Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Oxidative Trifluoromethylthiolation and Thiocyanation of Amines: a General Approach to N-S bond formation

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Supporting information

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1. General information

All reactions were carried out using oven-dried glassware and magnetic stirring under air unless otherwise stated. Reaction temperatures are reported as the temperature of the bath surrounding the vessel. Anhydrous acetonitrile was purchased from Acros Organics (Solvents Extra Dry over Molecular Sieve, AcroSeal®). Dichloromethane was purified by distillation over CaH_2 while tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone prior to use. Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with a $KMnO_4$ solution or a phosphomolybdic acid solution. Column chromatography was performed using 0.04–0.063 nm silica gel. NMR spectra were recorded on a Bruker DXP 300 MHz spectrometer. Chemical shifts (δ) are quoted in ppm relative to TMS (^{1}H) and $CFCl_3$ (^{19}F). Coupling constants (J) are quoted in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, m: multiplet. The residual solvent signals were used as references ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm or relative to external $CFCl_3$, δ_F = 0 ppm). High-resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. IR spectra were recorded on a PerkinElmer Spectrum 100, the wave numbers (ν) of recorded IR-signals (ATR) are quoted in cm^{-1}. Melting points were uncorrected and were reported for new compounds.

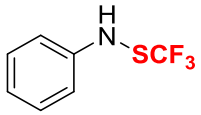
2. Preparation of substrates

$AgSCF_3$,[1a] *N*-chlorosaccharin,[1b] 1-(trifluoromethylthio)pyrrolidine-2,5-dione[1c] and chloramine-T[1d] were prepared according to previously reported procedures. All amine substrates and NCS were commercially available and were used as received unless otherwise stated.

3. General procedure for the trifluoromethylthiolation reaction of amine derivatives

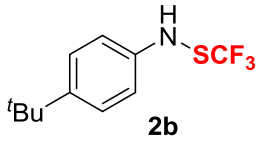
An oven-dried 10 mL glassware equipped with a stirring bar was charged with $AgSCF_3$ (50.2 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL). Amine derivatives **1** (0.2 mmol, 1 equiv) and *N*-chlorosuccinimide (32.1 mg, 0.24 mmol, 1.2 equiv) were added to the reaction mixture. The resulted reaction mixture was stirred at 25 °C until the TLC control showed complete conversion. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **2**. Note that, in the case of solid amines, these are added in the tube before the solvent. Caution: the products are volatile.

4. Purification and characterization of products 2



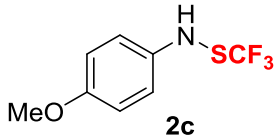
2a

***N*-[(Trifluoromethyl)thio]aniline 2a.**[1b,2,3,4] The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 91:9) as a pale yellow oil (35.2 mg, 91%, 2 h; 509.6 mg, 88%, on a 3 mmol scale, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.50. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.29 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 5.09 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ –53.4 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 145.0, 129.4 (q, J = 317.1 Hz), 129.3, 121.9, 115.1. **IR** (neat, cm^{-1}) ν: 2923, 2853, 1601, 1496, 1464, 1260, 1118, 1029, 800, 749. **HRMS** (CI) calcd for $C_7H_7F_3NS$ *m/z* 194.0246 $[M+H]^+$, Found 194.0260.



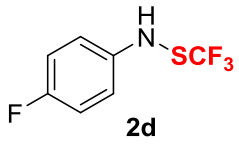
2b

4-*Tert*-butyl-*N*-[(trifluoromethyl)thio]aniline 2b.[1b] The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as an orange oil (39.7 mg, 80%, 20 h). R_f (petroleum ether/diethyl ether = 90:10): 0.62. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 5.05 (s, 1H), 1.34 (s, 9H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.5 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 144.8, 142.5, 129.4 (q, J = 317.9 Hz), 126.1, 114.8, 34.1, 31.4. **IR** (neat, cm^{-1}) ν: 3347, 2966, 1611, 1512, 1239, 1105, 923, 830, 748, 553. **HRMS** (CI) calcd for $C_{11}H_{15}F_3NS$ *m/z* 250.0872 $[M+H]^+$, Found 250.0871.



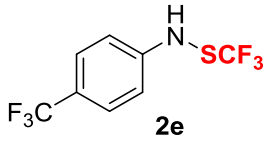
2c

4-Methoxy-*N*-[(trifluoromethyl)thio]aniline 2c.[2] The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 83:17) as an orange oil (40.4 mg, 91%, 2 h). R_f (petroleum ether/diethyl ether = 80:20): 0.47. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.02 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 4.95 (s, 1H), 3.78 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.5 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 155.0, 138.6, 129.5 (q, J = 317.9 Hz), 116.5, 114.6, 55.6. **IR** (neat, cm^{-1}) ν: 3327, 2841, 1506, 1444, 1285, 1225, 1109, 1028, 927, 816, 513. **HRMS** (CI) calcd for $C_8H_9F_3NOS$ *m/z* 224.0351 $[M+H]^+$, Found 224.0354.



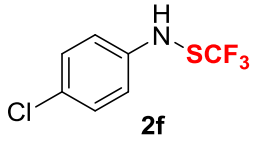
2d

4-Fluoro-*N*-[(trifluoromethyl)thio]aniline 2d.[2,4] The product was purified by flash column chromatography on silica gel (height 14 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as a yellow oil (38.9 mg, 92%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.50. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.12 – 6.87 (m, 4H), 5.04 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.4 (s), – 123.0 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 158.2 (d, J = 240.8 Hz), 141.1 (d, J = 2.3 Hz), 129.4 (q, J = 317.9 Hz), 116.4 (d, J = 8.3 Hz), 115.9 (d, J = 22.7 Hz). **IR** (neat, cm^{-1}) ν: 3415, 1863, 1505, 1453, 1376, 1281, 1210, 1108, 926, 824, 750, 509. **HRMS** (CI) calcd for $C_7H_6F_4NS$ *m/z* 212.0157 $[M+H]^+$, Found 212.0157.



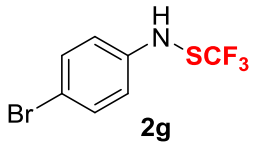
2e

4-Trifluoromethyl-*N*-[(trifluoromethyl)thio]aniline 2e. [2,4] The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as a yellow oil (38.1 mg, 73%, 24 h). R_f (petroleum ether/diethyl ether = 90:10): 0.43. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 5.33 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.1 (s), – 62.2 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.0, 129.1 (q, J = 317.1 Hz), 126.7 (q, J = 3.8 Hz), 124.2 (q, J = 271.8 Hz), 124.1 (q, J = 32.5 Hz), 114.9. **IR** (neat, cm^{-1}) ν: 3425, 1617, 1520, 1324, 1296, 1242, 1107, 1067, 1011, 832, 592. **HRMS** (CI) calcd for $C_8H_6F_6NS$ *m/z* 262.0125 $[M+H]^+$, Found 262.0128.



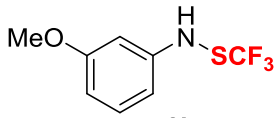
2f

4-Chloro-*N*-[(trifluoromethyl)thio]aniline 2f.[2,4] The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 91:9) as a pale yellow oil (38.7 mg, 85%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.39. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.24 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 5.10 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.3 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 143.7, 129.2, 129.2 (q, J = 317.1 Hz), 126.8, 116.3. **IR** (neat, cm^{-1}) ν: 3387, 1596, 1490, 1443, 1375, 1277, 1232, 1107, 927, 820, 658. **HRMS** (CI) calcd for $C_7H_6ClF_3NS$ *m/z* 227.9856 $[M+H]^+$, Found 227.9873.



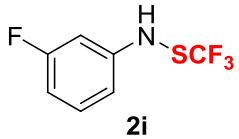
2g

4-Bromo-*N*-[(trifluoromethyl)thio]aniline 2g.[4] The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 91:9) as an orange oil (45.3 mg, 83%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.41. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.11 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.3 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 144.2, 132.1, 129.2 (q, J = 317.9 Hz), 116.8, 114.1. **IR** (neat, cm^{-1}) ν: 3380, 1591, 1485, 1440, 1232, 1107, 1005, 926, 816, 750, 635, 501. **HRMS** (CI) calcd for $C_7H_6BrF_3NS$ *m/z* 271.9351 $[M+H]^+$, Found 271.9362.



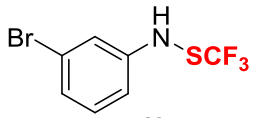
2h

3-Methoxy-*N*-[(trifluoromethyl)thio]aniline 2h.[4] The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 85:15) as a white solid (41.3 mg, 93%, 2 h). R_f (petroleum ether/diethyl ether = 80:20): 0.54. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.18 (t, J = 8.1 Hz, 1H), 6.73 – 6.62 (m, 2H), 6.53 (dd, J = 8.1, 1.8 Hz, 1H), 5.13 (s, 1H), 3.81 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.4 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 160.7, 146.5, 130.1, 129.3 (q, J = 317.1 Hz), 107.8, 107.2, 101.2, 55.2. **IR** (neat, cm^{-1}) ν: 3321, 2937, 1598, 1507, 1480, 1277, 1107, 1051, 836, 761, 685. **HRMS** (CI) calcd for $C_8H_9F_3NOS$ *m/z* 224.0351 $[M+H]^+$, Found 224.0356.



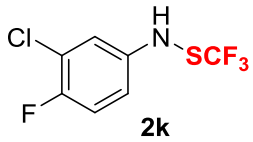
2i

3-Fluoro-*N*-[(trifluoromethyl)thio]aniline 2i. The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as a yellow oil (32.2 mg, 76%, 2 h). R_f (petroleum ether/diethyl ether = 94:6): 0.36. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 1H), 6.82 – 6.68 (m, 2H), 6.58 (td, J = 8.4, 2.1 Hz, 1H), 5.09 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.3 (s), – 112.2 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 163.7 (d, J = 245.4 Hz), 147.0 (d, J = 9.8 Hz), 130.5 (d, J = 9.8 Hz), 129.2 (q, J = 317.1 Hz), 110.9 (d, J = 2.3 Hz), 108.7 (d, J = 21.1 Hz), 102.5 (d, J = 26.4 Hz). **IR** (neat, cm^{-1}) ν: 3416, 2962, 1615, 1490, 1277, 1110, 972, 847, 768, 680. **HRMS** (CI) calcd for $C_7H_6F_4NS$ *m/z* 212.0152 $[M+H]^+$, Found 212.0160.



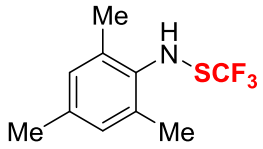
2j

3-Bromo-*N*-[(trifluoromethyl)thio]aniline 2j. The product was purified by flash column chromatography on silica gel (height 19 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as an orange oil (43.8 mg, 81%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.35. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.12 – 6.98 (m, 2H), 6.97 – 6.86 (m, 1H), 5.05 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.2 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 146.4, 130.6, 129.2 (q, J = 317.9 Hz), 125.0, 123.1, 118.2, 113.8. **IR** (neat, cm^{-1}) ν: 3379, 1594, 1474, 1457, 1281, 1108, 933, 850, 768, 679. **HRMS** (CI) calcd for $C_7H_6BrF_3NS$ *m/z* 271.9351 $[M+H]^+$, Found 271.9361.



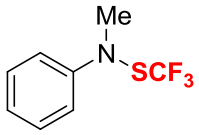
2k

3-Chloro-4-fluoro-*N*-[(trifluoromethyl)thio]aniline 2k. The product was purified by flash column chromatography on silica gel (height 20 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as a yellow oil (35.1 mg, 71%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.40. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.18 – 6.87 (m, 3H), 5.10 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.3 (s), – 125.4 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 153.6 (d, J = 242.4 Hz), 141.8 (d, J = 2.3 Hz), 129.2 (q, J = 317.9 Hz), 121.5 (d, J = 18.9 Hz), 117.0 (d, J = 22.5 Hz), 116.9, 114.5 (d, J = 6.8 Hz). **IR** (neat, cm^{-1}) ν: 3405, 1708, 1497, 1363, 1209, 1108, 943, 808, 751, 542. **HRMS** (CI) calcd for $C_7H_5ClF_4NS$ *m/z* 245.9762 $[M+H]^+$, Found 245.9772.



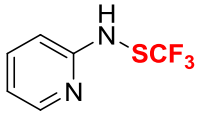
2l

2,4,6-Trimethyl-*N*-[(trifluoromethyl)thio]aniline 2l. The product was purified by flash column chromatography on silica gel (height 12 cm, width 1.5 cm, pentane/diethyl ether = 95:5) as an orange oil (27.3 mg, 58%, 24 h). R_f (petroleum ether/diethyl ether = 90:10): 0.68. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.59 (s, 1H), 2.32 (s, 6H), 2.26 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 52.6 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 139.4, 134.5, 131.5, 130.3 (q, J = 318.6 Hz), 129.6, 20.6, 18.1. **IR** (neat, cm^{-1}) ν: 3394, 2971, 1480, 1216, 1117, 849, 747, 581. **HRMS** (CI) calcd for $C_{10}H_{13}F_3NS$ *m/z* 236.0715 $[M+H]^+$, Found 236.0723.



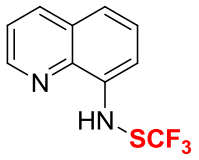
2m

***N*-Methyl-*N*-[(trifluoromethyl)thio]aniline 2m.** [1b,3,4] The product was purified by flash column chromatography on silica gel (height 14 cm, width 1.5 cm, pentane/diethyl ether = 85:15) as a colorless oil (18.3 mg, 44%, 12 h). R_f (petroleum ether/diethyl ether = 96:4): 0.67. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 4H), 6.87 (d, J = 7.2 Hz, 1H), 3.39 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 50.9 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.6, 130.3 (q, J = 320.9 Hz), 129.0, 121.2, 115.9, 46.1. **IR** (neat, cm^{-1}) ν: 2955, 1599, 1495, 1266, 1107, 1032, 873, 748, 689. **HRMS** (CI) calcd for $C_8H_9F_3NS$ *m/z* 208.0402 $[M+H]^+$, Found 208.0405.



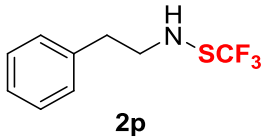
2n

***N*-[(Trifluoromethyl)thio]pyridin-2-amine 2n.** The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 60:40) as a yellow solid (26.3 mg, 68%, 8 h). mp: 81 – 83 °C. R_f (petroleum ether/diethyl ether = 70:30): 0.34. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.13 (d, J = 5.1 Hz, 1H), 7.65 – 7.54 (m, 1H), 7.27 – 7.17 (m, 1H), 6.82 (dd, J = 6.9, 5.1 Hz, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.4 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 158.5, 147.8, 138.7, 129.4 (q, J = 316.3 Hz), 117.1, 107.7. **IR** (neat, cm^{-1}) ν: 3134, 2848, 1604, 1584, 1500, 1448, 1299, 1112, 996, 945, 771, 591. **HRMS** (CI) calcd for $C_6H_6F_3N_2S$ *m/z* 195.0198 $[M+H]^+$, Found 195.0212.



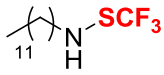
2o

***N*-[(Trifluoromethyl)thio]quinolin-8-amine 2o.** The product was purified by flash column chromatography on silica gel (height 12 cm, width 1.5 cm, pentane/diethyl ether = 60:40) as a colorless oil (19.6 mg, 40%, 20 h). R_f (petroleum ether/diethyl ether = 70:30): 0.73. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 8.79 (dd, J = 4.2, 1.5 Hz, 1H), 8.14 (dd, J = 8.4, 1.5 Hz, 1H), 7.65 – 7.32 (m, 5H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 52.9 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.2, 141.8, 138.9, 136.1, 129.4 (q, J = 317.1 Hz), 128.3, 127.1, 121.8, 119.3, 110.0. **IR** (neat, cm^{-1}) ν: 3341, 2917, 2160, 1418, 1324, 1235, 1099, 1008, 733, 669, 592. **HRMS** (CI) calcd for $C_{10}H_8F_3N_2S$ *m/z* 245.0355 $[M+H]^+$, Found 245.0353.



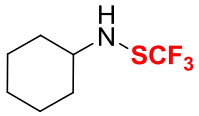
2p

***N*-[(Trifluoromethyl)thio]-2-phenylethan-1-amine 2p.**[1b] The product was purified by flash column chromatography on silica gel (height 14 cm, width 1.5 cm, pentane/diethyl ether = 90:10) as a colorless oil (40.8 mg, 92%, 2 h). R_f (petroleum ether/diethyl ether = 80:20): 0.80. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.19 – 7.05 (m, 3H), 3.32 – 3.16 (m, 2H), 2.76 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.0 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.4, 130.4 (q, J = 317.1 Hz), 128.8, 128.6, 126.5, 54.6, 36.6. **IR** (neat, cm^{-1}) ν: 3367, 2933, 1604, 1455, 1112, 746, 699, 560. **HRMS** (CI) calcd for $C_9H_{11}F_3NS$ *m/z* 222.0559 $[M+H]^+$, Found 222.0560.



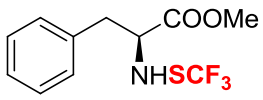
2q

***N*-[(Trifluoromethyl)thio]dodecan-1-amine 2q.**[3] The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 85:15) as a colorless oil (46.2 mg, 81%, 2 h). R_f (petroleum ether/diethyl ether = 90:10): 0.83. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 3.15 – 2.97 (m, 2H), 2.82 (s, 1H), 1.58 – 1.44 (m, 2H), 1.26 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 52.9 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 130.5 (q, J = 317.9 Hz), 53.7, 31.9, 30.2, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 26.5, 22.7, 14.1. **IR** (neat, cm^{-1}) ν: 2925, 2855, 1467, 1154, 1120, 722. **HRMS** (CI) calcd for $C_{13}H_{27}F_3NS$ *m/z* 286.1811 $[M+H]^+$, Found 286.1829.



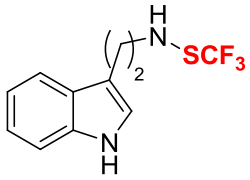
2r

***N*-[(Trifluoromethyl)thio]cyclohexanamine 2r.**[3] The product was purified by flash column chromatography on silica gel (height 15 cm, width 2.0 cm, pentane) as a colorless oil (86.2 mg, 87%, on a 0.5 mmol scale, 2 h). R_f (petroleum ether): 0.49. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 2.98 – 2.64 (m, 2H), 2.10 – 1.87 (m, 2H), 1.81 – 1.50 (m, 3H), 1.40 – 0.98 (m, 5H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.4 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 130.3 (q, J = 317.1 Hz), 59.5, 33.2, 25.6, 24.5. **IR** (neat, cm^{-1}) ν: 1264, 896, 731, 703. **HRMS** (CI) calcd for $C_7H_{13}F_3NS$ *m/z* 200.0721 $[M+H]^+$, Found 200.0715.



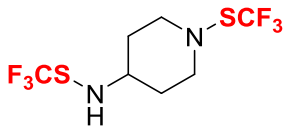
2s

Methyl *N*-[(trifluoromethyl)thio]-*L*-phenylalaninate 2s. The product was purified by flash column chromatography on silica gel (height 25 cm, width 2.0 cm, petroleum ether /acetone = 94:6) as a colorless oil (58.3 mg, 42%, on a 0.5 mmol scale starting from *L*-phenylalanine methyl ester hydrochloride, Et_3N (50.6 mg, 0.2 mmol, 1 equiv) and 2.4 equiv instead of 1.2 equiv of $AgSCF_3$ were added, 4 h). R_f (petroleum ether/ acetone = 95:5): 0.47. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 3H), 7.20 – 7.08 (m, 2H), 4.05 – 3.89 (m, 1H), 3.73 (s, 3H), 3.34 (d, J = 8.1 Hz, 1H), 3.07 (qd, J = 13.8, 6.6 Hz, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 54.0 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 172.9, 135.6, 129.8 (q, J = 314.8 Hz), 129.2, 128.6, 127.1, 66.6, 52.2, 39.3. **IR** (neat, cm^{-1}) ν: 3347, 2964, 1738, 1497, 1439, 1214, 1155, 1116, 743, 699. **HRMS** (CI) Calcd for $C_{11}H_{13}F_3NO_2S$ *m/z* 280.0619 $[M+H]^+$, Found 280.0632. Note that Et_3N was added in the reaction mixture 2 h before addition of the NCS and $AgSCF_3$.



2t

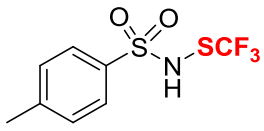
***N*-[(Trifluoromethyl)thio]-2-(1*H*-indol-3-yl)ethan-1-amine 2t.**[3] The product was purified by flash column chromatography on silica gel (height 15 cm, width 1.5 cm, pentane/diethyl ether = 67:33) as a colorless oil (43.3 mg, 83%, 2 h). R_f (petroleum ether/diethyl ether = 67:33): 0.35. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.29 – 7.11 (m, 2H), 7.02 (d, J = 1.8 Hz, 1H), 3.49 – 3.35 (m, 2H), 3.02 (t, J = 6.8 Hz, 2H), 2.94 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 53.0 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.3, 130.4 (q, J = 317.9 Hz), 127.2, 122.2, 122.0, 119.5, 118.6, 112.5, 111.2, 53.6, 26.2. **IR** (neat, cm^{-1}) ν: 3398, 3326, 2929, 1458, 1338, 1108, 809, 749, 581. **HRMS** (CI) calcd for $C_{11}H_{12}F_3N_2S$ *m/z* 261.0668 $[M+H]^+$, Found 261.0684.



2u

***S*-(Trifluoromethyl)-*N*-(1-[(trifluoromethyl)thio]piperidin-4-yl)thiohydroxylamine 2u.** The product was purified by flash column chromatography on silica gel (height 14 cm, width 2.0 cm, pentane/diethyl ether = 95:5) as a colorless oil (72.1 mg, 48%, on a 0.5 mmol scale, 2.4 equiv of $AgSCF_3$ and 2.4 equiv of NCS were used, 4 h). R_f (petroleum ether/diethyl ether = 90:10): 0.62. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 3.44

– 3.28 (m, 2H), 3.26 – 3.07 (m, 2H), 3.04 – 2.77 (m, 2H), 2.08 – 1.86 (m, 2H), 1.61 – 1.42 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 47.0 (s), – 53.1 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 131.4 (q, J = 323.1 Hz), 130.1 (q, J = 316.3 Hz), 55.9, 55.7, 33.3. **IR** (neat, cm^{-1}) ν: 3373, 2932, 2854, 1375, 1101, 949, 744. **HRMS** (CI) calcd for $C_7H_{11}F_6N_2S_2$ *m/z* 301.0268 $[M+H]^+$, Found 301.0260.



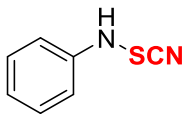
2v

4-methyl-*N*-(trifluoromethylthio)benzenesulfonamide 2v. An oven-dried 10 mL glassware equipped with a stirring bar was charged with $AgSCF_3$ (62.7 mg, 0.3 mmol, 1.5 equiv), chloramine-T[1d] (45.5 mg, 0.2 mmol, 1 equiv) and THF (2 mL) under air. The obtained reaction mixture was stirred at 25 °C for 2h. The crude was directly purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 50:50) and **2v** was obtained as a white solid (16.6 mg, 31%). R_f (petroleum ether/diethyl ether = 50:50): 0.38. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.32 (s, 1H), 2.45 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 51.9 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 145.1, 135.0, 129.9, 128.0 (q, J = 314.8 Hz), 127.9, 21.7. **IR** (neat, cm^{-1}) ν: 3225, 2922, 1597, 1389, 1331, 1086, 880, 812, 663, 534. **HRMS** (CI) calcd for $C_8H_9F_3NO_2S_2$ m/z 272.0021 $[M+H]^+$, Found 272.0014.

5. General procedure for the thiocyanation reaction of aniline derivatives

An oven-dried 50 mL flask equipped with a stirring bar was charged with AgSCN (398.3 mg, 2.4 mmol, 1.2 equiv) and THF (20 mL). Amine derivatives **1** (2 mmol, 1 equiv) and *N*-chlorosuccinimide (320.5 mg, 2.4 mmol, 1.2 equiv) were added to the reaction mixture. The obtained reaction mixture was stirred at 25 °C until the TLC control showed complete conversion. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **3**.

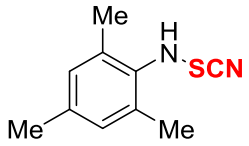
6. Purification and characterization of products 3



3a

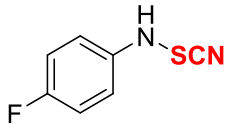
***N*-(Cyanosulfanyl)aniline 3a.** The product was purified by flash column chromatography on silica gel (height 18 cm, width 2.0 cm, pentane/diethyl ether = 50:50) as a white solid (343.8 mg, 76%, on a 3 mmol scale, 2 h). mp: 75 – 76 °C. R_f

(petroleum ether/diethyl ether = 50:50): 0.39. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 2H), 7.16 – 7.03 (m, 3H), 5.10 (s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 143.3, 129.6, 123.2, 116.5, 113.3. **IR** (neat, cm^{-1}) ν: 3259, 2849, 2152, 1501, 1469, 1209, 1101, 912, 826, 762, 611. **HRMS** (CI) calcd for $C_7H_7N_2S$ *m/z* 151.0324 $[M+H]^+$, Found 151.0335.



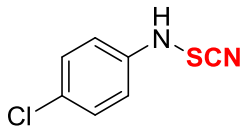
3b

***N*-(Cyanosulfanyl)-2,4,6-trimethylaniline 3b.** The product was purified by flash column chromatography on silica gel (height 15 cm, width 2.0 cm, pentane/diethyl ether = 50:50) as a yellow solid (271.2 mg, 71%, 18 h). mp: 79 – 80 °C. R_f (petroleum ether/diethyl ether = 50:50): 0.75. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 6.89 (s, 2H), 4.93 (s, 1H), 2.34 (s, 6H), 2.27 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.2, 135.8, 132.0, 129.9, 114.4, 20.7, 17.9. **IR** (neat, cm^{-1}) ν: 3318, 2964, 2915, 2140, 1481, 1209, 883, 723, 603, 568. **HRMS** (CI) calcd for $C_{10}H_{13}N_2S$ *m/z* 193.0794 $[M+H]^+$, Found 193.0786.



3c

***N*-(Cyanosulfanyl)-4-fluoroaniline 3c.** The product was purified by flash column chromatography on silica gel (height 18 cm, width 2.0 cm, pentane/diethyl ether = 50:50) as a yellow solid (293.8 mg, 87%, 2 h). mp: 77 – 78 °C. R_f (petroleum ether/diethyl ether = 50:50): 0.50. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.12 – 6.96 (m, 4H), 5.15 (s, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ – 120.6 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 159.1 (d, J = 242.4 Hz), 139.5 (d, J = 2.3 Hz), 118.3 (d, J = 8.3 Hz), 116.3 (d, J = 22.7 Hz), 113.3. **IR** (neat, cm^{-1}) ν: 3260, 2151, 1502, 1209, 1100, 911, 827, 763, 610, 505. **HRMS** (CI) calcd for $C_7H_6FN_2S$ *m/z* 169.0230 $[M+H]^+$, Found 169.0229.



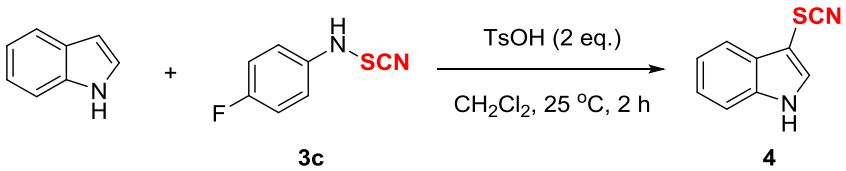
3d

***N*-(Cyanosulfanyl)-4-chloroaniline 3d.** The product was purified by flash column chromatography on silica gel (height 18 cm, width 1.5 cm, pentane/diethyl ether = 50:50) as a pale yellow solid (288.4 mg, 78%, 2 h). mp: 81 – 82 °C. R_f (petroleum ether/diethyl ether = 50:50): 0.37. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 7.30 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 5.24 (s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 142.0,

129.6, 128.4, 117.8, 113.0. **IR** (neat, cm^{-1}) ν: 3288, 2153, 1595, 1488, 1283, 1231, 1092, 916, 815, 563. **HRMS** (CI) calcd for $C_7H_6ClN_2S$ *m/z* 184.9935 $[M+H]^+$, Found 184.9947.

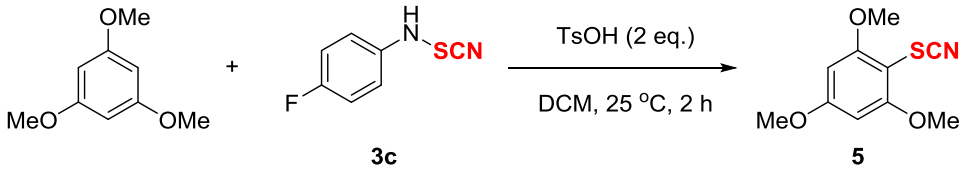
7. Post-functionalizations

7a. Thiocyanation of indole



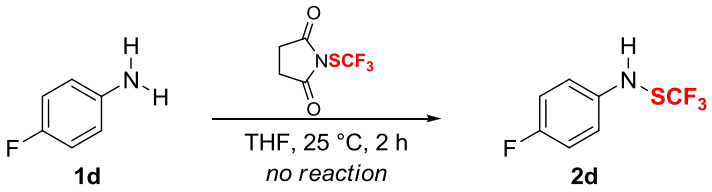
3-Thiocyanato-1*H*-indole 4.[5] An oven-dried 10 mL glassware equipped with a stirring bar was charged with indole (23.4 mg, 0.2 mmol, 1 equiv), CH_2Cl_2 (2 mL), *N*-(cyanosulfanyl)-4-fluoroaniline **3c** (67.3 mg, 0.4 mmol, 2 equiv) and TsOH (68.9 mg, 0.4 mmol, 2 equiv). The resulted reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (height 13 cm, width 1.5 cm, petroleum ether/diethyl ether = 80:20) as a white solid (28.9 mg, 83%). R_f (petroleum ether/diethyl ether = 65:35): 0.21. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.86 – 7.74 (m, 1H), 7.50 – 7.27 (m, 4H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.0, 131.0, 127.6, 123.8, 121.8, 118.6, 112.1, 91.8. One carbon is overlapped. **IR** (neat, cm^{-1}) ν: 3370, 3047, 1577, 1503, 1467, 1380, 1317, 1112, 822, 793, 757, 459. **HRMS** (CI) calcd for $C_9H_7N_2S$ *m/z* 175.0330 $[M+H]^+$, Found 175.0324.

7b. Thiocyanation of 1,3,5-trimethoxybenzene

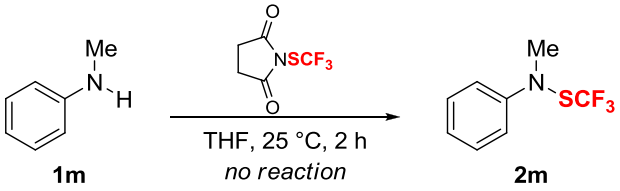


2,4,6-Trimethoxy-phenylthiocyanate 5.[6] An oven-dried 10 mL glassware equipped with a stirring bar was charged with 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol, 1 equiv), CH_2Cl_2 (2 mL), *N*-(cyanosulfanyl)-4-fluoroaniline **3c** (67.3 mg, 0.4 mmol, 2 equiv) and TsOH (68.9 mg, 0.4 mmol, 2 equiv). The resulted reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (height 15 cm, width 1.5 cm, petroleum ether/diethyl ether = 50:50) as a yellow solid (41.4 mg, 92%). R_f (petroleum ether/diethyl ether = 67:33): 0.18. **^{1}H NMR** (300.13 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.91 (s, 6H), 3.84 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 164.2, 161.3, 111.8, 91.2, 89.5, 56.3, 55.5. **IR** (neat, cm^{-1}) ν: 2924, 2149, 1583, 1456, 1415, 1344, 1205, 1127, 1085, 914, 821, 804. **HRMS** (CI) calcd for $C_{10}H_{12}NO_3S$ *m/z* 226.0538 $[M+H]^+$, Found 226.0532.

8. Control experiments :



An oven-dried 10 mL glassware equipped with a stirring bar was charged with 1-((trifluoromethyl)thio)pyrrolidine-2,5-dione (23.9 mg, 0.12 mmol, 1.2 equiv) and THF (1 mL). 4-Fluoroaniline **1d** (11.1 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture. The resulted reaction mixture was stirred at 25 °C for 2 h. The desired product **2d** was not observed.



An oven-dried 10 mL glassware equipped with a stirring bar was charged with 1-((trifluoromethyl)thio)pyrrolidine-2,5-dione (47.8 mg, 0.24 mmol, 1.2 equiv) and THF (2 mL). *N*-methylaniline **1m** (21.4 mg, 0.2 mmol, 1 equiv) was added to the reaction mixture. The resulted reaction mixture was stirred at 25 °C for 2 h. The desired product **2m** was not observed.

9. References

(1) (a) G. Teverovskiy, D. S. Surry and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2011, **50**, 7312; (b) C. Xu, B. Ma and Q. Shen, *Angew. Chem. Int. Ed.*, 2014, **53**, 9316; (c) C. Xu and Q. Shen, *Org. Lett.*, 2014, **16**, 2046; (d) A. Shiri and A. Khoramabadi-zad, *Synthesis*, 2009, **16**, 2797.

(2) A. Ferry, T. Billard, B. R. Langlois and E. Bacqué, *J. Org. Chem.*, 2008, **73**, 9362.

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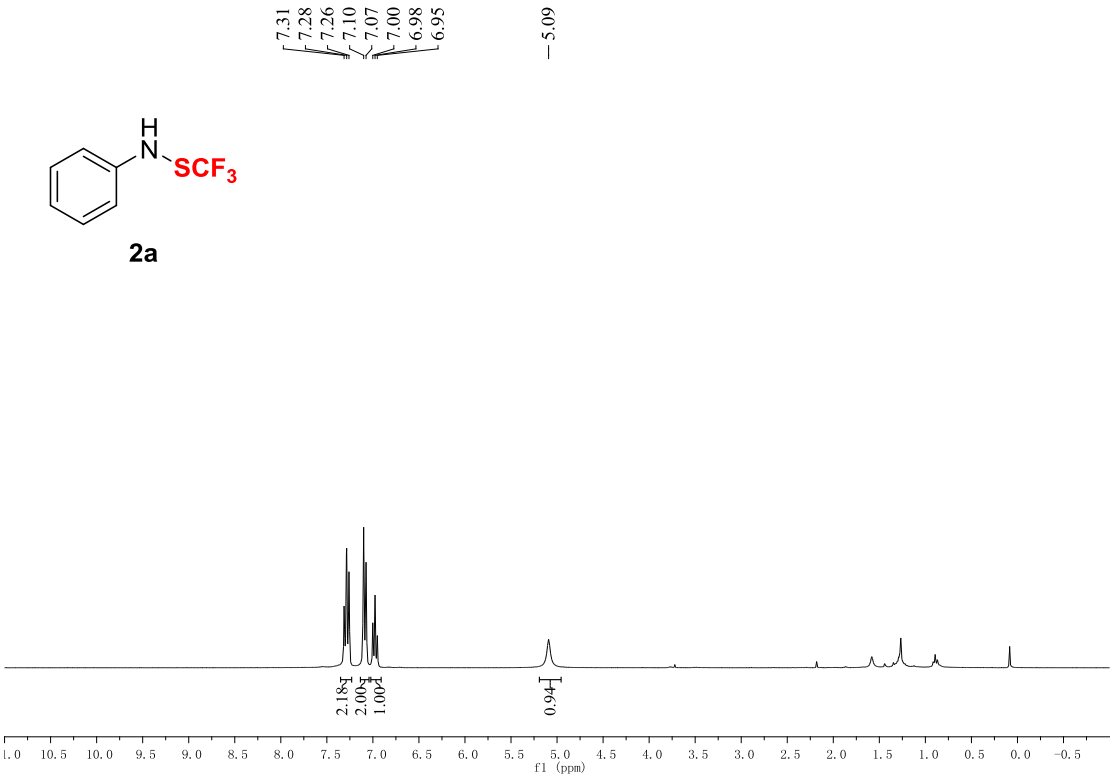
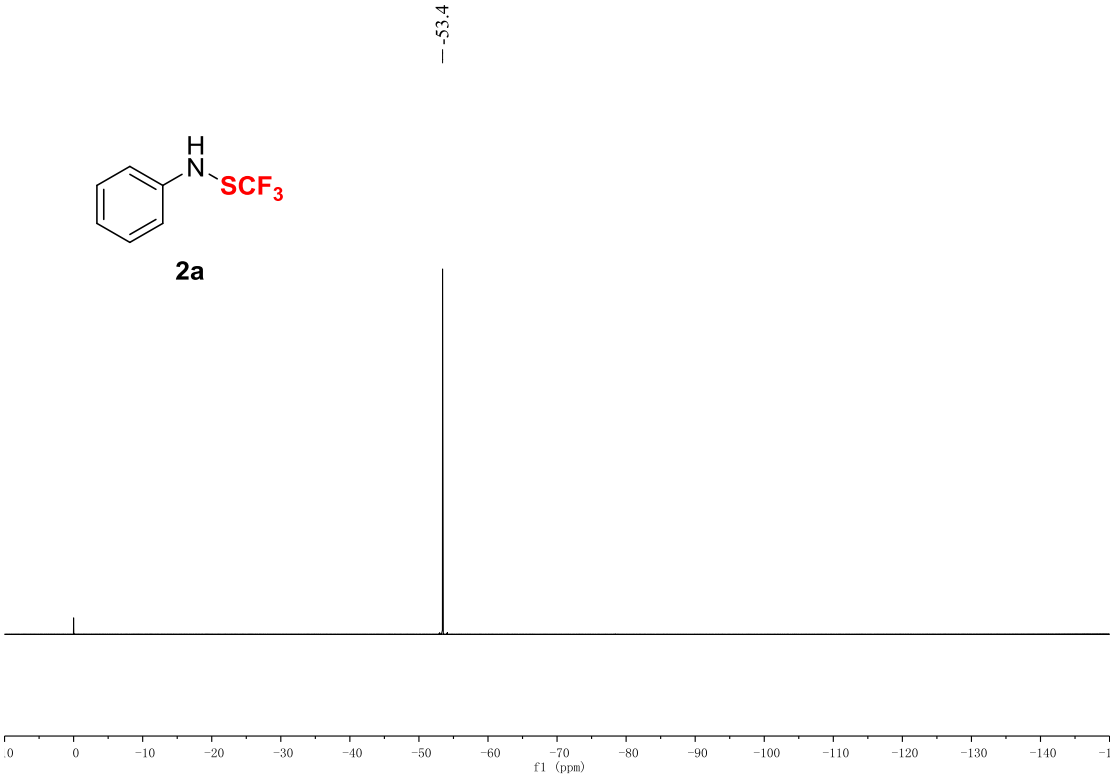
(4) Z. Huang, Y.-D. Yang, E. Tokunaga and N. Shibata, *Asian J. Org. Chem.*, 2015, **4**, 525.

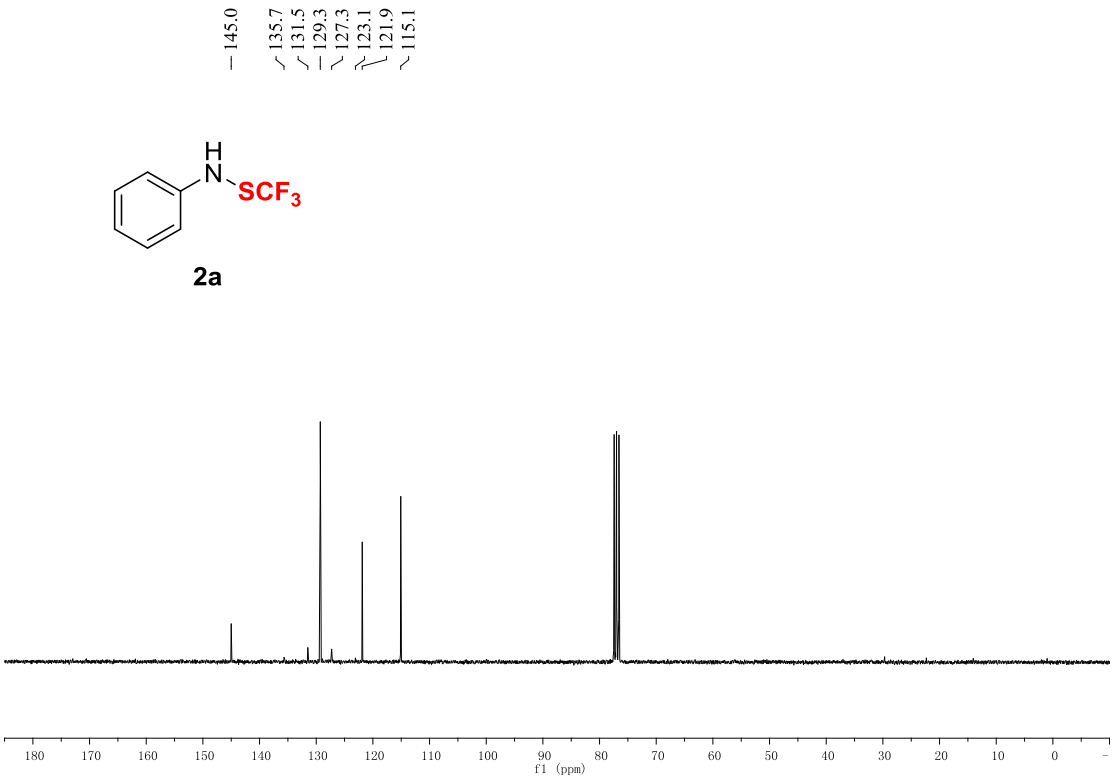
(5) D. Yang, K. Yan, W. Wei, G. Li, S. Lu, C. Zhao, L. Tian and H. Wang, *J. Org. Chem.*, 2015, **80**, 11073.

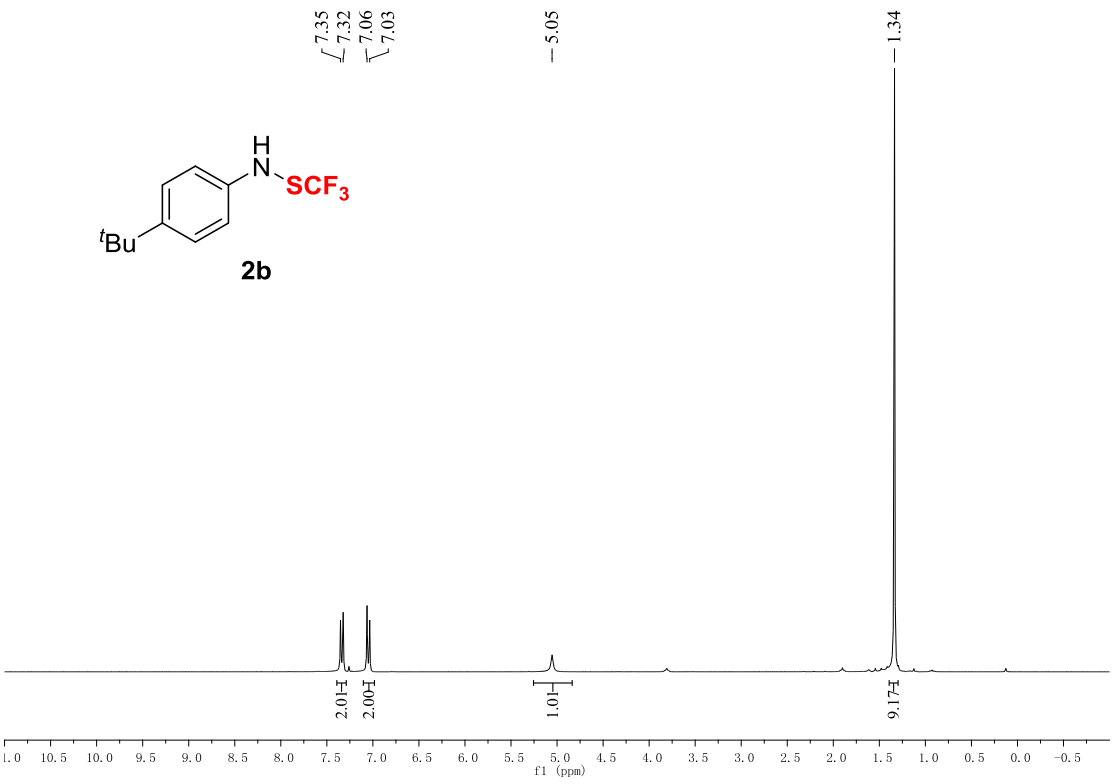
(6) X.-K. Guo, D.-Y. Zhao, J.-H. Li, X.-G. Zhang, C.-L. Deng and R.-Y. Tang, *Synlett*, 2012, 627.

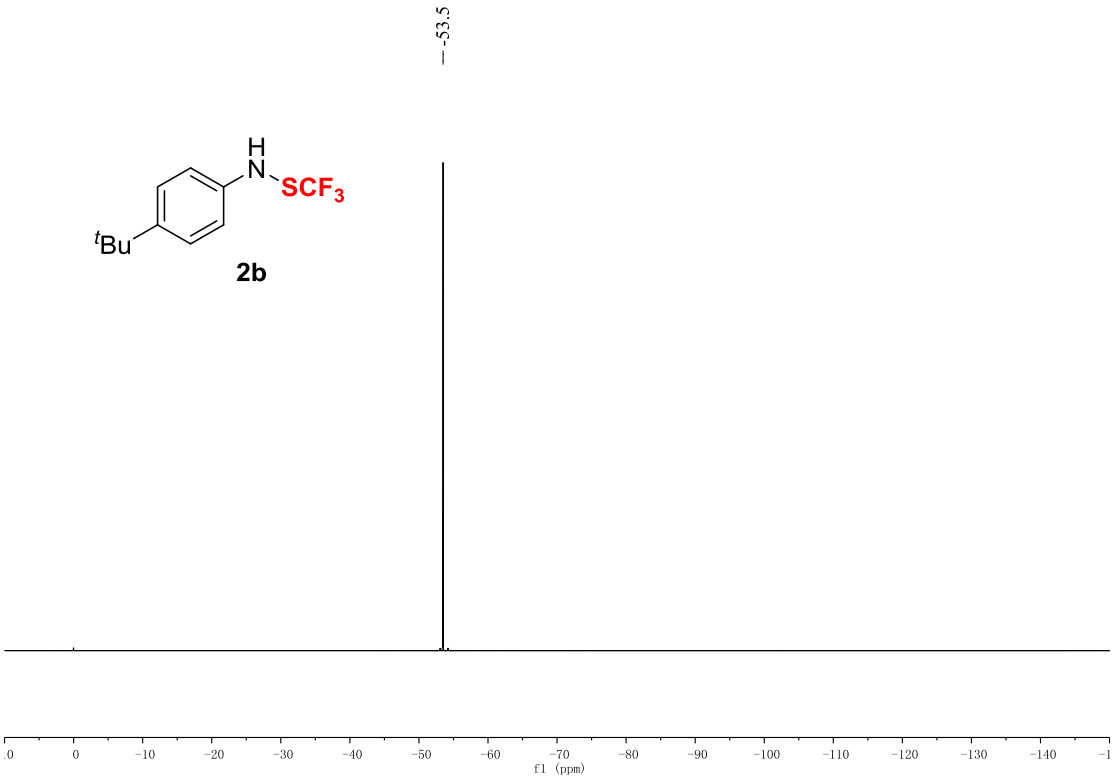
10. NMR Spectra of the corresponding compounds

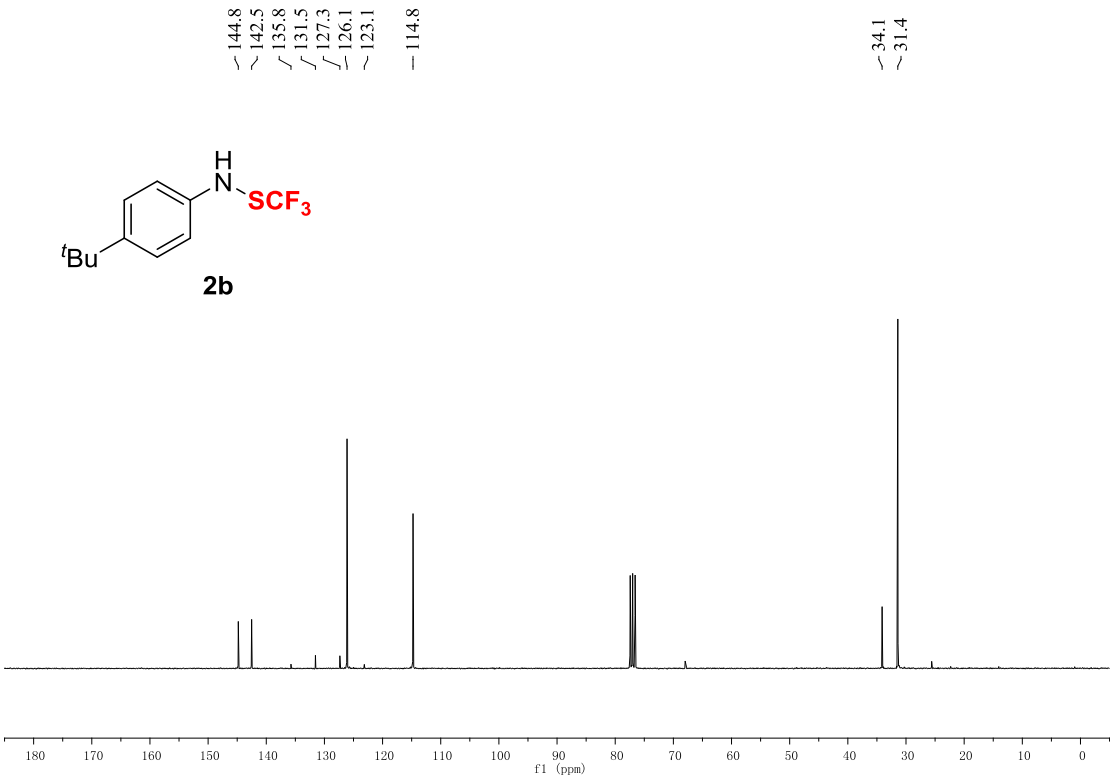


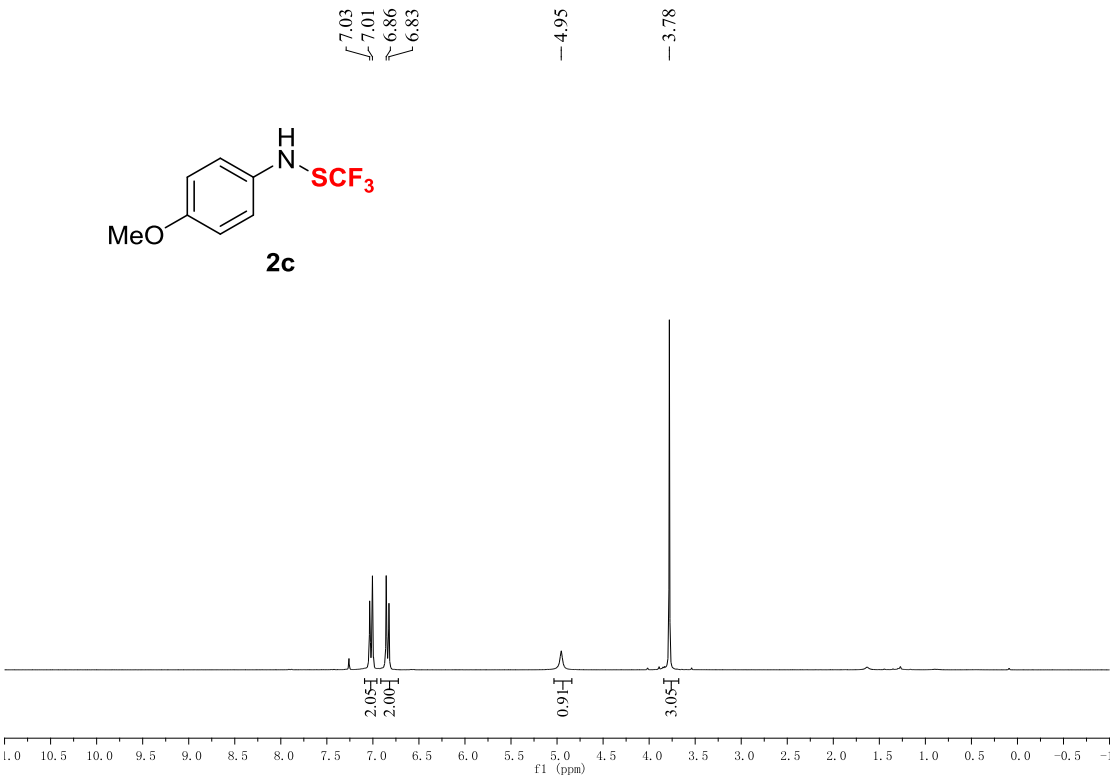


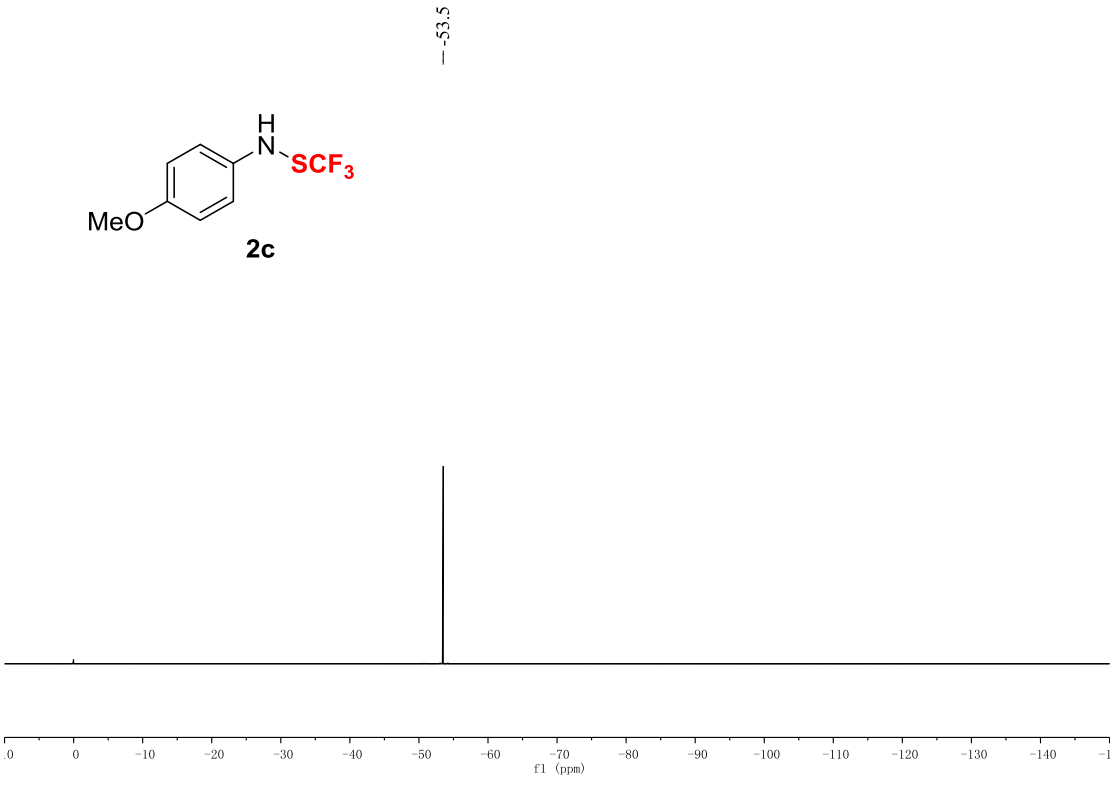

145.0
135.7
131.5
129.3
127.3
123.1
121.9
115.1
H
N
SCF3
2a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

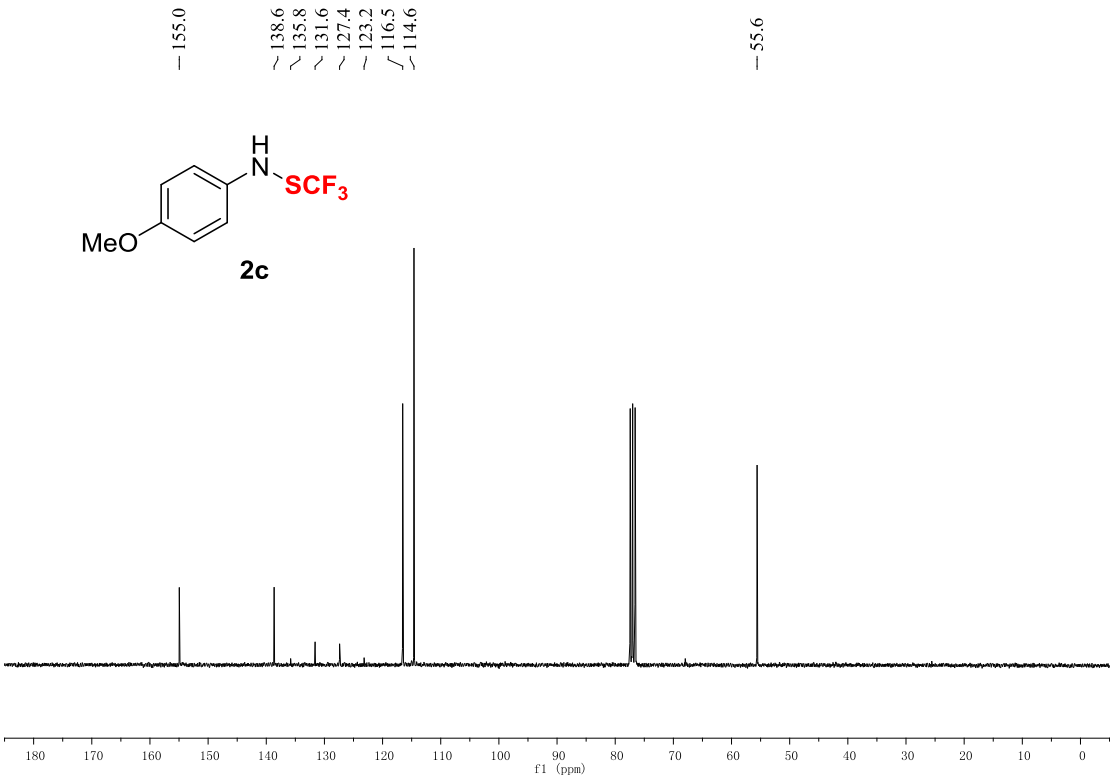

7.35
7.32
7.06
7.03
5.05
1.34
H
N
SCF3
tBu
2b
2.01
2.00
1.01
9.17
f1 (ppm)

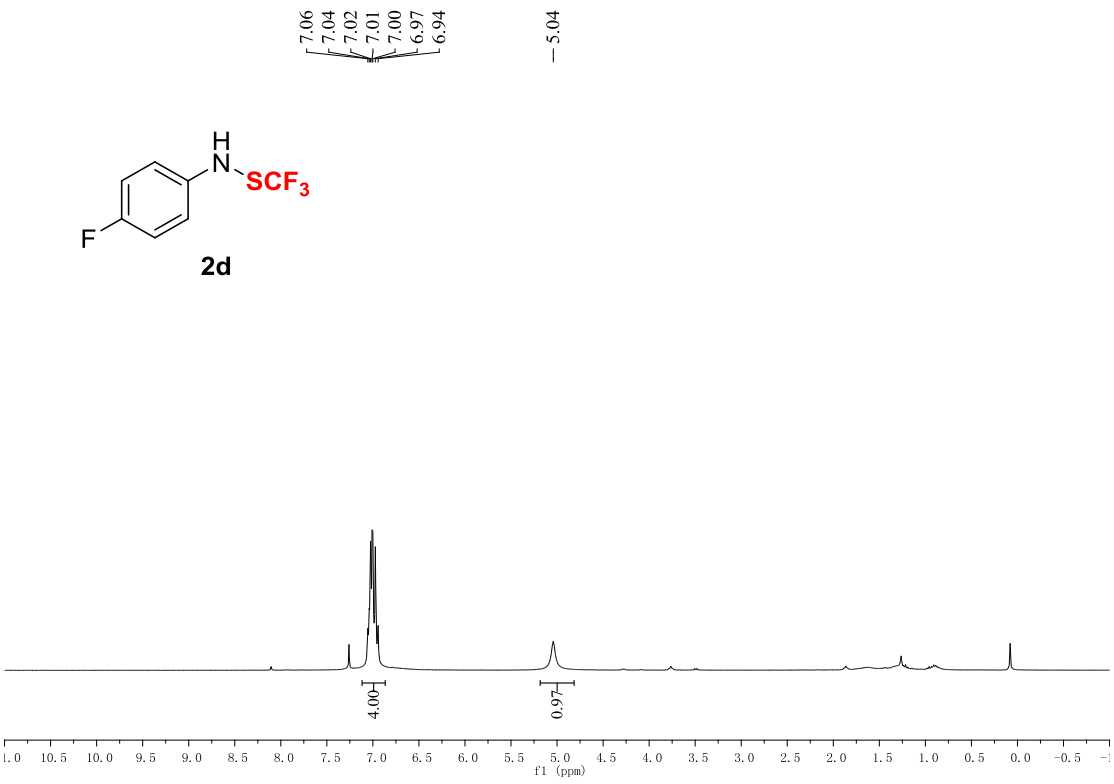

-53.5
H
N
SCF3
tBu
2b
f1 (ppm)

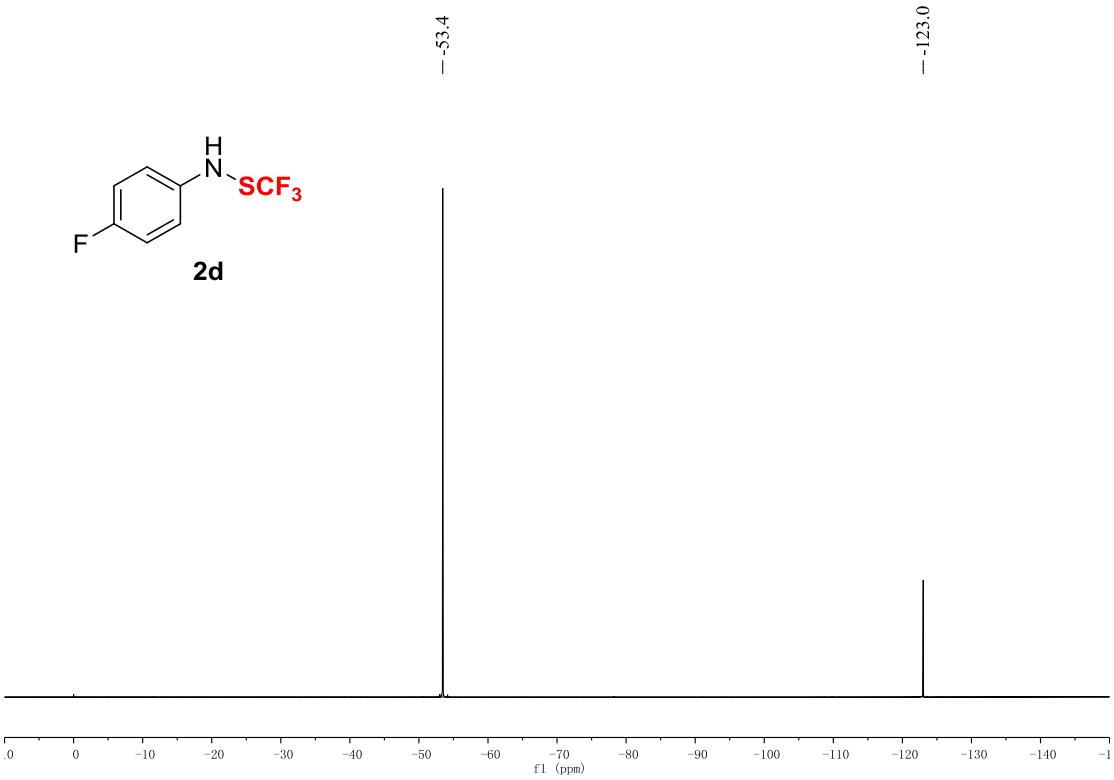

144.8
142.5
135.8
131.5
127.3
126.1
123.1
114.8
34.1
31.4
H
N
SCF3
tBu
2b
f1 (ppm)

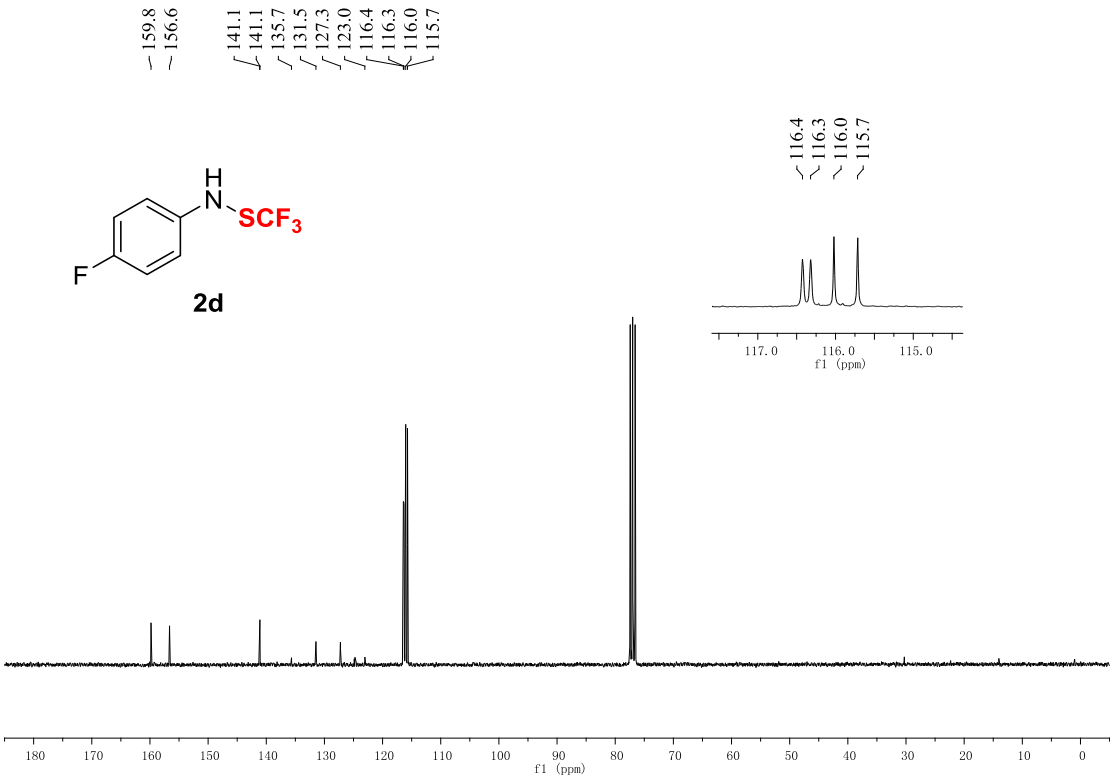

7.03
7.01
6.86
6.83
4.95
3.78
H
N
SCF3
MeO
2c
2.05
2.00
0.91
3.05
f1 (ppm)

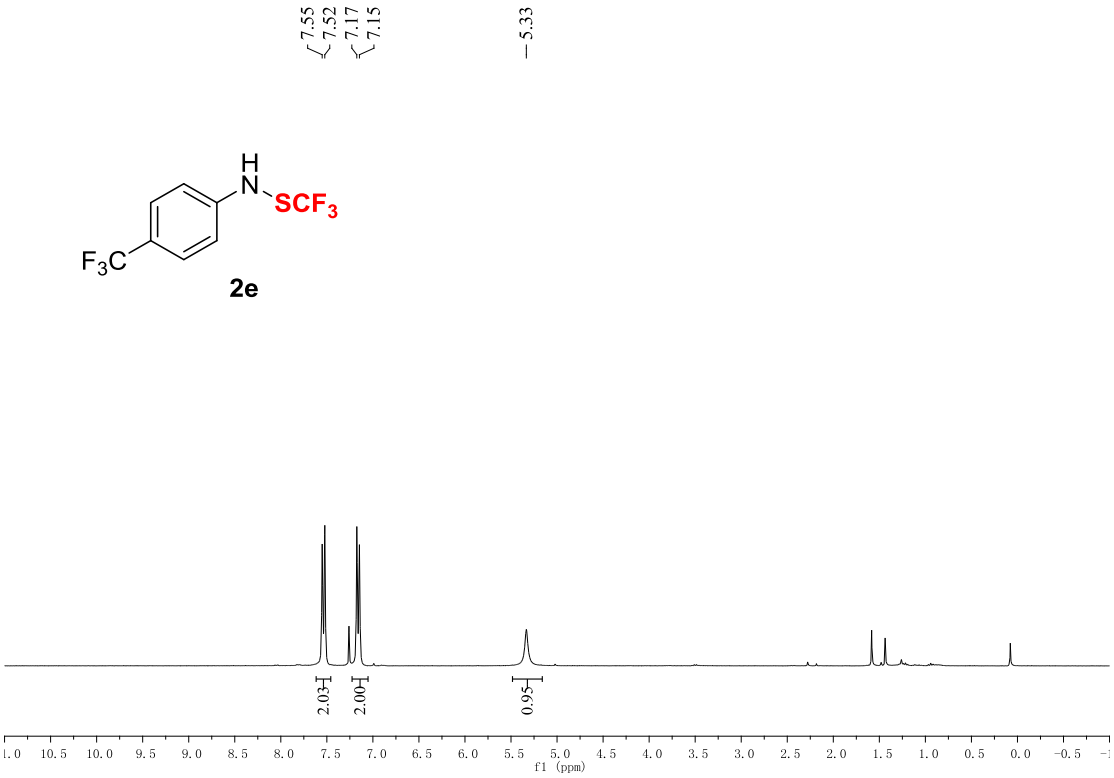

-53.5
H
N
SCF3
MeO
2c
f1 (ppm)

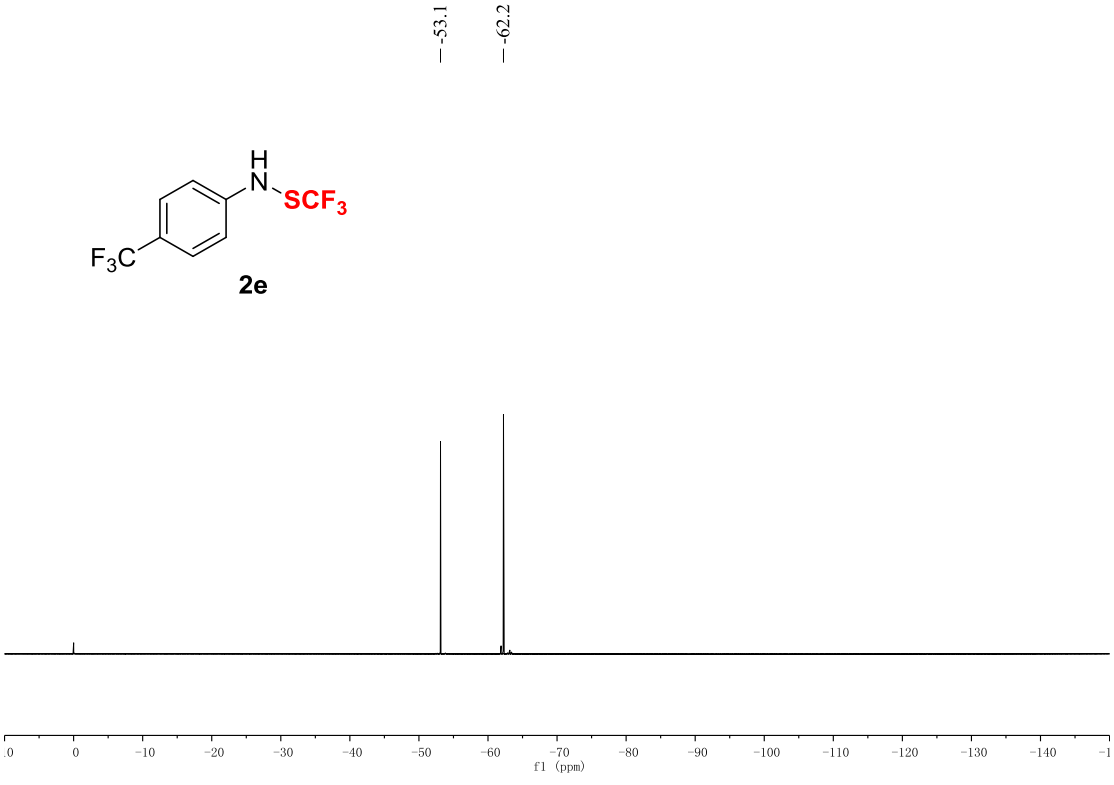

155.0
138.6
135.8
131.6
127.4
123.2
116.5
114.6
55.6
H
N
SCF3
MeO
2c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

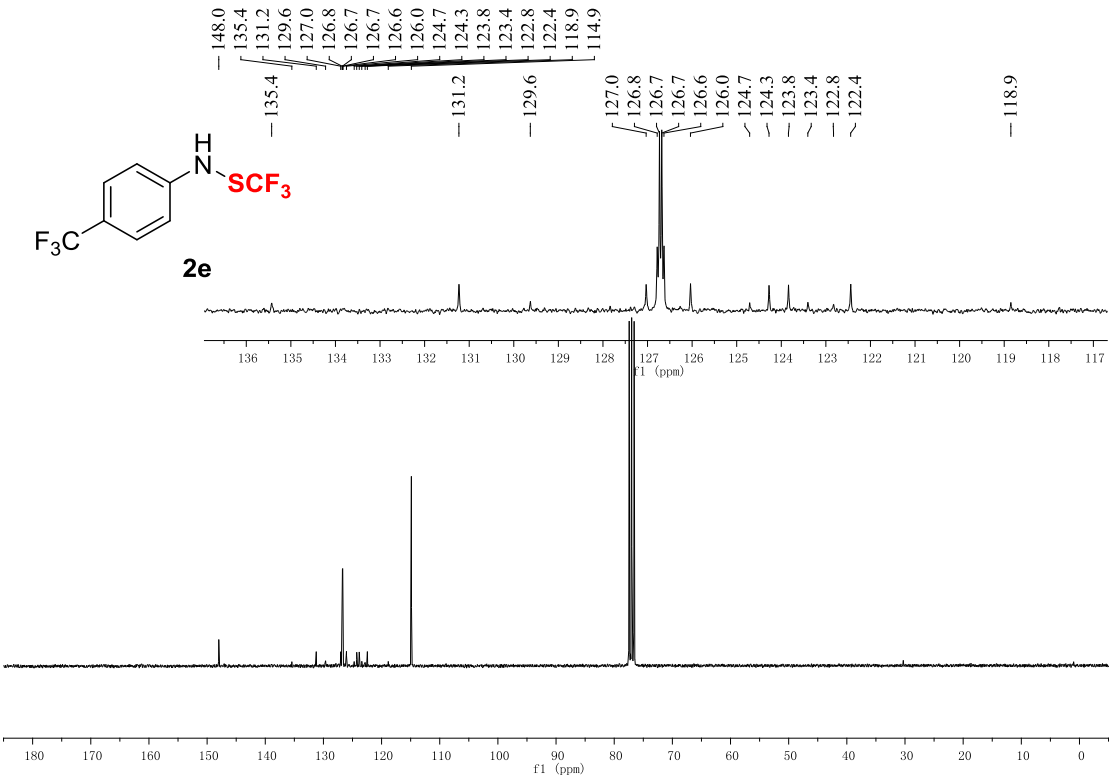

7.06
7.04
7.02
7.01
7.00
6.97
6.94
5.04
H
N
SCF3
F
2d
4.00
0.97
f1 (ppm)

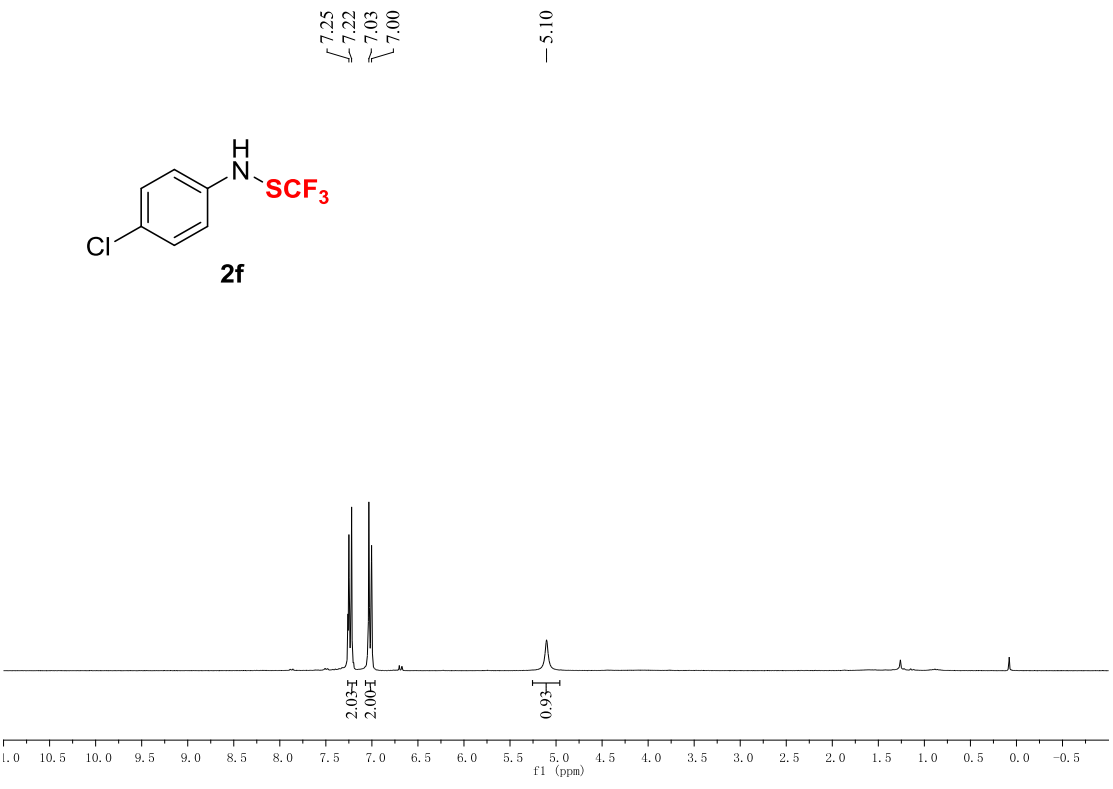

-53.4
-123.0
H
N
SCF3
F
2d
f1 (ppm)

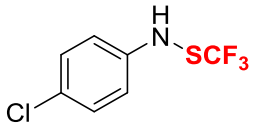

159.8
156.6
141.1
141.1
135.7
131.5
127.3
123.0
116.4
116.3
116.0
115.7
H
N
SCF3
F
2d
116.4
116.3
116.0
115.7
117.0
116.0
115.0
f1 (ppm)
f1 (ppm)


7.55
7.52
7.17
7.15
5.33
H
N
SCF3
F3C
2e
2.03
2.00
0.95
f1 (ppm)


-53.1
-62.2
H
N
SCF3
F3C
2e
f1 (ppm)

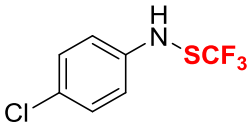

148.0
135.4
131.2
129.6
127.0
126.8
126.7
126.7
126.6
126.0
124.7
124.3
123.8
123.4
122.8
122.4
118.9
114.9
H
N
SCF3
F3C
2e
f1 (ppm)
f1 (ppm)


7.25
7.22
7.03
7.00
5.10
H
N
SCF3
Cl
2f
2.03
2.00
0.93
f1 (ppm)


H
N
SCF3
Cl

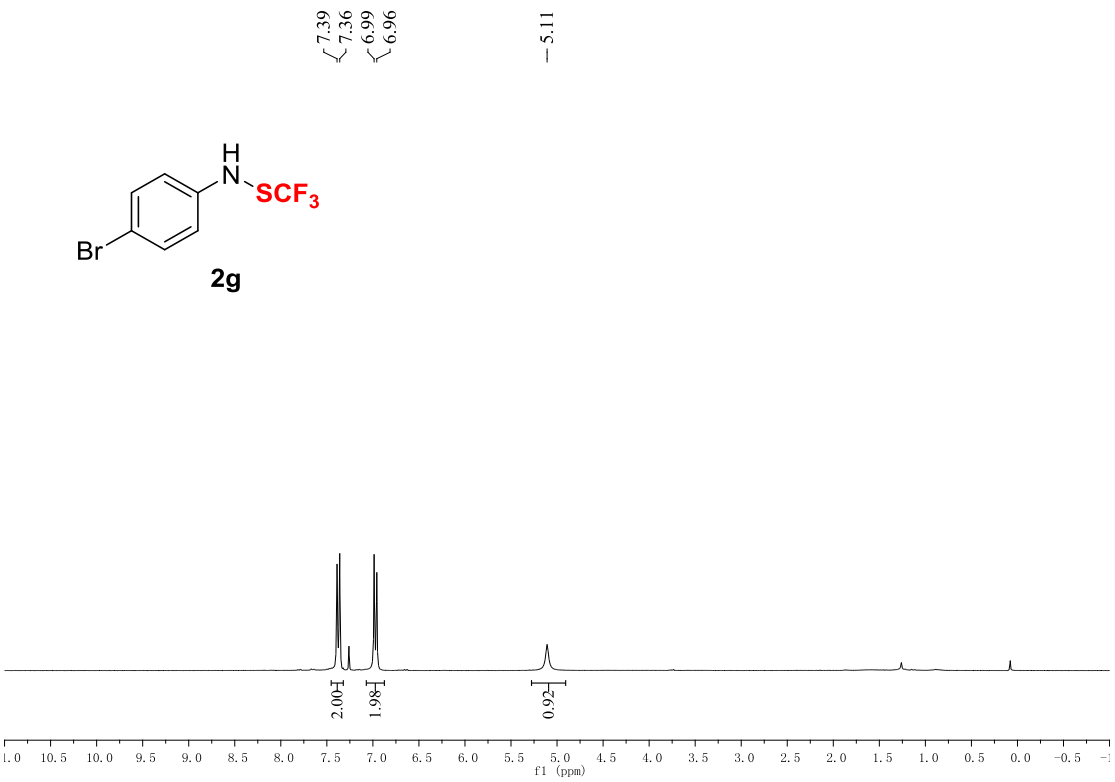
2f

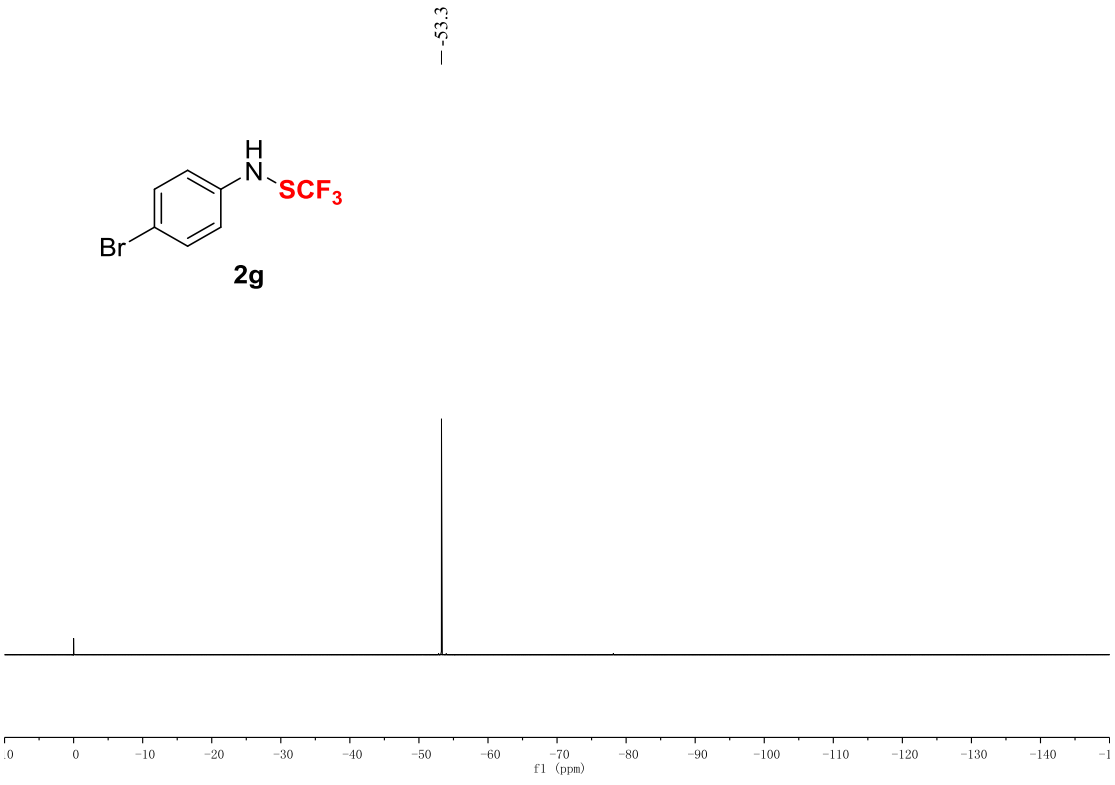
-53.3
.0
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−1
f1 (ppm)

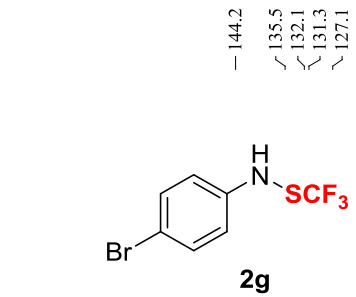

H
N
SCF3
Cl

2f

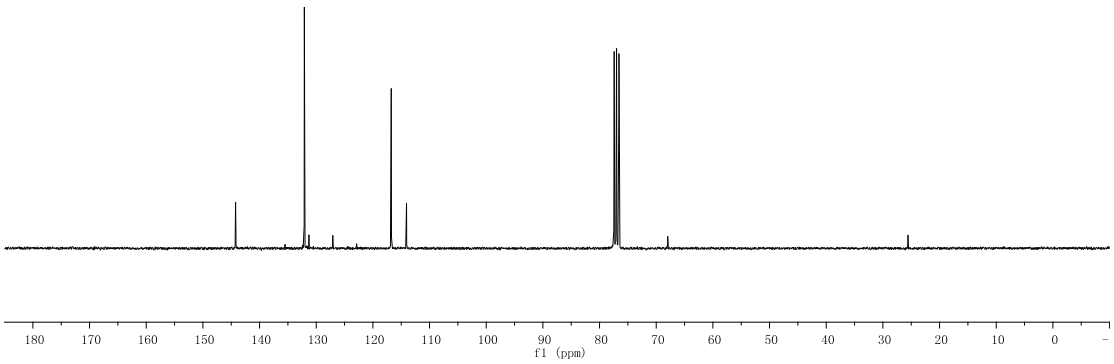
143.7
135.5
131.3
129.2
127.1
126.8
122.9
116.3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

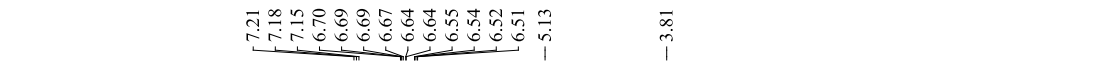

7.39
7.36
6.99
6.96
5.11
H
N
SCF3
Br
2g
2.00
1.98
0.92
f1 (ppm)

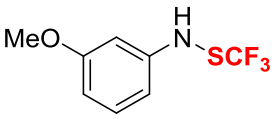

-53.3
H
N
SCF3
Br
2g
f1 (ppm)


144.2
135.5
132.1
131.3
127.1
116.8
114.1
H
N
SCF3
Br

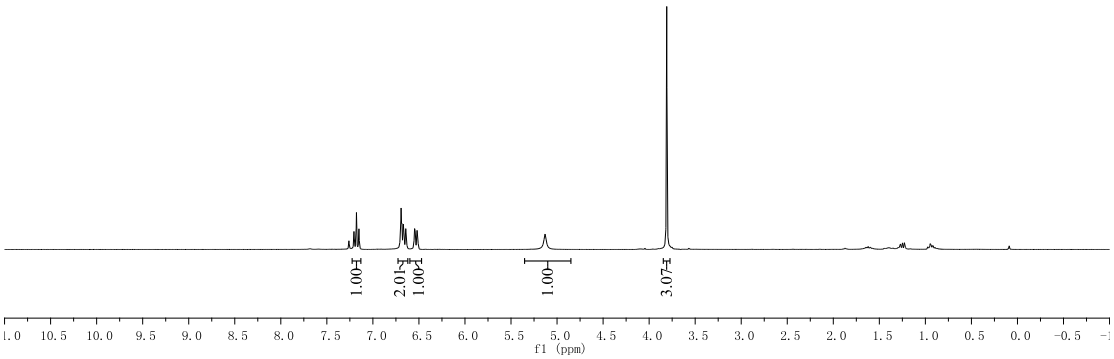
2g

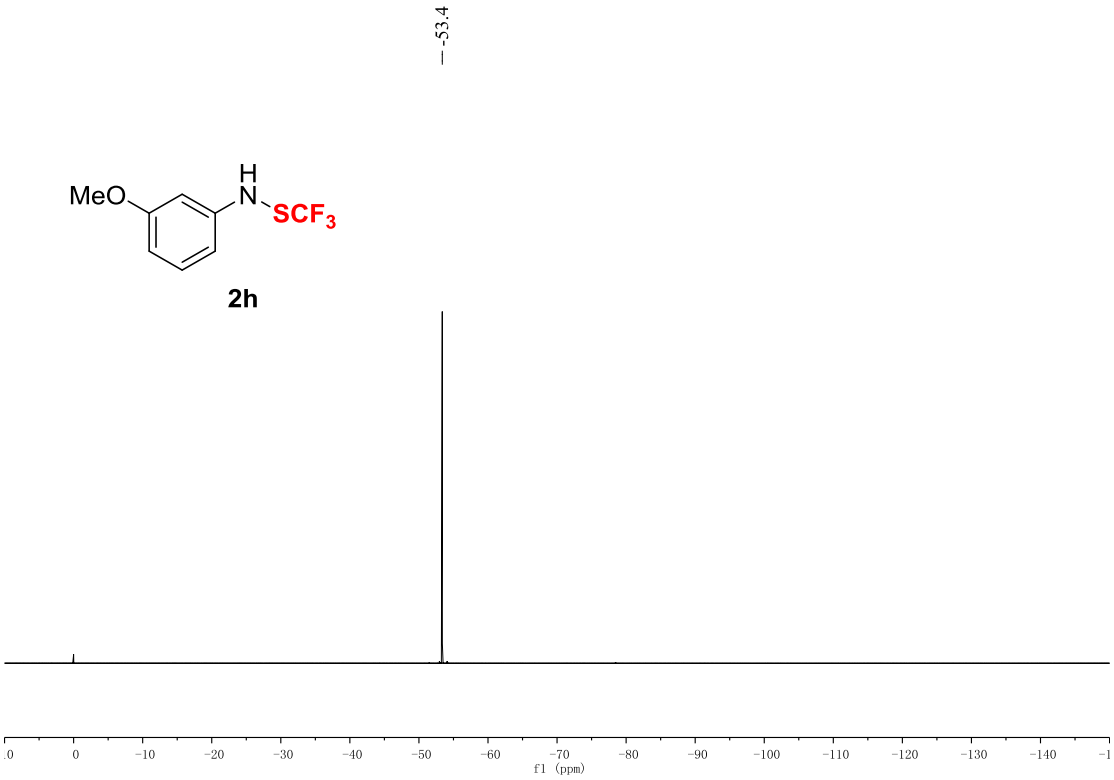

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

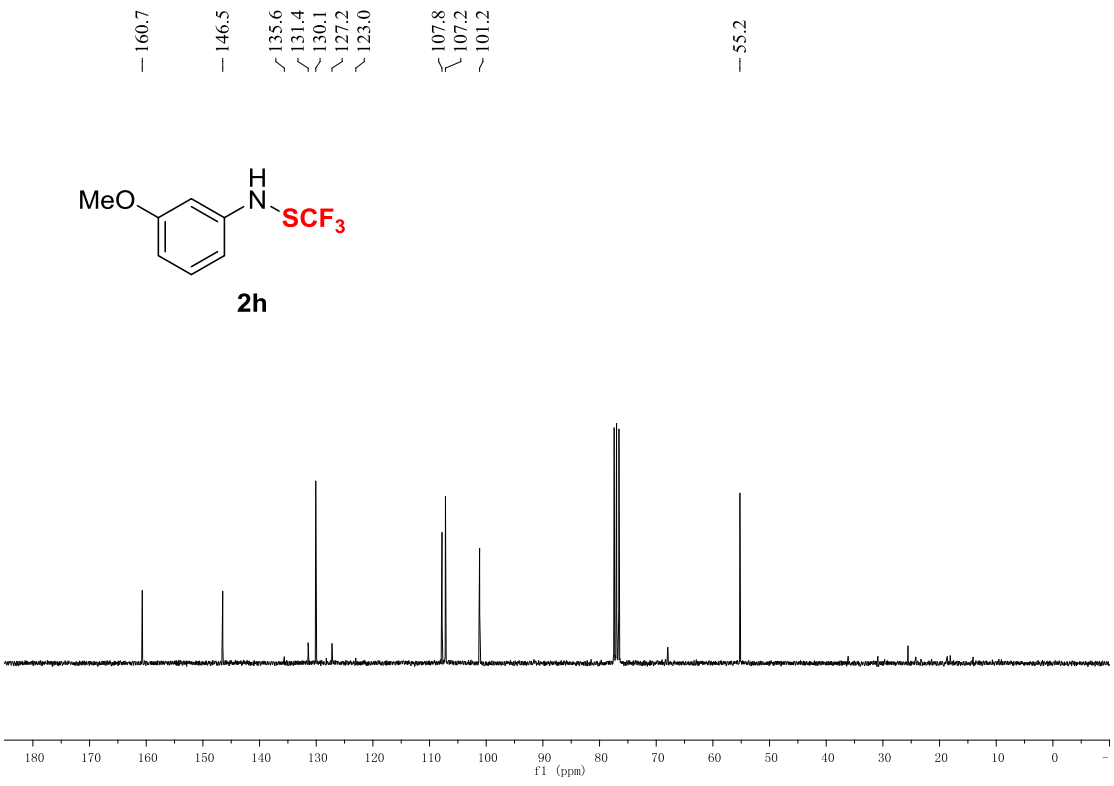

7.21
7.18
7.15
6.70
6.69
6.69
6.67
6.64
6.64
6.55
6.54
6.52
6.51
5.13
3.81


MeO
H
N
SCF3

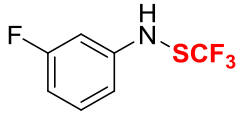
2h


1.00
2.01
1.00
1.00
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

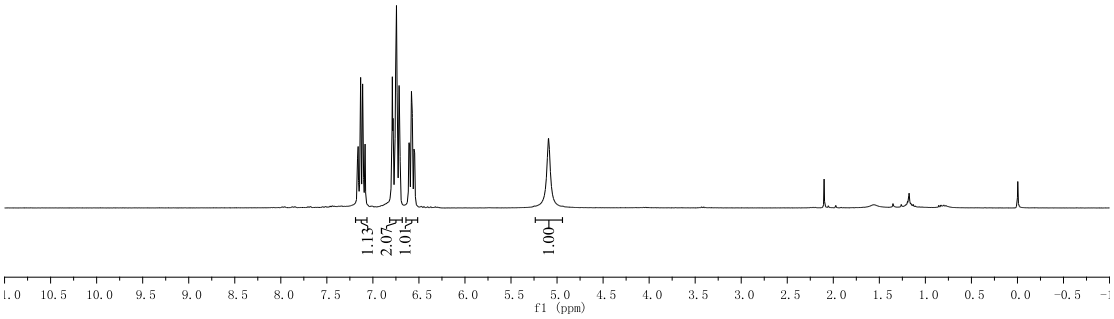

-53.4
MeO
H
N
SCF3
2h
f1 (ppm)

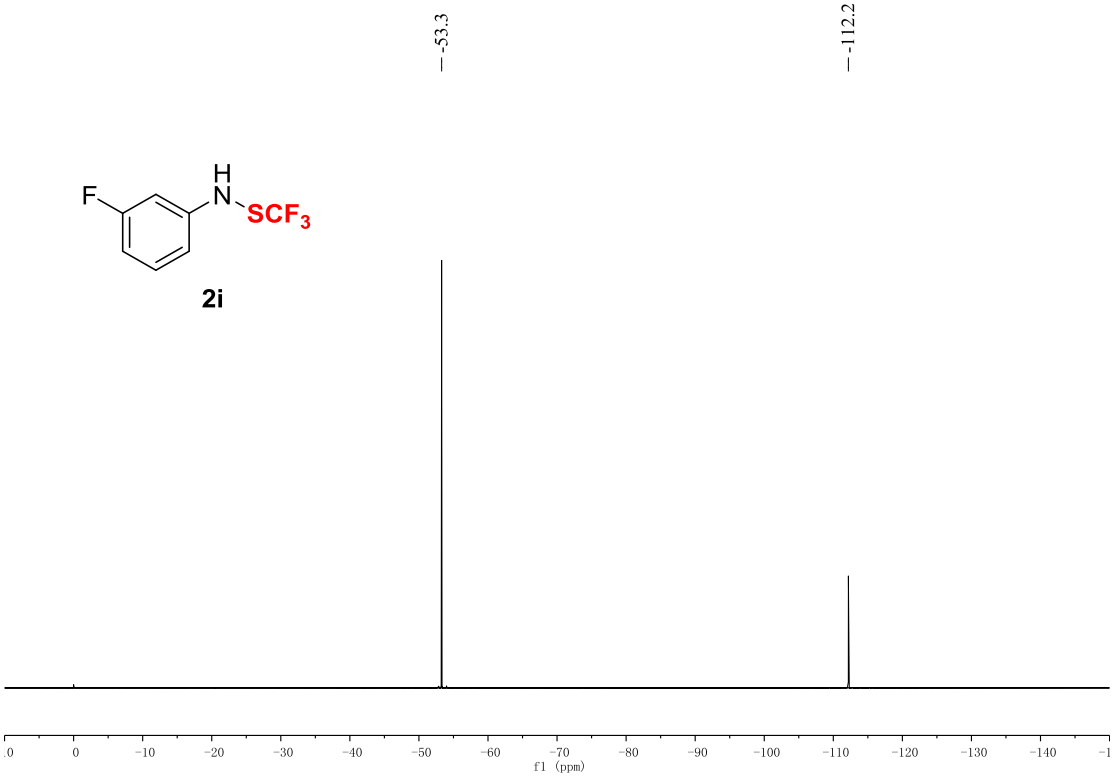

160.7
146.5
135.6
131.4
130.1
127.2
123.0
107.8
107.2
101.2
55.2
MeO
H
N
SCF3
2h
f1 (ppm)


7.17
7.16
7.13
7.11
7.08
6.80
6.79
6.78
6.75
6.74
6.72
6.71
6.61
6.60
6.58
6.57
6.55
6.55
5.09


F
H
N
SCF3

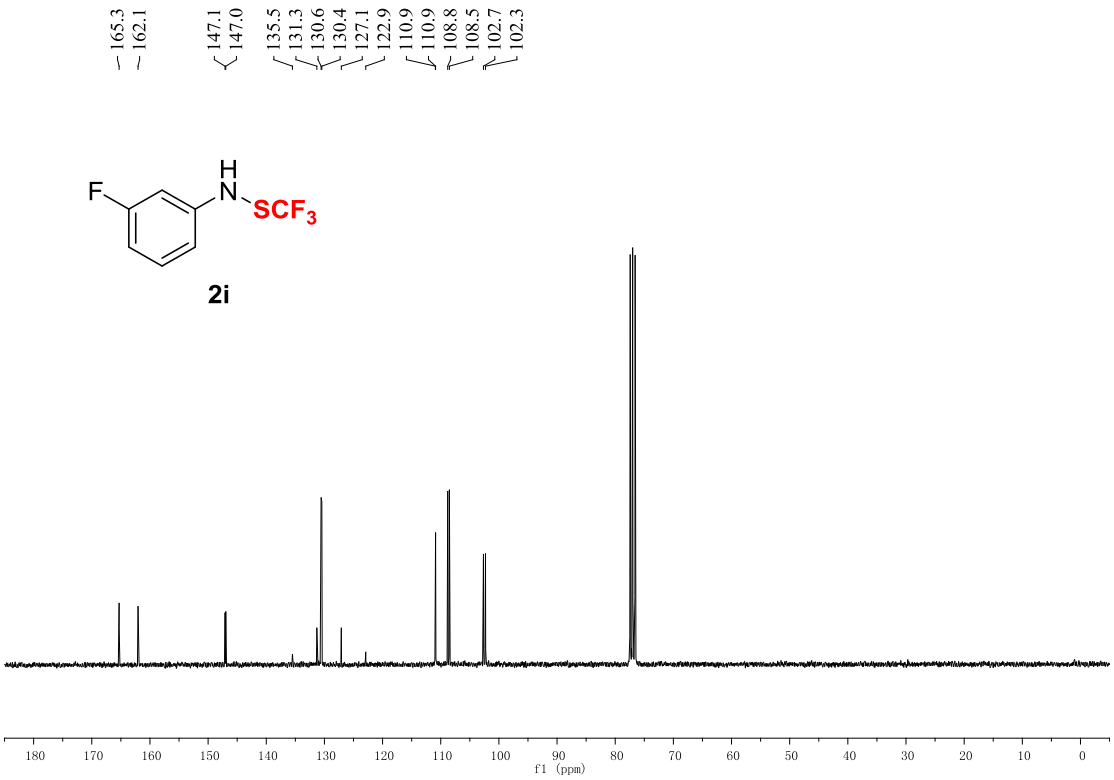
2i


1.13
2.07
1.01
1.00
f1 (ppm)

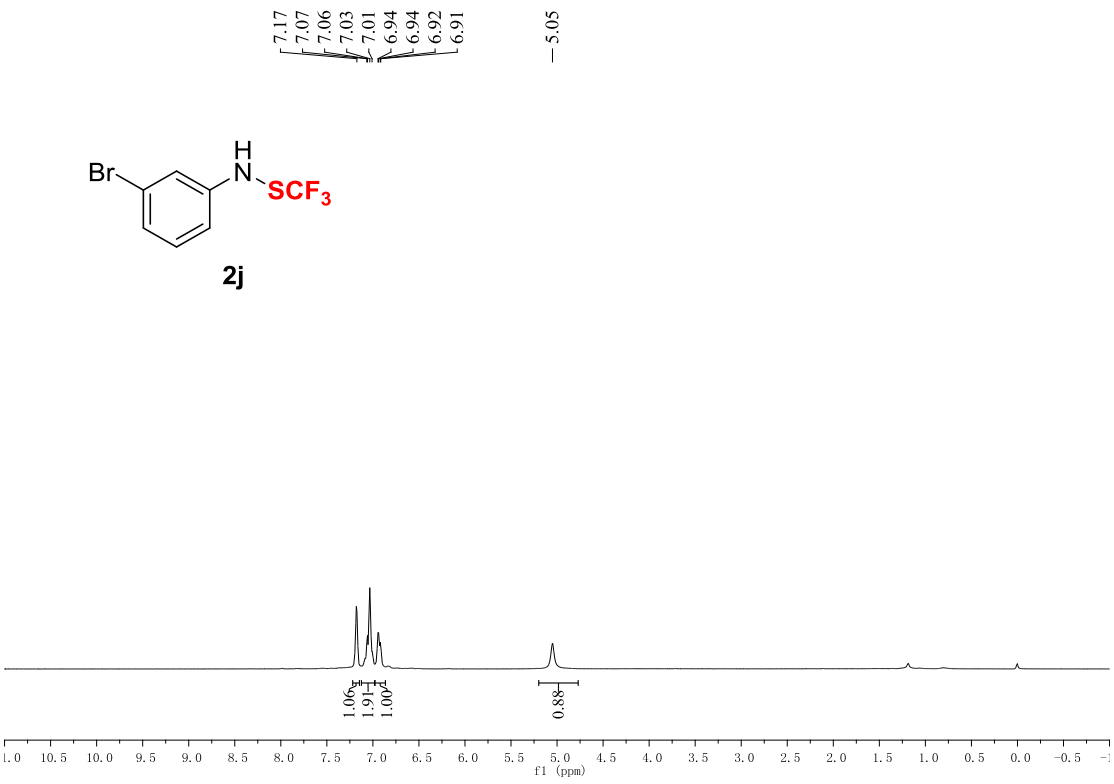

-53.3
-112.2
f1 (ppm)

F
H
N
SCF3

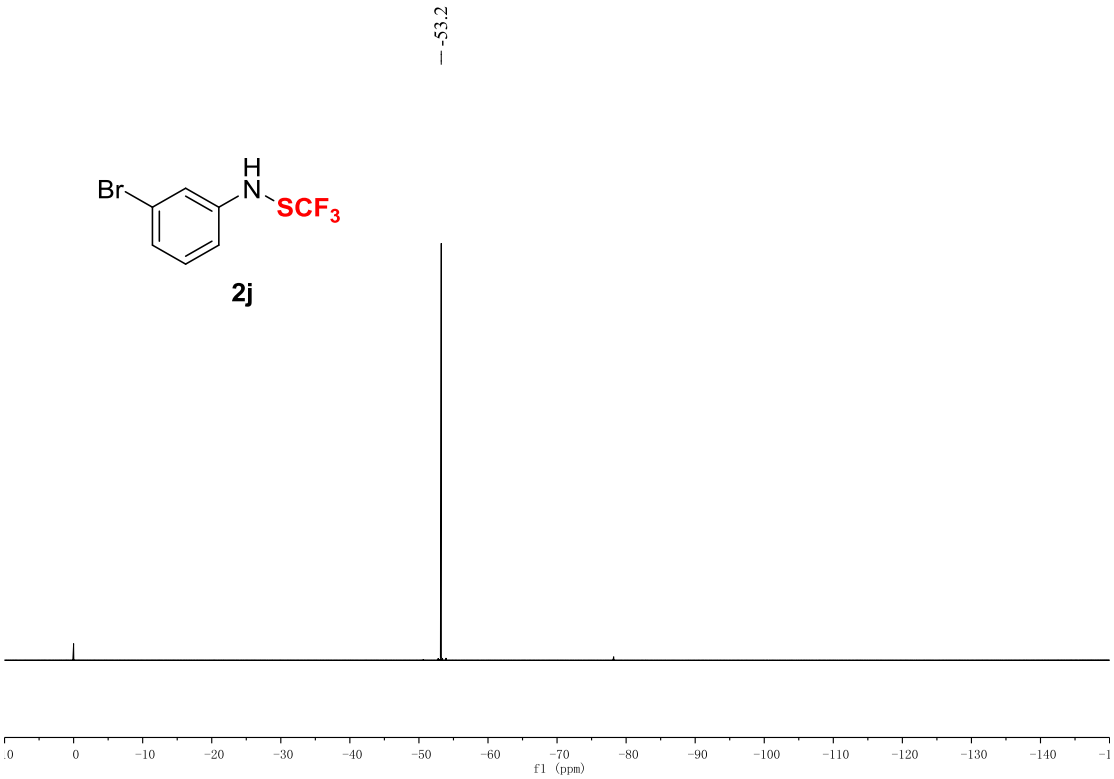
2i

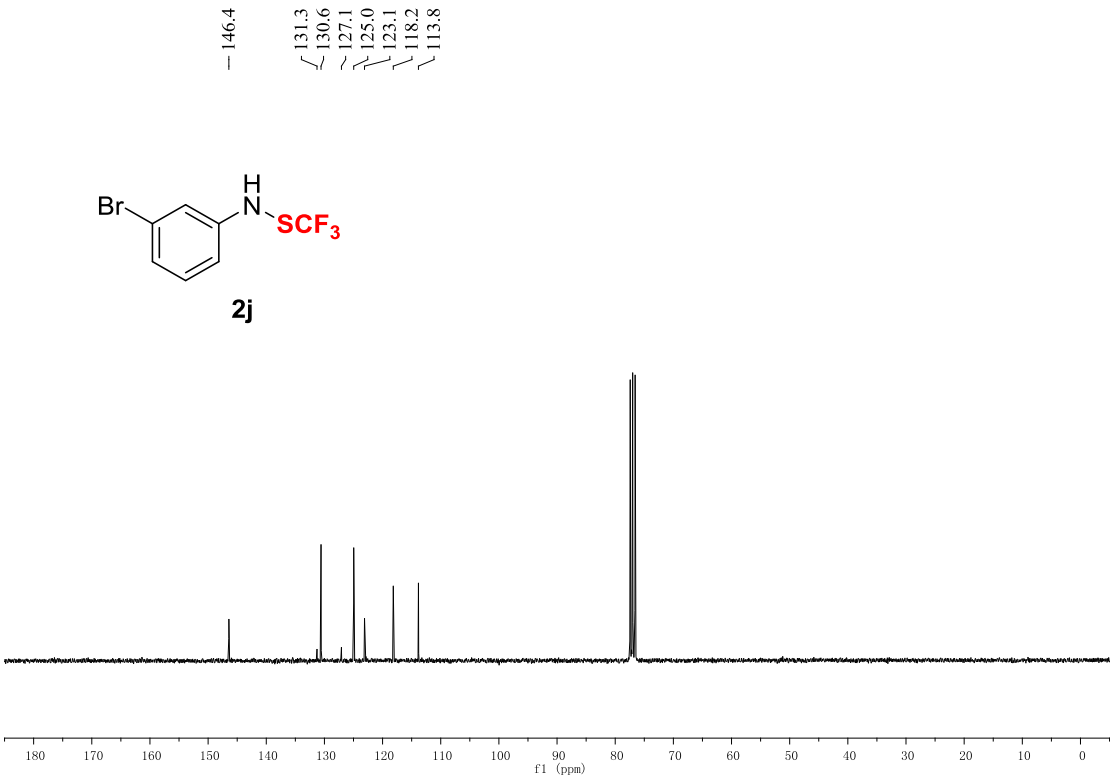

165.3
162.1
147.1
147.0
135.5
131.3
130.6
130.4
127.1
122.9
110.9
110.9
108.8
108.5
102.7
102.3
F
H
N
SCF3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

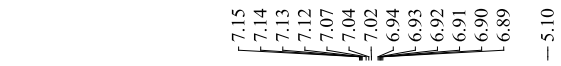
2i


7.17
7.07
7.06
7.03
7.01
6.94
6.94
6.92
6.91
5.05
Br
H
N
SCF3
1.06
1.91
1.00
0.88
f1 (ppm)

2j

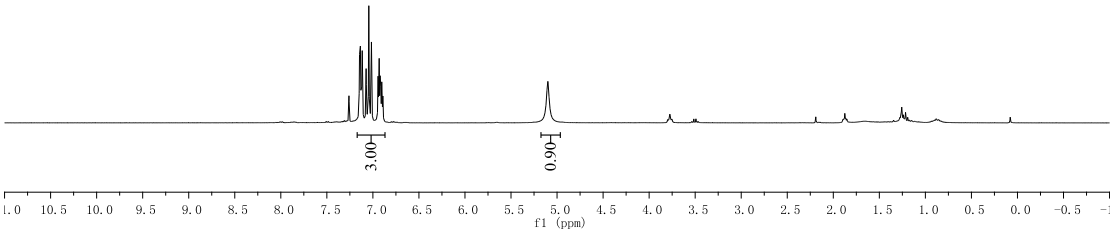

-53.2
Br
H
N
SCF3
2j
f1 (ppm)

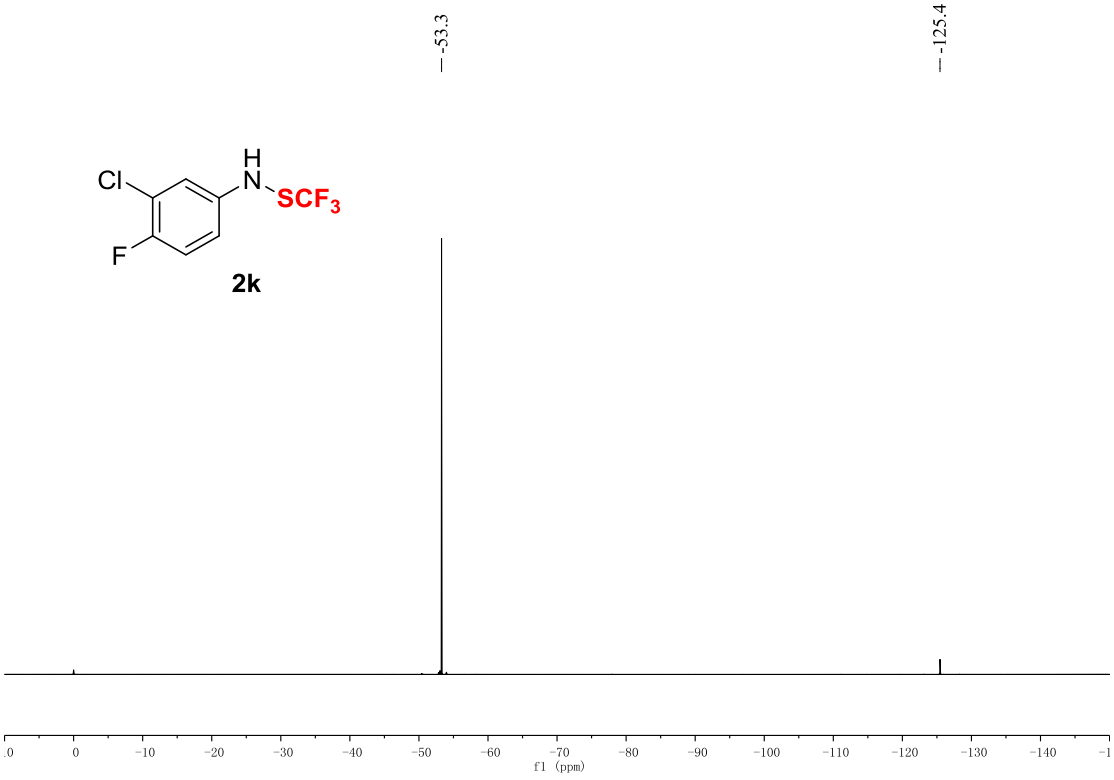

146.4
131.3
130.6
127.1
125.0
123.1
118.2
113.8
Br
H
N
SCF3
2j
f1 (ppm)


7.15
7.14
7.13
7.12
7.07
7.04
7.02
6.94
6.93
6.92
6.91
6.90
6.89
5.10


Cl
H
N
SCF3
F

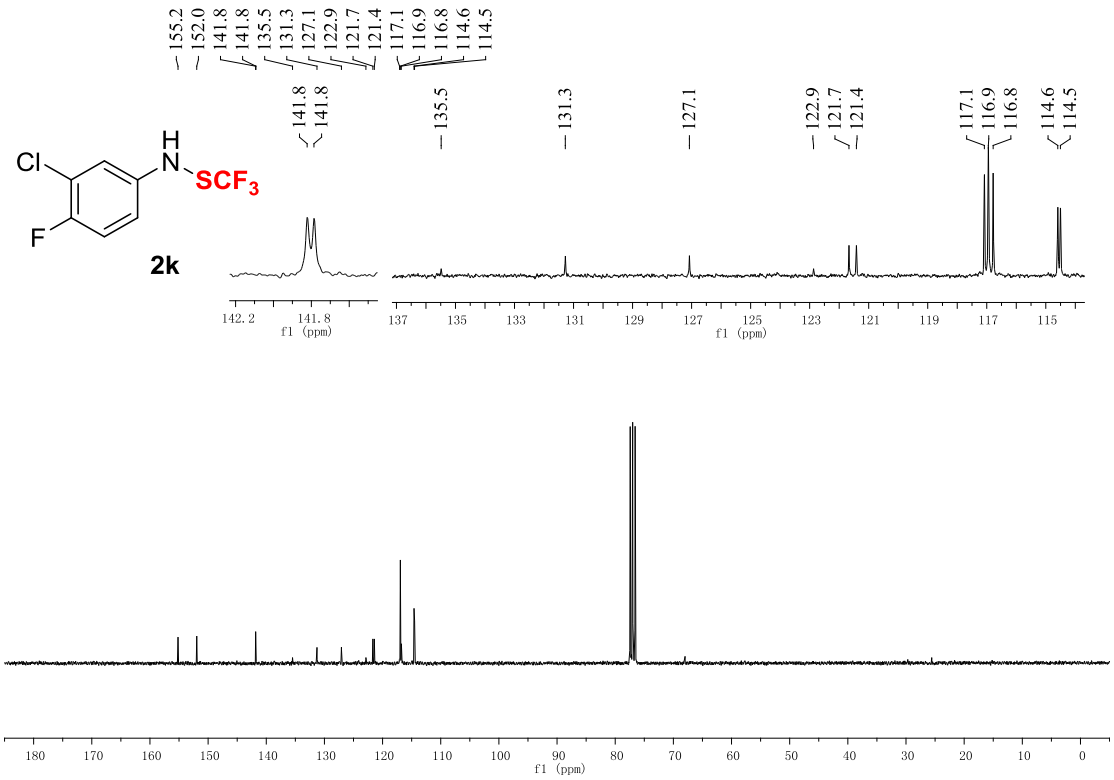
2k


3.00
0.90
f1 (ppm)

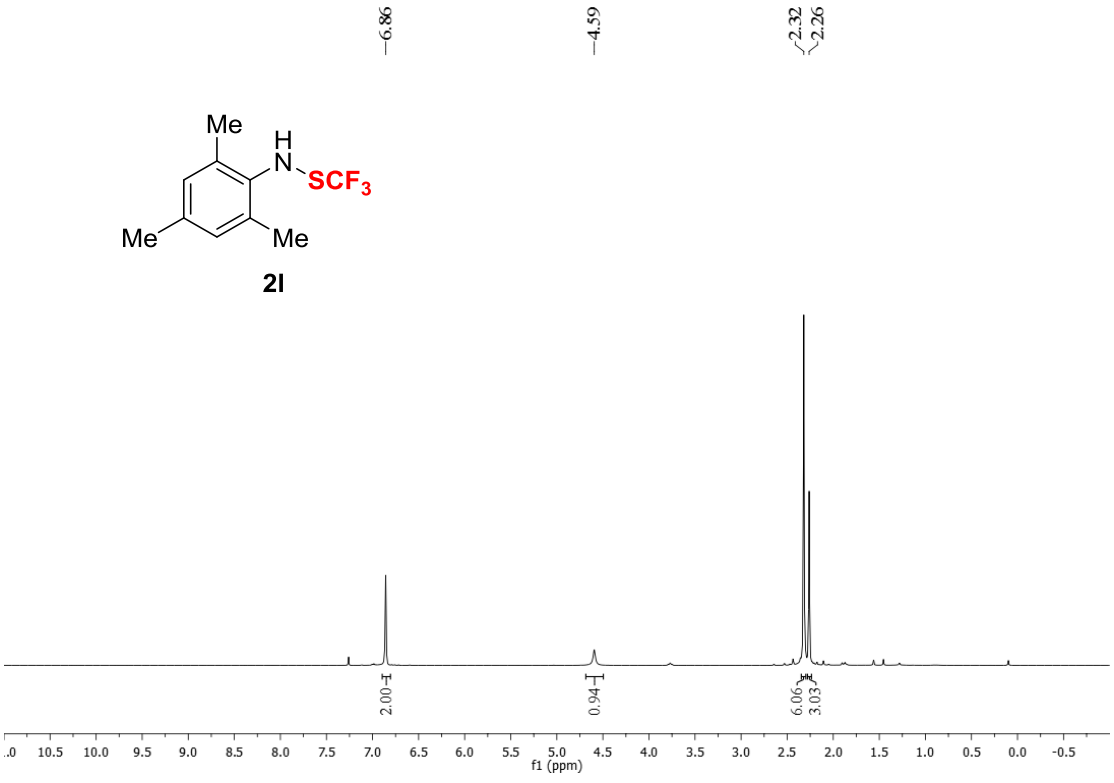

-53.3
-125.4
f1 (ppm)

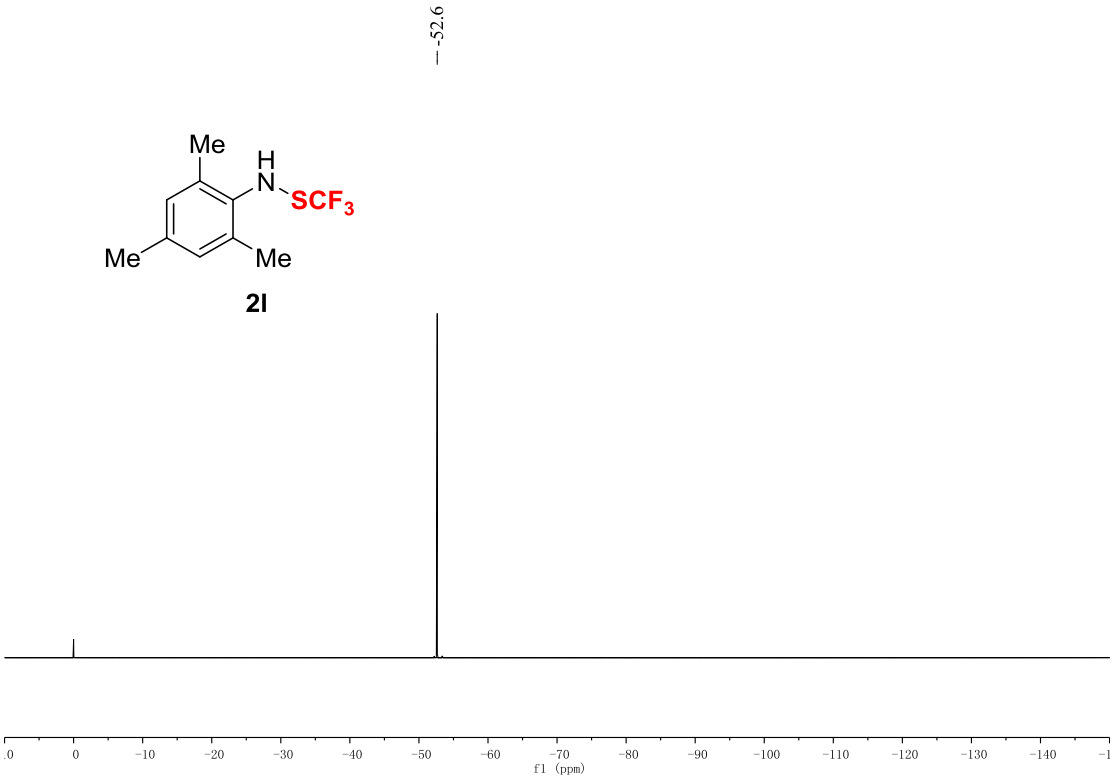
Cl
H
N
SCF3
F

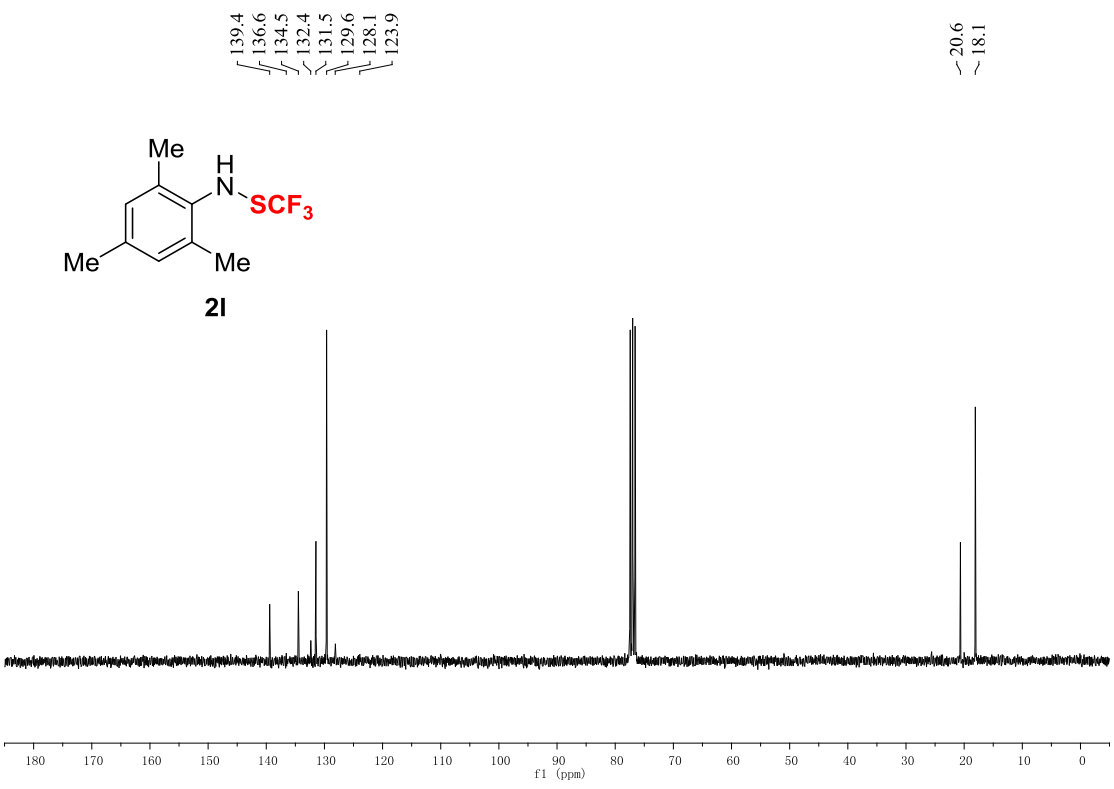
2k

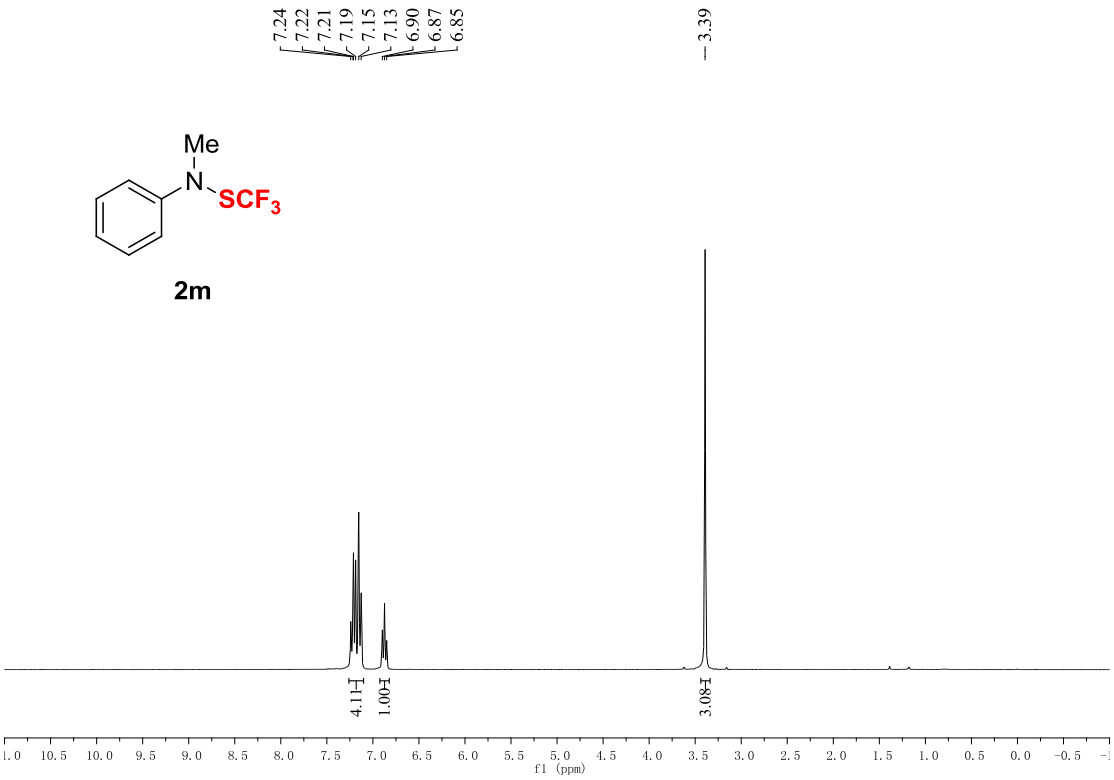

155.2
152.0
141.8
141.8
135.5
131.3
127.1
122.9
121.7
121.4
117.1
116.9
116.8
114.6
114.5
Cl
F
H
N
SCF3
2k
f1 (ppm)

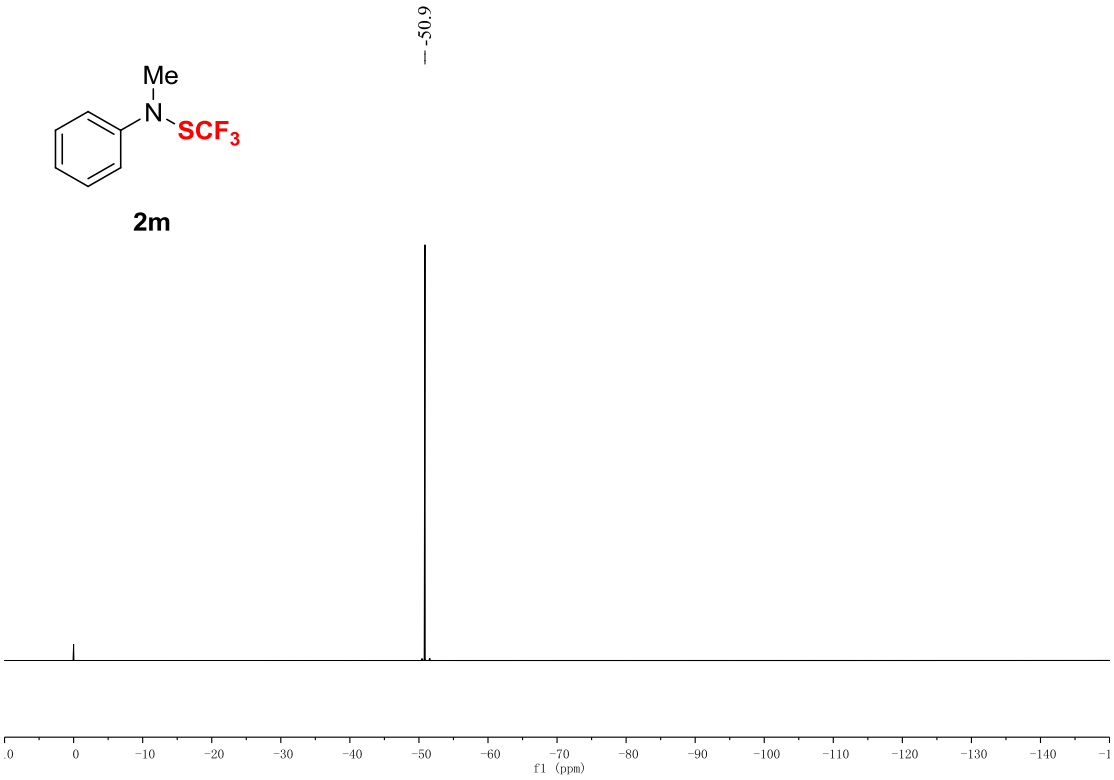
f1 (ppm)

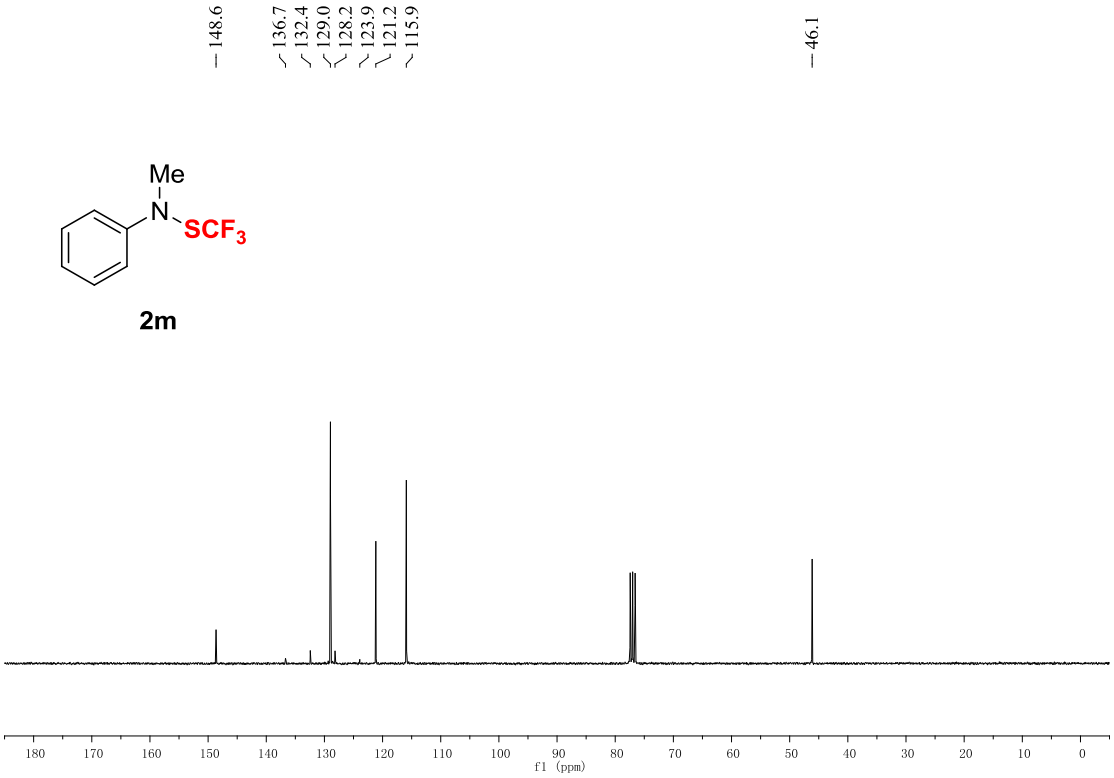

6.86
4.59
2.32
2.26
Me
H
N
SCF3
Me
Me
2l
2.00
0.94
6.06
3.03
f1 (ppm)


-52.6
Me
H
N
SCF3
Me
Me
2l
f1 (ppm)

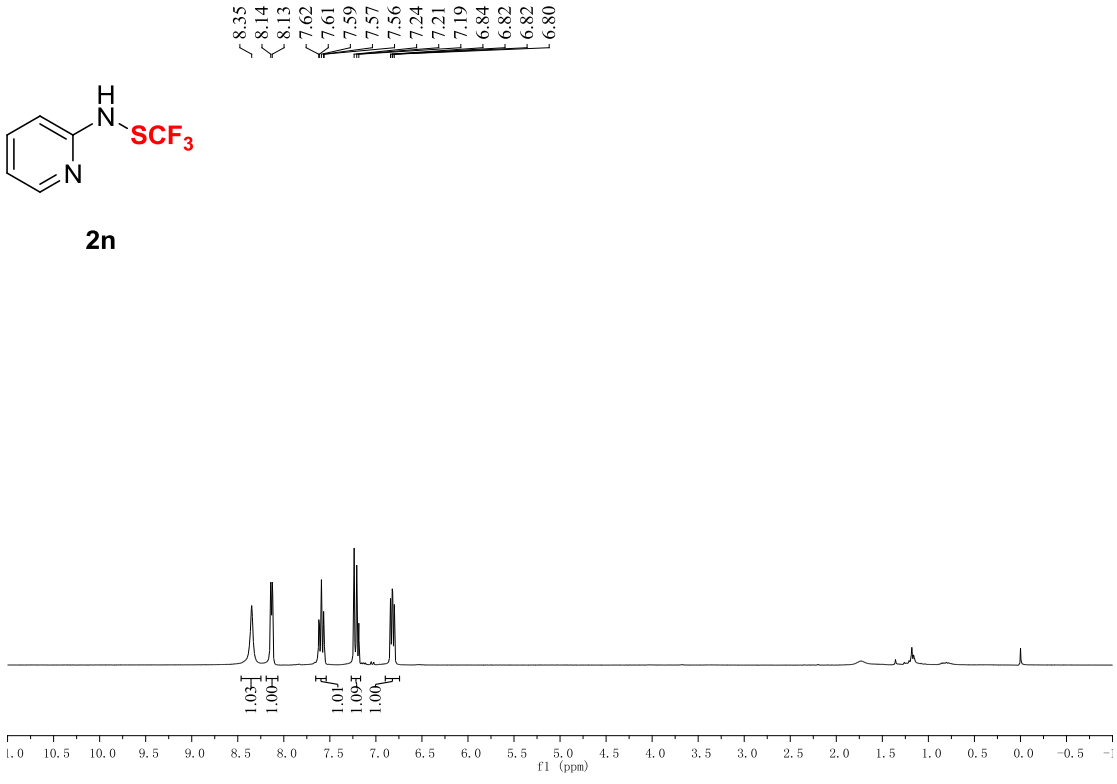

139.4
136.6
134.5
132.4
131.5
129.6
128.1
123.9
20.6
18.1
Me
H
N
SCF3
Me
Me
2l
f1 (ppm)


7.24
7.22
7.21
7.19
7.15
7.13
6.90
6.87
6.85
3.39
Me
N
SCF3
2m
4.11
1.00
3.08
f1 (ppm)

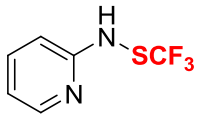

-50.9
Me
N
SCF3
2m
f1 (ppm)


148.6
136.7
132.4
129.0
128.2
123.9
121.2
115.9
46.1
Me
N
SCF3
f1 (ppm)

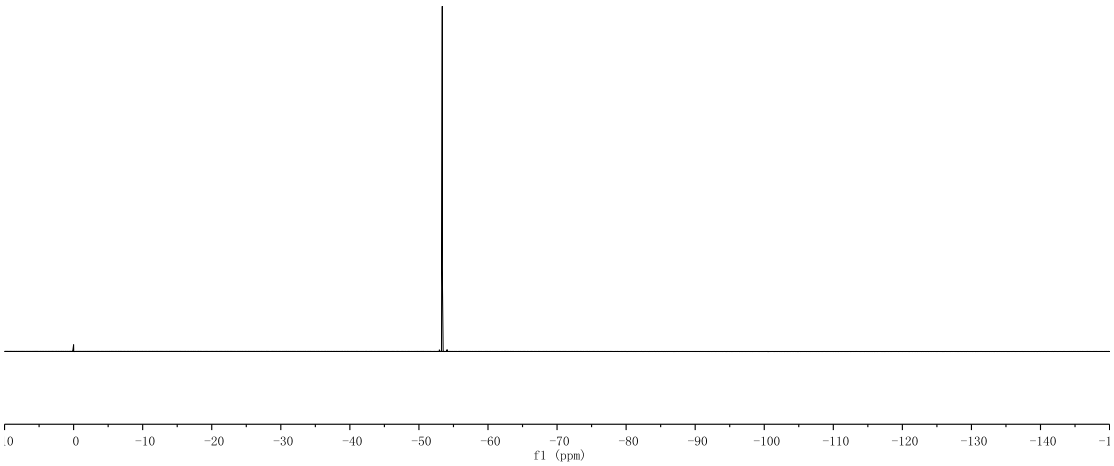
2m

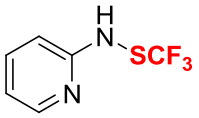

8.35
8.14
8.13
7.62
7.61
7.59
7.57
7.56
7.24
7.21
7.19
6.84
6.82
6.80
H
N
SCF3
N
1.03
1.00
1.01
1.09
1.00
f1 (ppm)

2n

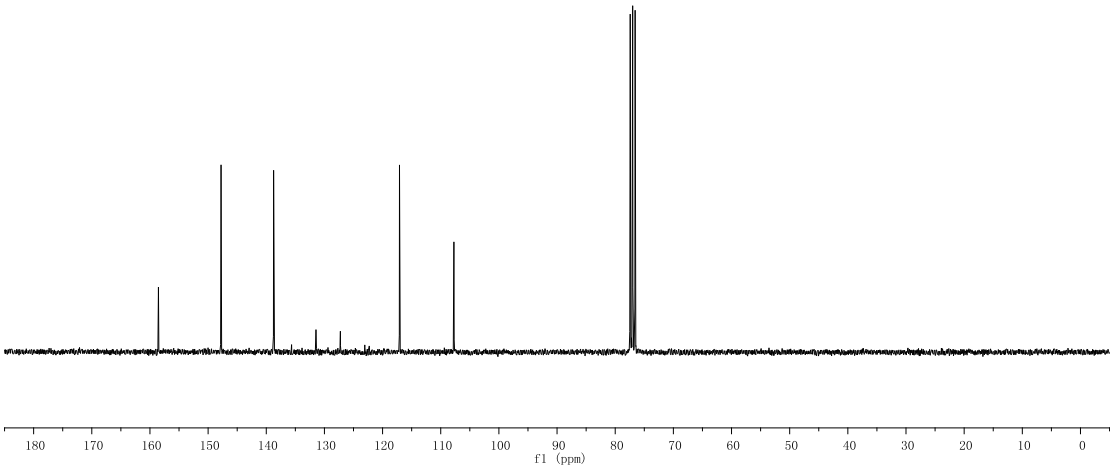

H
N
SCF3
N

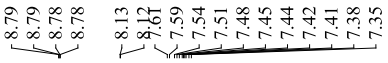
2n

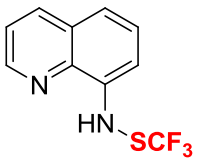

-53.4
f1 (ppm)


H
N
SCF3
N

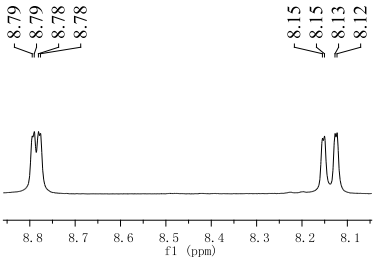
2n

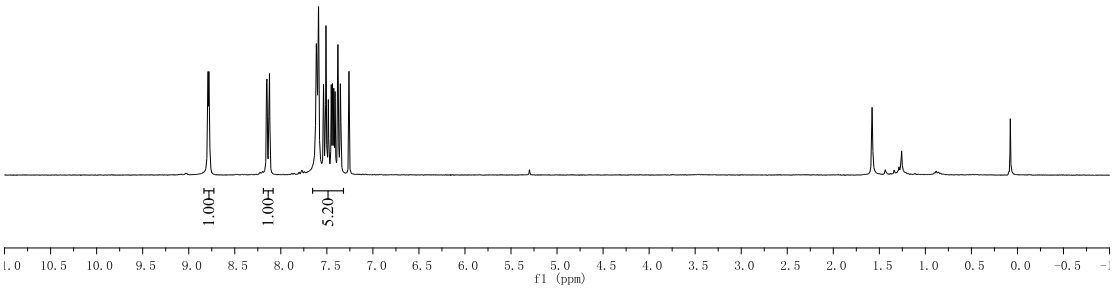

158.5
147.8
138.7
135.6
131.5
127.3
123.1
117.1
107.7
f1 (ppm)

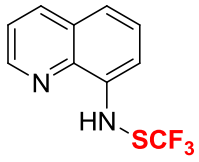

8.79
8.79
8.78
8.78
8.13
8.12
7.61
7.59
7.54
7.51
7.48
7.45
7.44
7.42
7.41
7.38
7.35


N
HN
SCF3

2o

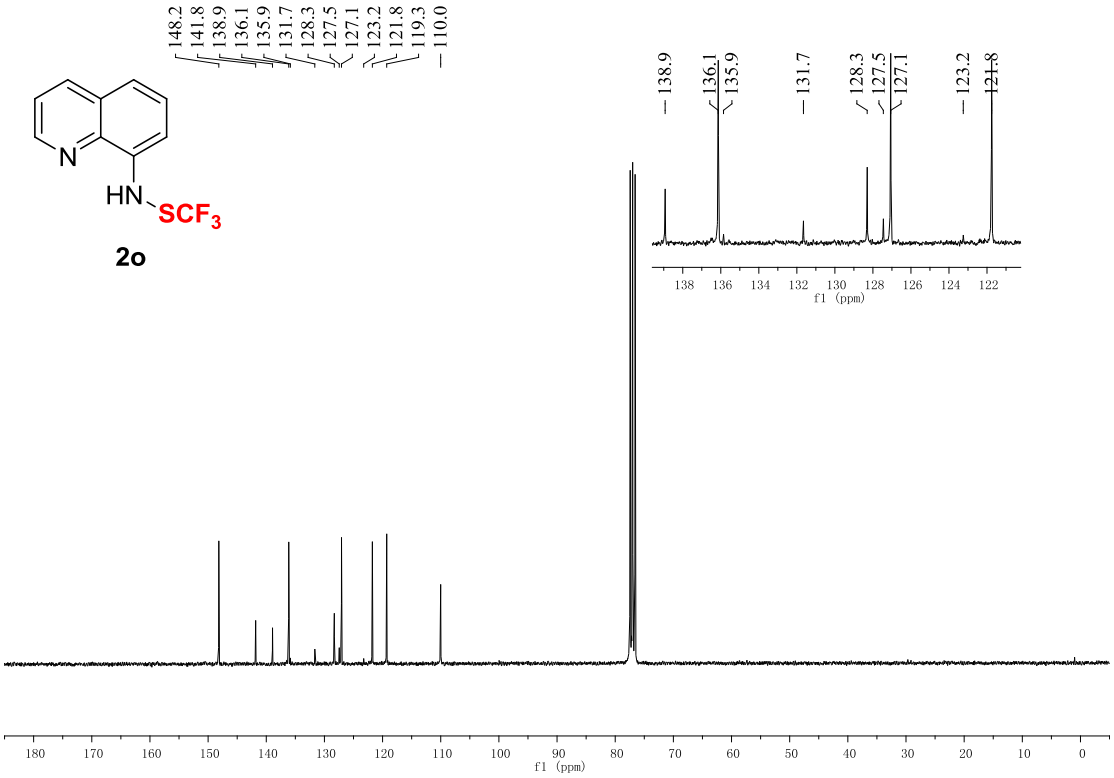

8.79
8.79
8.78
8.78
8.15
8.15
8.13
8.12
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1
f1 (ppm)


1.00
1.00
5.20
f1 (ppm)

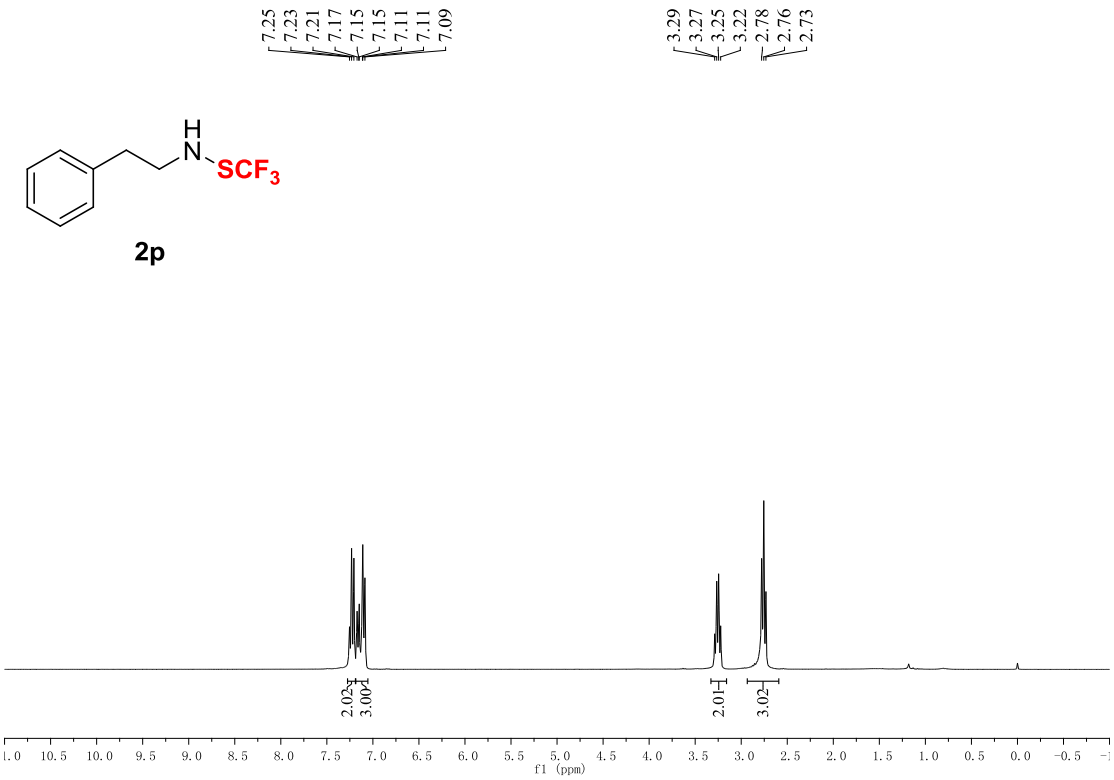

N
HN
SCF3

2o

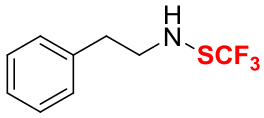
-52.9
f1 (ppm)


148.2
141.8
138.9
136.1
135.9
131.7
128.3
127.5
127.1
123.2
121.8
119.3
110.0
N
HN
SCF3
138.9
136.1
135.9
131.7
128.3
127.5
127.1
123.2
121.8
f1 (ppm)
f1 (ppm)

2o

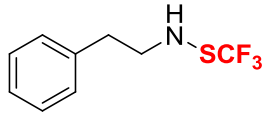

7.25
7.23
7.21
7.17
7.15
7.15
7.11
7.11
7.09
3.29
3.27
3.25
3.22
2.78
2.76
2.73
H
N
SCF3
2.02
3.00
2.01
3.02
f1 (ppm)

2p


H
N
SCF3

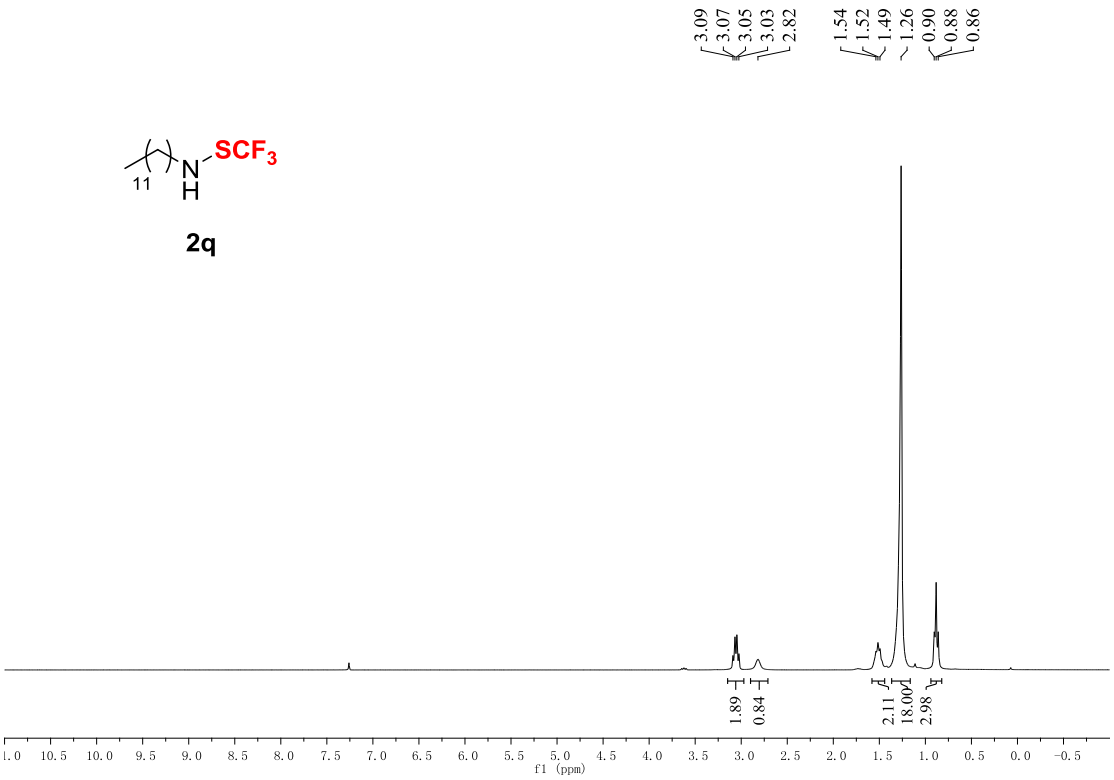
2p

-53.0
f1 (ppm)

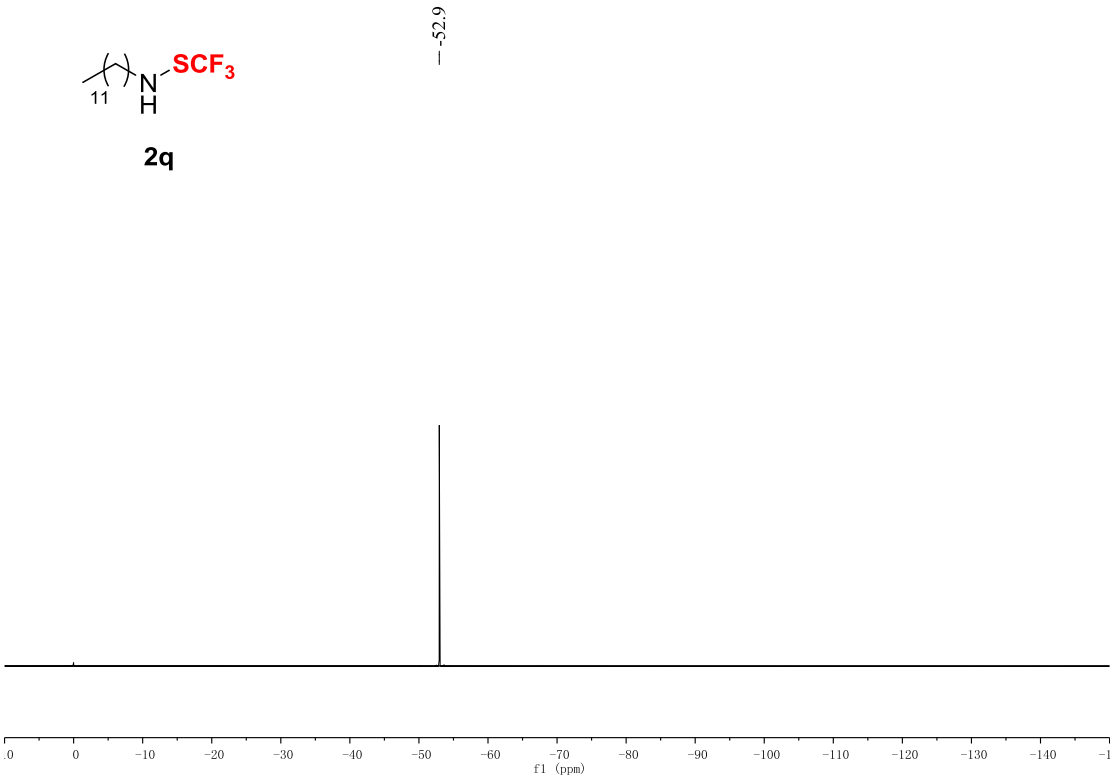

H
N
SCF3

2p

138.4
136.7
132.5
128.8
128.6
128.3
126.5
124.1
54.6
36.6
f1 (ppm)


3.09
3.07
3.05
3.03
2.82
1.54
1.52
1.49
1.26
0.90
0.88
0.86
11
N
H
SCF3
1.89
0.84
2.11
18.00
2.98
f1 (ppm)

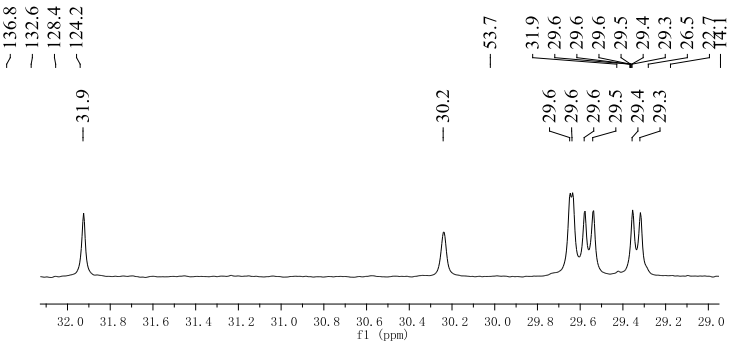
2q

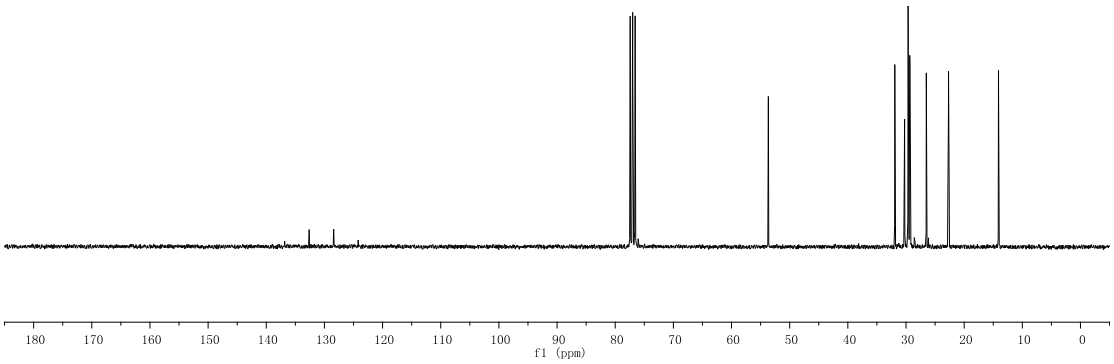

-52.9
11
N
H
SCF3
f1 (ppm)

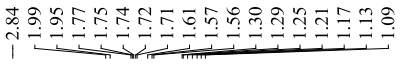
2q

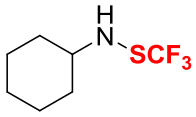

11
N
H
SCF3

2q

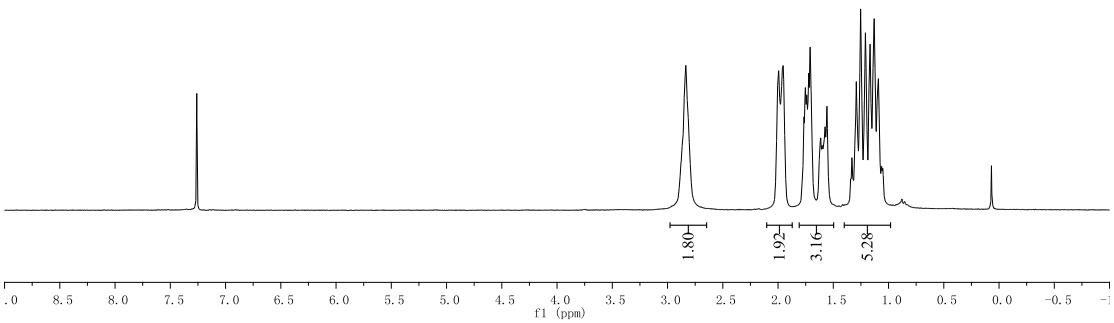

136.8
132.6
128.4
124.2
31.9
30.2
53.7
31.9
29.6
29.6
29.6
29.5
29.4
29.3
26.5
22.7
14.1
32.0 31.8 31.6 31.4 31.2 31.0 30.8 30.6 30.4 30.2 30.0 29.8 29.6 29.4 29.2 29.0
f1 (ppm)

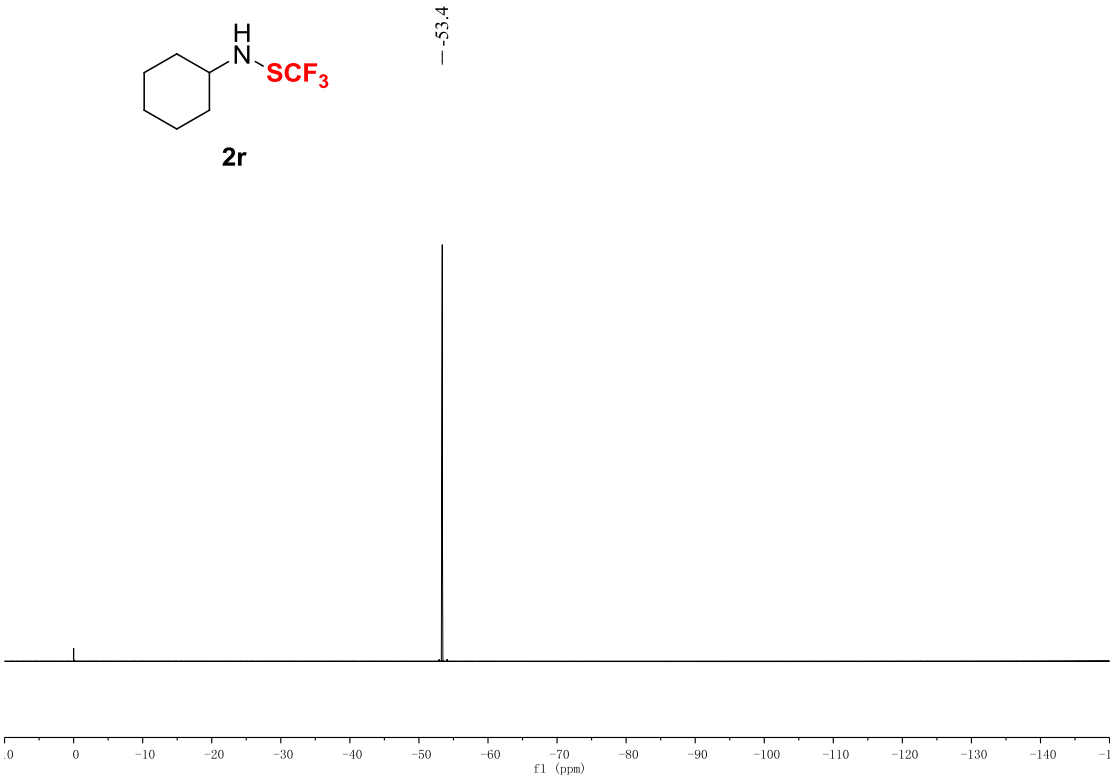

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

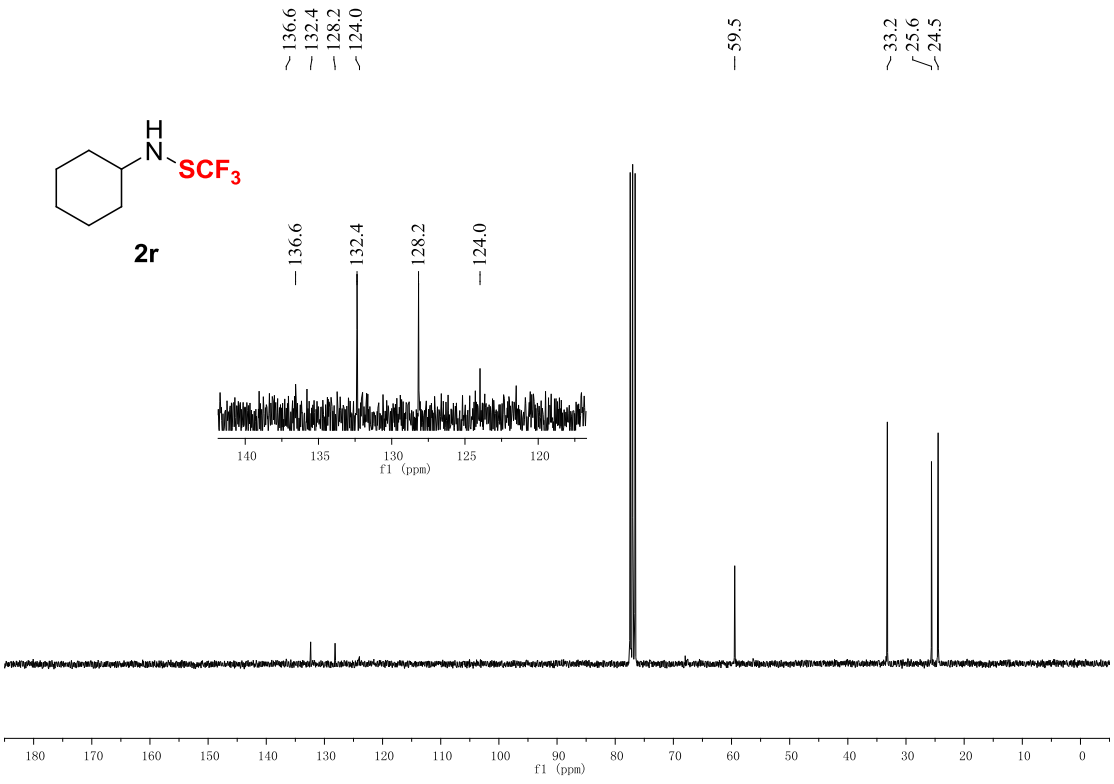

2.84
1.99
1.95
1.77
1.75
1.74
1.72
1.71
1.61
1.57
1.56
1.30
1.29
1.25
1.21
1.17
1.13
1.09

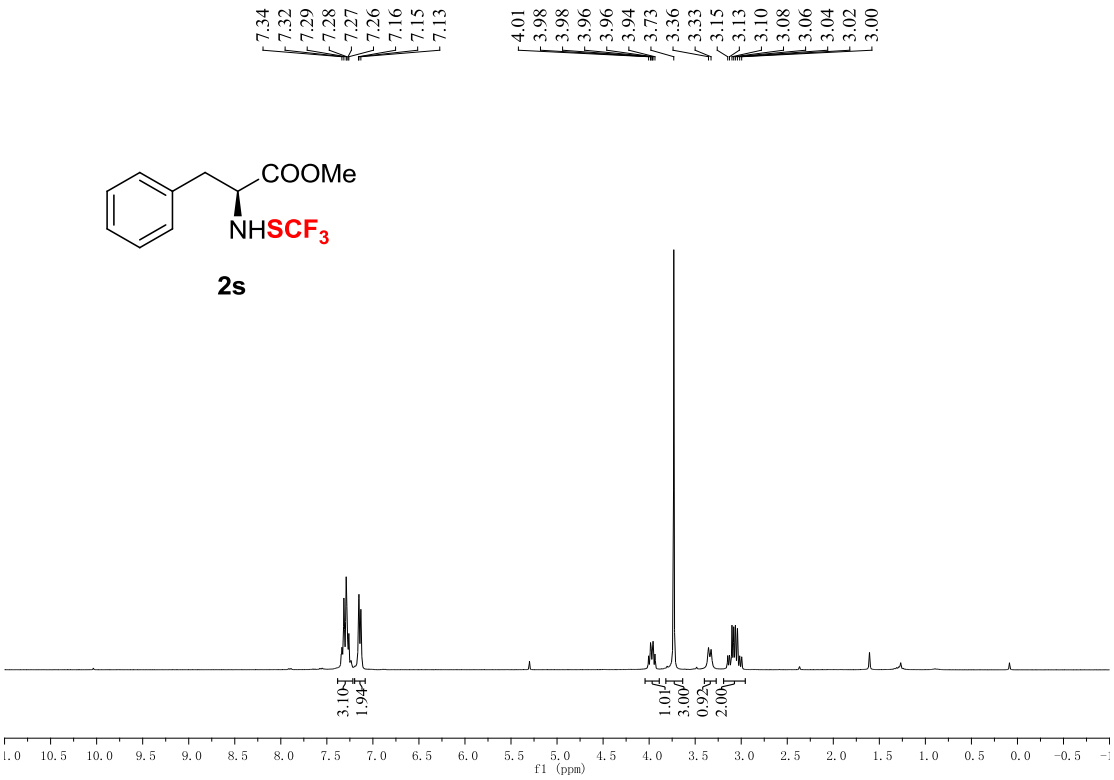

H
N
SCF3

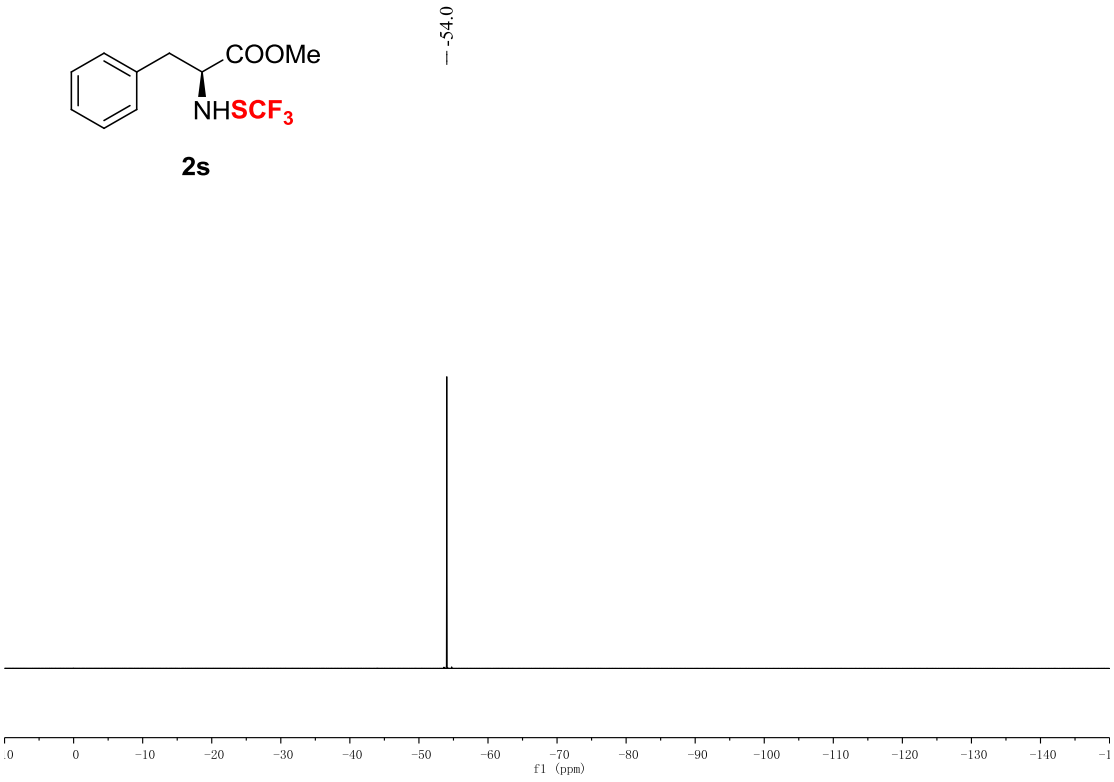
2r

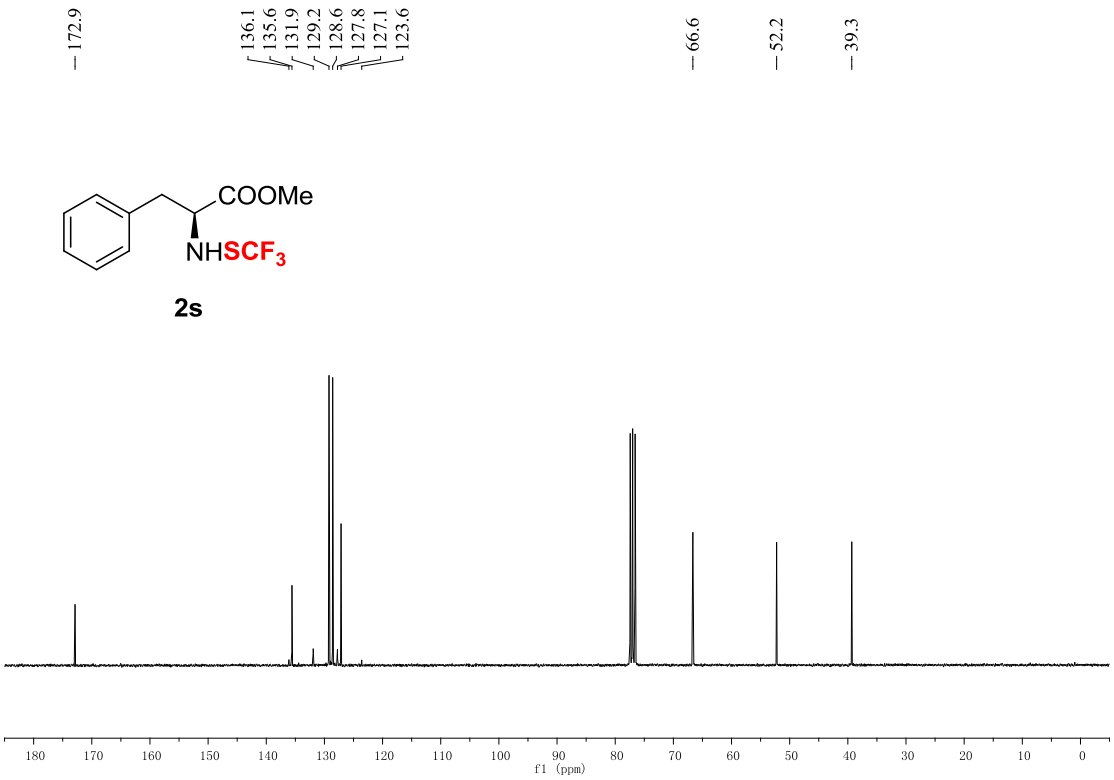

1.80
1.92
3.16
5.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

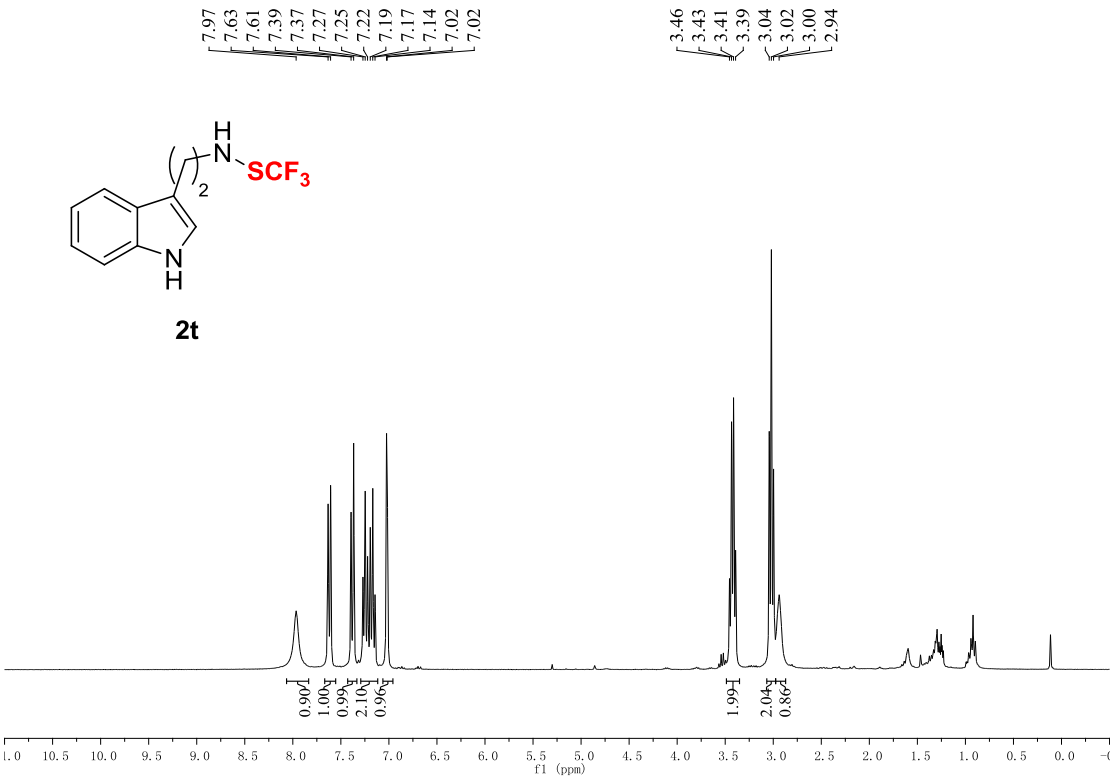

H
N
SCF3
2r
-53.4
f1 (ppm)

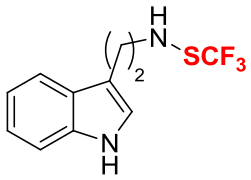

136.6
132.4
128.2
124.0
59.5
33.2
25.6
24.5
H
N
SCF3
2r
f1 (ppm)
f1 (ppm)


7.34
7.32
7.29
7.28
7.27
7.26
7.16
7.15
7.13
4.01
3.98
3.98
3.96
3.96
3.94
3.73
3.36
3.33
3.15
3.13
3.10
3.08
3.06
3.04
3.02
3.00
COOMe
NHSCF3
2s
3.10
1.94
1.01
3.00
0.92
2.00
f1 (ppm)

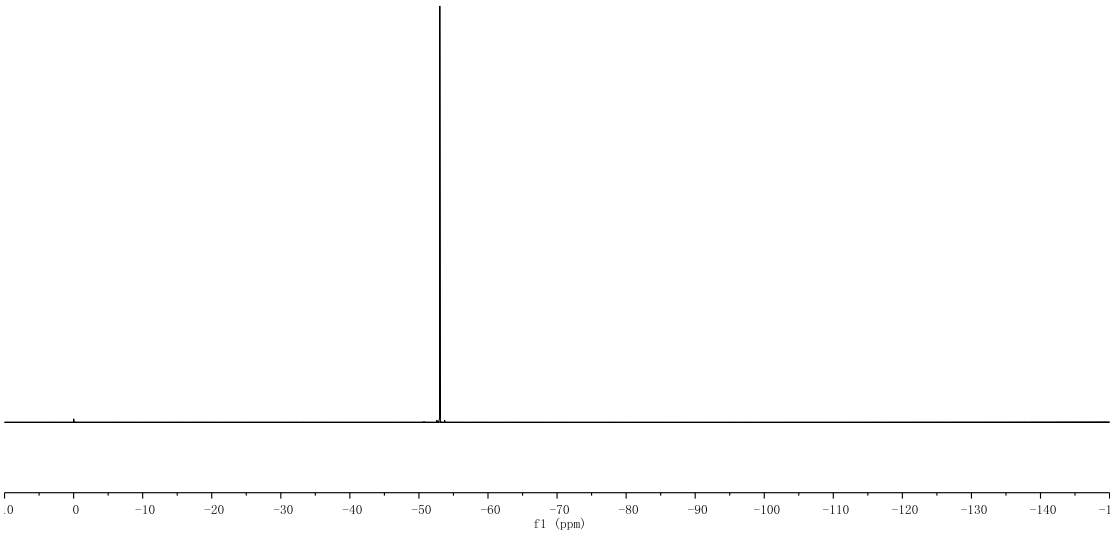

-54.0
COOMe
NHSCF3
2s
f1 (ppm)

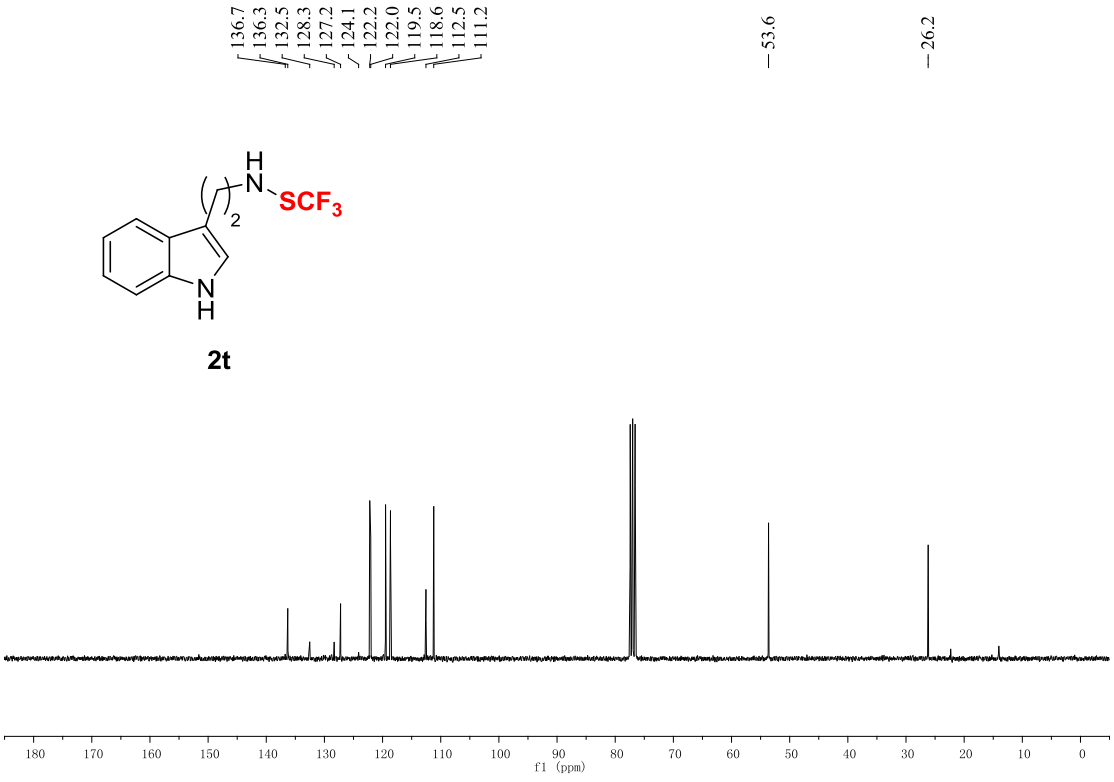

172.9
136.1
135.6
131.9
129.2
128.6
127.8
127.1
123.6
66.6
52.2
39.3
COOMe
NHSCF3
2s
f1 (ppm)


7.97
7.63
7.61
7.39
7.37
7.27
7.25
7.22
7.19
7.17
7.14
7.02
7.02
3.46
3.43
3.41
3.39
3.04
3.02
3.00
2.94
H
N
SCF3
2
N
H
2t
0.90
1.00
0.99
2.10
0.96
1.99
2.04
0.86
f1 (ppm)


H
N
SCF3
2
N
H

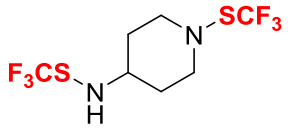
2t


-53.0
.0
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−1
f1 (ppm)

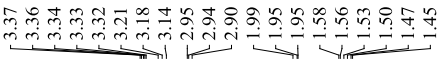

136.7
136.3
132.5
128.3
127.2
124.1
122.2
122.0
119.5
118.6
112.5
111.2
53.6
26.2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

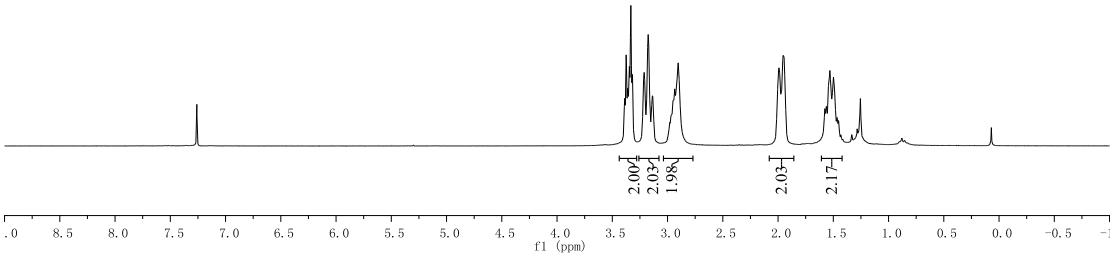
H
N
SCF3
2
N
H

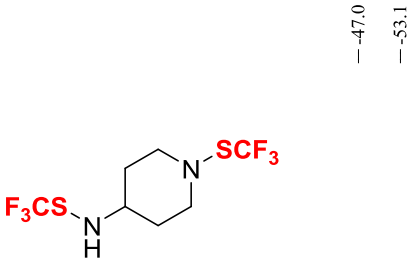
2t


SCF3
F3CS
N
H

2u

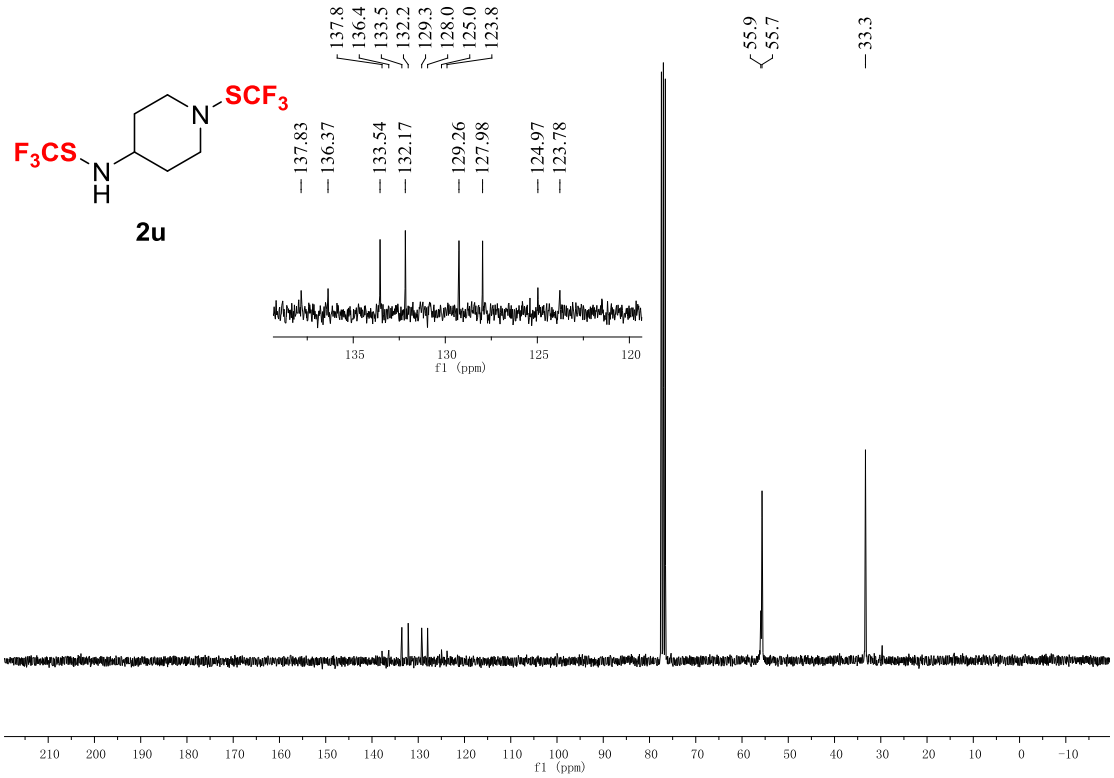

3.37
3.36
3.34
3.33
3.32
3.21
3.18
3.14
2.95
2.94
2.90
1.99
1.95
1.95
1.58
1.56
1.53
1.50
1.47
1.45

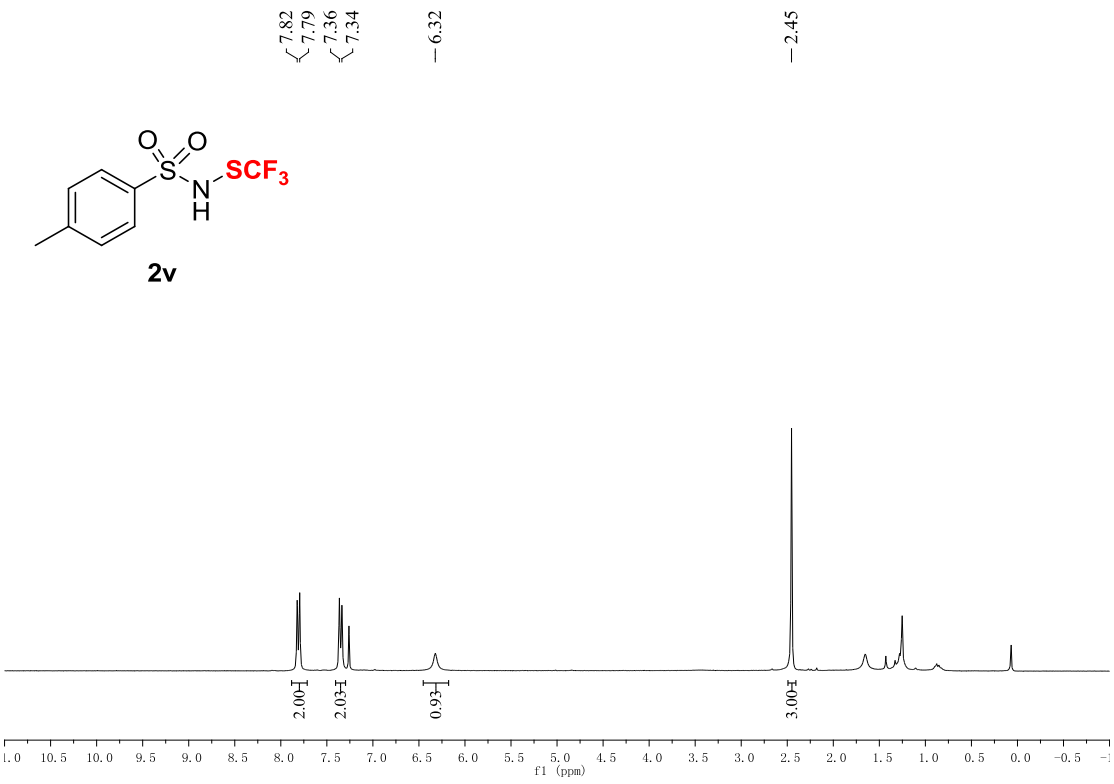

2.00
2.03
1.98
2.03
2.17
f1 (ppm)

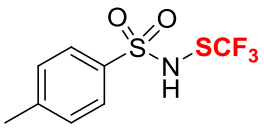

SCF3
F3CS
N
H

2u

-47.0
-53.1
0.90
1.00
f1 (ppm)

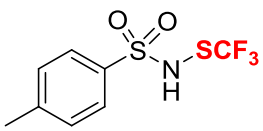

137.8
136.4
133.5
132.2
129.3
128.0
125.0
123.8
55.9
55.7
33.3
137.83
136.37
133.54
132.17
129.26
127.98
124.97
123.78
SCF3
F3CS
N
H
2u
135
130
125
120
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.82
7.79
7.36
7.34
6.32
2.45
O
O
S
N
H
SCF3
2v
2.00
2.03
0.93
3.00
f1 (ppm)


O
O
S
N
H
SCF3

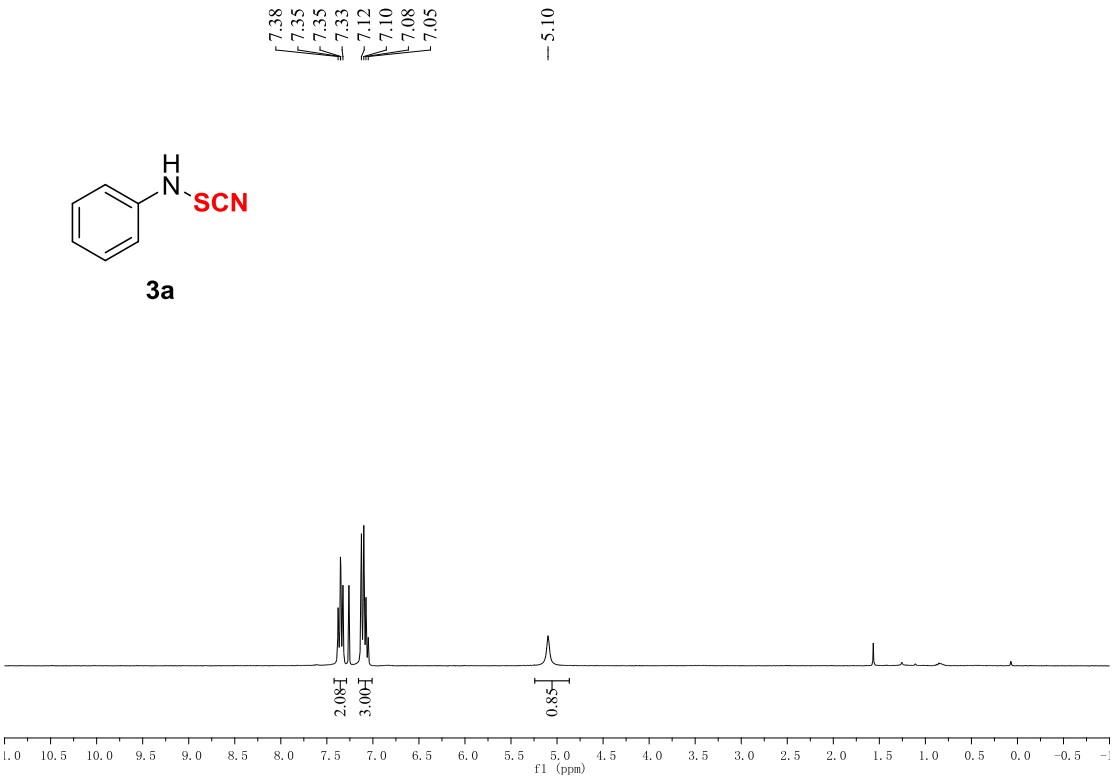
2v

-51.9
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

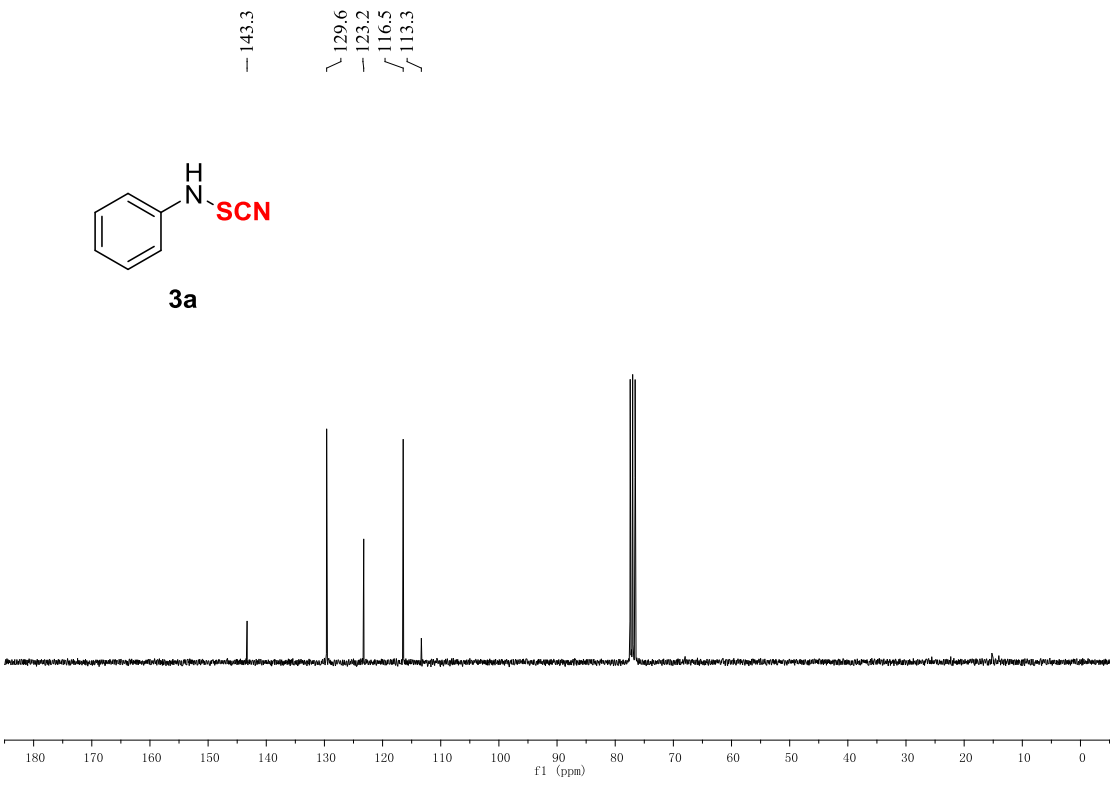

O
O
S
N
H
SCF3

2v

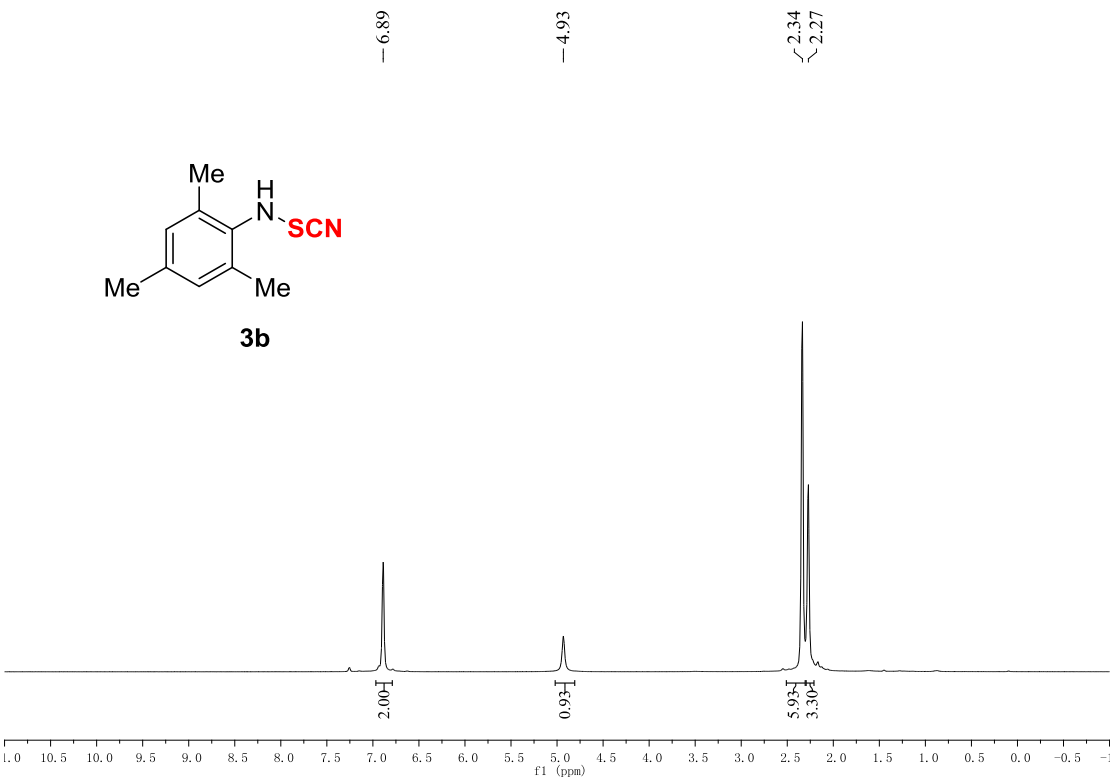
145.1
135.0
130.1
129.9
127.9
125.9
21.7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

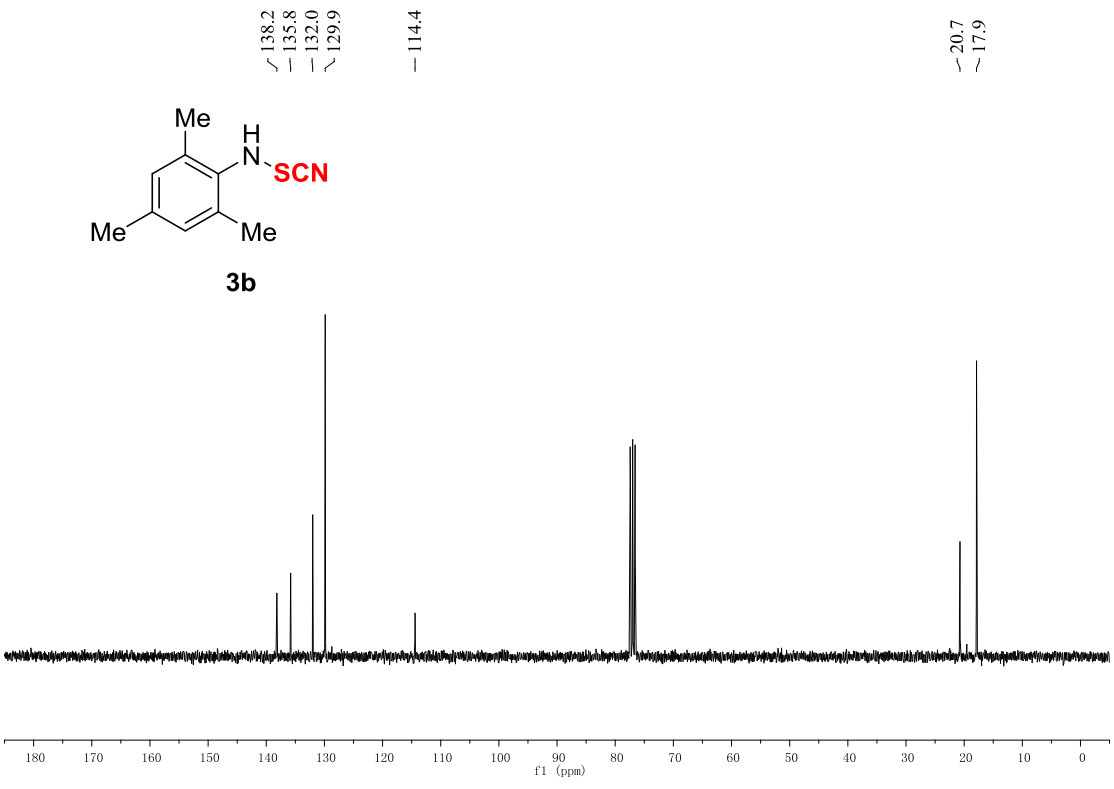

7.38
7.35
7.35
7.33
7.12
7.10
7.08
7.05
5.10
H
N
SCN
2.08
3.00
0.85
f1 (ppm)

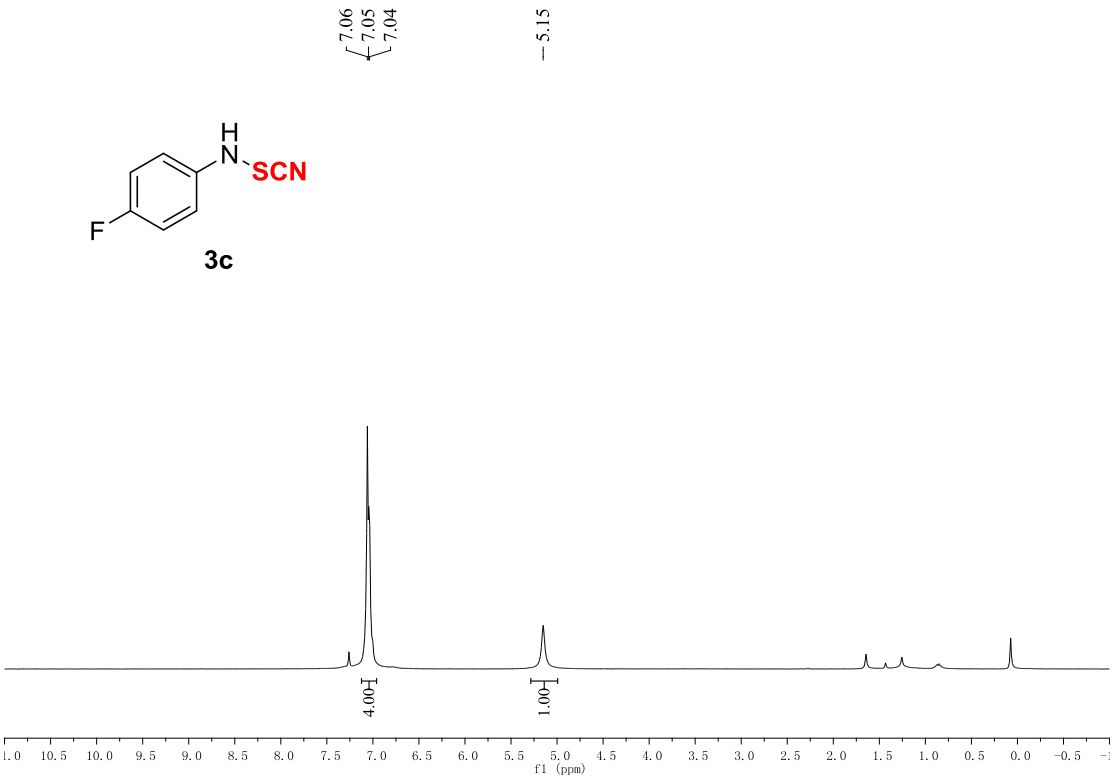
3a

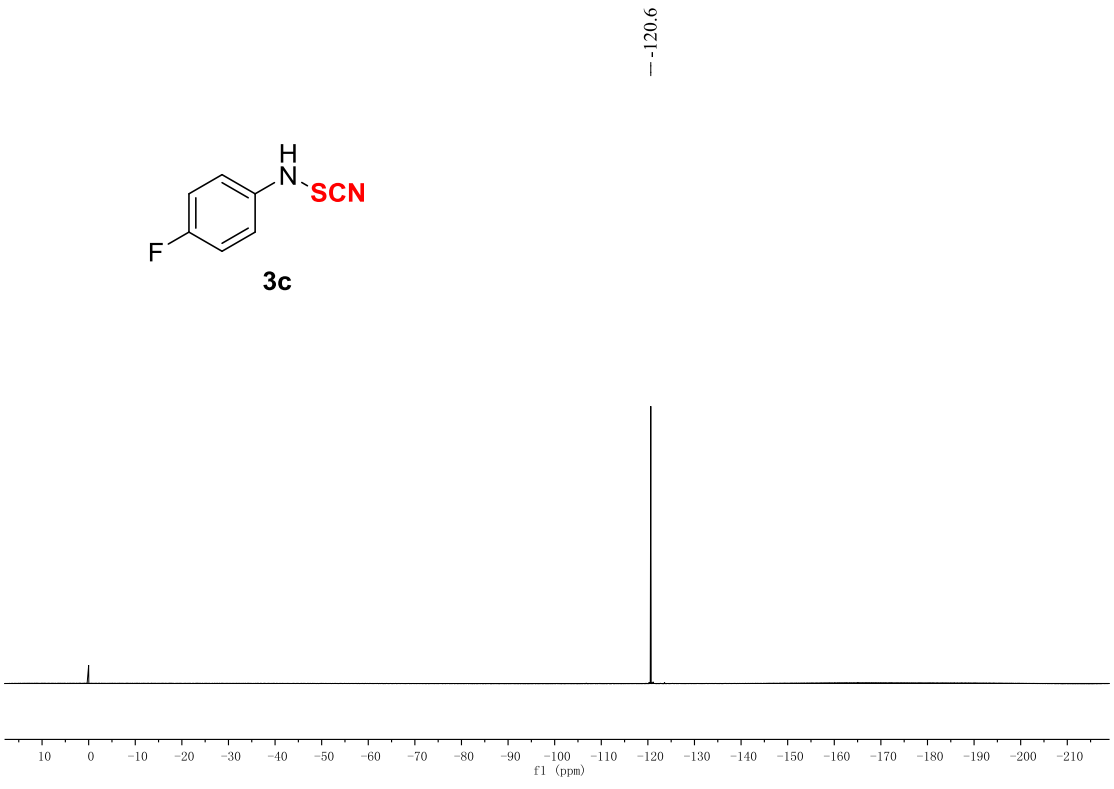

143.3
129.6
123.2
116.5
113.3
H
N
SCN
f1 (ppm)

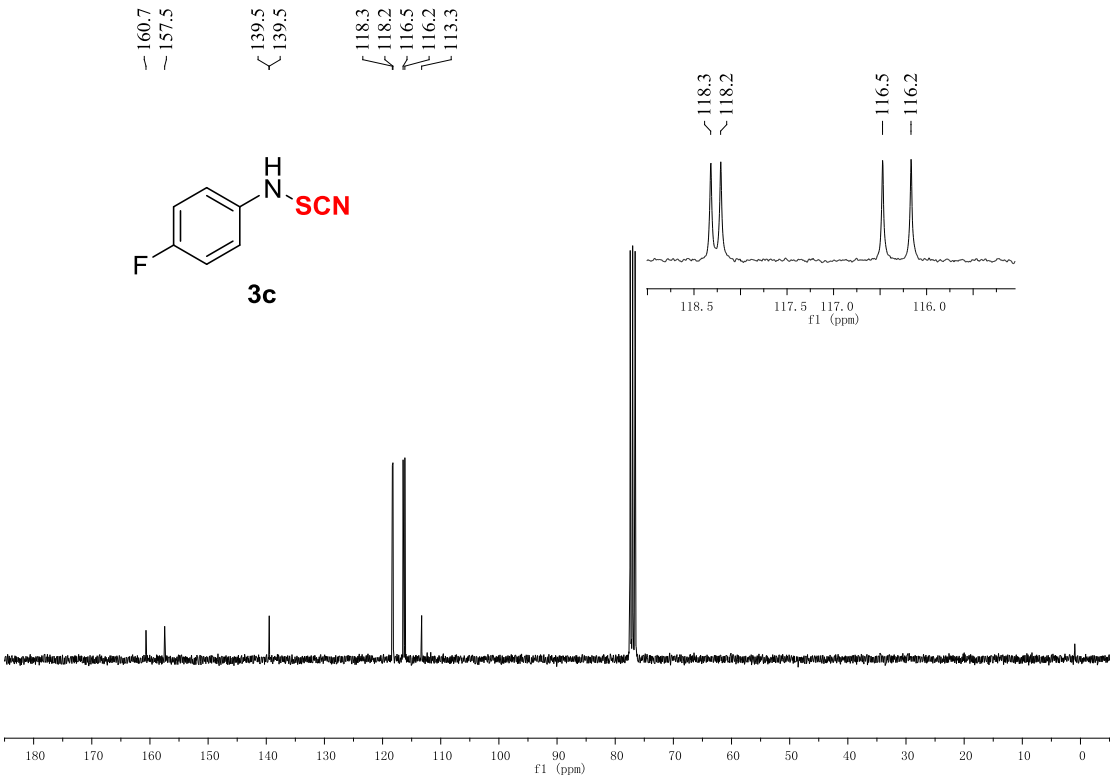
3a

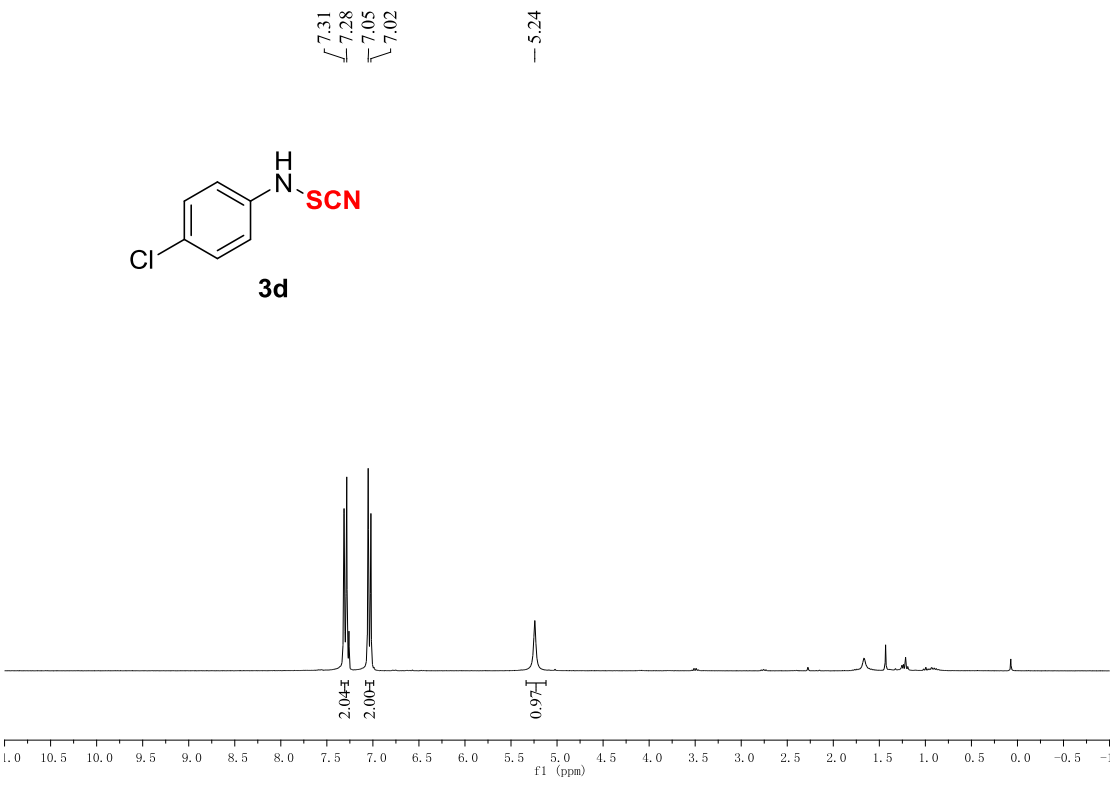

6.89
4.93
2.34
2.27
Me
H
N
SCN
Me
Me
3b
2.00
0.93
5.93
3.30
f1 (ppm)

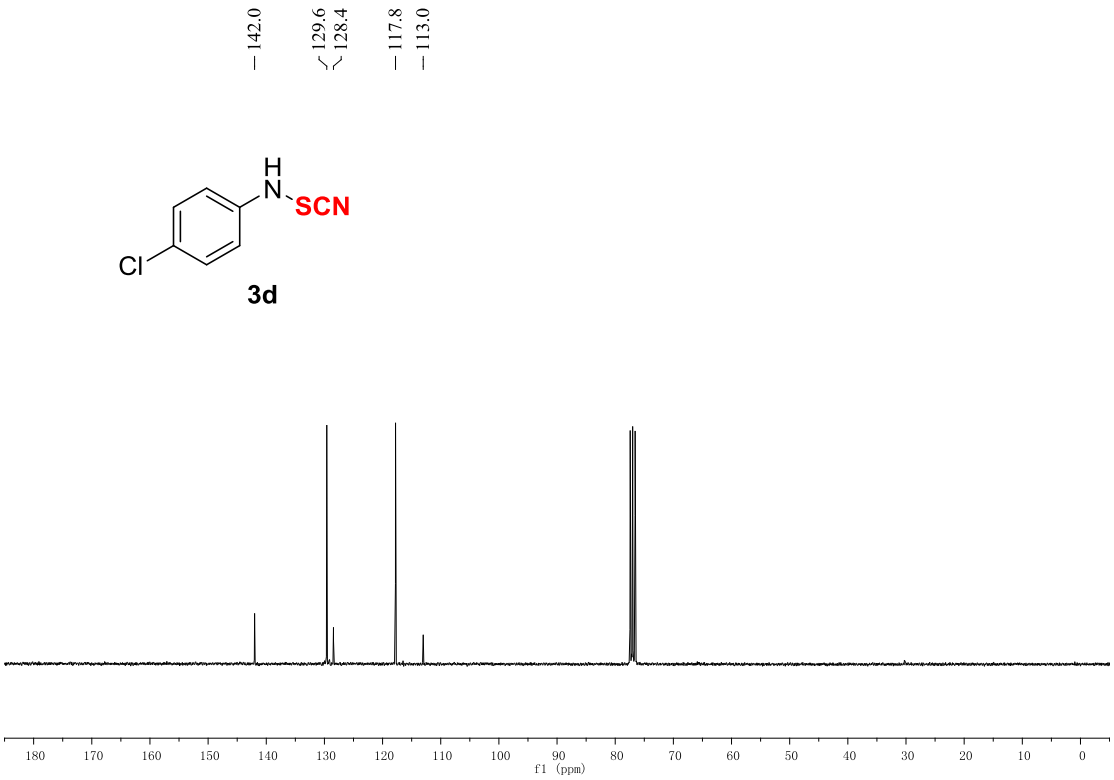

138.2
135.8
132.0
129.9
114.4
20.7
17.9
Me
H
N
SCN
Me
Me
3b
f1 (ppm)

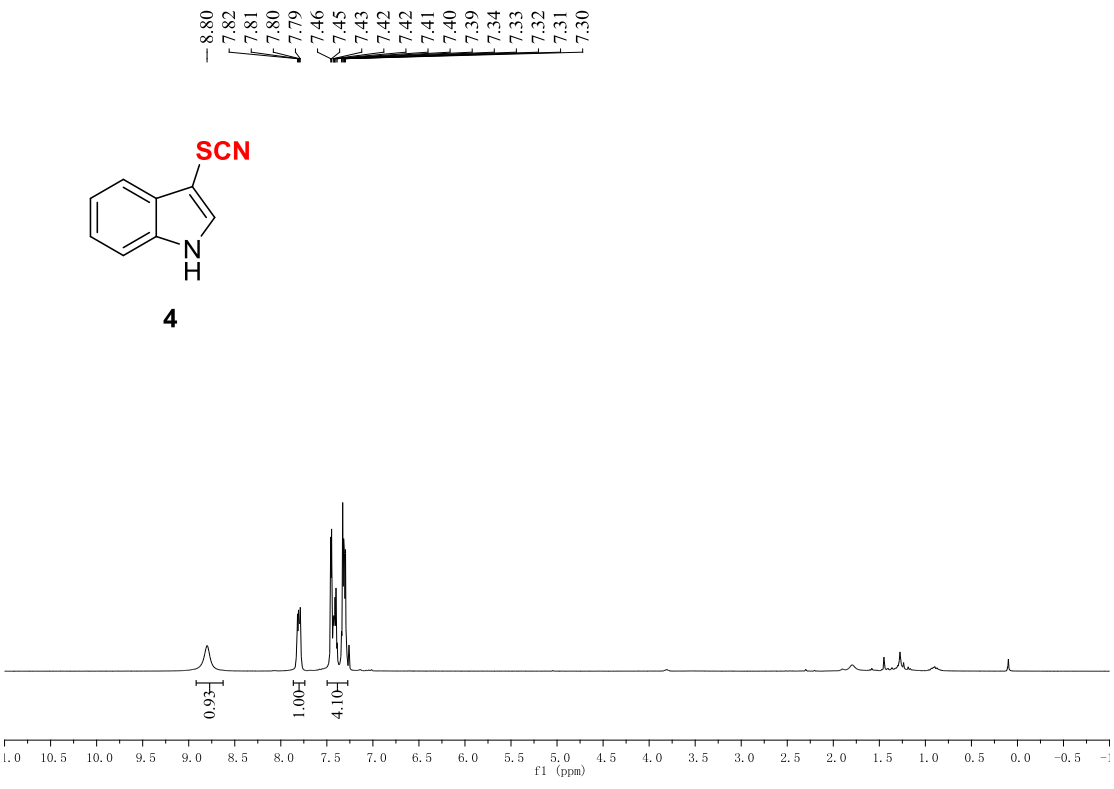

7.06
7.05
7.04
5.15
H
N
SCN
F
3c
4.00
1.00
f1 (ppm)

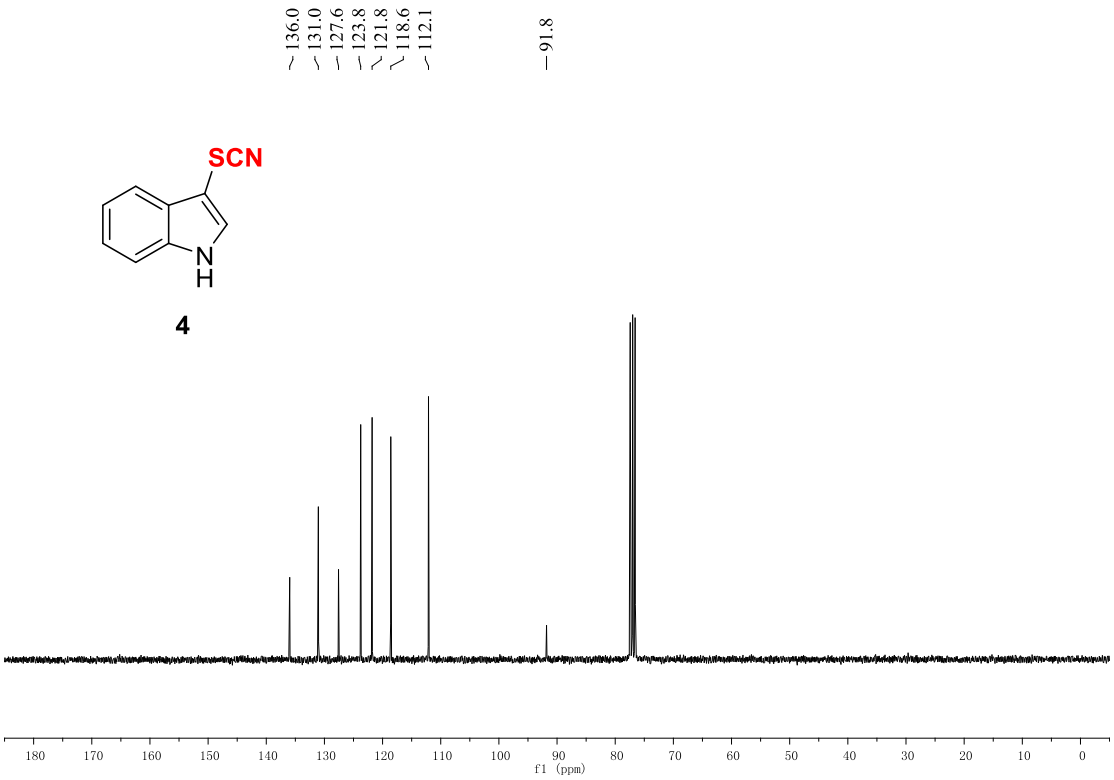

-120.6
H
N
SCN
F
3c
f1 (ppm)

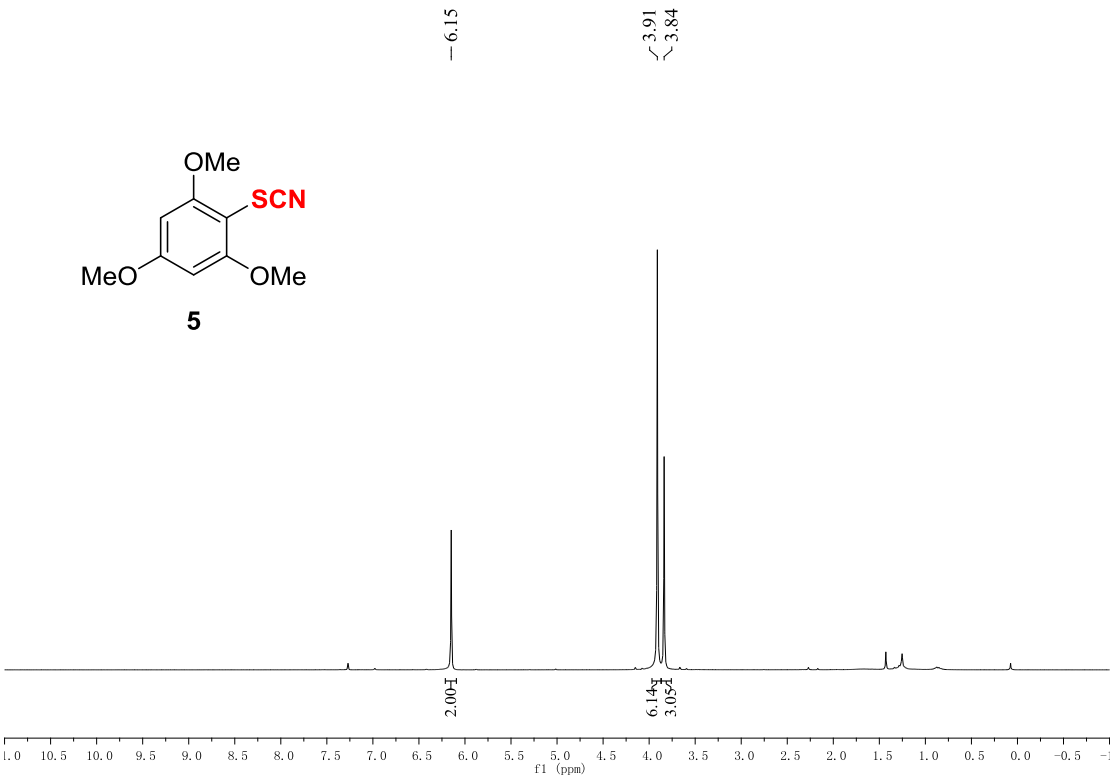

160.7
157.5
139.5
139.5
118.3
118.2
116.5
116.2
113.3
H
N
SCN
F
3c
118.3
118.2
116.5
116.2
118.5
117.5
117.0
116.0
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

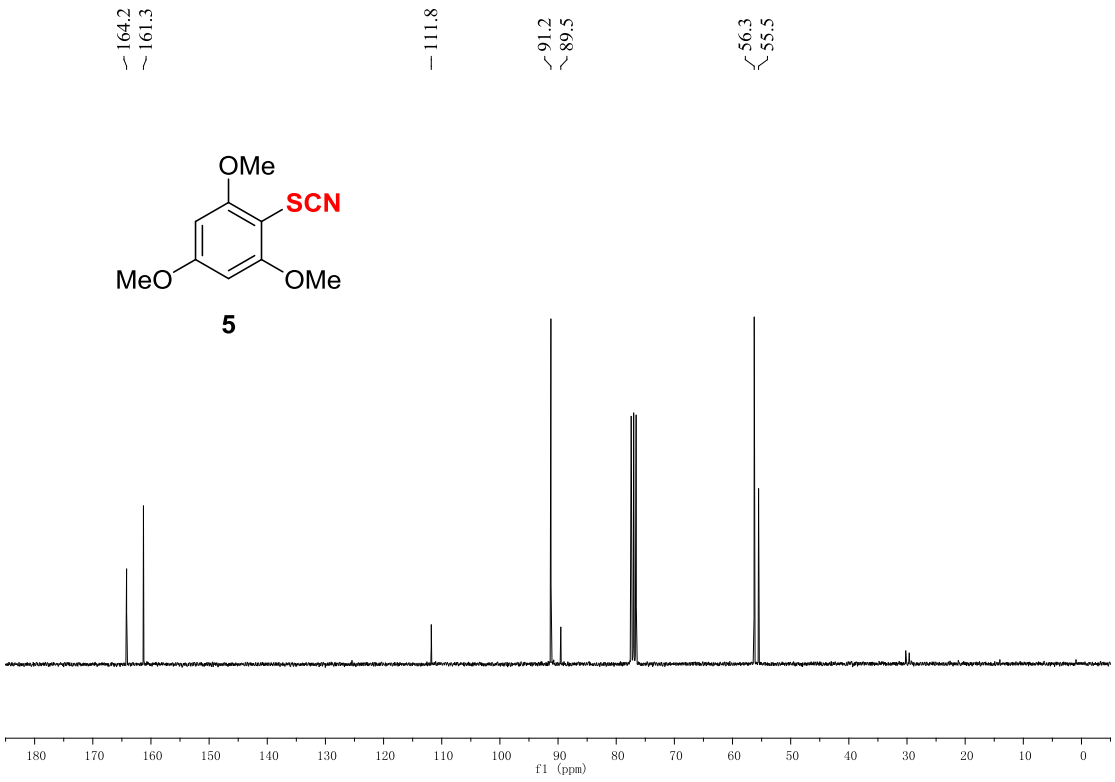

7.31
7.28
7.05
7.02
5.24
H
N
SCN
Cl
3d
2.04
2.00
0.97
f1 (ppm)


142.0
129.6
128.4
117.8
113.0
H
N
SCN
Cl
3d
f1 (ppm)


8.80
7.82
7.81
7.80
7.79
7.46
7.45
7.43
7.42
7.42
7.41
7.40
7.39
7.34
7.33
7.32
7.31
7.30
SCN
N
H
4
0.93
1.00
4.10
f1 (ppm)


136.0
131.0
127.6
123.8
121.8
118.6
112.1
91.8
SCN
N
H
4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.15
3.91
3.84
OMe
SCN
MeO
OMe
5
2.00
6.14
3.05
f1 (ppm)


164.2
161.3
111.8
91.2
89.5
56.3
55.5
OMe
SCN
MeO
OMe
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)