

Supporting Information

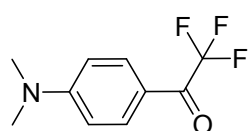
1: General information	S2
2: Characterization results of the products	S2-S4
3: NMR Spectra	S5-S18

1: General information: Unless otherwise stated, reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. NMR spectra were recorded on Varian Mercury 400 (400 MHz) spectrophotometers. All chemical shift (δ) are reported in ppm and coupling constants (J) in Hz; All chemical shifts are relative to solvent peaks [chloroform: 7.26 (^1H), 77.00 (^{13}C); methanol: 3.31 (^1H), 48.80 (^{13}C)], respectively. Mass spectra were measured on a MS spectrometer.

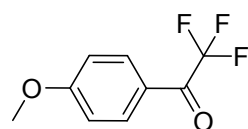
Reagents: Unless otherwise statement, commercial reagents were used without purification.

2: Characterization results of the products

A 30 mL autoclave was charged with Aryl iodides (0.2 mmol), $(\text{PPh}_3)_3\text{CuCF}_3$ (0.3 mmol), $(\text{PPh}_3)_2\text{PdI}_2$ (0.01 mmol), xylene (5 mL) and a magnetic stirring bar. Once sealed, the autoclave was purged 3 times with CO, then pressurized to 20 bar and heated at 70 °C for 24h. After reaction, the autoclave was cooled to room temperature and depressurized. An additional of methyl iodide (0.5 mL) was added and reacted for a further 2 hs. The mixture was then filtered through celite using EtOAc and the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the corresponding compound.

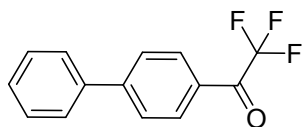


petroleum ether/EtOAc=5/1 as eluant. **Yield:** 75% , pale yellow soild. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.96 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 9.2$ Hz, 2H), 3.10 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 177.81 (q, $J = 34.3$ Hz), 154.62, 132.68, 117.45(q, $J = 292.9$ Hz), 117.17, 110.58, 39.76; $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -71.03; HRMS-EI (m/z): Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{NO}$, 217.0714. Found: 217.0715.



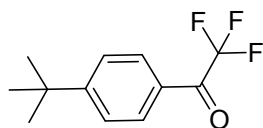
petroleum ether/ CH_2Cl_2 =2/1. **Yield:** 96% , colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.00 (d, $J = 9.0$ Hz, 2H), 3.93 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.88 (q, $J = 34.3$ Hz),

165.18, 132.73, 122.68, 116.85 (q, $J = 292.9$ Hz), 55.61; ^{19}F NMR (376 MHz, CDCl_3): δ -71.81; **HRMS-EI** (m/z): Calcd for $\text{C}_9\text{H}_7\text{F}_3\text{O}_2$, 204.0398. Found: 204.0402



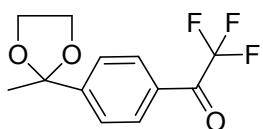
petroleum ether/ $\text{CH}_2\text{Cl}_2=2/1$. **Yield:** 78%, white soild. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.44 (s, 1H);

^{13}C NMR (101 MHz, CDCl_3): δ 180.03 (q, $J = 34.3$ Hz), 148.16, 139.04, 130.72, 129.08, 128.87, 128.45, 127.59, 127.31, 116.7 (q, $J = 292.9$ Hz); ^{19}F NMR (376 MHz, CDCl_3): δ -71.73; **HRMS-EI** (m/z): Calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{O}$, 250.0605. Found: 250.0608.



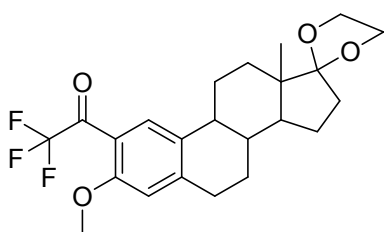
petroleum ether/ $\text{CH}_2\text{Cl}_2=2/1$. **Yield:** 80%, colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 180.06 (q, $J = 34.3$ Hz),

159.79, 130.13, 127.20, 126.19, 121.07, 116.73 (q, $J = 292.2$ Hz), 35.31, 30.70; ^{19}F NMR (376 MHz, CDCl_3): δ -72.17; **HRMS-EI** (m/z): Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}$, 230.0918. Found: 230.0916.



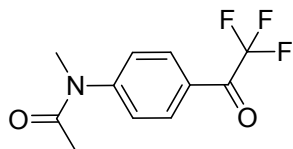
petroleum ether/ $\text{CH}_2\text{Cl}_2=2/1$. **Yield:** 77%, pale yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 2H), 4.07 (t, $J = 7.0$ Hz, 2H), 3.76 (t, $J = 6.9$ Hz, 2H), 1.65 (s, 3H); ^{13}C

NMR (101 MHz, CDCl_3): δ 180.1 (q, $J = 34.3$ Hz), 151.36, 130.25, 129.37, 126.10, 116.6 (q, $J = 292.2$ Hz), 108.21, 64.65, 27.27; ^{19}F NMR (376 MHz, CDCl_3): δ -71.98; **HRMS-EI** (m/z): Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_3$, 260.0660. Found: 260.0660.

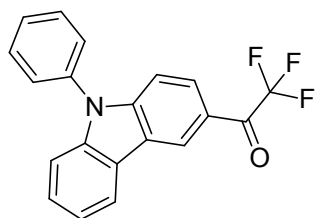


petroleum ether/ $\text{EtOAc}=5/1$. **Yield:** 45%, white soild. ^1H NMR (400 MHz, CDCl_3): δ 7.62 (s, 1H), 6.71 (s, 1H), 4.18-3.72 (m, 7H), 2.46-1.10 (m, 15H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 181.85 (q, $J = 36.4$ Hz), 157.83, 146.55, 133.22, 128.75, 119.20, 116.37 (q, $J = 292.2$ Hz),

112.16, 65.24, 64.57, 55.82, 49.17, 46.02, 43.17, 38.66, 34.15, 30.43, 30.28, 26.50, 25.84, 22.26, 14.22; ^{19}F NMR (376 MHz, CDCl_3): δ -74.38; HRMS-EI (m/z): Calcd for $\text{C}_{23}\text{H}_{27}\text{F}_3\text{O}_4$, 424.1861. Found: 424.1858

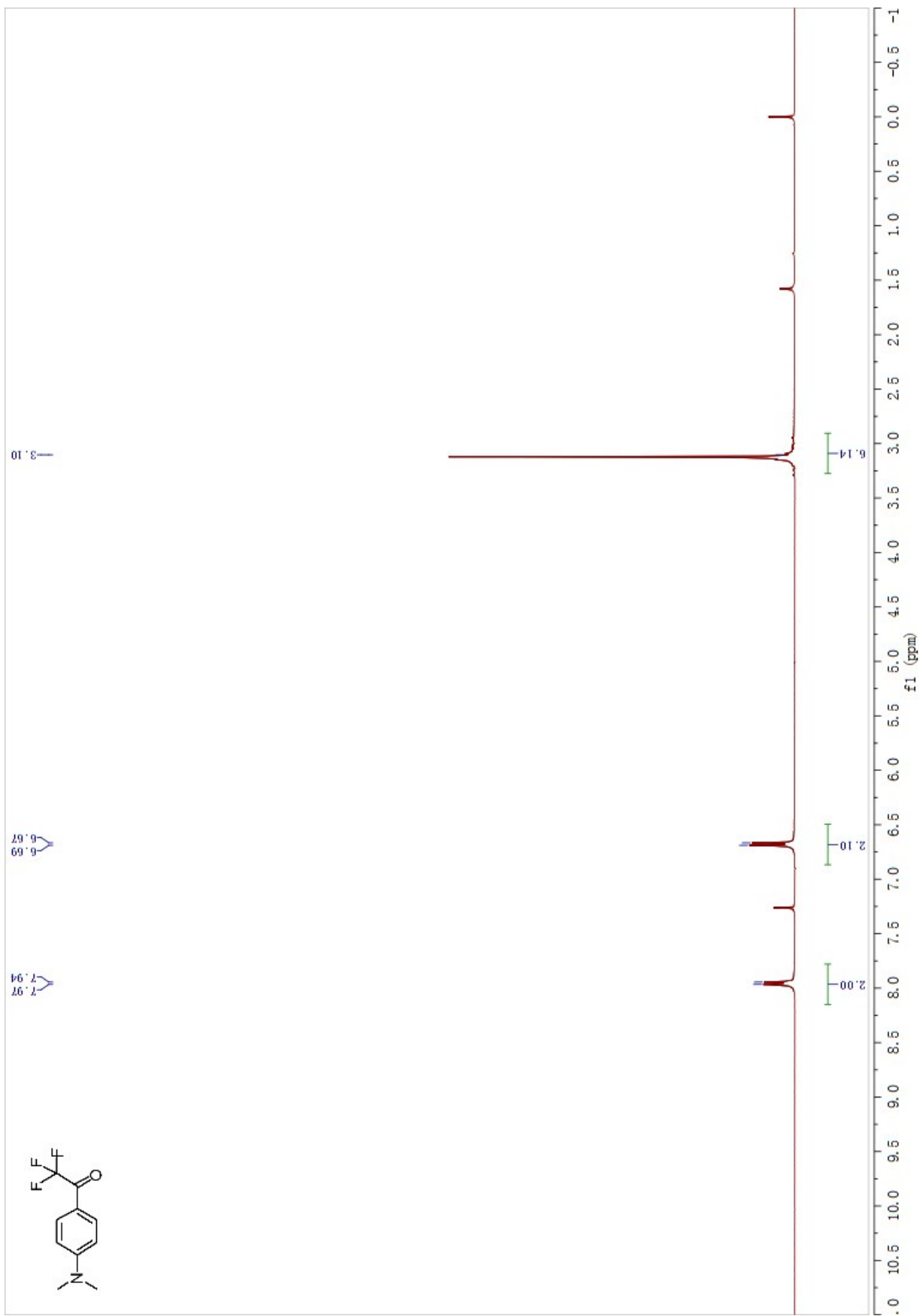


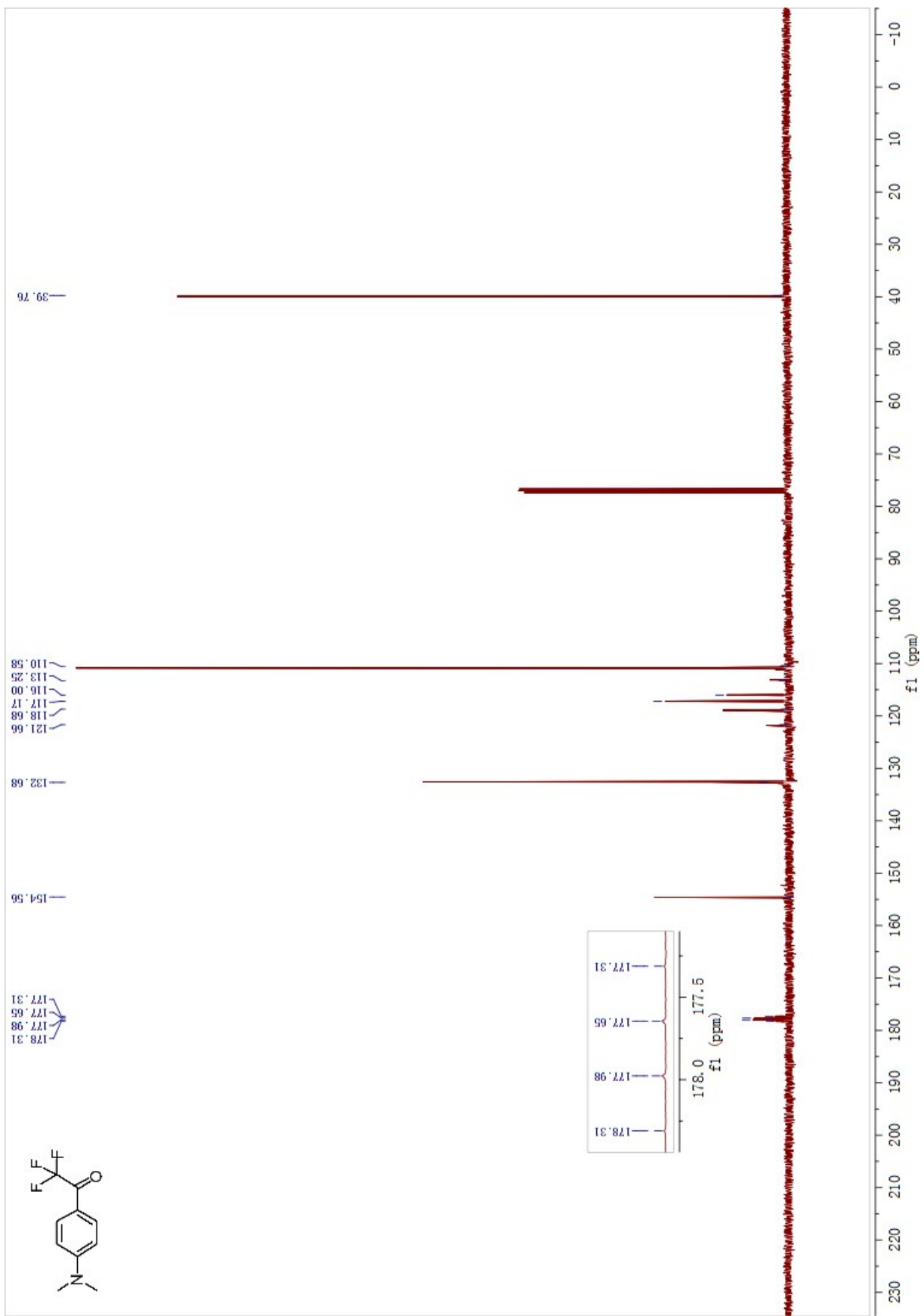
petroleum ether/EtOAc=1/2. Yield: 78%, white solid. ^1H NMR (400 MHz, CD_3COD): δ 9.13 (d, J = 8.2 Hz, 2H), 8.81 (d, J = 8.4 Hz, 2H), 6.31 (s, 3H), 4.78 (s, 3H); ^{13}C NMR (101 MHz, CD_3COD): δ 172.84, 146.58, 136.07, 130.98, 124.31(q, J = 287.9 Hz), 97.67(q, J = 34.0 Hz), 37.54, 22.35; ^{19}F NMR (376 MHz, CD_3COD): δ -84.83; HRMS-EI (m/z): Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NO}_2$, 245.0664. Found: 245.0664.

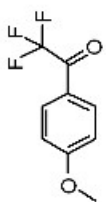


petroleum ether/EtOAc=5/1. Yield: 86%, white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.90 (s, 1H), 8.23 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 7.71-7.61 (m, 2H), 7.55 (t, J = 6.5 Hz, 3H), 7.48 (d, J = 8.7 Hz, 1H), 7.42 (t, J = 8.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 179.63 (q, J = 36.4 Hz), 144.64, 141.86, 136.22, 130.15, 128.51, 128.10, 127.30, 126.99, 124.04, 123.48, 123.02, 121.84, 120.70, 117.21(q, J = 292.9 Hz), 110.51, 110.09; ^{19}F NMR (376 MHz, CDCl_3): δ -70.37; HRMS-EI (m/z): Calcd for $\text{C}_{20}\text{H}_{12}\text{F}_3\text{NO}$, 339.0871. Found: 339.0873.

4: NMR Spectra



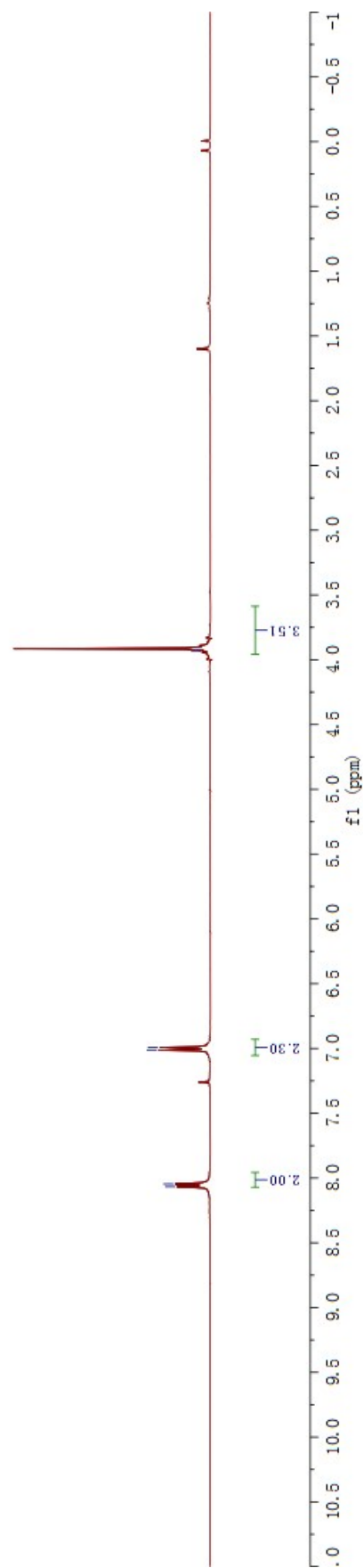


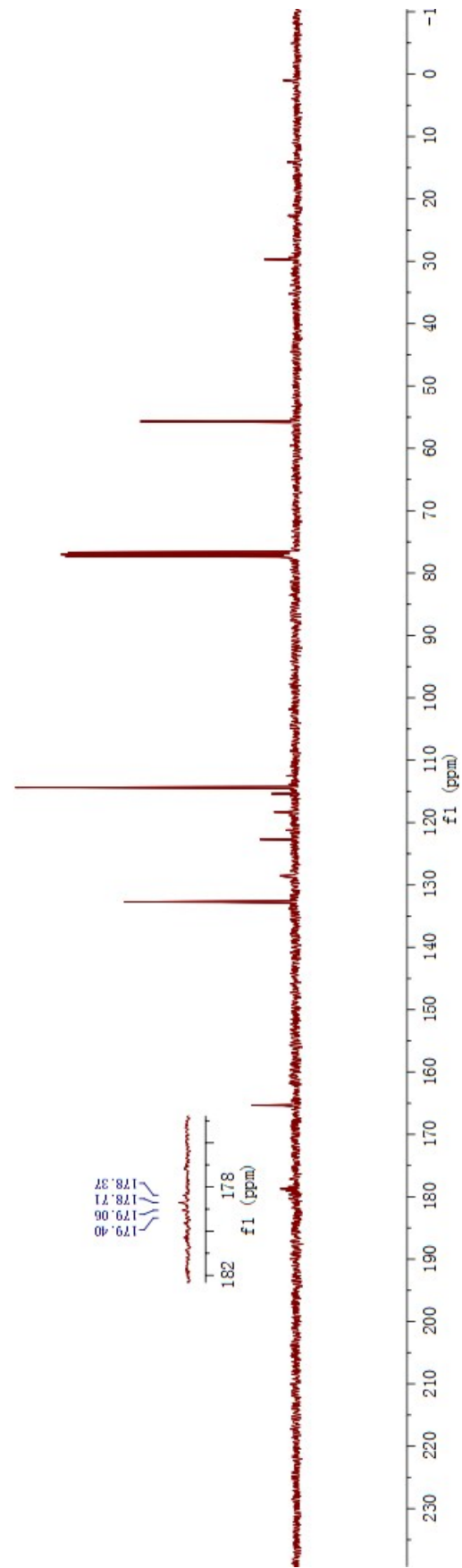
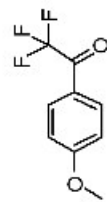


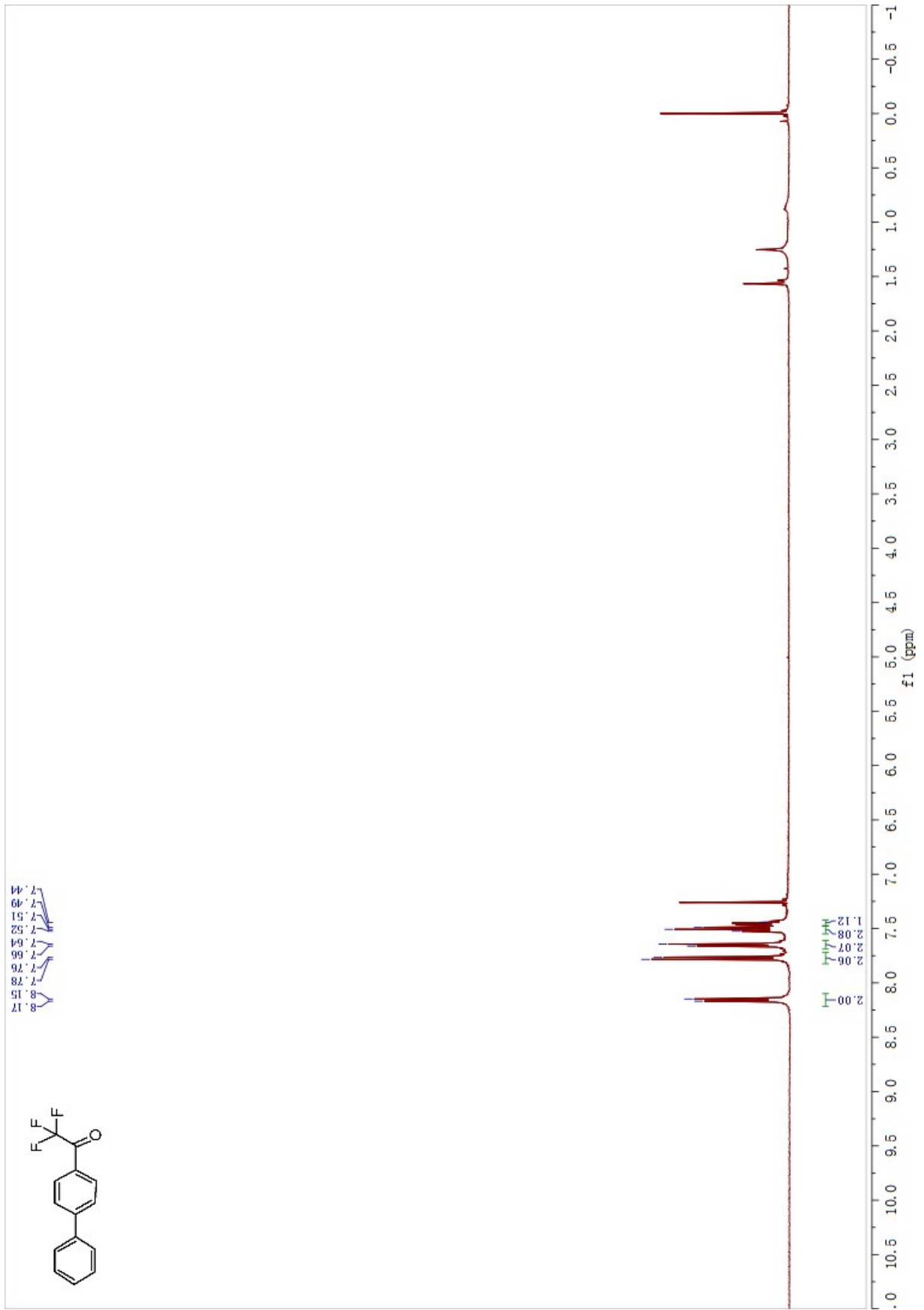
8.07
8.05

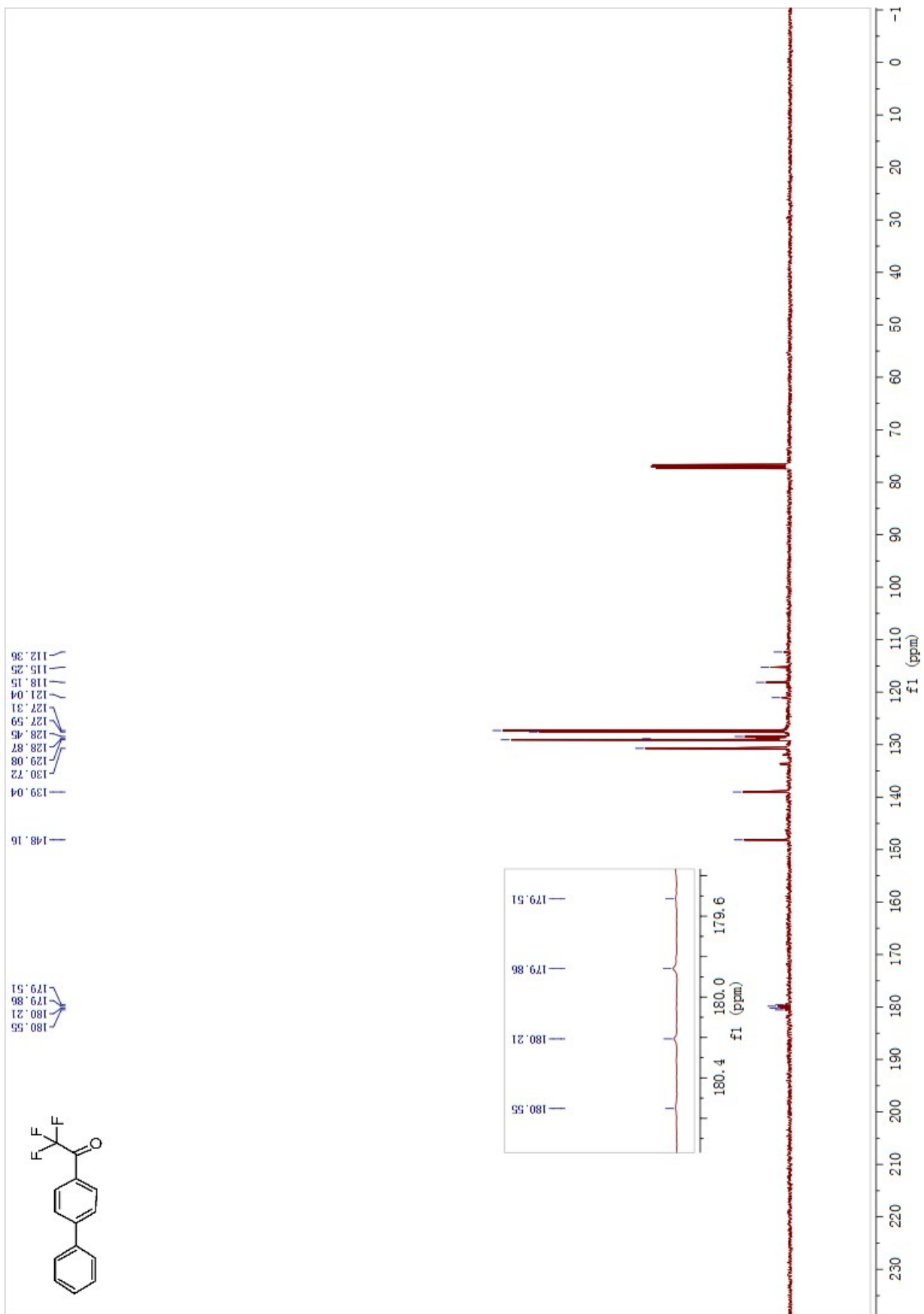
7.01
6.99

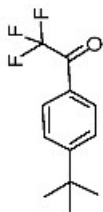
3.93











8.03
8.01
7.58
7.55
7.26

1.36

