71 (s, 3H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9 (s), 146.0 (s), 136.3 (s), 134.9 (s), 131.4 (s), 130.7 (s), 130.0 (s), 127.3 (s), 127.2 (s), 122.2 (s), 122.0 (q, *J* = 337.3 Hz), 121.0 (s), 115.3 (s), 107.1 (s), 52.1 (s), 40.8 (s), 21.7 (s). IR (ATR): *v* 2924, 2852, 1734, 1595, 1493, 1452, 1440, 1384, 1278, 1195, 1175, 1133, 1083, 1042, 1016, 975, 811, 737, 676, 661, 598, 573 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd. for $C_{19}H_{15}BrF_3NNaO_4SSe^+$: 591.8915; found: 591.8909.



2-bromo-5-ethyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2e)

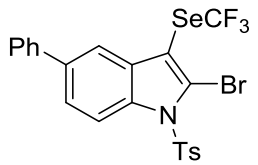
Obtained as a white solid in 77% yield (120.5 mg). Mp: 152.4 – 153.8 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.42 (s, 1H), 7.30 – 7.22 (m, 3H), 2.76 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ

-34.8 (s, 3F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 145.8 (s), 141.1 (s), 135.5 (s), 135.0 (s), 131.3 (s), 129.9 (s), 127.2 (s), 126.2 (s), 122.0 (q, *J* = 338.3 Hz), 121.6 (s), 119.0 (s), 115.0 (s), 107.4 (d, *J* = 1.9 Hz), 28.6 (s), 21.6 (s), 15.8 (s). IR (ATR): *v* 2965, 2924, 1594, 1492, 1450, 1380, 1306, 1210, 1169, 1147, 1083, 1037, 955, 811, 777, 736, 674, 658, 576 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{18}H_{15}BrF_3NO_2SSe^+$: 524.9119; found: 524.9116.



2-bromo-5-(*tert*-butyl)-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2f)

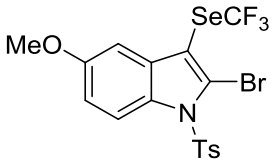
Obtained as a white solid in 74% yield (122.6 mg). Mp: 153.2 – 154.8 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.46 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 2.38 (s, 3H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0 (s), 145.8 (s), 135.2 (s), 135.1 (s), 130.8 (s), 130.0 (s), 127.3 (s), 123.9 (s), 122.1 (q, *J* = 337.3 Hz), 121.3 (s), 116.7 (s), 114.7 (s), 107.6 (s), 34.7 (s), 31.5 (s), 21.7 (s). IR (ATR): *v* 2961, 2925, 1596, 1445, 1385, 1224, 1195, 1139, 1101, 1085, 1045, 964, 856, 811, 744, 701, 664, 590, 579 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{20}H_{19}BrF_3NO_2SSe^+$: 552.9432; found: 552.9433.



2-bromo-5-phenyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2g)

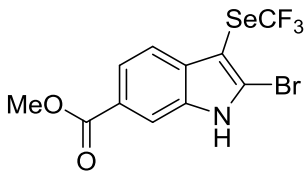
Obtained as a white solid in 96% yield (217.7 mg). Mp: 216.3 – 216.8 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J*

= 8.8 Hz, 1H), 7.87 – 7.79 (m, 3H), 7.70 – 7.55 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.1 (s), 140.5 (s), 138.2 (s), 136.6 (s), 134.9 (s), 131.7 (s), 130.1 (s), 128.9 (s), 127.5 (s), 127.4 (s), 127.3 (s), 125.3 (s), 122.4 (s), 122.1 (q, *J* = 336.2 Hz), 118.7 (s), 115.5 (s), 107.7 (d, *J* = 1.9 Hz), 21.7 (s). IR (ATR): *v* 2926, 2910, 1727, 1596, 1492, 1442, 1385, 1265, 1218, 1193, 1162, 1128, 1101, 1088, 1044, 1017, 878, 823, 760, 736, 700, 675, 663, 623, 595 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd. for $C_{22}H_{15}BrF_3NNaO_2SSe^+$: 595.9016; found: 595.9013.



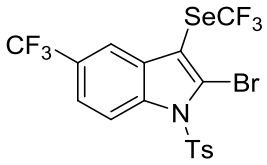
2-bromo-5-methoxy-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2h)

Obtained as a white solid in 78% yield (123.2 mg). Mp: 180.1 – 181.6 ℃. R_f (petroleum ether/ ethyl acetate = 15:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.96 (m, 2H), 3.86 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.8 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.4 (s), 145.9 (s), 134.8 (s), 132.4 (s), 131.7 (s), 129.9 (s), 127.2 (s), 122.1 (s), 122.0 (q, *J* = 336.3 Hz), 116.4 (s), 115.0 (s), 107.5 (d, *J* = 1.9 Hz), 102.4 (s), 55.7 (s), 21.6 (s). IR (ATR): *v* 2922, 2852, 1722, 1610, 1596, 1493, 1457, 1430, 1382, 1296, 1259, 1195, 1150, 1083, 1041, 969, 810, 788, 737, 702, 663, 592 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{17}H_{13}BrF_3NO_3SSe^+$: 526.8912; found: 526.8914.



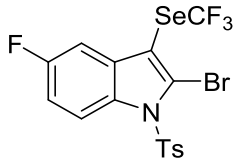
methyl 2-bromo-3-((trifluoromethyl)selanyl)-1*H*-indole-6-carboxylate (2i)

Obtained as a white solid in 43% yield (51.6 mg). Mp: 243.8 – 245.0 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.25. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.21 (s, 1H), 8.00 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -36.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 167.0 (s), 136.3 (s), 134.2 (s), 126.3 (s), 124.3 (s), 123.0 (q, J = 336.9 Hz), 122.4 (s), 119.1 (s), 113.6 (s), 95.1 (s), 52.5 (s). IR (ATR): v 2923, 2852, 1713, 1620, 1507, 1434, 1379, 1352, 1292, 1246, 1133, 1090, 1024, 1006, 894, 813, 768, 737, 702, 664, 577 cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd. for $C_{11}H_7BrF_3NO_2Se^+$: 400.8772; found: 400.8773.



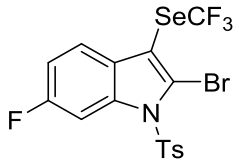
2-bromo-1-tosyl-5-(trifluoromethyl)-3-((trifluoromethyl)selanyl)-1*H*-indole (2j)

Obtained as a white solid in 33% yield (56.3 mg). Mp: 176.3 – 177.8 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.9 Hz, 1H), 7.91 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F), -61.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.5 (s), 138.6 (s), 134.6 (s), 131.1 (s), 130.2 (s), 127.4 (s), 127.1 (s), 124.5 (q, J = 273.2 Hz), 124.0 (s), 122.5 (q, J = 3.5 Hz), 121.9 (q, J = 337.3 Hz), 118.0 (q, J = 4.3 Hz), 115.7 (s), 107.2 (s), 21.7 (s). IR (ATR): v 2959, 2924, 1619, 1596, 1493, 1441, 1385, 1331, 1258, 1195, 1172, 1157, 1121, 1084, 1063, 1042, 1016, 960, 892, 811, 779, 738, 704, 663, 585 cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd. for $C_{17}H_{10}BrF_6NO_2SSe^+$: 564.8685; found: 564.8680.



2-bromo-5-fluoro-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2k)

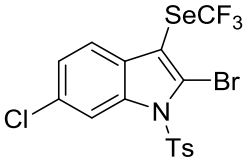
Obtained as a white solid in 66% yield (68.0 mg). Mp: 193.4 – 194.1 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 9.3, 4.3 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.13 (td, *J* = 9.1, 2.7 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F), -117.1 (td, *J* = 8.6, 4.4 Hz, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3 (d, *J* = 244.2 Hz), 146.2 (s), 134.6 (s), 133.4 (d, *J* = 1.8 Hz), 132.5 (d, *J* = 10.3 Hz), 130.1 (s), 127.3 (s), 123.5 (s), 121.9 (q, *J* = 337.3 Hz), 116.7 (d, *J* = 9.0 Hz), 113.9 (d, *J* = 25.3 Hz), 106.2 (d, *J* = 25.2 Hz), 21.7 (s). IR (ATR): *v* 2924, 2852, 1615, 1596, 1455, 1436, 1384, 1193, 1182, 1168, 1146, 1130, 1088, 1043, 1016, 979, 857, 738, 664, 599, 580 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}BrF_4NO_2SSe^+$: 514.8711; found: 514.8712.



2-bromo-6-fluoro-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2l)

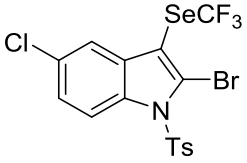
Obtained as a yellow solid in 73% yield (113.5 mg). Mp:169.7 – 171.6 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 10.2, 2.3 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.12 (td, *J* = 8.8, 2.3 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F), -114.1 (td, *J* = 9.6, 5.4 Hz, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.7 Hz), 146.3 (s), 137.0 (d, *J* = 12.8 Hz), 134.7 (s), 130.1 (s), 127.5 (s), 127.4 (s), 127.0 (s), 121.8 (q, *J* = 338.3 Hz), 121.5 (d, *J* = 9.8 Hz), 113.3 (d, *J* = 24.4 Hz), 107.0 (s), 102.8 (d, *J* = 29.9 Hz), 21.7 (s). IR (ATR): *v* 2923, 2853, 1614, 1595, 1584, 1482, 1413, 1383, 1298, 1266, 1234, 1193, 1174, 1128, 1084,

1040, 980, 853, 810, 673, 575 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}BrF_4NO_2SSe^+$: 514.8711; found: 514.8715.



2-bromo-6-chloro-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2m)

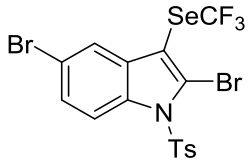
Obtained as a white solid in 48% yield (51.4 mg). Mp: 200.1 – 202.3 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.3 (s), 137.2 (s), 134.7 (s), 132.1 (s), 130.1 (s), 129.7 (s), 127.4 (s), 125.5 (s), 122.4 (s), 121.9 (q, *J* = 337.3 Hz), 121.3 (s), 115.3 (s), 107.0 (s), 21.7 (s). IR (ATR): *v* 2925, 2852, 1723, 1596, 1482, 1454, 1406, 1388, 1294, 1264, 1197, 1172, 1133, 1086, 1038, 948, 809, 736, 644, 572 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}BrClF_3NO_2SSe^+$: 530.8416; found: 530.8414.



2-bromo-5-chloro-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2n)

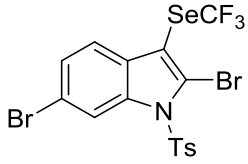
Obtained as a white solid in 53% yield (39.1 mg). Mp: 219.2 – 221.0 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.36 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.3 (s), 135.5 (s), 134.6 (s), 132.5 (s),

130.9 (s), 130.1 (s), 127.3 (s), 126.1 (s), 123.4 (s), 121.9 (q, *J* = 337.3 Hz), 120.1 (s), 116.4 (s), 106.6 (s), 21.7 (s). IR (ATR): *v* 2922, 2852, 1721, 1595, 1492, 1432, 1388, 1183, 1160, 1138, 1084, 1037, 964, 811, 749, 664, 597, 574 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}BrClF_3NO_2SSe^+$: 530.8416; found: 530.8418.



2,5-dibromo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2o)

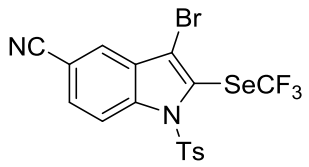
Obtained as a white solid in 82% yield (142.2 mg). Mp: 226.7 – 227.4 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.3 (s), 135.9 (s), 134.6 (s), 132.9 (s), 130.1 (s), 128.8 (s), 127.3 (s), 123.3 (s), 123.1 (s), 121.9 (q, *J* = 338.3 Hz), 118.5 (s), 116.7 (s), 106.4 (d, *J* = 1.8 Hz), 21.7 (s). IR (ATR): *v* 2923, 2855, 1731, 1594, 1492, 1428, 1386, 1183, 1159, 1136, 1127, 1084, 1062, 1037, 968, 944, 809, 727, 663, 571 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}Br_2F_3NO_2SSe^+$: 574.7911; found: 574.7908.



2,6-dibromo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (2p)

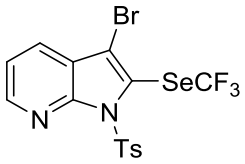
Obtained as a white solid in 44% yield (76.2 mg). Mp: 203.4 – 204.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.4

(s), 137.5 (s), 134.6 (s), 130.2 (s), 130.1 (s), 128.2 (s), 127.4 (s), 122.4 (s), 122.0 (q, *J* = 336.2 Hz), 121.6 (s), 119.8 (s), 118.1 (s), 107.1 (d, *J* = 2.0 Hz), 21.7 (s). IR (ATR): *v* 2923, 2852, 1595, 1561, 1492, 1449, 1386, 1295, 1262, 1194, 1171, 1135, 1086, 1040, 966, 939, 867, 809, 728, 663, 570 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{16}H_{10}Br_2F_3NO_2SSe^+$: 574.7911; found: 574.7902.



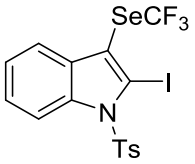
3-bromo-1-tosyl-2-((trifluoromethyl)selanyl)-1*H*-indole-5-carbonitrile (2q′)

Obtained as a white solid in 65% yield (100.3 mg). Mp: 185.0 – 186.3 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.9 Hz, 1H), 7.96 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -33.8 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.5 (s), 139.9 (s), 135.1 (s), 130.4 (s), 130.2 (s), 128.6 (s), 127.5 (s), 126.3 (s), 121.3 (q, *J* = 338.6 Hz), 119.8 (s), 118.4 (s), 117.2 (s), 116.6 (s), 108.2 (s), 21.7 (s). IR (ATR): *v* 2955, 2916, 2850, 2228, 1734, 1595, 1437, 1378, 1234, 1193, 1175, 1145, 1083, 1039, 813, 739, 663, 595, 582 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd. for $C_{17}H_{10}BrF_3N_2O_2SSeNa^+$: 544.8656; found: 544.8647.



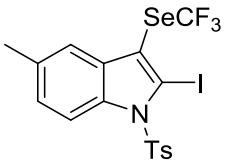
3-bromo-1-tosyl-2-((trifluoromethyl)selanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (2r′)

Obtained as a yellow solid in 73% yield (109.3 mg). Mp: 203.2 – 204.6 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.9 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.89 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.39 – 7.24 (m, 3H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -33.9. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.1 (s), 148.2 (s), 145.7 (s), 135.6 (s), 129.7 (s), 129.7 (s), 128.3 (s), 121.7 (q, *J* = 338.2 Hz), 121.4 (s), 120.1 (s), 118.1 (s), 114.7 (s), 21.7 (s). IR (ATR): *v* 2952, 2917, 2849, 1733, 1594, 1571, 1384, 1320, 1274, 1192, 1179, 1158, 1084, 1035, 940, 767, 710, 662, 568 cm^{-1}. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd. for $C_{15}H_{11}BrF_3N_2O_2SSe^+$: 498.8836; found: 498.8827.



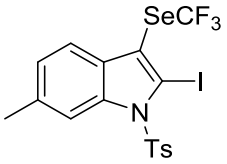
2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3a)

Obtained as a yellow solid in 90% yield (149.2 mg). Mp: 123.1 –124.5 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.30 (m, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.8 (s), 138.7 (s), 134.9 (s), 132.3 (s), 129.9 (s), 127.4 (s), 125.7 (s), 124.6 (s), 122.3 (q, *J* = 337.3 Hz), 121.1 (s), 116.40 (s), 115.6 (s), 95.8 (s), 21.7 (s). IR (ATR): ν 2924, 1596, 1492, 1427, 1377, 1132, 1081, 1031, 935, 810, 737, 668, 657, 562 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{11}F_3INO_2SSe^+$ [M]$^+$: 544.8667; found: 544.8668.



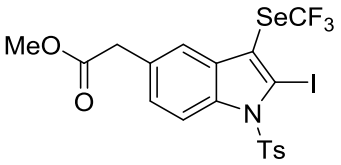
2-iodo-5-methyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3b)

Obtained as a white solid in 39% yield (65.9 mg). Mp: 232.1 – 233.7 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 137.0 (s), 134.9 (s), 134.5 (s), 132.4 (s), 129.9 (s), 127.3 (s), 127.1 (s), 122.4 (q, *J* = 337.3 Hz), 120.7 (s), 116.1 (s), 115.3 (s), 95.6 (s), 21.7 (s), 21.2 (s). IR (ATR): ν 2921, 2850, 1722, 1597, 1461, 1376, 1264, 1178, 1089, 1040, 966, 810, 737, 703, 673, 593 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{17}H_{13}F_3INO_2SSe^+$ [M]$^+$: 558.8829; found:558.8824.



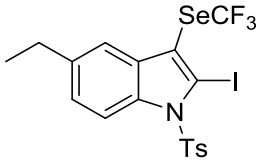
2-iodo-6-methyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3c)

Obtained as a white solid in 79% yield (132.8 mg). Mp: 231.3 – 232.9 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 2.52 (s, 3H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 139.1 (s), 136.1 (s), 135.1 (s), 130.2 (s), 129.9 (s), 127.3 (s), 126.1 (s), 122.4 (q, *J* = 337.3 Hz), 120.6 (s), 116.3 (d, *J* = 1.7 Hz), 115.6 (s), 94.5 (s), 22.0 (s), 21.6 (s). IR (ATR): ν 2925, 2853, 1379, 1264, 1141, 1088, 1042, 895, 812, 731, 702, 675, 576 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{17}H_{13}F_3INO_2SSe^+$ [M]$^+$: 558.8829; found: 558.8828.



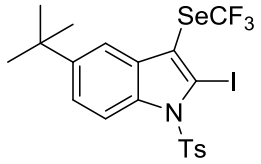
methyl 2-(2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indol-5-yl)acetate (3d)

Obtained as a yellow solid in 55% yield (101.9 mg). Mp: 162.8 – 163.8 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.30 – 7.23 (m, 3H), 3.75 (s, 2H), 3.70 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9 (s), 145.9 (s), 137.8 (s), 134.9 (s), 132.5 (s), 130.6 (s), 130.0 (s), 127.4 (s), 127.0 (s), 122.4 (q, *J* = 336.5 Hz), 121.5 (s), 115.9 (d, *J* = 1.7 Hz), 115.6 (s), 96.1 (s), 52.1 (s), 40.7 (s), 21.7 (s). IR (ATR): ν 2952, 2927, 1732, 1595, 1492, 1433, 1380, 1274, 1179, 1131, 1083, 1037, 1016, 973, 893, 811, 737, 659, 586 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{16}F_3INO_4SSe^+$ [M + H]$^+$: 617.8957; found: 617.8953.



5-ethyl-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3e)

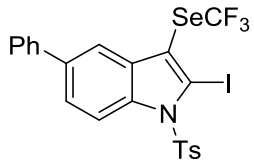
Obtained as a white solid in 68% yield (116.5 mg). Mp: 167.3 – 168.5 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.43 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 141.0 (s), 137.1 (s), 135.0 (s), 132.4 (s), 129.9 (s), 127.4 (s), 126.1 (s), 120.8 (q, *J* = 337.3 Hz), 119.5 (s), 116.2 (d, *J* = 1.7 Hz), 115.4 (s), 95.5 (s), 28.6 (s), 21.6 (s), 15.8 (s). IR (ATR): ν 2923, 2853, 1596, 1434, 1379, 1264, 1213, 1193, 1179, 1137, 1086, 1036, 812, 777, 735, 702, 670, 590, 576 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{18}H_{15}F_3INO_2SSe^+$ [M]$^+$: 572.8980; found: 572.8979.



5-(*tert*-butyl)-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3f)

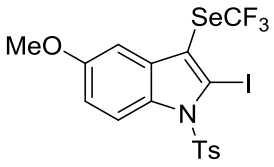
Obtained as a white solid in 49% yield (87.5 mg). Mp: 153.1 – 154.4 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.61 (s, 1H), 7.39 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 1.37 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.9 (s), 145.7 (s), 136.7 (s), 135.1 (s), 131.9 (s), 129.9 (s), 127.4 (s), 123.7 (s), 120.8 (q, *J* = 338.3 Hz), 117.2 (s), 116.4 (d, *J* = 1.8 Hz), 115.0 (s), 95.1 (s), 34.7 (s), 31.5 (s), 21.7 (s). IR (ATR): ν 2962, 2926, 1596, 1435, 1381, 1264, 1222, 1193, 1180, 1142, 1101, 1086, 1042, 962, 851, 812,

736, 702, 665, 591 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{20}H_{19}F_3INO_2SSe^+$ $[M]^+$: 600.9293; found: 600.9294.



2-iodo-5-phenyl-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3g)

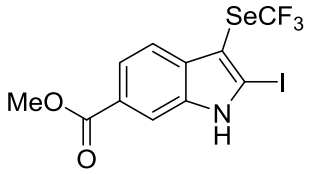
Obtained as a white solid in 52% yield (96.6 mg). Mp: 168.2 – 170.1 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.9 (s), 140.4 (s), 138.0 (s), 134.9 (s), 132.8 (s), 130.0 (s), 128.9 (s), 127.5 (s), 127.4 (s, 2C), 125.1 (s), 122.4 (q, *J* = 337.3 Hz), 119.2 (s), 116.5 (s), 115.9 (s), 96.3 (s), 21.7 (s). IR (ATR): ν 2958, 2922, 1724, 1596, 1492, 1473, 1379, 1264, 1214, 1191, 1178, 1126, 1098, 1085, 1038, 1017, 965, 878, 822, 808, 759, 735, 673, 614, 586 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{16}F_3INO_2SSe^+$ $[M + H]^+$: 621.9058; found: 621.9056.



2-iodo-5-methoxy-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3h)

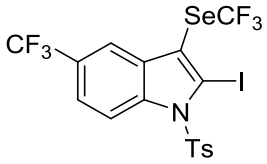
Obtained as a white solid in 50% yield (85.8 mg). Mp: 202.1 – 203.4 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.93 (dd, *J* = 9.2, 2.6 Hz, 1H), 3.85 (s, 3H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.3 (s), 145.8 (s), 134.8

(s), 133.4 (s), 133.3 (s), 129.9 (s), 127.3 (s), 122.4 (q, J = 336.5 Hz), 116.7 (s), 116.2 (d, J = 1.6 Hz), 115.0 (s), 102.8 (s), 96.0 (d, J = 1.5 Hz), 55.7 (s), 21.6 (s). IR (ATR): ν 2927, 2853, 1609, 1424, 1381, 1264, 1193, 1155, 1087, 1039, 895, 843, 812, 731, 702, 591 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{17}H_{13}F_3INO_3SSe^+$ $[M]^+$: 574.8773; found: 574.8771.



methyl 2-iodo-3-((trifluoromethyl)selanyl)-1*H*-indole-6-carboxylate (3i)

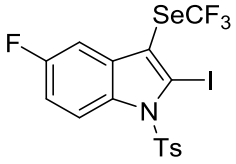
Obtained as a white solid in 27% yield (36.0 mg). Mp: 253.8 – 254.9 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.20. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.96 (s, 1H), 8.01 (s, 1H), 7.76 (d, J = 6.8 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -36.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 167.0 (s), 138.7 (s), 134.4 (s), 123.8 (s), 123.3 (q, J = 338.3 Hz), 122.2 (s), 119.2 (s), 113.4 (s), 103.9 (s), 102.2 (s), 52.5 (s). IR (ATR): ν 2926, 2855, 1715, 1421, 1379, 1133, 1092, 895, 731, 702, 606, 580 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{11}H_7F_3INO_2Se^+$ $[M]^+$: 448.8633; found: 448.8634.



2-iodo-1-tosyl-5-(trifluoromethyl)-3-((trifluoromethyl)selanyl)-1*H*-indole (3j)

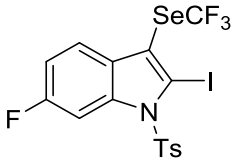
Obtained as a white solid in 11% yield (41.6 mg). Mp: 181.1 – 181.9 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.9 Hz, 1H), 7.93 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.5 (s, 3F), -61.5 (s,

3F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.4 (s), 140.1 (s), 134.6 (s), 132.1 (s), 130.1 (s), 127.5 (s), 127.3 (s), 127.0 (s), 124.0 (q, *J* = 272.2 Hz), 122.3 (d, *J* = 3.5 Hz), 122.3 (q, *J* = 336.4 Hz), 118.6 (q, *J* = 4.2 Hz), 116.1 (s), 98.1 (s), 21.7 (s). IR (ATR): ν 2917, 2848, 1595, 1491, 1436, 1384, 1333, 1259, 1225, 1174, 1156, 1125, 1097, 1086, 1064, 1040, 892, 815, 737, 704, 664, 582 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{17}H_{10}F_6INO_2SSe^+$ $[M]^+$: 612.8541; found: 612.8542.



5-fluoro-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3k)

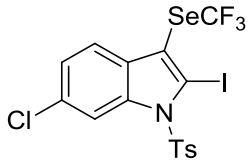
Obtained as a white solid in 79% yield (133.8 mg). Mp: 187.6 – 189.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 9.2, 4.3 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.22 (m, 3H), 7.06 (td, *J* = 9.1, 2.7 Hz, 1H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F), -117.3 – -117.5 (m, 1F). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 244.3 Hz), 146.1 (s), 135.0 (s), 134.6 (s), 133.5 (d, *J* = 10.2 Hz), 130.0 (s), 127.4 (s), 122.3 (q, *J* = 336.4 Hz), 117.0 (d, *J* = 9.0 Hz), 115.8 (s), 113.8 (d, *J* = 25.4 Hz), 106.6 (d, *J* = 25.1 Hz), 97.7 (s), 21.7 (s). IR (ATR): ν 2922, 2849, 1614, 1595, 1430, 1379, 1264, 1190, 1177, 1164, 1146, 1129, 1087, 1036, 1015, 977, 849, 800, 736, 701, 676, 582 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}F_4INO_2SSe^+$ $[M]^+$: 562.8573; found: 562.8576.



6-fluoro-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3l)

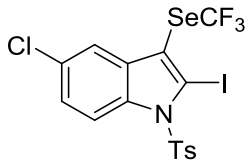
Obtained as a yellow solid in 72% yield (122.0 mg). Mp: 175.1 – 177.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J*

= 10.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 8.7 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F), -114.5 – -114.6 (m, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 245.0 Hz), 146.2 (s), 138.3 (d, *J* = 12.7 Hz), 134.7 (s), 130.0 (s), 128.7 (s), 127.5 (s), 121.9 (d, *J* = 10.0 Hz), 120.7 (q, *J* = 337.3 Hz) 115.8 (s), 113.2 (d, *J* = 24.4 Hz), 103.0 (d, *J* = 29.8 Hz), 95.0 (d, *J* = 3.3 Hz), 21.7 (s). IR (ATR): ν 2927, 2855, 1612, 1596, 1482, 1409, 1382, 1264, 1193, 1180, 1132, 1097, 1087, 1037, 979, 812, 732, 702, 672, 577 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}F_4INO_2SSe^+$ $[M]^+$: 562.8573; found: 562.8577.



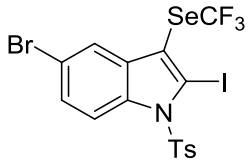
6-chloro-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3m)

Obtained as a white solid in 63% yield (108.6 mg). Mp: 200.9 –203.2 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 1.8 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.27 (m, 3H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.6 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.2 (s), 138.6 (s), 134.7 (s), 132.0 (s), 130.8 (s), 130.1 (s), 127.5 (s), 125.4 (s), 124.8 (s), 122.3 (q, *J* = 337.3 Hz), 121.8 (s), 115.6 (s), 96.2 (s), 21.7 (s). IR (ATR): ν 2925, 2854, 1596, 1454, 1400, 1380, 1264, 1192, 1180 ,1157, 1088, 1036, 950, 895, 812, 732, 702, 665, 574 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}ClF_3INO_2SSe^+$ $[M]^+$: 578.8277; found: 578.8279.



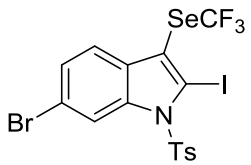
5-chloro-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3n)

Obtained as a white solid in 48% yield (83.0 mg). Mp: 228.2 – 230.6 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.47. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 2.2 Hz, 1H), 7.48 – 7.40 (m, 3H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -35.4 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.0 (s), 136.6 (s), 134.3 (s), 133.7 (s), 130.9 (s), 129.9 (s), 127.5 (s), 126.0 (s), 123.3 (q, J = 337.3 Hz), 120.2 (s), 117.3 (s), 115.7 (s), 103.7 (s), 21.5 (s). IR (ATR): ν 2925, 2853, 1596, 1424, 1379, 1264, 1191, 1179, 1137, 1089, 1074, 1035, 895, 811, 792, 702, 664, 579 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}ClF_3INO_2SSe^+$ $[M]^+$: 578.8277; found: 578.8278.



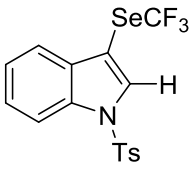
5-bromo-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3o)

Obtained as a white solid in 51% yield (89.2 mg). Mp: 239.3 – 240.1 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.52. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 2.1 Hz, 1H), 7.55 (dd, J = 9.0, 2.1 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -35.4 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.0 (s), 137.0 (s), 134.3 (s), 134.1 (s), 130.9 (s), 128.7 (s), 127.5, 123.3 (q, J = 338.3 Hz), 123.2 (s), 118.0 (s), 117.6 (s), 115.6 (d, J = 2.1 Hz), 103.6 (s), 21.5 (s). IR (ATR): ν 2927, 2853, 1595, 1421, 1378, 1264, 1214, 1197, 1179, 1137, 1089, 1033, 895, 810 ,733, 703, 664, 571 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}BrF_3INO_2SSe^+$ $[M]^+$: 622.7772; found: 622.7775.



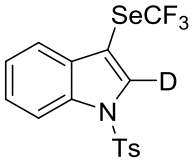
6-bromo-2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3p)

Obtained as a white solid in 57% yield (105.9 mg). Mp: 212.3 – 213.6 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.60. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (d, J = 1.6 Hz, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -35.4 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.0 (s), 138.5 (s), 134.3 (s), 131.5 (s), 130.9 (s), 128.4 (s), 127.7 (s), 123.3 (q, J = 337.3 Hz), 122.8 (s), 119.0 (s), 117.9 (s), 116.4 (s), 102.5 (s), 21.6 (s). IR (ATR): ν 2925, 2854, 1595, 1449, 1398, 1379, 1264, 1191, 1180, 1157, 1087, 1037, 940, 895, 811, 733, 703, 644, 573 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{10}BrF_3INO_2SSe^+$ $[M]^+$: 622.7772; found: 622.7776.



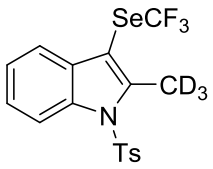
1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (4a)

Obtained as a white solid in 82% yield (103.2 mg). Mp: 187.4–188.3 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.98 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.32 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.1 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 134.8 (s), 134.6 (s), 134.0 (s), 131.9 (s), 130.1 (s), 127.0 (s), 125.6 (s), 124.2 (s), 121.9 (q, *J* = 334.7 Hz), 120.9 (s), 113.5 (s), 100.4 (d, *J* = 2.0 Hz), 21.6 (s). IR (ATR): ν 3131, 2925, 1597, 1515, 1493, 1472, 1442, 1373, 1263, 1188, 1174, 1130, 1087, 1034, 1016, 931, 811, 754, 744, 704, 659, 583 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{12}F_3NO_2SSe^+$ $[M]^+$: 418.9701; found: 418.9705.



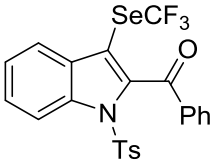
1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole-2-*d* (4b)

Obtained as a white solid in 73% yield (46.1 mg). Mp: 187.3 – 188.1 ℃. R_f (petroleum ether/ethyl acetate = 15:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.2 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7 (s), 134.7 (s), 134.6 (s), 131.9 (s), 130.2 (s), 127.0 (s), 125.6 (s), 124.2 (s), 121.9 (q, *J* = 334.8 Hz), 120.9 (s), 113.5 (s), 100.2 (q, *J* = 1.6 Hz), 21.6 (s). IR (ATR): ν 2924, 2851, 1597, 1493, 1468, 1438, 1373, 1364, 1236, 1187, 1173, 1115, 1088, 1032, 961, 873, 811, 754, 703, 658, 578 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{11}DF_3NO_2SSe^+$ $[M]^+$: 419.9763; found: 419.9764.



2-(methyl-d_3)-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (4c)

Obtained as a white solid in 52% yield (68.2 mg). Mp: 162.2 – 163.1 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.39 – 7.29 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.0 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.4 (s), 144.3 (s), 136.2 (s), 135.7 (s), 131.3 (s), 130.1 (s), 126.4 (s), 125.1 (s), 124.2 (s), 122.1 (q, *J* = 335.4 Hz), 120.2 (s), 114.4 (s), 102.1 (s), 21.6 (s). IR (ATR): ν 2926, 2856, 1596, 1543, 1493, 1447, 1374, 1298, 1236, 1217, 1188, 1175, 1111, 1083, 1040, 942, 848, 744, 686, 656, 581 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{17}H_{11}D_3F_3NO_2SSe^+$ $[M]^+$: 436.0051; found: 436.0045.



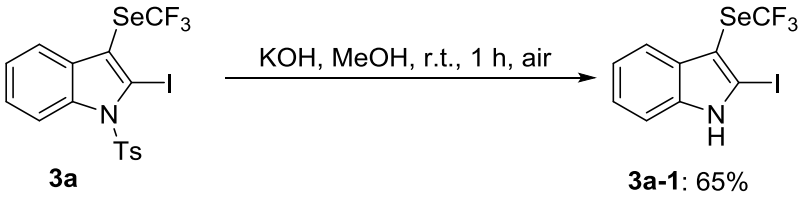
phenyl(1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indol-2-yl)methanone (4d)

Obtained as a white solid in 60% yield (93.8 mg). Mp: 196.8 – 197.9 ℃. R_f (petroleum ether:ethyl acetate = 15:1) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -34.1 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.6 (s), 145.9 (s), 142.5 (s), 137.3 (s), 135.1 (s), 134.2 (s), 133.8 (s), 131.1 (s), 130.0 (s), 129.8 (s), 128.7 (s), 127.6 (s), 126.8 (s), 125.0 (s), 121.7 (q, *J* = 336.2 Hz), 121.6 (s), 114.3 (s), 102.7 (s), 21.7 (s). IR (ATR): ν 2923,

2853, 1724, 1673, 1596, 1583, 1522, 1493, 1445, 1379, 1321, 1255, 1176, 1150, 1086, 954, 814, 730, 574 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{23}H_{16}F_3NNaO_3SSe^+$ $[M + Na]^+$: 545.9860; found: 545.9858.

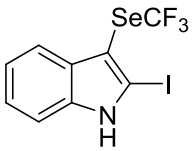
Procedures for derivatization of 3a

(a)



3a **3a-1**: 65%

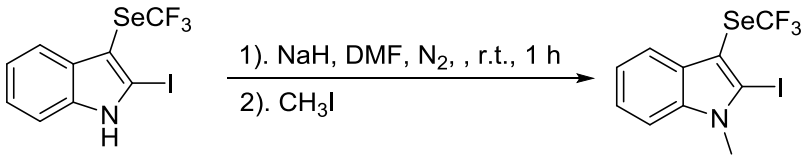
To a solution of 2-iodo-1-tosyl-3-((trifluoromethyl)selanyl)-1*H*-indole (**3a**) (217.9 mg, 0.40 mmol, 1.0 equiv) in MeOH (4 mL) was added KOH (673.3 mg, 12.0 mmol, 30.0 equiv) in a Schlenk tube equipped with a stir bar, and the mixture was stirred at r.t. for 4 h. The reaction mixture was neutralized with the addition of HCl (3.0 M, 3 mL), and the solution was extracted with ethyl acetate (3 × 15 mL). Organic layers were washed with brine and dried over Na_2SO_4. The solvents were filtered and evaporated under reduced pressure. The obtained residue was purified by column chromatography on silica gel with petroleum ether/ ethyl acetate (20:1) to give product **3a-1**.



2-iodo-3-((trifluoromethyl)selanyl)-1*H*-indole (3a-1)

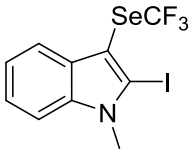
Obtained as a white solid in 65% yield (100.9 mg). Mp: 97.5 – 98.7 ℃. R_f (petroleum ether/ethyl acetate = 20:1) = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.14 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.1 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.8 (s), 130.8 (s), 123.4 (s), 122.8 (q, *J* = 336.7 Hz), 121.9 (s), 120.0 (s), 110.7 (s), 104.1 (s), 94.1 (s). IR (ATR): *v* 2916, 1848, 1708, 1466, 1432, 1394, 1335, 1302, 1275, 1224, 1115, 1090, 743 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $C_9H_6F_3INSe^+$: 391.8657; found: 391.8645.

(b)



3a-1 **3a-2**: 89%

To a stirred solution of 2-iodo-3-((trifluoromethyl)selanyl)-1*H*-indole (**3a-1**) (39.8 mg, 0.10 mmol, 1.0 equiv) in dry DMF (1.0 mL) was added NaH (3.6 mg, 0.15 mmol, 1.0 equiv) under a nitrogen atmosphere at room temperature, and the resulting reaction mixture was stirred at room temperature for 1 h. CH_3I (9.3 μL, 0.15 mmol, 1.0 equiv) was added, and then the reaction mixture was stirred at room temperature for overnight. The reaction was quenched with water (5 mL), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The obtained residue was purified by column chromatography on silica gel with petroleum ether to give product **3a-2**.



2-iodo-1-methyl-3-((trifluoromethyl)selanyl)-1*H*-indole (3a-2)

Obtained as a white solid in 89% yield (36.2 mg). Mp: 152.4 – 156.3 ℃. R_f (petroleum ether) = 0.82. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 6.9 Hz, 1H), 7.33 (d, J = 5.6 Hz, 1H), 7.27 – 7.15 (m, 2H), 3.86 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.7 (s), 131.4 (s), 122.9 (s), 122.7 (q, J = 337.1 Hz), 121.6 (s), 120.2 (s), 110.1 (s), 103.4 (s), 102.5 (s), 36.0 (s). IR (ATR): v 1461, 1448, 1417, 1348, 1327, 1306, 1233, 1160, 1116, 1090, 1011, 741 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{10}H_8F_3INSe$: 405.8813; found: 405.8801.

Crystal Structure Analyses

The suitable crystals of **1a-S** (CCDC 2267469), **1p-Ph** (CCDC 2353238), **2a** (CCDC 2160368), **2a'** (CCDC 2125422), **2a-S'** (CCDC 2267084), **2f** (CCDC 2179736), **2l** (CCDC 2179735), **2q'** (CCDC 2353239), **2r'** (CCDC 2278531), **3a** (CCDC 2165430), **3i** (CCDC 2267080), **4a** (CCDC 2160370), **4a'** (CCDC 2125421), **4a-Ph'** (CCDC 2353240), **4b** (CCDC 2179724), **4c** (CCDC 2246259), **4d** (CCDC 2129692), **4p-Ph** (CCDC 2353241), and **5** (CCDC 2184810) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX or a Rigaku diffractometer, equipped with a CCD detector at r.t., using CuKα radiation (λ 1.54178 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[6] Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

Some alert level B and the residuals were appeared in the check cif file of compounds **3i** (CCDC 2267080) and **5** (CCDC 2184810). We still did not solve these problems when we tried to give additional refinement cycles or use new space group. But we have given sufficient evidence to prove the accuracy of this structure by ^{1}H, ^{13}C and ^{19}F NMR.

ORTEP diagrams

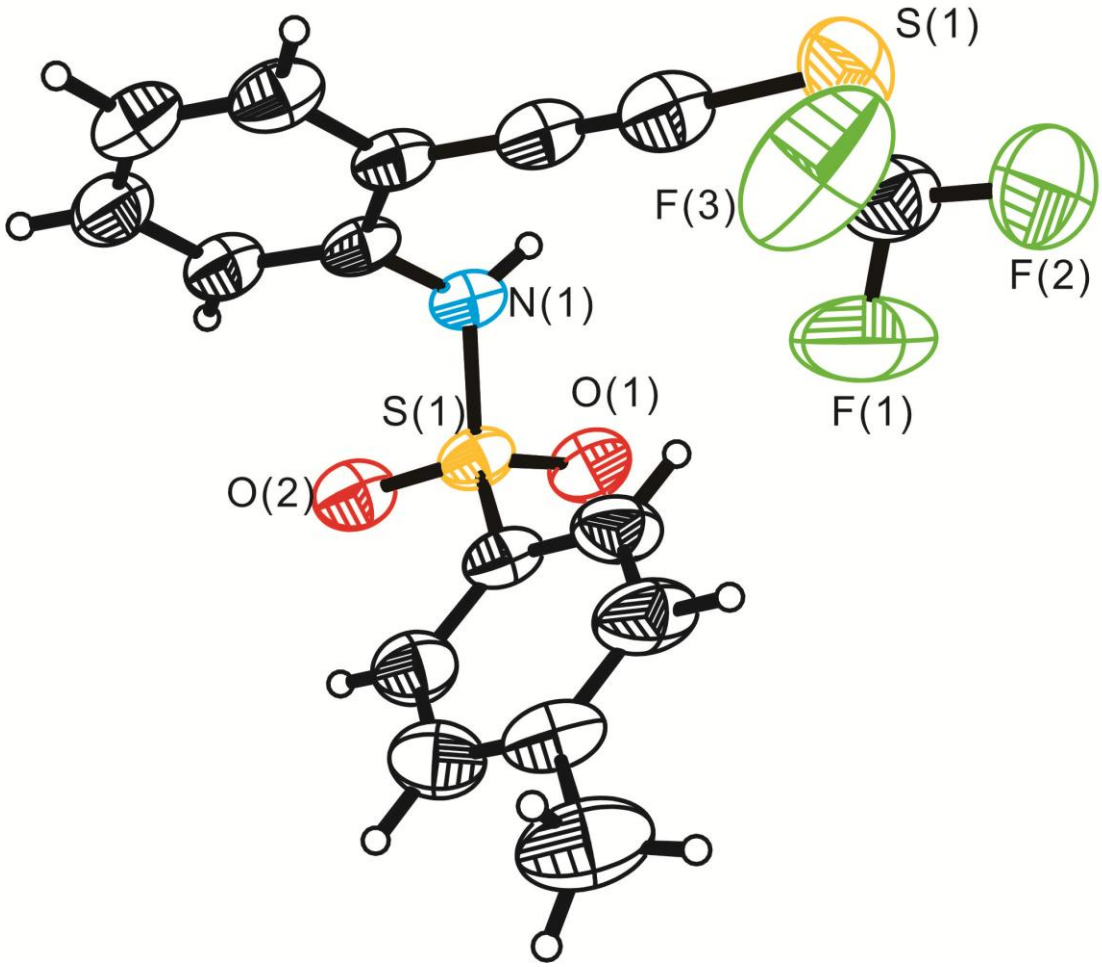


Figure S1. ORTEP diagram of 1a-S with thermal ellipsoids at the 40% probability level

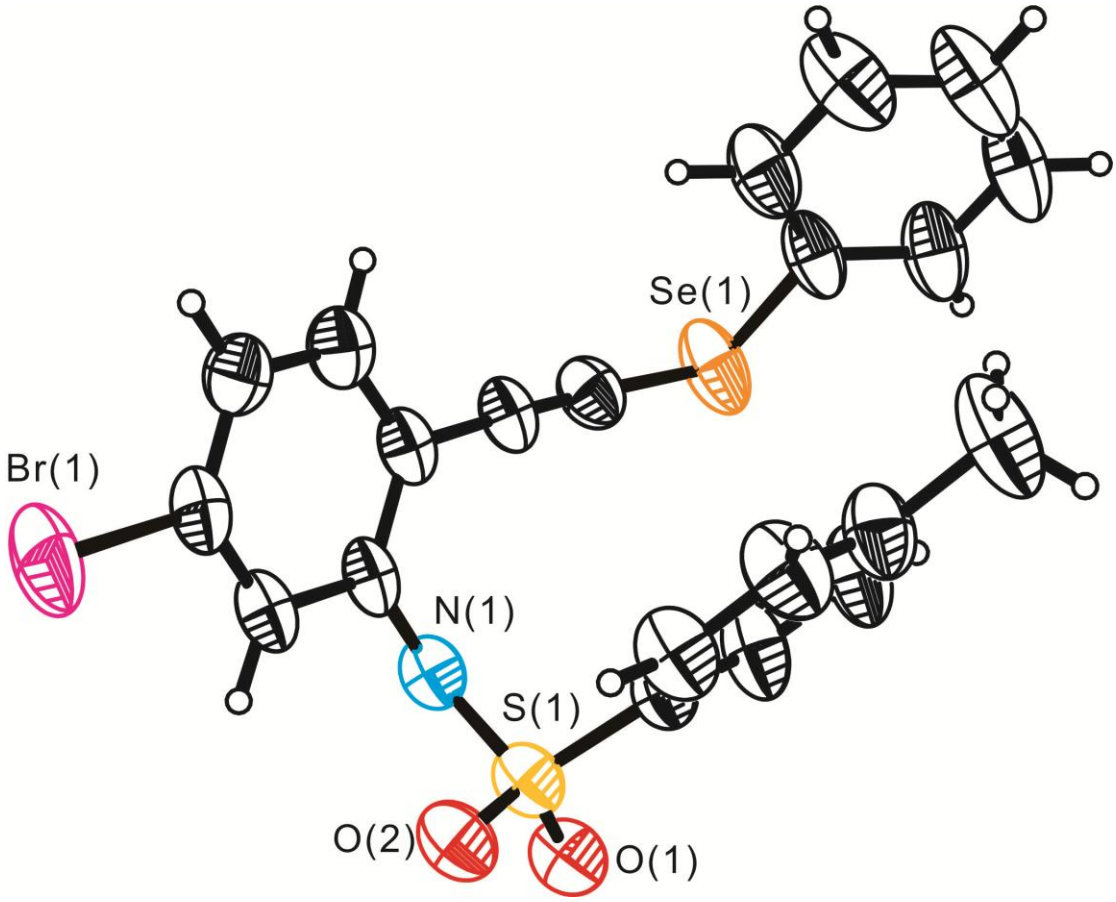


Figure S2. ORTEP diagram of 1p-Ph with thermal ellipsoids at the 40% probability level

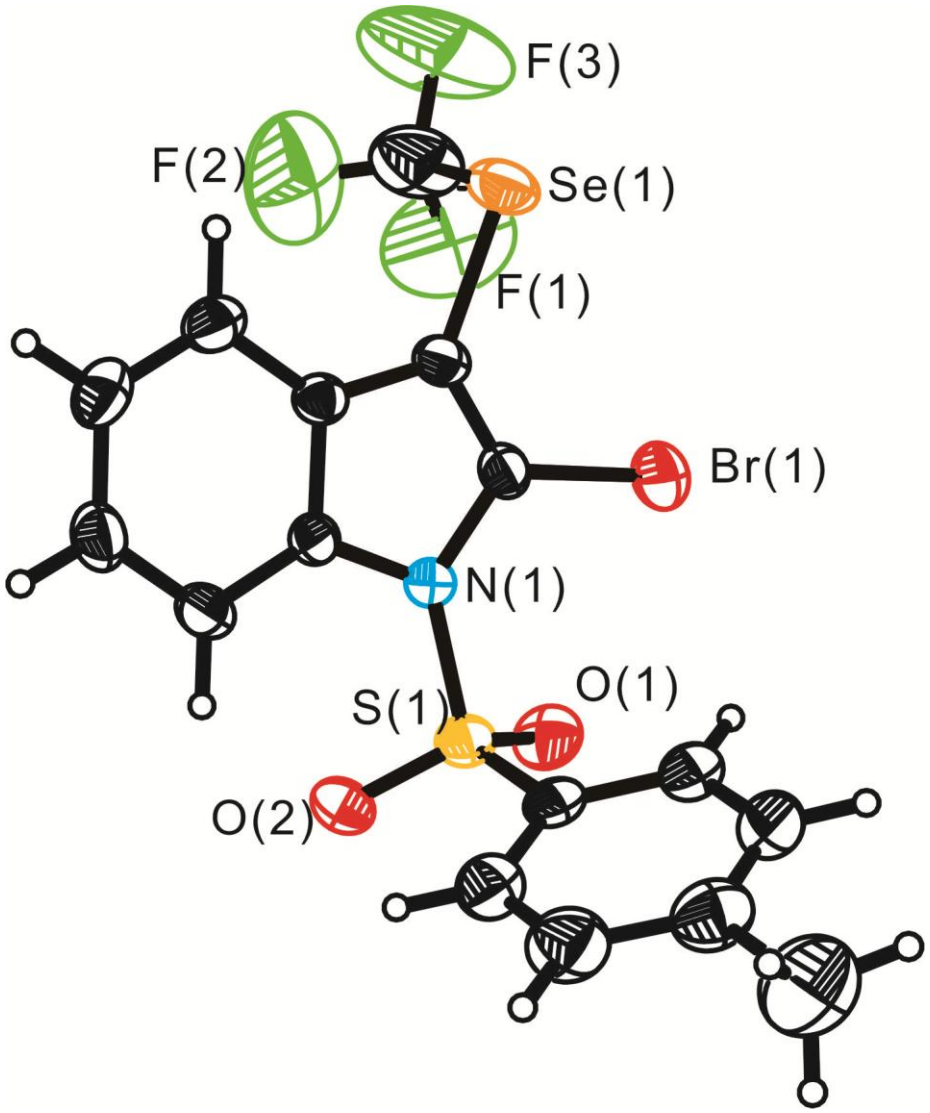


Figure S3. ORTEP diagram of 2a with thermal ellipsoids at the 40% probability level

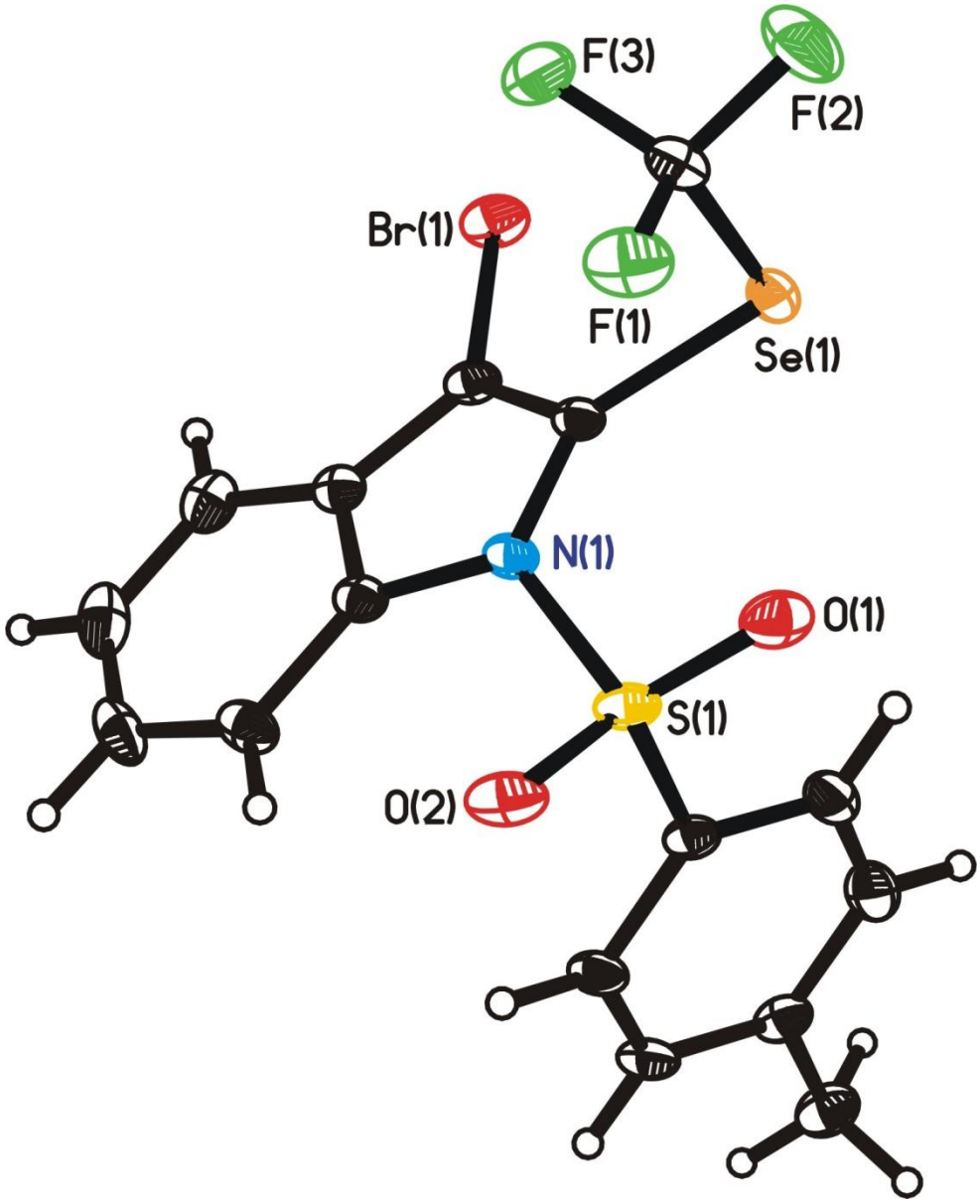


Figure S4. ORTEP diagram of 2a′ with thermal ellipsoids at the 40% probability level

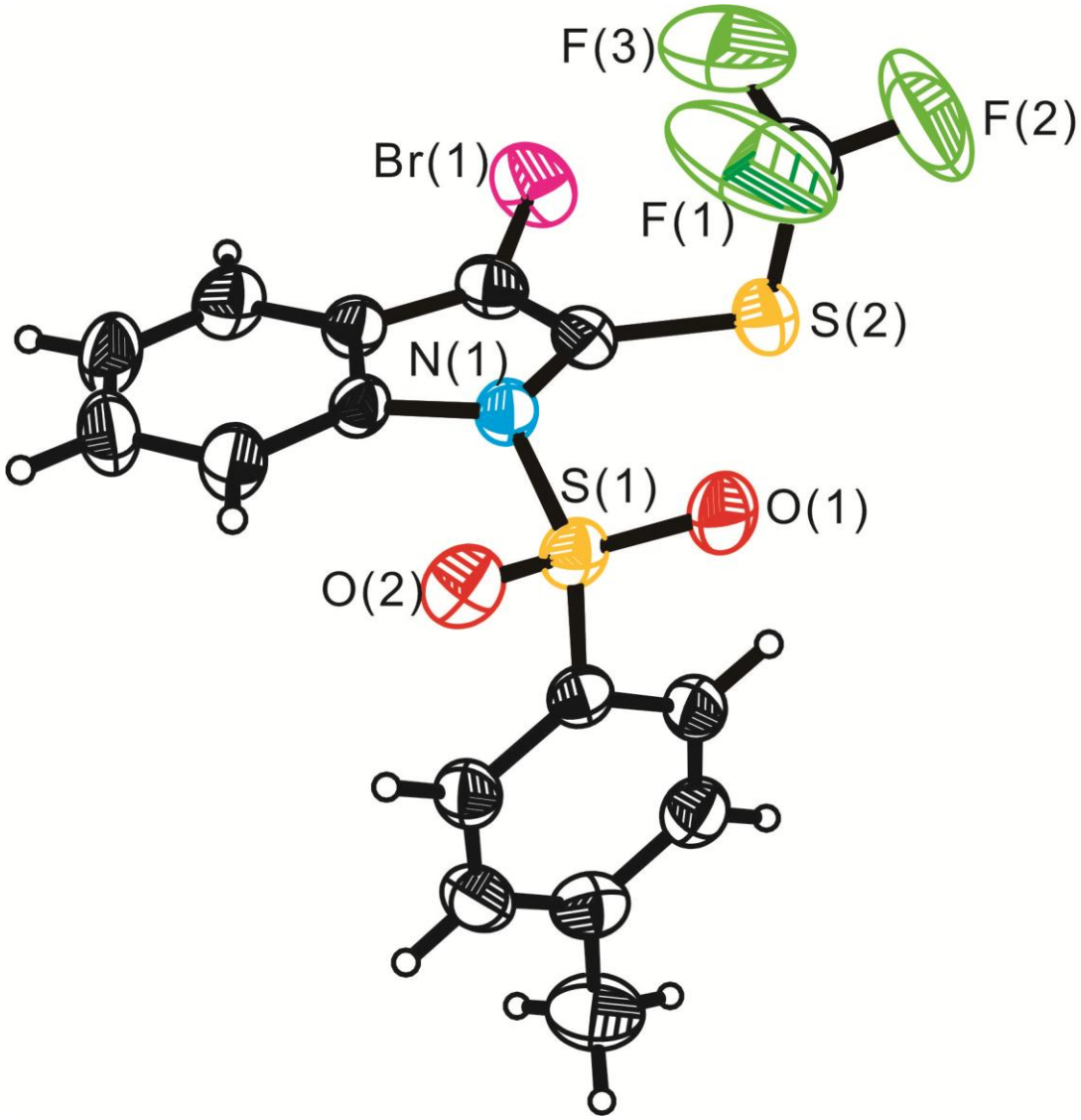


Figure S5. ORTEP diagram of 2a-S' with thermal ellipsoids at the 40% probability level

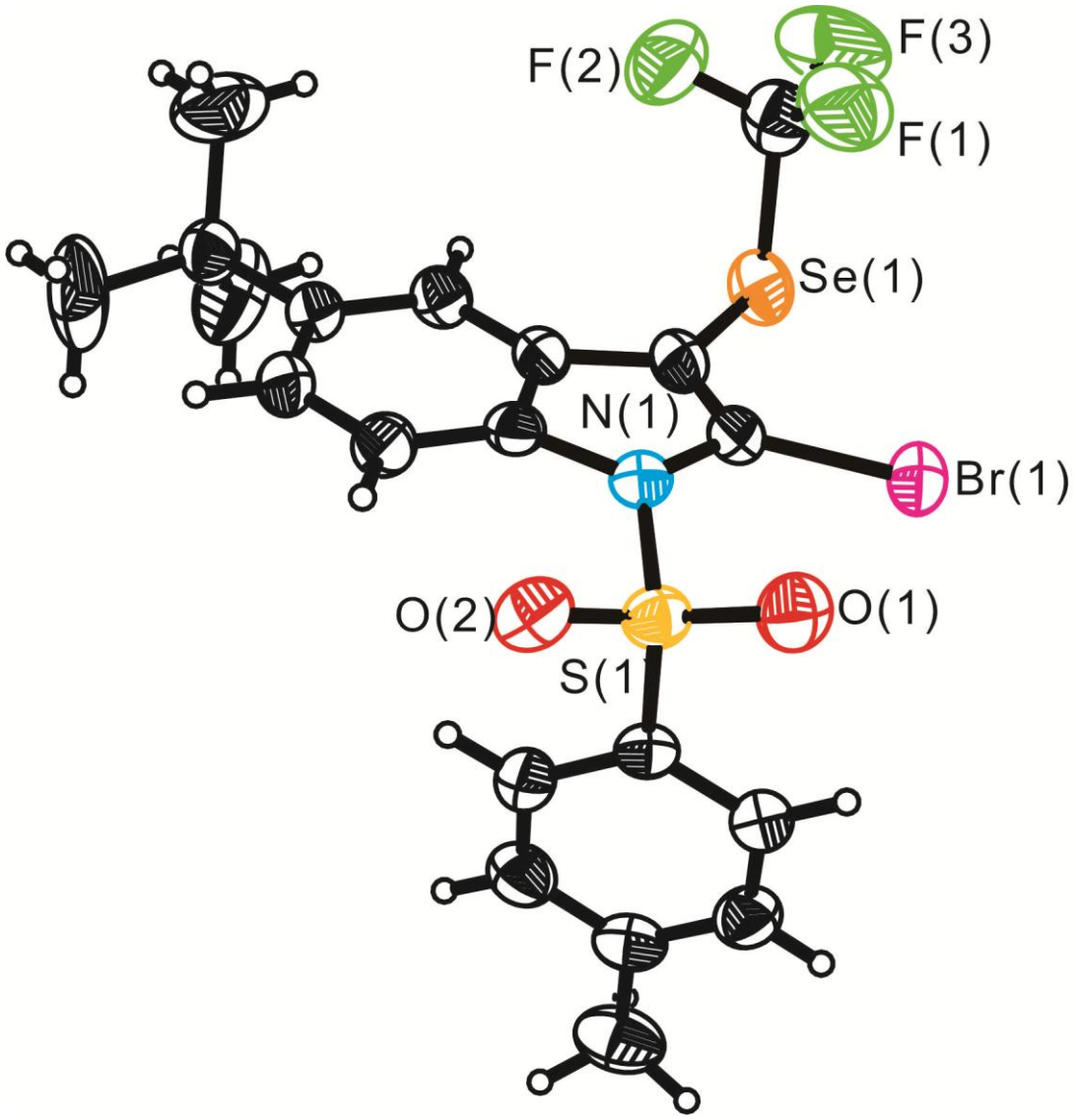


Figure S6. ORTEP diagram of 2f with thermal ellipsoids at the 40% probability level

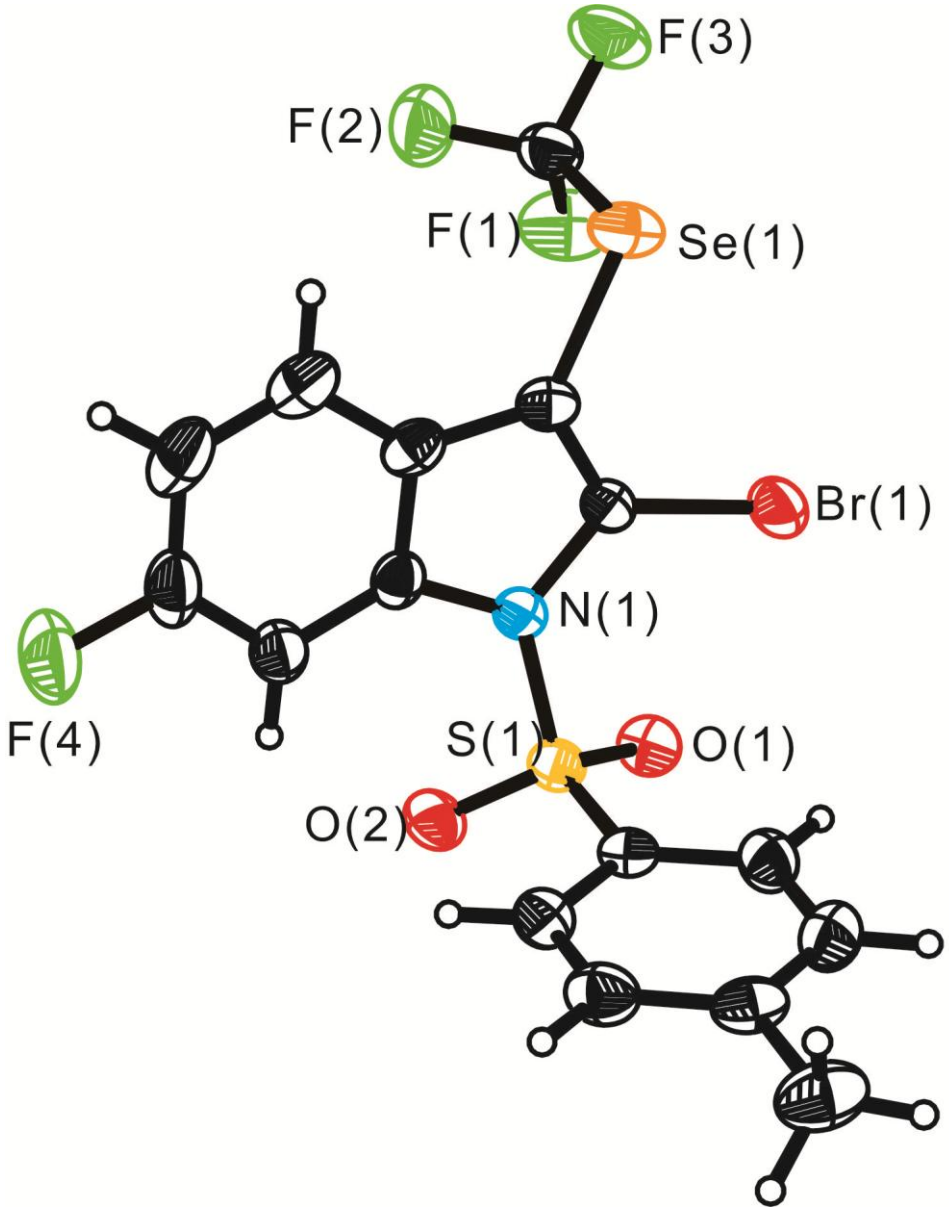


Figure S7. ORTEP diagram of 2l with thermal ellipsoids at the 40% probability level

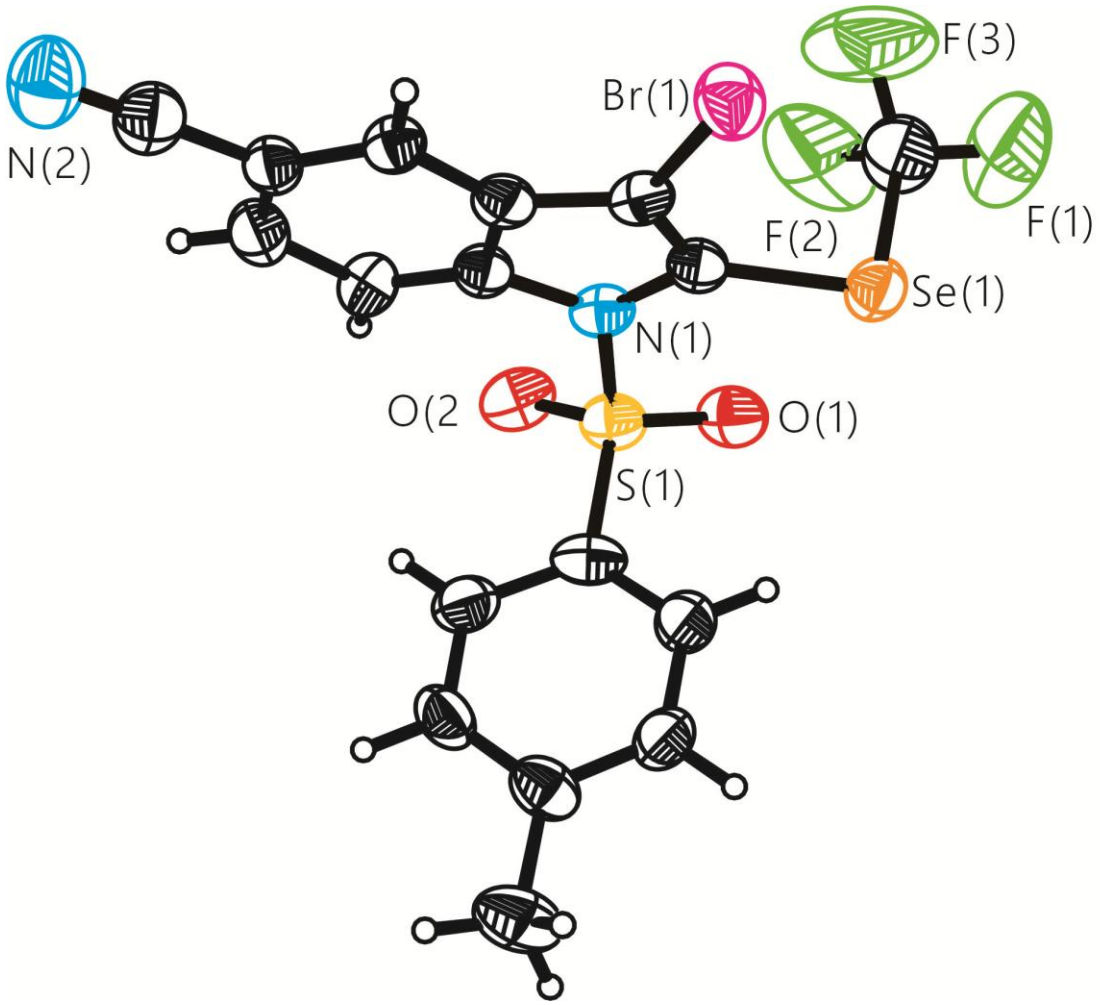


Figure S8. ORTEP diagram of 2q′ with thermal ellipsoids at the 40% probability level

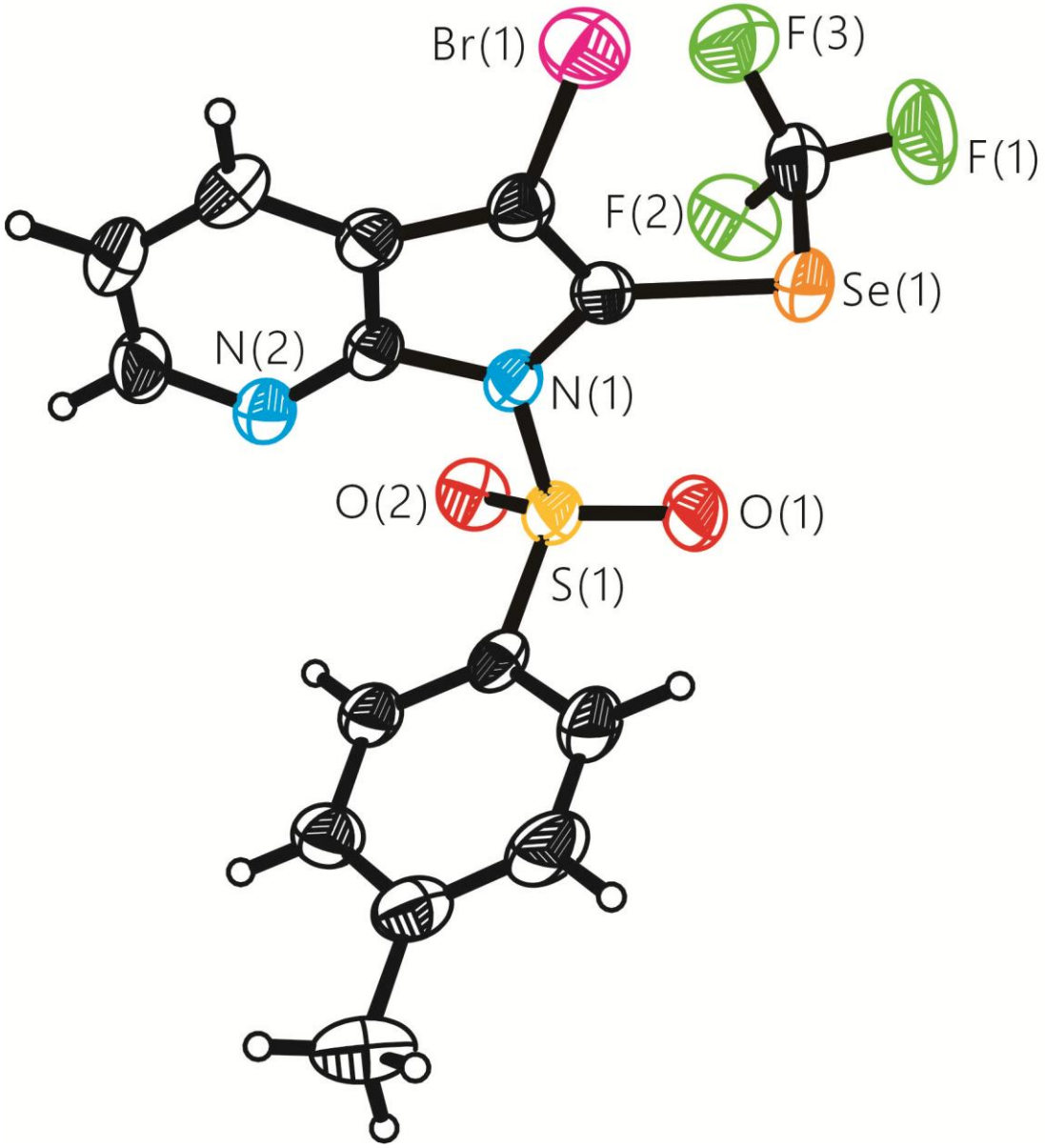


Figure S9. ORTEP diagram of 2r′ with thermal ellipsoids at the 40% probability level

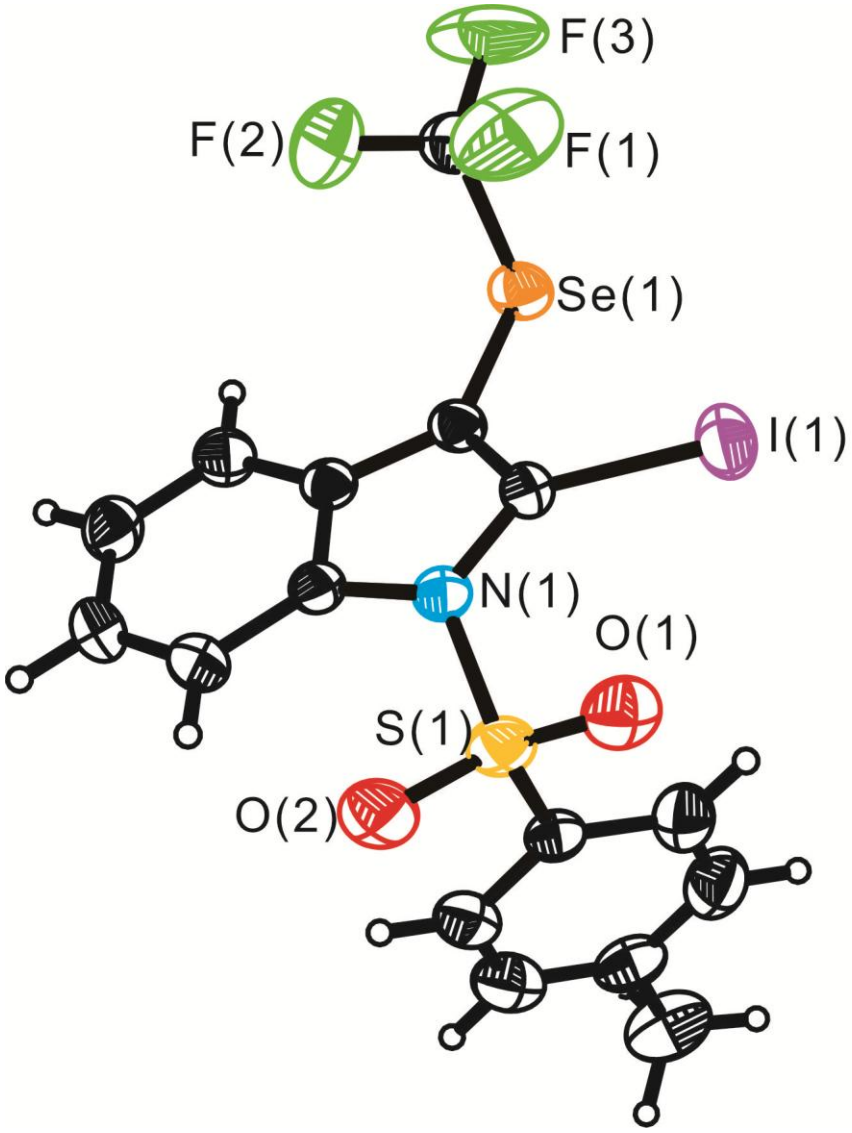


Figure S10. ORTEP diagram of 3a with thermal ellipsoids at the 40% probability level

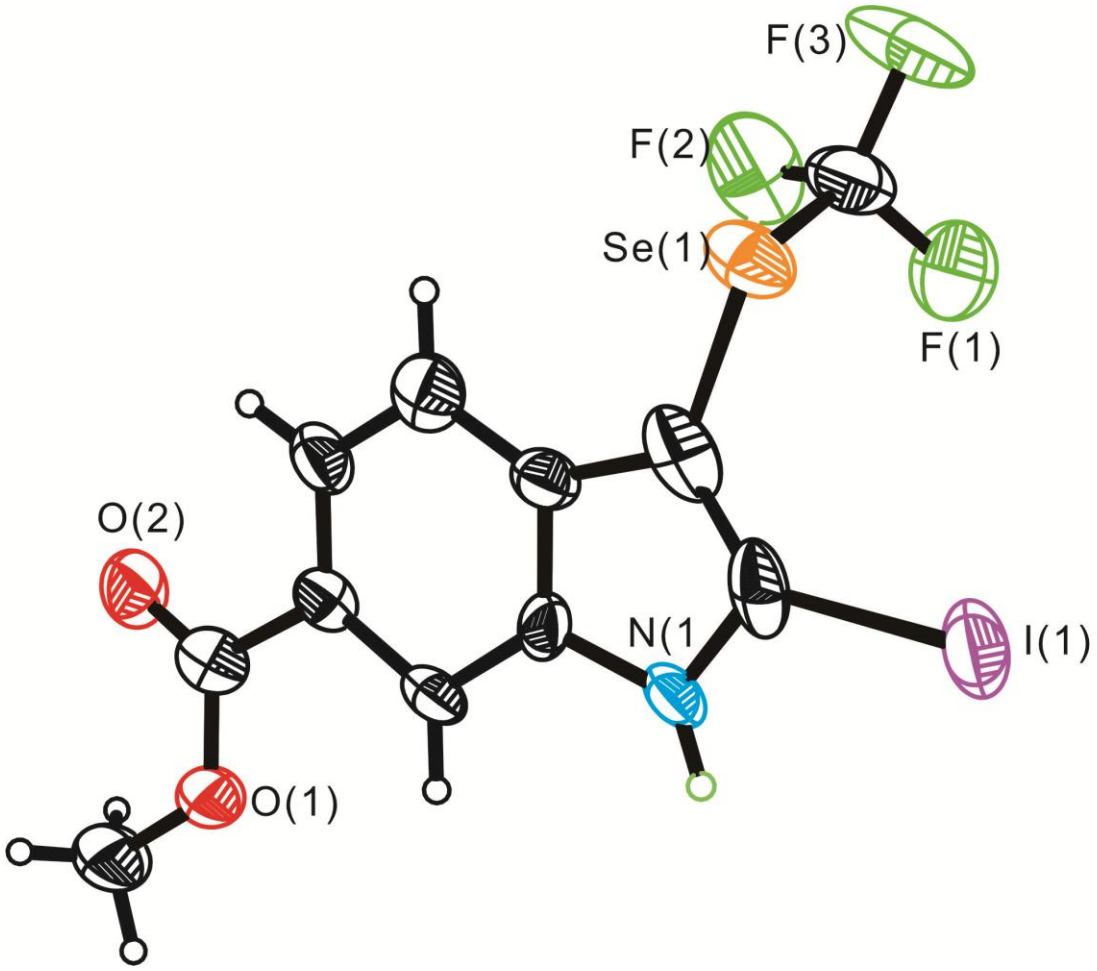


Figure S11. ORTEP diagram of 3i with thermal ellipsoids at the 40% probability level

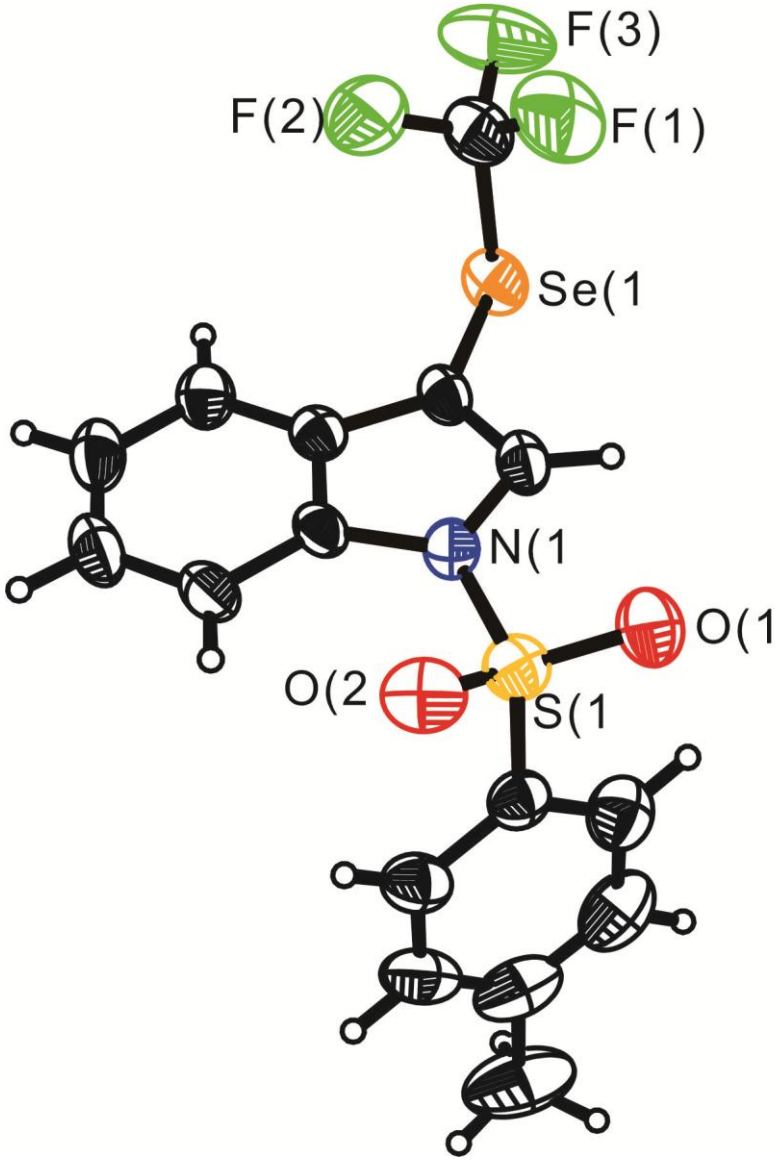


Figure S12. ORTEP diagram of 4a with thermal ellipsoids at the 40% probability level

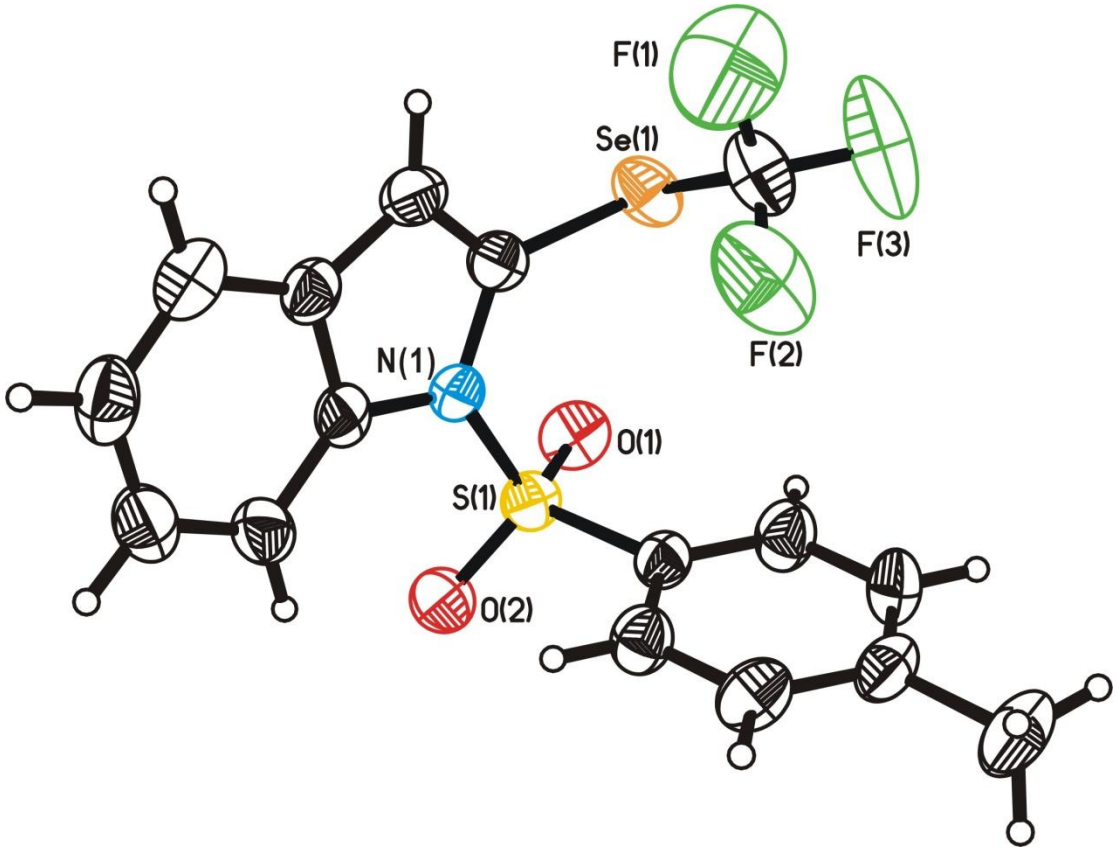


Figure S13. ORTEP diagram of 4a′ with thermal ellipsoids at the 40% probability level

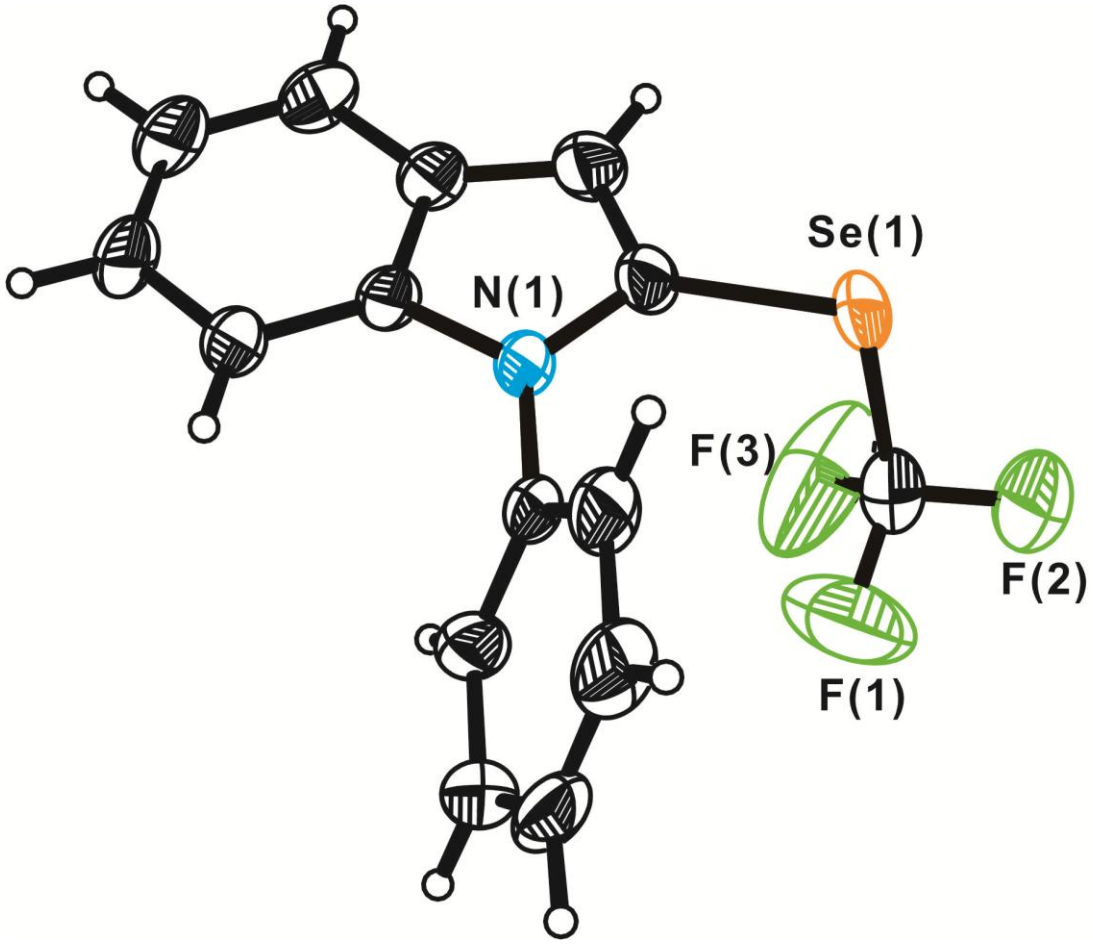


Figure S14. ORTEP diagram of 4a-Ph′ with thermal ellipsoids at the 40% probability level

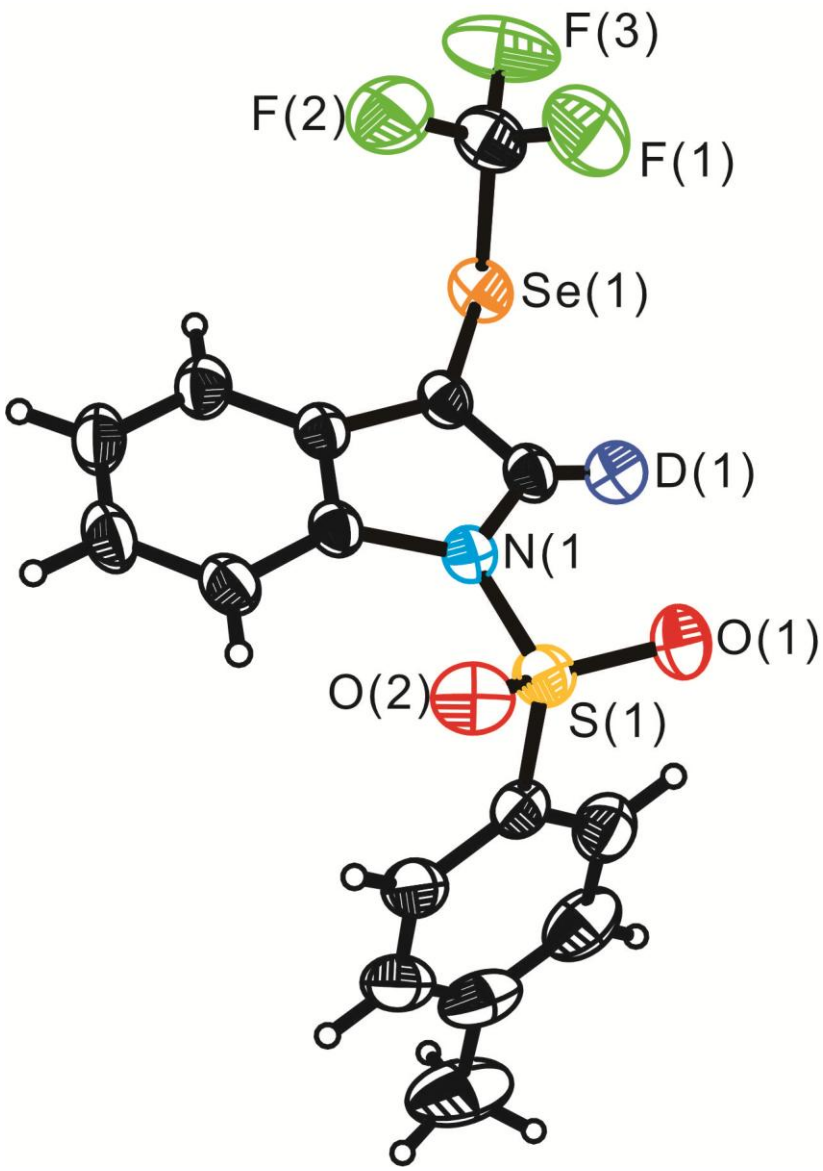


Figure S15. ORTEP diagram of 4b with thermal ellipsoids at the 40% probability level

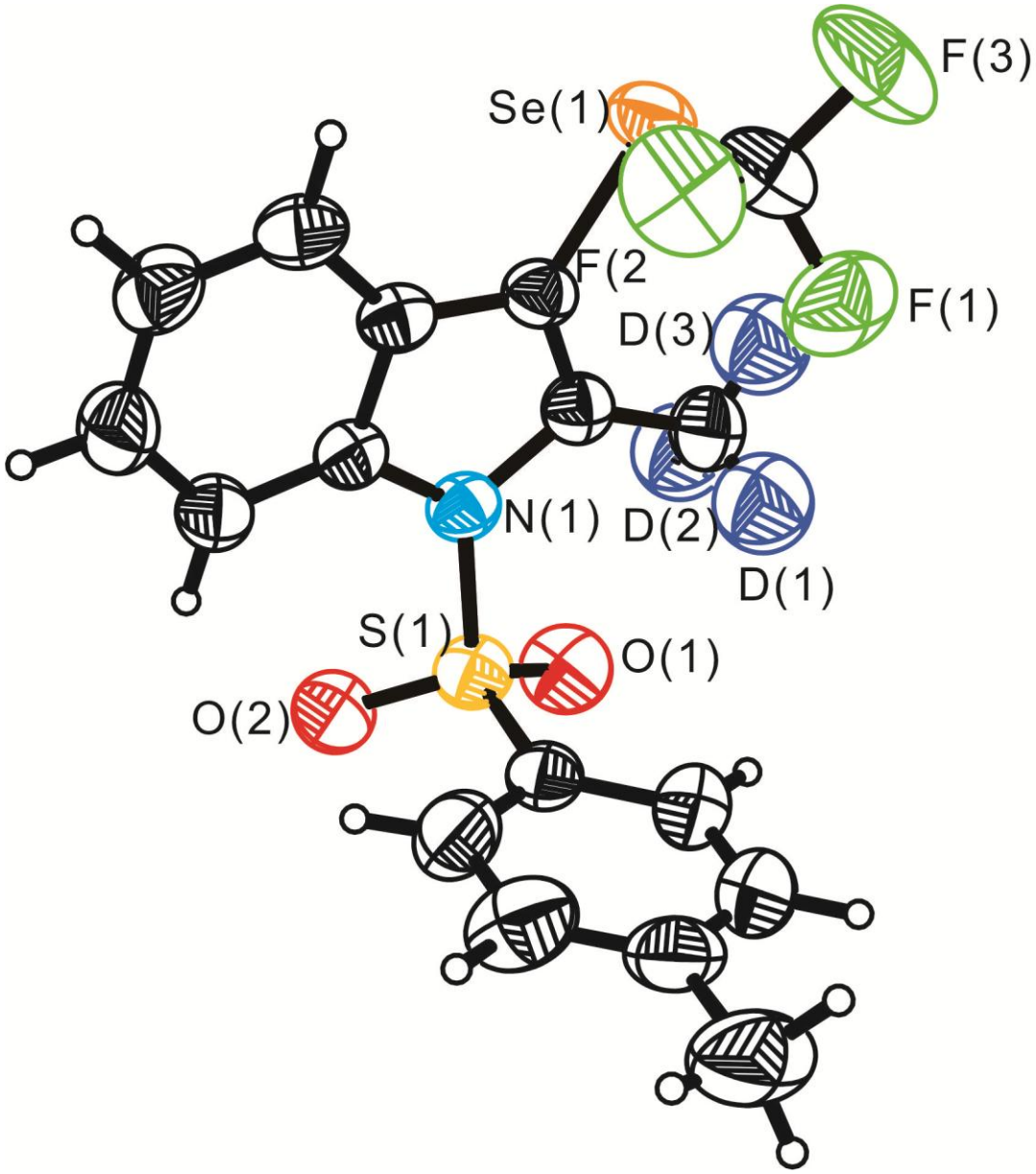


Figure S16. ORTEP diagram of 4c with thermal ellipsoids at the 40% probability level

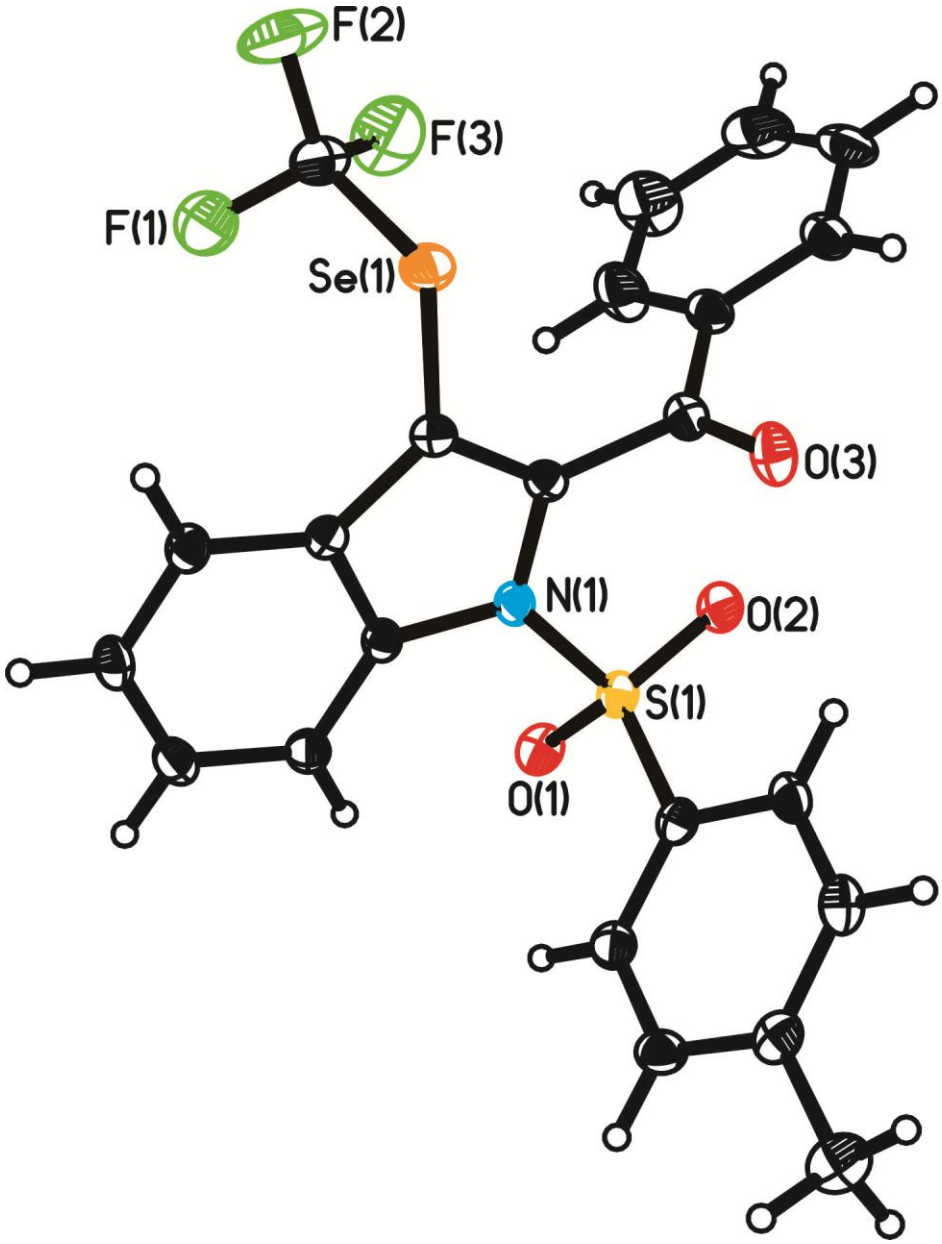


Figure S17. ORTEP diagram of 4d with thermal ellipsoids at the 40% probability level

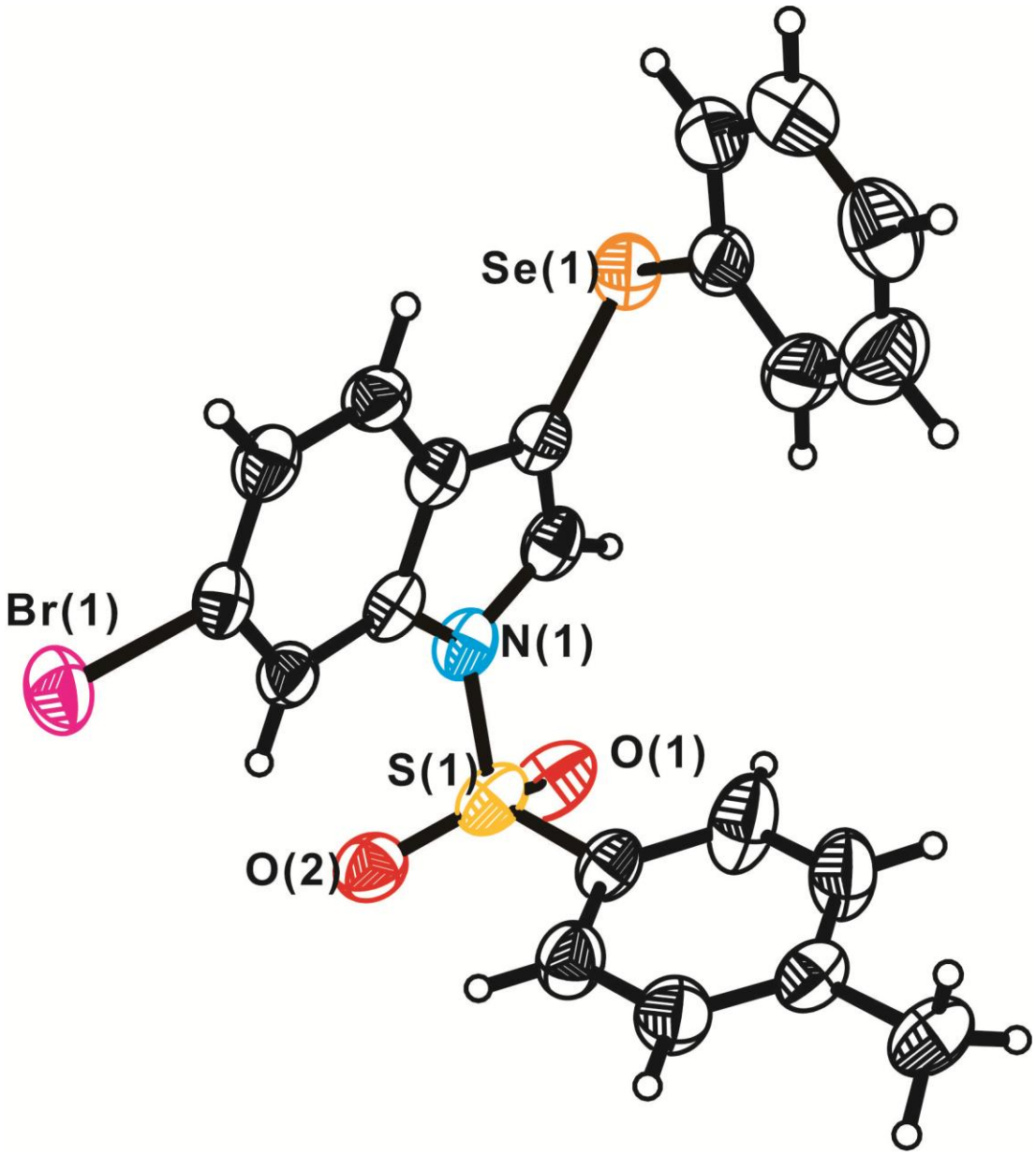


Figure S18. ORTEP diagram of 4p-Ph with thermal ellipsoids at the 40% probability level

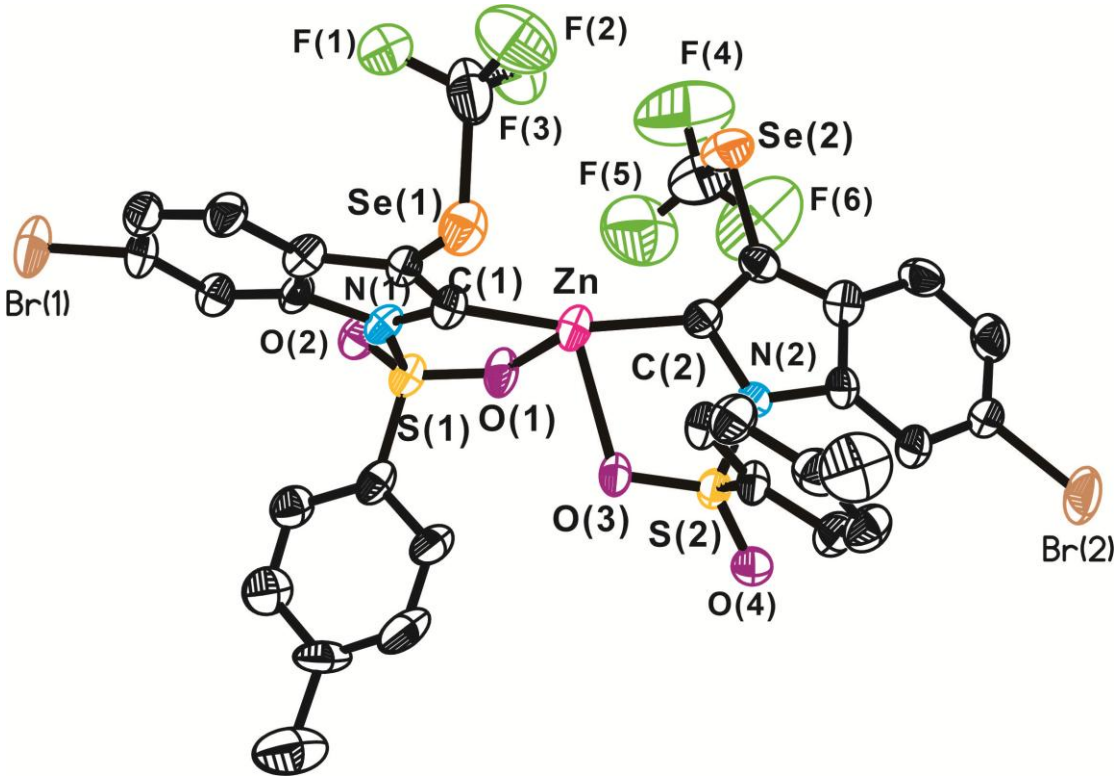


Figure S19. ORTEP diagram of 5 with thermal ellipsoids at the 40% probability level

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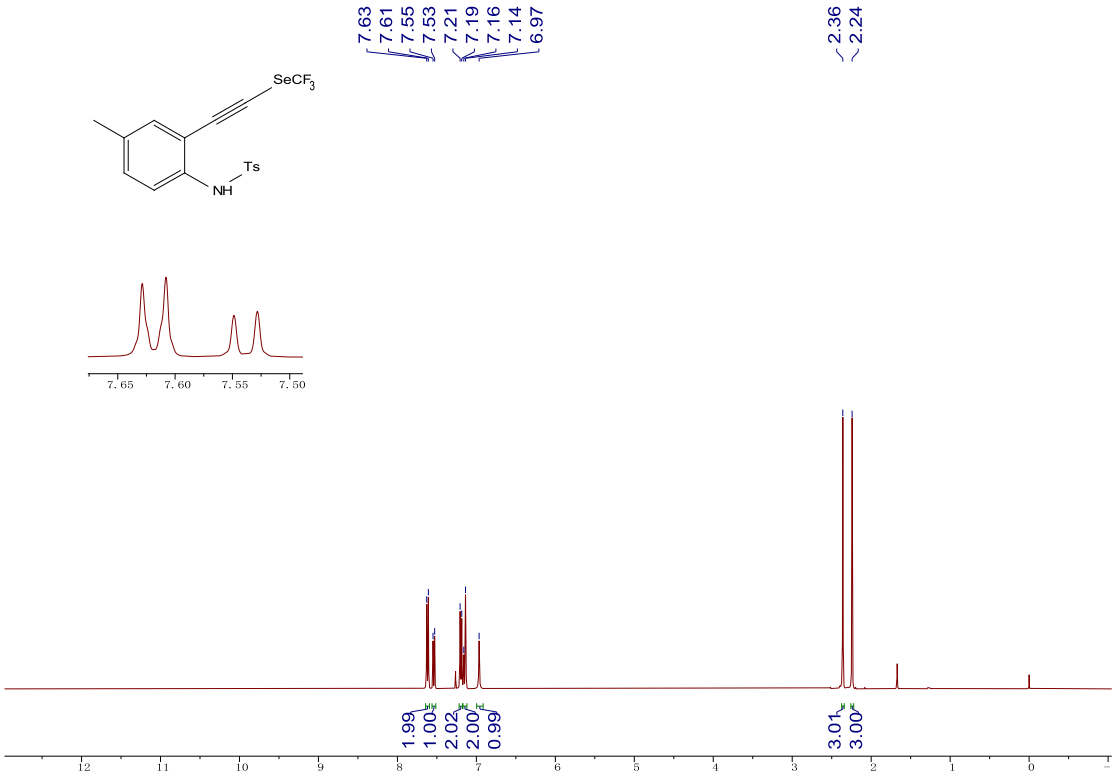
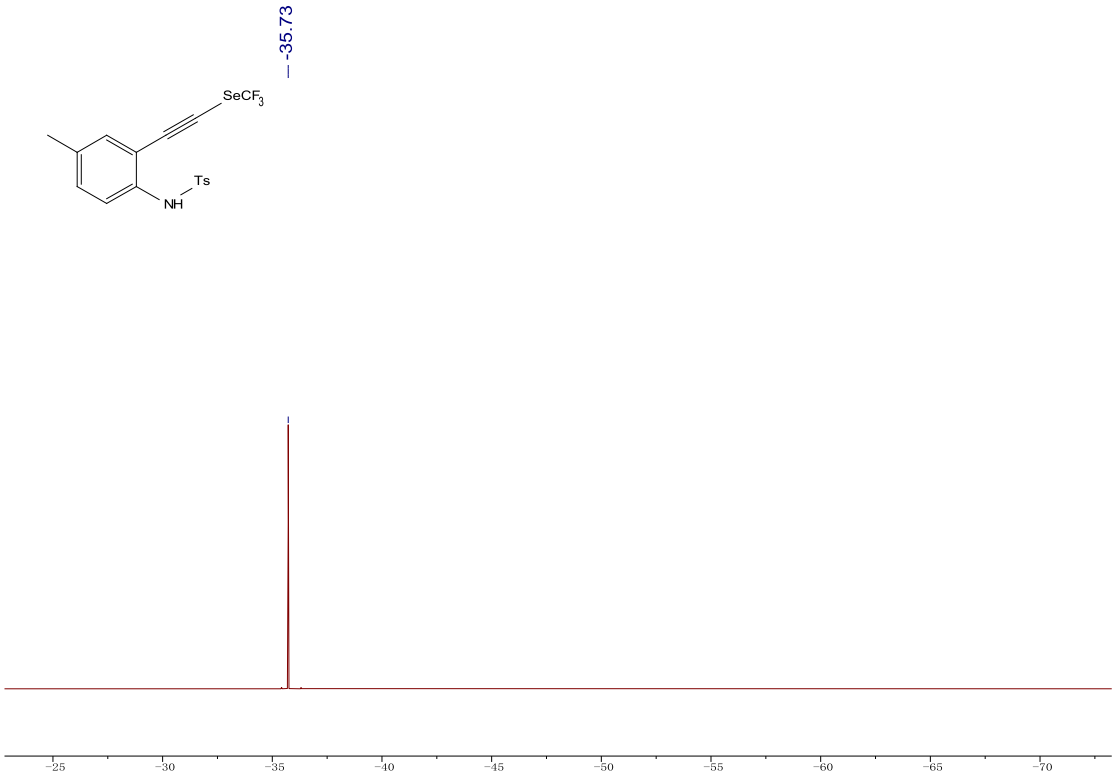
Copies of ^{1}H NMR, ^{19}FNMR and ^{13}C NMR spectra

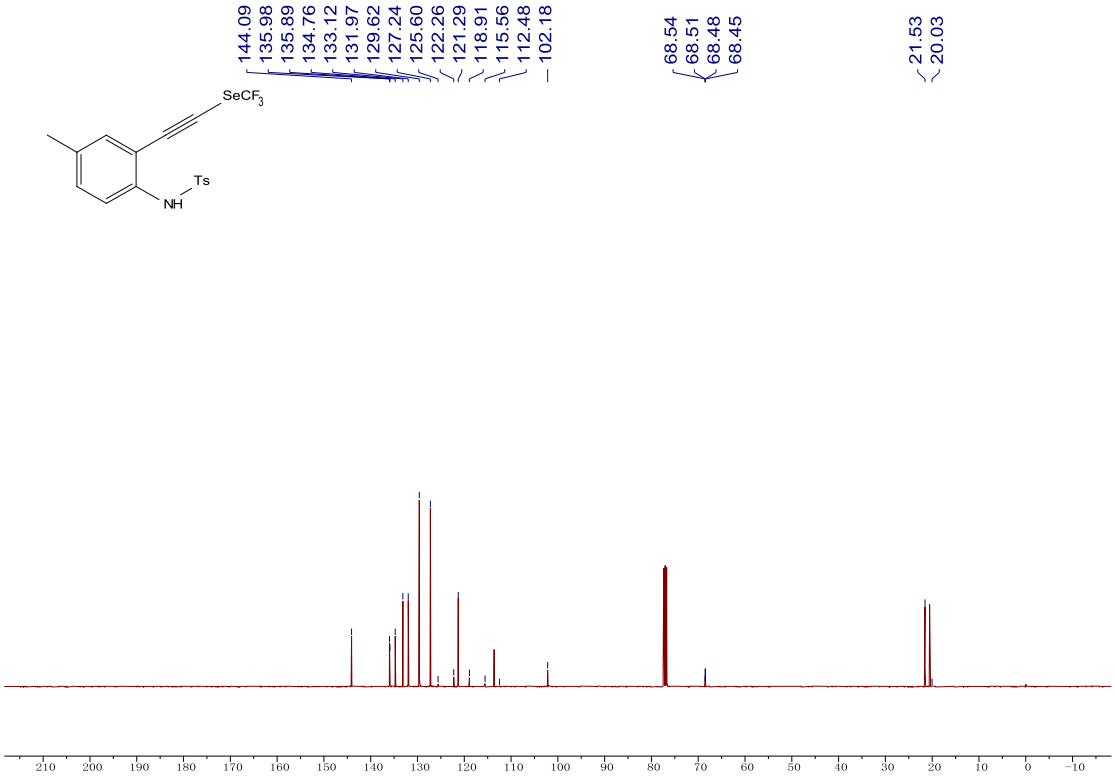
^{1}H NMR spectra of **1b** (400 MHz, $CDCl_3$)



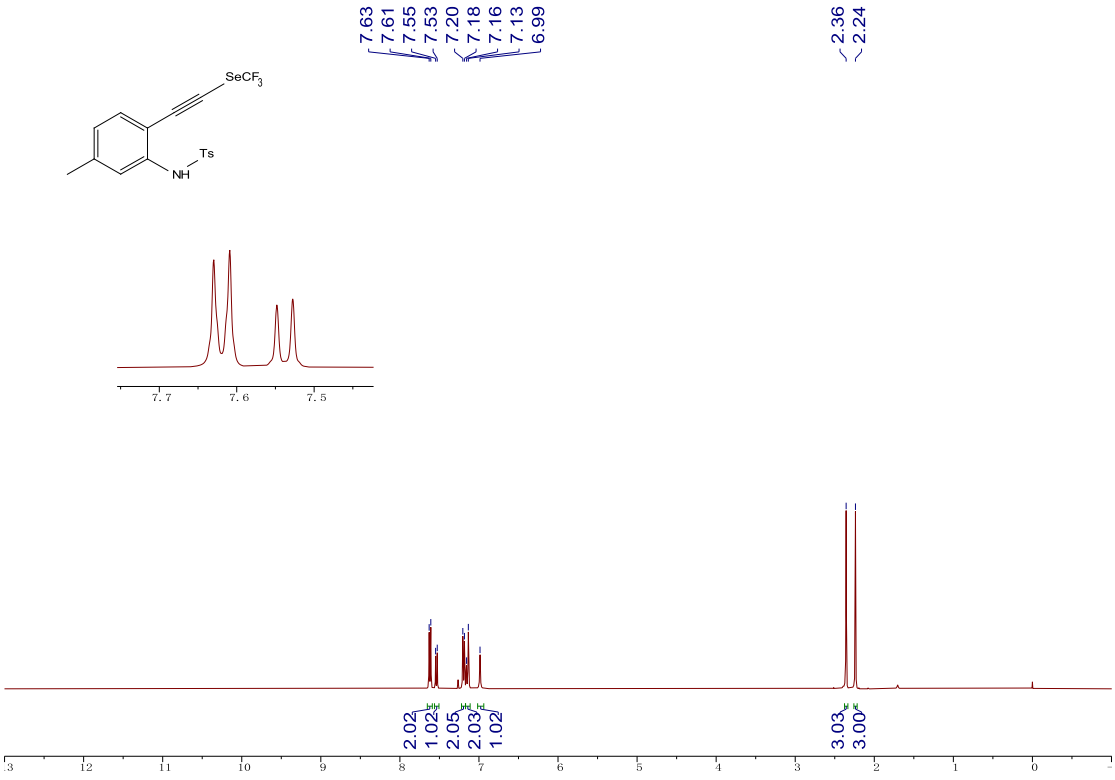
^{19}F NMR spectra of **1b** (376 MHz, $CDCl_3$)



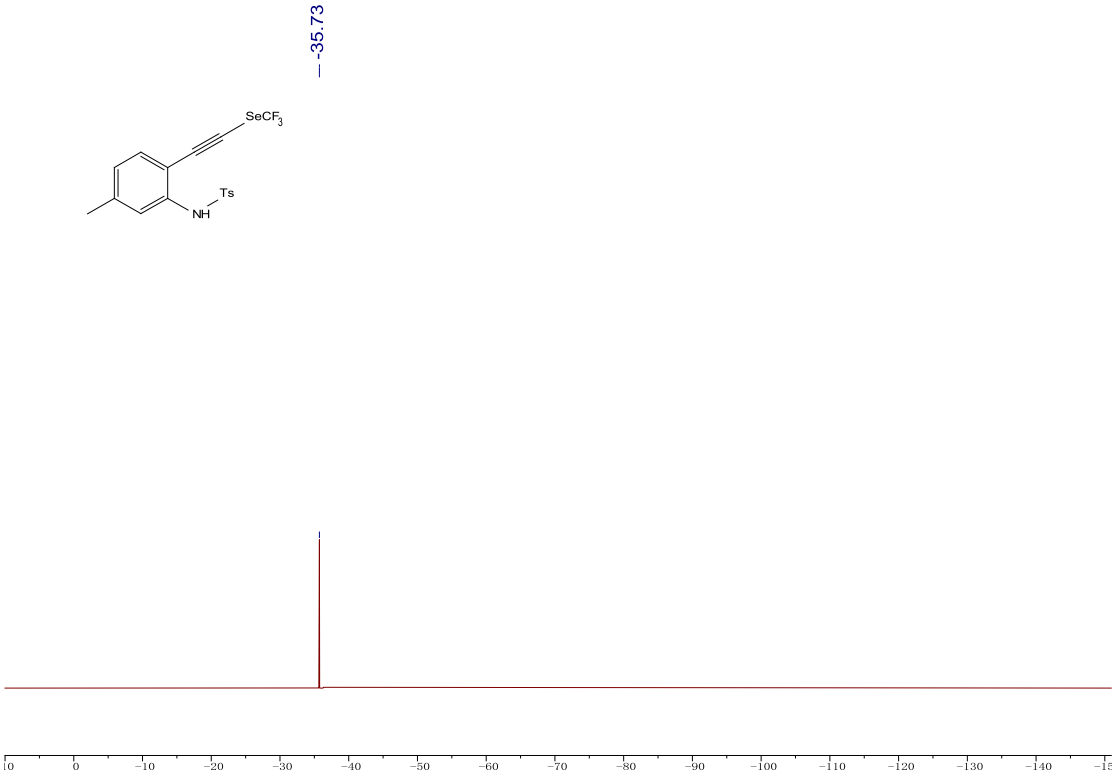
$^{13}C\{^{1}H\}$ NMR spectra of **1b** (101 MHz, $CDCl_3$)



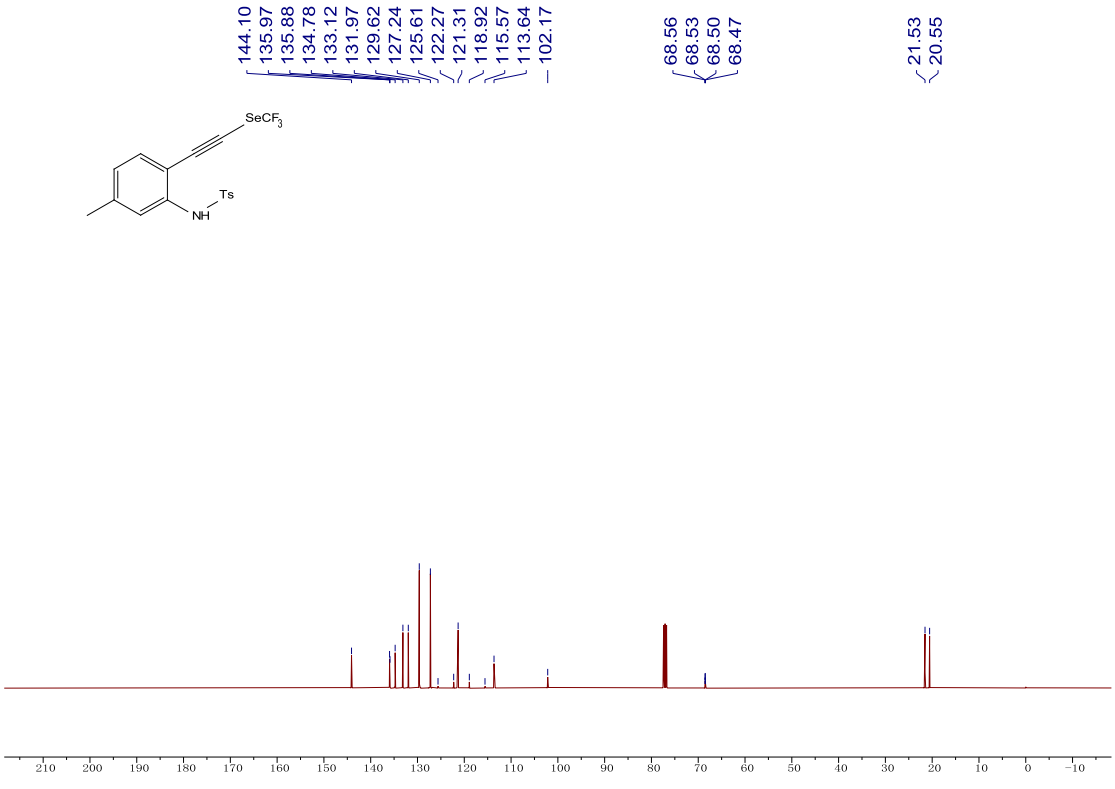
^{1}H NMR spectra of **1c** (400 MHz, $CDCl_3$)



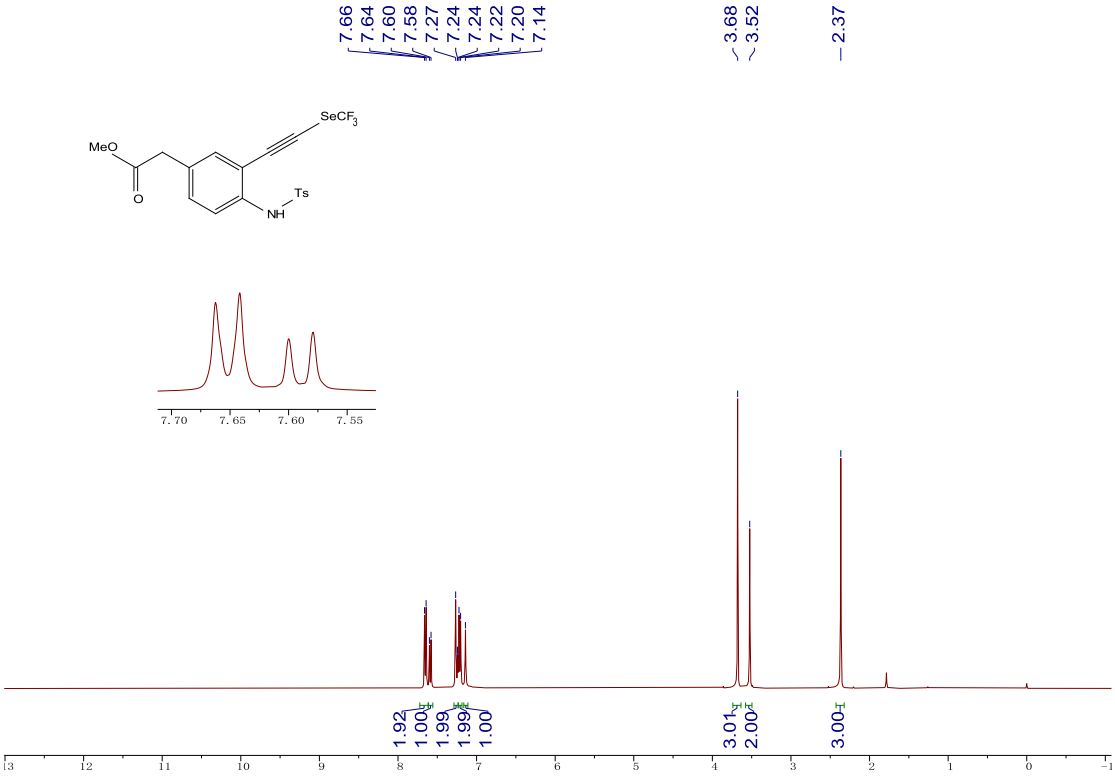
^{19}F NMR spectra of **1c** (376 MHz, $CDCl_3$)



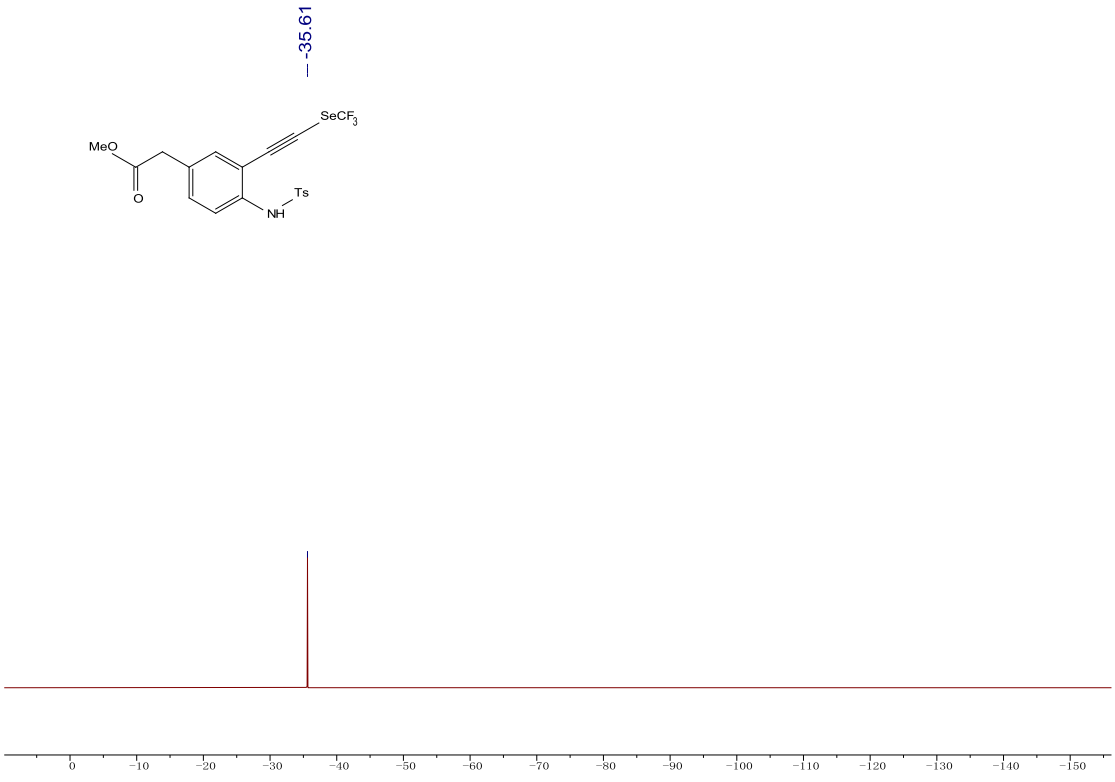
$^{13}C\{^{1}H\}$ NMR spectra of **1c** (101 MHz, $CDCl_3$)



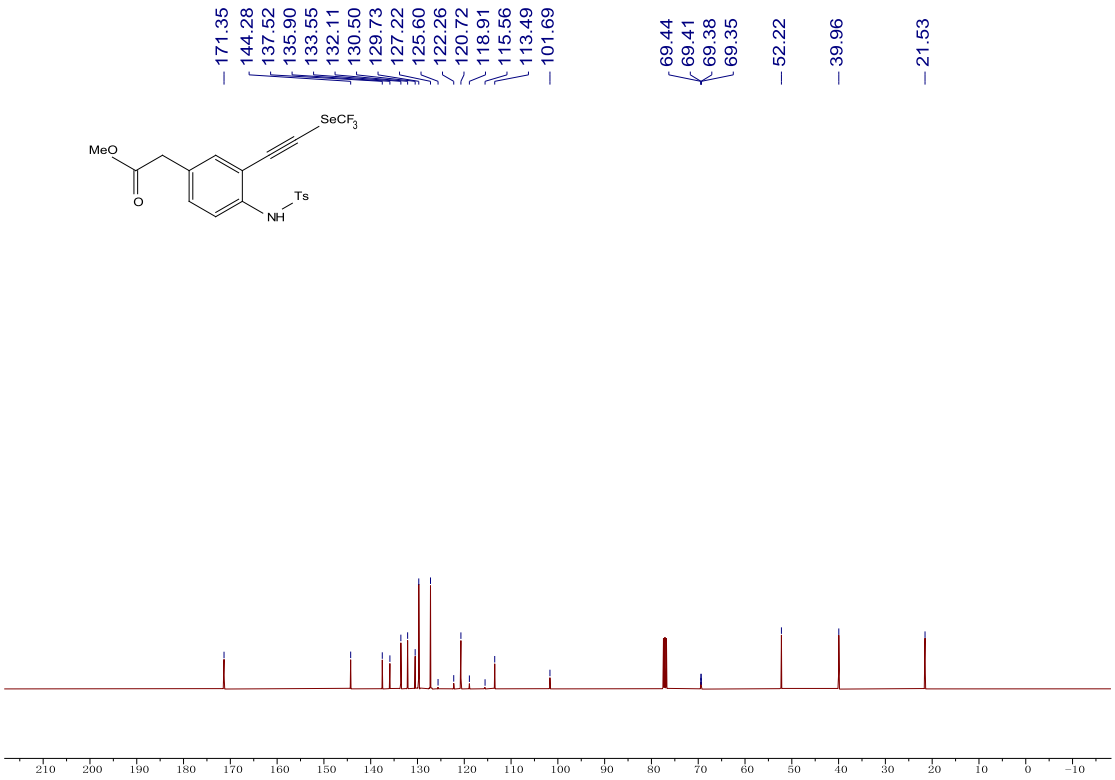
^{1}H NMR spectra of **1d** (400 MHz, $CDCl_3$)



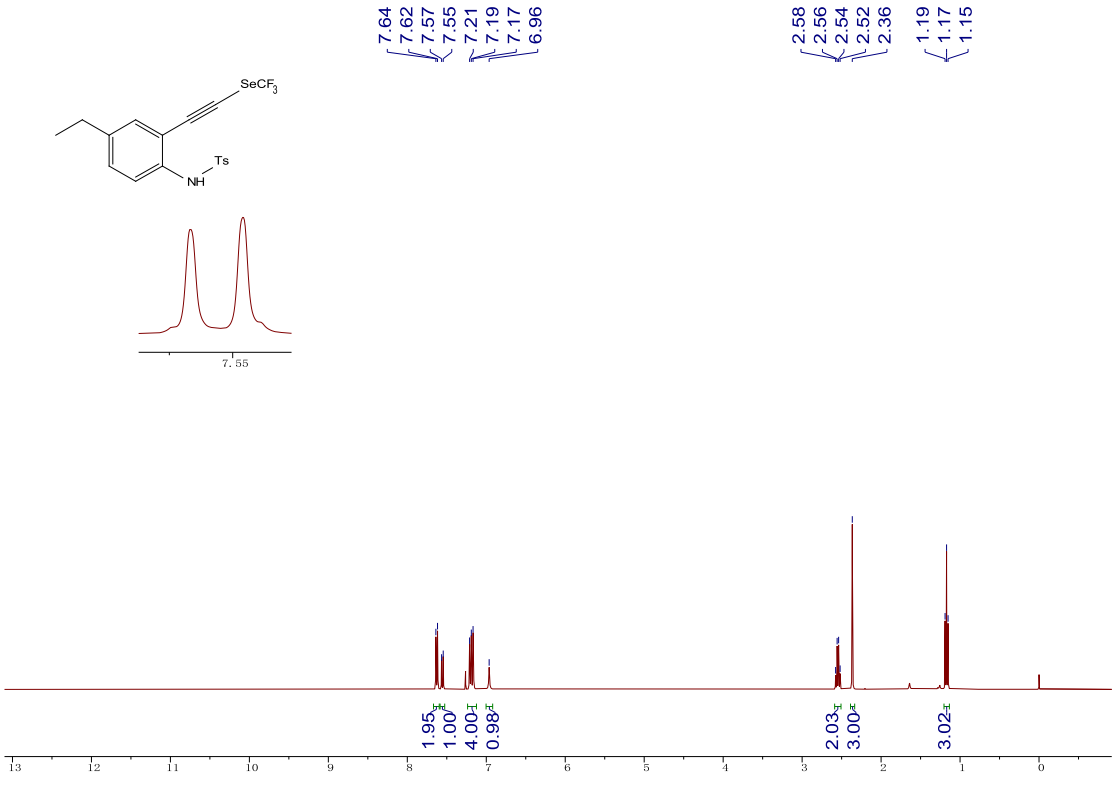
^{19}F NMR spectra of **1d** (376 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of **1d** (101 MHz, $CDCl_3$)



^{1}H NMR spectra of **1e** (400 MHz, $CDCl_3$)



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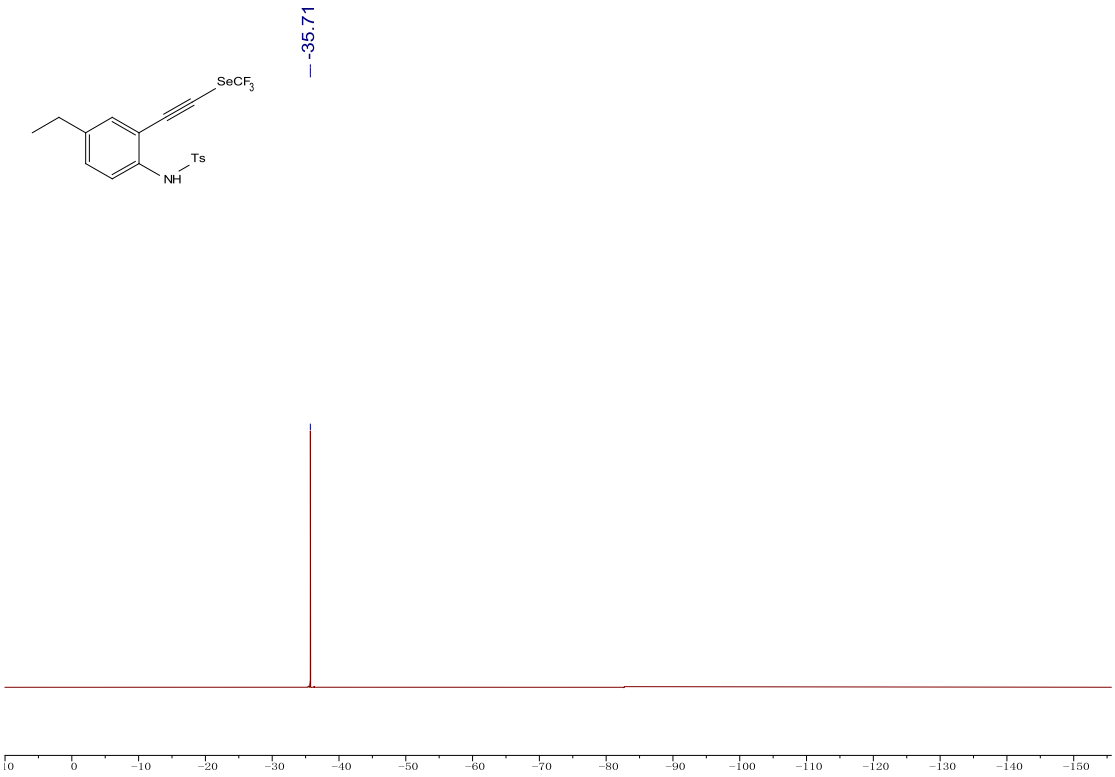
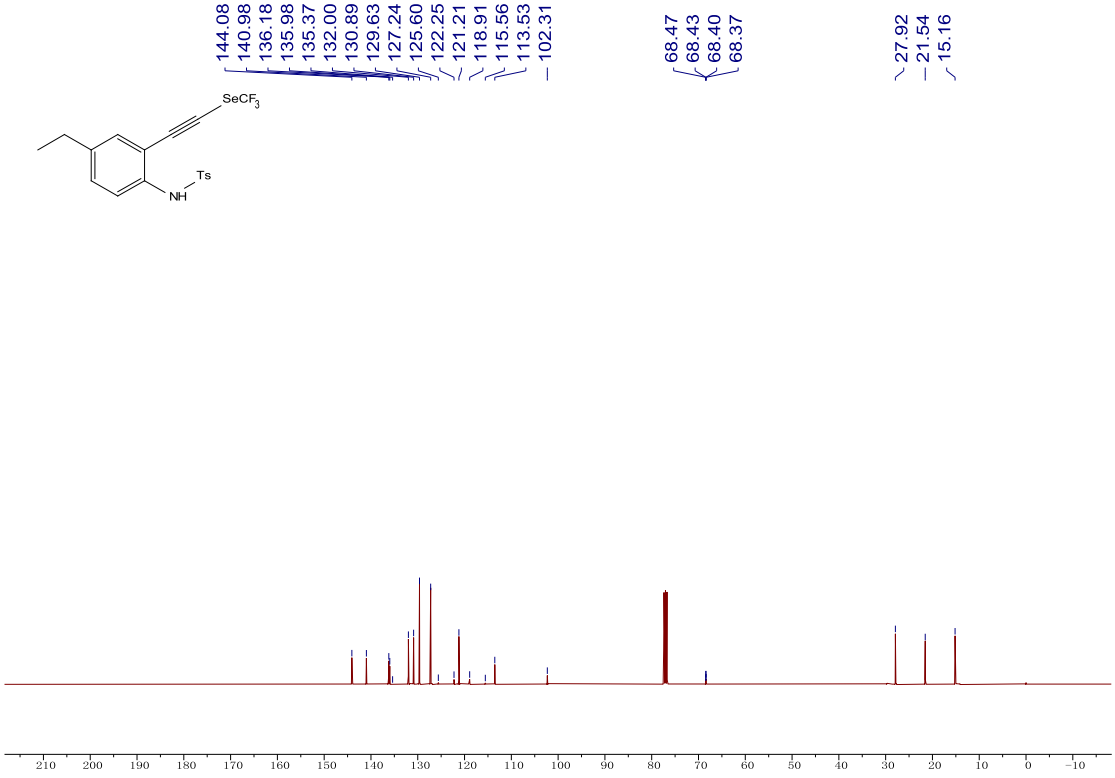


$^{13}C\{^1H\}$ NMR spectra of **1e** (101 MHz, $CDCl_3$)



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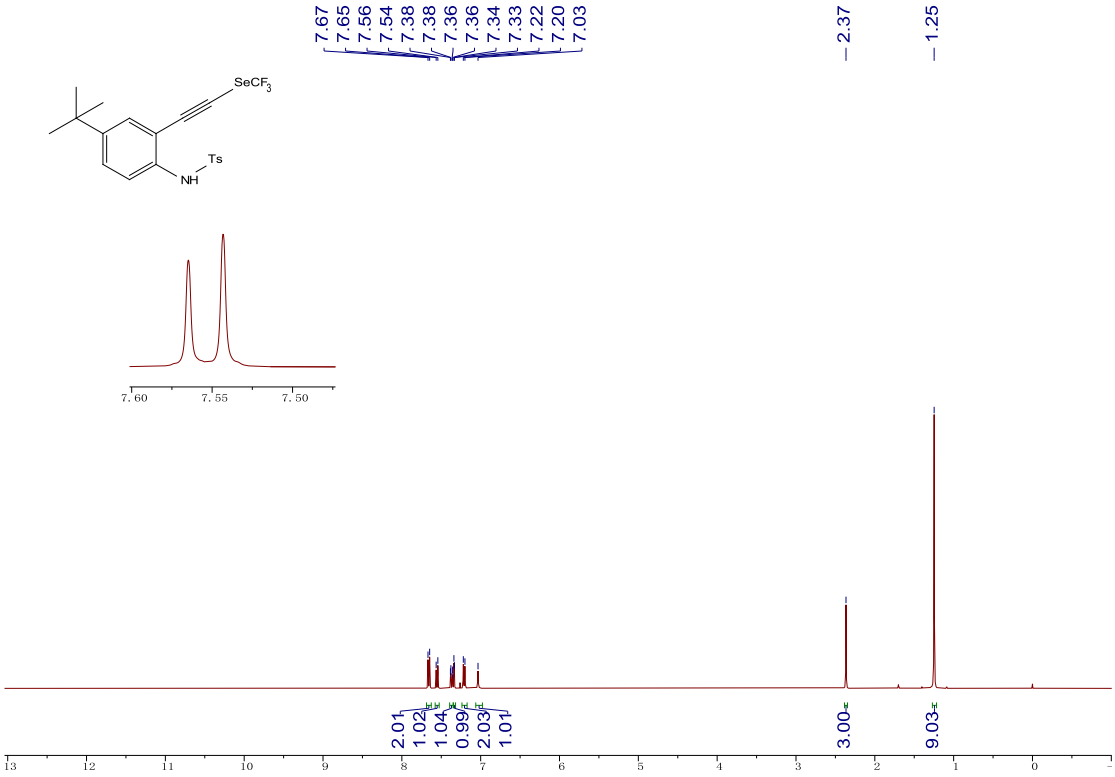

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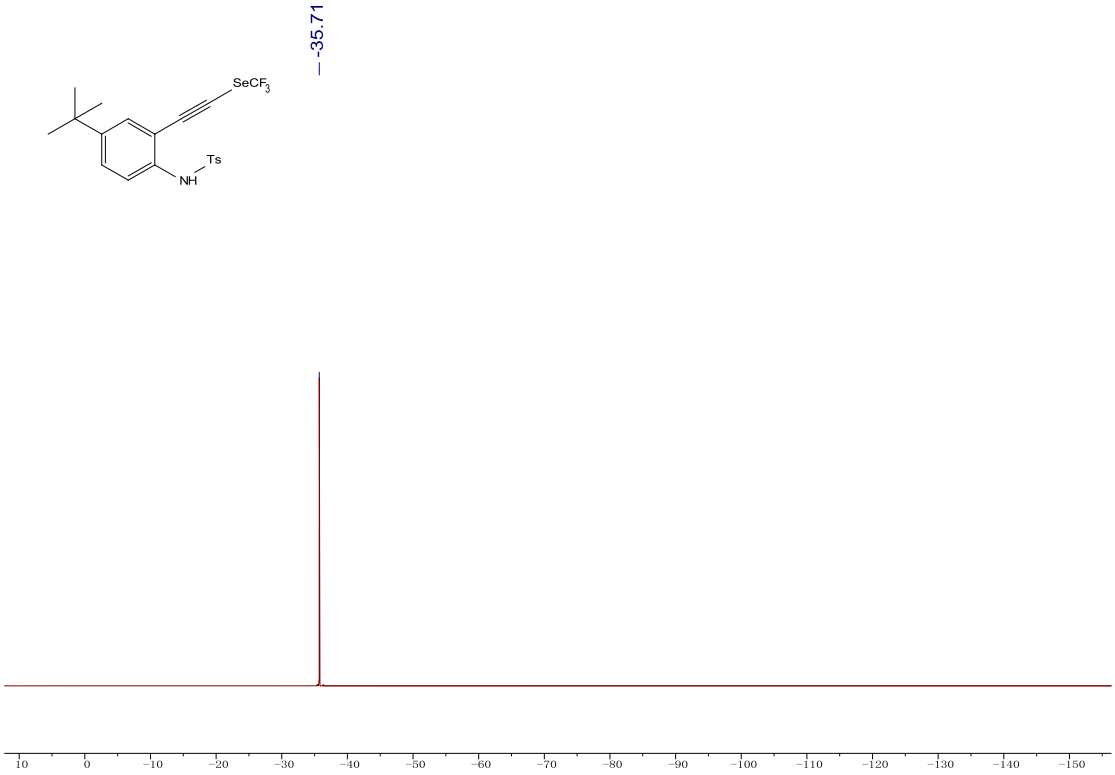

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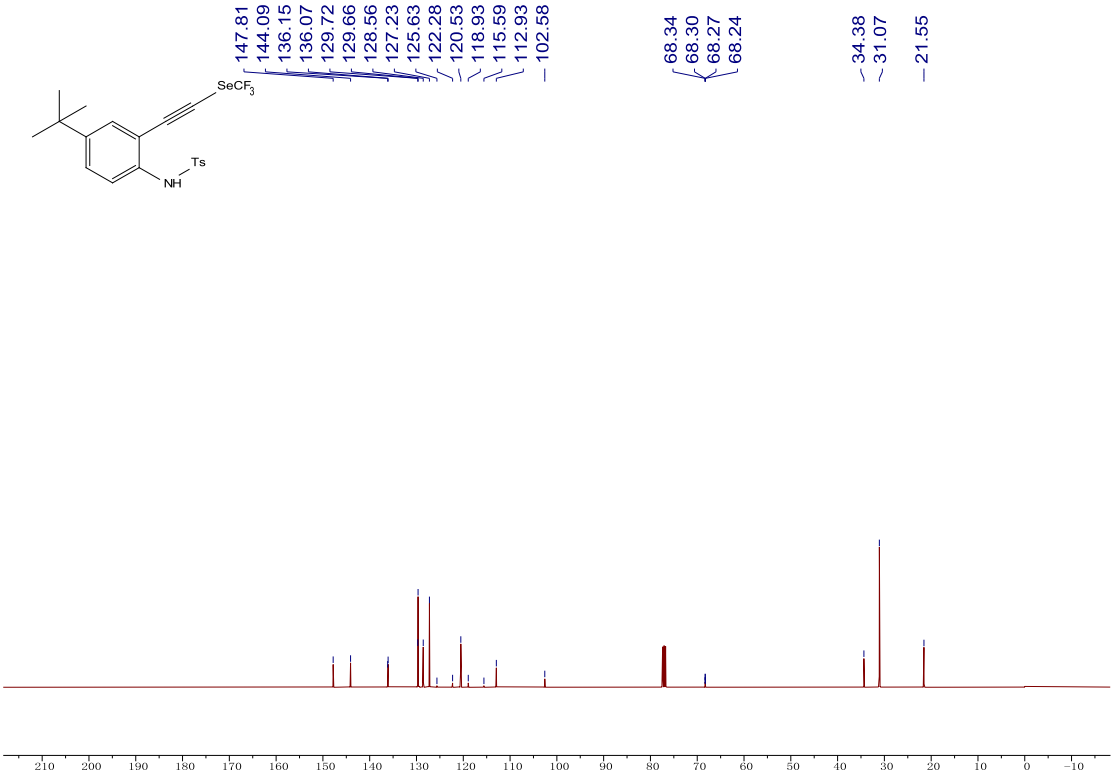

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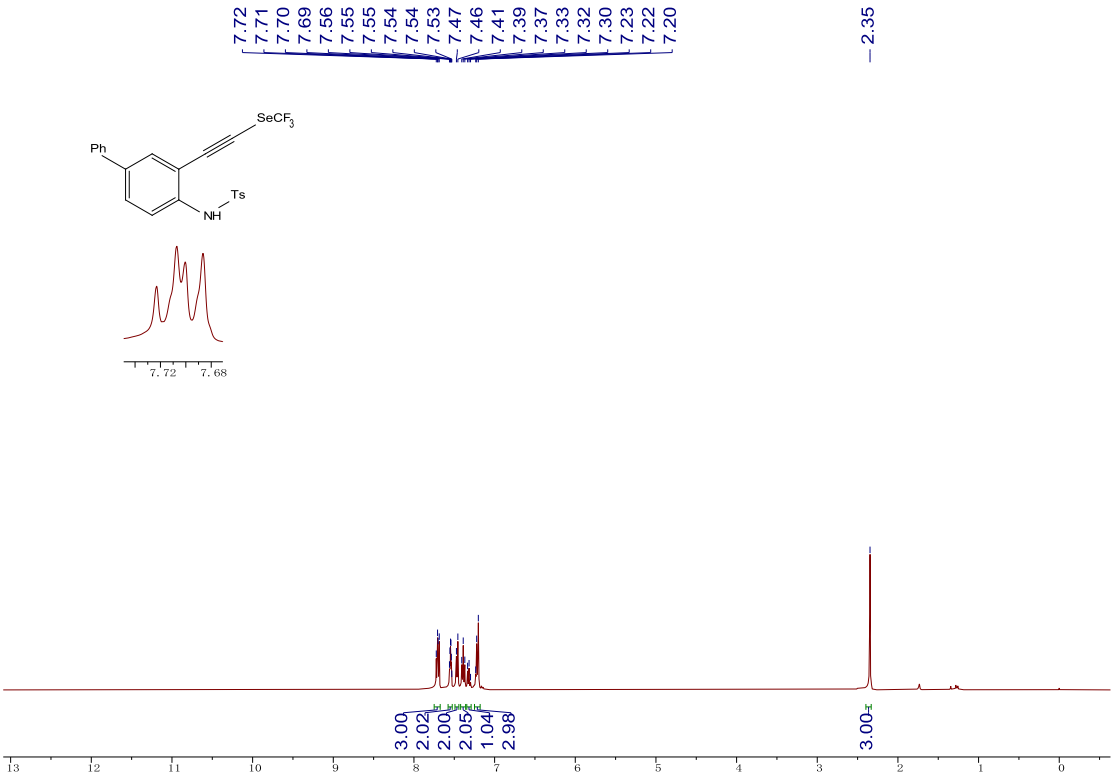
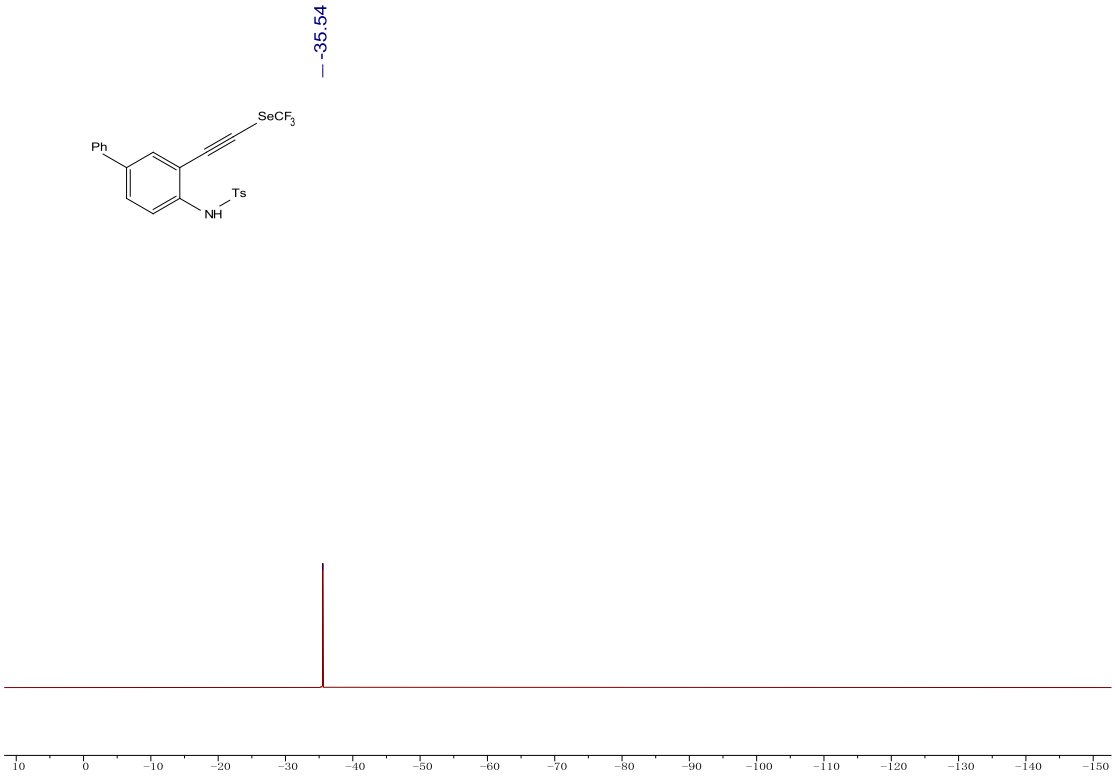


^{19}F NMR spectra of **1g** (376 MHz, $CDCl_3$)



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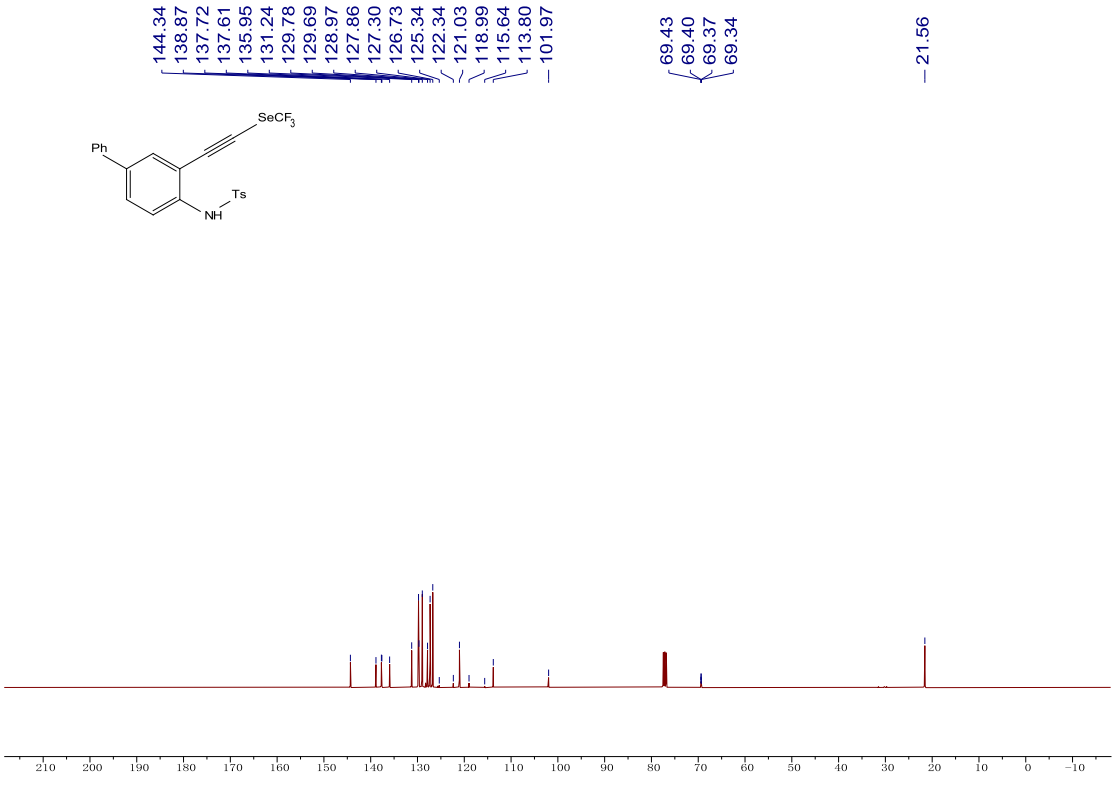

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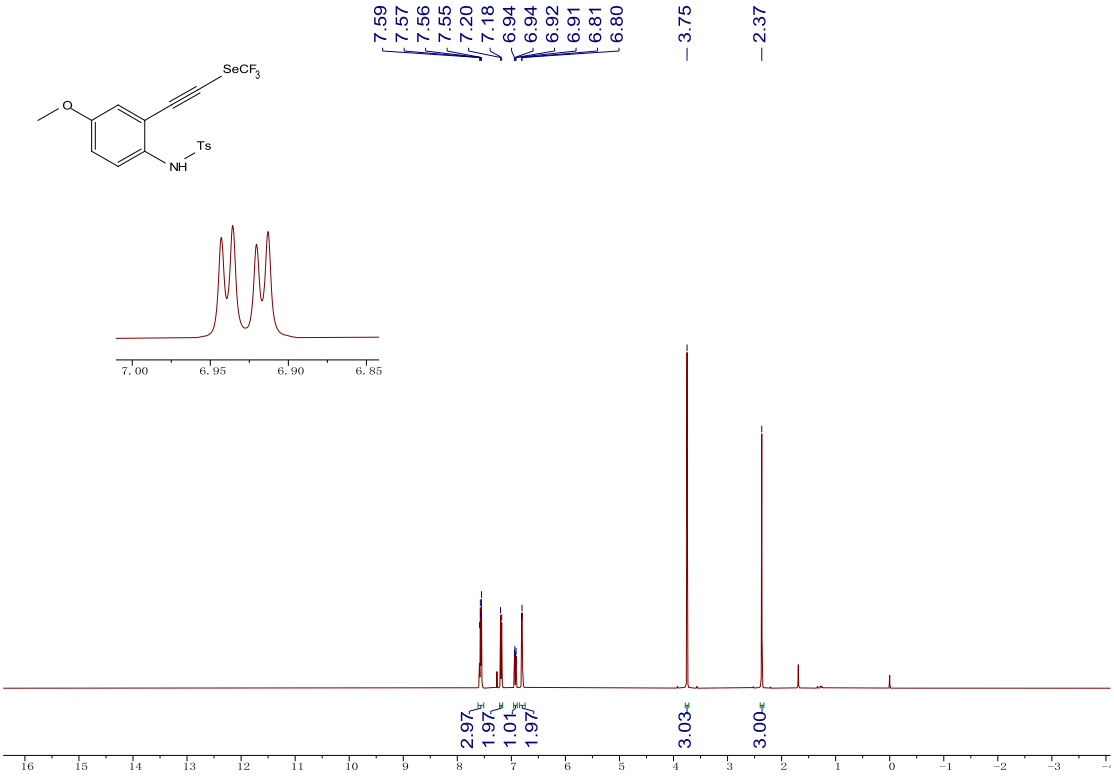

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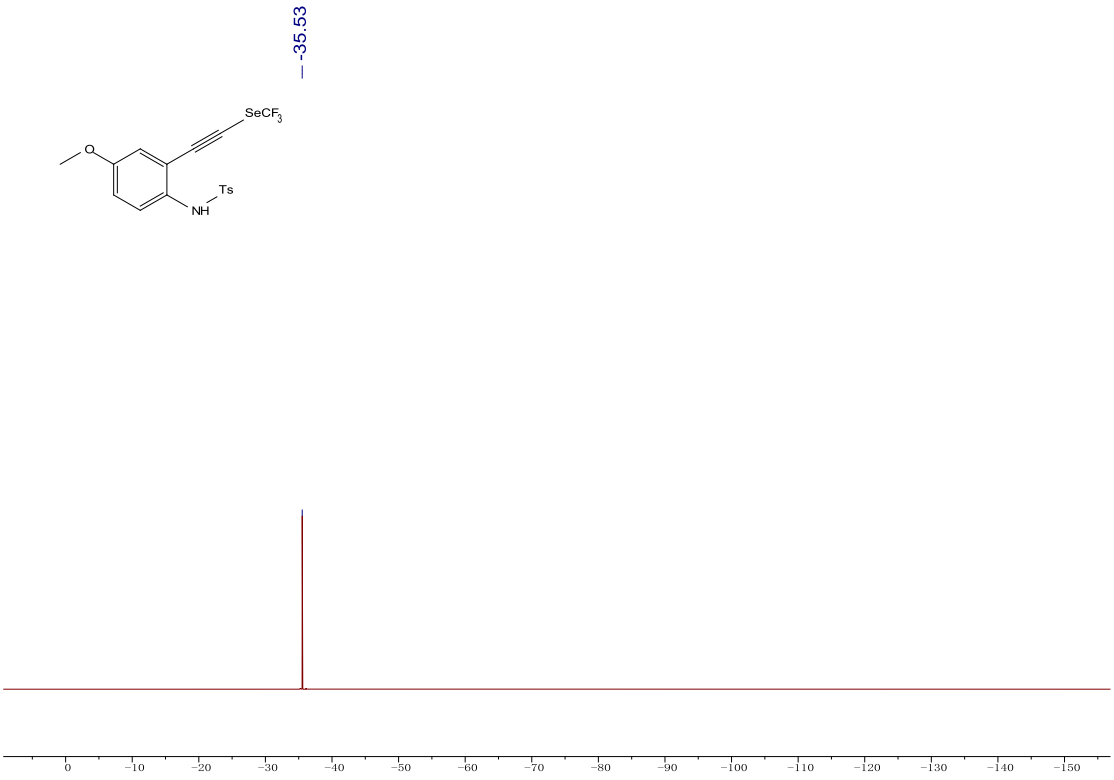

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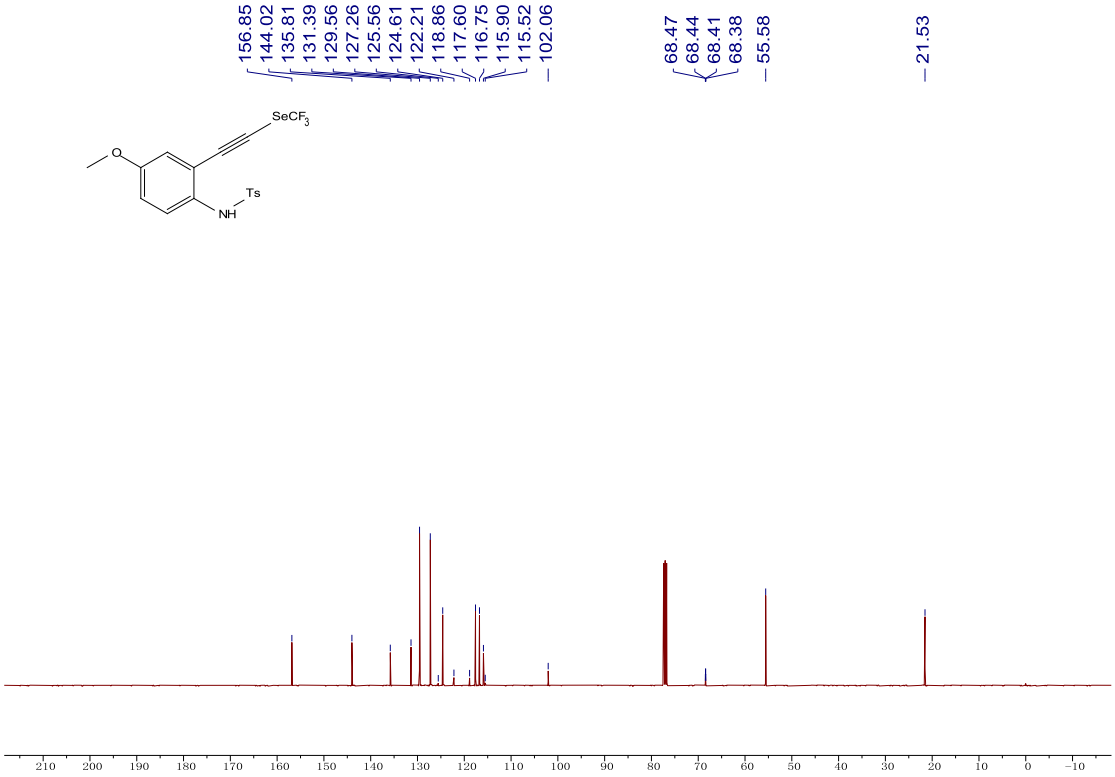
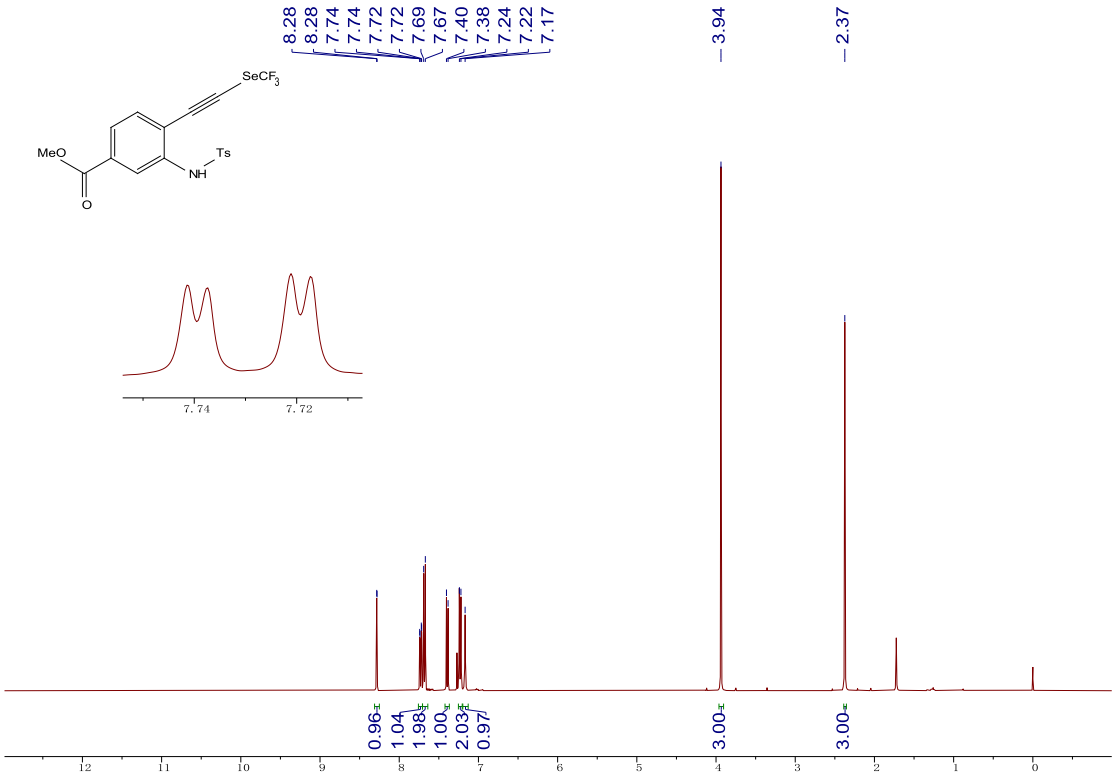


^{1}H NMR spectra of **1i** (400 MHz, $CDCl_3$)



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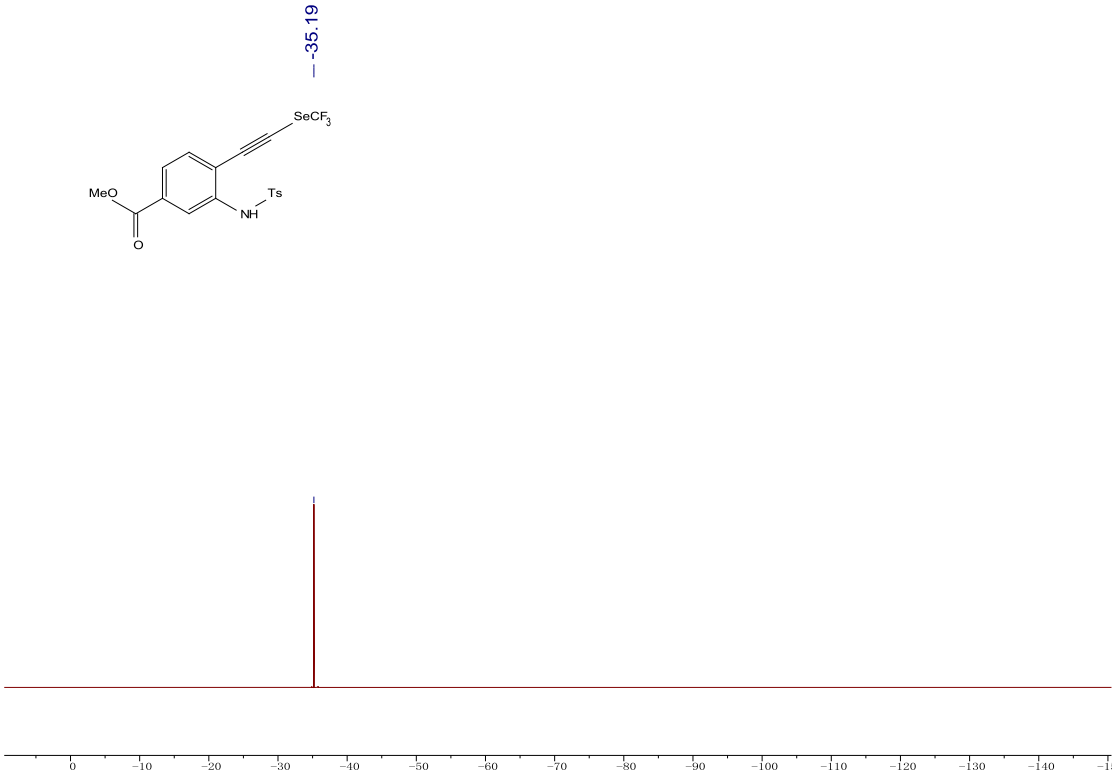

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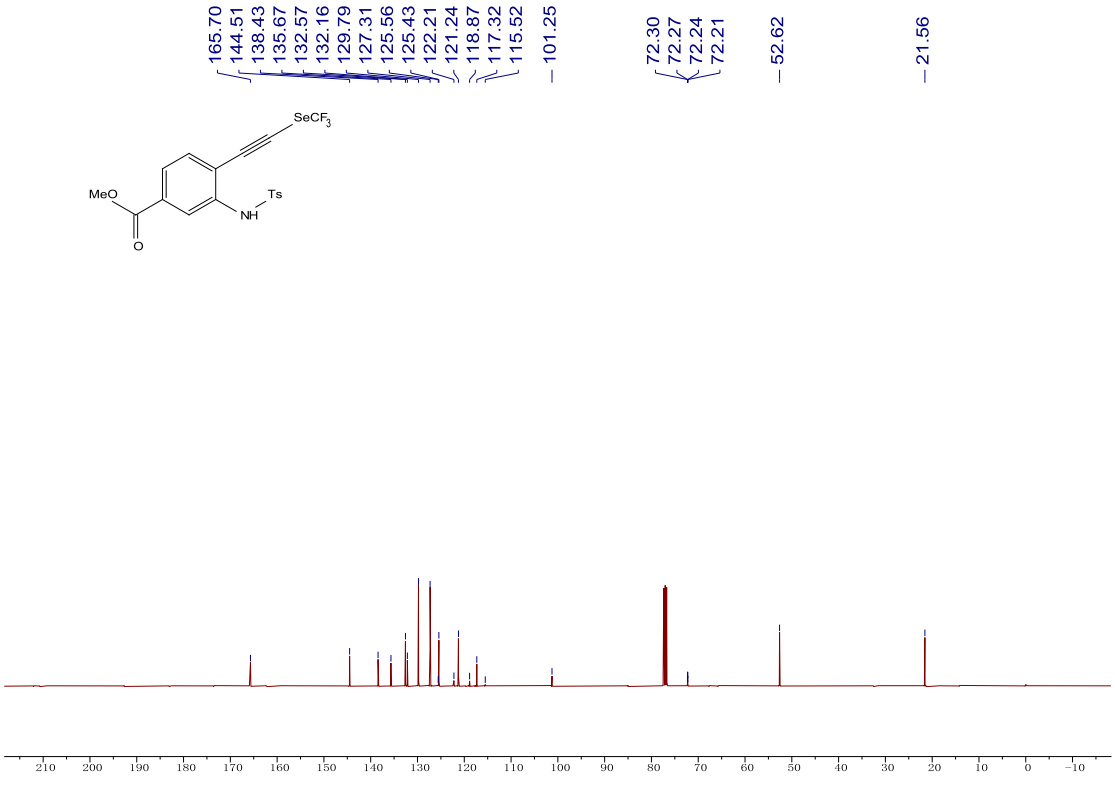

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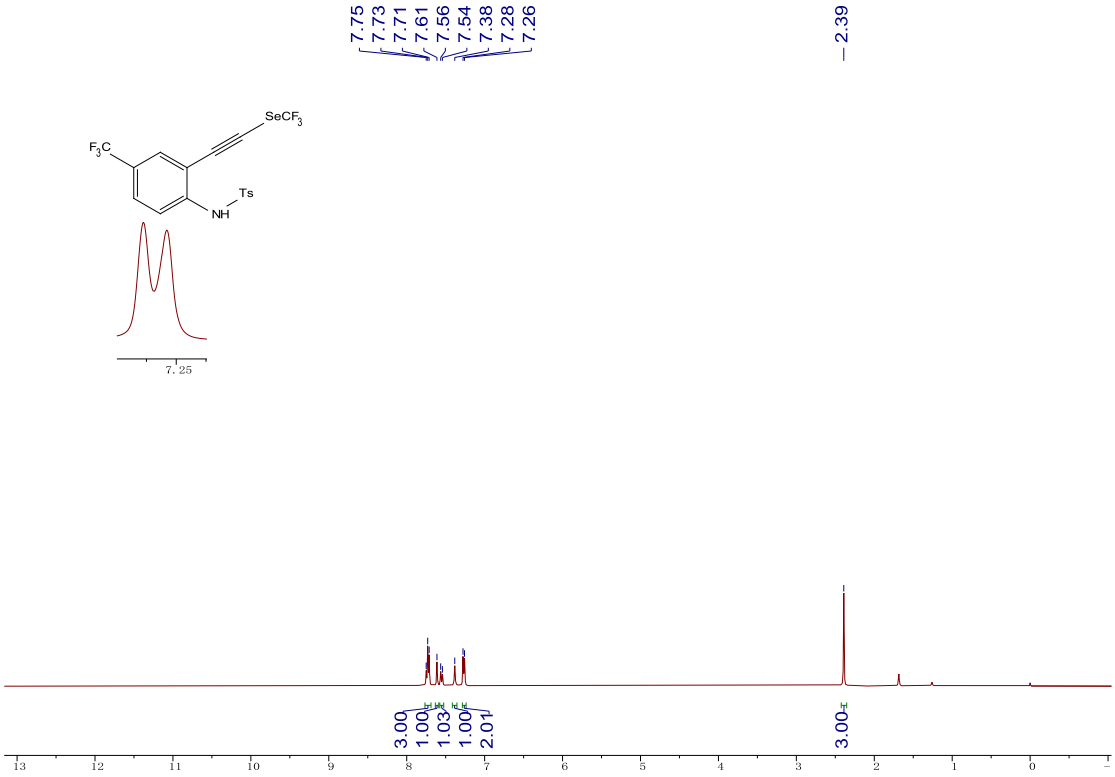

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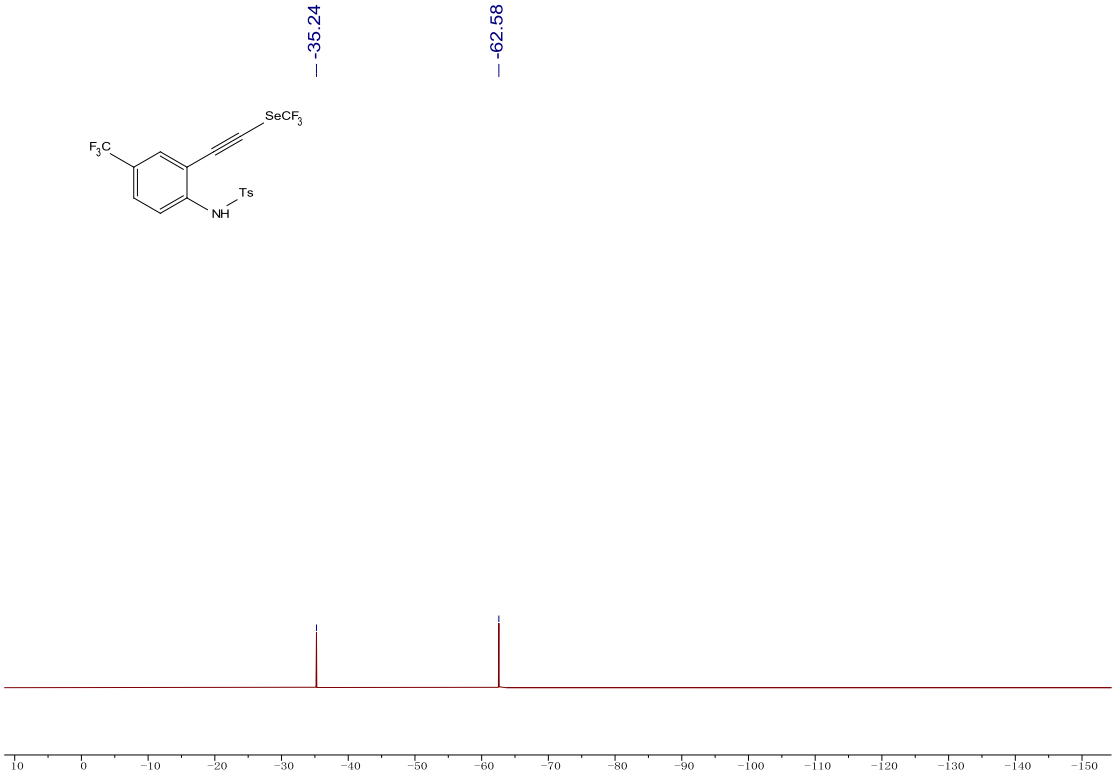

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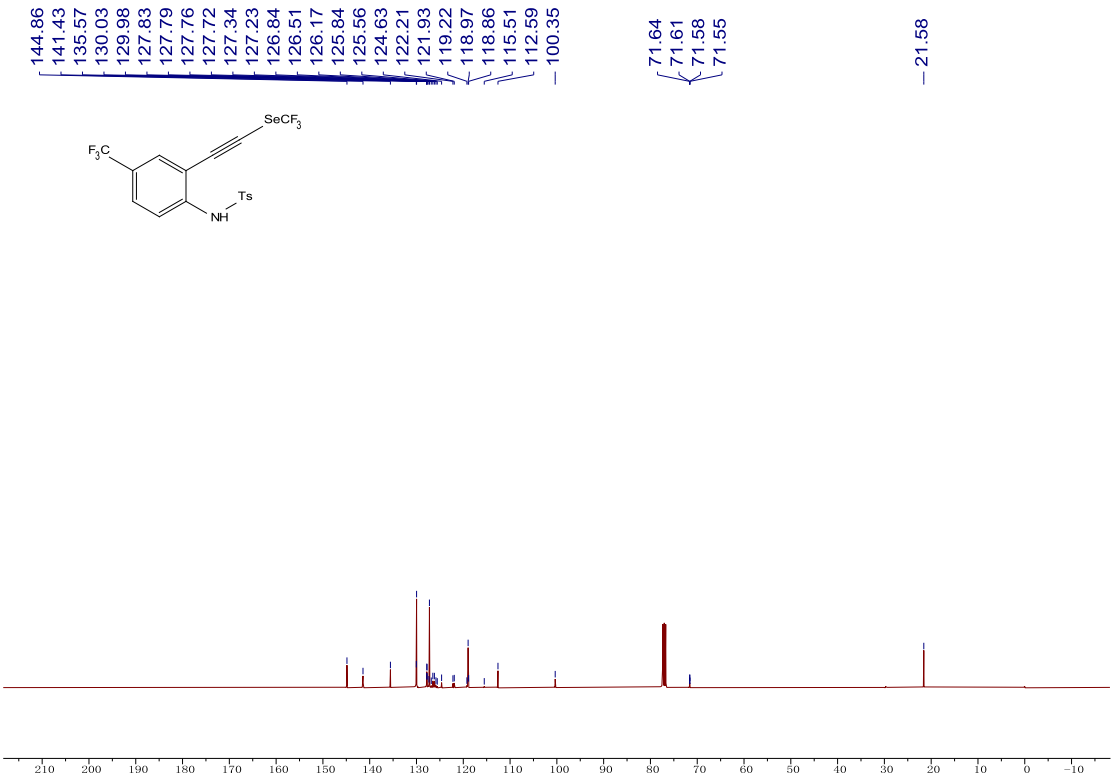

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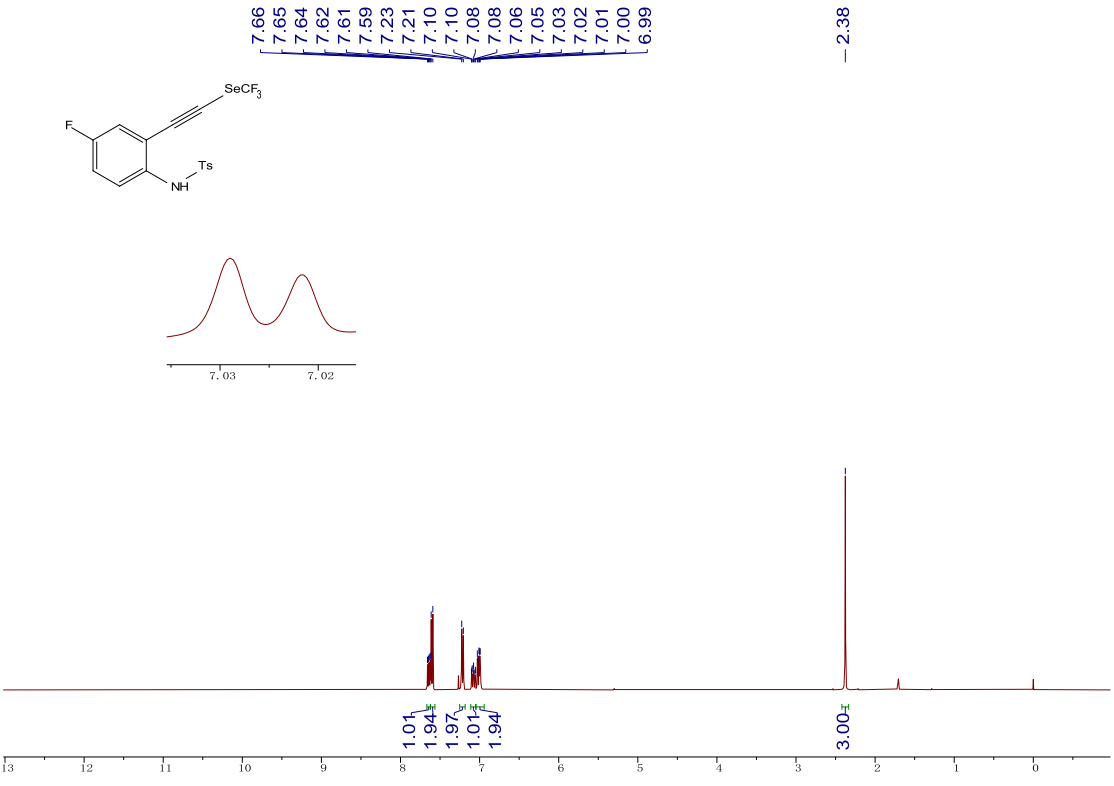

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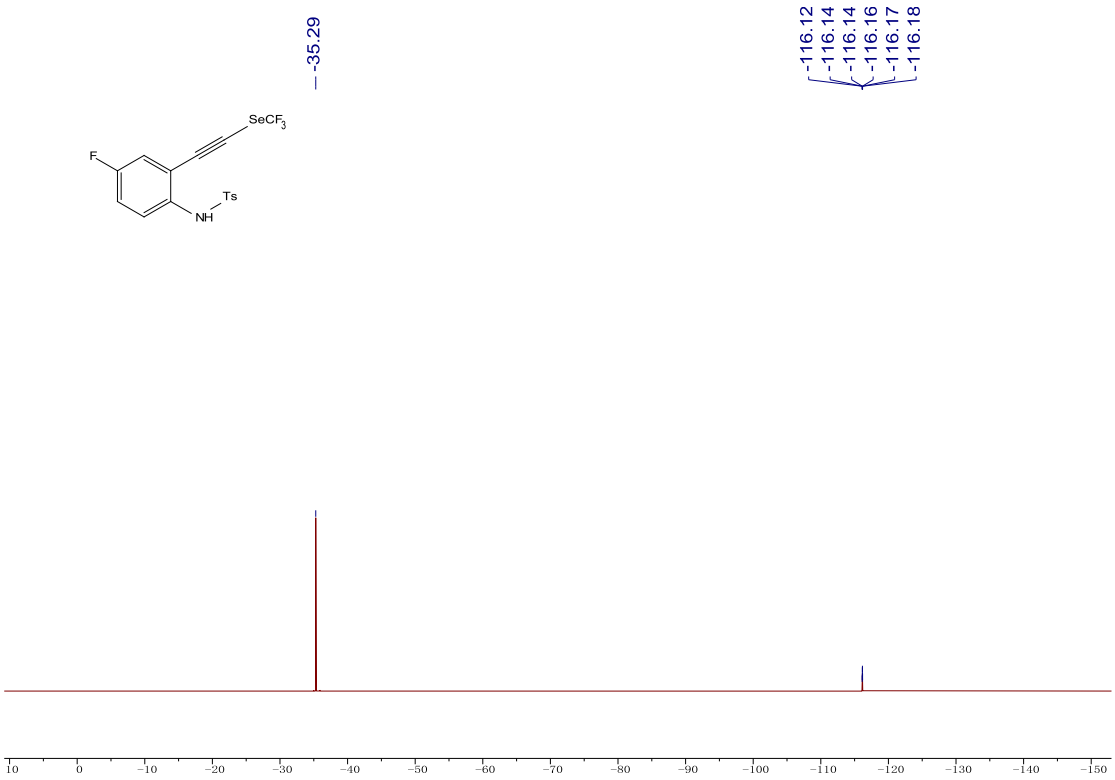

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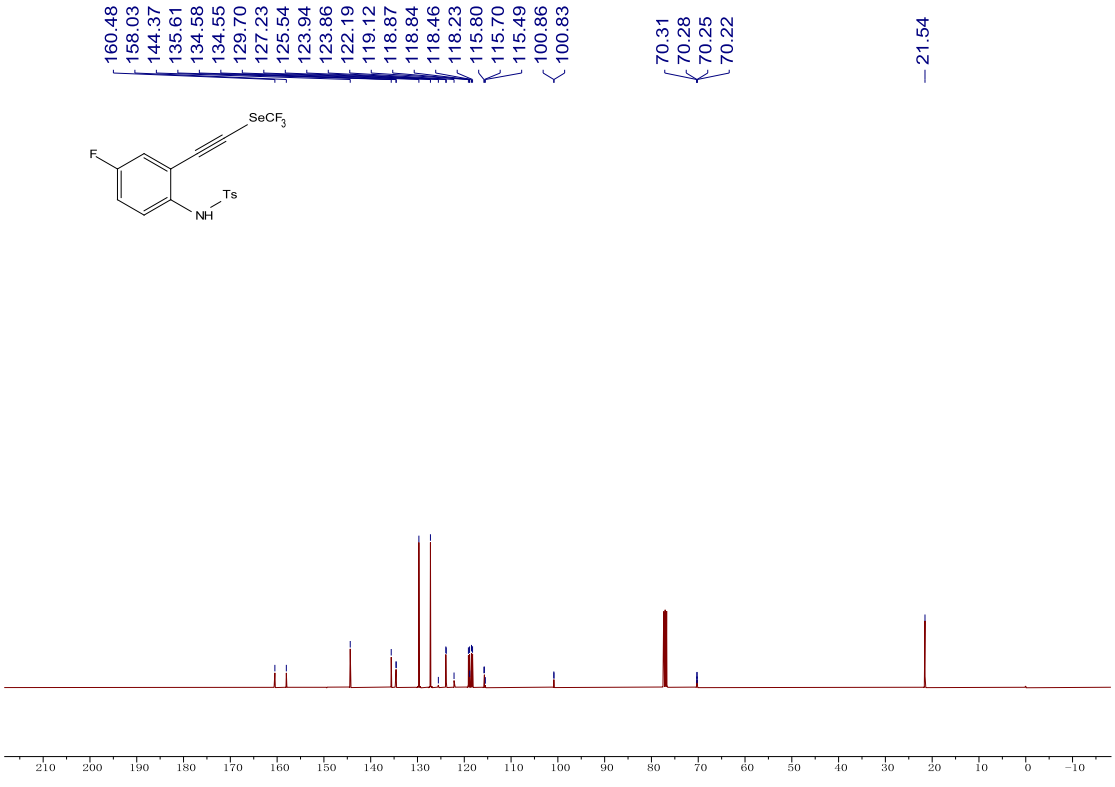

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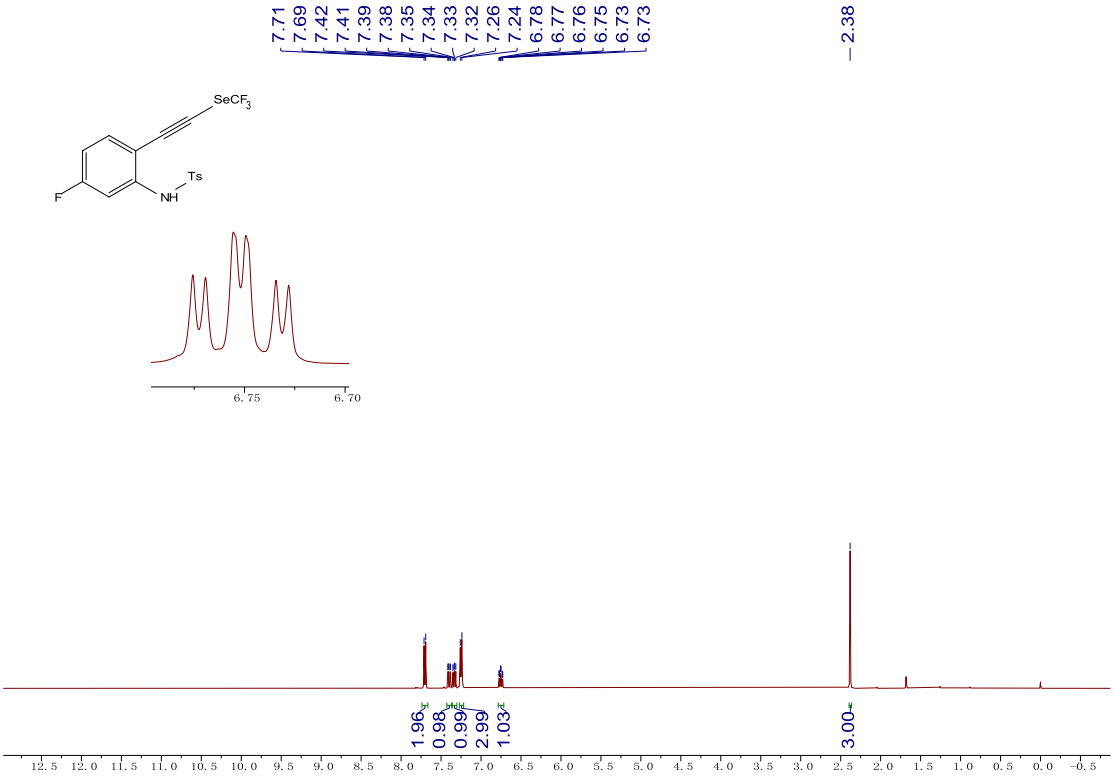

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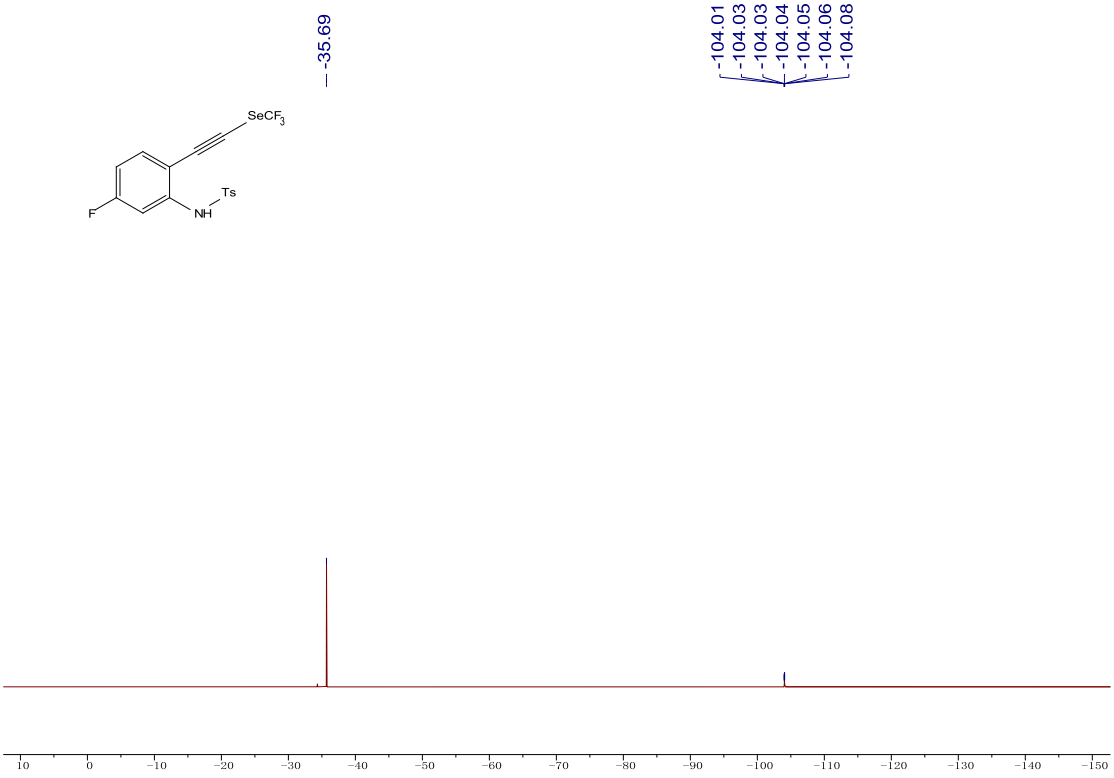

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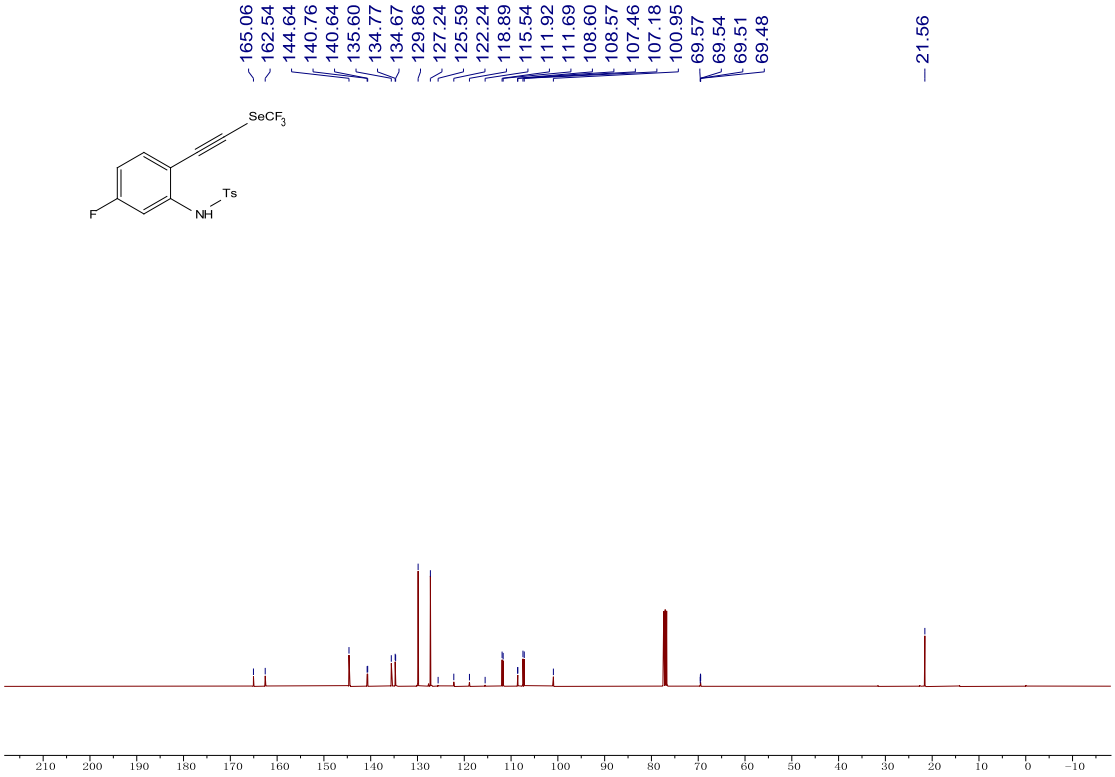

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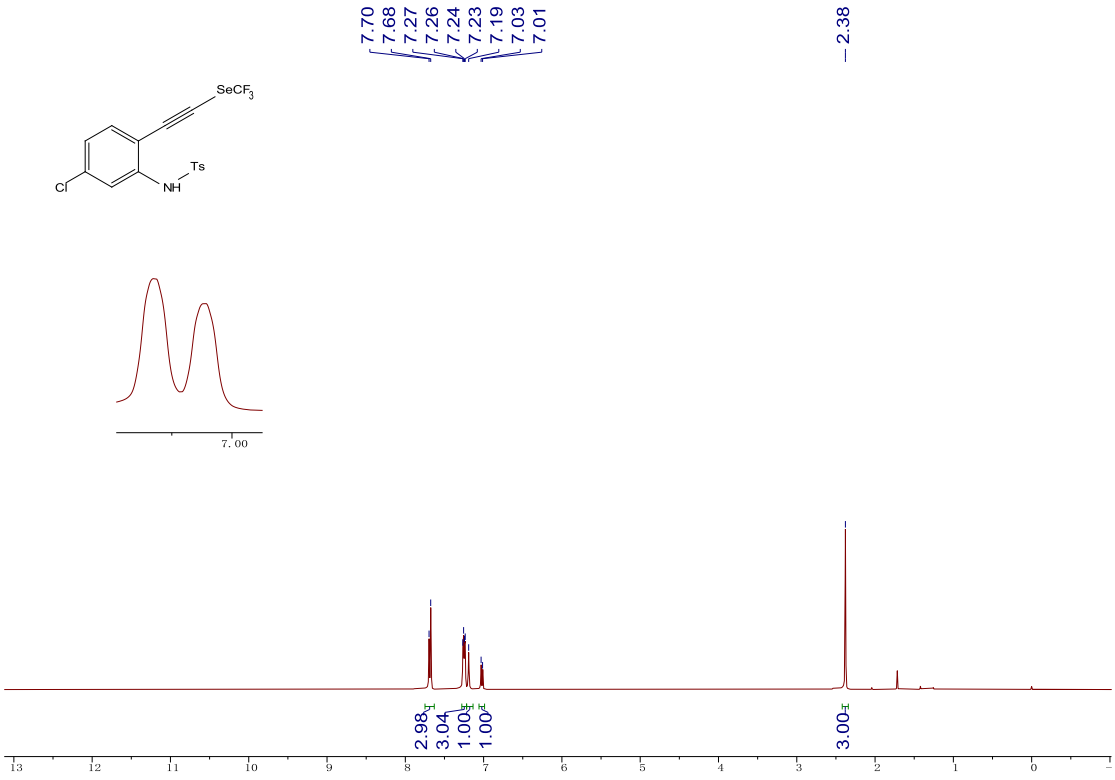

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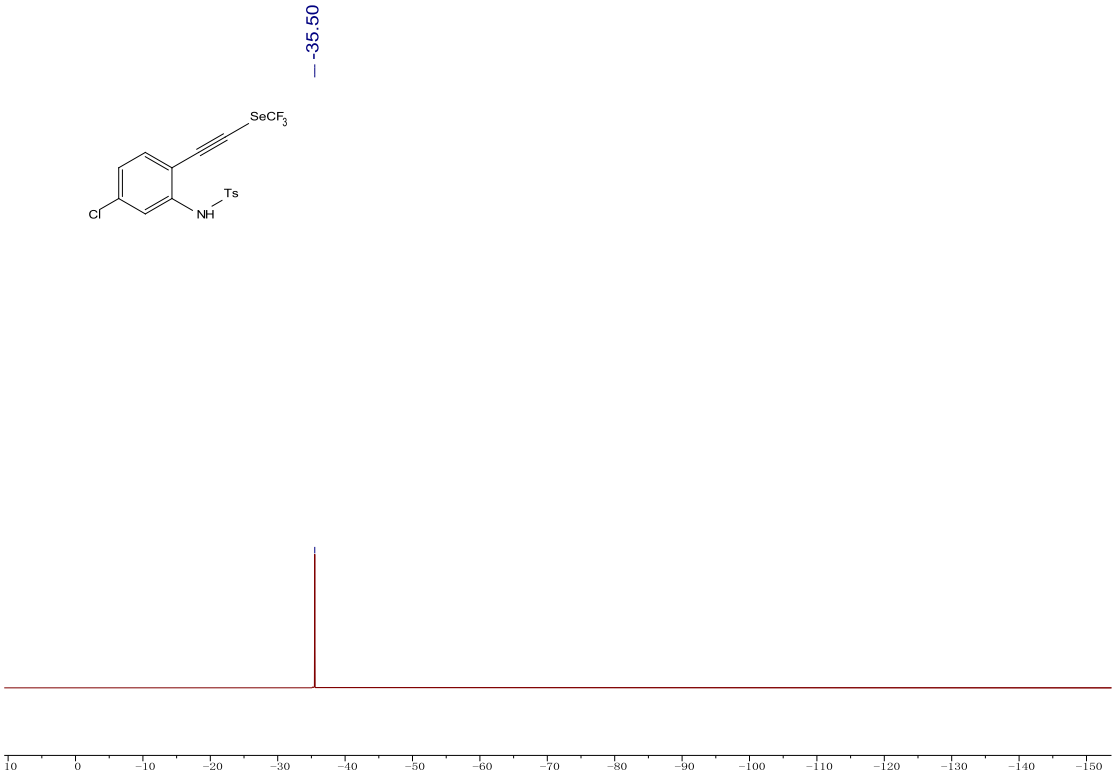

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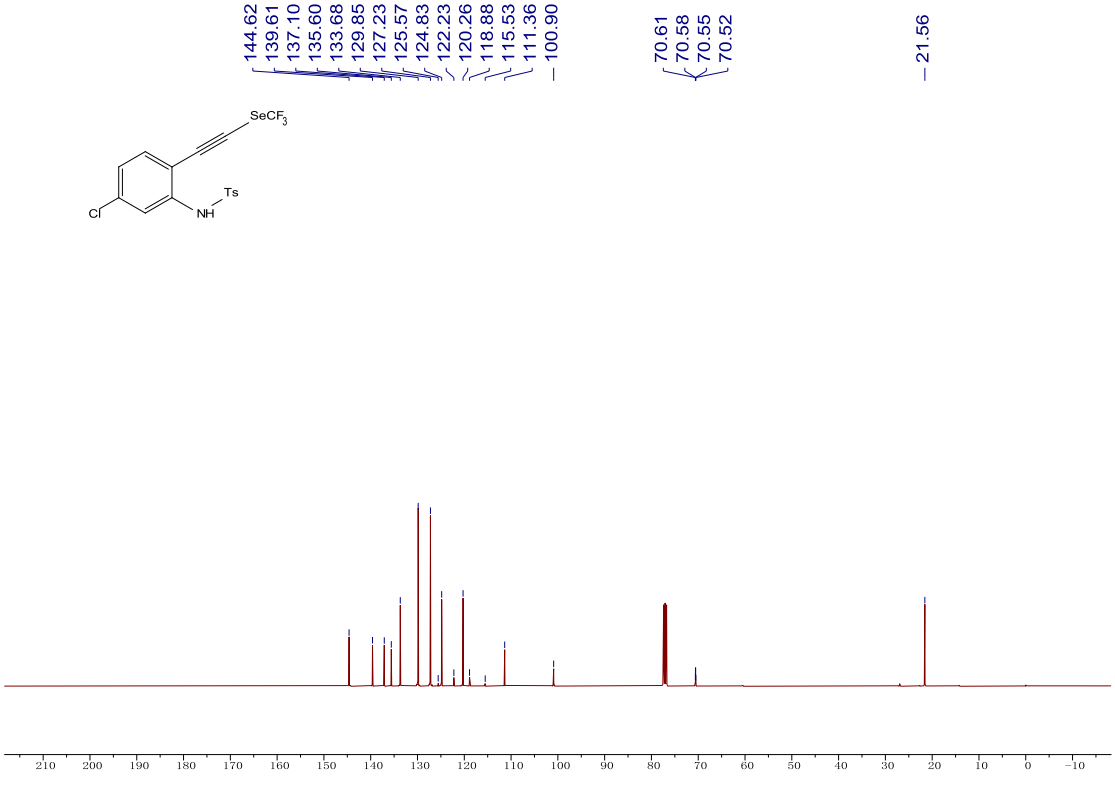

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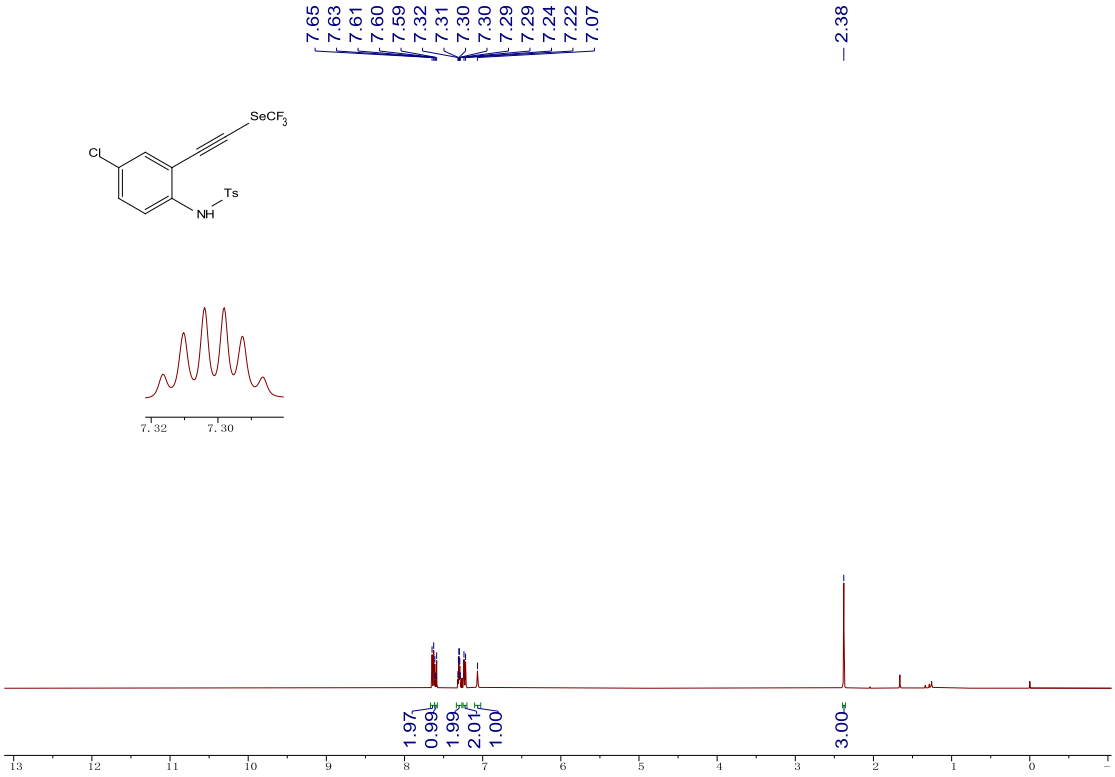
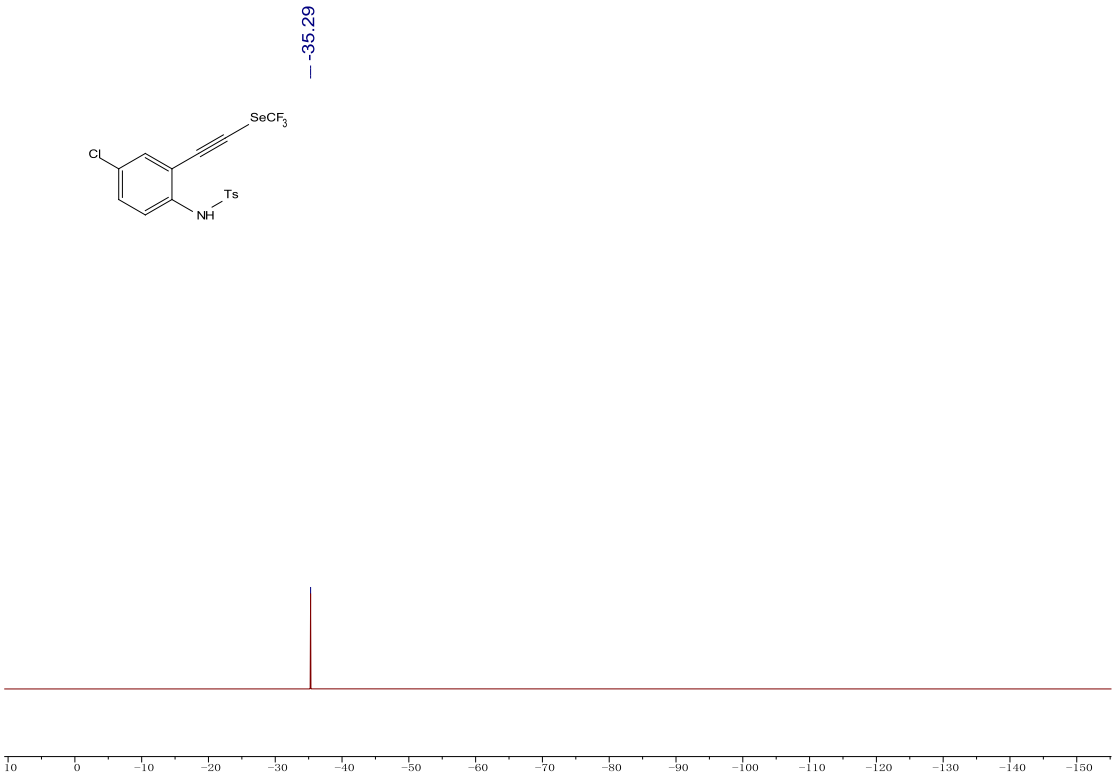
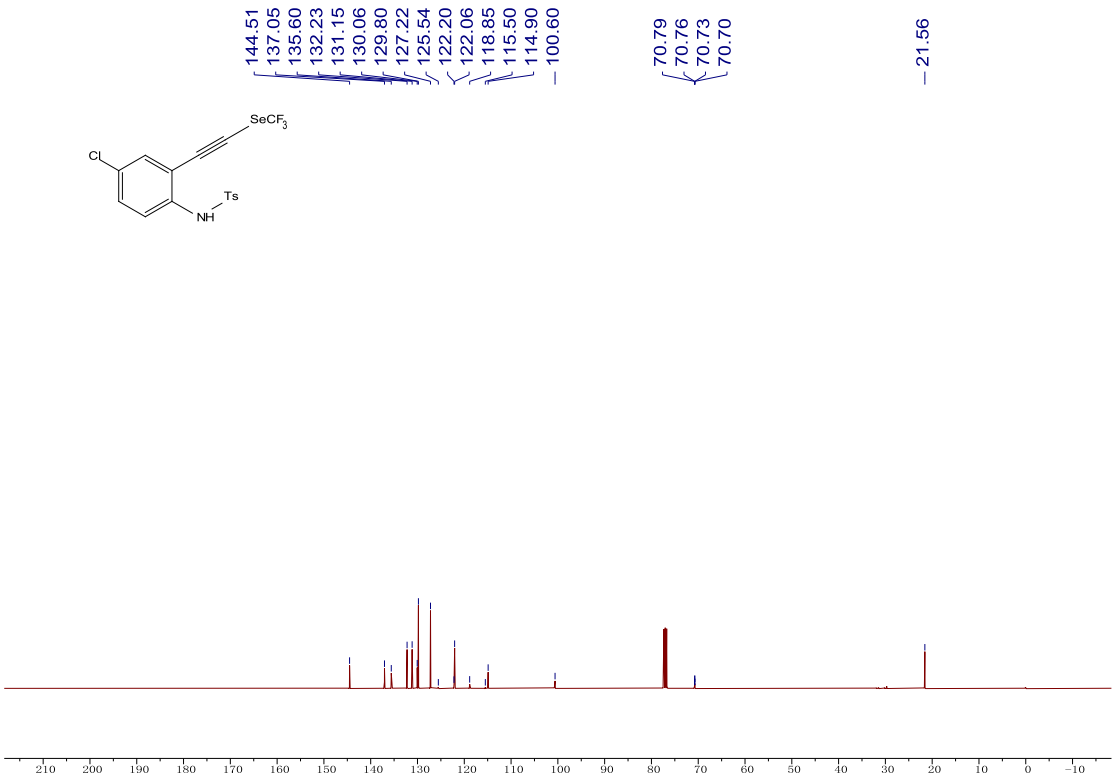


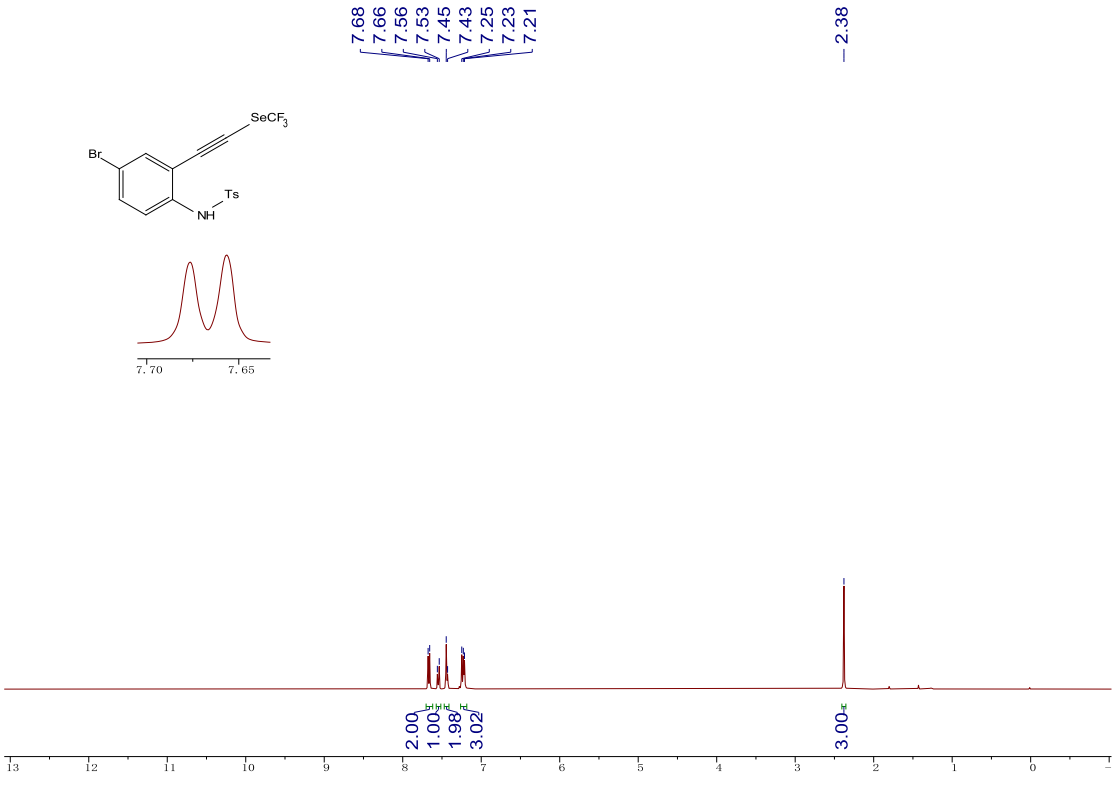
^{19}F NMR spectra of **1n** (376 MHz, $CDCl_3$)



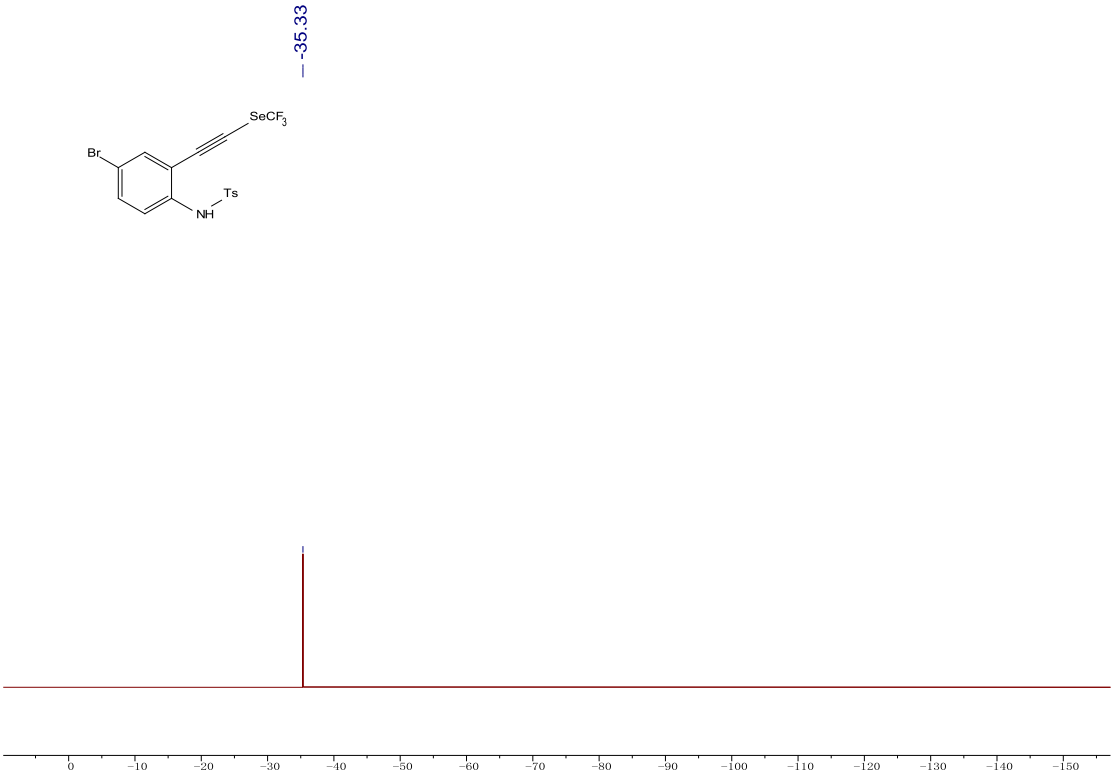
$^{13}C\{^{1}H\}$ NMR spectra of **1n** (101 MHz, $CDCl_3$)



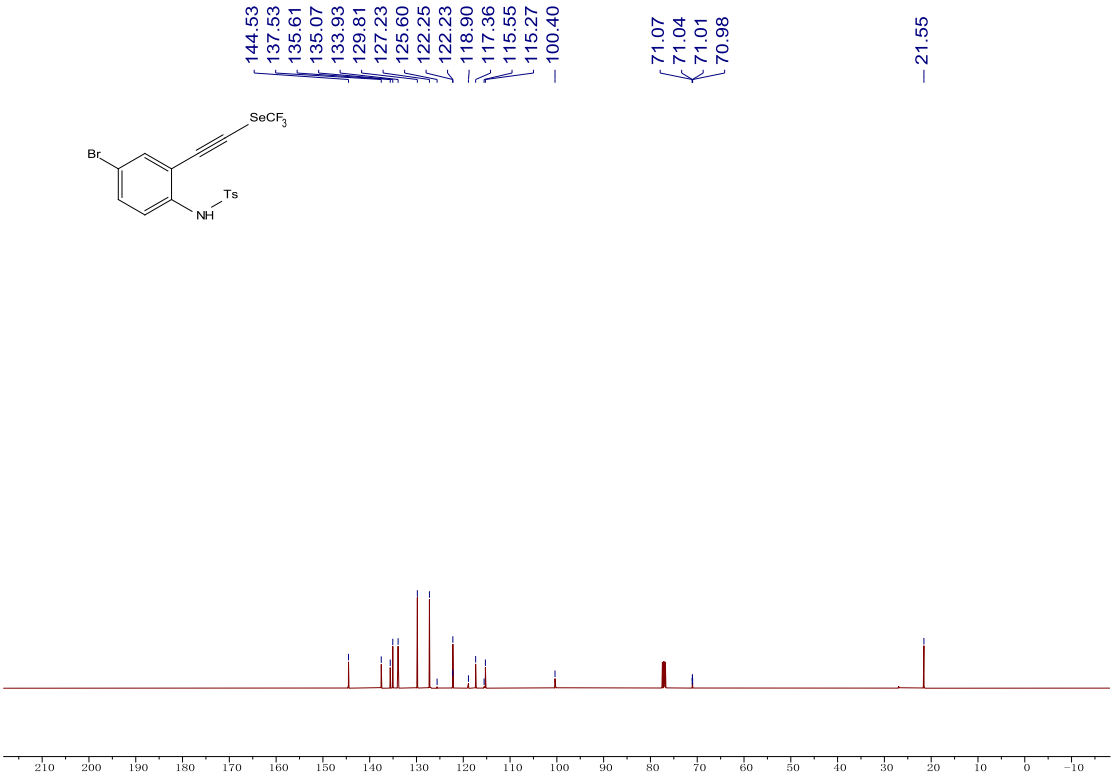
^{1}H NMR spectra of **1o** (400 MHz, $CDCl_3$)



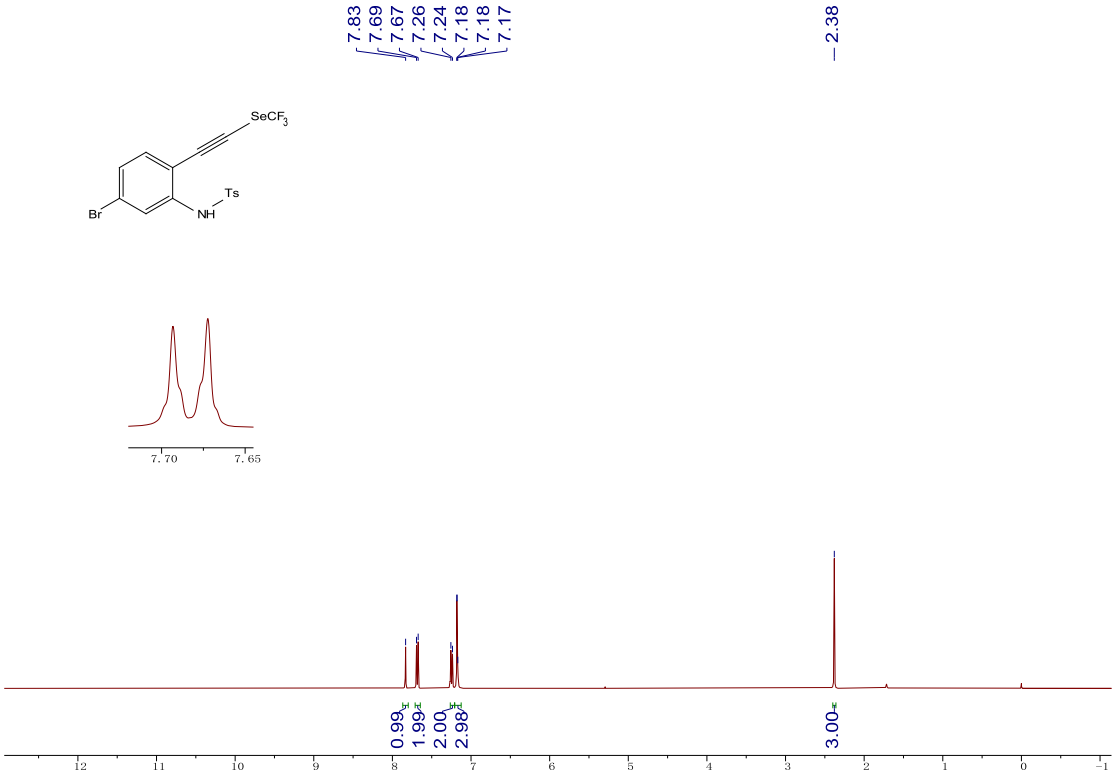
^{19}F NMR spectra of **1o** (376 MHz, $CDCl_3$)



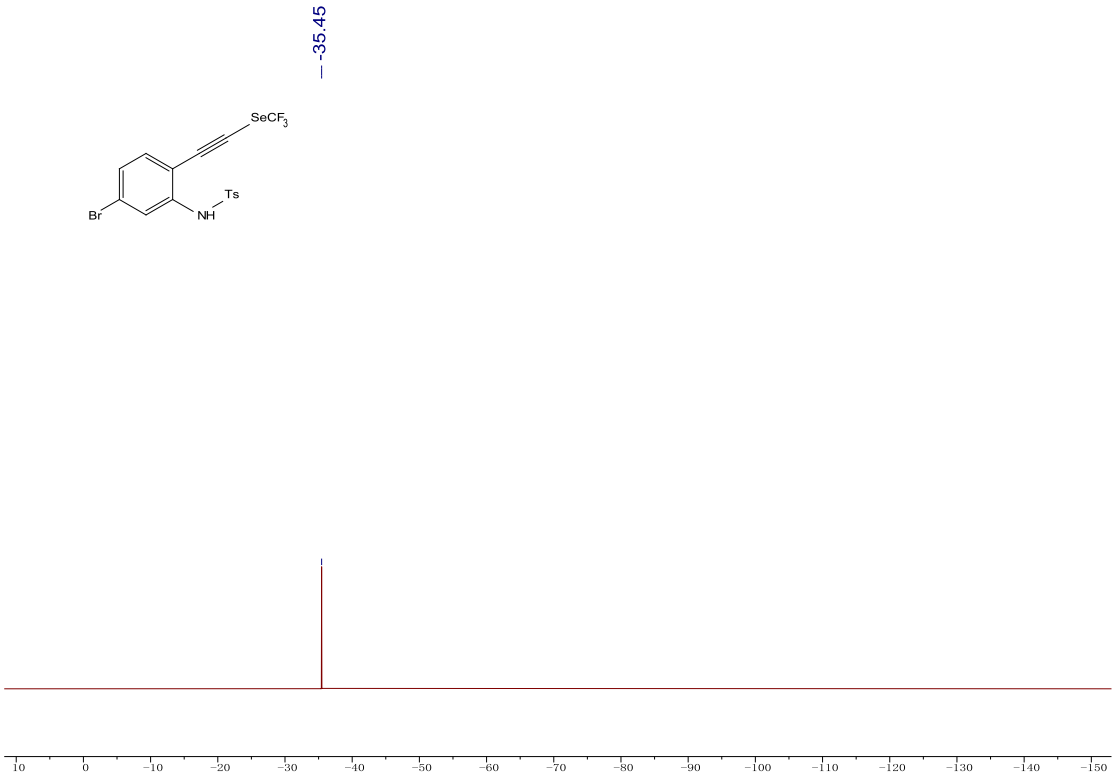
$^{13}C\{^1H\}$ NMR spectra of **1o** (101 MHz, $CDCl_3$)



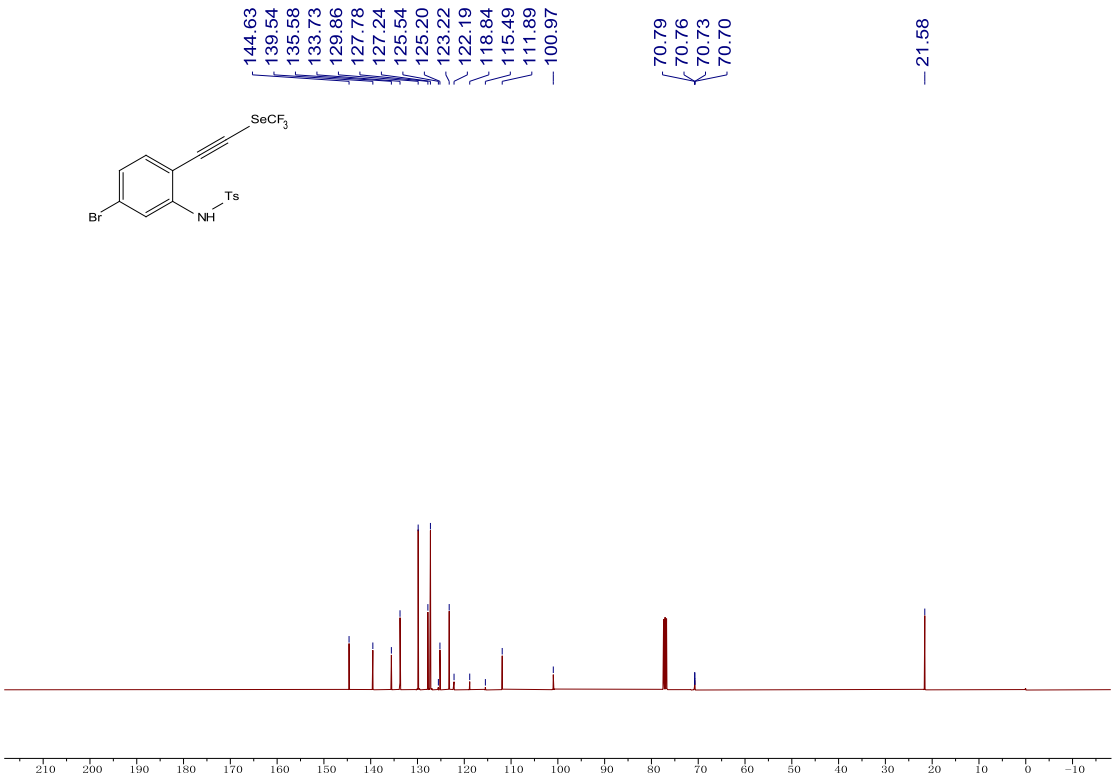
^{1}H NMR spectra of **1p** (400 MHz, $CDCl_3$)



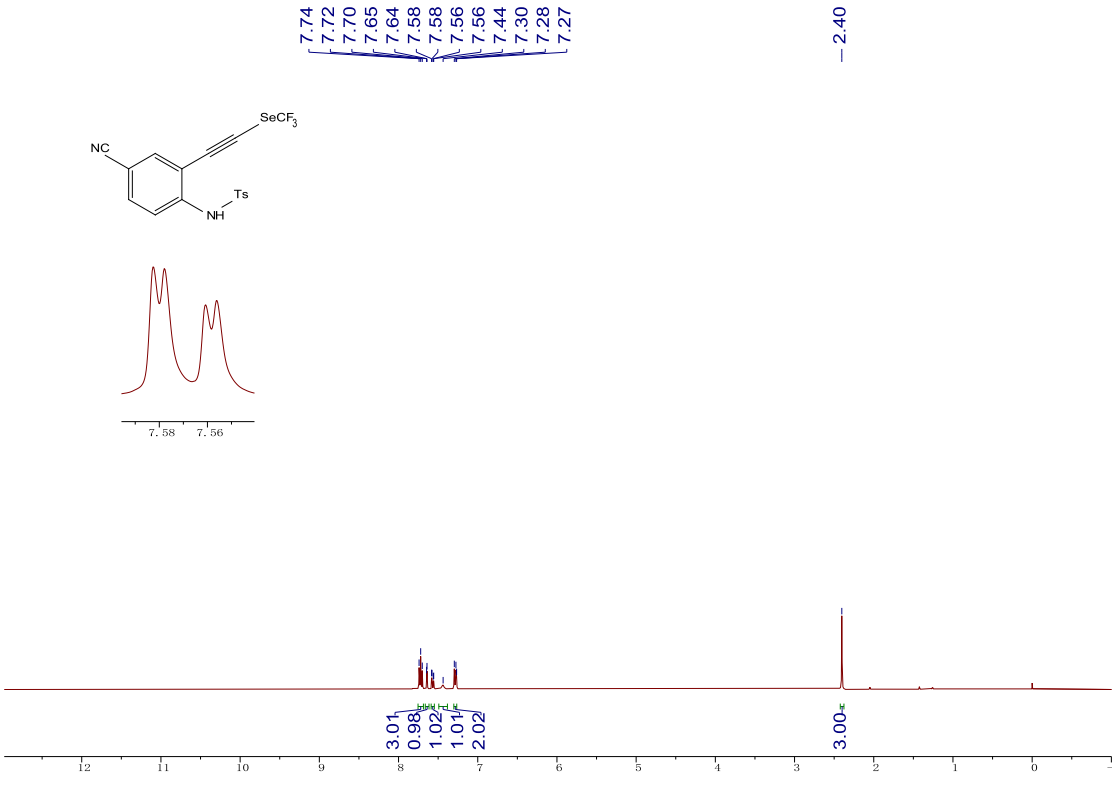
^{19}F NMR spectra of **1p** (376 MHz, $CDCl_3$)



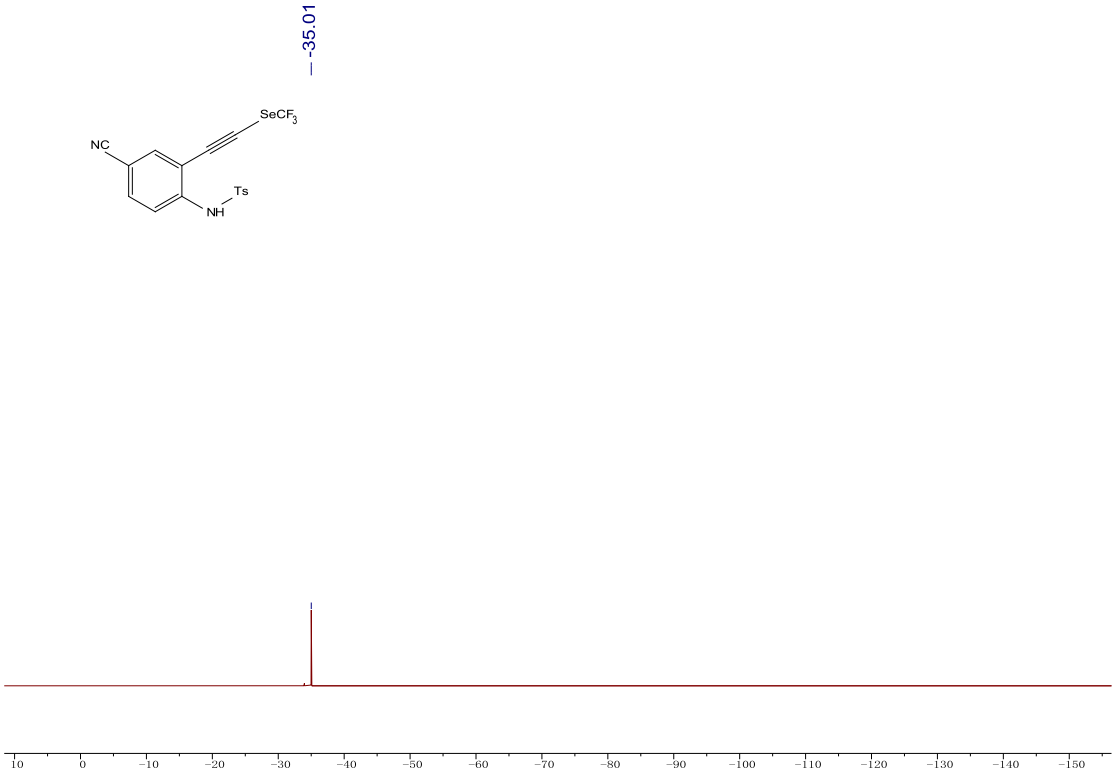
$^{13}C\{^{1}H\}$ NMR spectra of **1p** (101 MHz, $CDCl_3$)



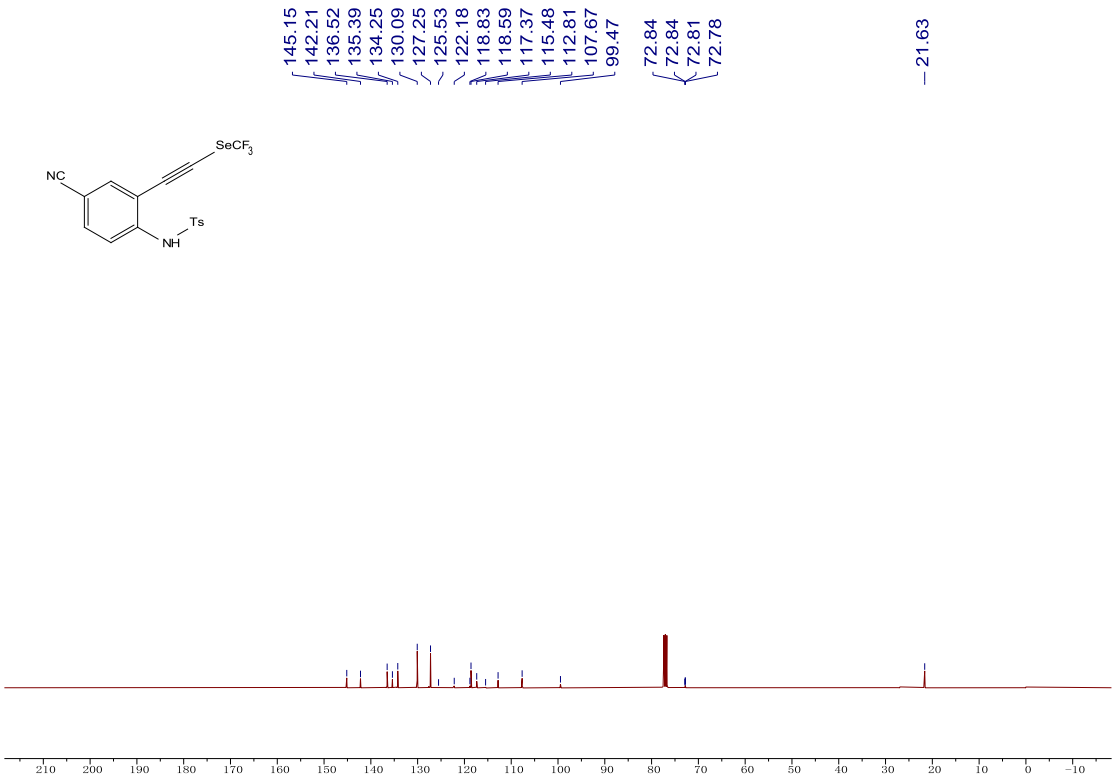
^{1}H NMR spectra of **1q** (400 MHz, $CDCl_3$)



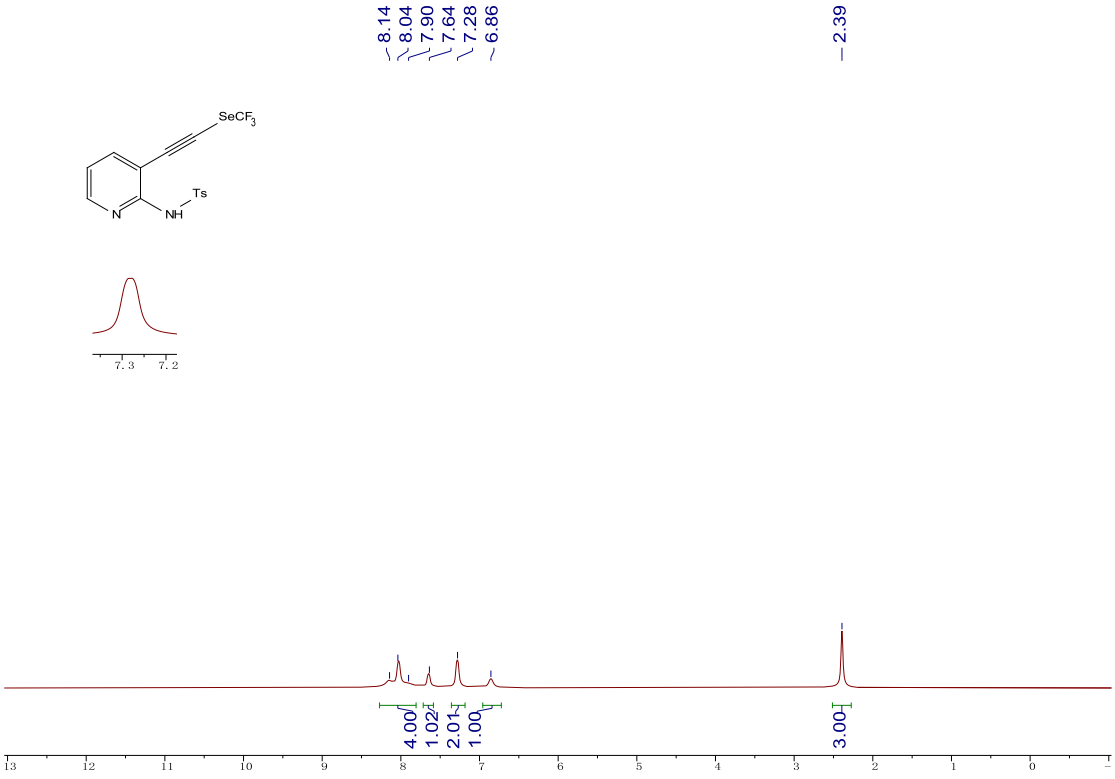
^{19}F NMR spectra of **1q** ($CDCl_3$)



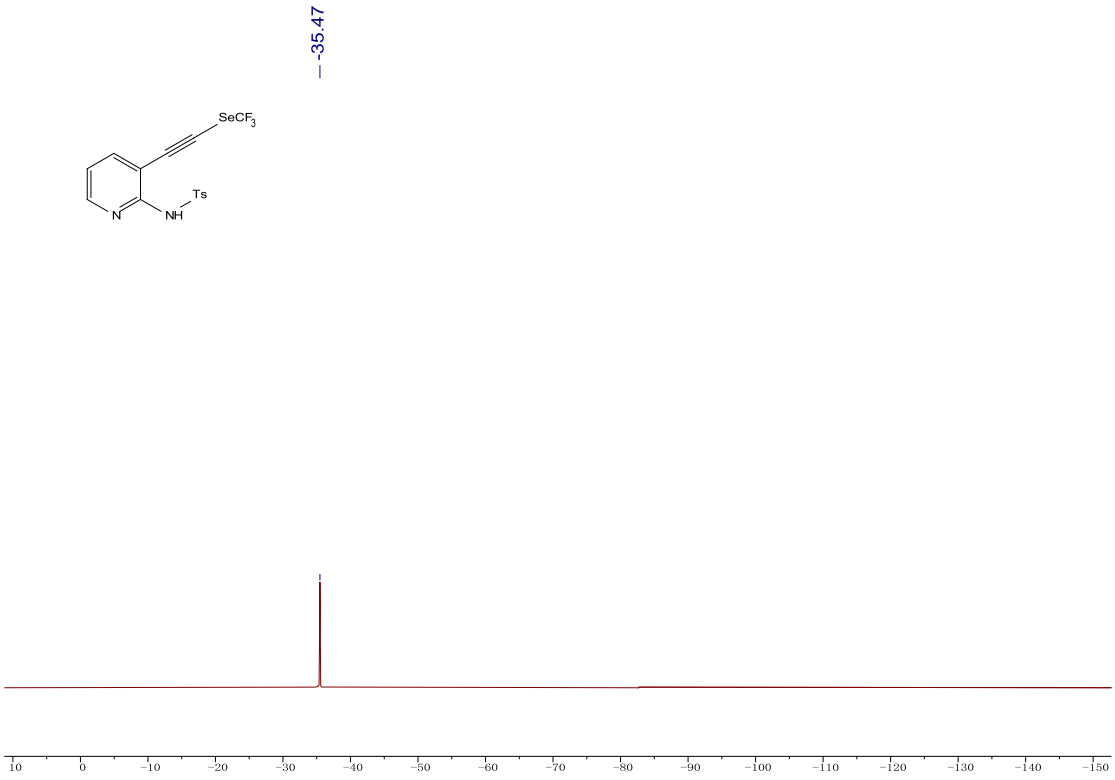
$^{13}C\{^1H\}$ NMR spectra of **1q** ($CDCl_3$)



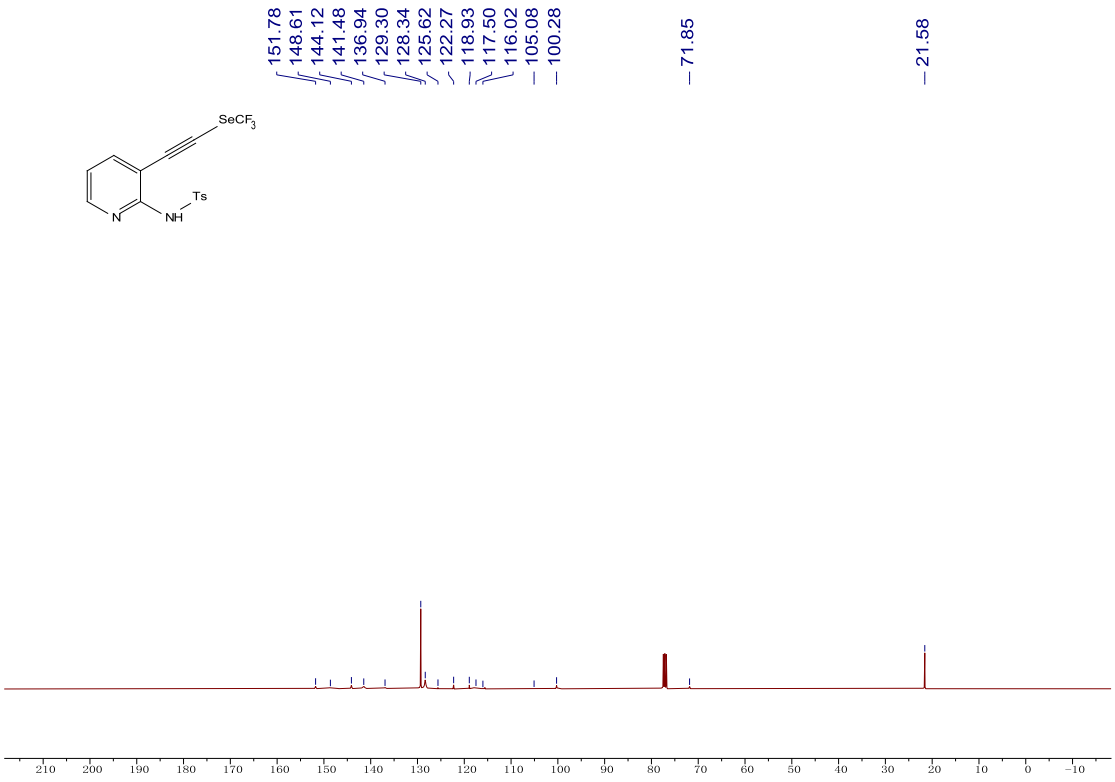
^{1}H NMR spectra of **1r** (400 MHz, $CDCl_3$)



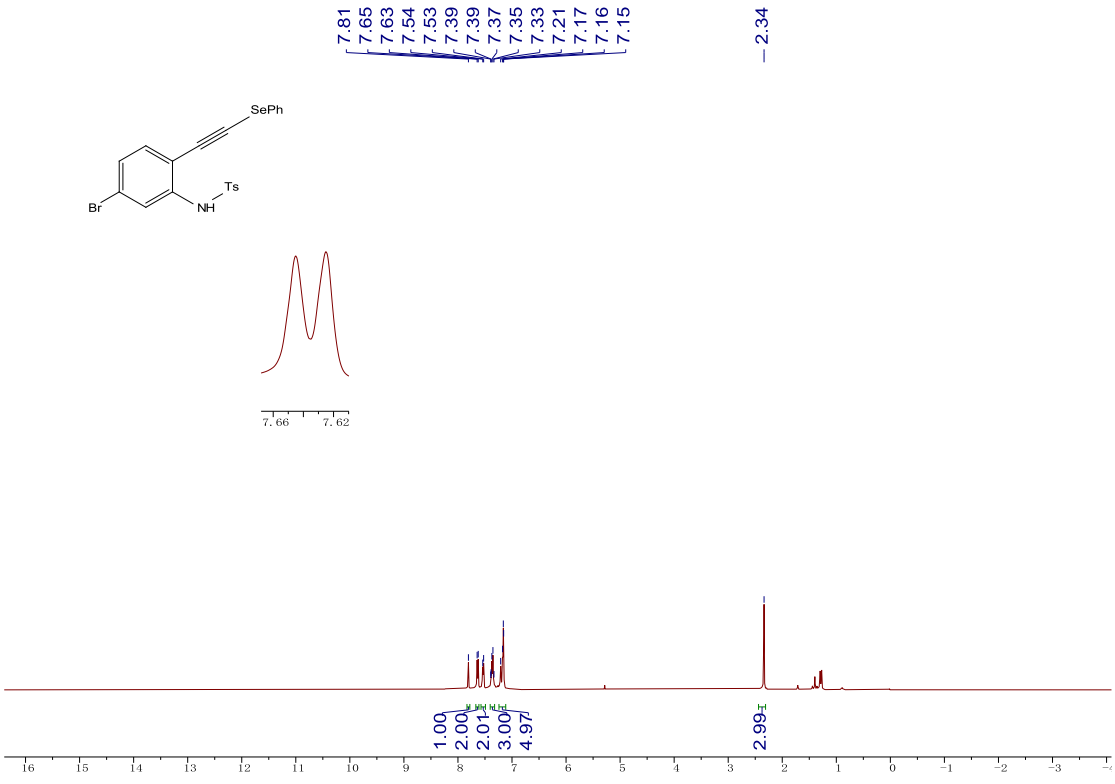
^{19}F NMR spectra of **1r** (376 MHz, $CDCl_3$)



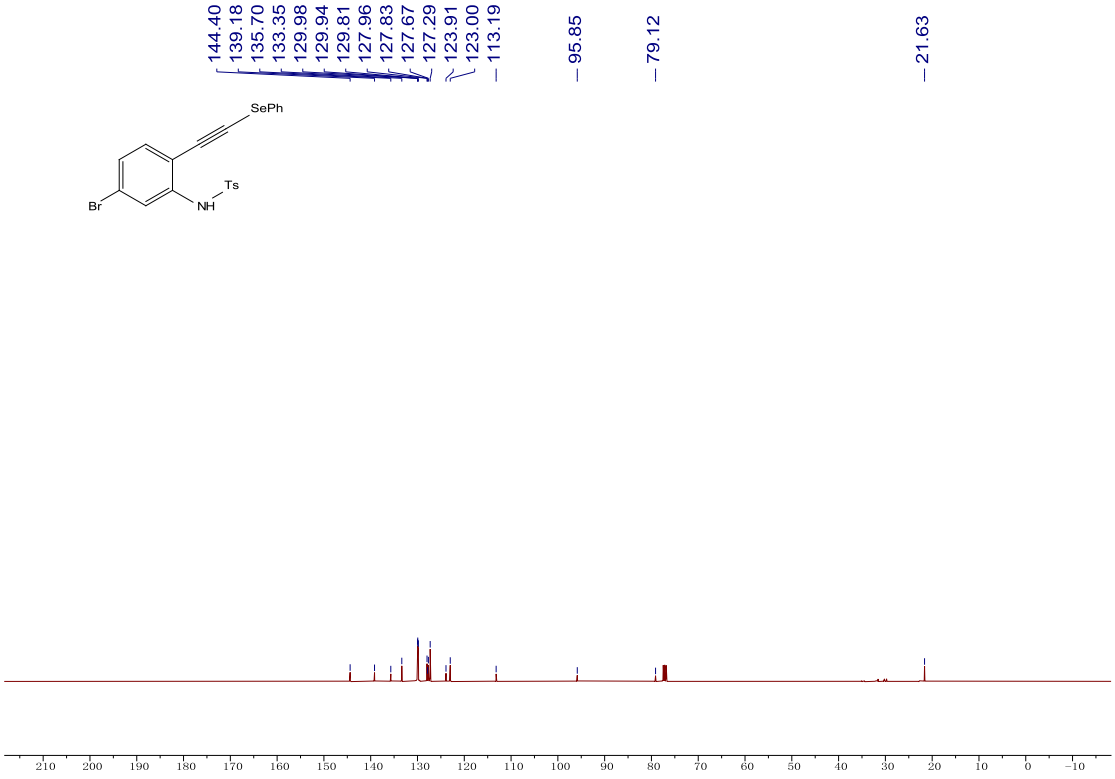
$^{13}C\{^{1}H\}$ NMR spectra of **1r** (101 MHz, $CDCl_3$)



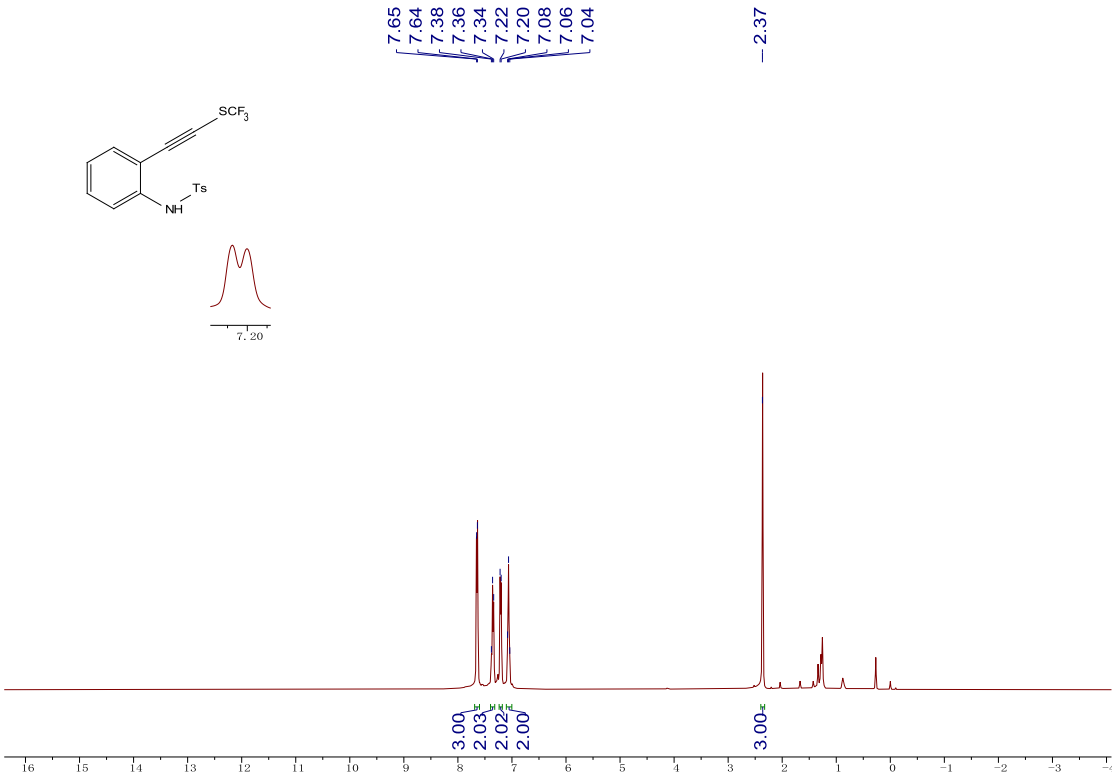
^{1}H NMR spectra of **1p-Ph** (400 MHz, $CDCl_3$)



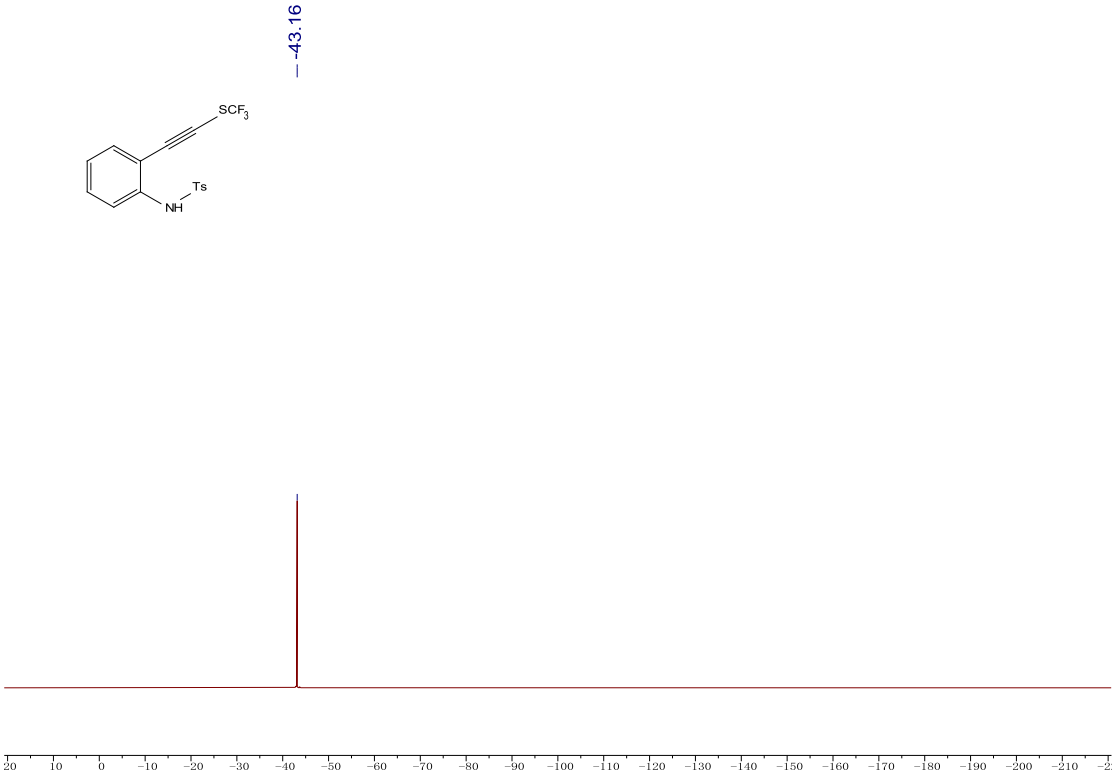
$^{13}C\{^{1}H\}$ NMR spectra of **1p-Ph** (101 MHz, $CDCl_3$)



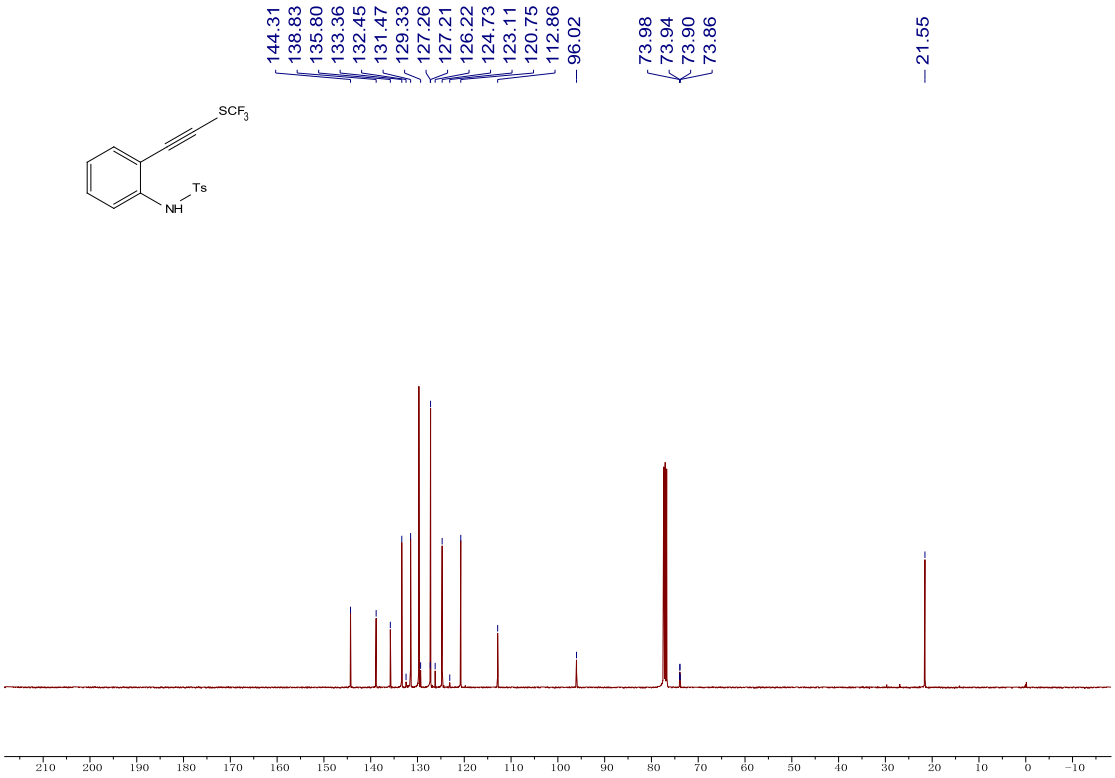
^{1}H NMR spectra of **1a-S** (400 MHz, $CDCl_3$)



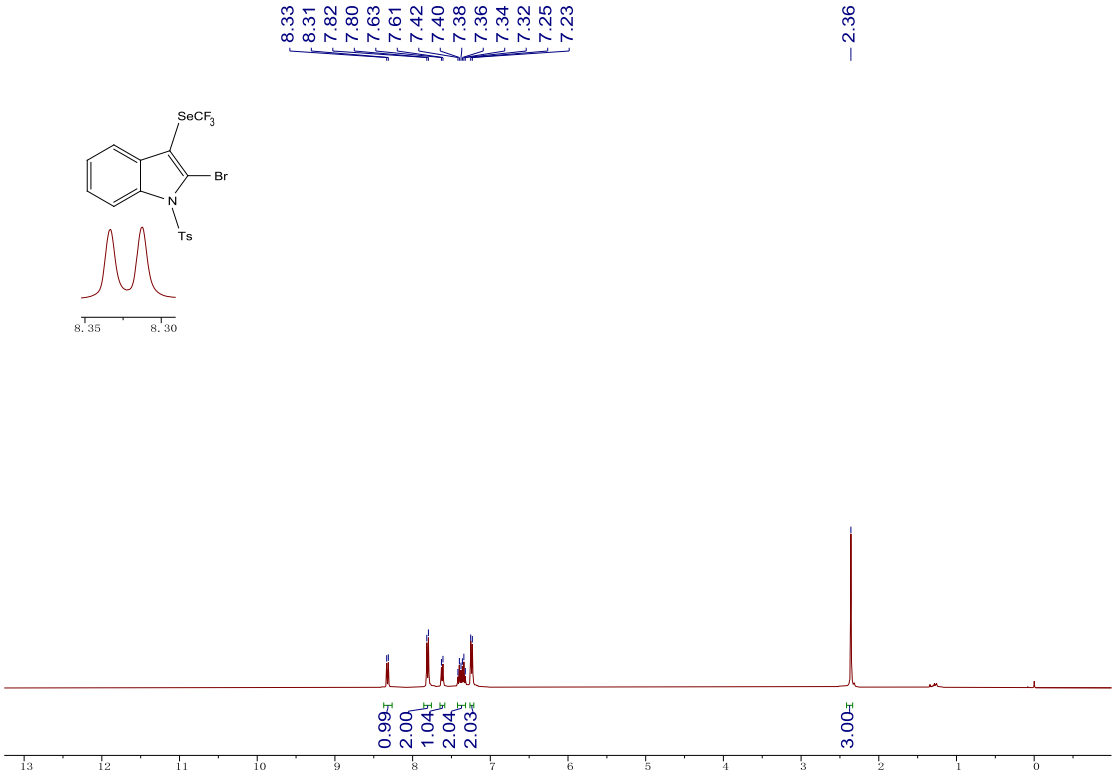
^{19}F NMR spectra of **1a-S** (376 MHz, $CDCl_3$)



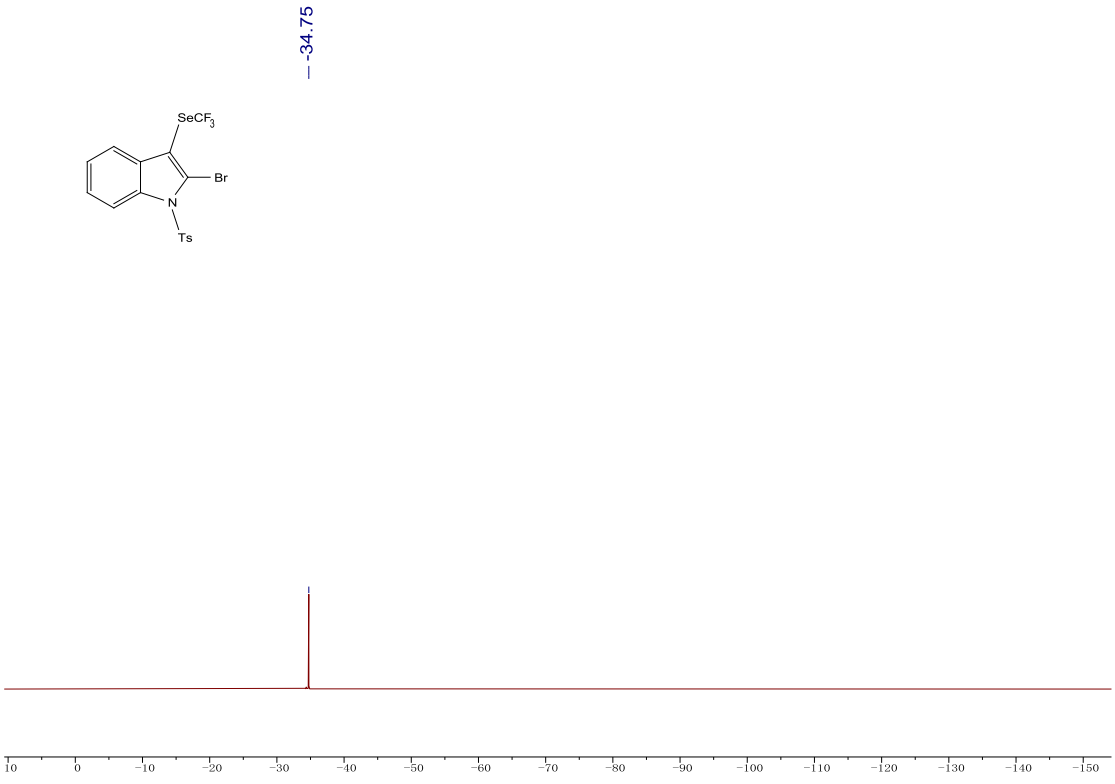
$^{13}C\{^1H\}$ NMR spectra of **1a-S** (101 MHz, $CDCl_3$)



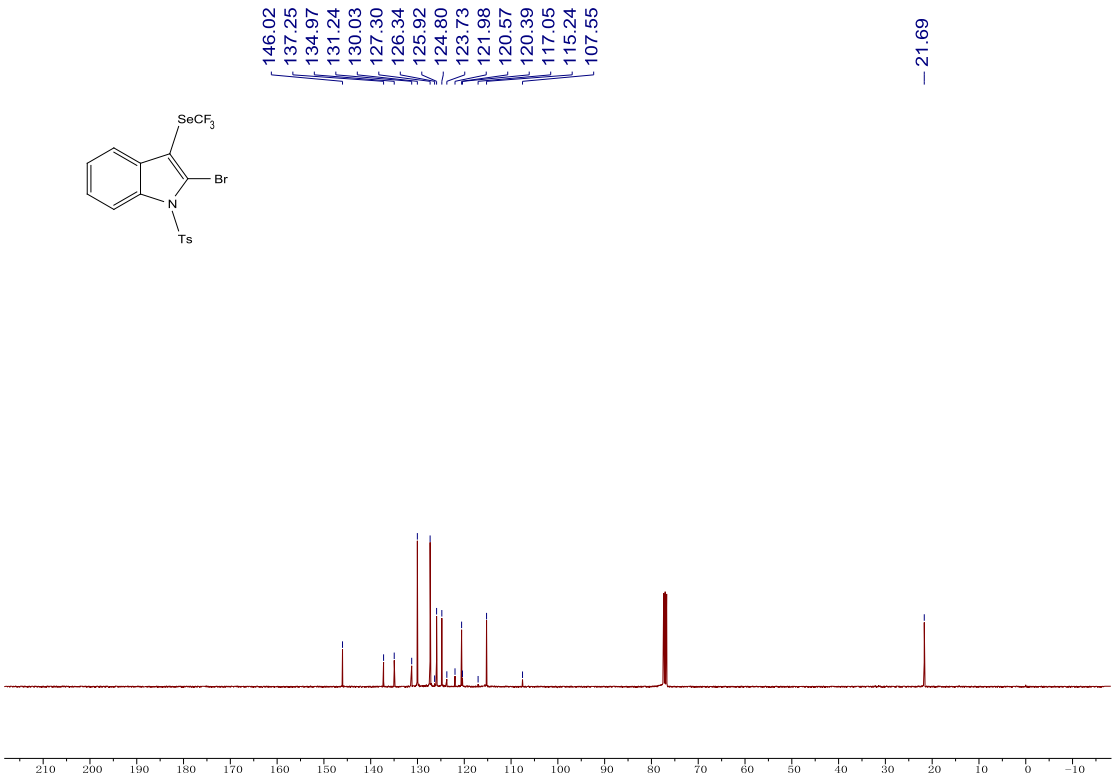
^{1}H NMR spectra of **2a** (400 MHz, $CDCl_3$)



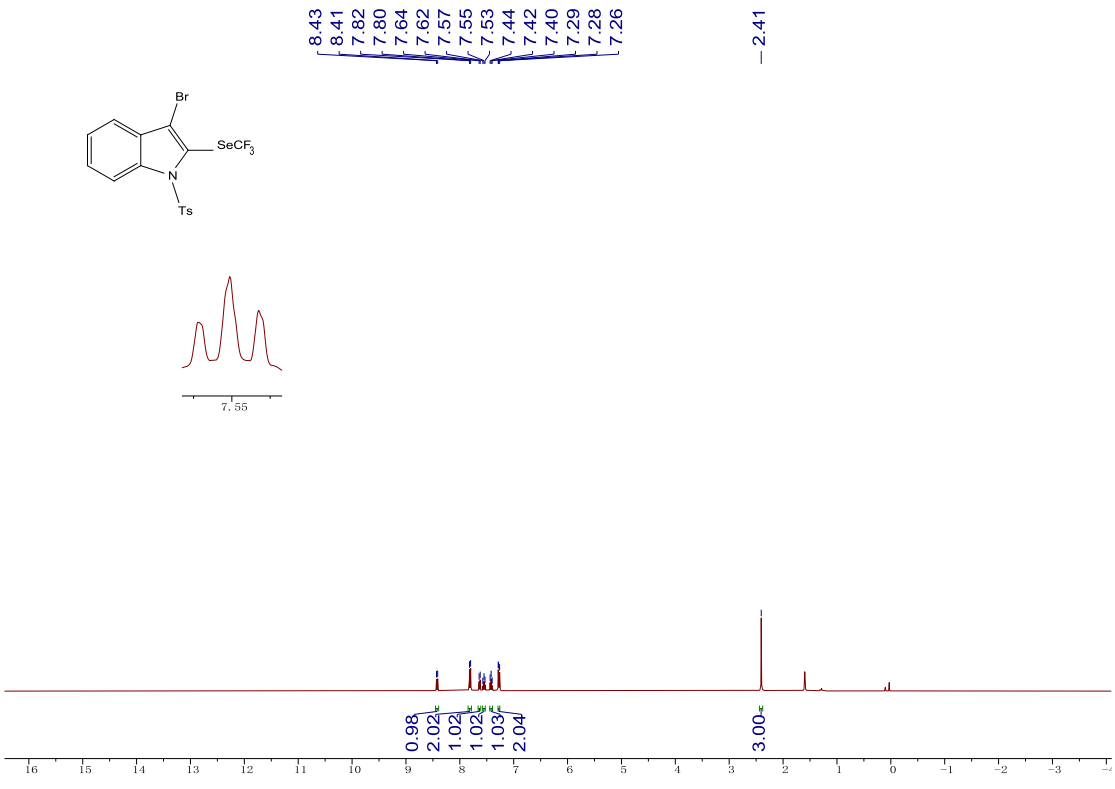
^{19}F NMR spectra of **2a** (376 MHz, $CDCl_3$)



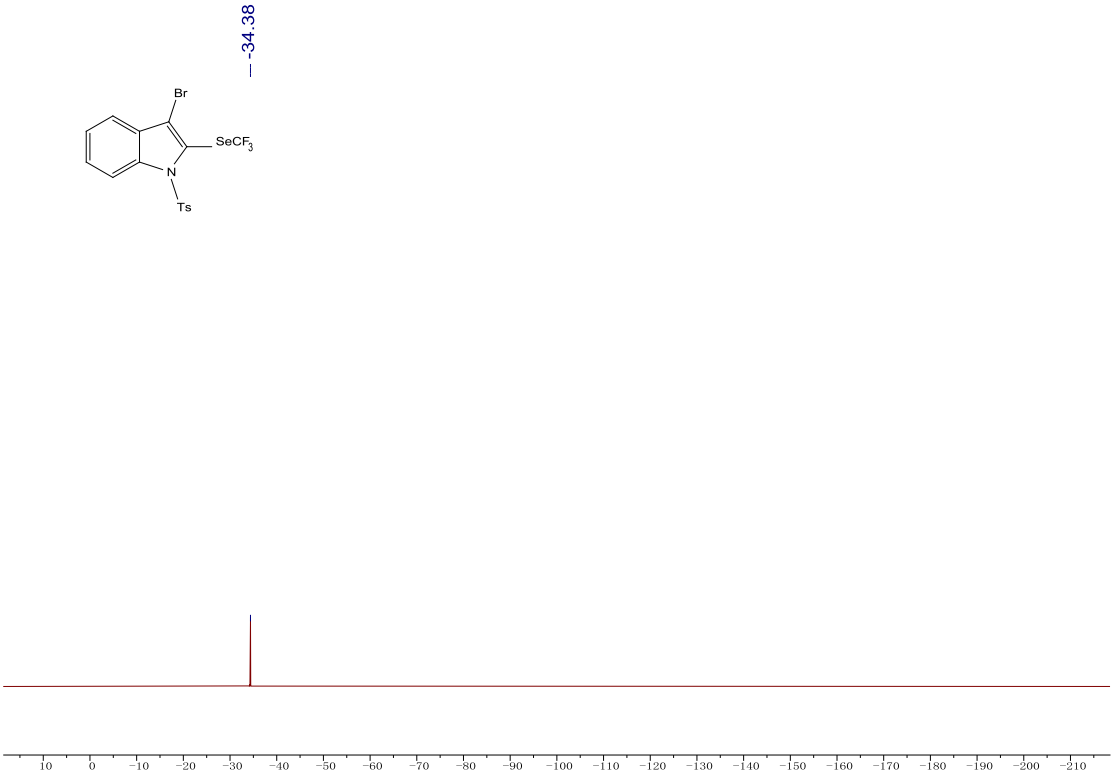
$^{13}C\{^{1}H\}$ NMR spectra of **2a** (101 MHz, $CDCl_3$)



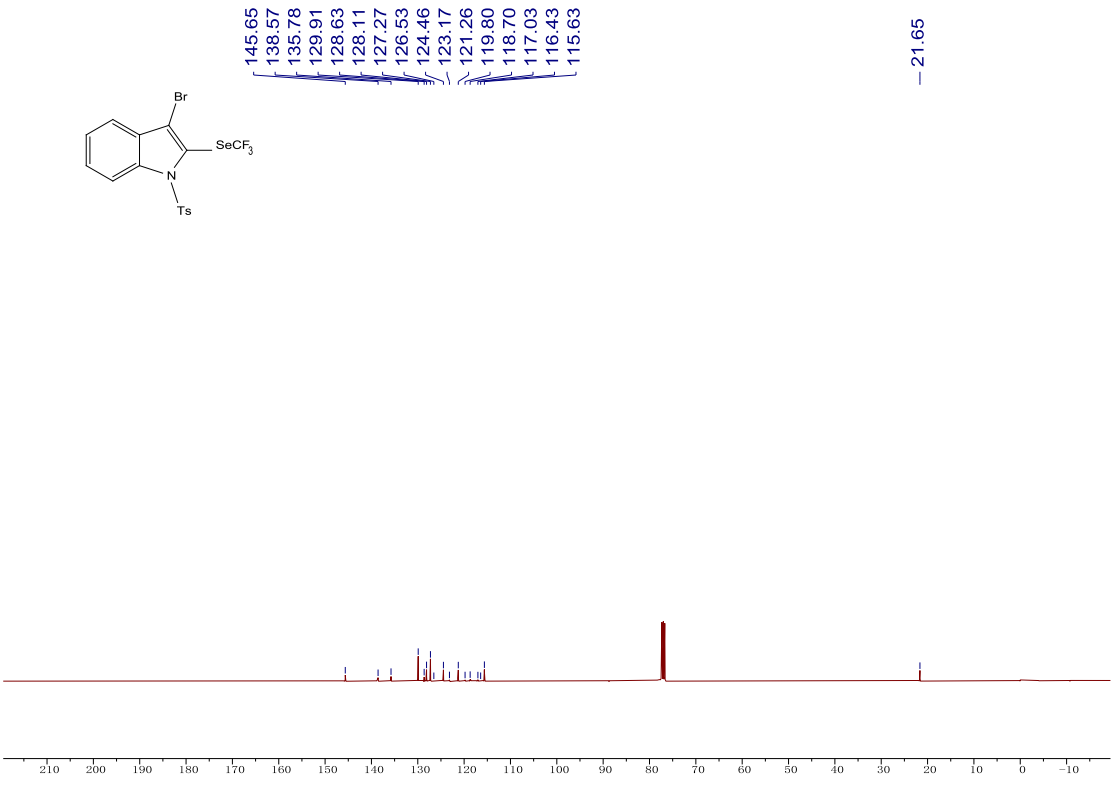
^{1}H NMR spectra of **2a′** (400 MHz, $CDCl_3$)



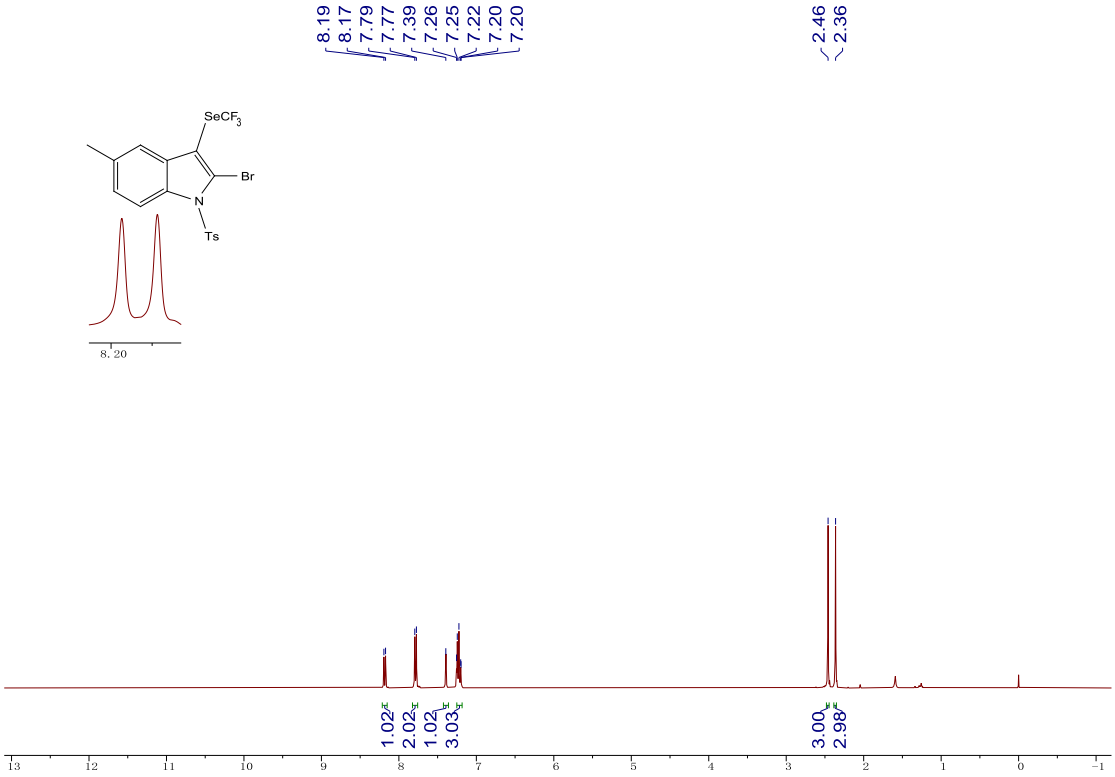
^{19}F NMR spectra of **2a′** (376 MHz, $CDCl_3$)



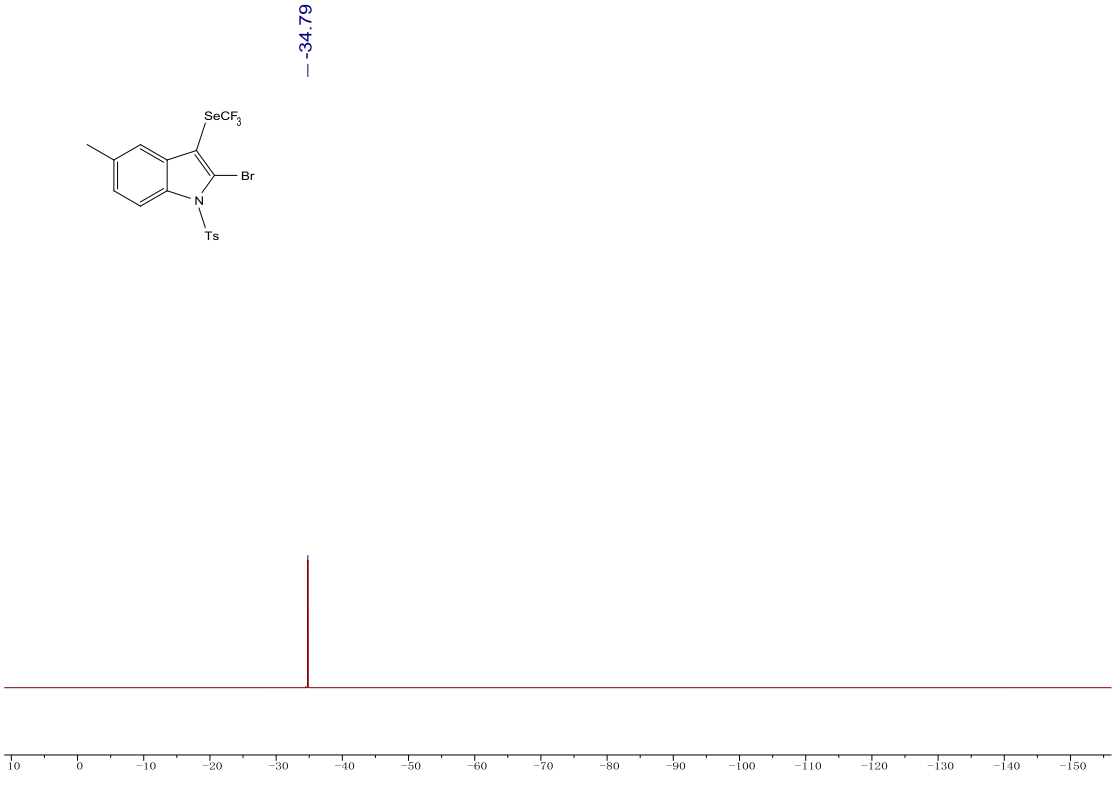
$^{13}C\{^1H\}$ NMR spectra of **2a′** (101 MHz, $CDCl_3$)



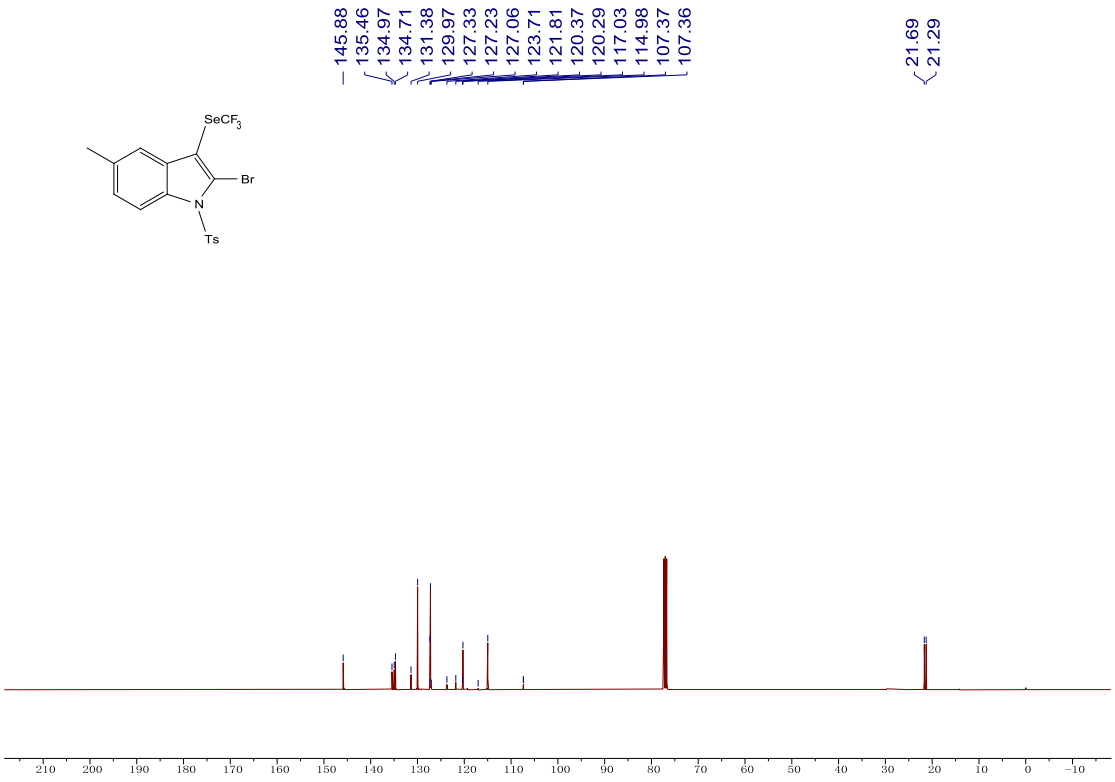
^{1}H NMR spectra of **2b** (400 MHz, $CDCl_3$)



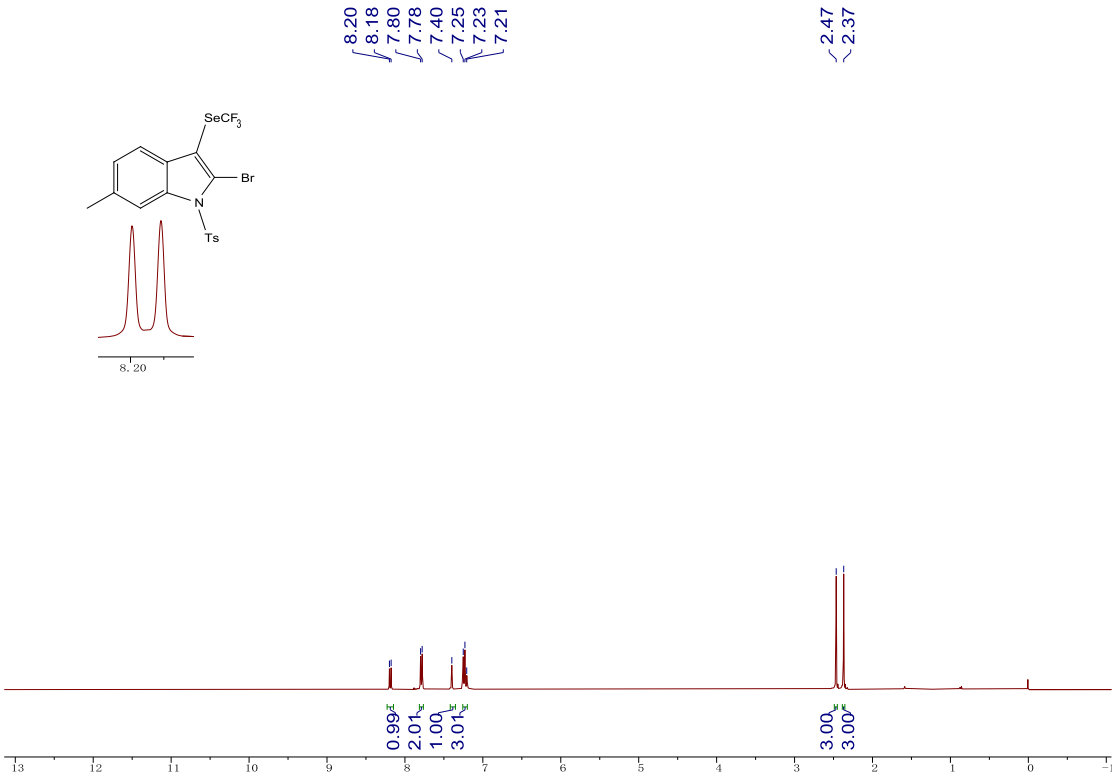
^{19}F NMR spectra of **2b** (376 MHz, $CDCl_3$)



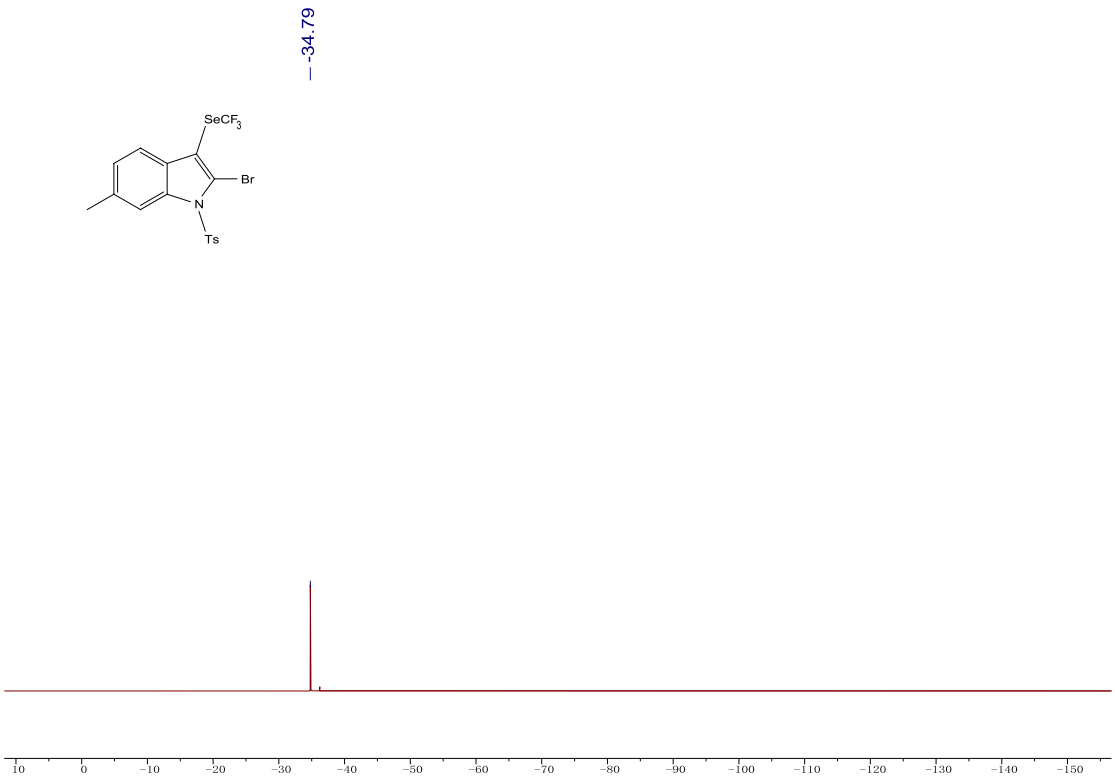
$^{13}C\{^{1}H\}$ NMR spectra of **2b** (101 MHz, $CDCl_3$)



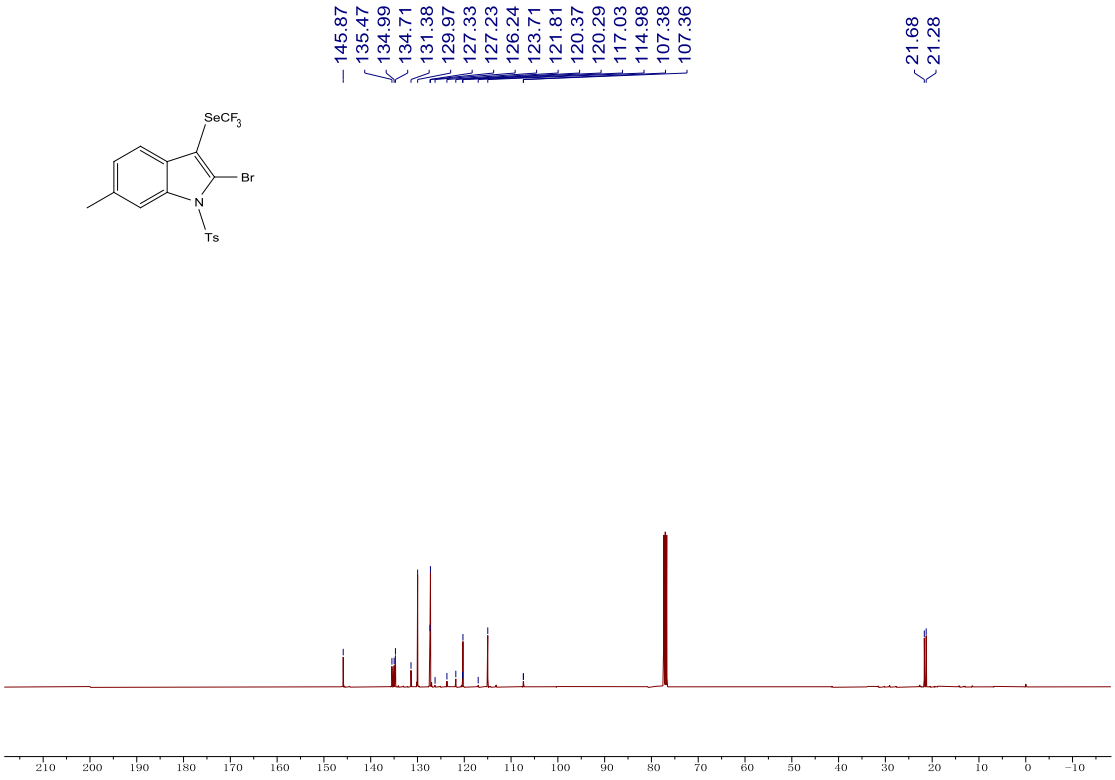
^{1}H NMR spectra of **2c** (400 MHz, $CDCl_3$)



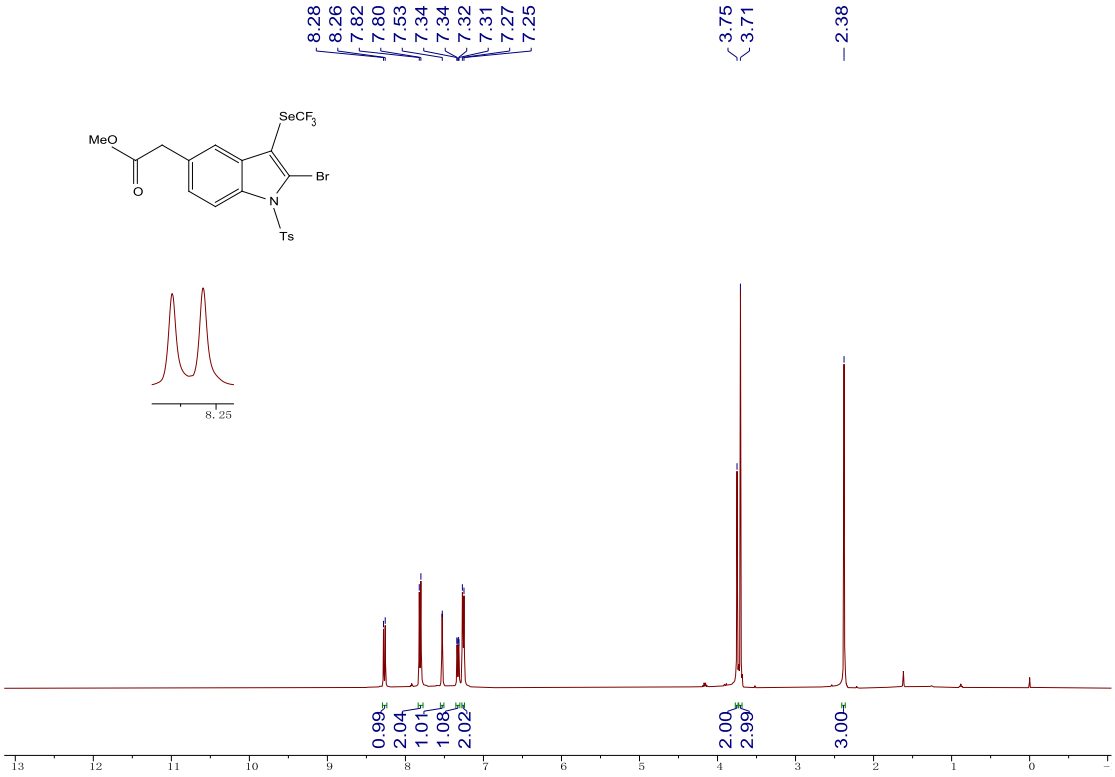
^{19}F NMR spectra of **2c** (376 MHz, $CDCl_3$)



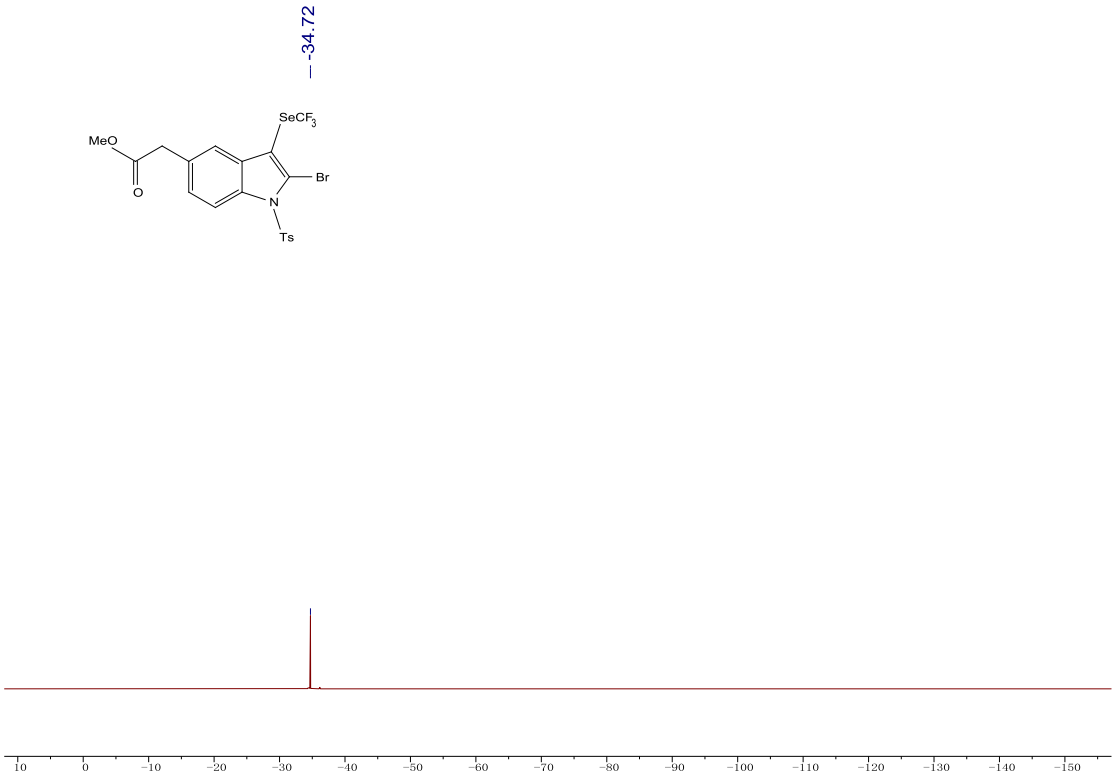
$^{13}C\{^1H\}$ NMR spectra of **2c** (101 MHz, $CDCl_3$)



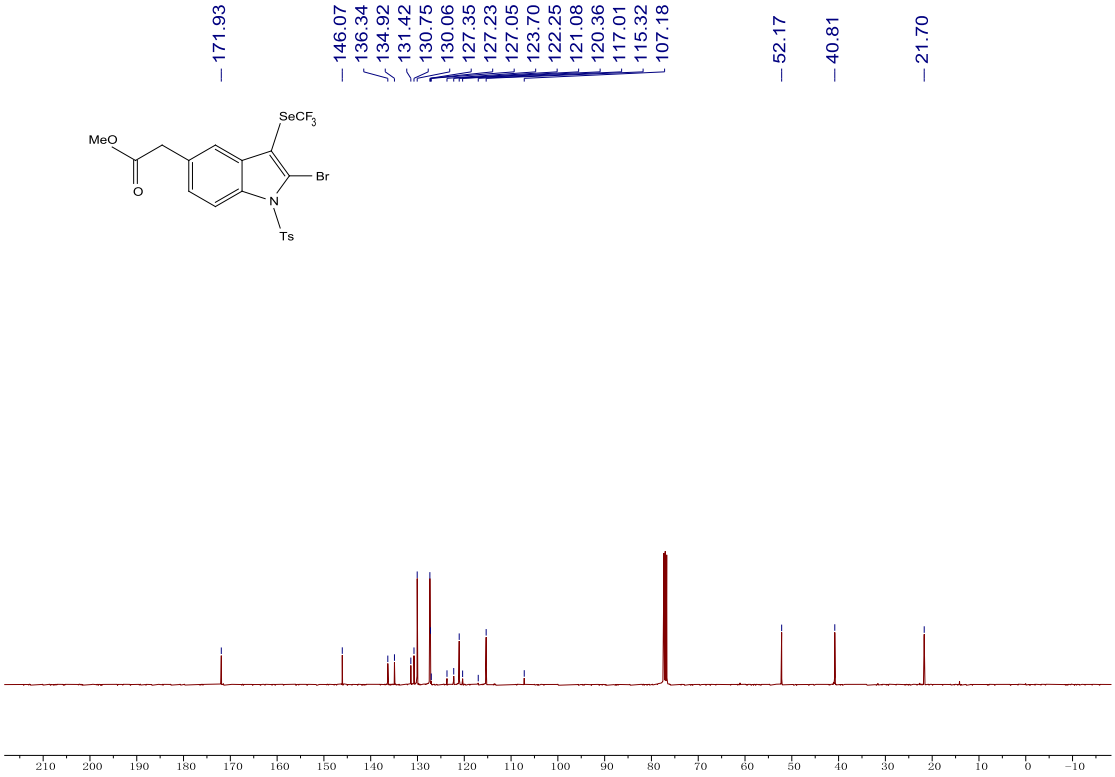
^{1}H NMR spectra of **2d** (400 MHz, $CDCl_3$)



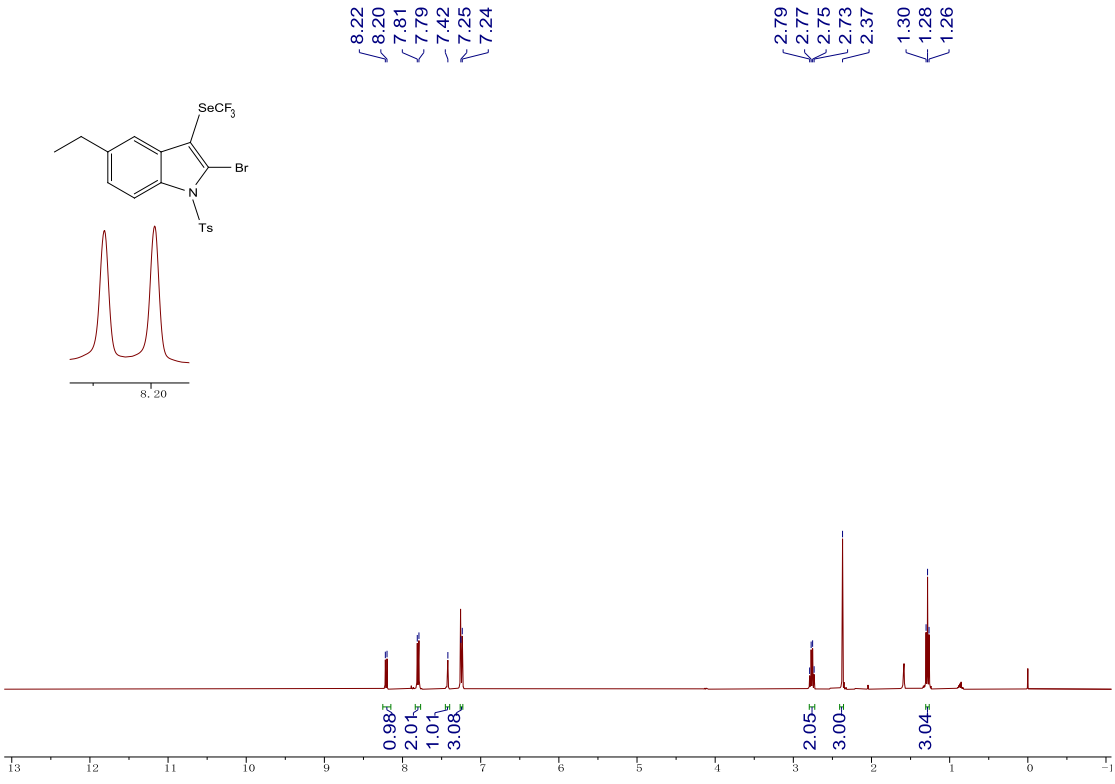
^{19}F NMR spectra of **2d** (376 MHz, $CDCl_3$)



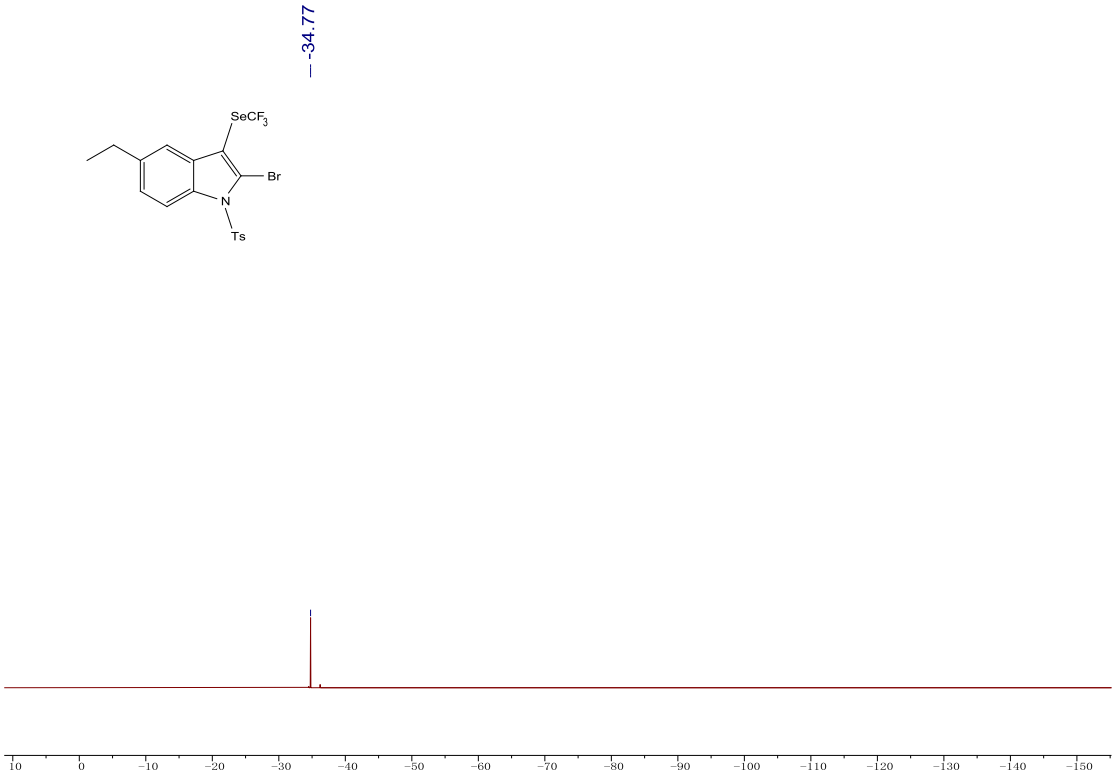
$^{13}C\{^{1}H\}$ NMR spectra of **2d** (101 MHz, $CDCl_3$)



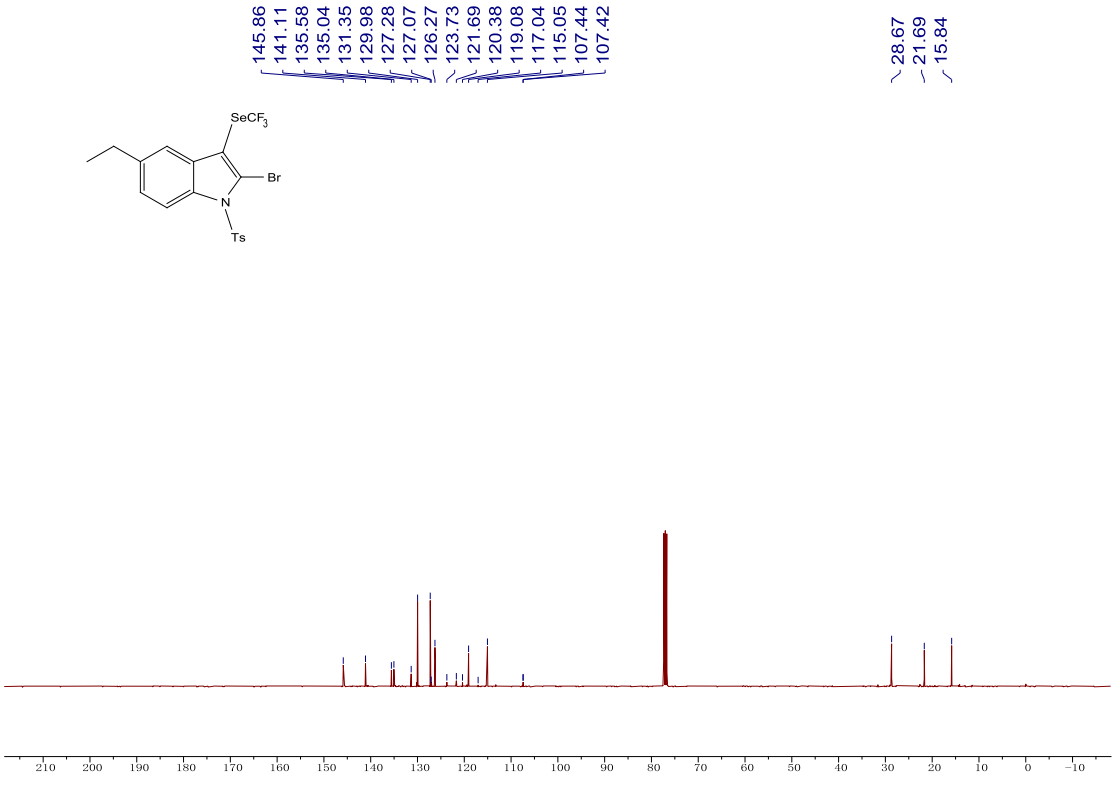
^{1}H NMR spectra of **2e** (400 MHz, $CDCl_3$)



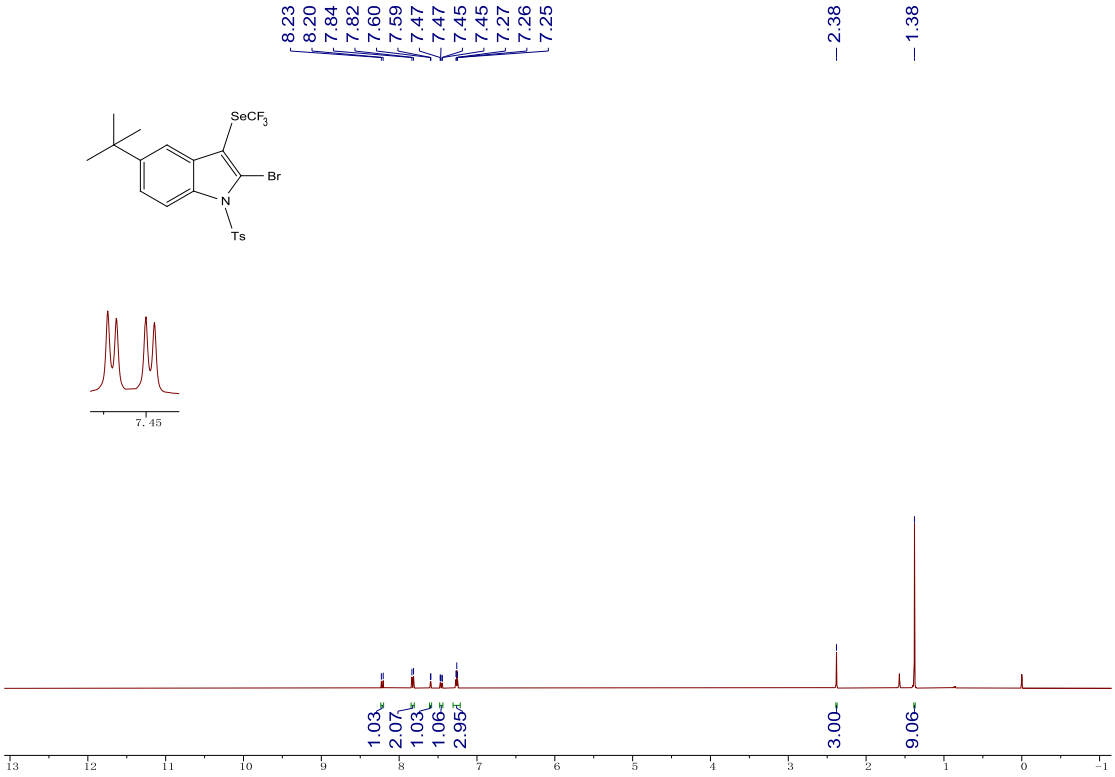
^{19}F NMR spectra of **2e** (376 MHz, $CDCl_3$)



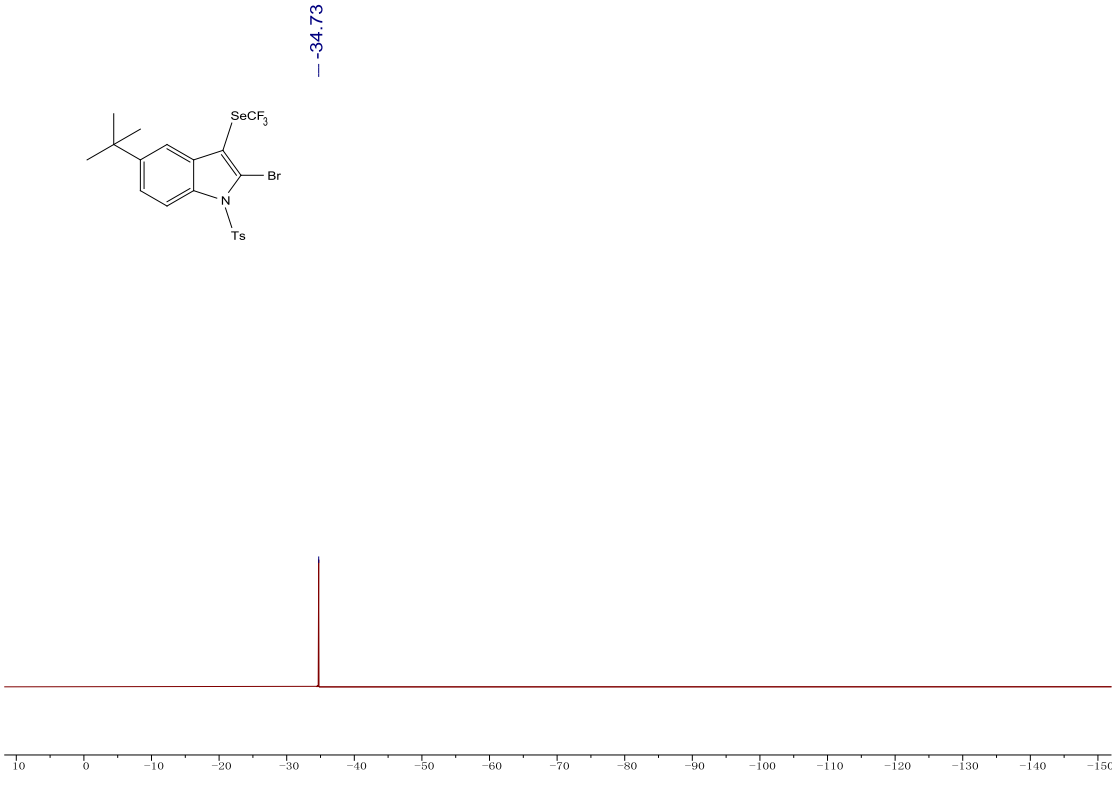
$^{13}C\{^1H\}$ NMR spectra of **2e** (101 MHz, $CDCl_3$)



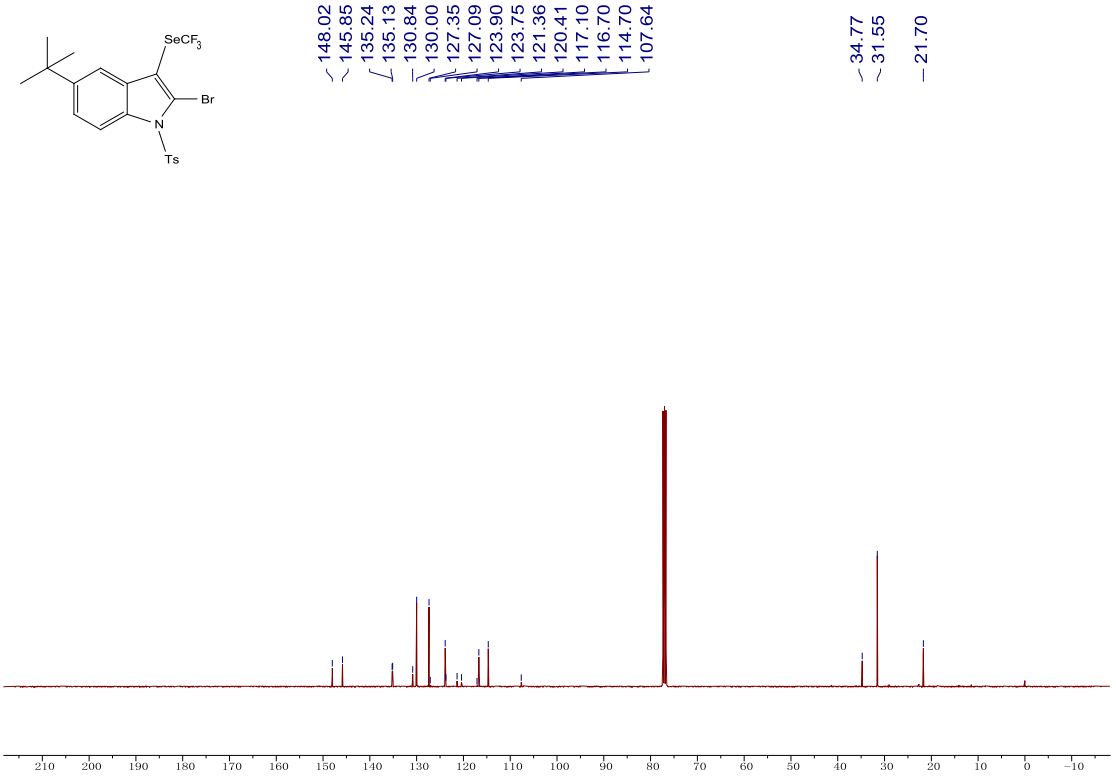
^{1}H NMR spectra of **2f** (400 MHz, $CDCl_3$)



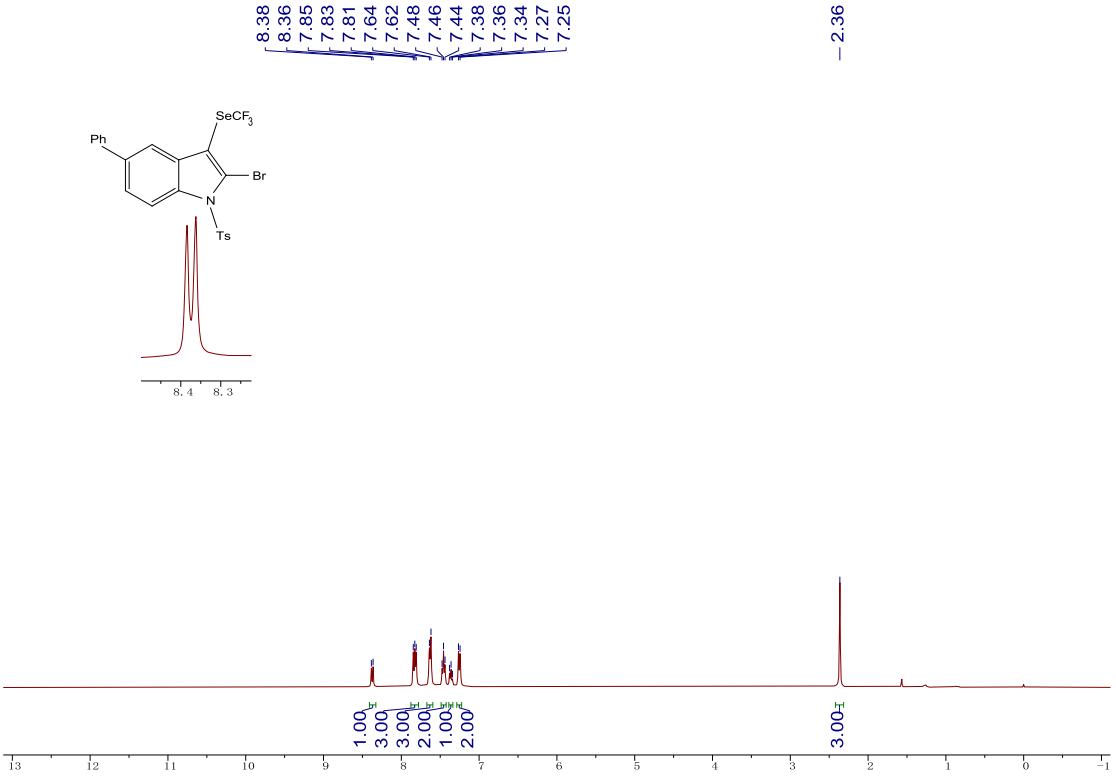
^{19}F NMR spectra of **2f** (376 MHz, $CDCl_3$)



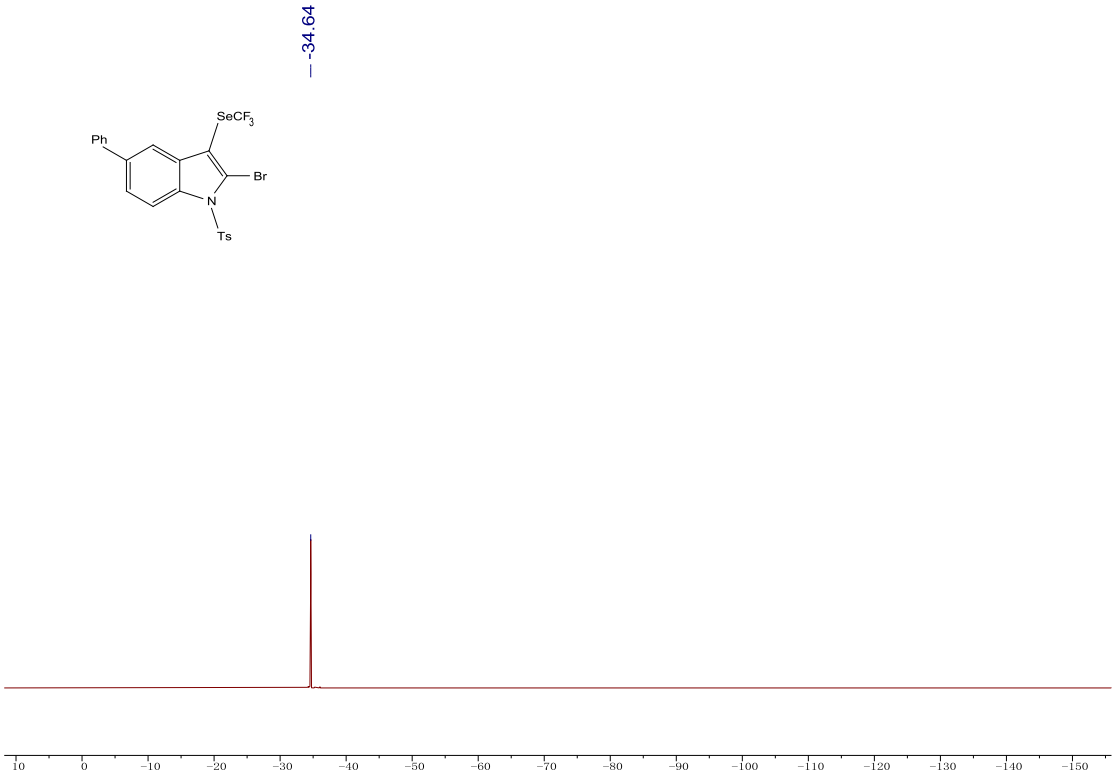
$^{13}C\{^{1}H\}$ NMR spectra of **2f** (101 MHz, $CDCl_3$)



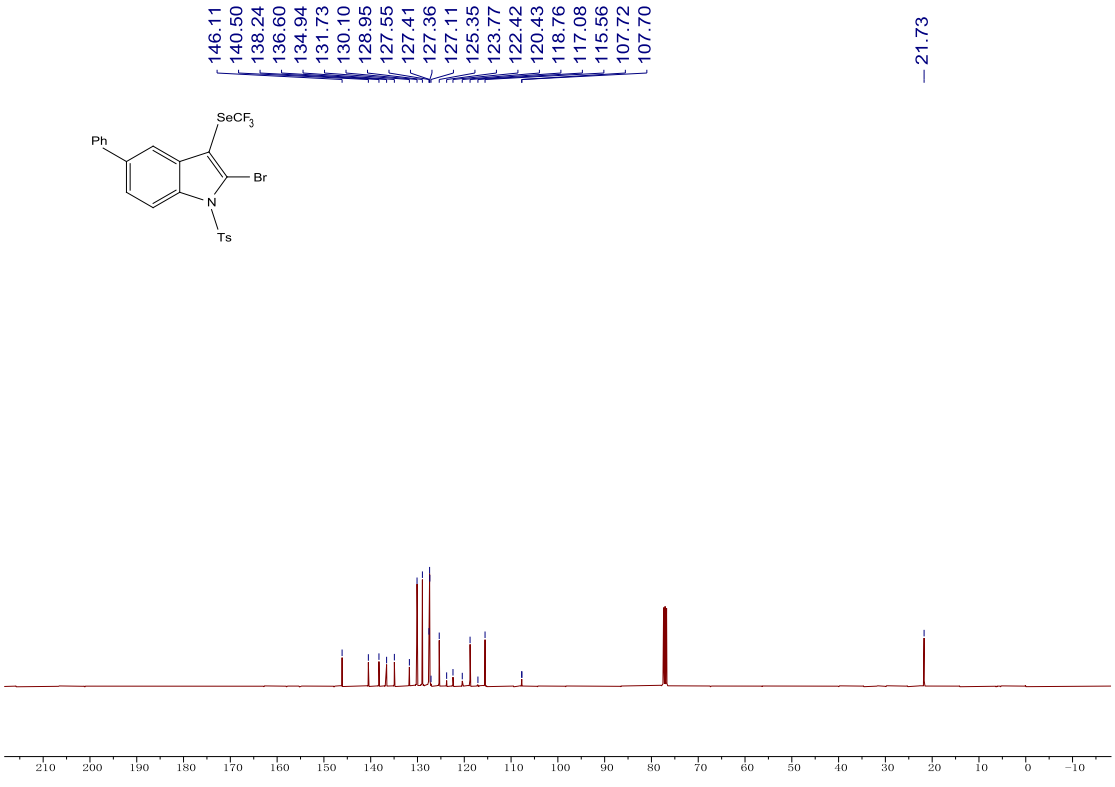
^{1}H NMR spectra of **2g** (400 MHz, $CDCl_3$)



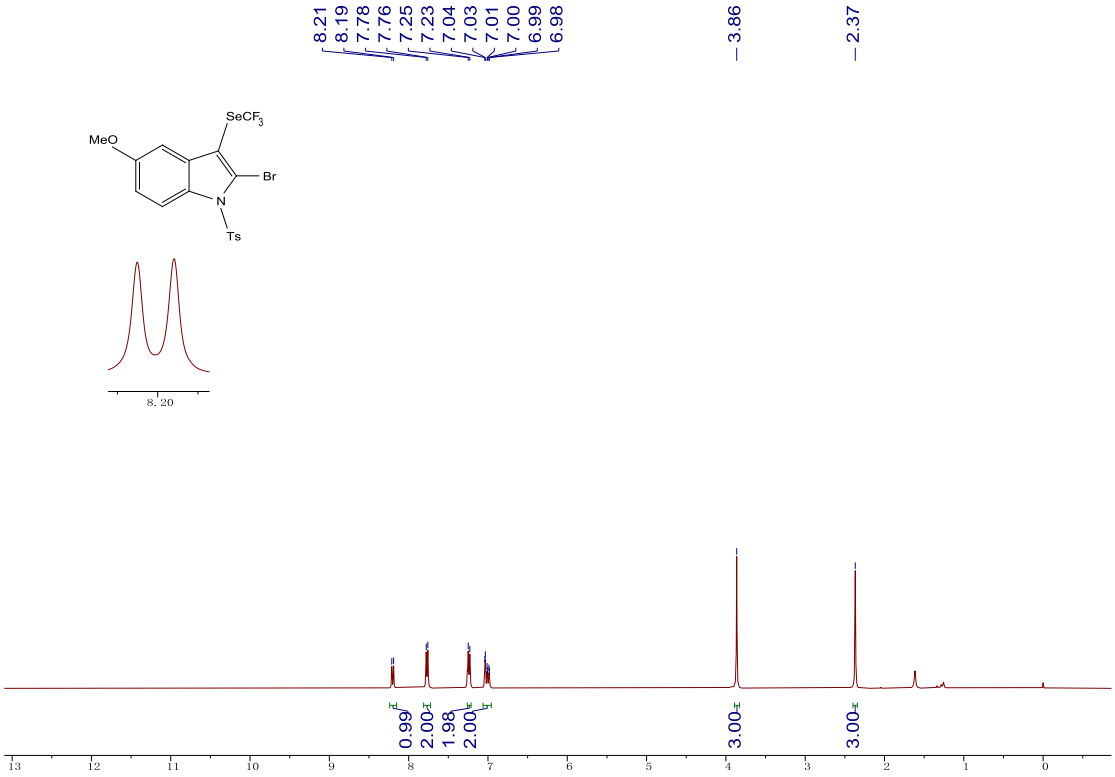
^{19}F NMR spectra of **2g** (376 MHz, $CDCl_3$)



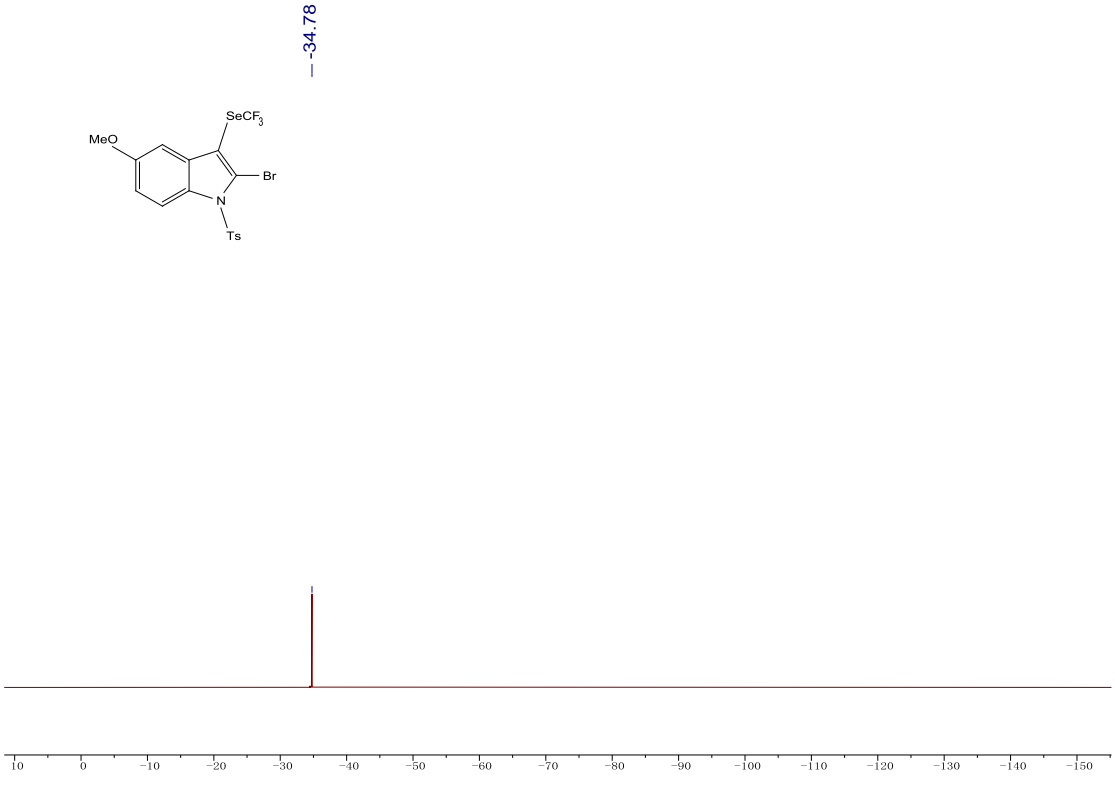
$^{13}C\{^1H\}$ NMR spectra of **2g** (101 MHz, $CDCl_3$)



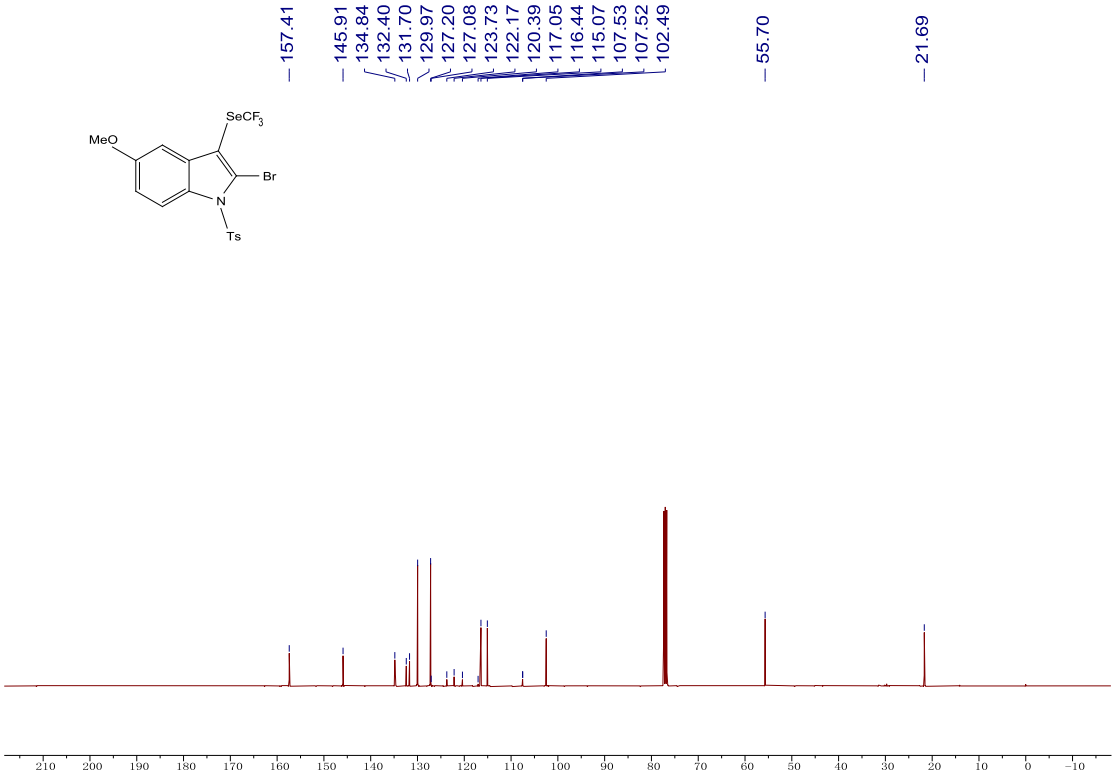
^{1}H NMR spectra of **2h** (400 MHz, $CDCl_3$)



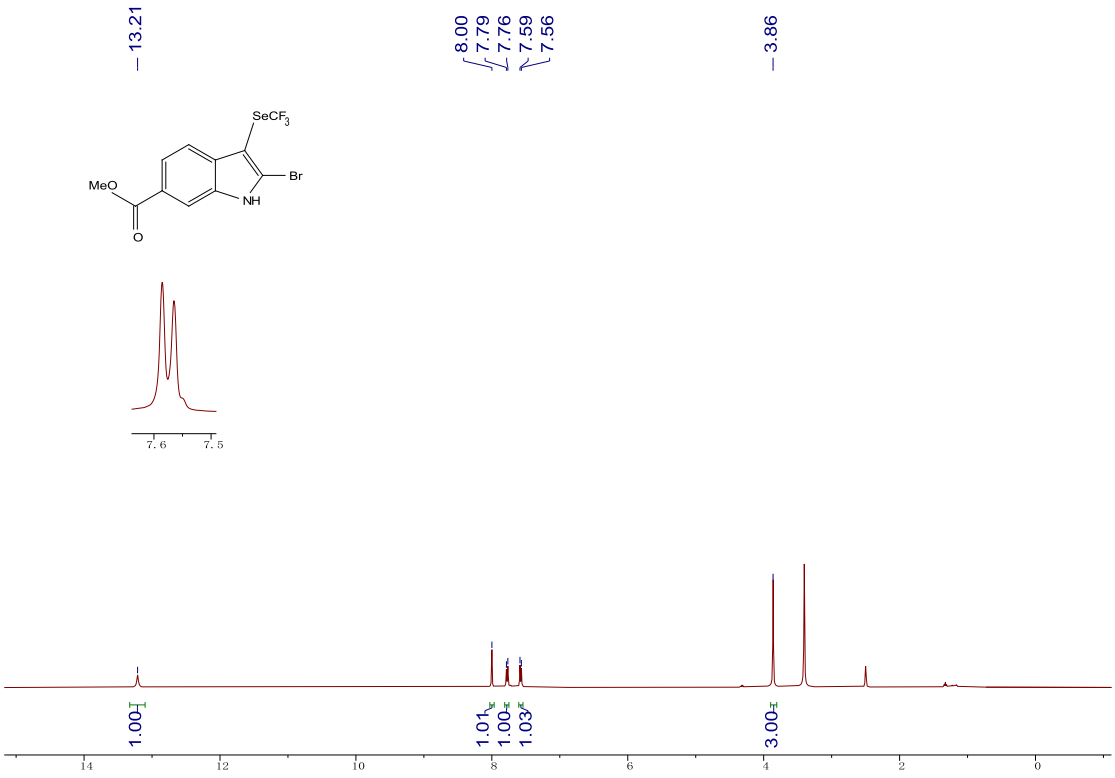
^{19}F NMR spectra of **2h** (376 MHz, $CDCl_3$)



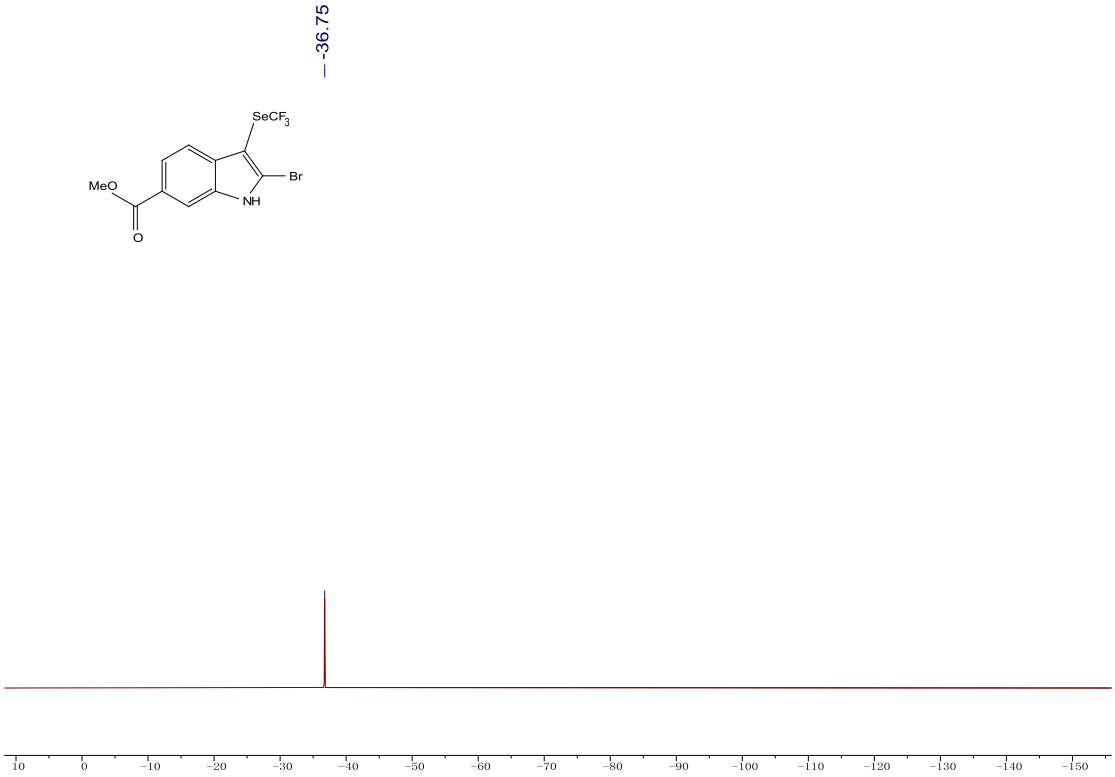
$^{13}C\{^{1}H\}$ NMR spectra of **2h** (101 MHz, $CDCl_3$)



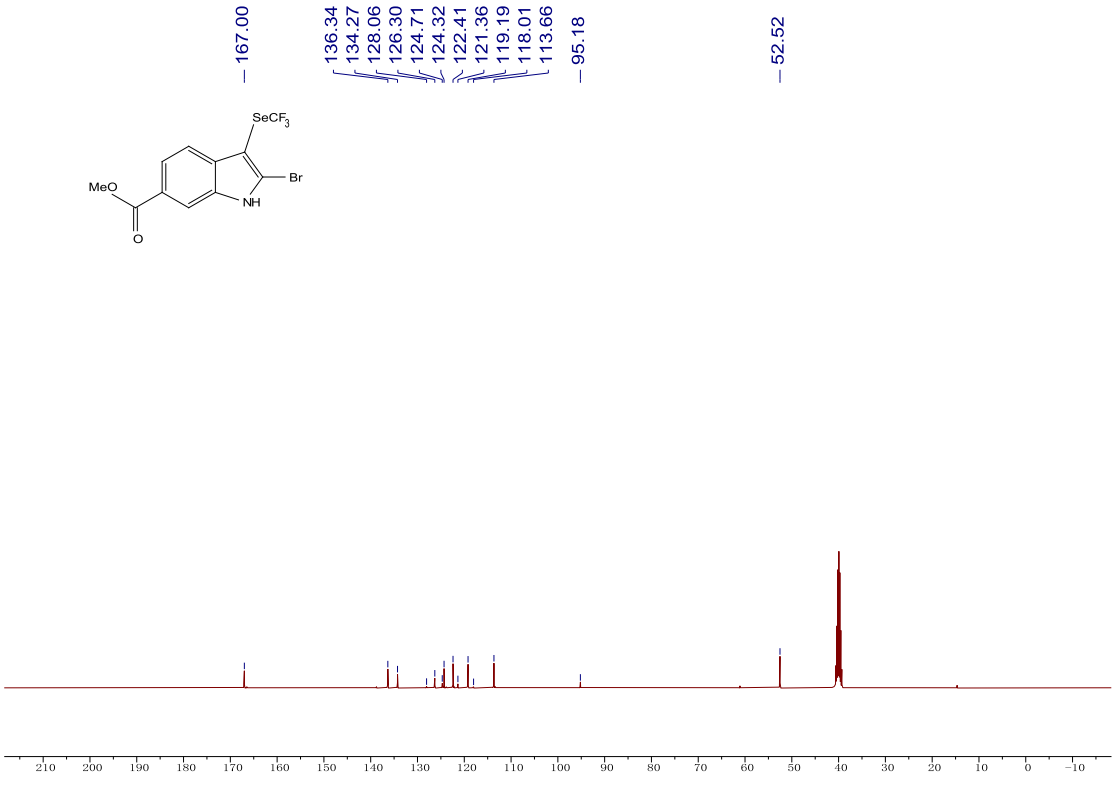
^{1}H NMR spectra of **2i** (400 MHz, DMSO-d_6)



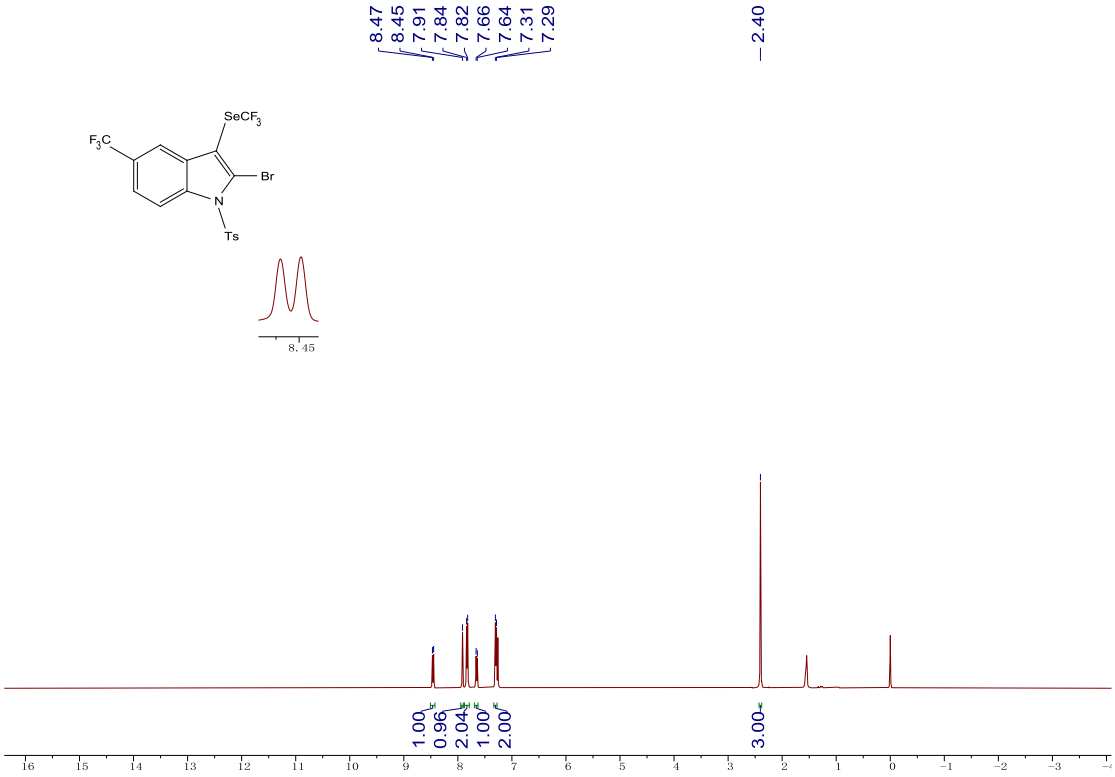
^{19}F NMR spectra of **2i** (376 MHz, DMSO-d_6)



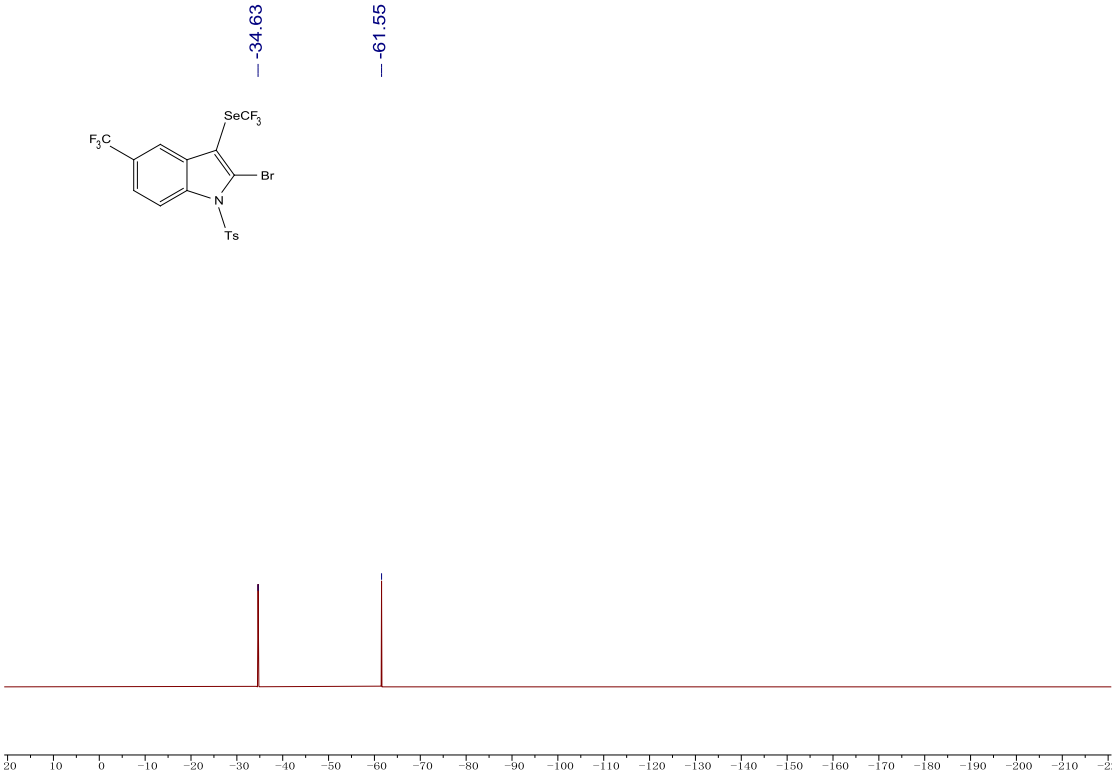
^{13}C{^{1}H} NMR spectra of **2i** (101 MHz, DMSO-d_6)



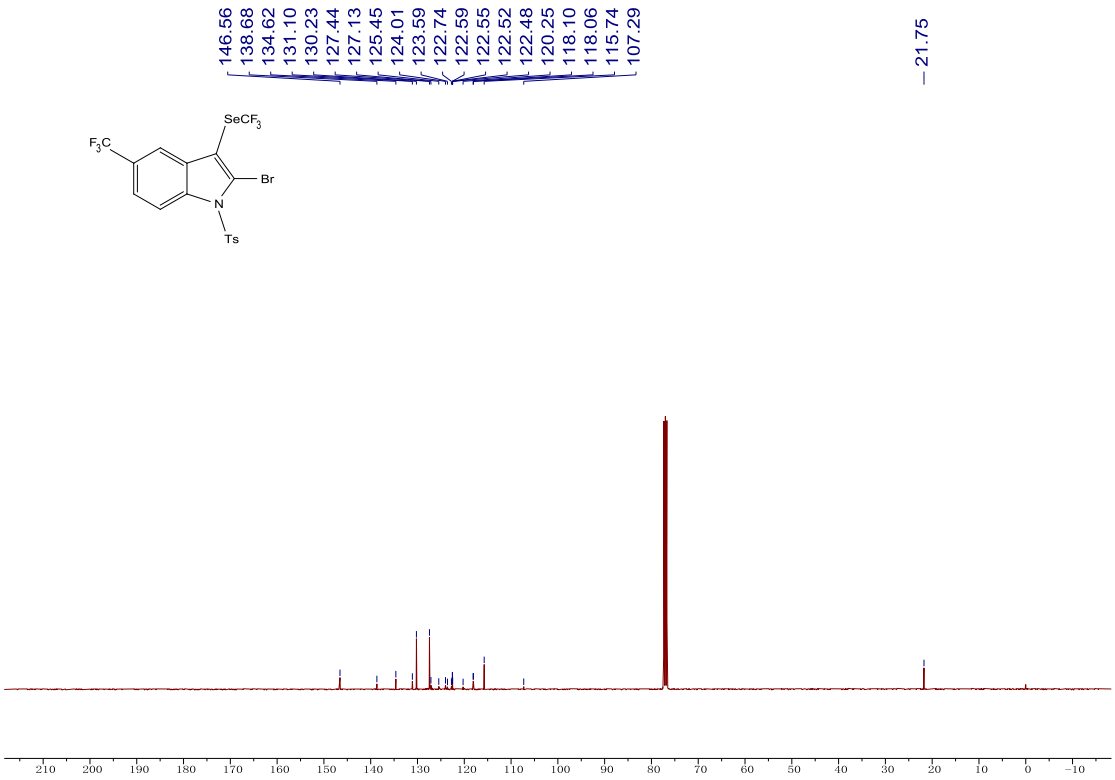
^{1}H NMR spectra of **2j** (400 MHz, $CDCl_3$)



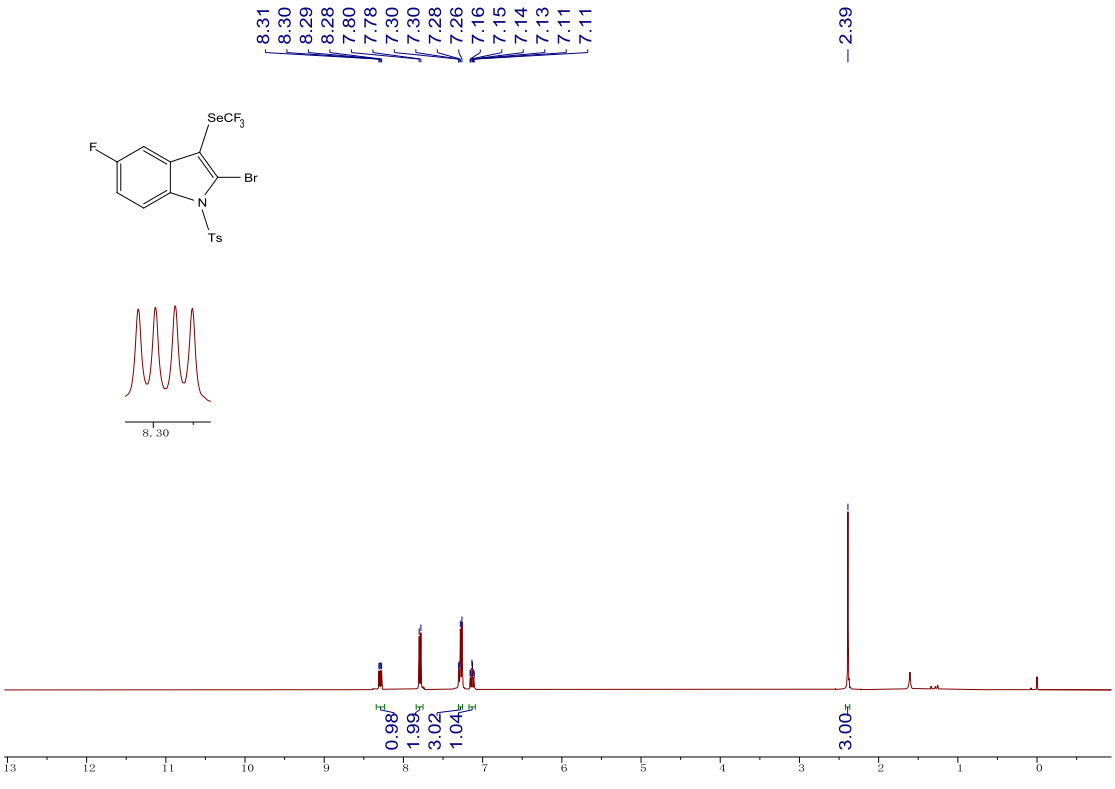
^{19}F NMR spectra of **2j** (376 MHz, $CDCl_3$)



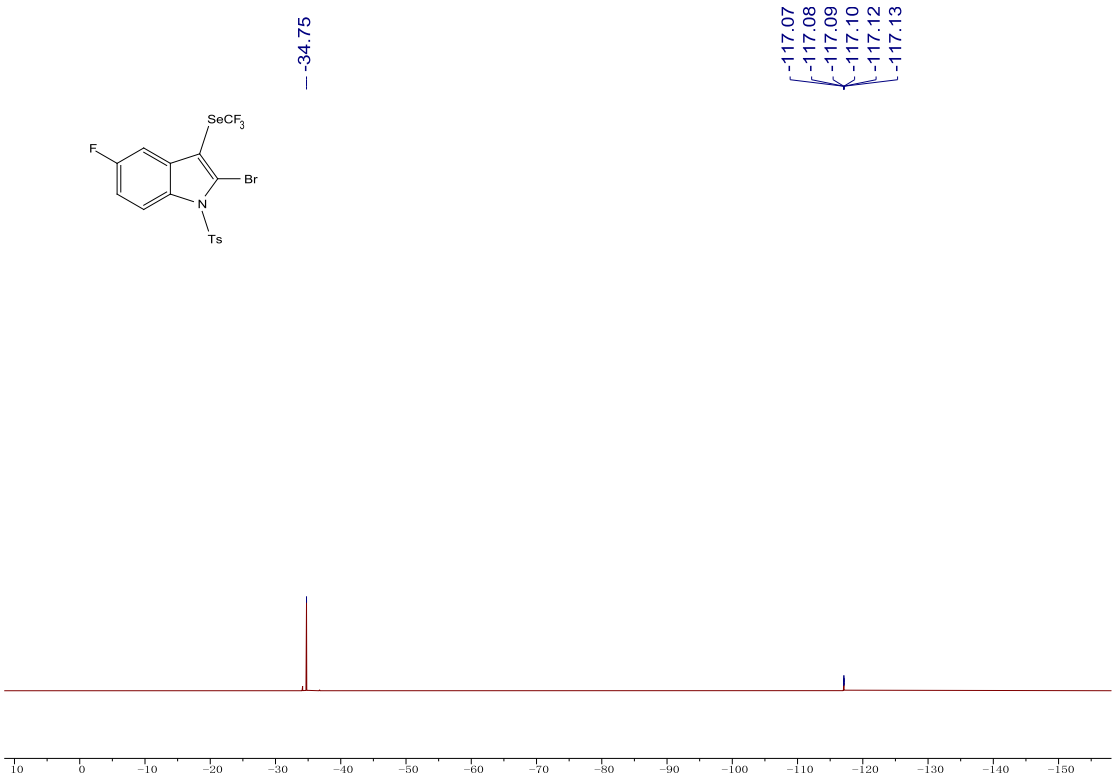
$^{13}C\{^{1}H\}$ NMR spectra of **2j** (101 MHz, $CDCl_3$)



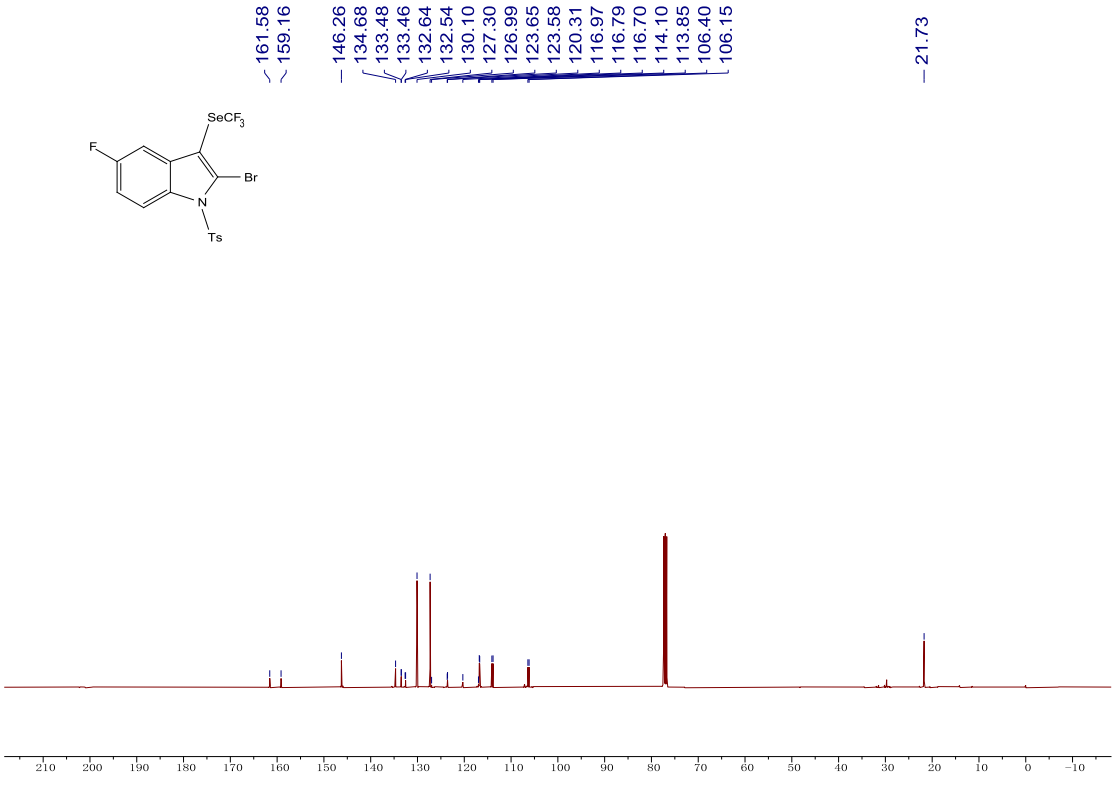
^{1}H NMR spectra of **2k** (400 MHz, $CDCl_3$)



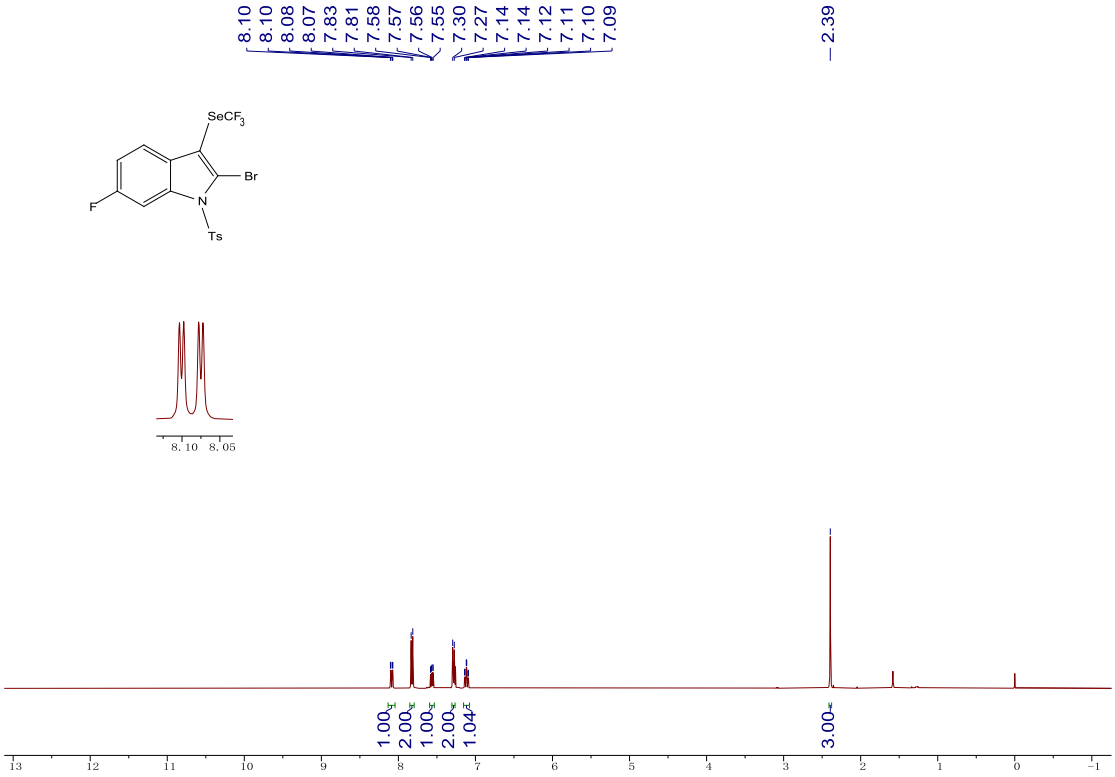
^{19}F NMR spectra of **2k** (376 MHz, $CDCl_3$)



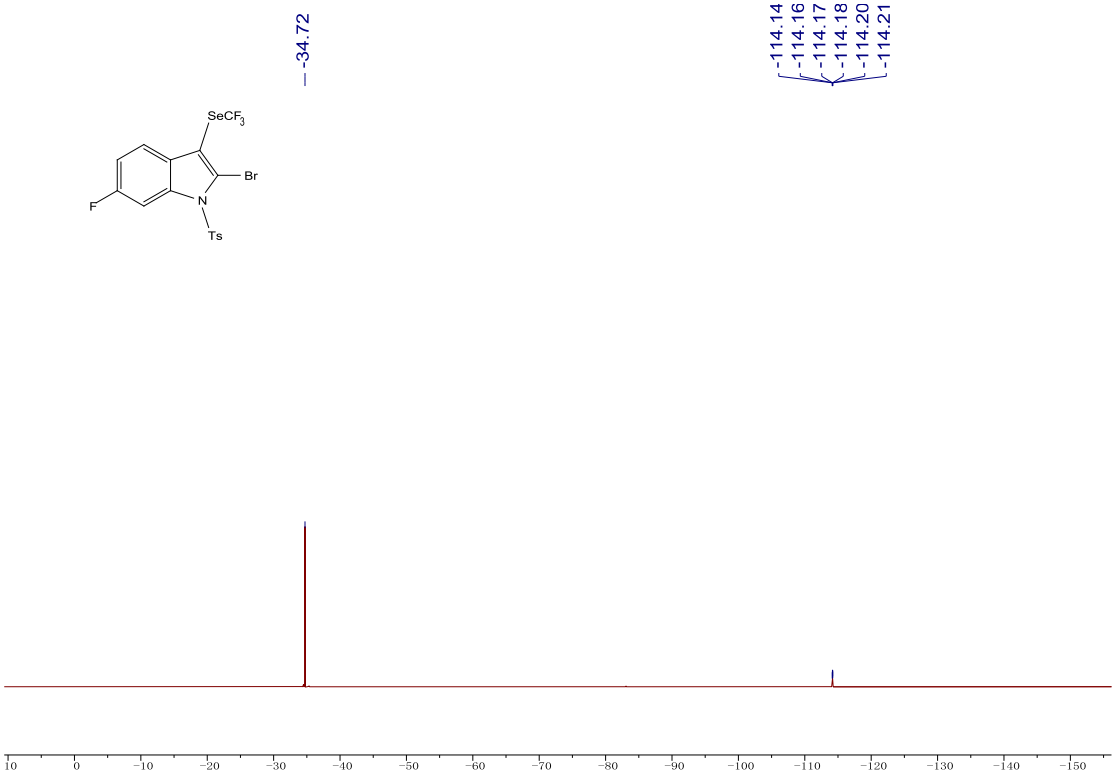
$^{13}C\{^1H\}$ NMR spectra of **2k** (101 MHz, $CDCl_3$)



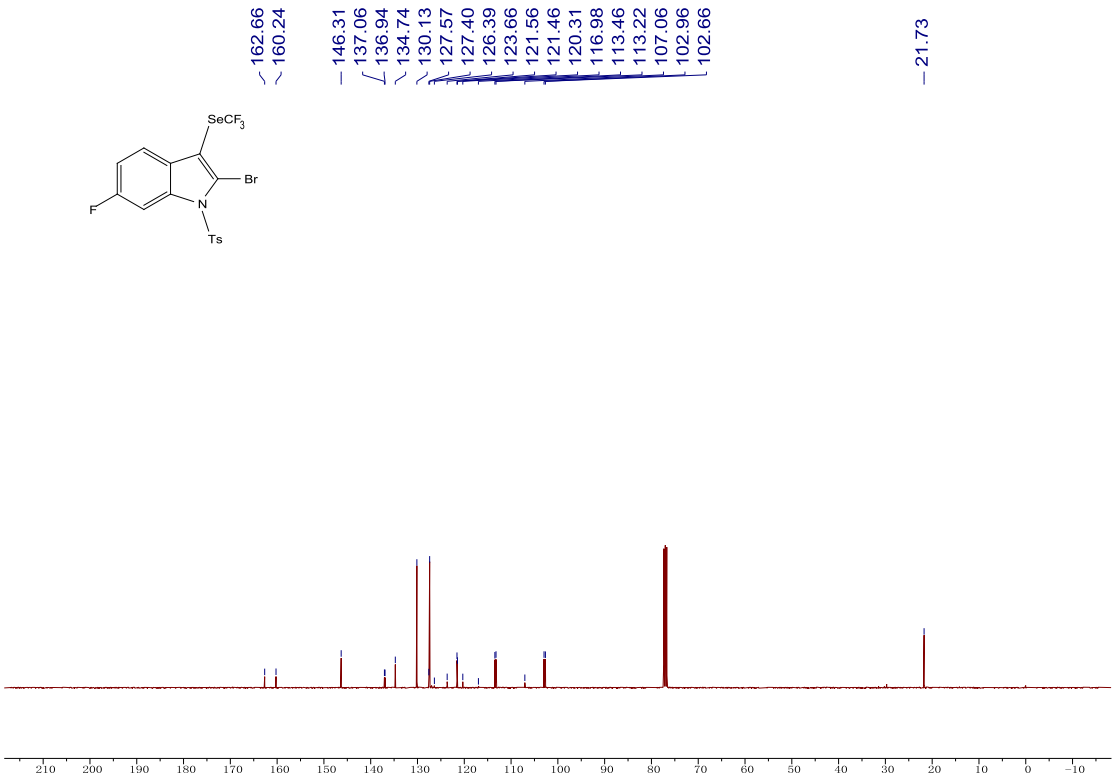
^{1}H NMR spectra of **2l** (400 MHz, $CDCl_3$)



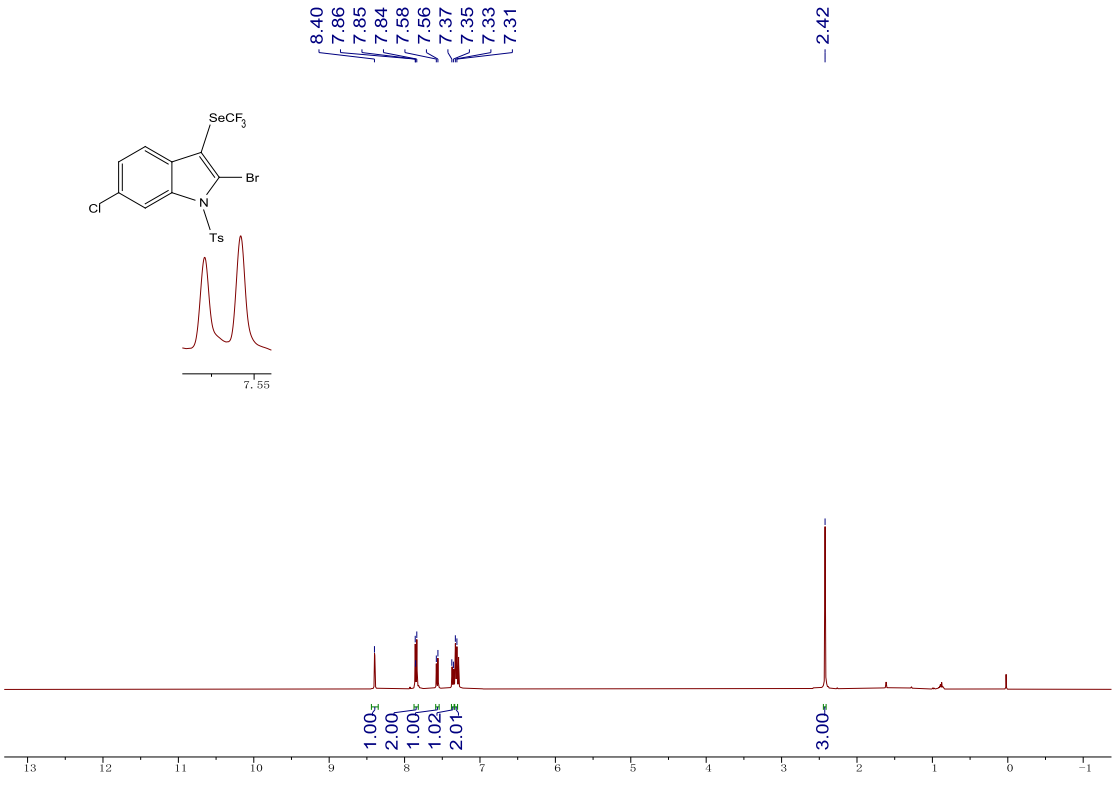
^{19}F NMR spectra of **2l** (376 MHz, $CDCl_3$)



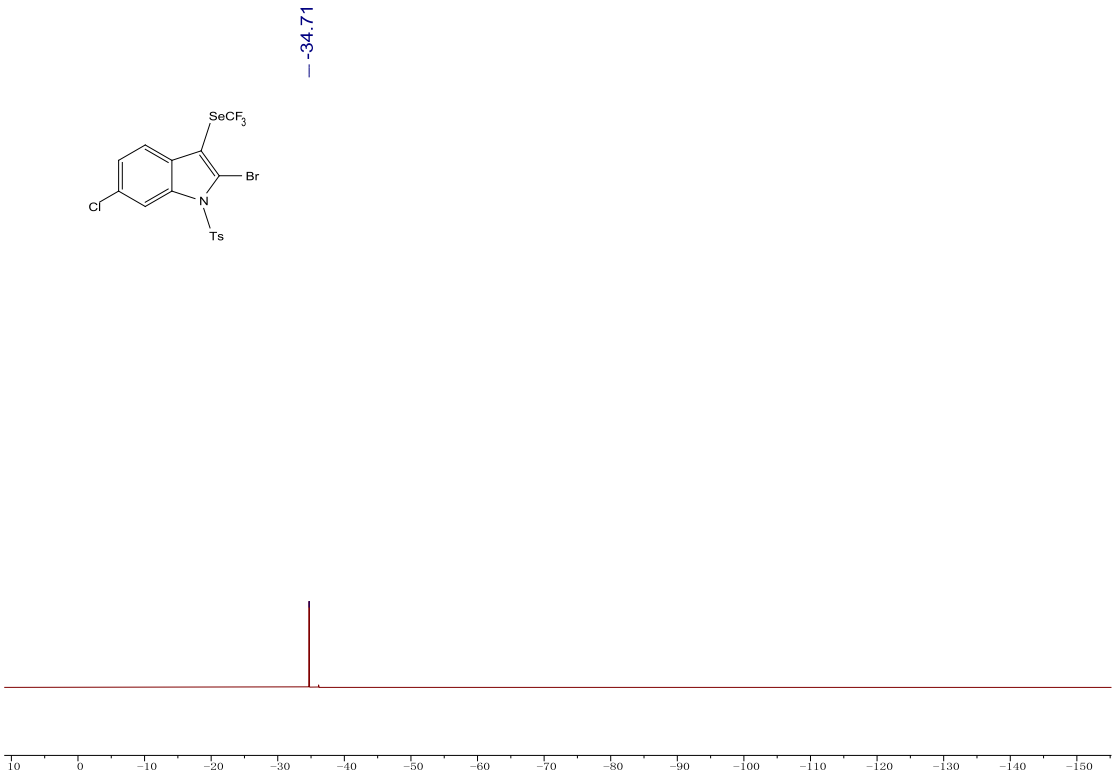
$^{13}C\{^{1}H\}$ NMR spectra of **2l** (101 MHz, $CDCl_3$)



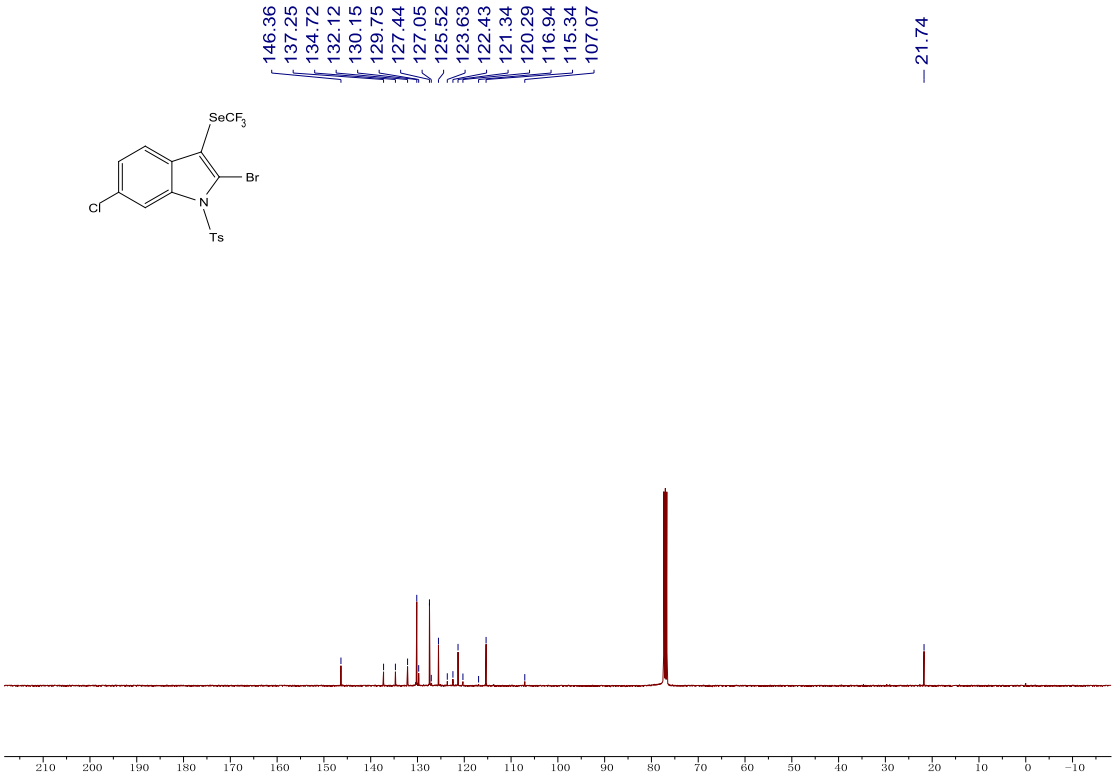
^{1}H NMR spectra of **2m** (400 MHz, $CDCl_3$)



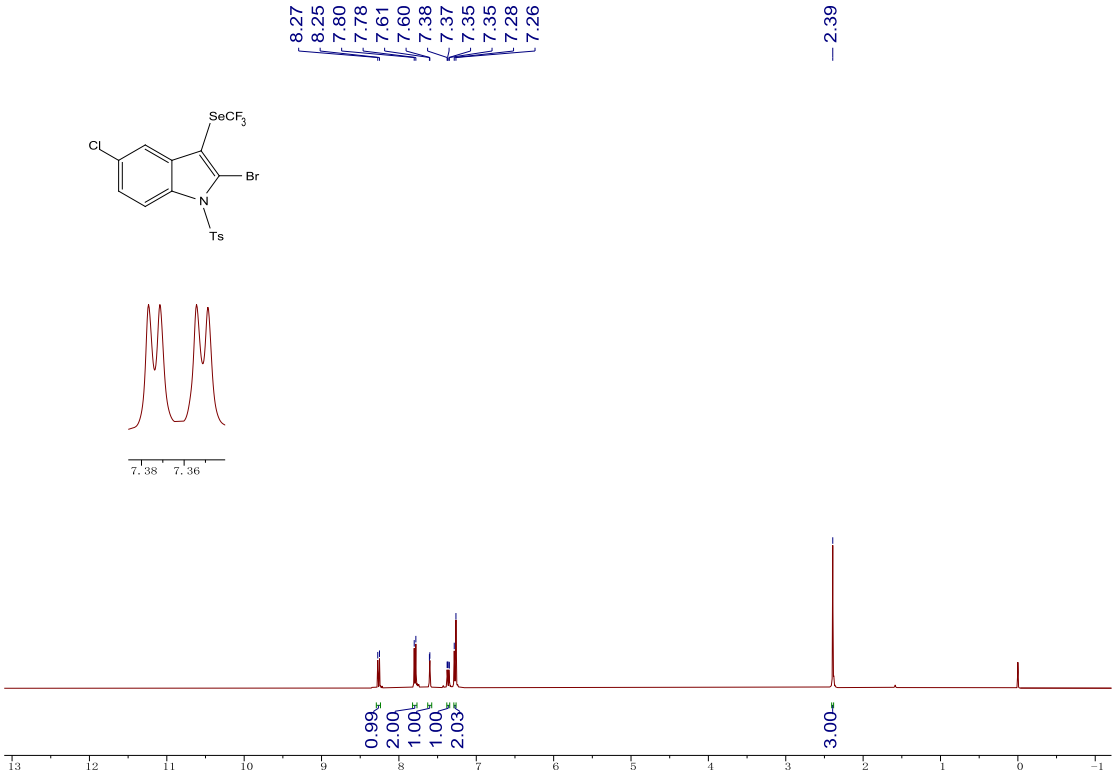
^{19}F NMR spectra of **2m** (376 MHz, $CDCl_3$)



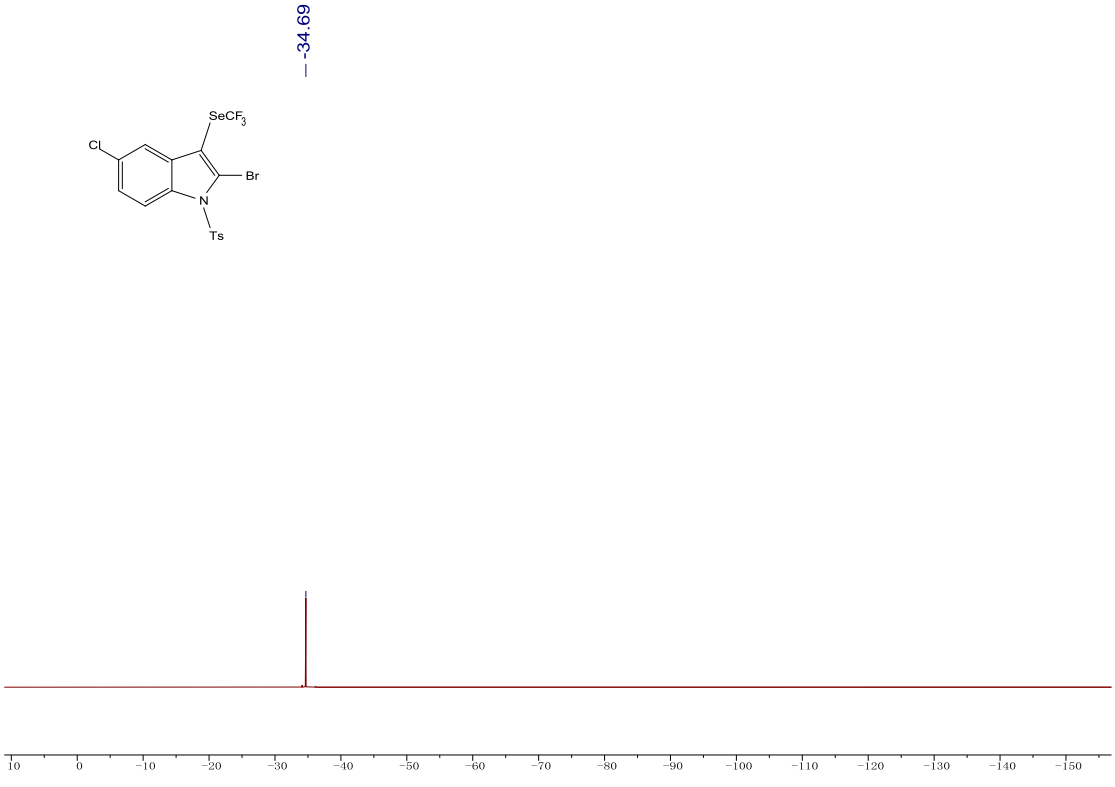
^{13}C NMR spectra of **2m** (101 MHz, $CDCl_3$)



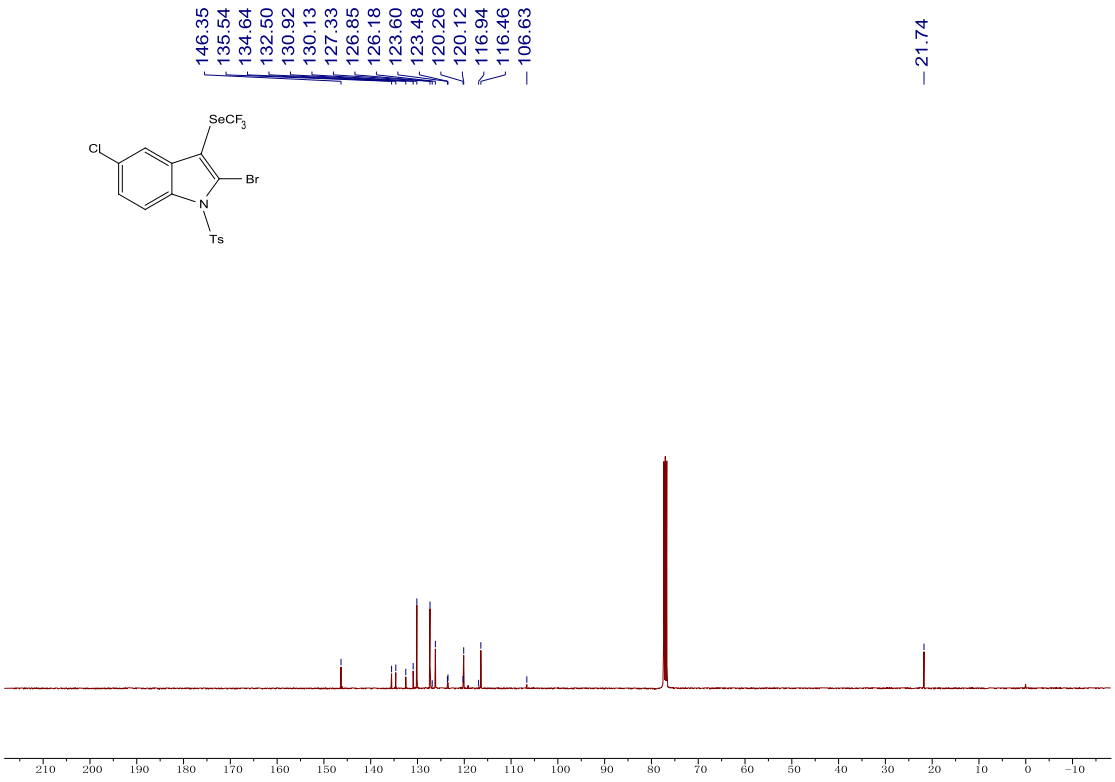
^{1}H NMR spectra of **2n** (400 MHz, $CDCl_3$)



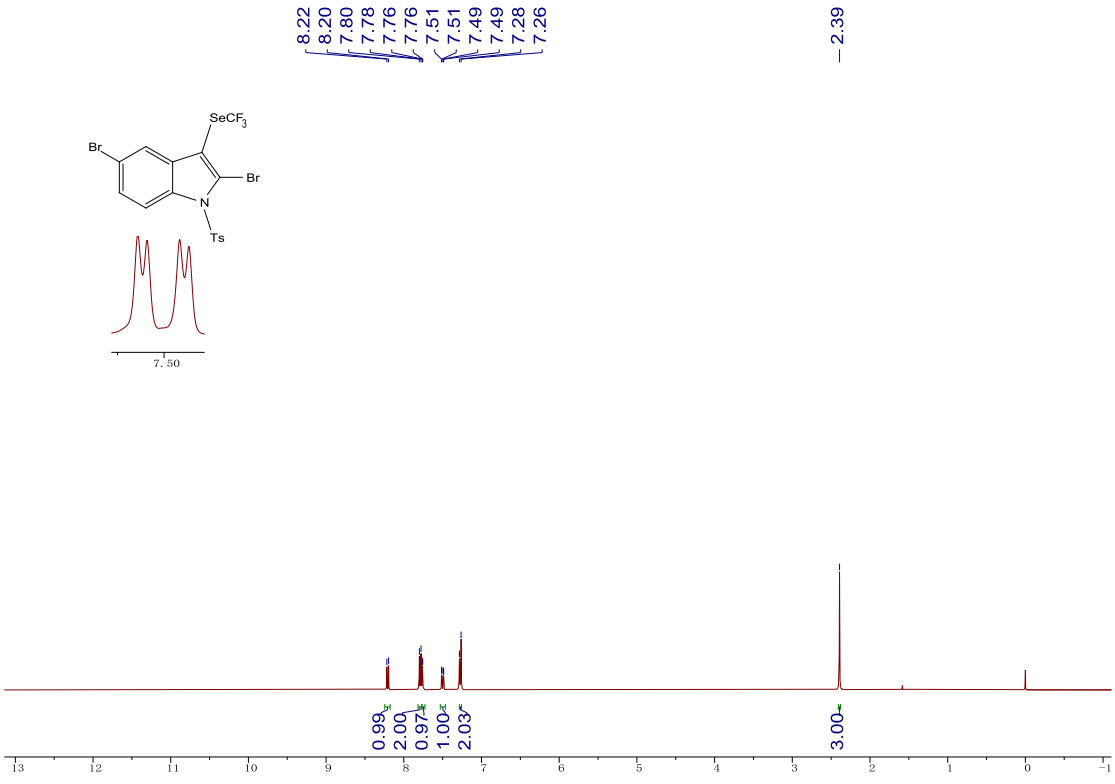
^{19}F NMR spectra of **2n** (376 MHz, $CDCl_3$)



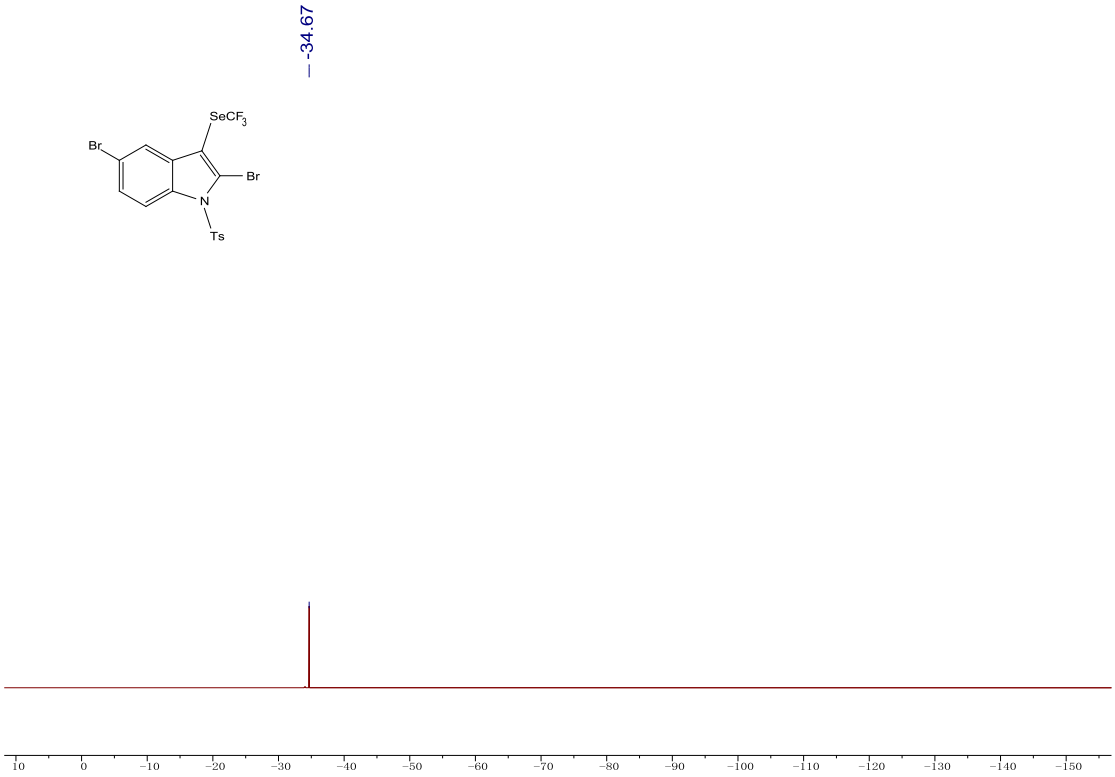
$^{13}C\{^{1}H\}$ NMR spectra of **2n** (101 MHz, $CDCl_3$)



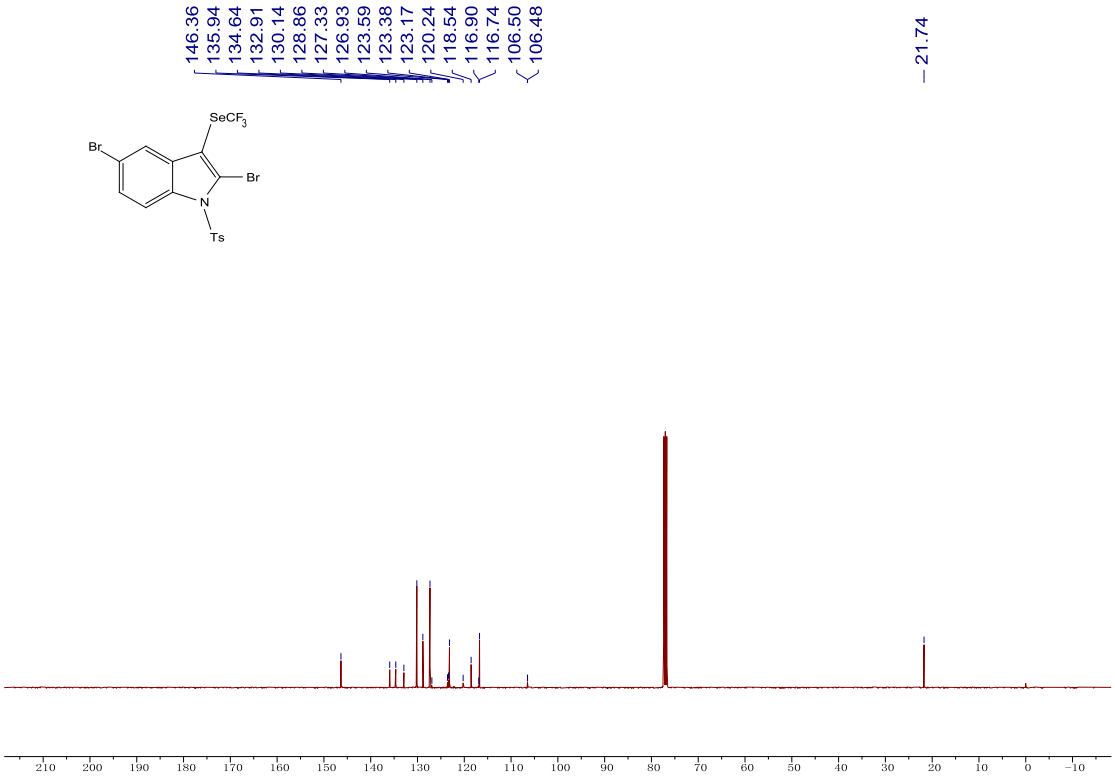
^{1}H NMR spectra of **2o** (400 MHz, $CDCl_3$)



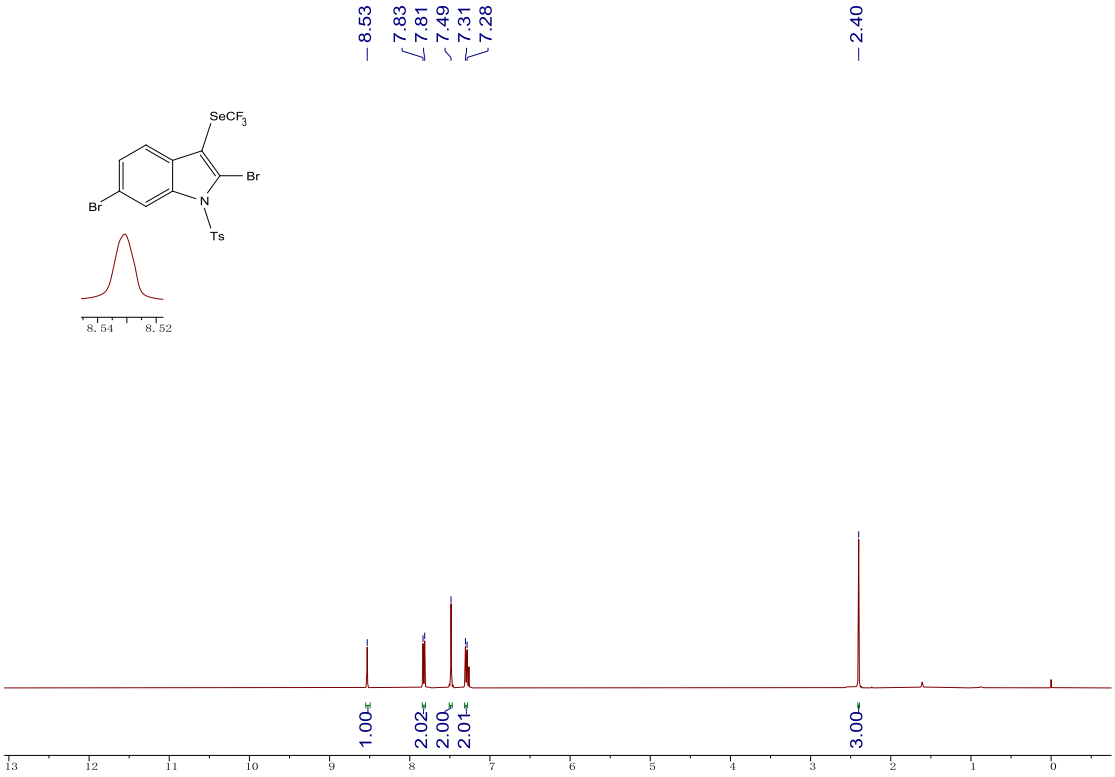
^{19}F NMR spectra of **2o** (376 MHz, $CDCl_3$)



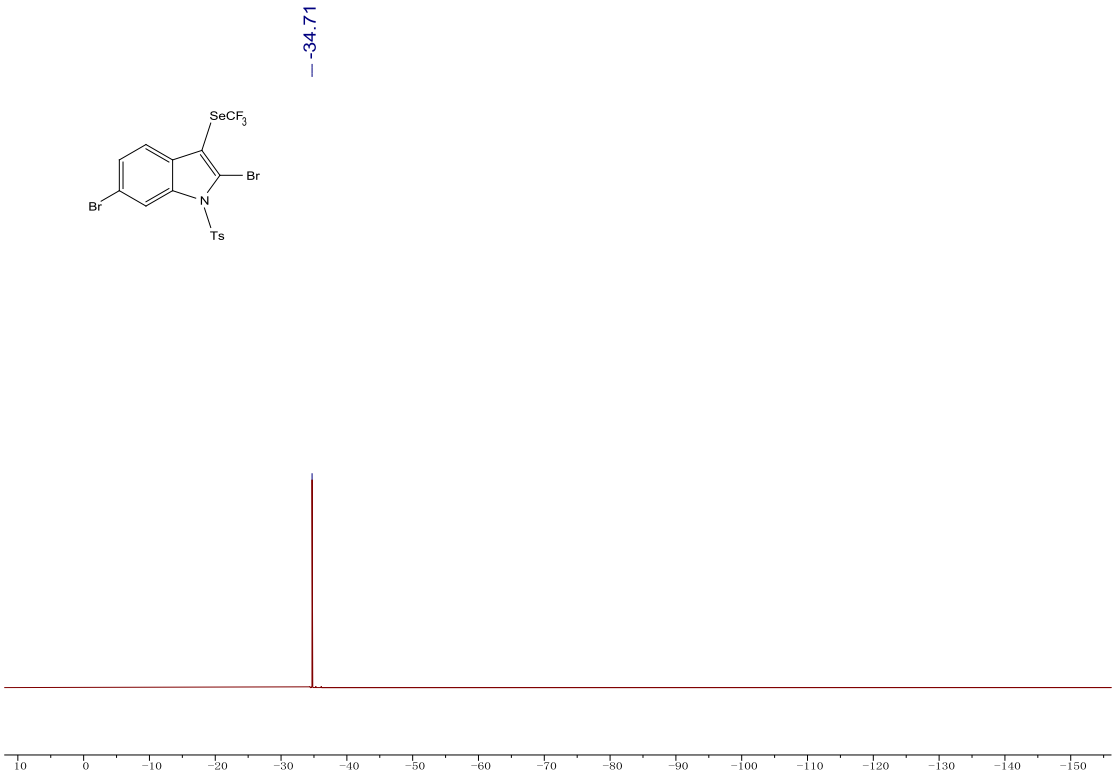
$^{13}C\{^1H\}$ NMR spectra of **2o** (101 MHz, $CDCl_3$)



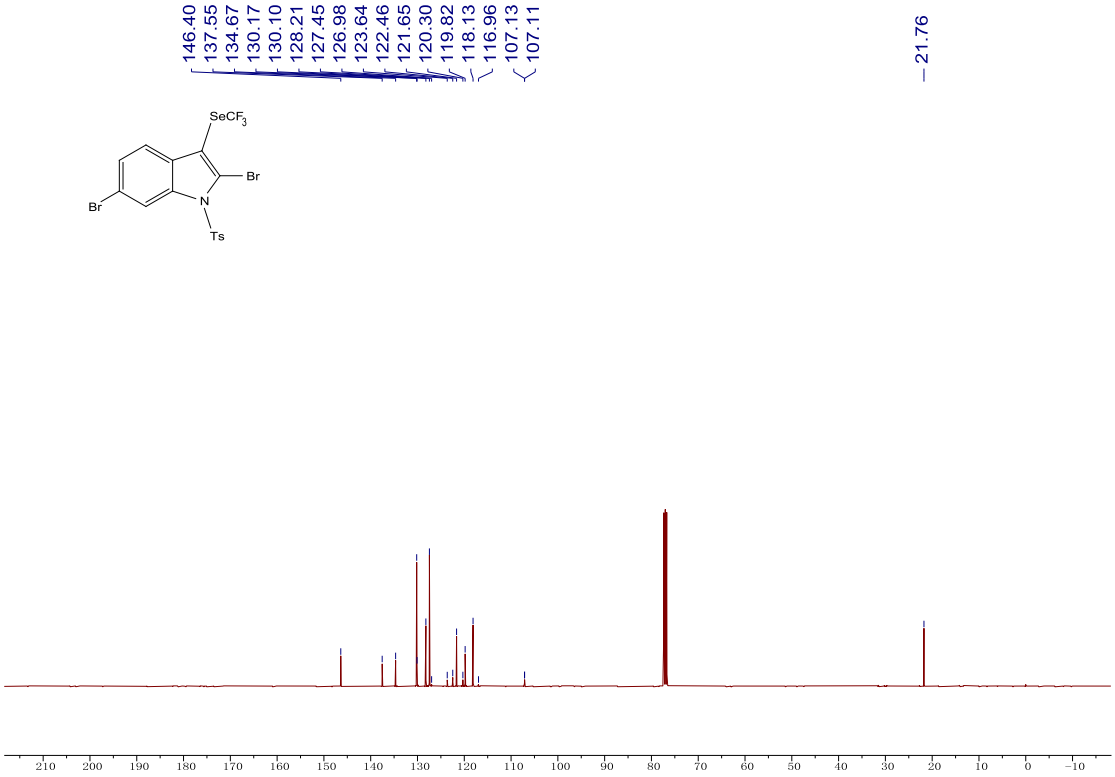
^{1}H NMR spectra of **2p** (400 MHz, $CDCl_3$)



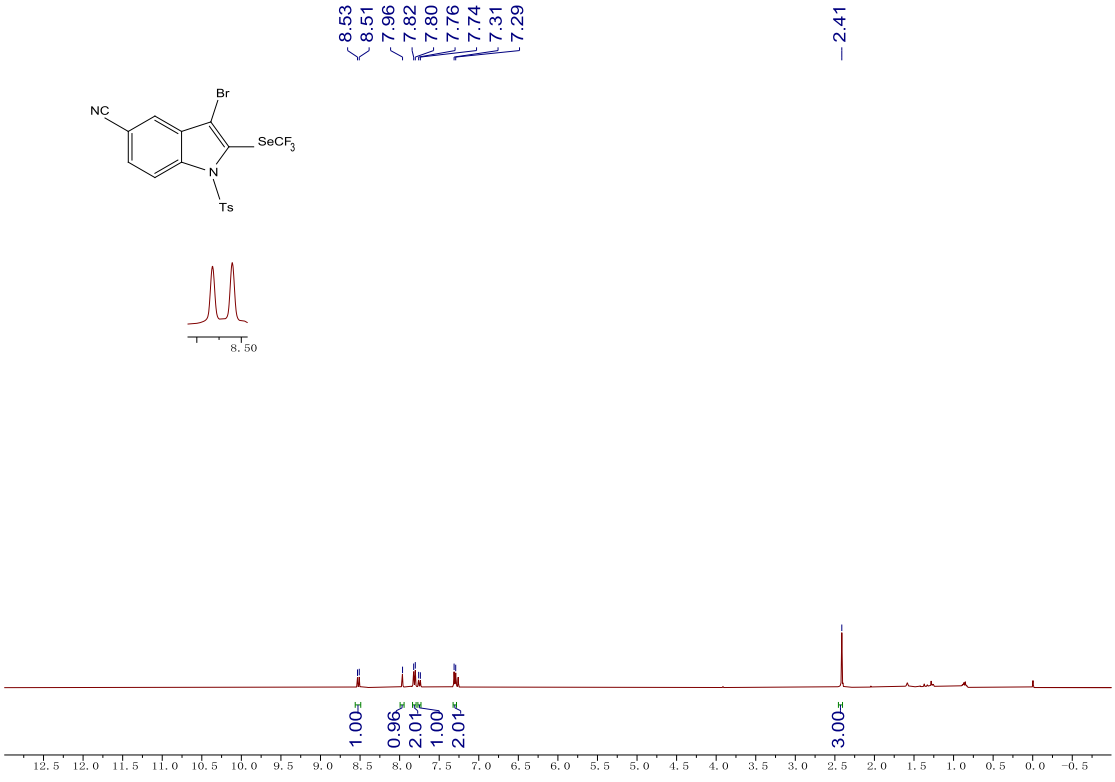
^{19}F NMR spectra of **2p** (376 MHz, $CDCl_3$)



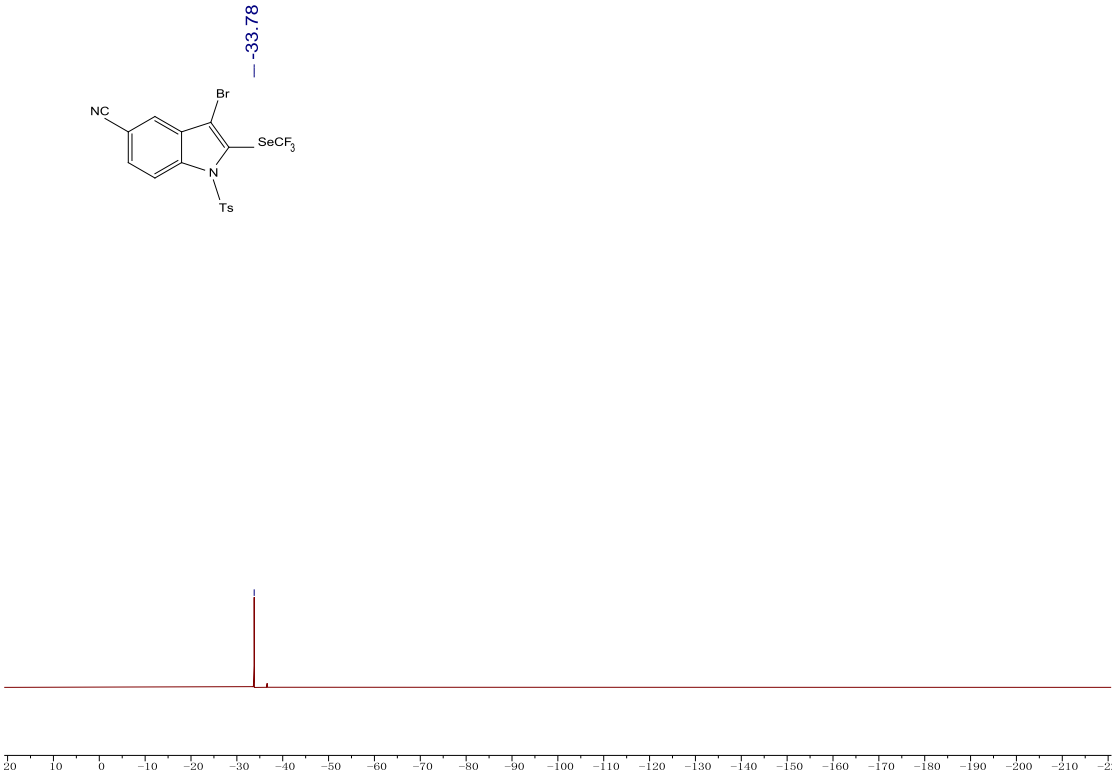
$^{13}C\{^{1}H\}$ NMR spectra of **2p** (101 MHz, $CDCl_3$)



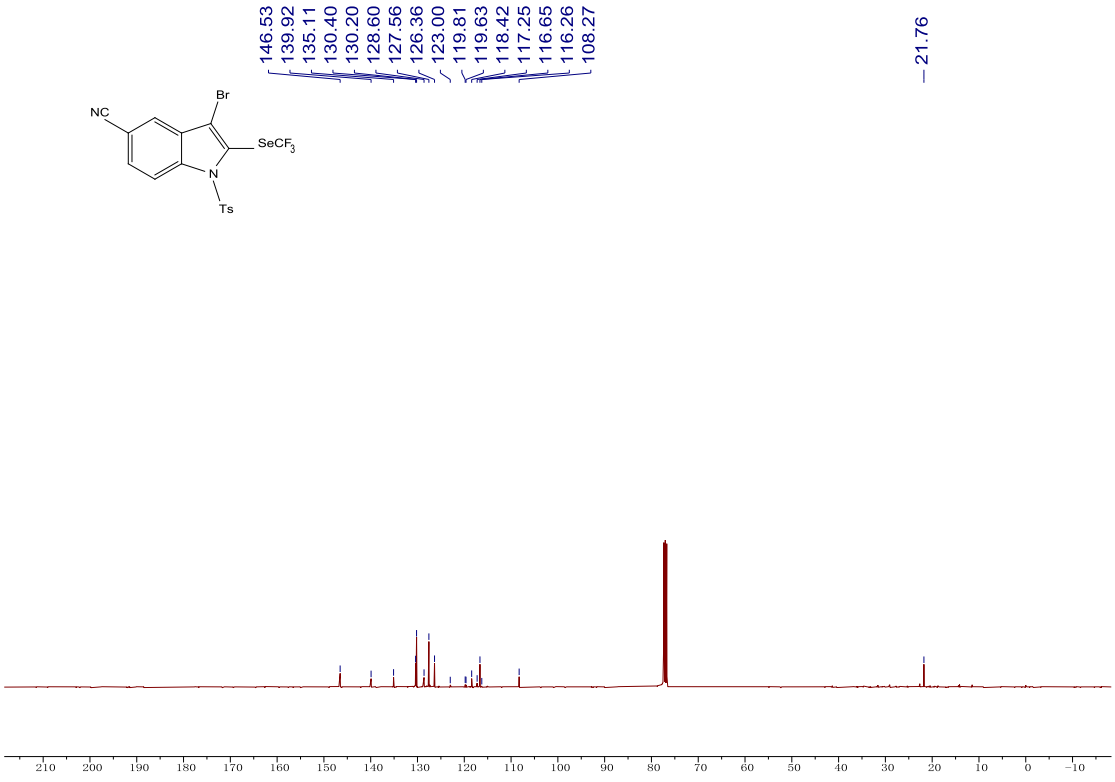
^{1}H NMR spectra of **2q′** (400 MHz, $CDCl_3$)



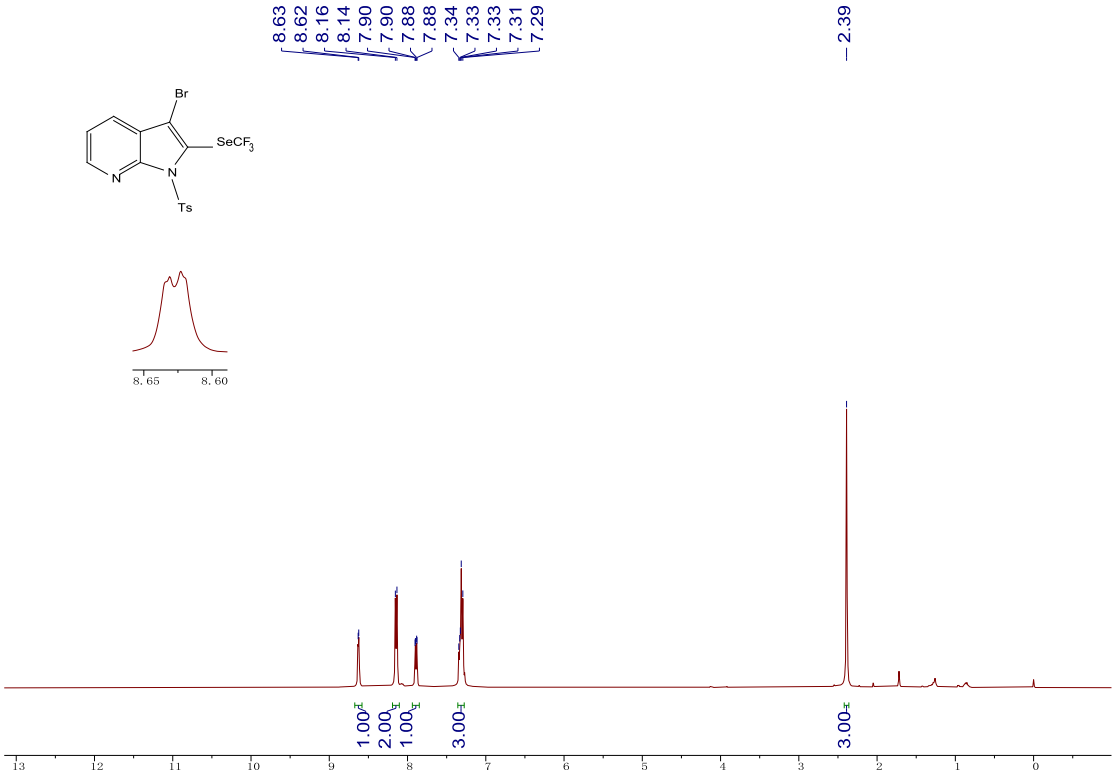
^{19}F NMR spectra of **2q′** (376 MHz, $CDCl_3$)



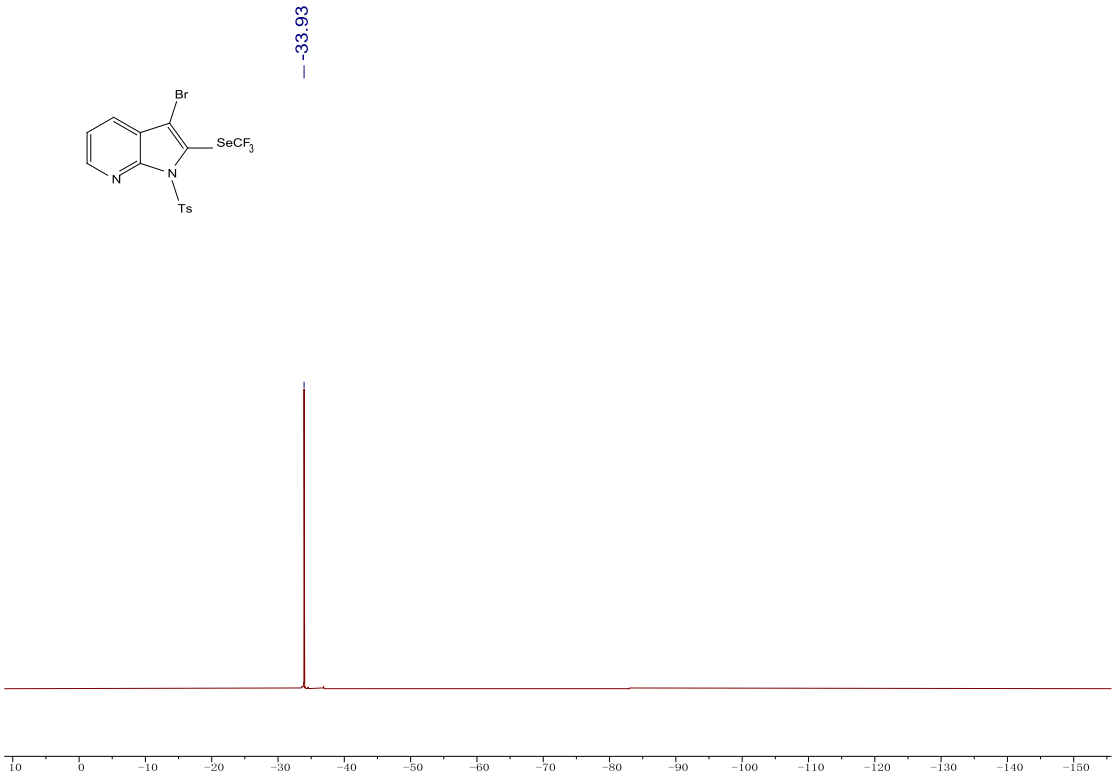
$^{13}C\{^1H\}$ NMR spectra of **2q′** (101 MHz, $CDCl_3$)



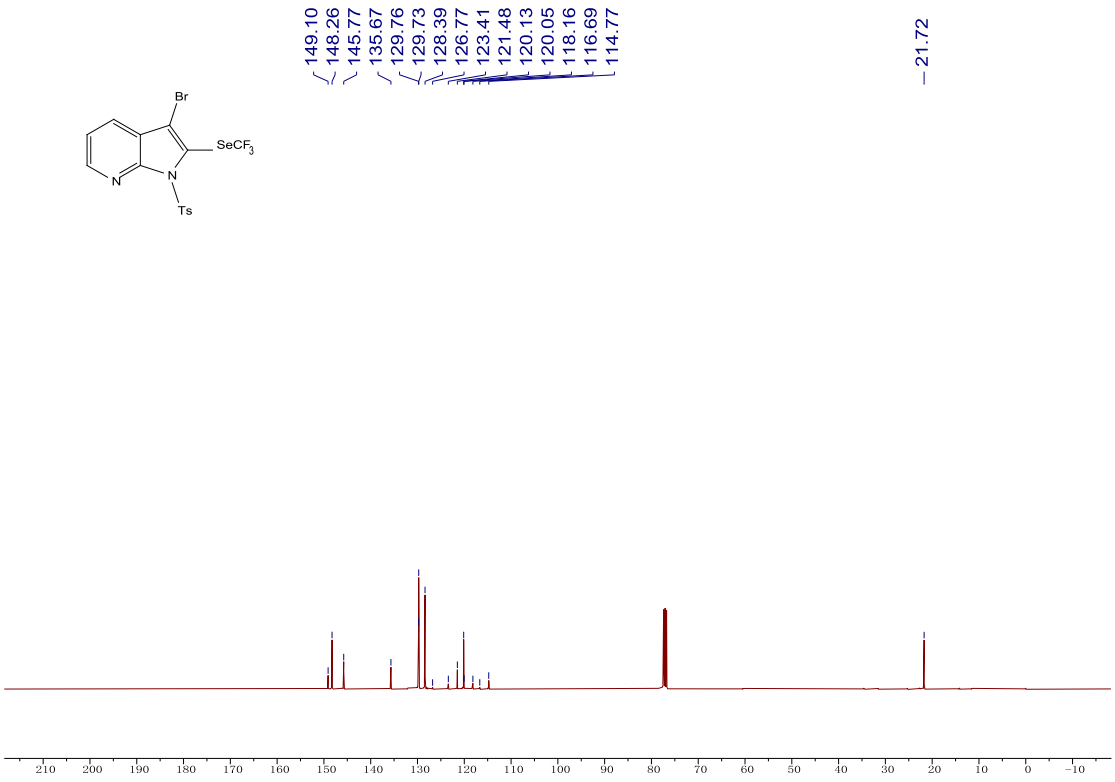
^{1}H NMR spectra of **2r′** (400 MHz, $CDCl_3$)



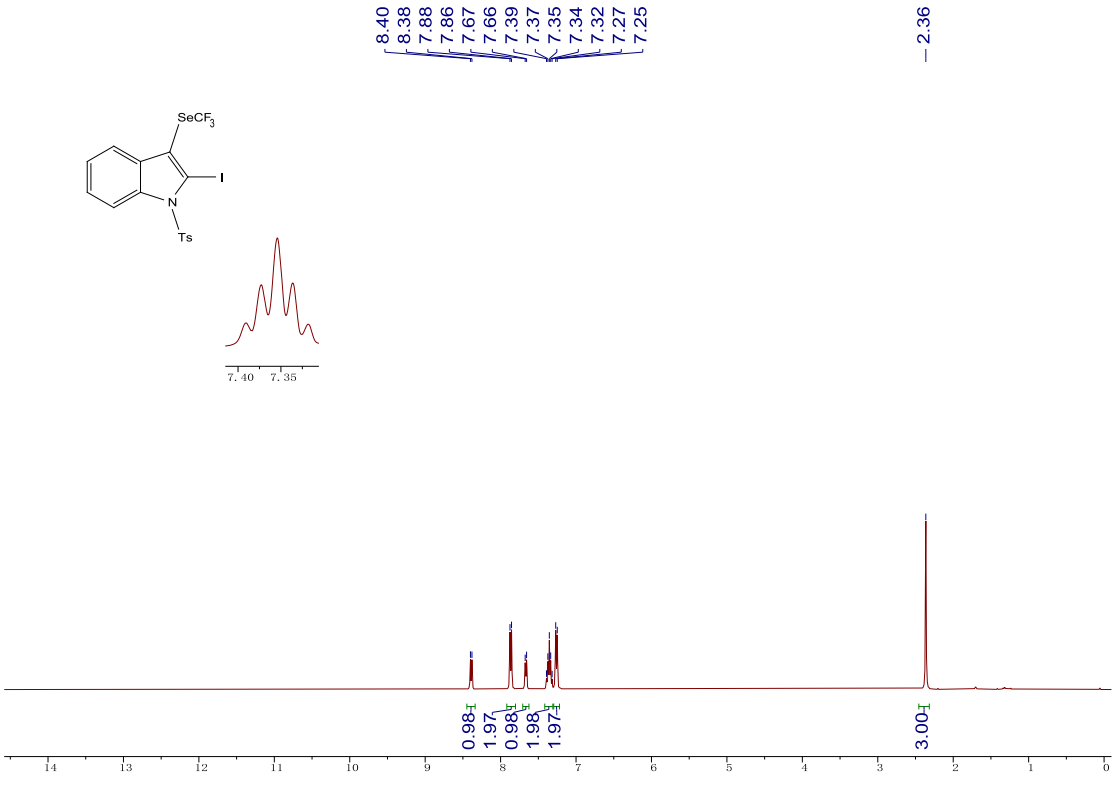
^{19}F NMR spectra of **2r′** (376 MHz, $CDCl_3$)



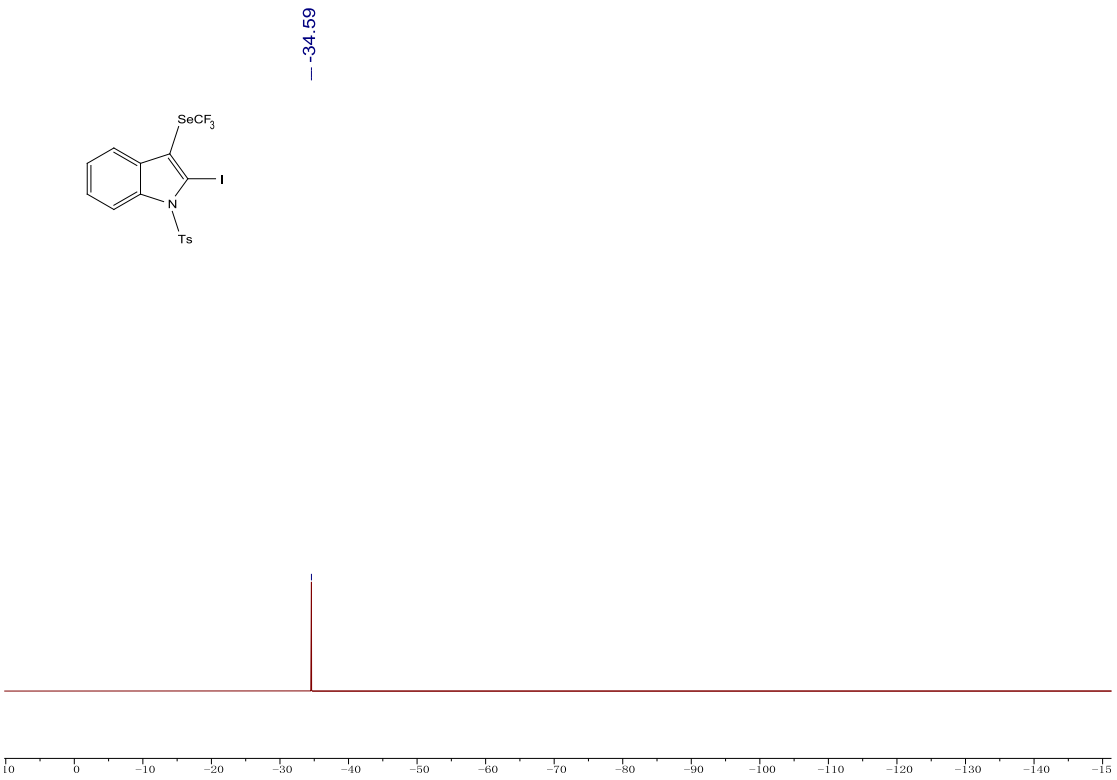
$^{13}C\{^{1}H\}$ NMR spectra of **2r′** (101 MHz, $CDCl_3$)



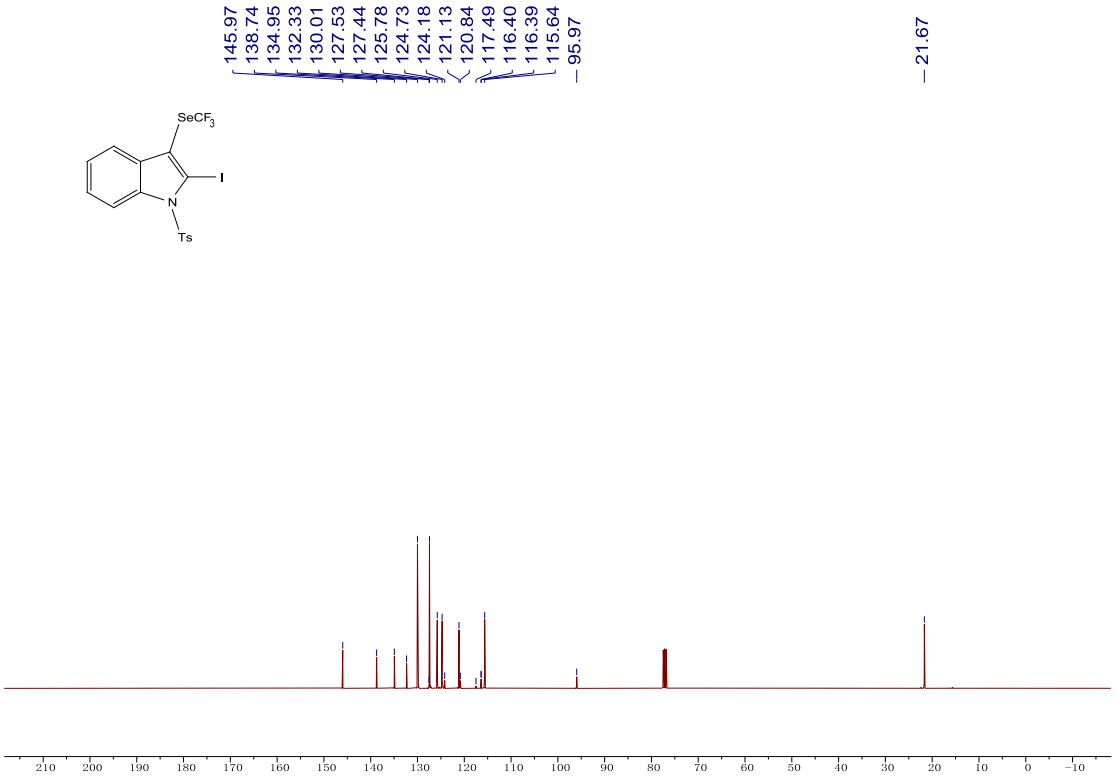
^{1}H NMR spectra of **3a** (400 MHz, $CDCl_3$)



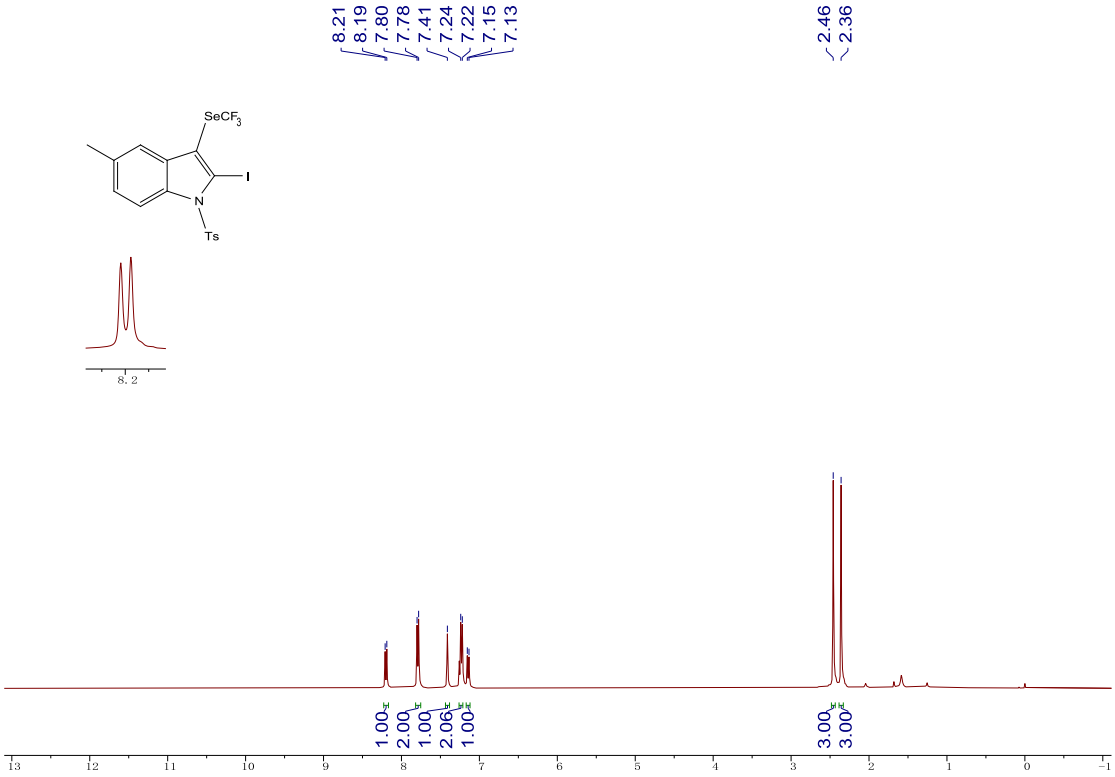
^{19}F NMR spectra of **3a** (376 MHz, $CDCl_3$)



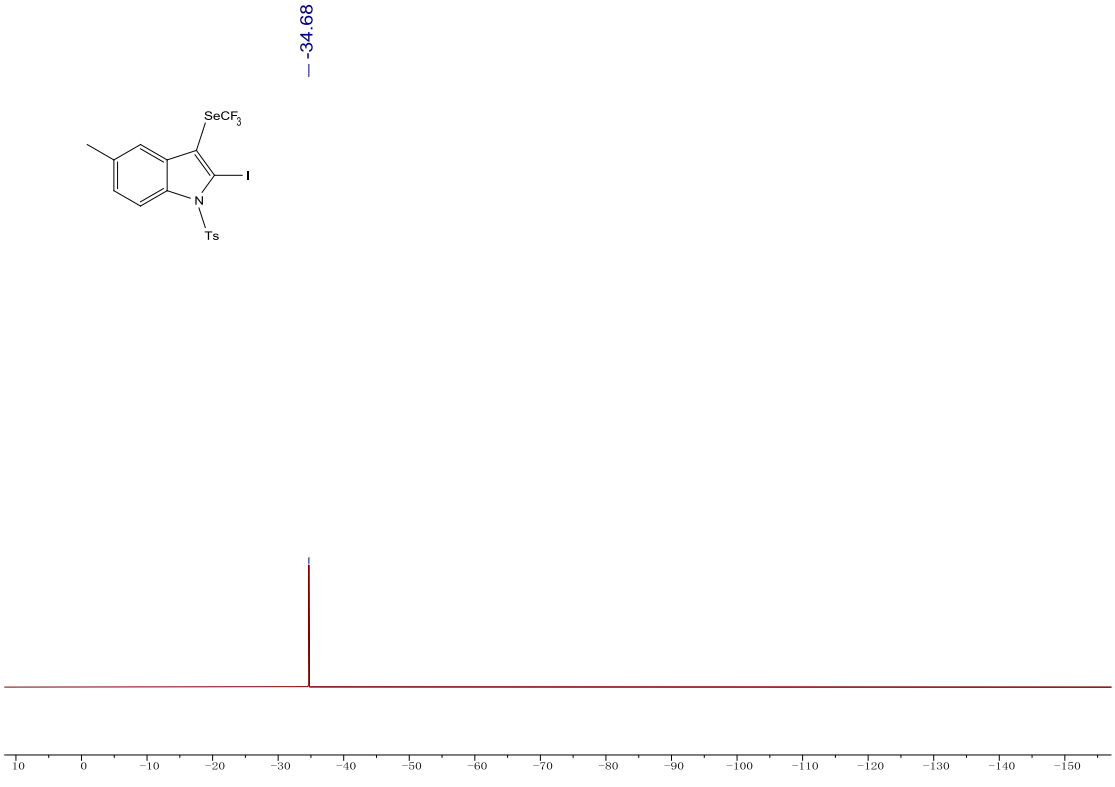
$^{13}C\{^1H\}$ NMR spectra of **3a** (101 MHz, $CDCl_3$)



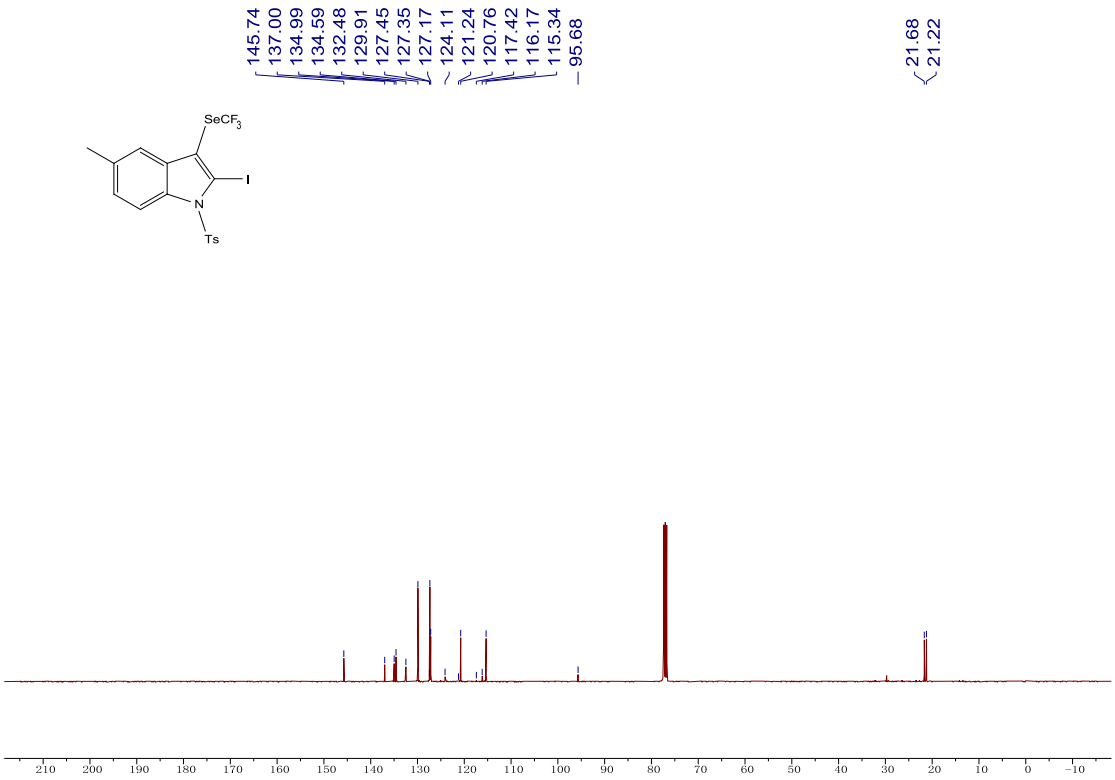
^{1}H NMR spectra of **3b** (400 MHz, $CDCl_3$)



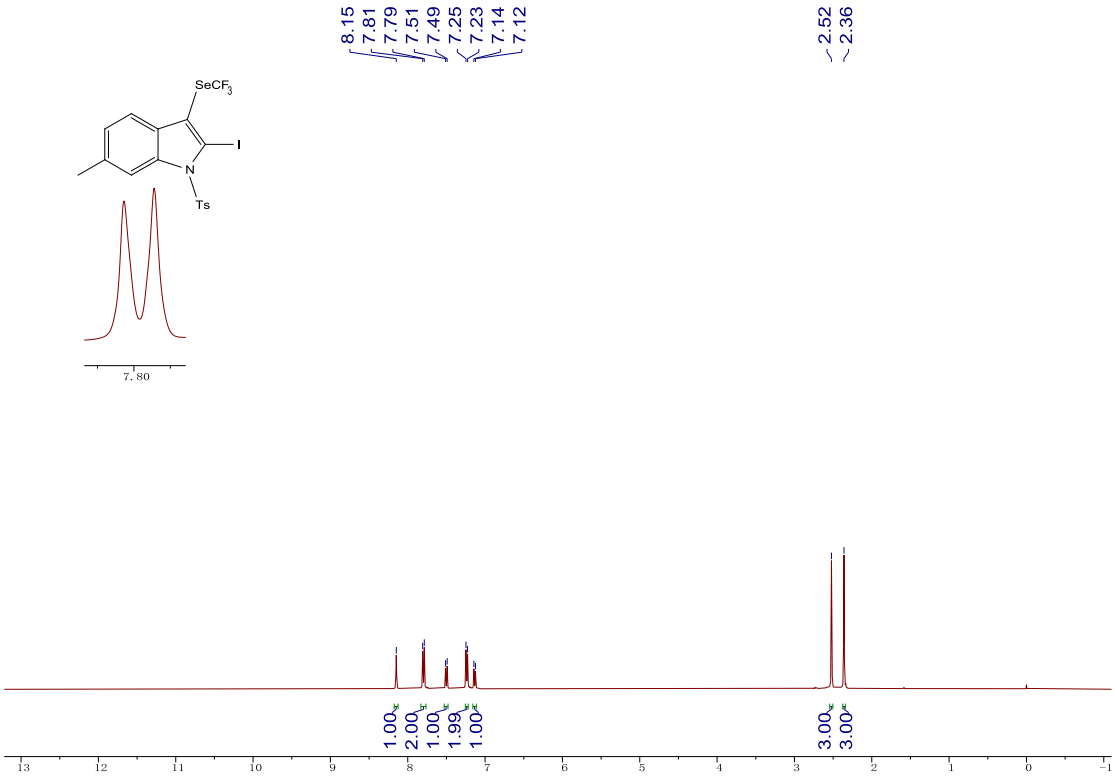
^{19}F NMR spectra of **3b** (376 MHz, $CDCl_3$)



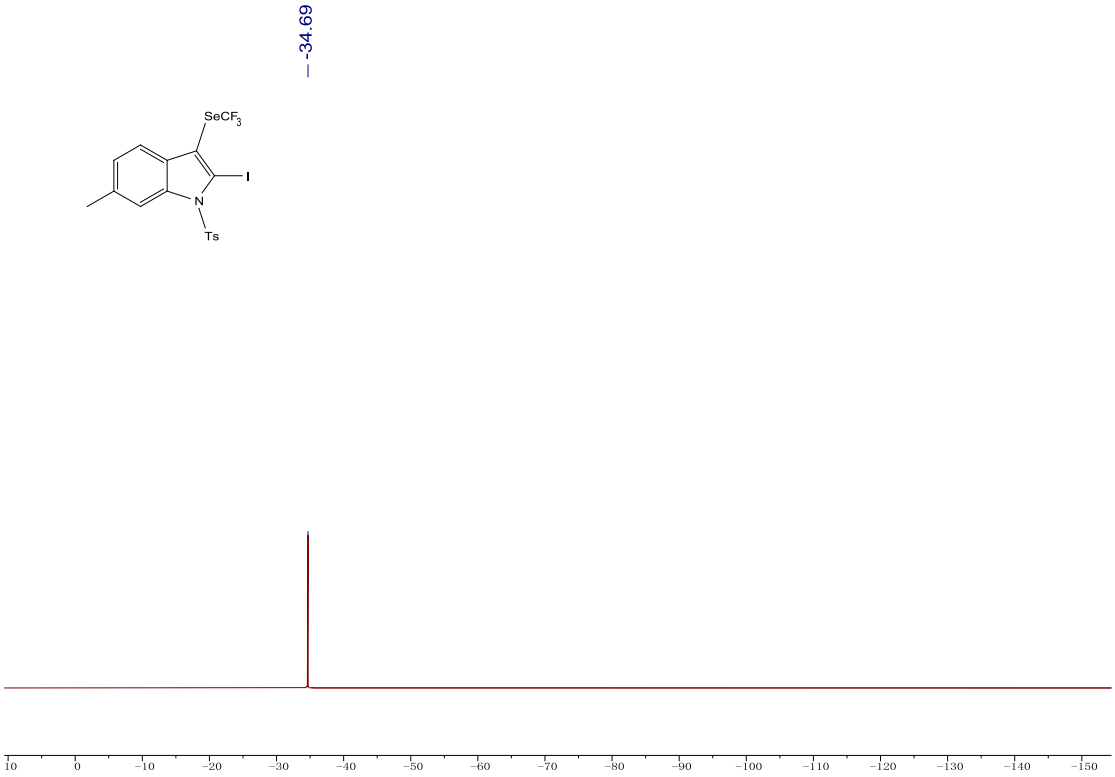
$^{13}C\{^{1}H\}$ NMR spectra of **3b** (101 MHz, $CDCl_3$)



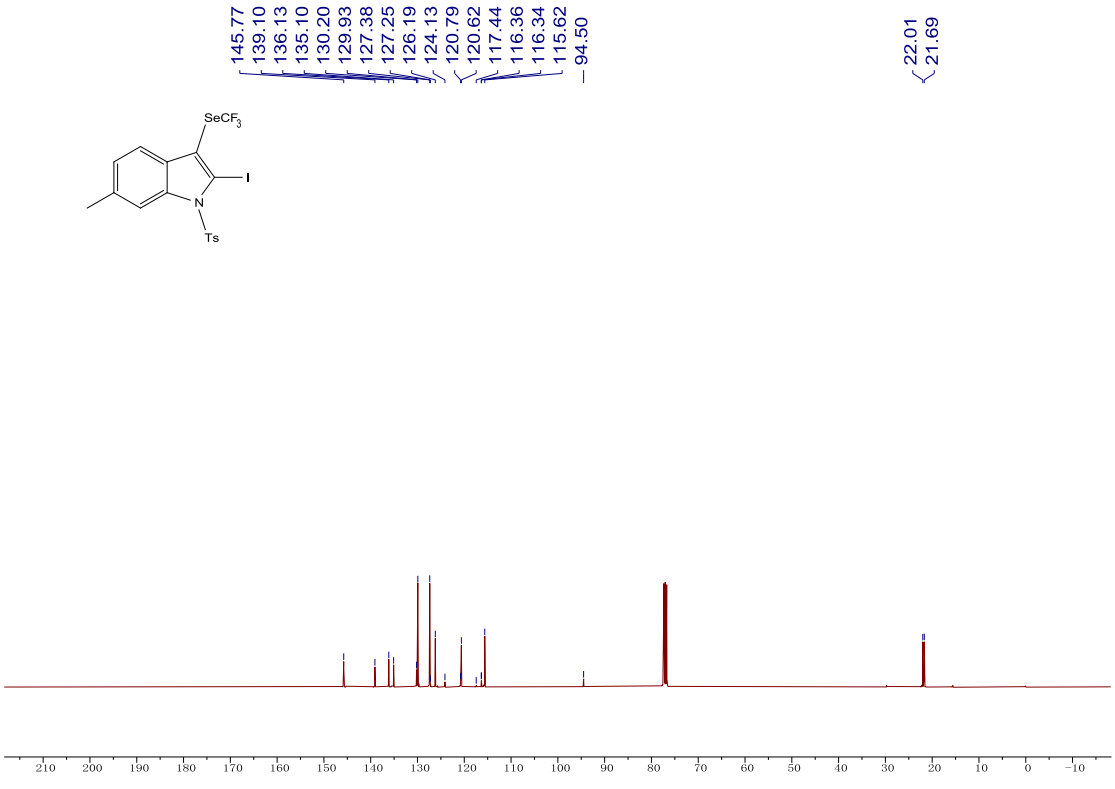
^{1}H NMR spectra of **3c** (400 MHz, $CDCl_3$)



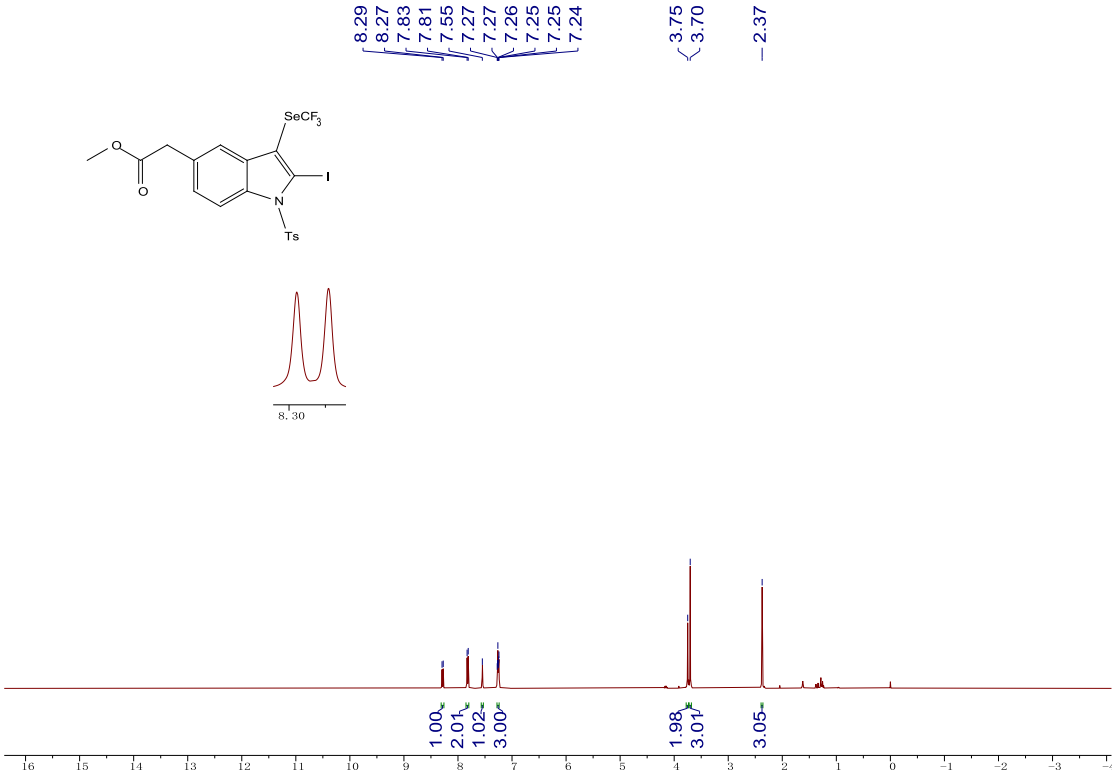
^{19}F NMR spectra of **3c** (376 MHz, $CDCl_3$)



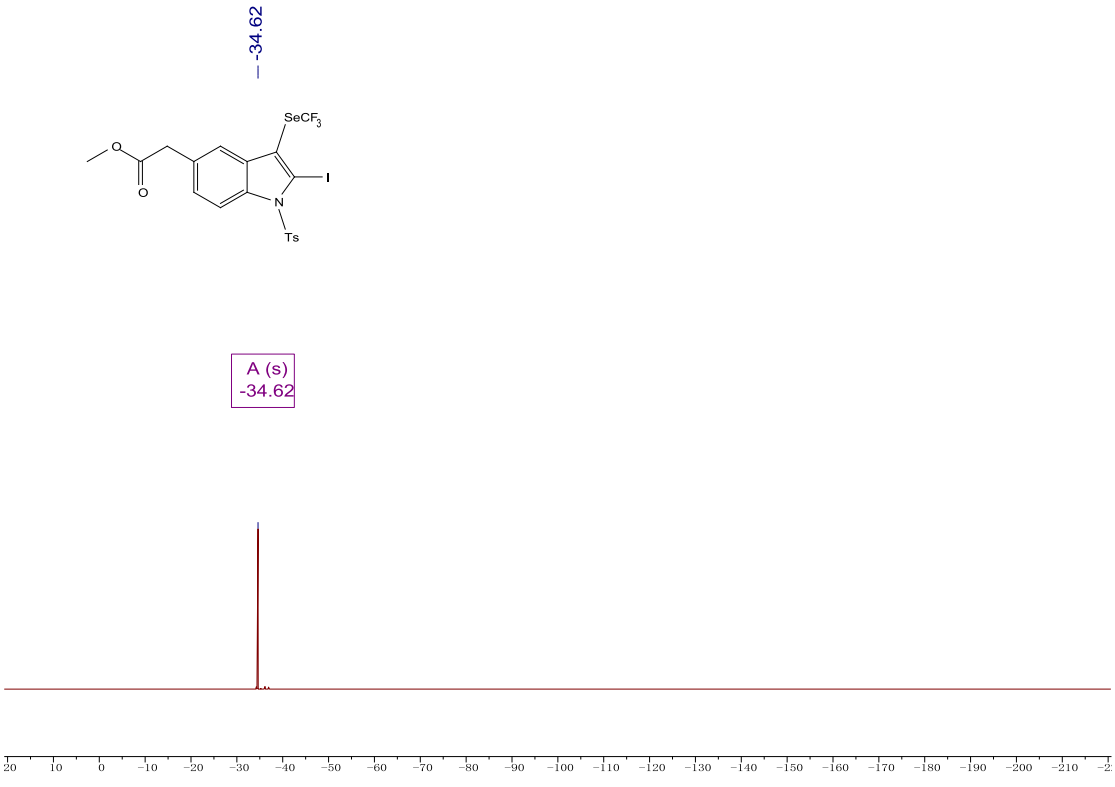
$^{13}C\{^1H\}$ NMR spectra of **3c** (101 MHz, $CDCl_3$)



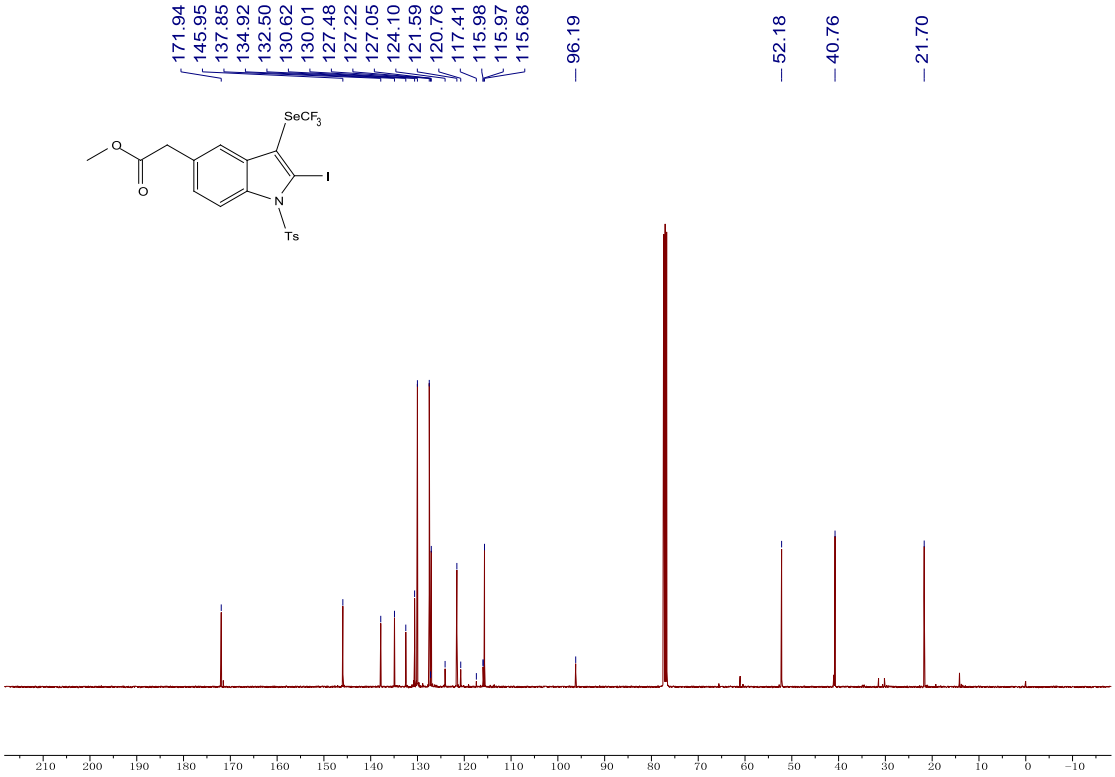
^{1}H NMR spectra of **3d** (400 MHz, $CDCl_3$)



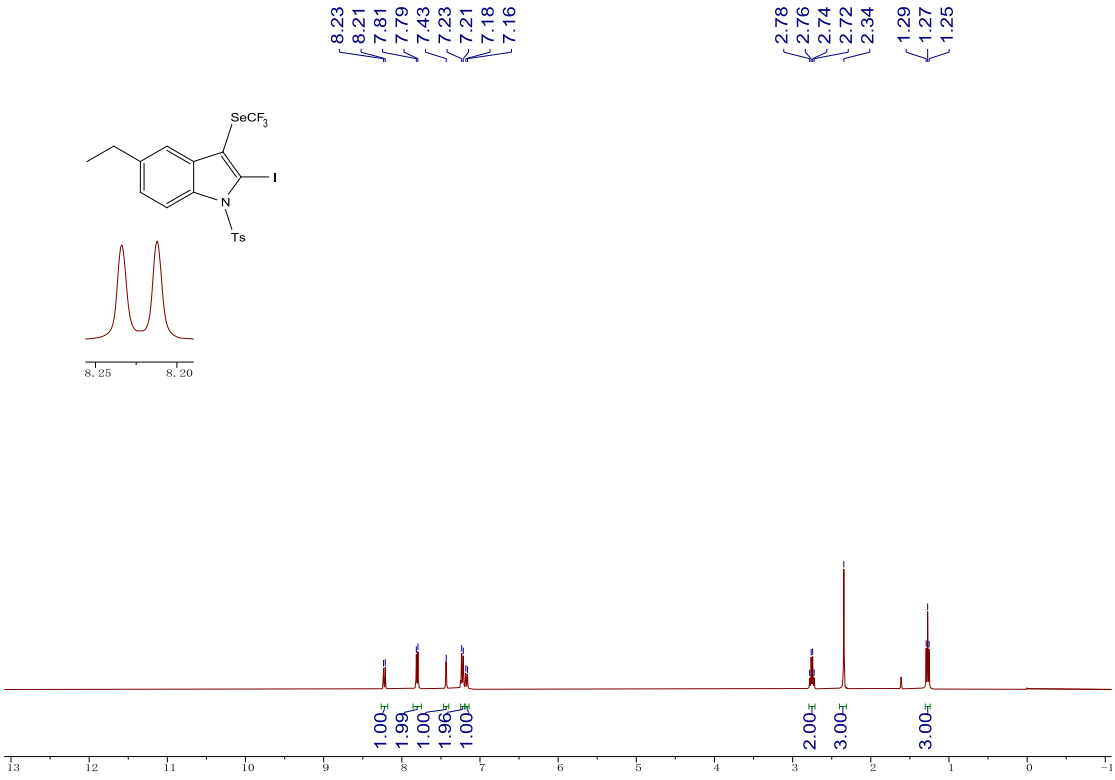
^{19}F NMR spectra of **3d** (376 MHz, $CDCl_3$)



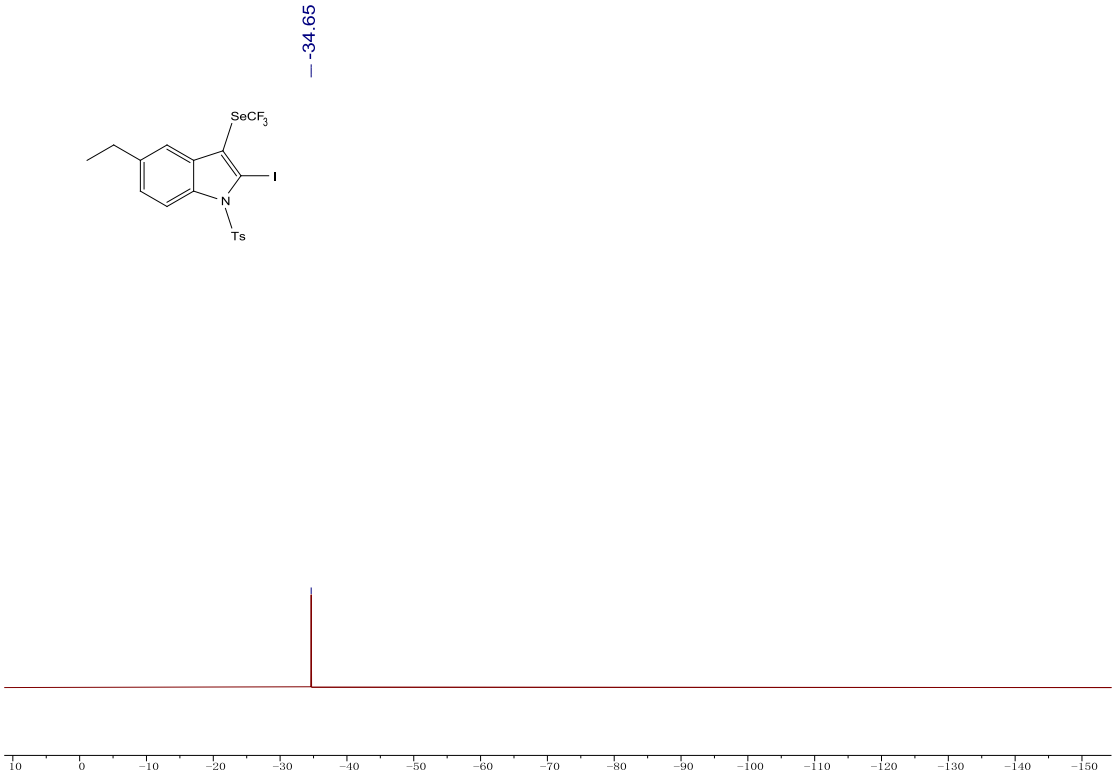
$^{13}C\{^{1}H\}$ NMR spectra of **3d** (101 MHz, $CDCl_3$)



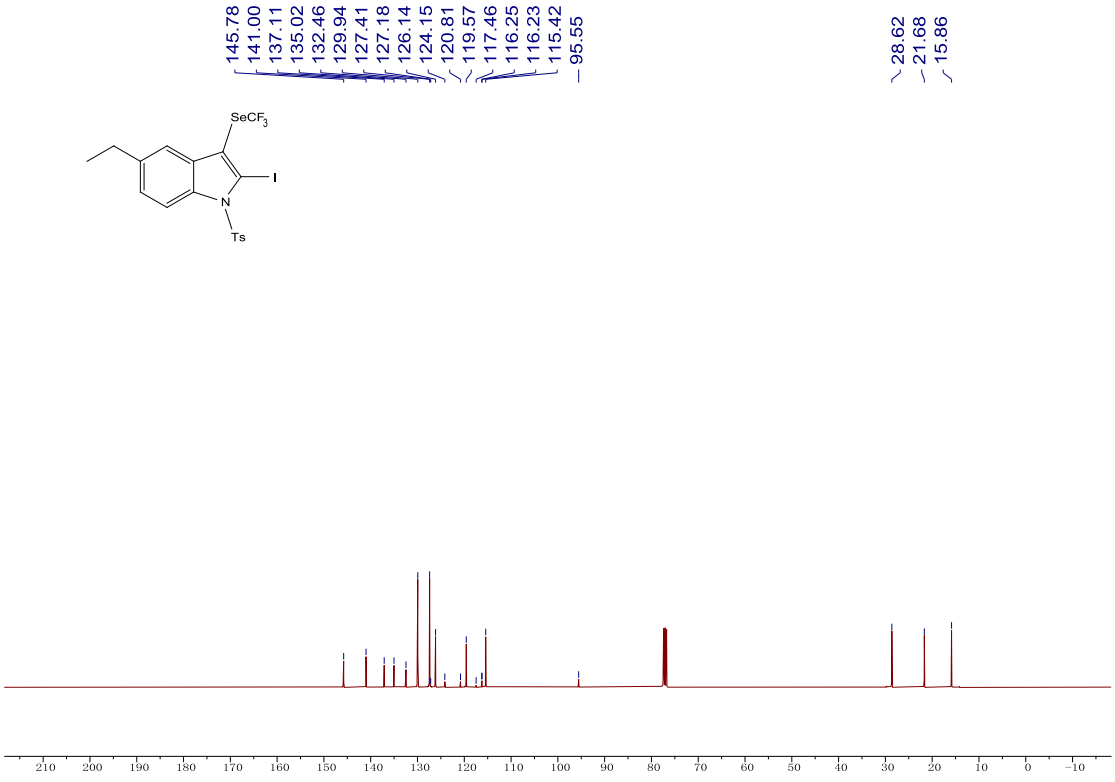
^{1}H NMR spectra of **3e** (400 MHz, $CDCl_3$)



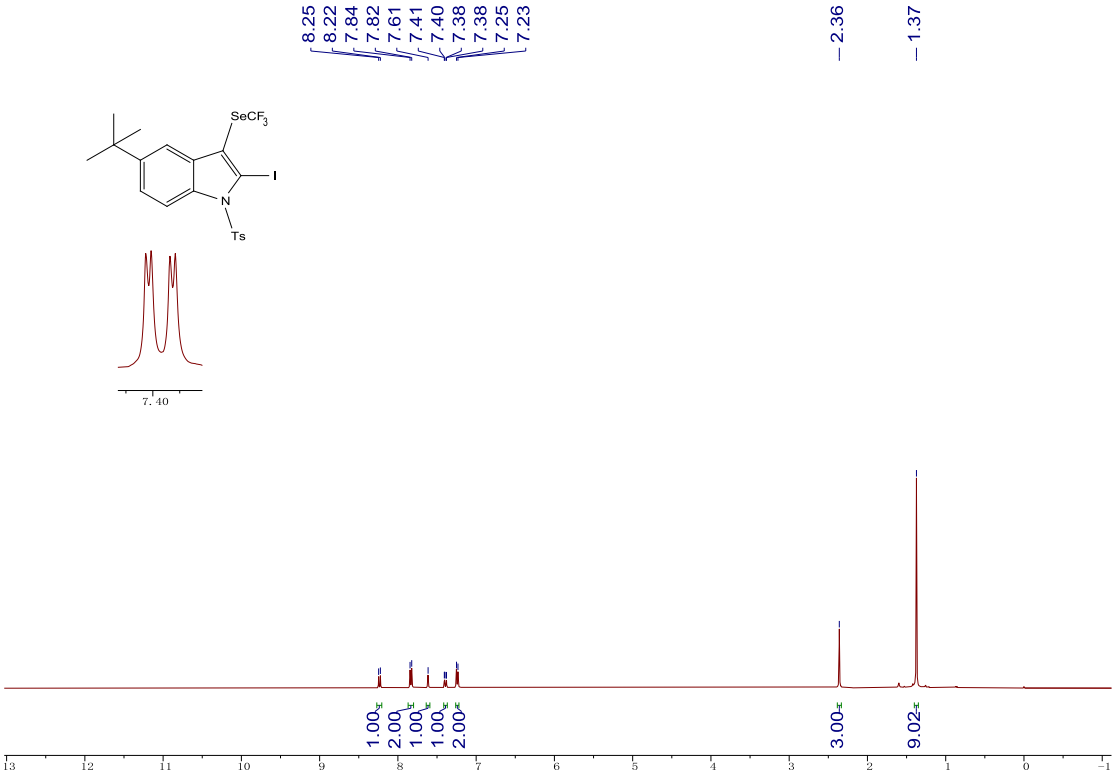
^{19}F NMR spectra of **3e** (376 MHz, $CDCl_3$)



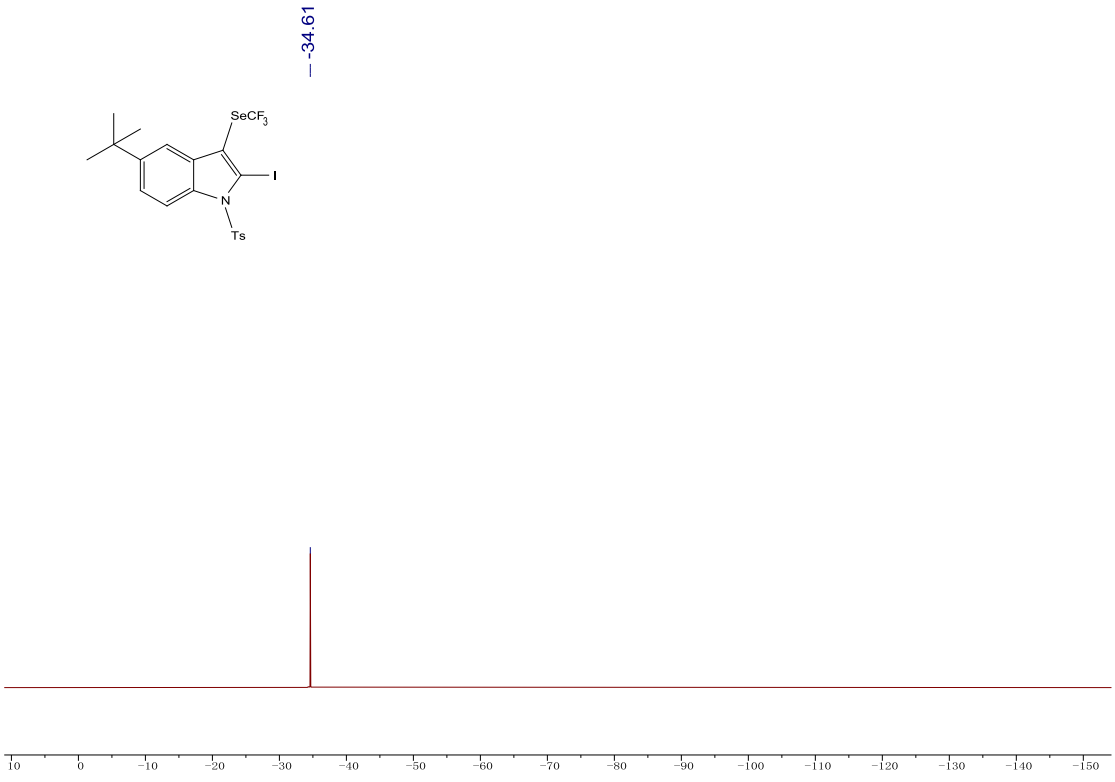
$^{13}C\{^1H\}$ NMR spectra of **3e** (101 MHz, $CDCl_3$)



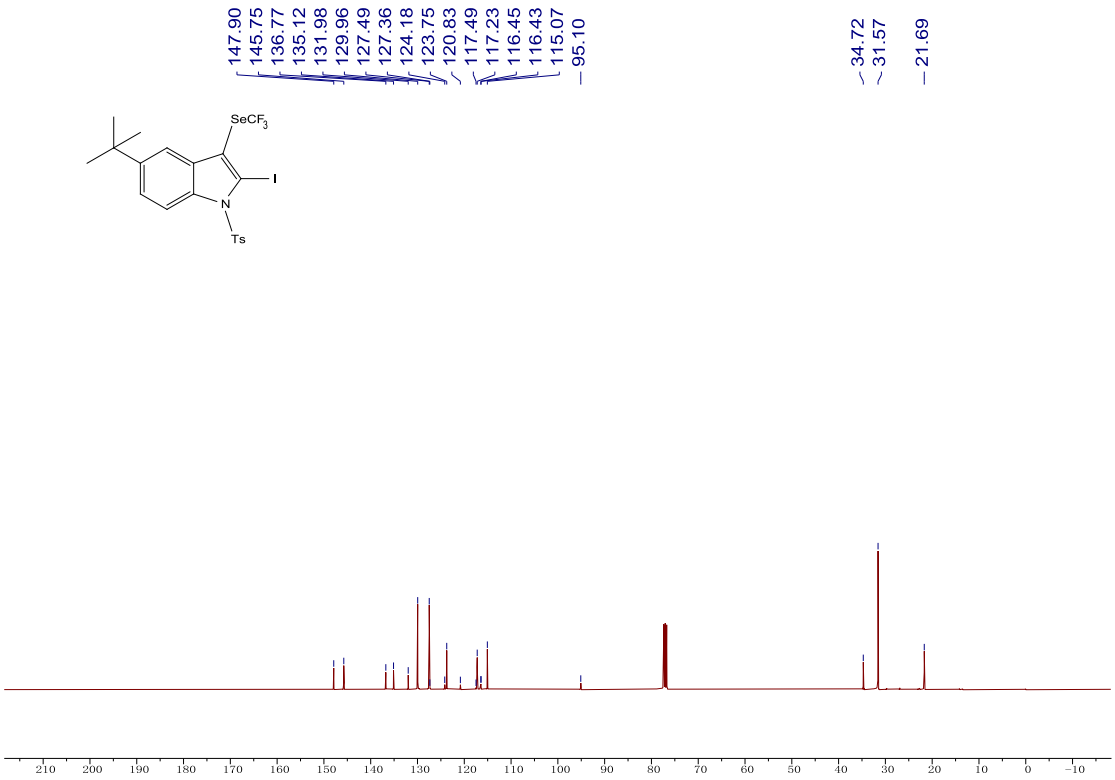
^{1}H NMR spectra of **3f** (400 MHz, $CDCl_3$)



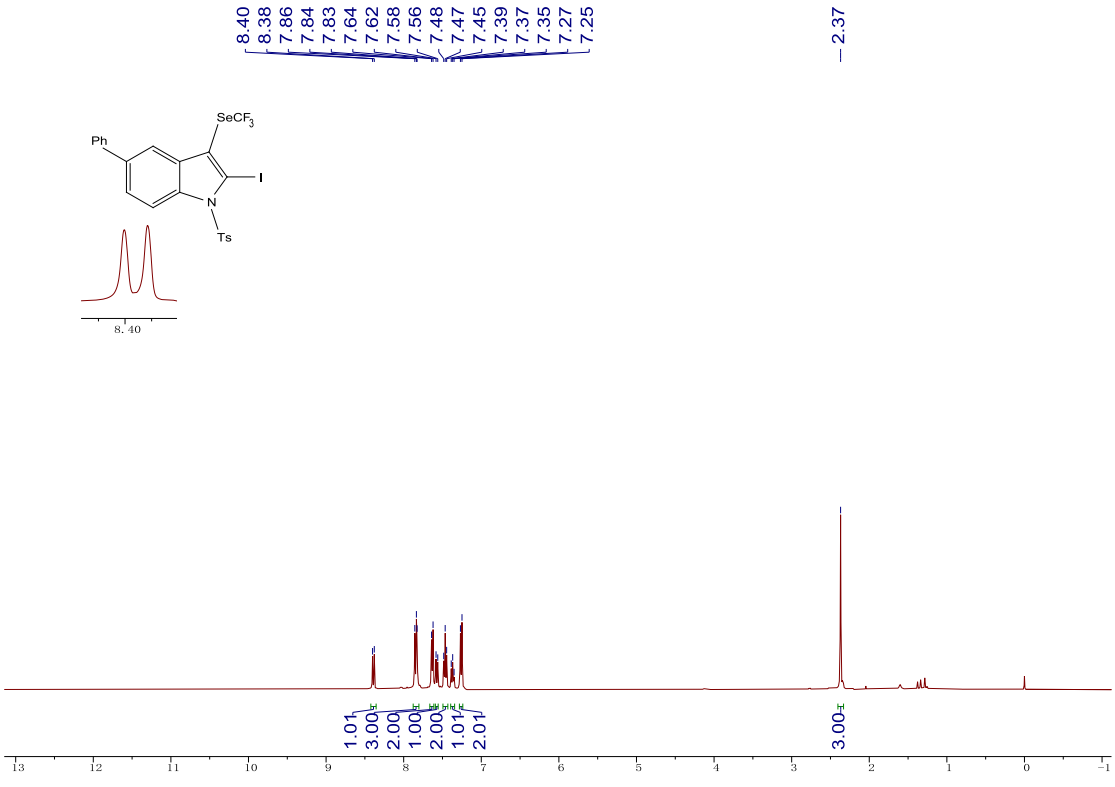
^{19}F NMR spectra of **3f** (376 MHz, $CDCl_3$)



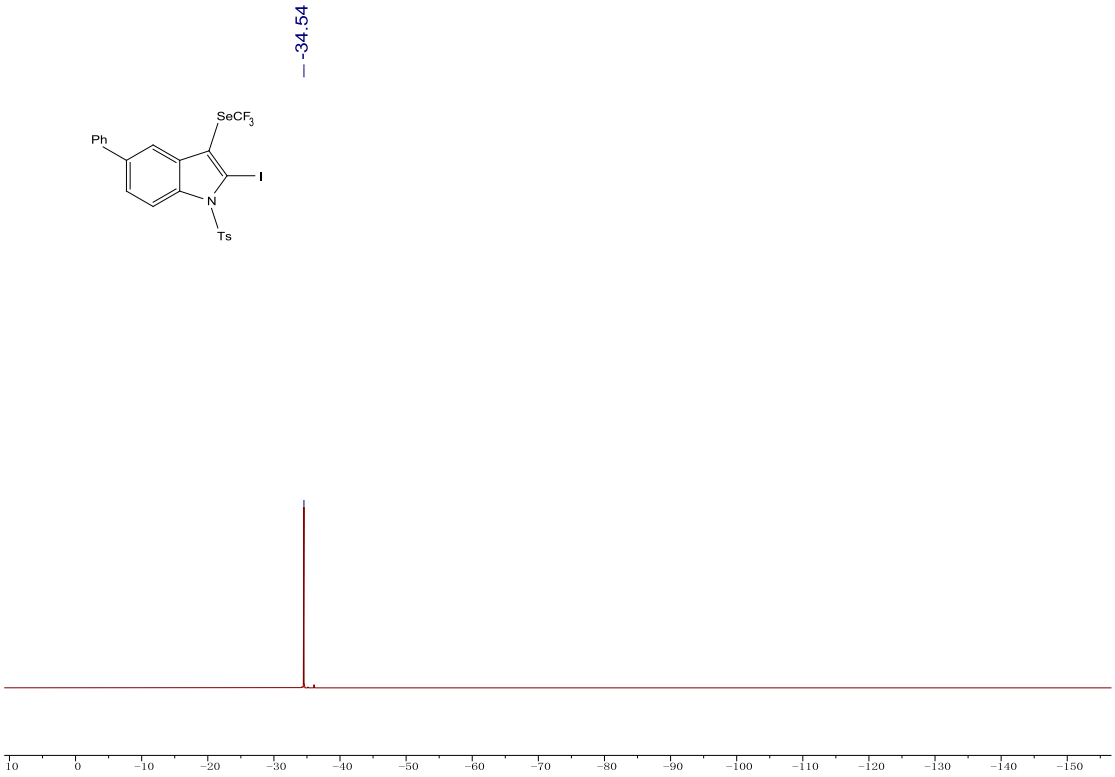
$^{13}C\{^{1}H\}$ NMR spectra of **3f** (101 MHz, $CDCl_3$)



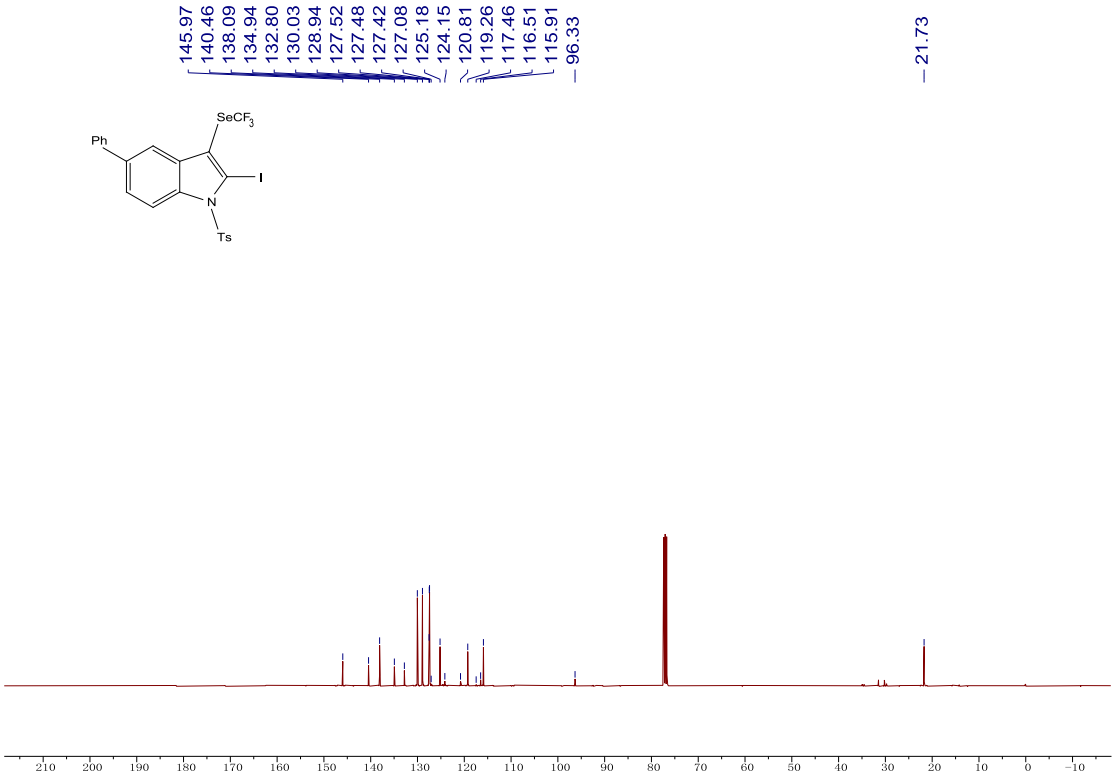
^{1}H NMR spectra of **3g** (400 MHz, $CDCl_3$)



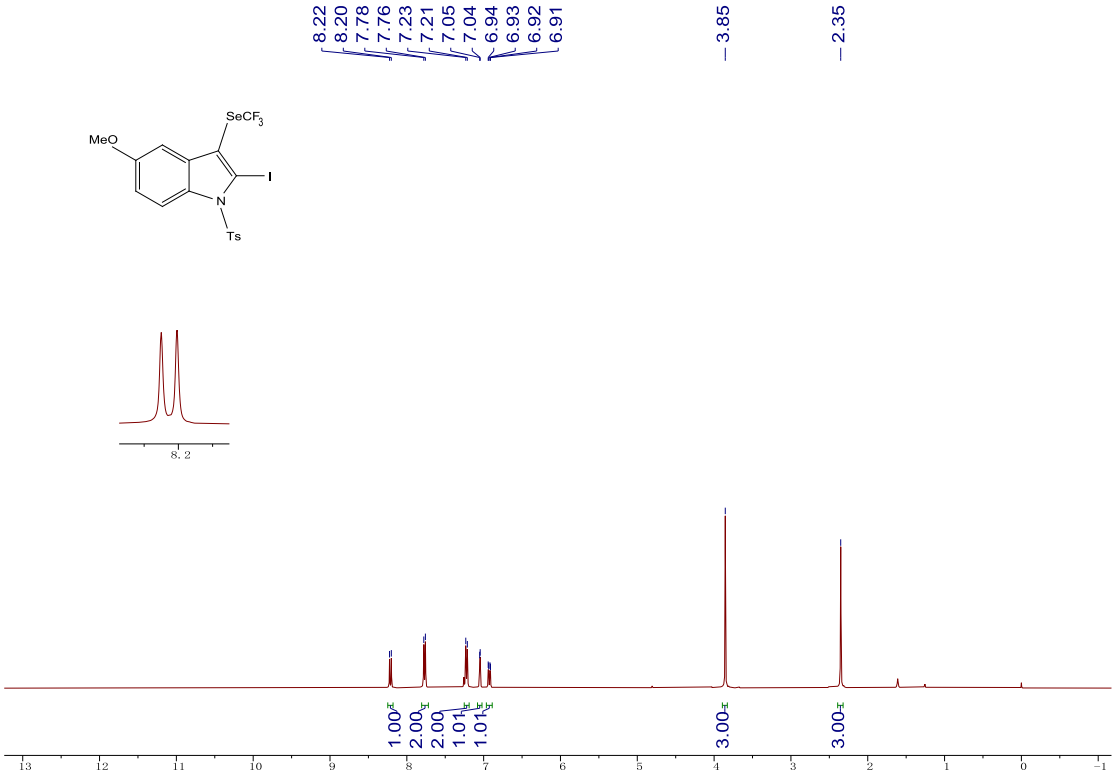
^{19}F NMR spectra of **3g** (376 MHz, $CDCl_3$)



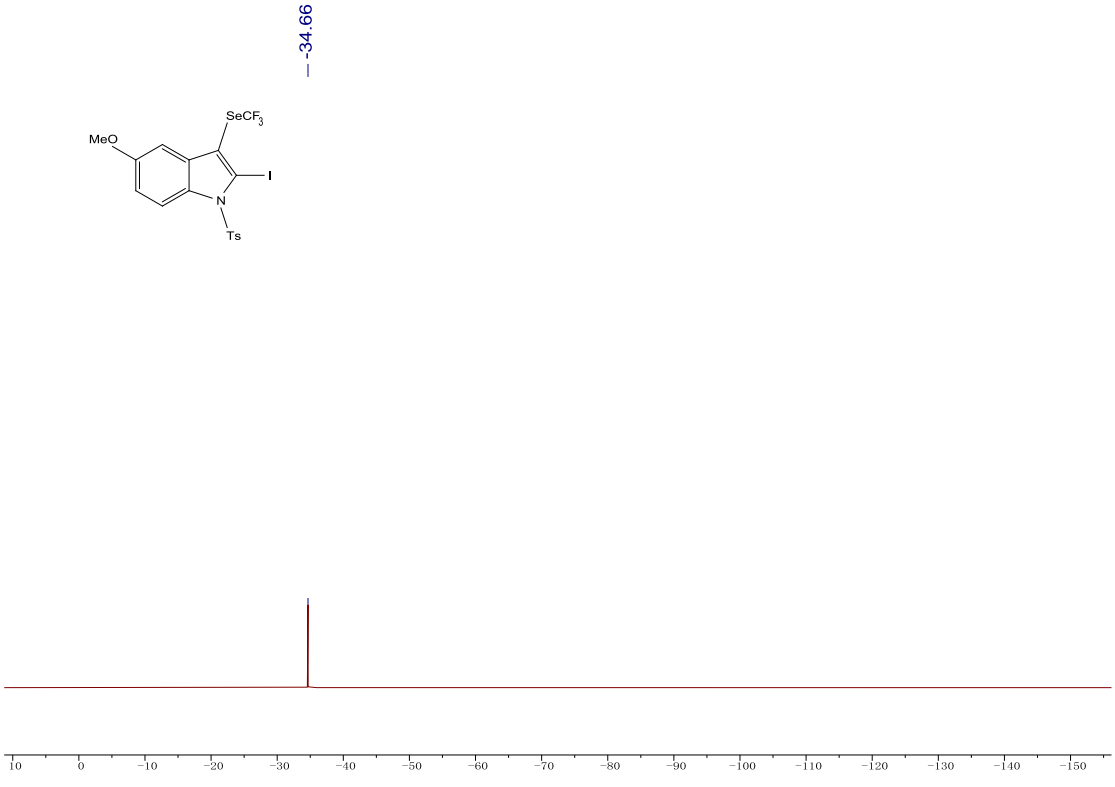
$^{13}C\{^1H\}$ NMR spectra of **3g** (101 MHz, $CDCl_3$)



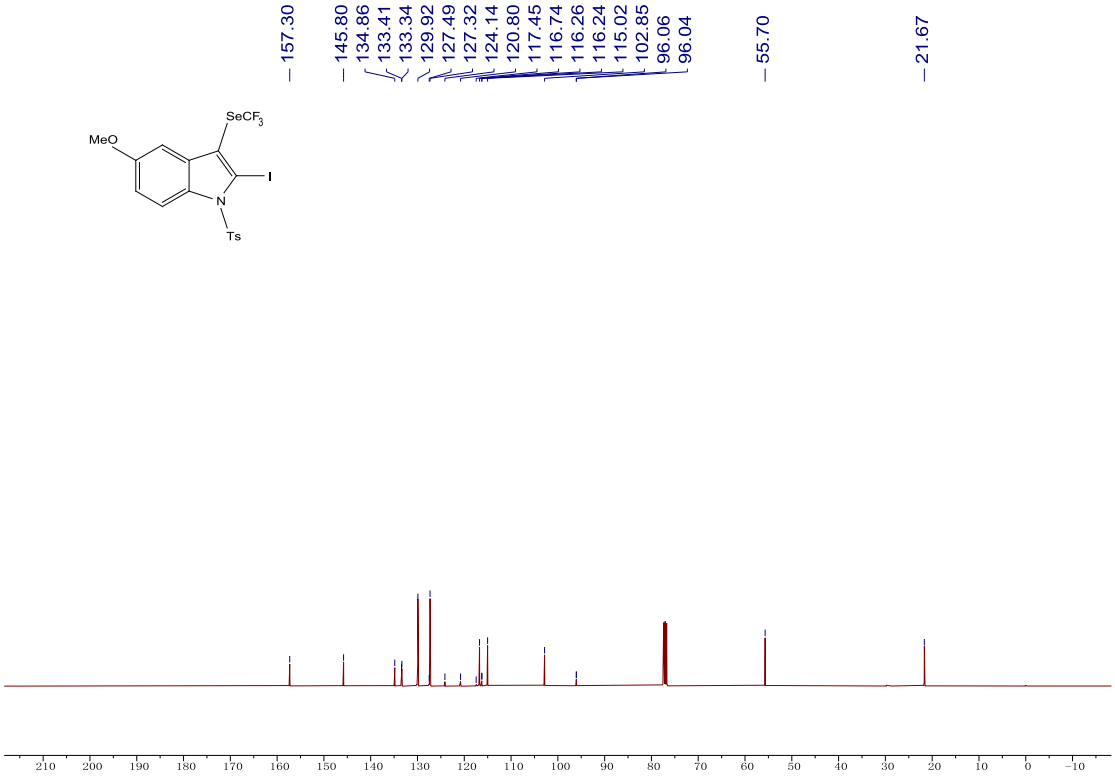
^{1}H NMR spectra of **3h** (400 MHz, $CDCl_3$)



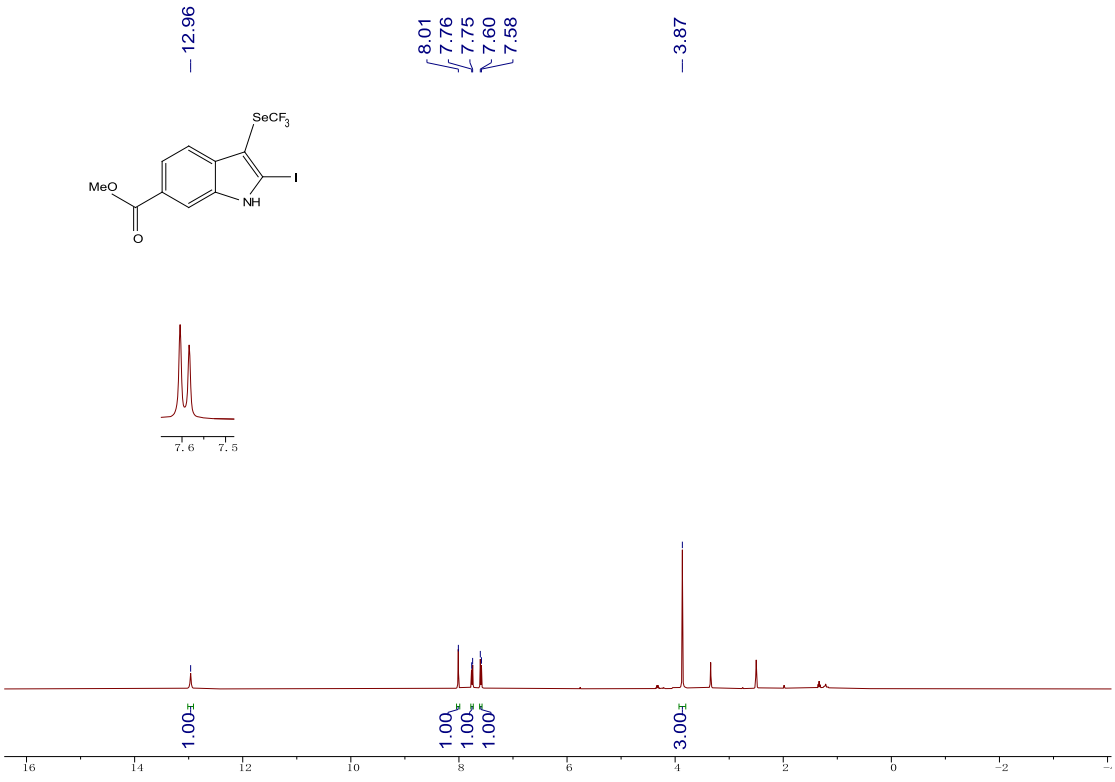
^{19}F NMR spectra of **3h** (376 MHz, $CDCl_3$)



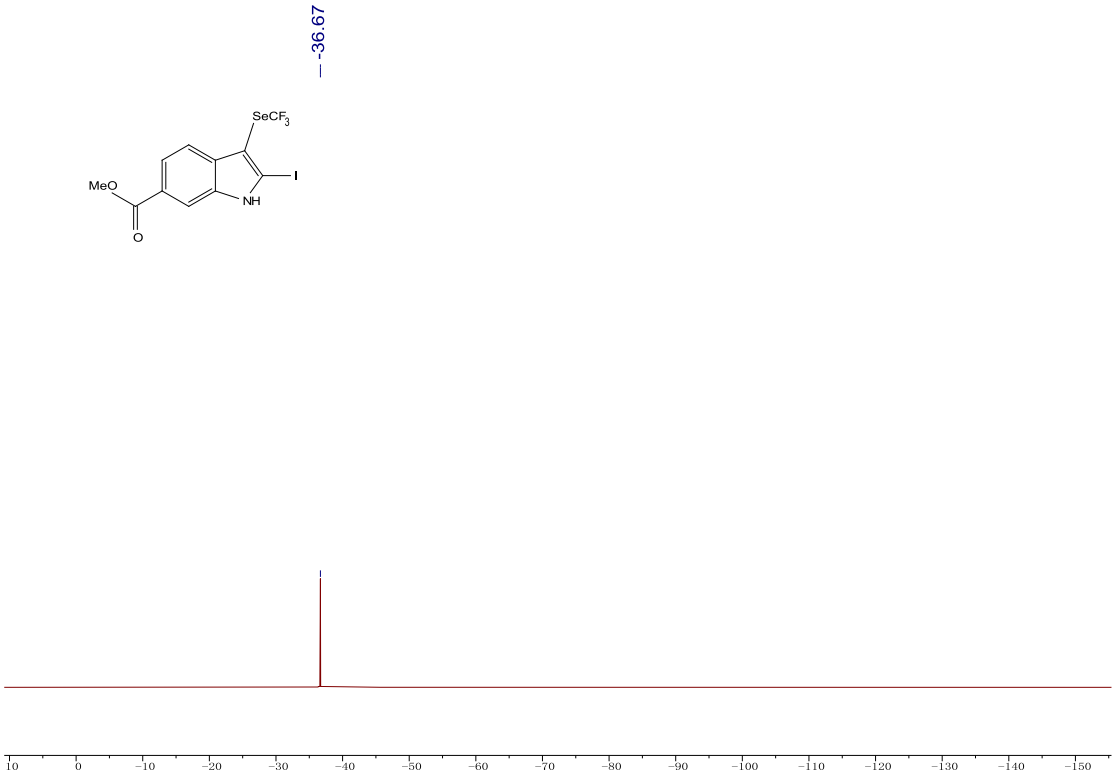
$^{13}C\{^{1}H\}$ NMR spectra of **3h** (101 MHz, $CDCl_3$)



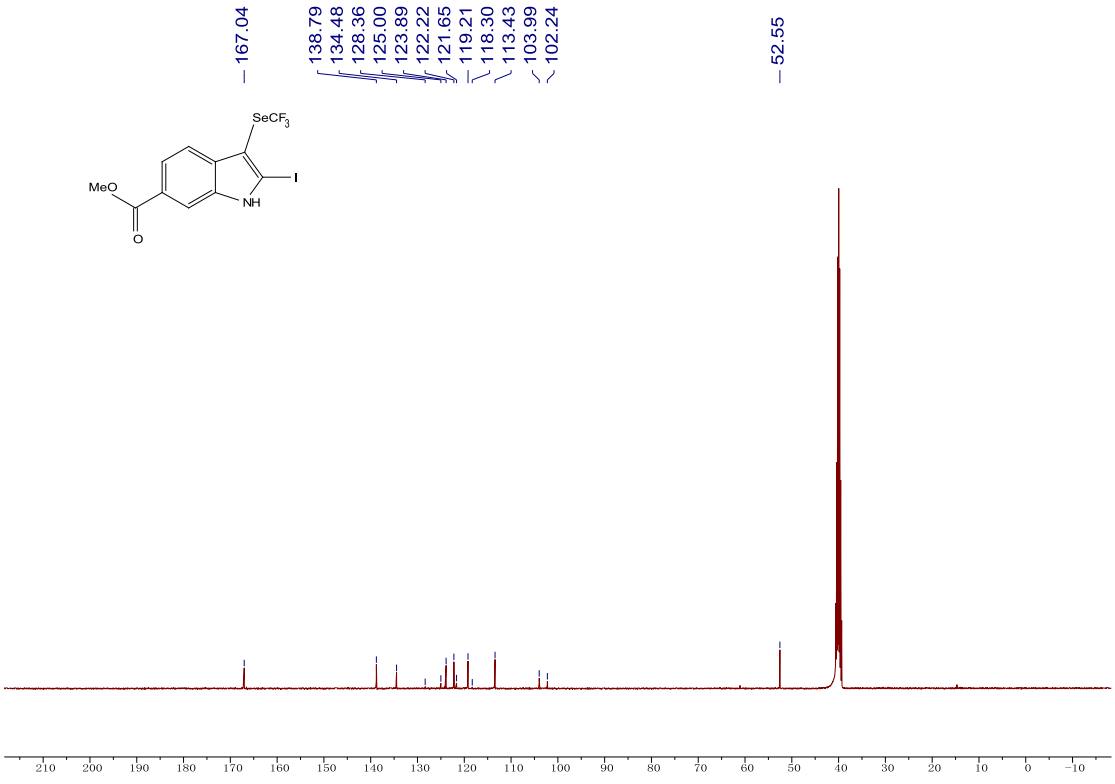
^{1}H NMR spectra of **3i** (400 MHz, DMSO-d_6)



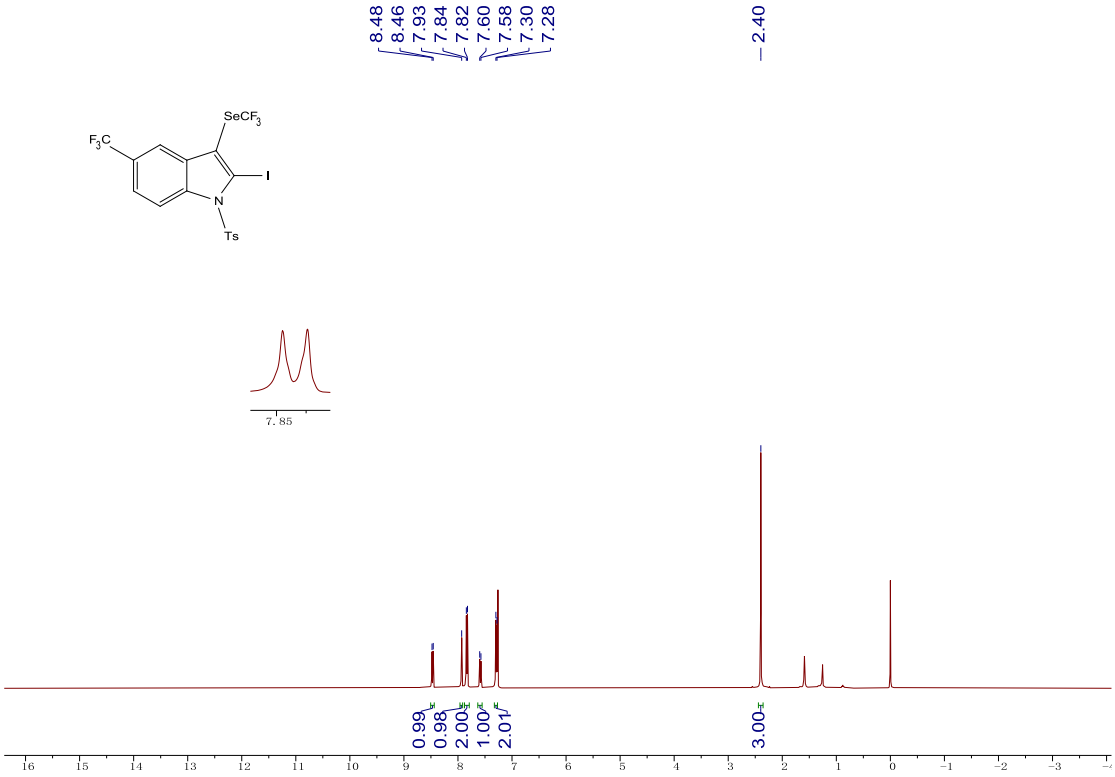
^{19}F NMR spectra of **3i** (376 MHz, DMSO-d_6)



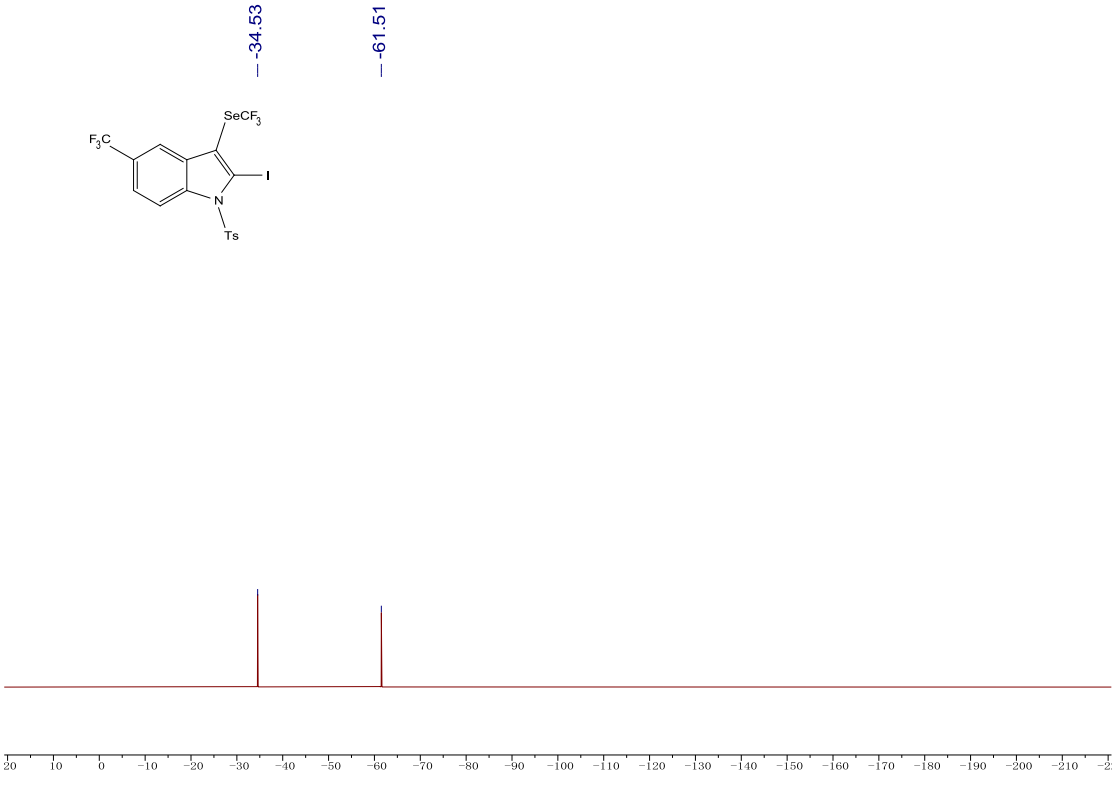
^{13}C{^{1}H} NMR spectra of **3i** (101 MHz, DMSO-d_6)



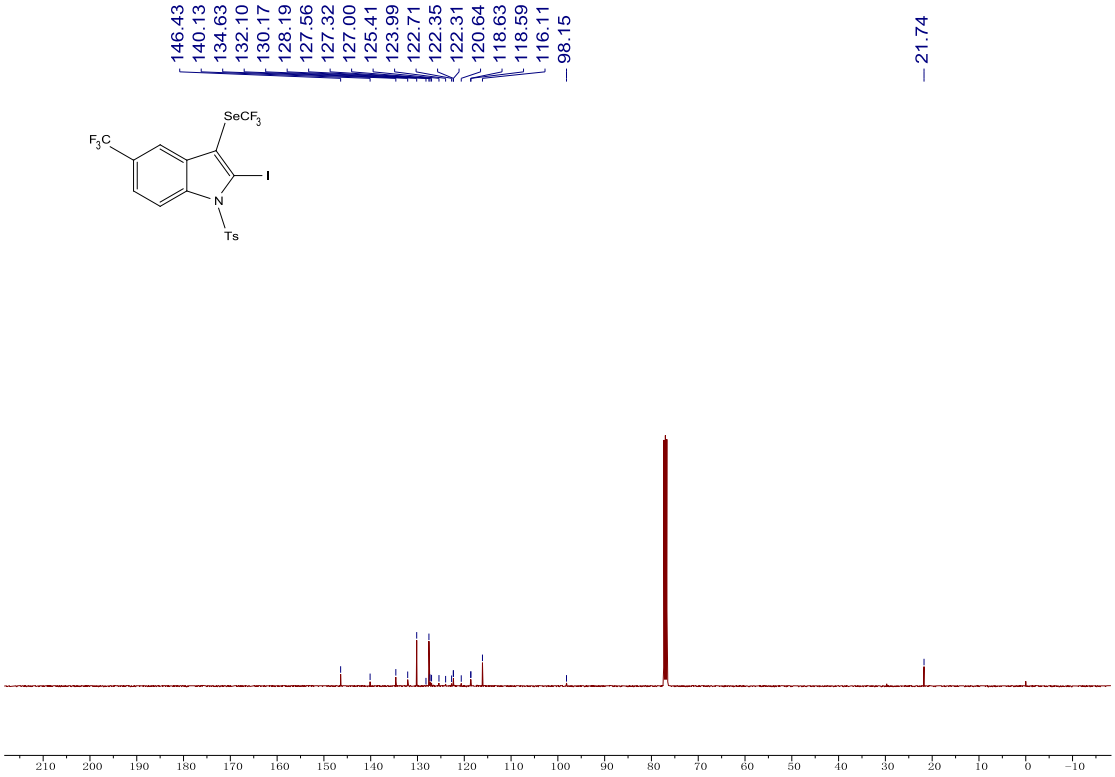
^{1}H NMR spectra of **3j** (400 MHz, $CDCl_3$)



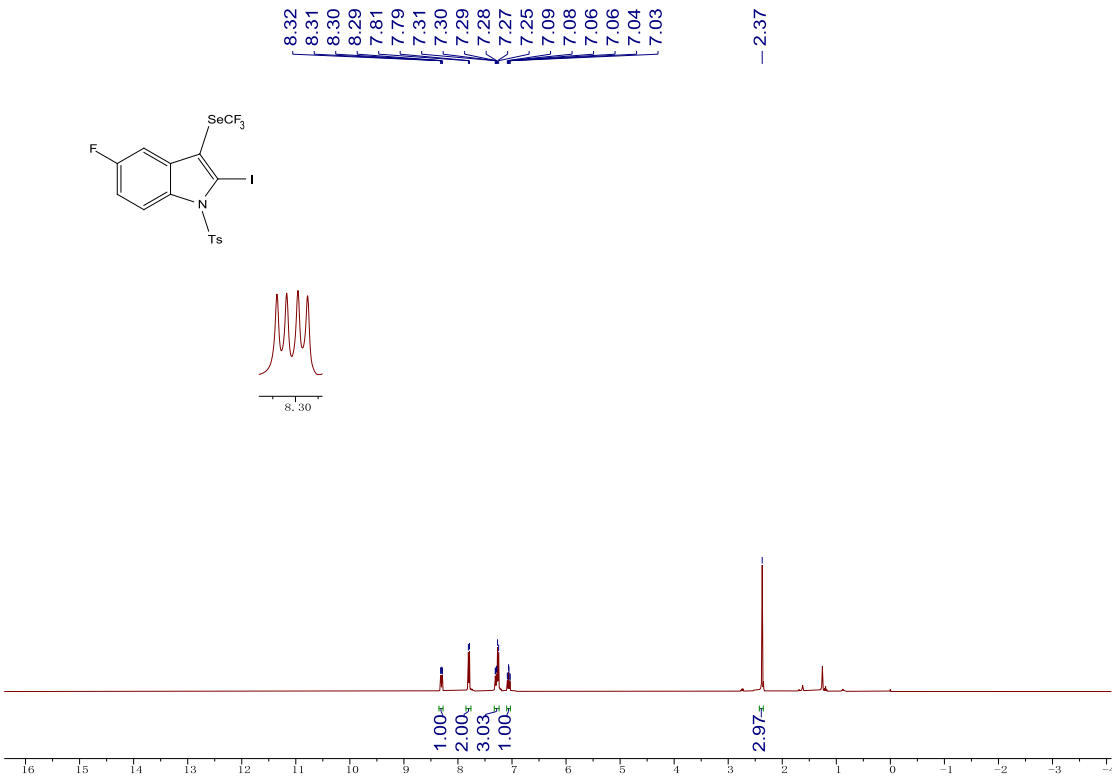
^{19}F NMR spectra of **3j** (376 MHz, $CDCl_3$)



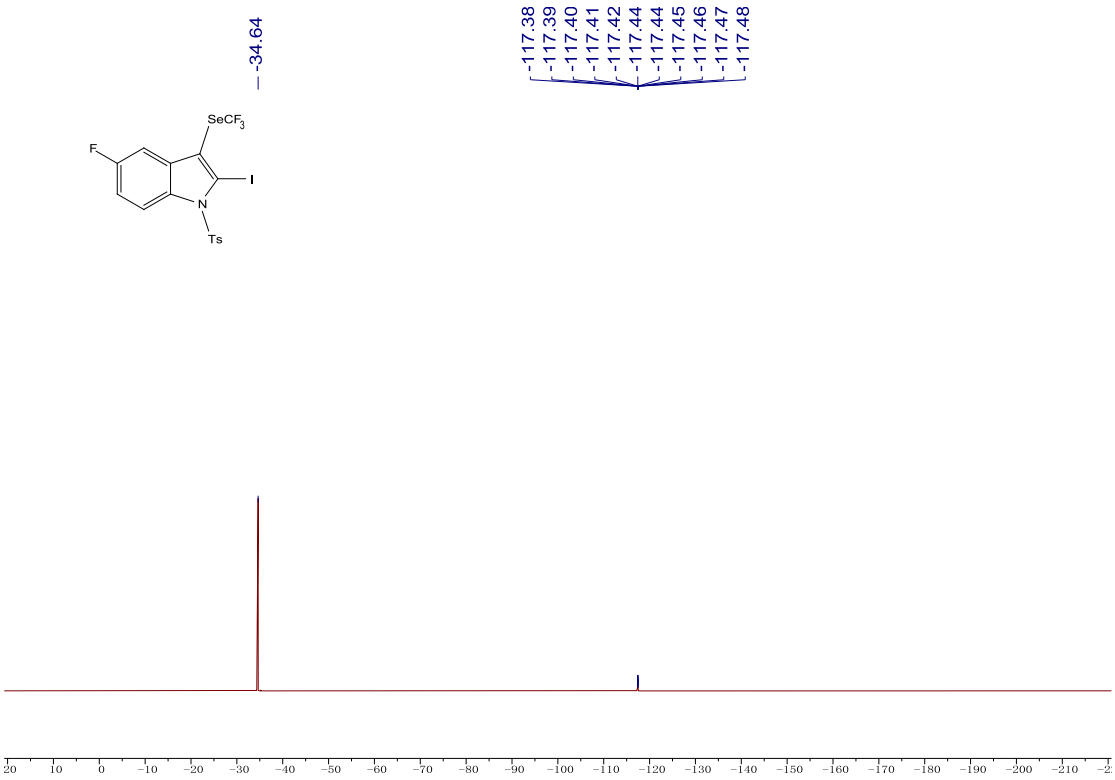
$^{13}C\{^{1}H\}$ NMR spectra of **3j** (101 MHz, $CDCl_3$)



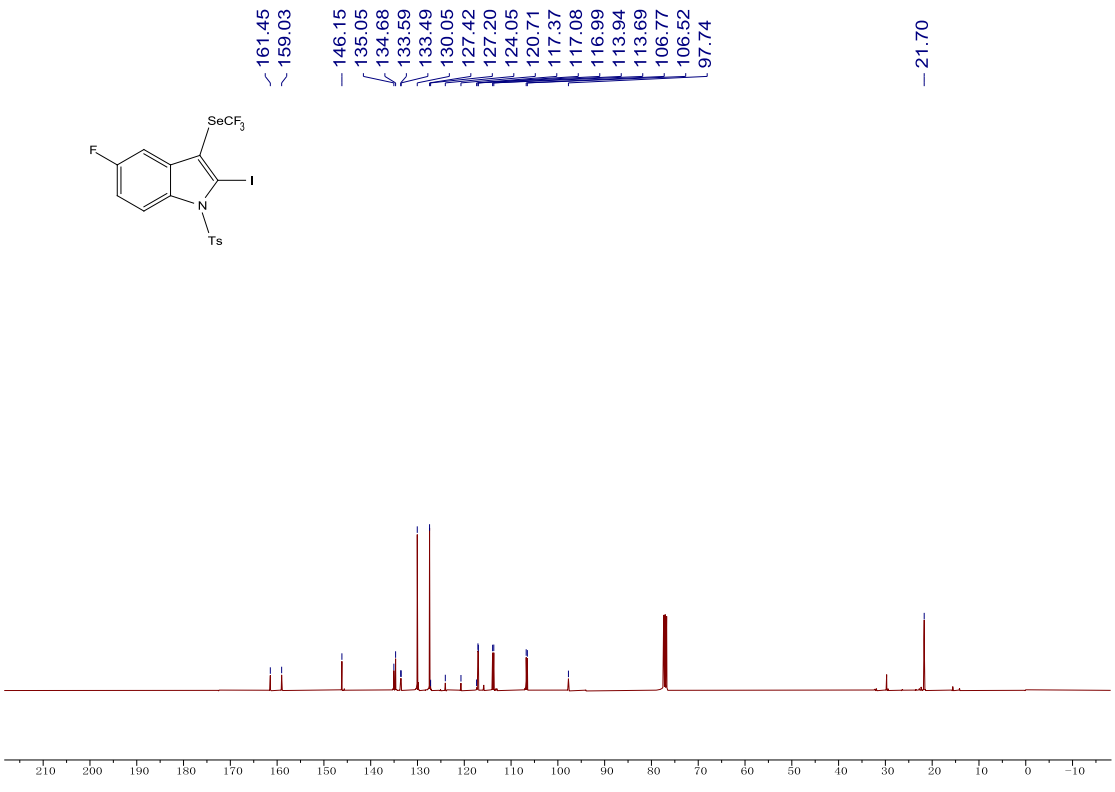
^{1}H NMR spectra of **3k** (400 MHz, $CDCl_3$)



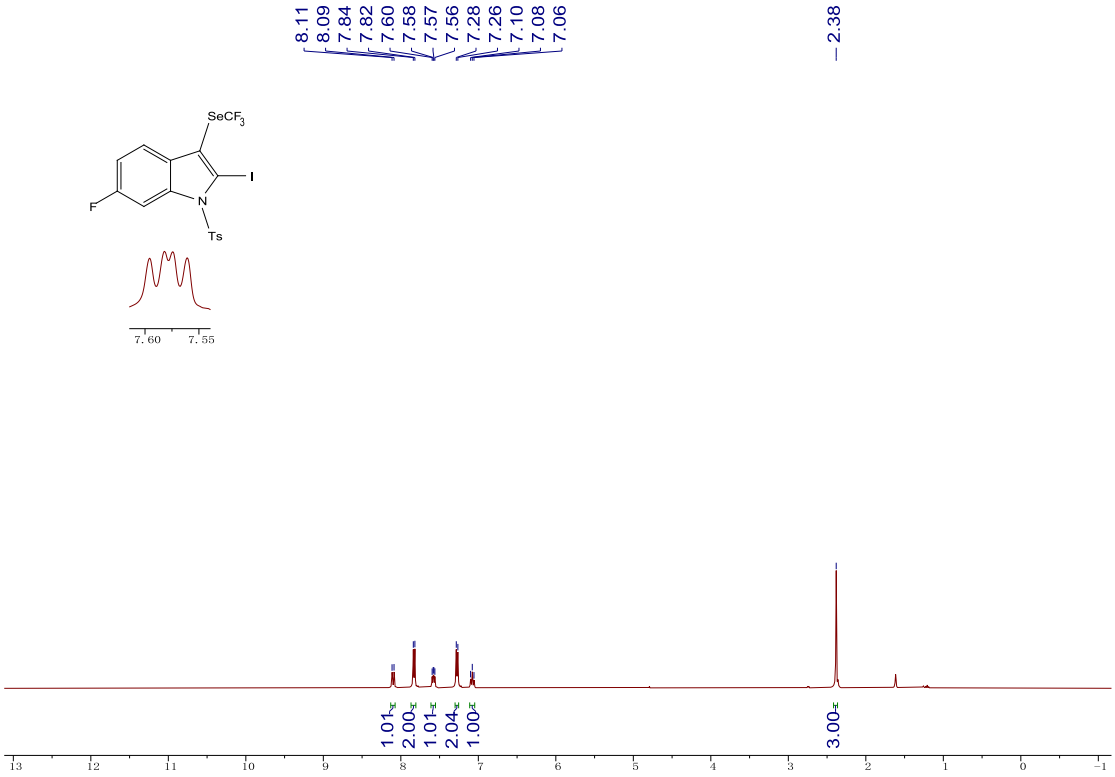
^{19}F NMR spectra of **3k** (376 MHz, $CDCl_3$)



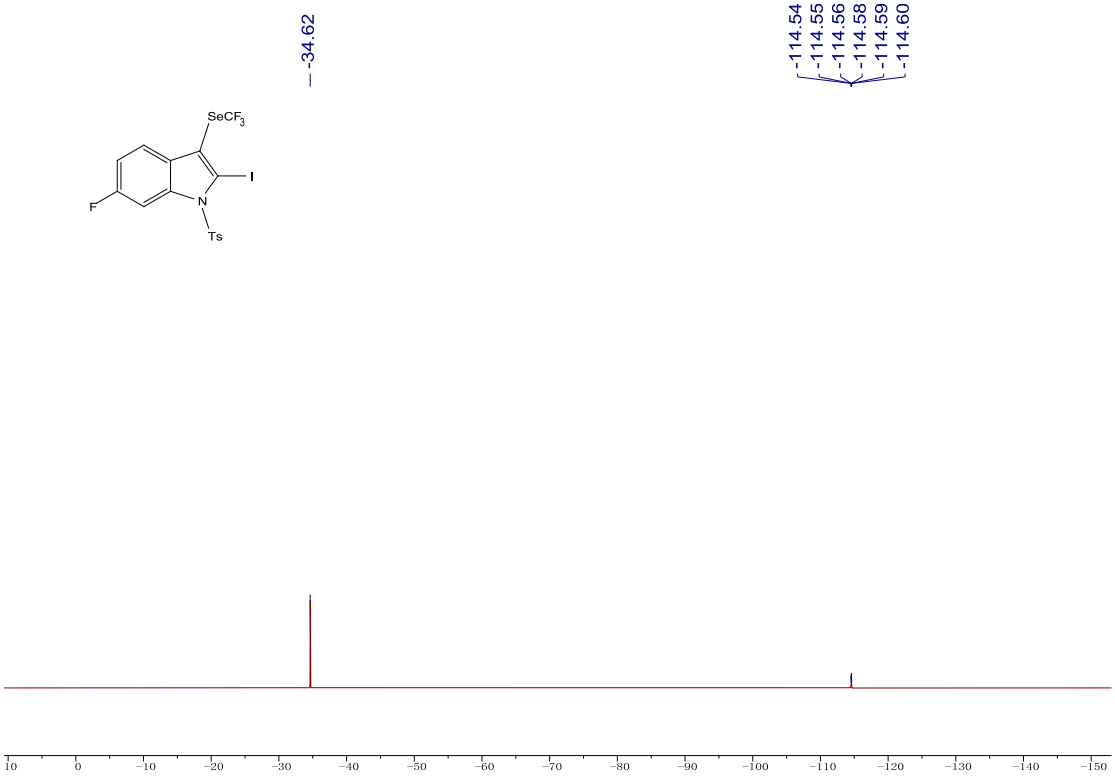
$^{13}C\{^1H\}$ NMR spectra of **3k** (101 MHz, $CDCl_3$)



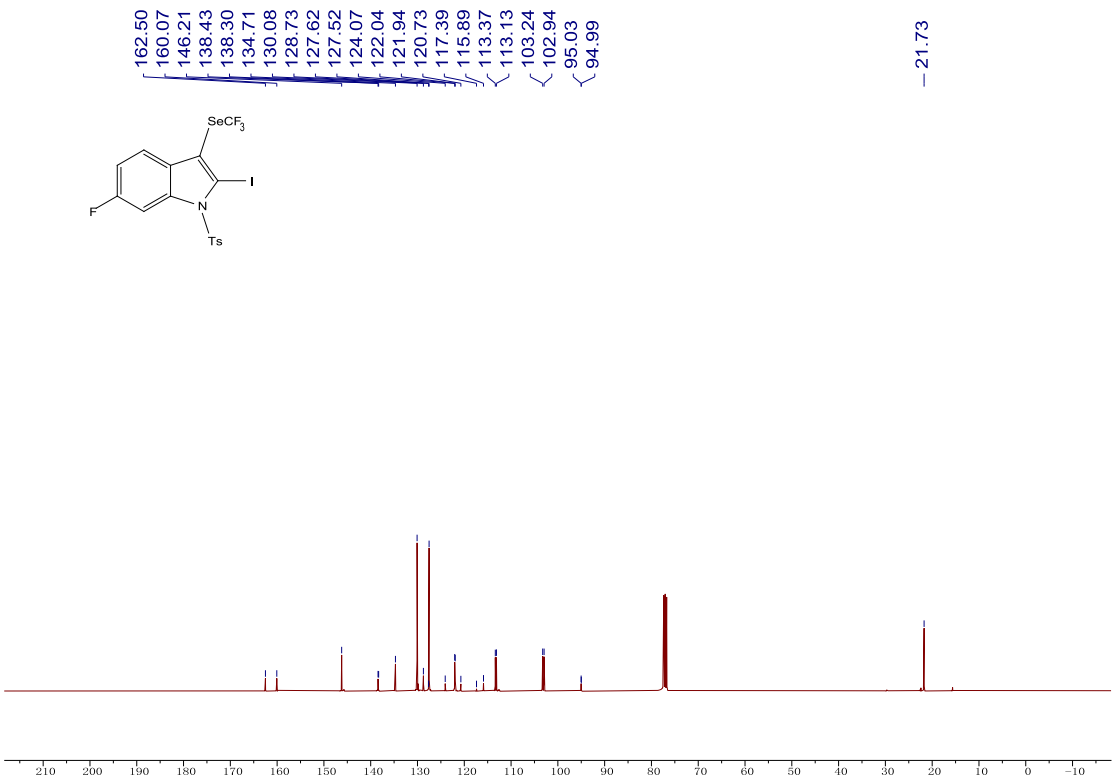
^{1}H NMR spectra of **3l** (400 MHz, $CDCl_3$)



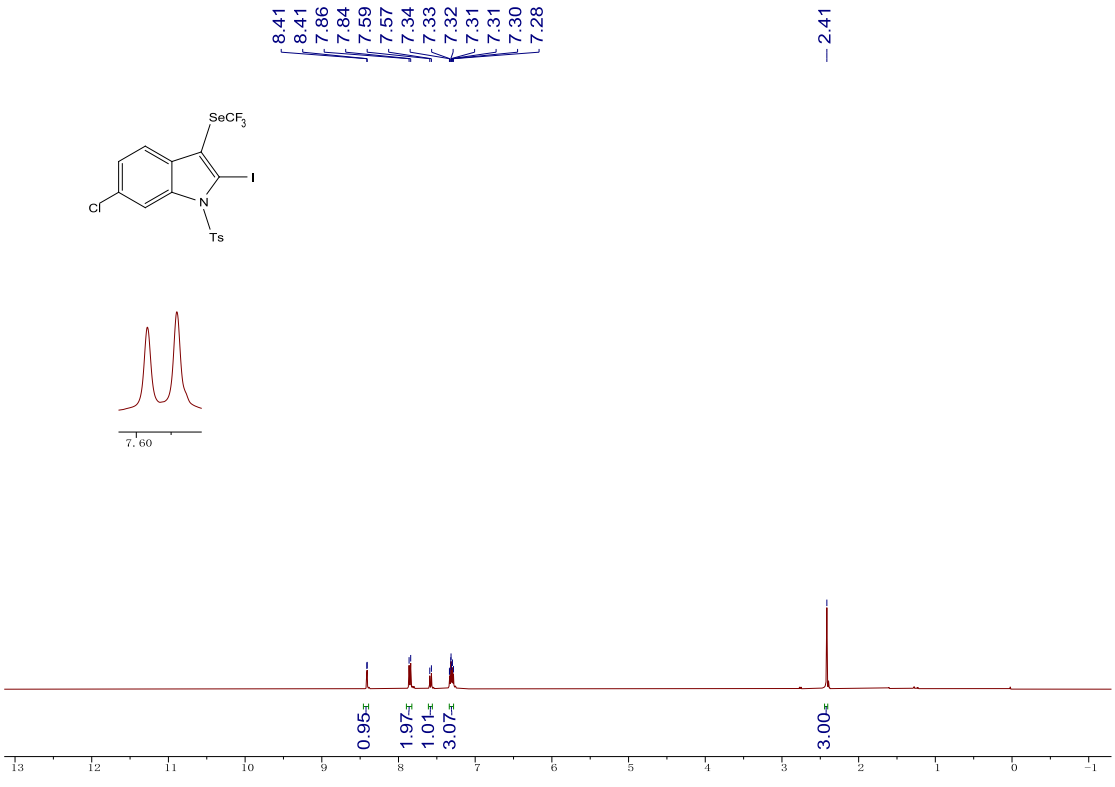
^{19}F NMR spectra of **3l** (376 MHz, $CDCl_3$)



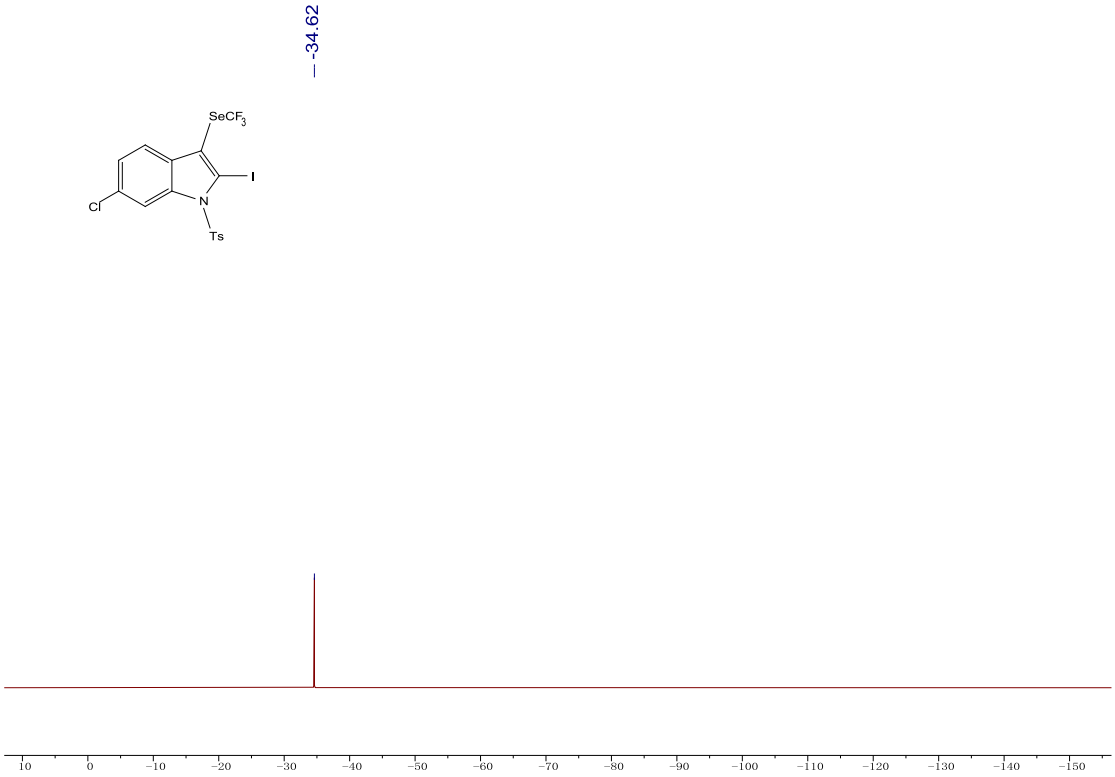
$^{13}C\{^{1}H\}$ NMR spectra of **3l** (101 MHz, $CDCl_3$)



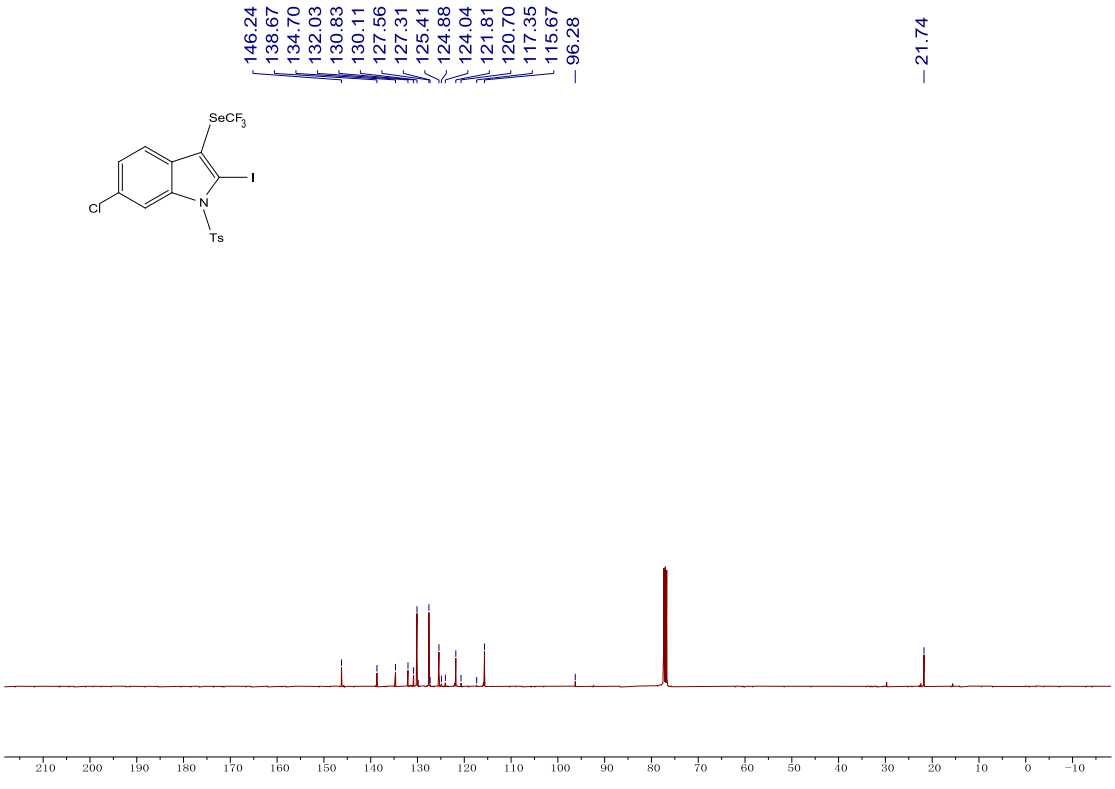
^{1}H NMR spectra of **3m** (400 MHz, $CDCl_3$)



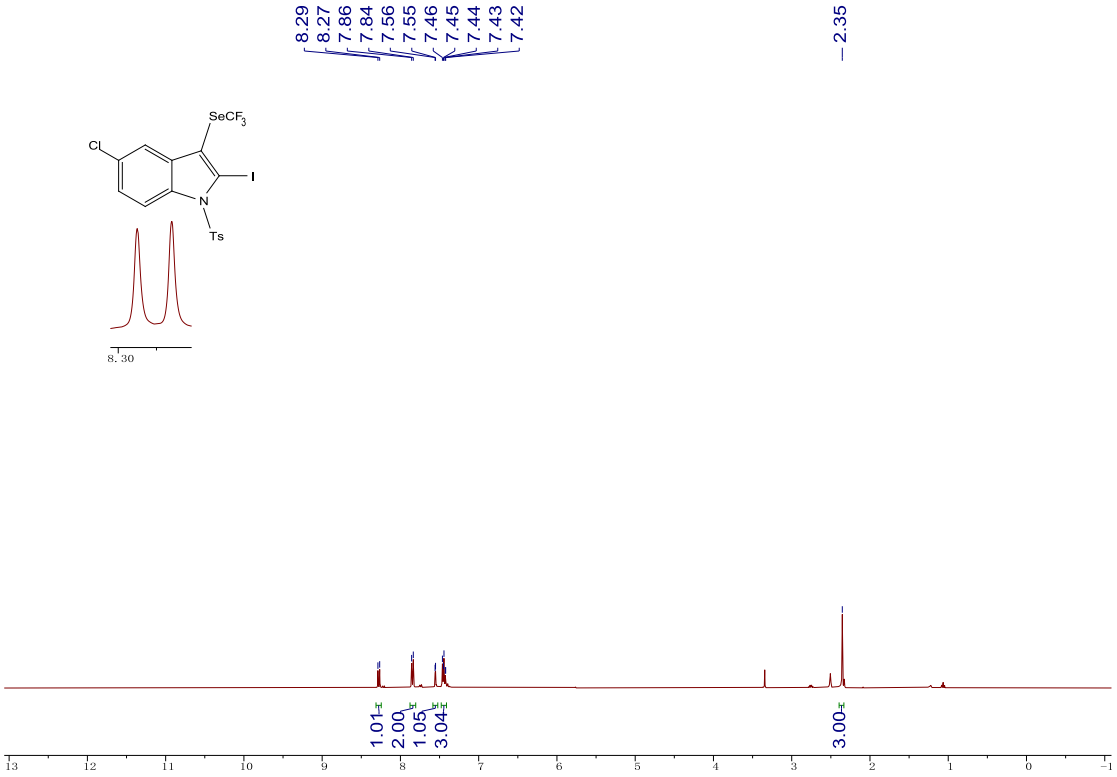
^{19}F NMR spectra of **3m** (376 MHz, $CDCl_3$)



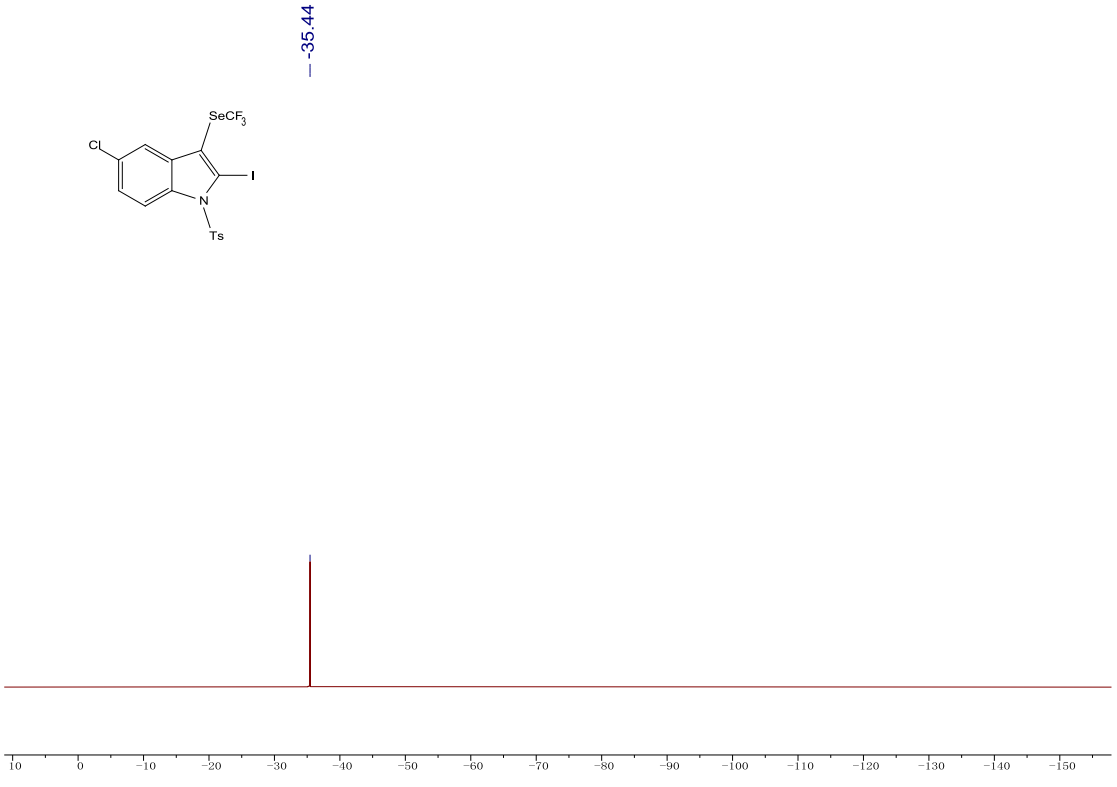
$^{13}C\{^1H\}$ NMR spectra of **3m** (101 MHz, $CDCl_3$)



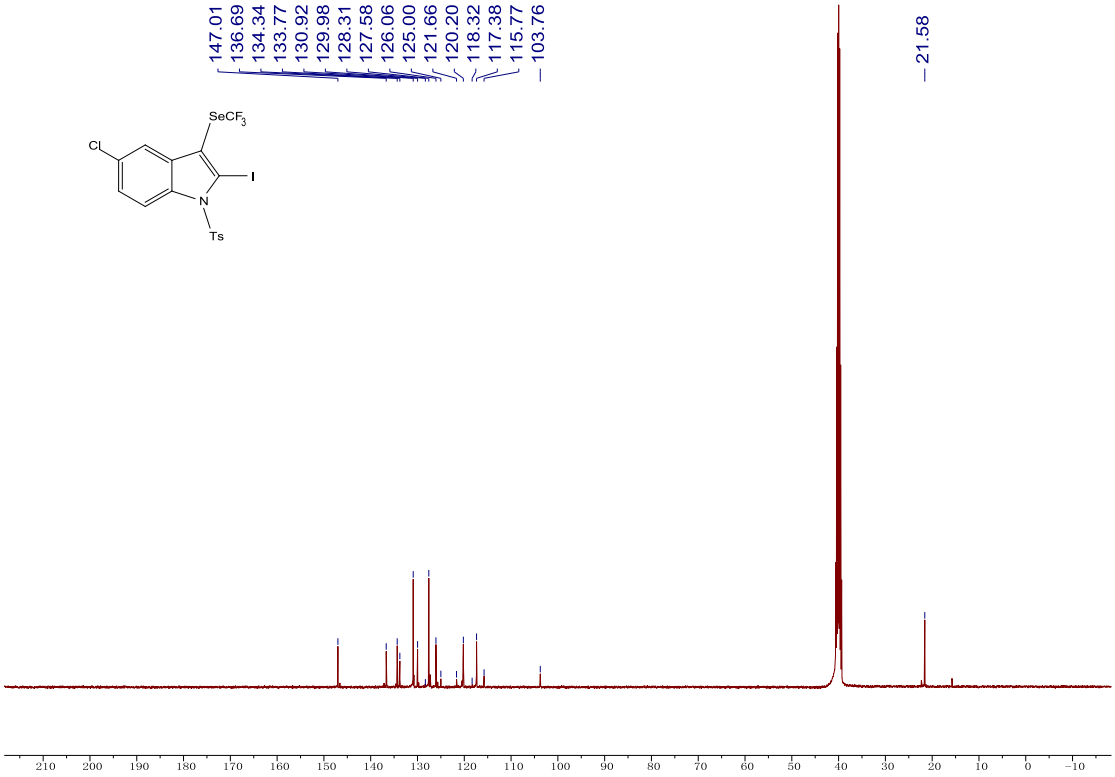
^{1}H NMR spectra of **3n** (400 MHz, DMSO-d_6)



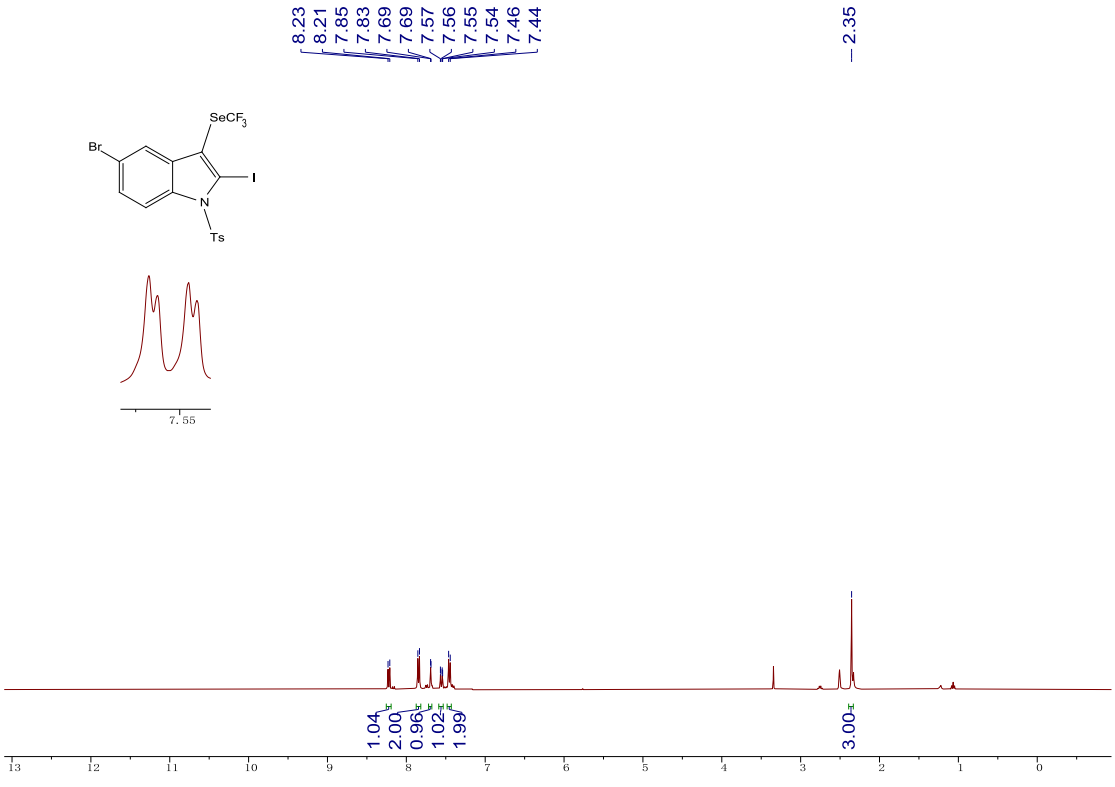
^{19}F NMR spectra of **3n** (376 MHz, DMSO-d_6)



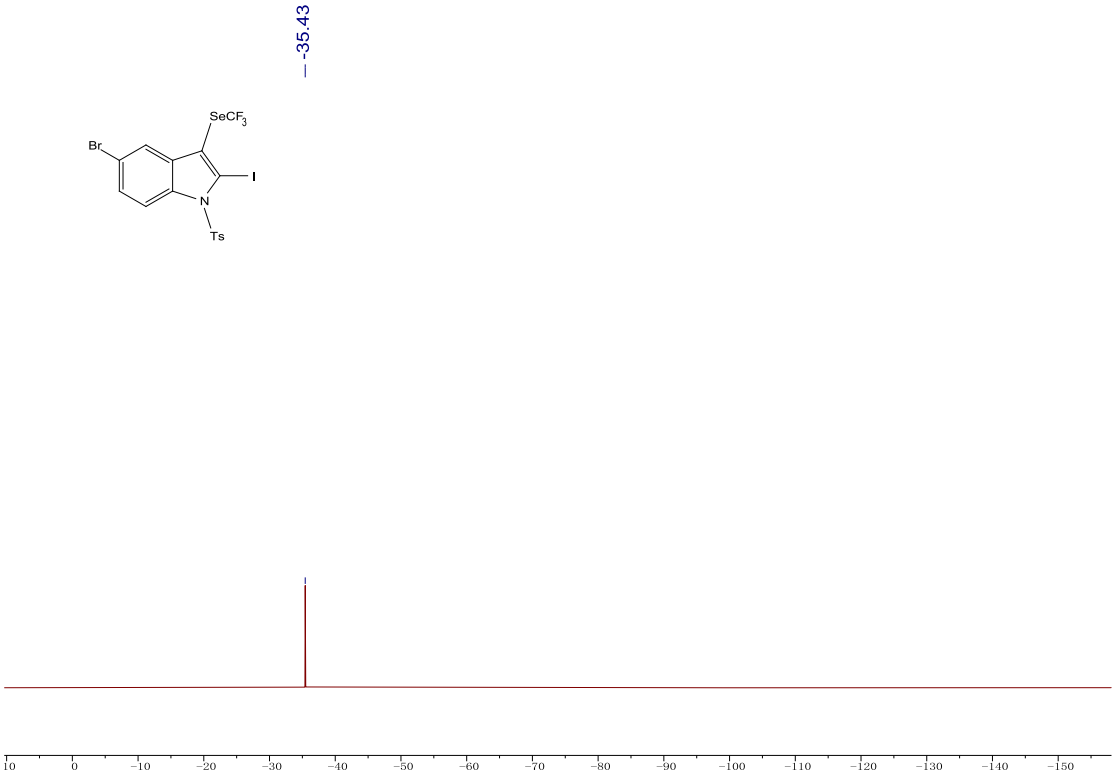
$^{13}C\{^{1}H\}$ NMR spectra of **3n** (101 MHz, DMSO-d_6)



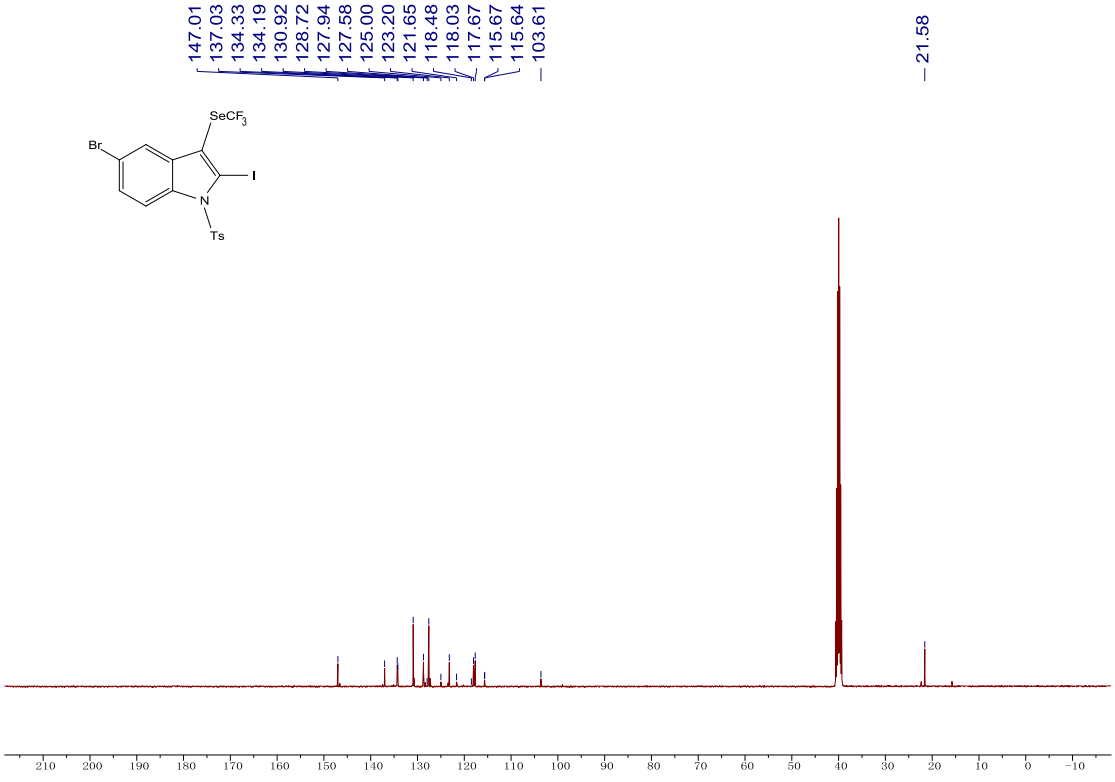
^{1}H NMR spectra of **3o** (400 MHz, DMSO-d_6)



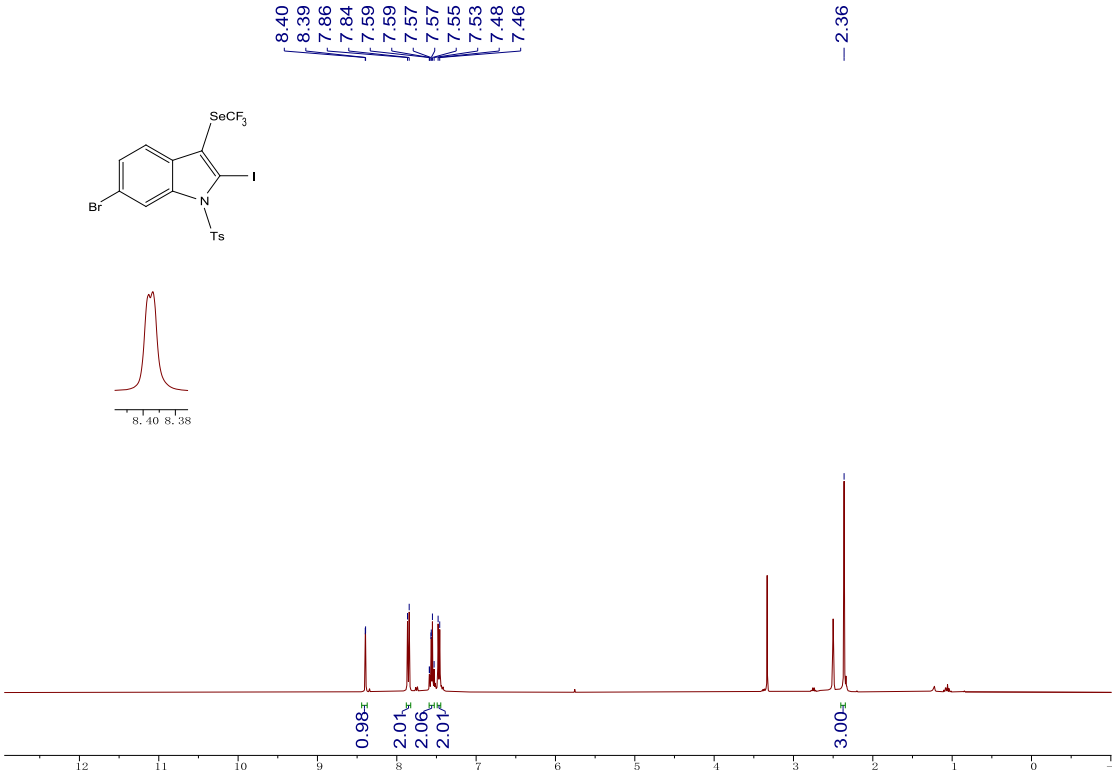
^{19}F NMR spectra of **3o** (376 MHz, DMSO-d_6)



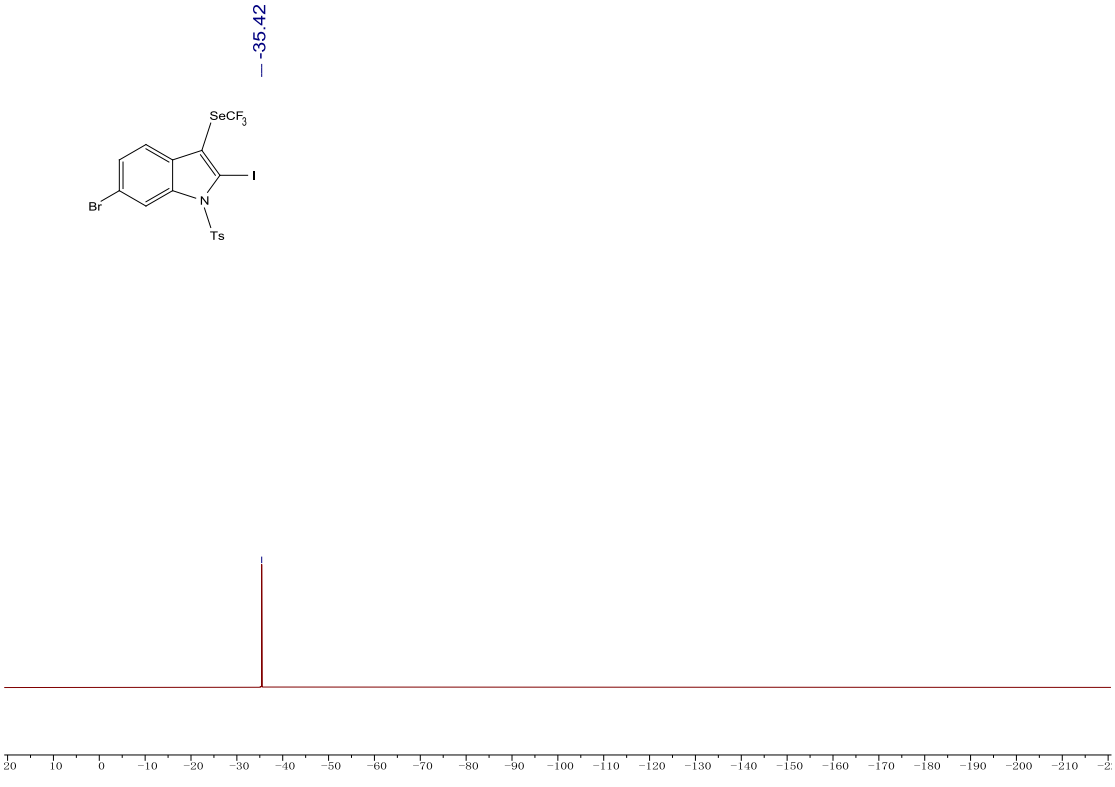
^{13}C{^{1}H} NMR spectra of **3o** (101 MHz, DMSO-d_6)



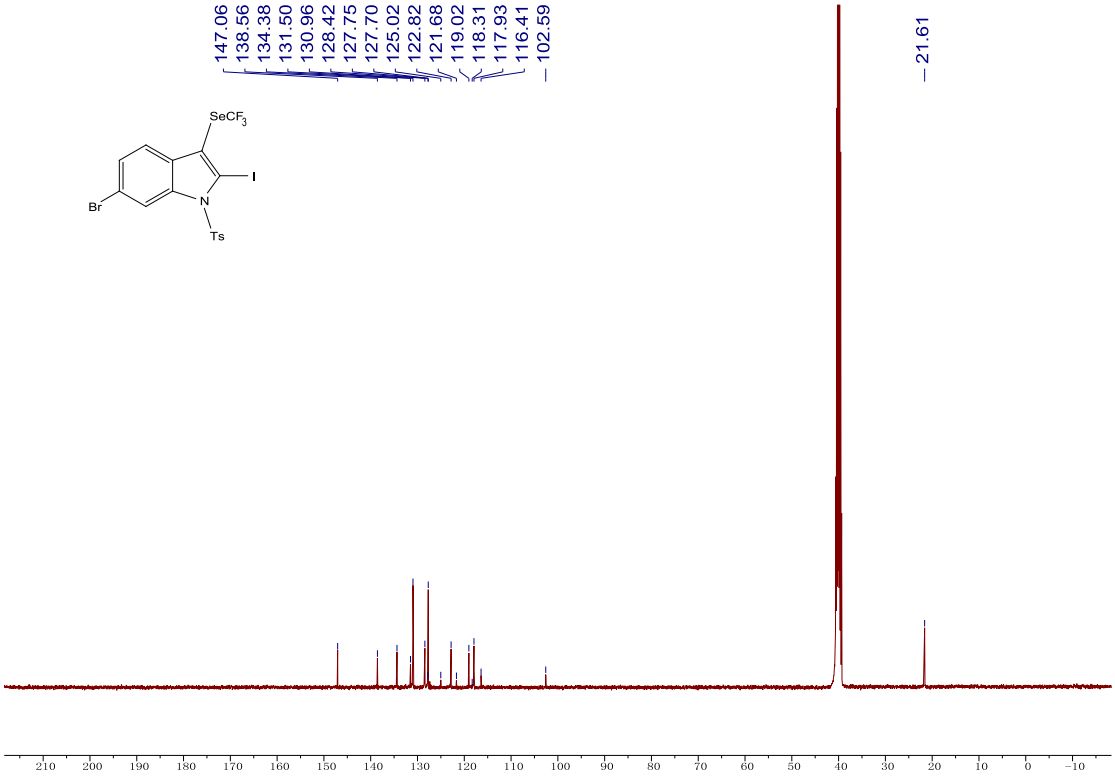
^{1}H NMR spectra of **3p** (400 MHz, DMSO-d_6)



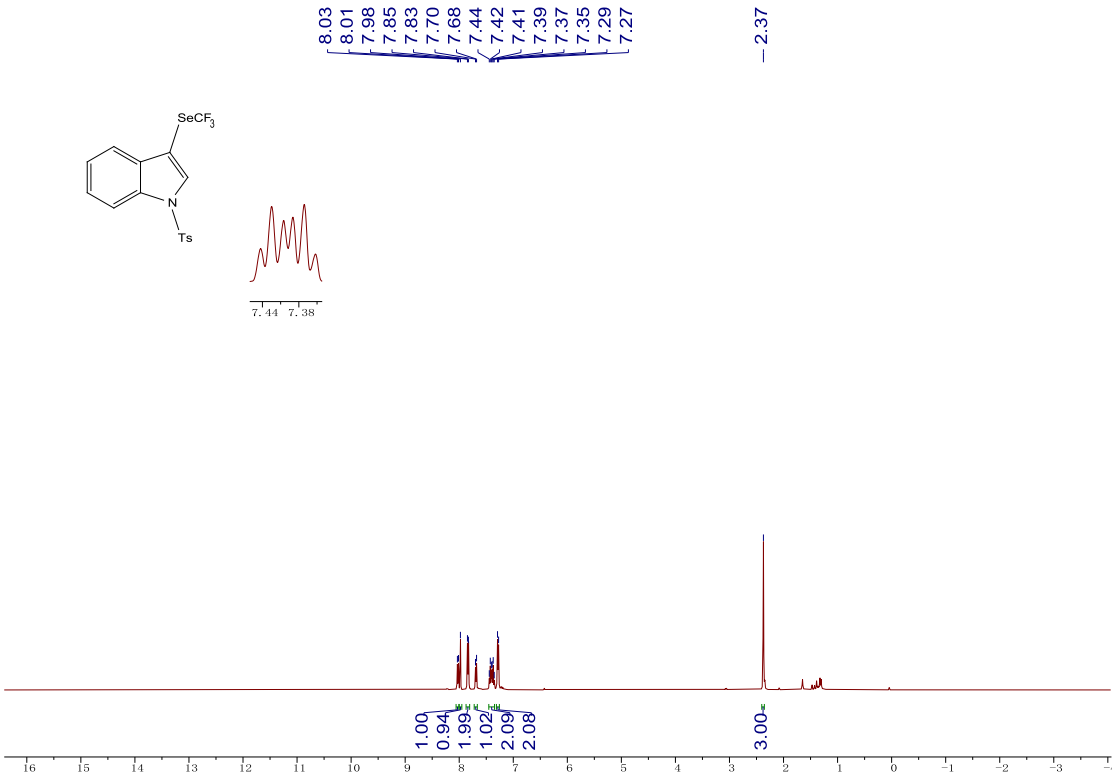
^{19}F NMR spectra of **3p** (376 MHz, DMSO-d_6)



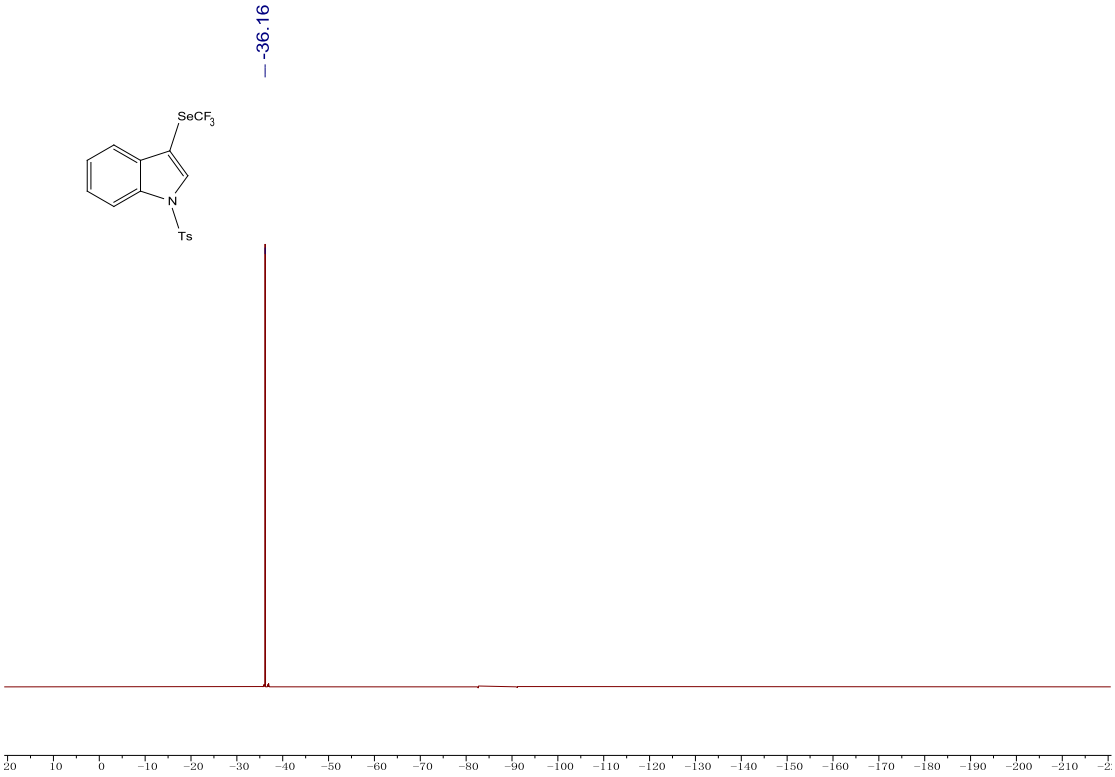
$^{13}C\{^{1}H\}$ NMR spectra of **3p** (101 MHz, DMSO-d_6)



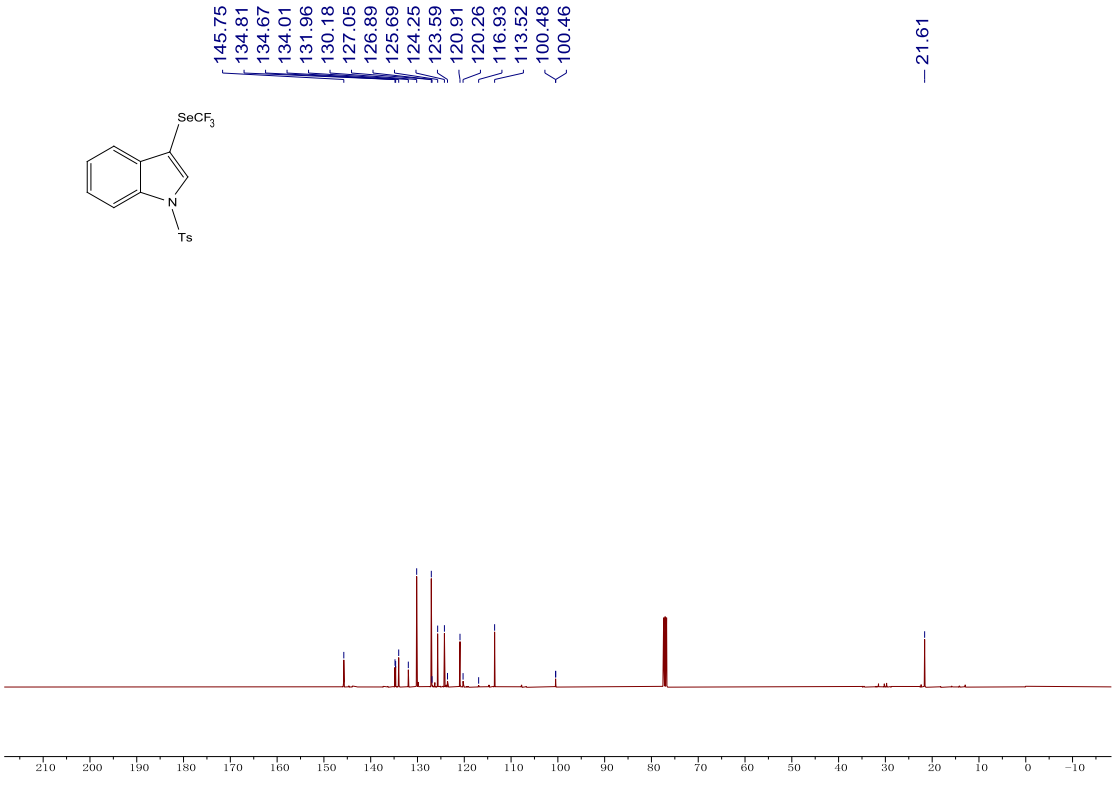
^{1}H NMR spectra of **4a** (400 MHz, $CDCl_3$)



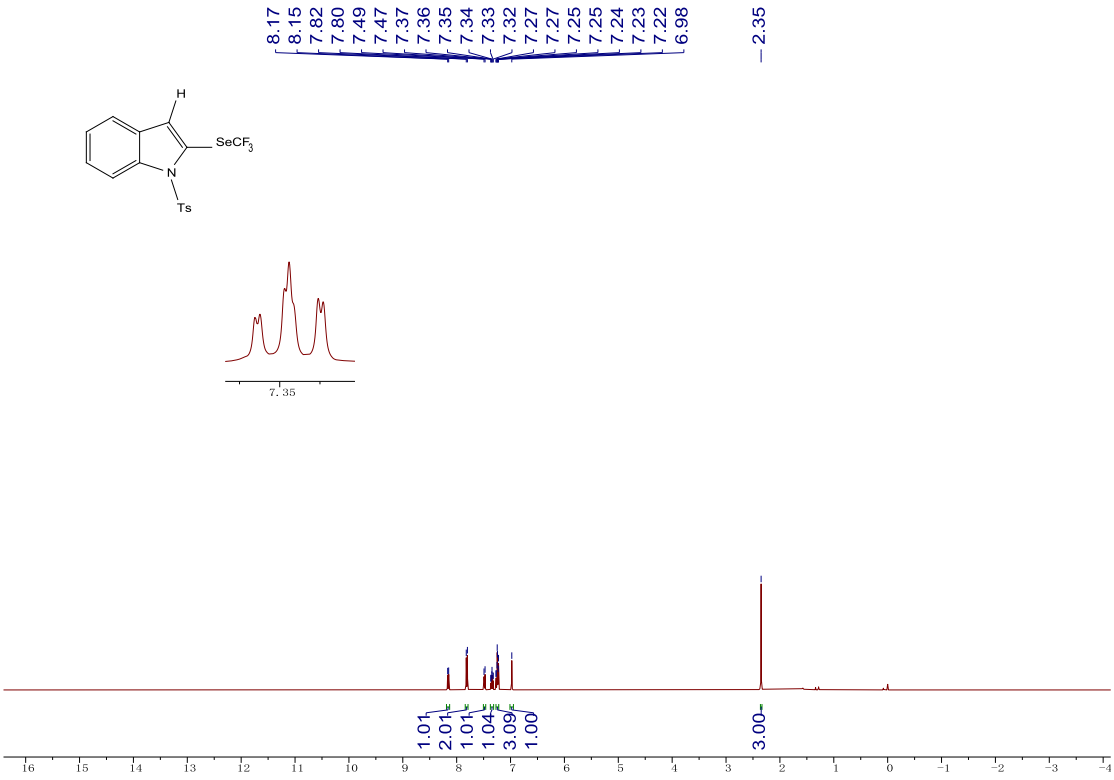
^{19}F NMR spectra of **4a** (376 MHz, $CDCl_3$)



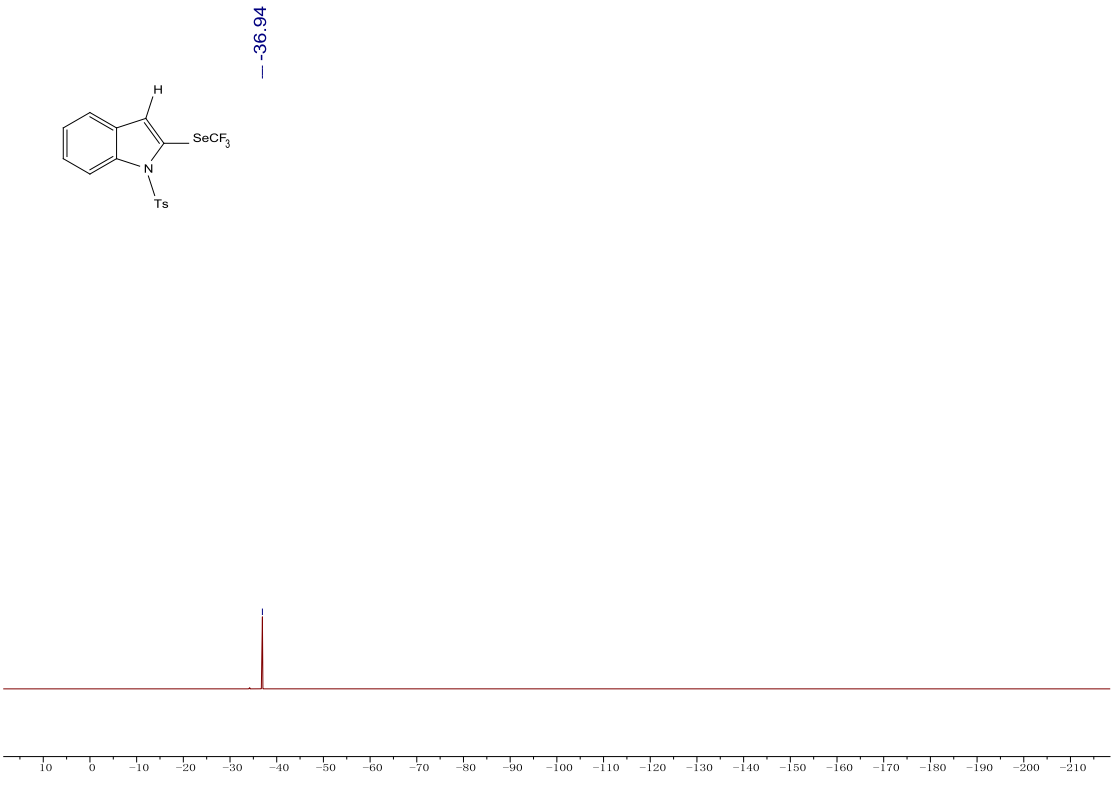
$^{13}C\{^1H\}$ NMR spectra of **4a** (101 MHz, $CDCl_3$)



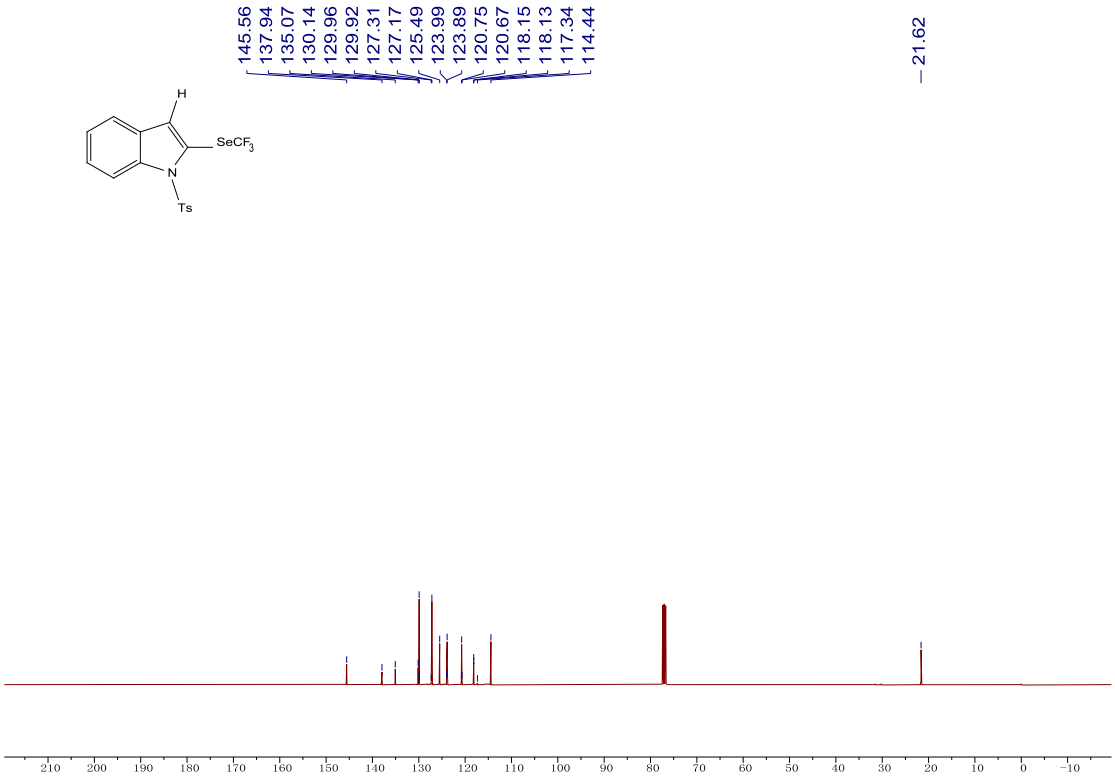
^{1}H NMR spectra of **4a′** (400 MHz, $CDCl_3$)



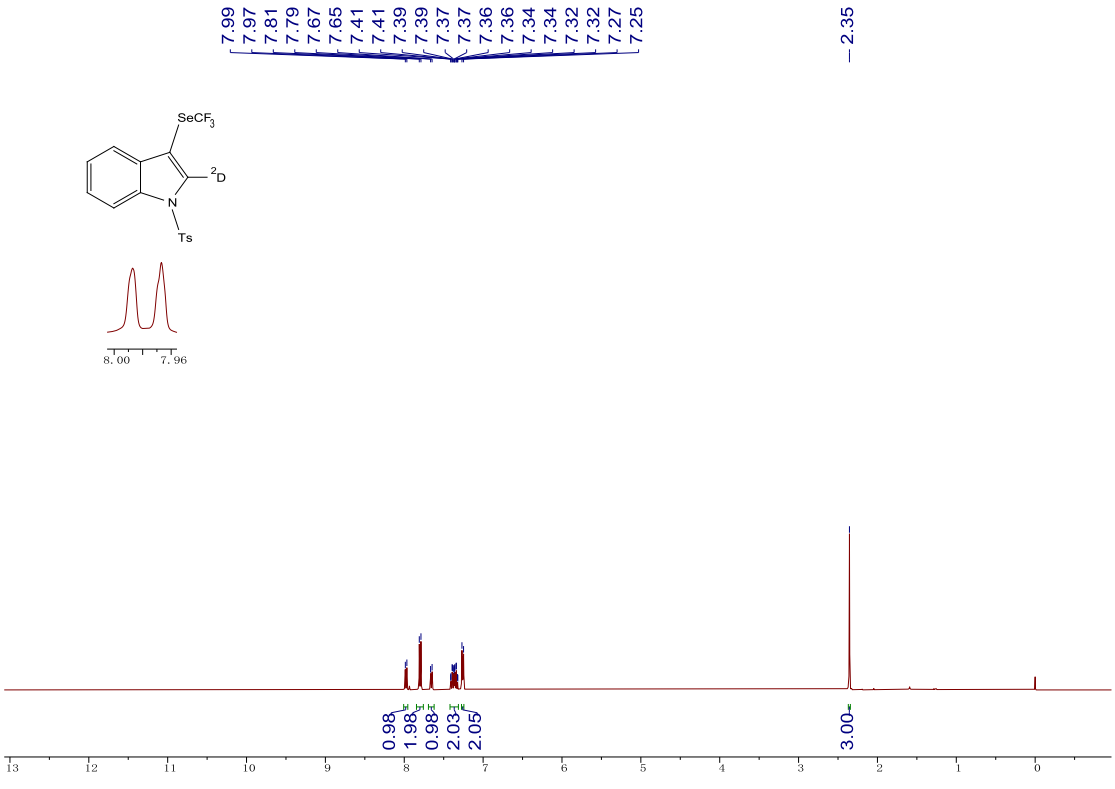
^{19}F NMR spectra of **4a′** (376 MHz, $CDCl_3$)



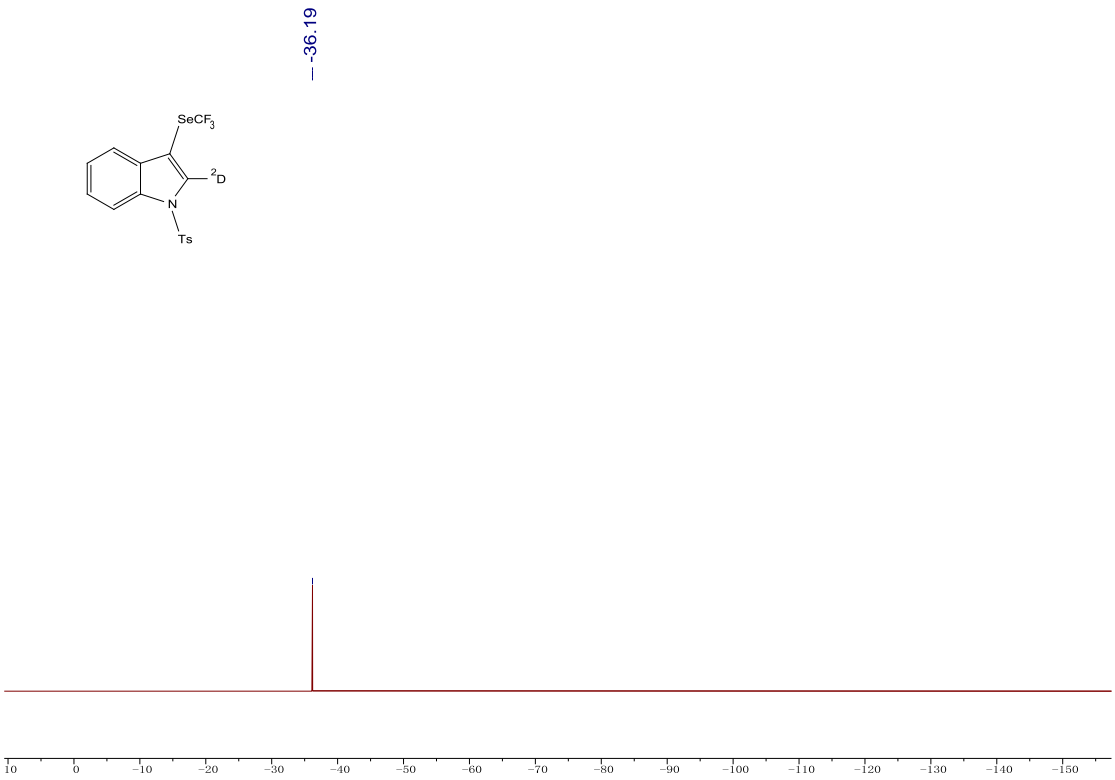
$^{13}C\{^{1}H\}$ NMR spectra of **4a′** (101 MHz, $CDCl_3$)



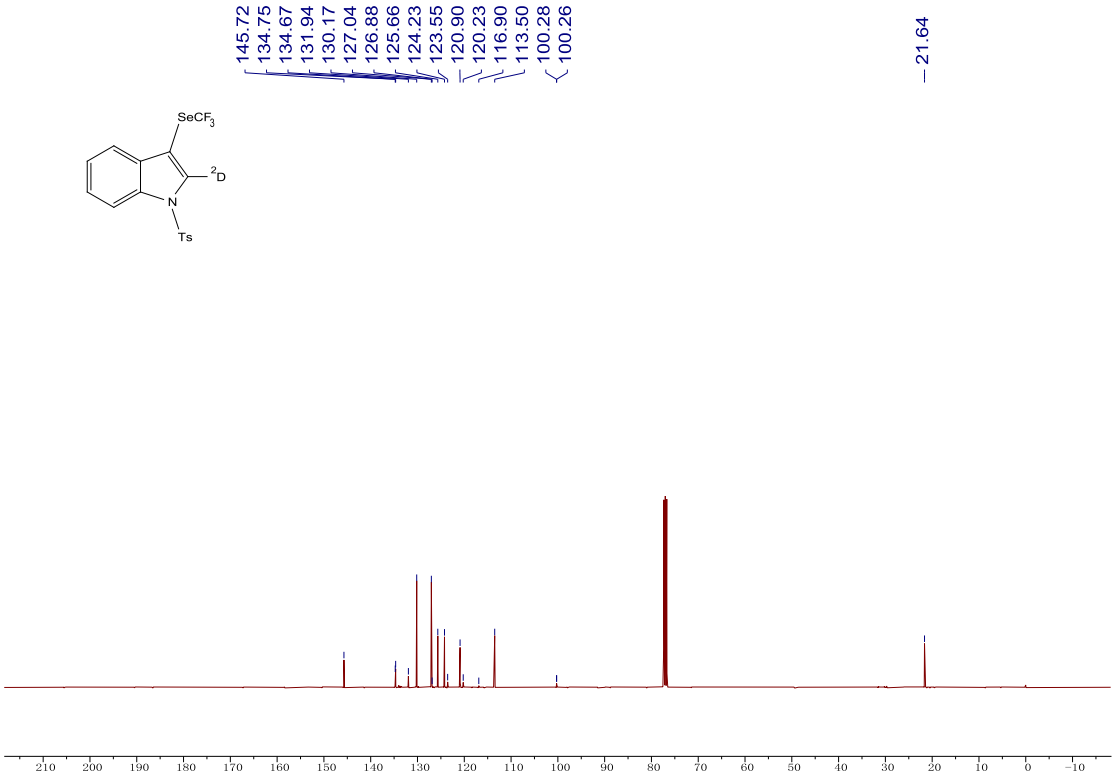
^{1}H NMR spectra of **4b** (400 MHz, $CDCl_3$)



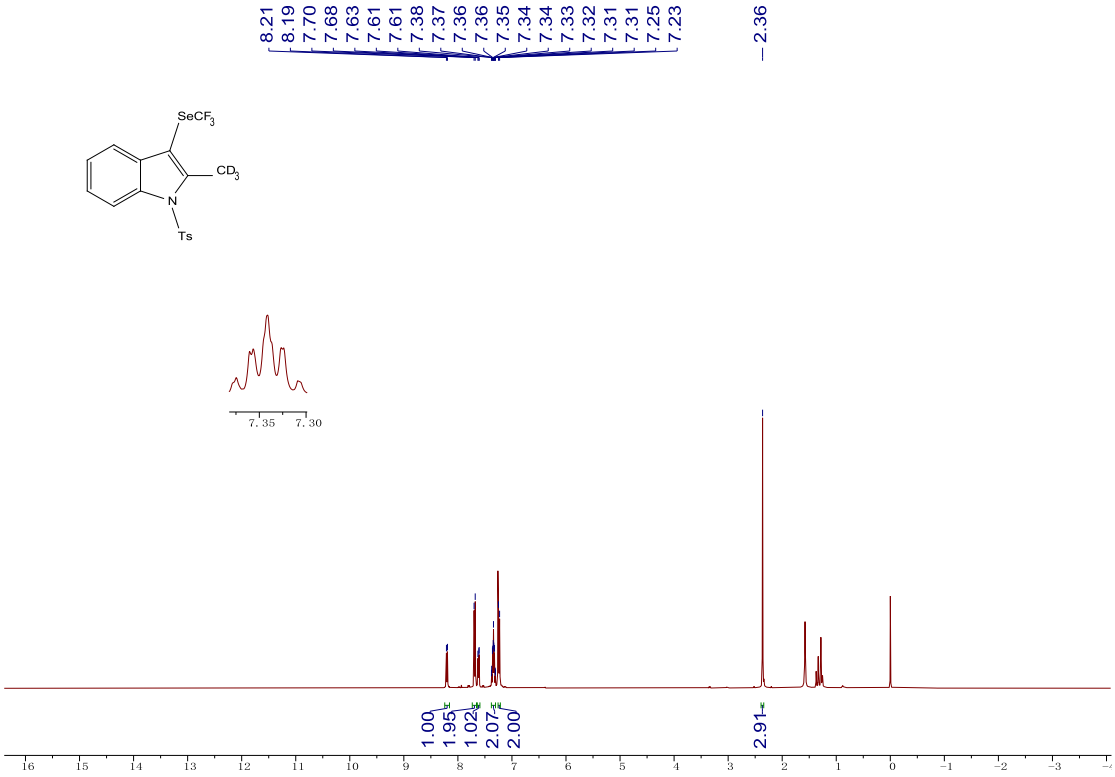
^{19}F NMR spectra of **4b** (376 MHz, $CDCl_3$)



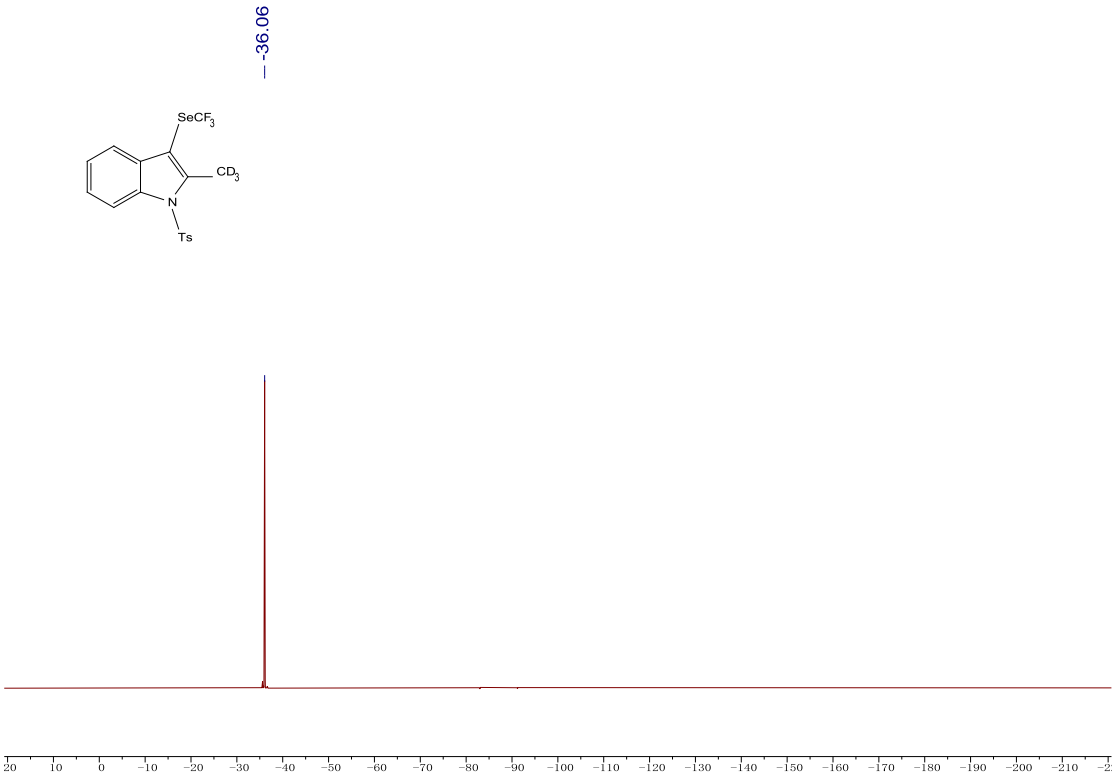
$^{13}C\{^1H\}$ NMR spectra of **4b** (101 MHz, $CDCl_3$)



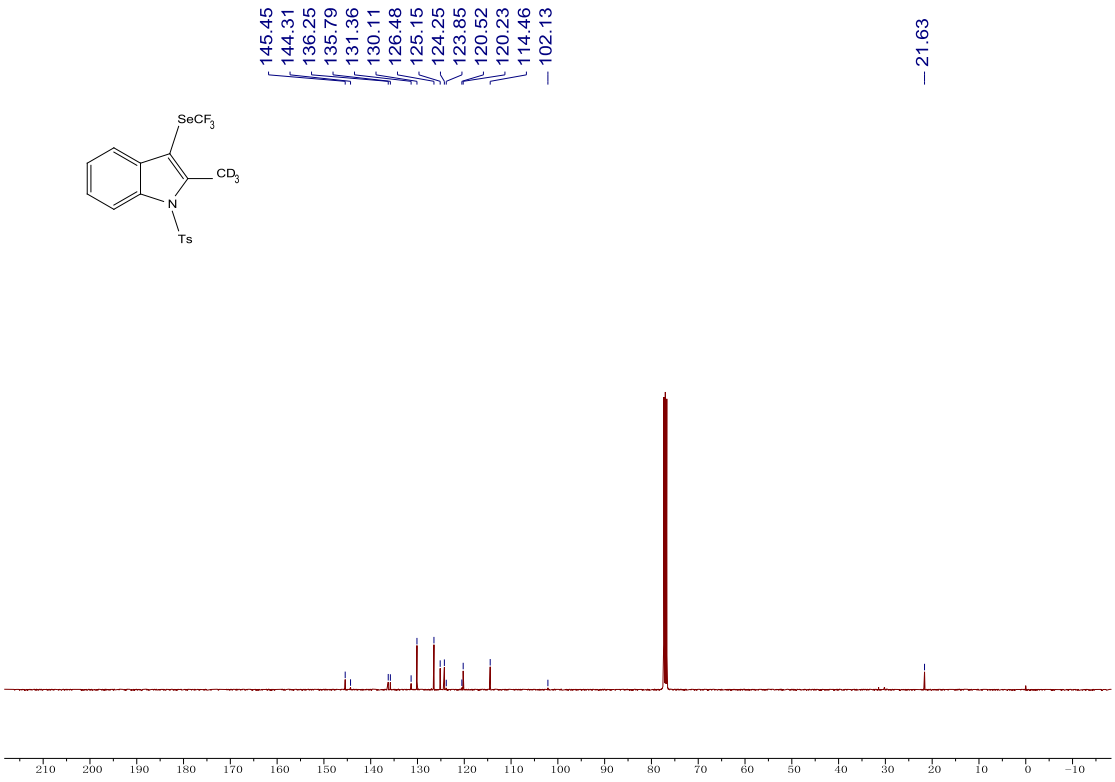
^{1}H NMR spectra of **4c** (400 MHz, $CDCl_3$)



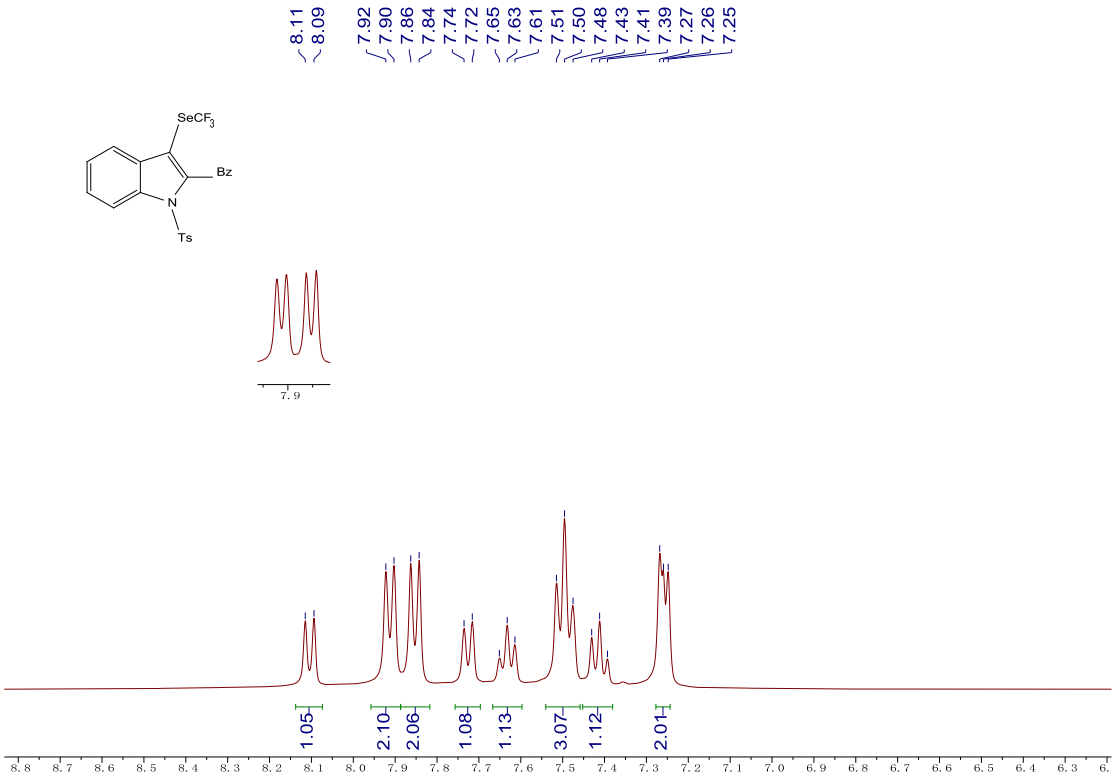
^{19}F NMR spectra of **4c** (376 MHz, $CDCl_3$)



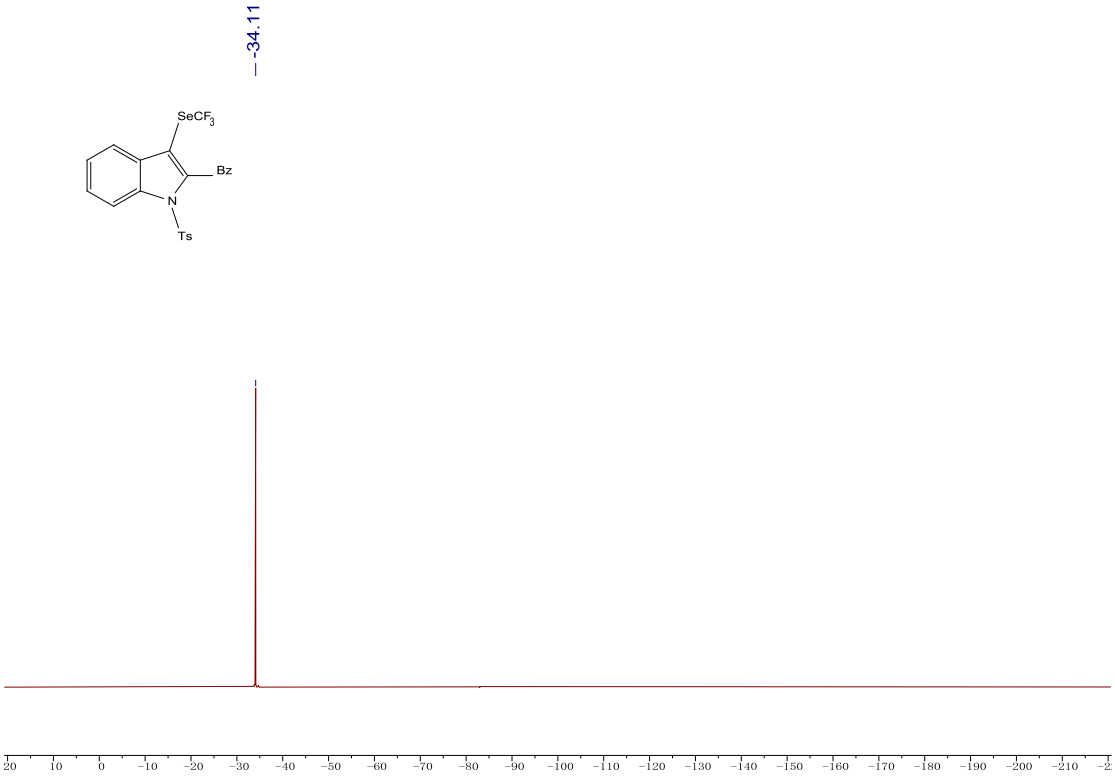
$^{13}C\{^{1}H\}$ NMR spectra of **4c** (101 MHz, $CDCl_3$)



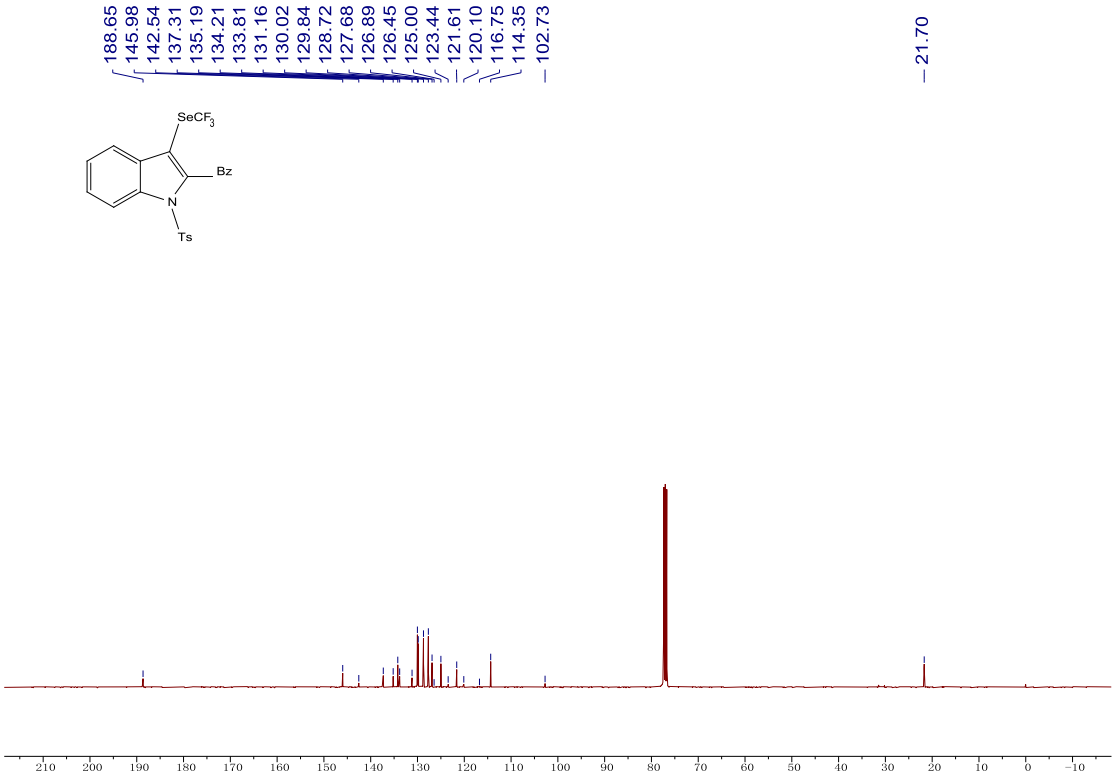
^{1}H NMR spectra of **4d** (400 MHz, $CDCl_3$)



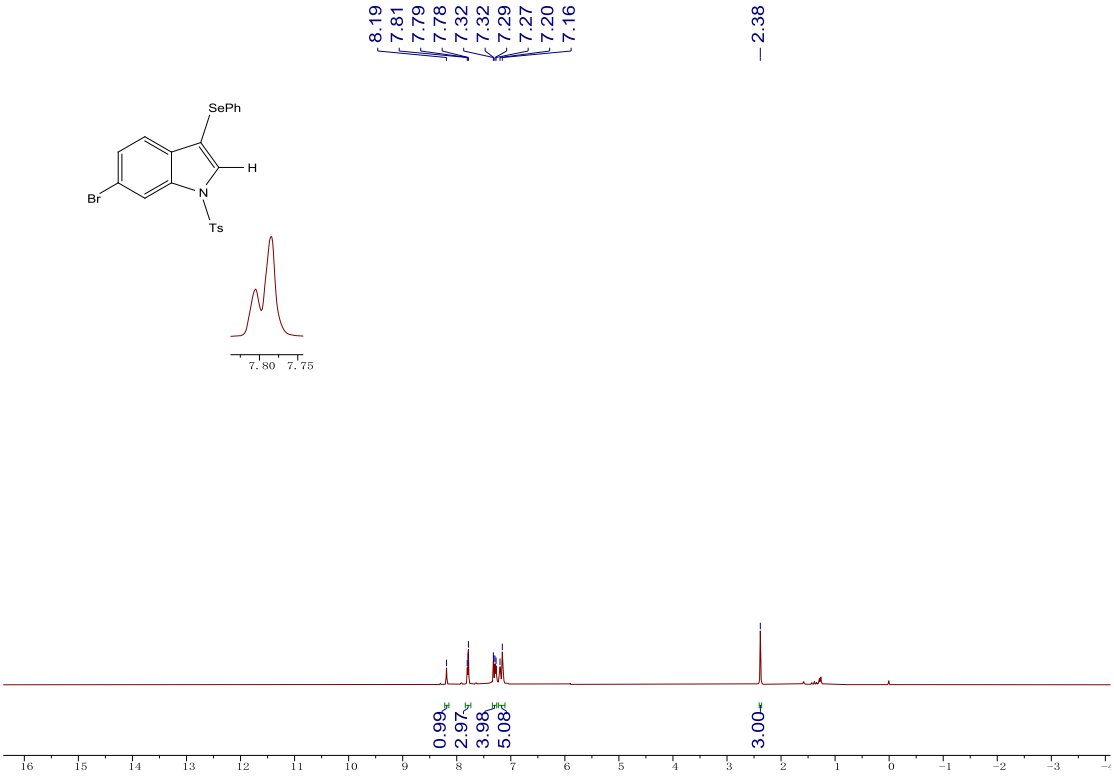
^{19}F NMR spectra of **4d** (376 MHz, $CDCl_3$)



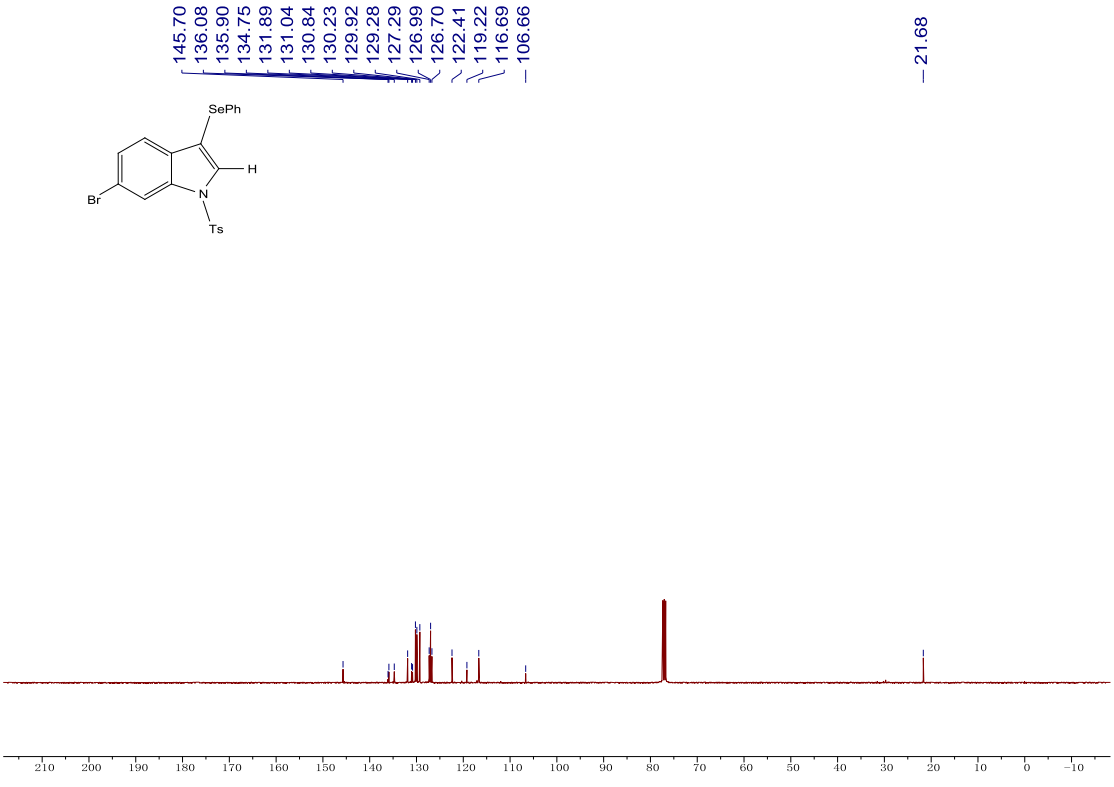
$^{13}C\{^1H\}$ NMR spectra of **4d** (101 MHz, $CDCl_3$)



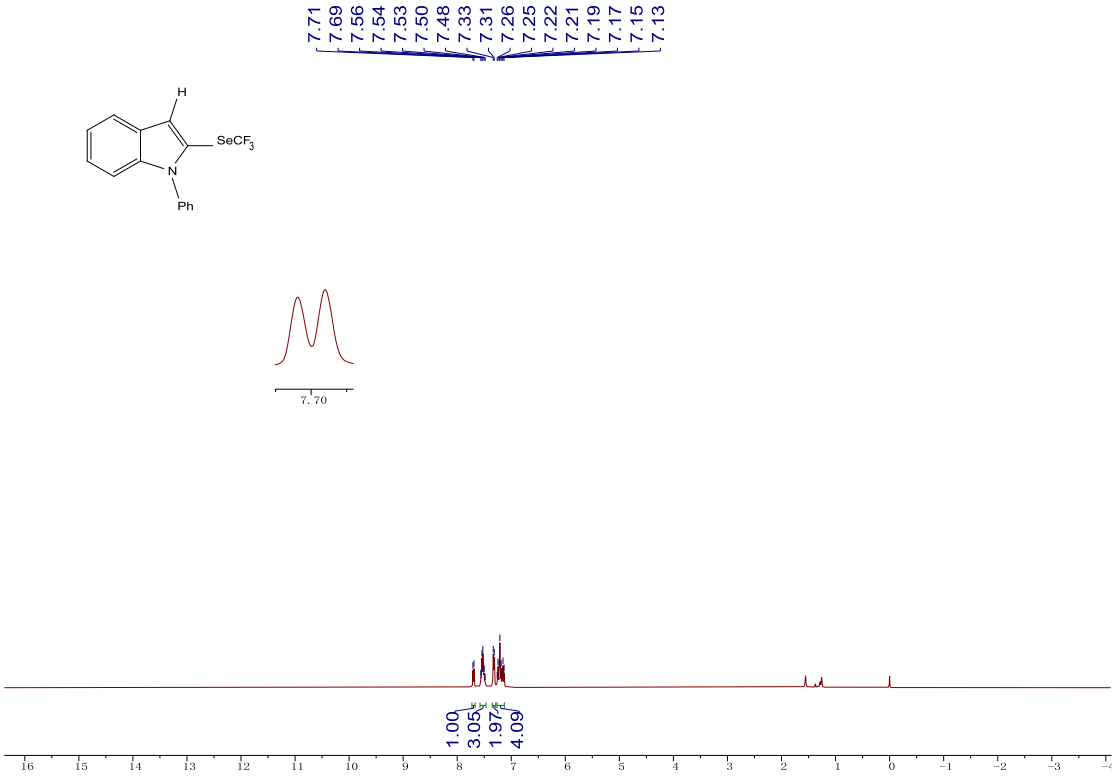
^{1}H NMR spectra of **4p-Ph** (400 MHz, $CDCl_3$)



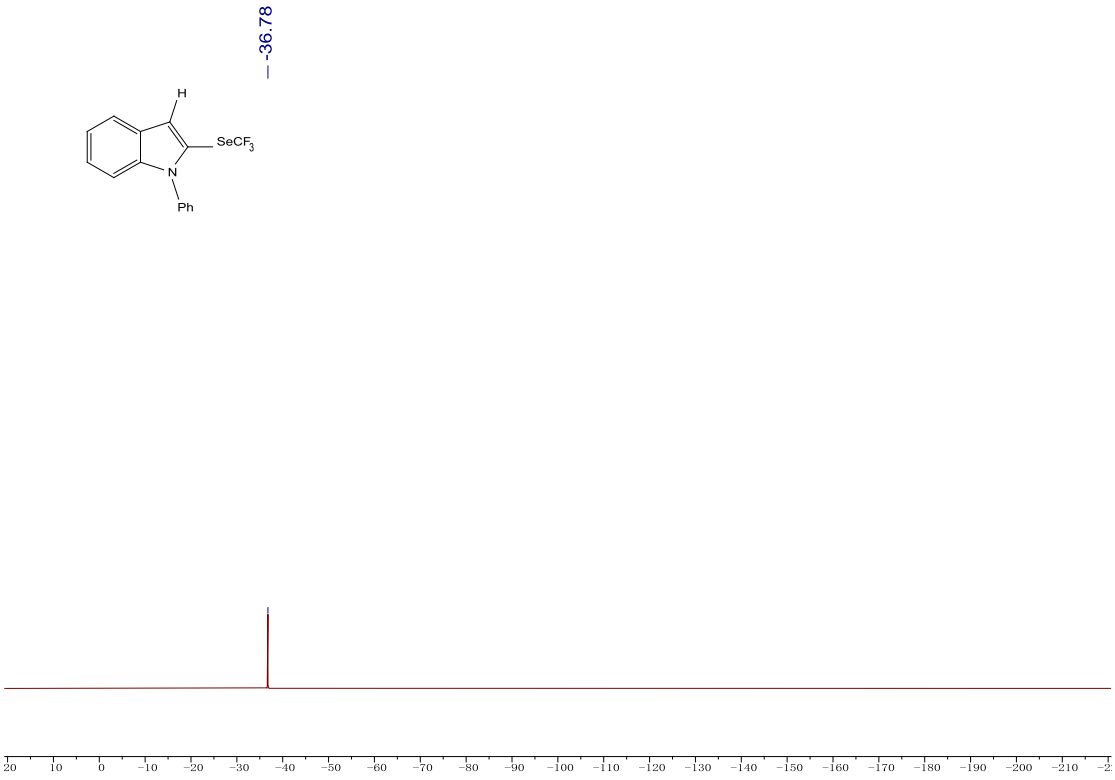
^{13}C{^{1}H} NMR spectra of **4p-Ph** (101 MHz, $CDCl_3$)



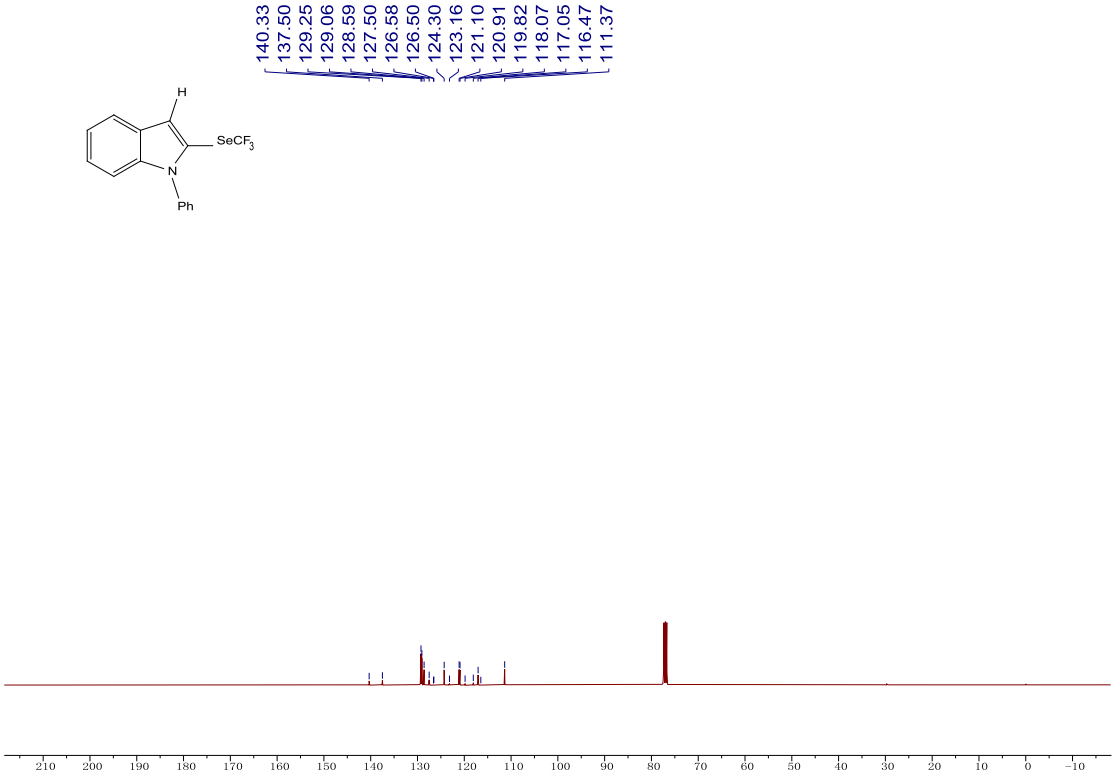
^{1}H NMR spectra of **4a-Ph′** (400 MHz, $CDCl_3$)



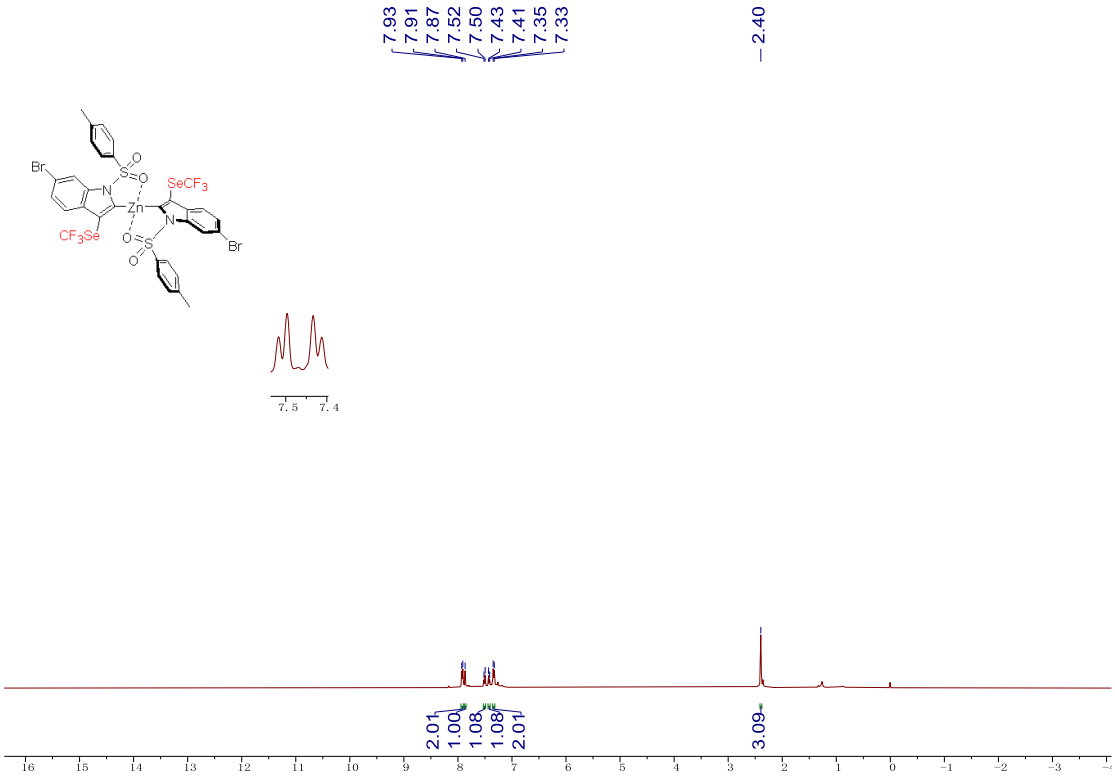
^{19}F NMR spectra of **4a-Ph′** (376 MHz, $CDCl_3$)



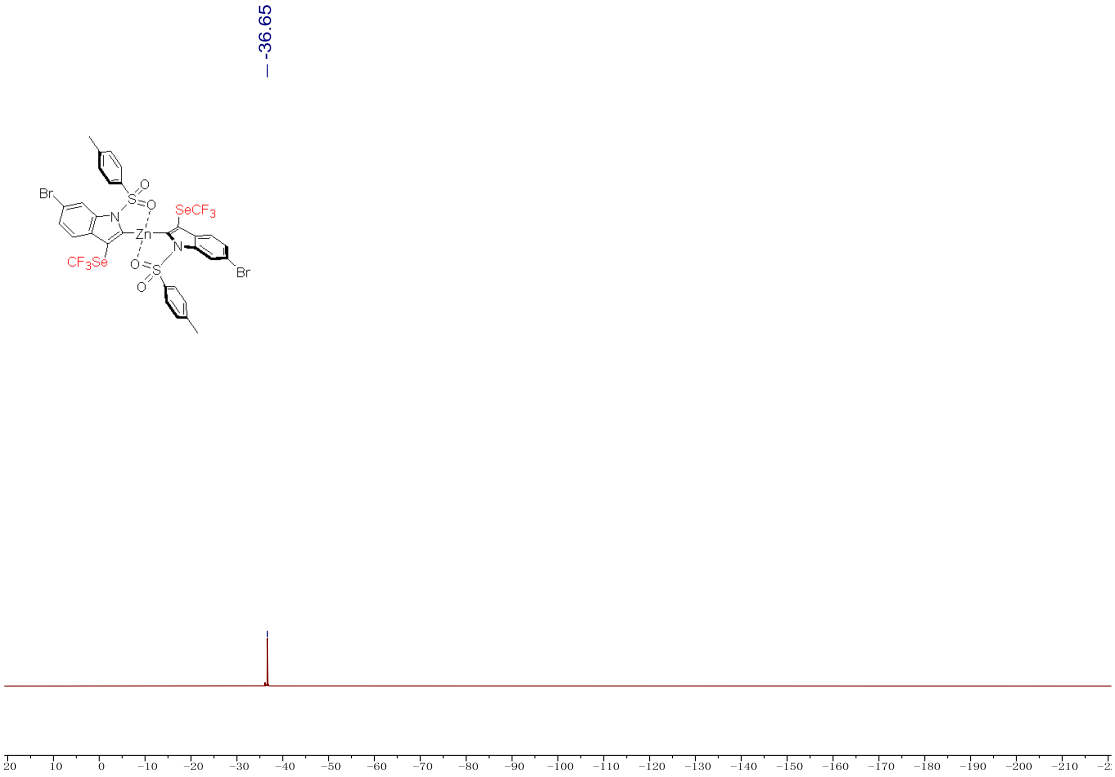
$^{13}C\{^{1}H\}$ NMR spectra of **4a-Ph′** (101 MHz, $CDCl_3$)



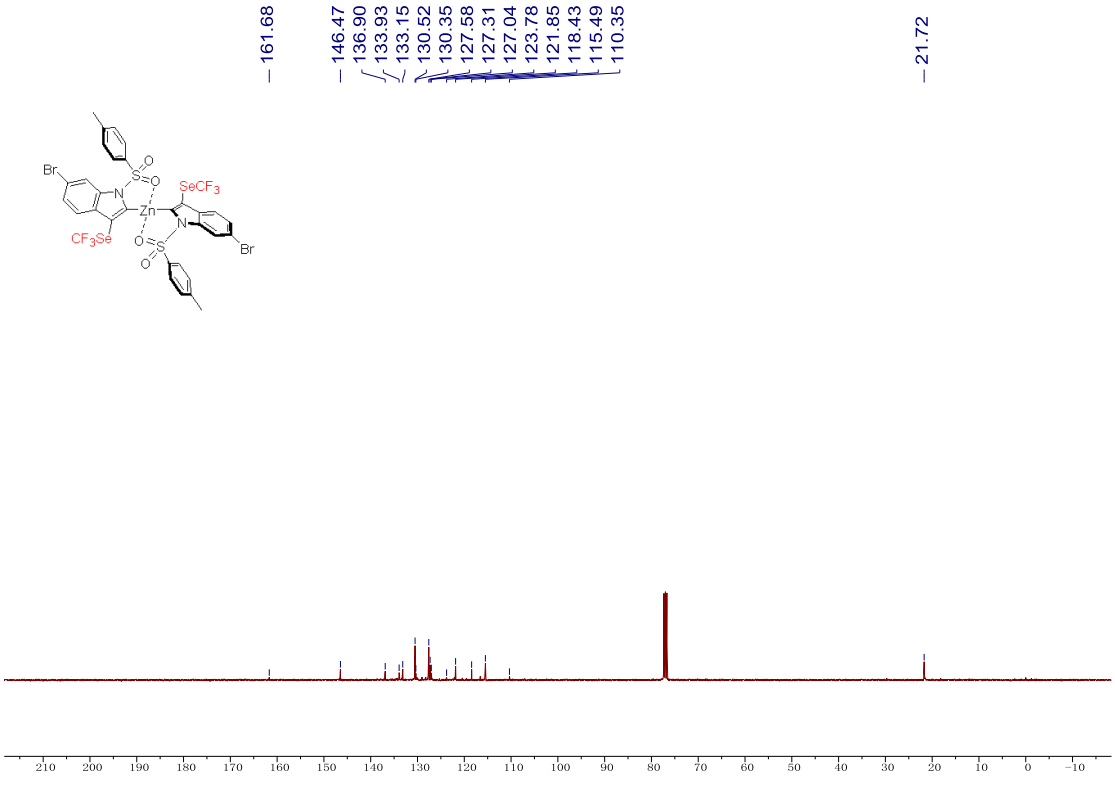
^{1}H NMR spectra of **5** (400 MHz, $CDCl_3$)



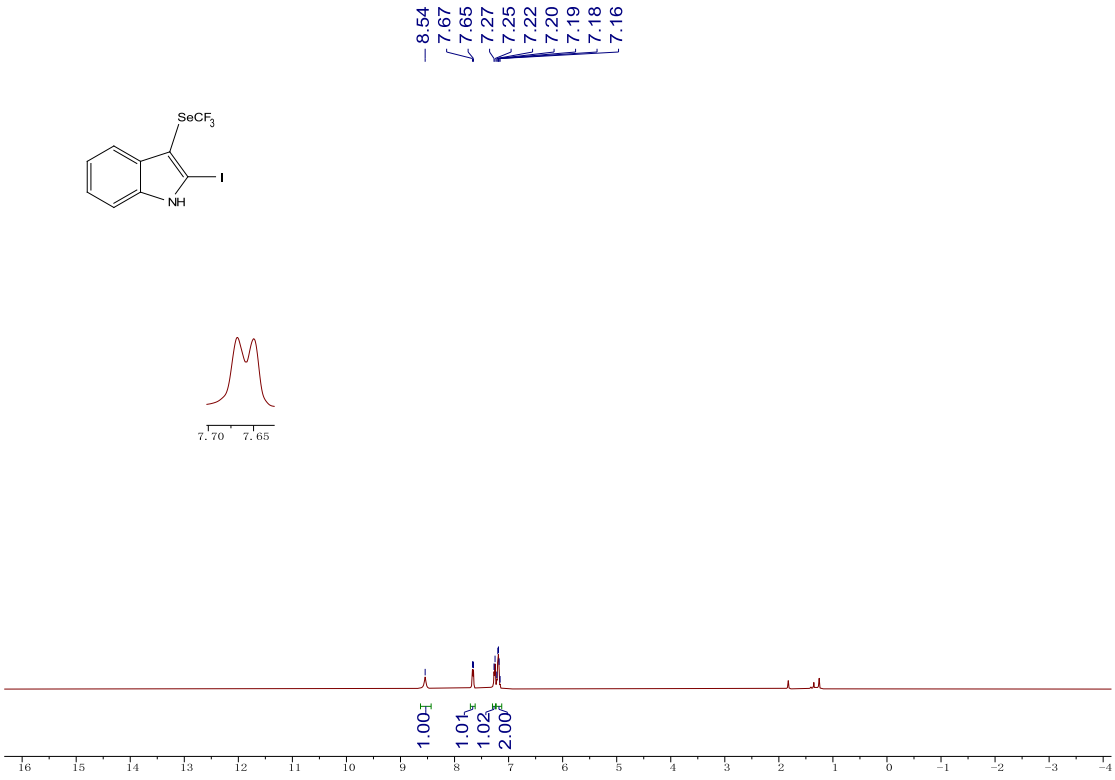
^{19}F NMR spectra of **5** (376 MHz, $CDCl_3$)



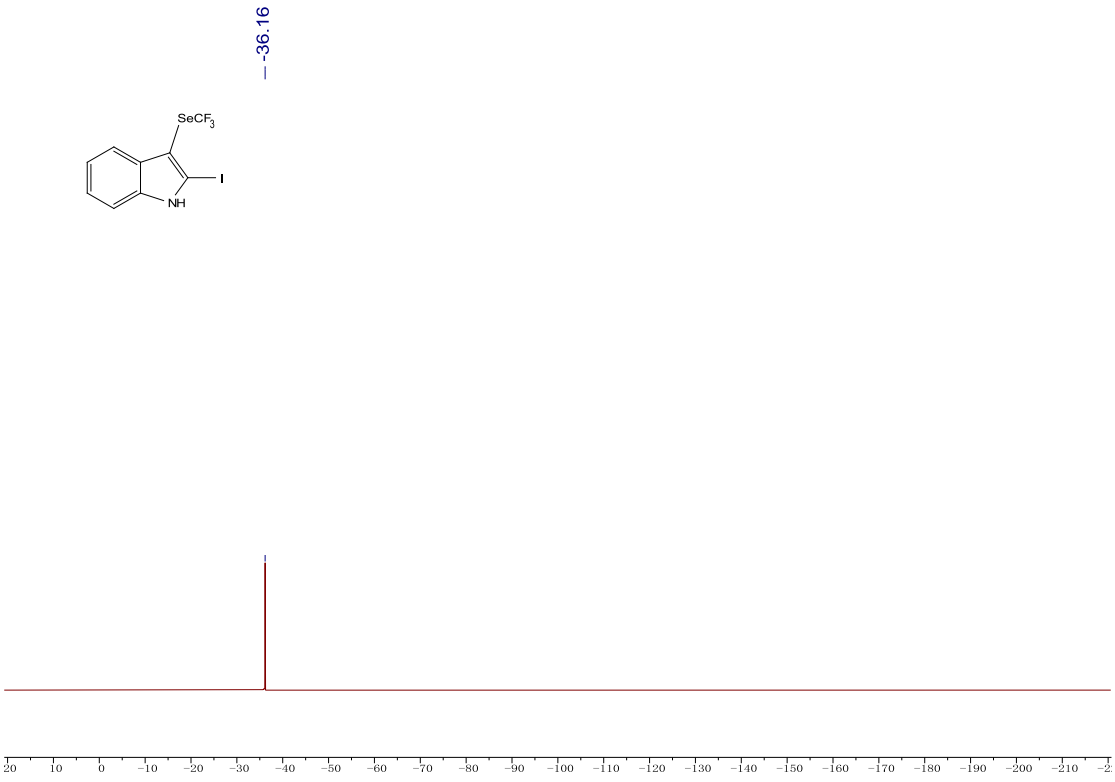
$^{13}C\{^1H\}$ NMR spectra of **5** (101 MHz, $CDCl_3$)



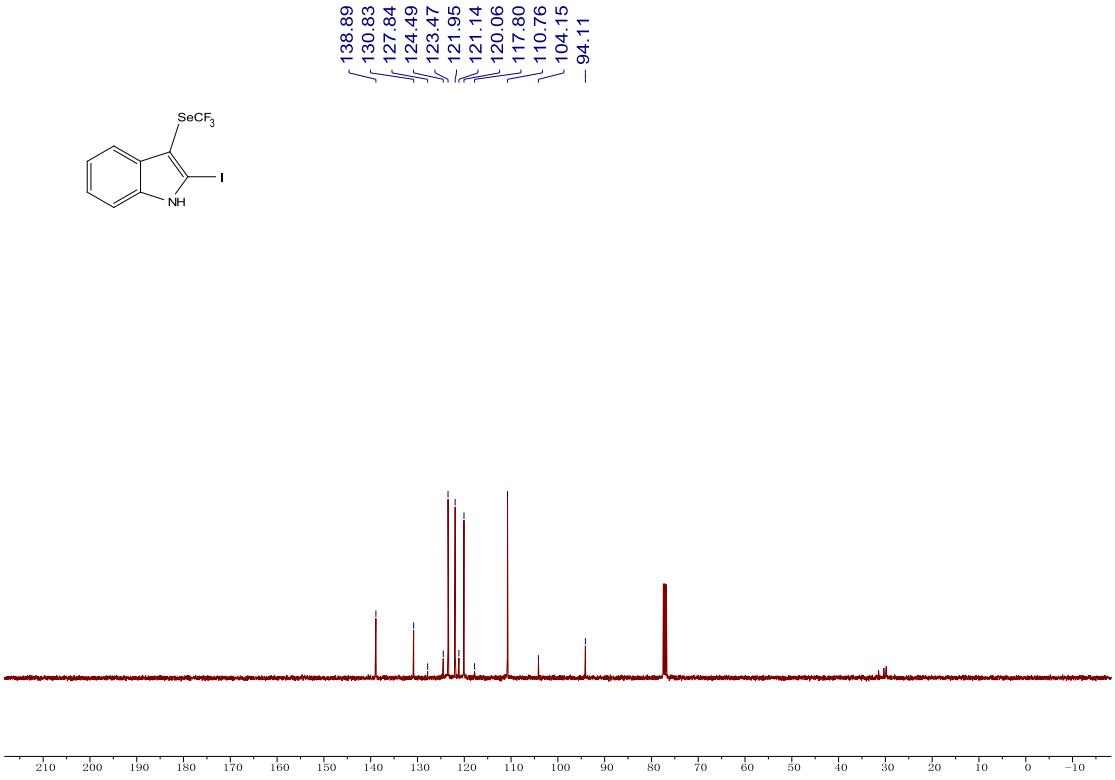
^{1}H NMR spectra of **3a-1** (400 MHz, $CDCl_3$)



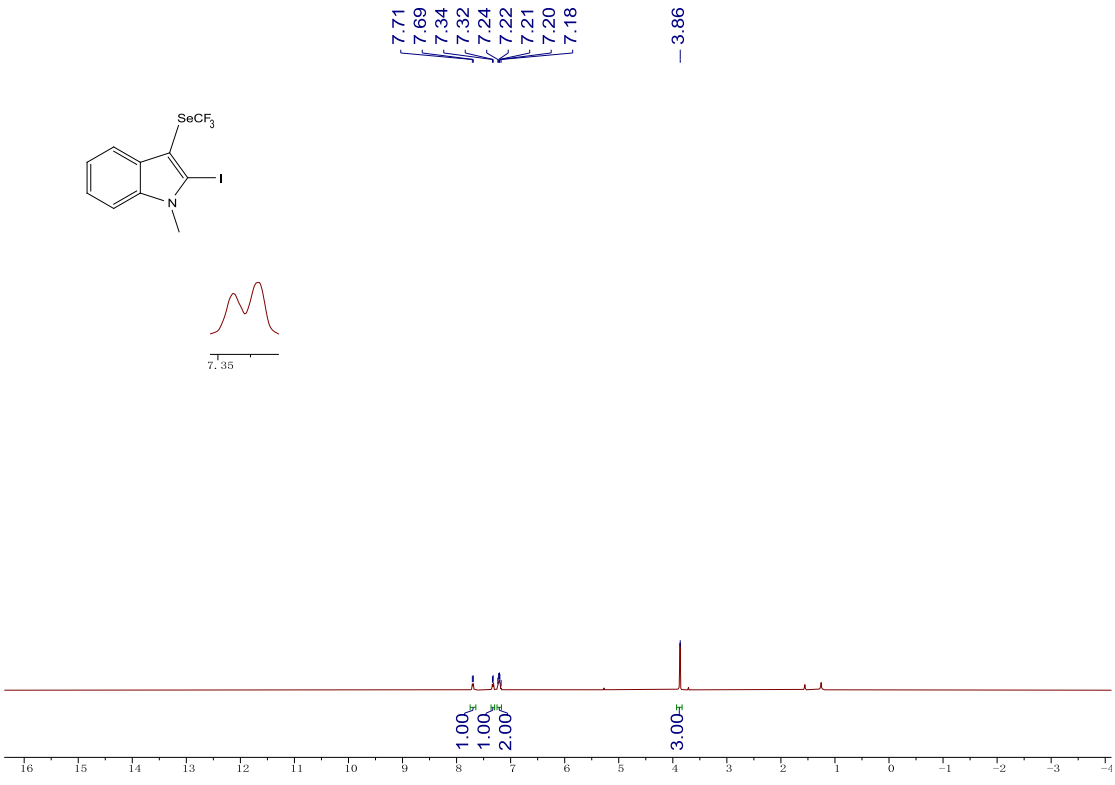
^{19}F NMR spectra of **3a-1** (376 MHz, $CDCl_3$)



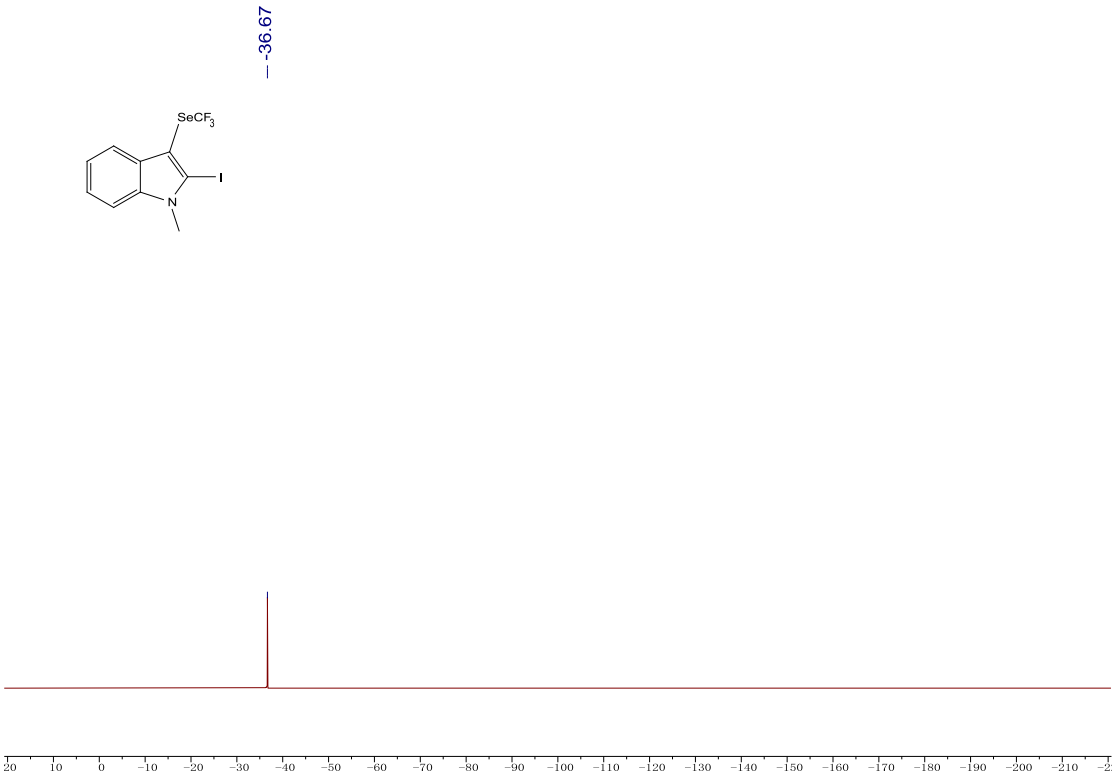
$^{13}C\{^{1}H\}$ NMR spectra of **3a-1** (101 MHz, $CDCl_3$)



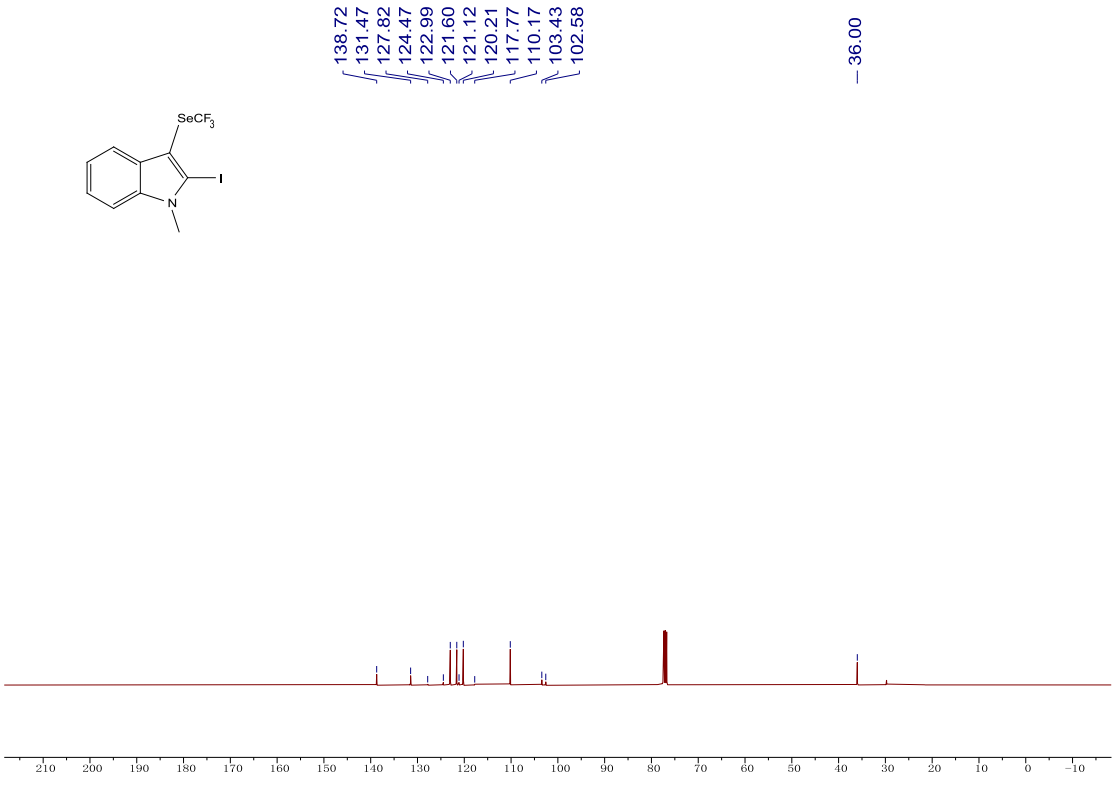
^{1}H NMR spectra of **3a-2** (400 MHz, $CDCl_3$)



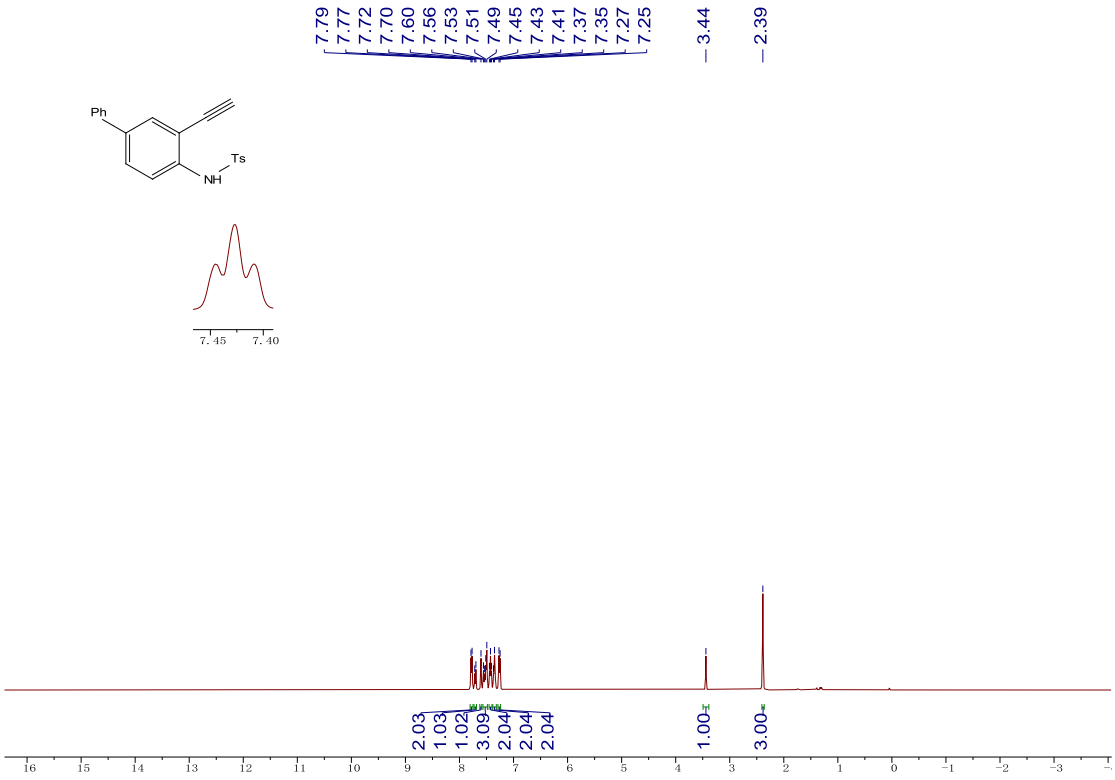
^{19}F NMR spectra of **3a-2** (376 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of **3a-2** (101 MHz, $CDCl_3$)



^{1}H NMR spectra of *N*-(3-ethynyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectra of *N*-(3-ethynyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (101 MHz, $CDCl_3$)