Supplementary information

Electrochemical cross-dehydrogenative coupling of arenes and carboxylic acids for the synthesis of aryl esters

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Contents

I. General Information

All reagents and solvents were commercially available and used as received. Flash column chromatography was performed with silica gel (200−300 mesh). NMR spectra were recorded on Bruker AV-400 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm), $CDCl_3$ (7.26 ppm) for ^1H and $CDCl_3$ (77.2 ppm) for ^{13}C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, ABq = AB quartet. High resolution mass spectra (ESI) were recorded on an Agilent 6500 series Q-TOF. Cyclic voltammograms were recorded on a CHI 760E potentiostat. Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer.

II. Procedures for the Electrolysis

General procedure for the electrolysis. A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with arene (0.2 mmol, 1.0 equiv.), carboxylic acid (0.3 mmol, 1.5 equiv.), 2,6-lutidine (0.3 mmol, 1.5 equiv.) and Et_4NPF_6 (0.06 mmol, 0.3 equiv.). The Schlenk tube was equipped with a reticulated vitreous carbon (RVC, 100 PPI) anode (1.0 cm × 1.0 cm × 1.2 cm) and a platinum plate (1.0 cm × 1.0 cm) cathode and sealed. The reaction mixture was degassed via vacuum evacuation and backfilled with nitrogen three times. MeCN (4.0 mL) and HFIP (1 mL) were added. The constant current (7.5 mA) electrolysis was carried out at room temperature for 1.8 to 5.8 h. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the product.

Gram scale synthesis of 35. The electrolysis was conducted in a 250 mL four-necked flask cell with three sets of parallel electrodes (RVC anode (100 PPI, 1.0 cm × 1.0 cm × 1.2 cm), Pt plate cathode (1.0 cm × 1.0 cm)), and a constant current of 7.5 mA (Figure S1). The reaction mixture consisted of **43** (0.77 g, 6.0 mmol), **44** (2.32 g, 9.0 mmol), 2,6-lutidine (0.96 g, 9.0 mmol), Et_4NPF_6 (0.55 g, 1.8 mmol), MeCN (120 mL) and HFIP (30 mL). The reaction was carried out at room temperature for 18 h. The reaction mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and H_2O. The phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the product **35** as a white solid (77% yield, 1.78 g).

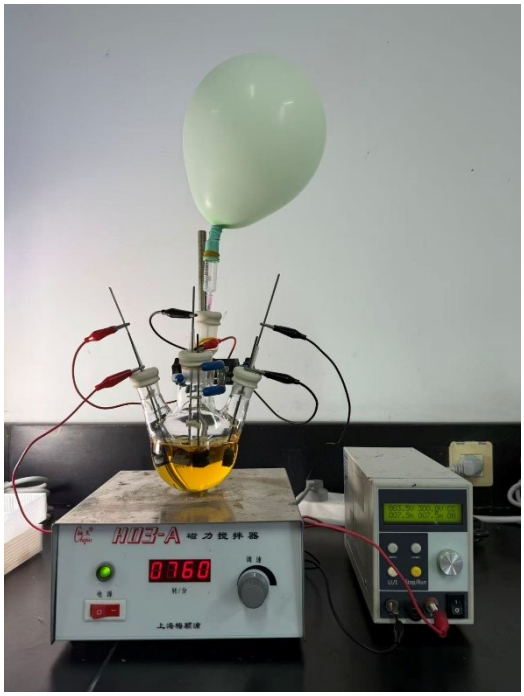
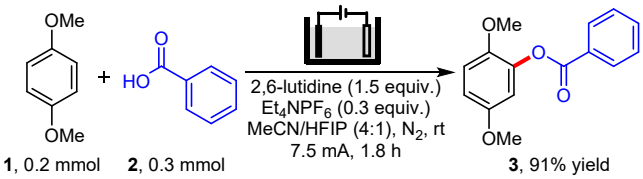


Figure S1. Scale up reaction.

III. Faradaic Efficiency



1, 0.2 mmol **2**, 0.3 mmol **3**, 91% yield

The Faradaic efficiency (FE) of a two-electron oxidation reaction can be calculated by the following equation:

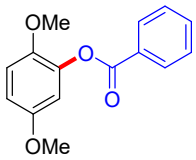
$$\mathrm{FE} = \frac{2nF \times y}{It}$$

where n is the mole of substrate, y is the yield of reaction and F is Faraday constant and equals 96455 C mol^{-1}.

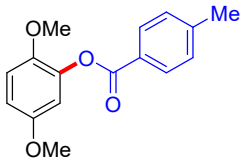
So, the FE of this electrochemical acyloxylation reaction can be calculated as:

$$\mathrm{FE} = \frac{2nF \times y}{It} = \frac{2 \times 0.2 \times 10^{-3} \times 96455 \times 0.91}{7.5 \times 10^{-3} \times 1.8 \times 3600} = 72.2\%$$

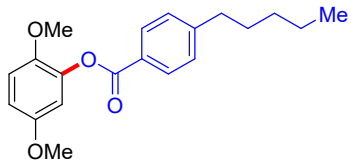
IV. Characterization Data for the Electrolysis Products



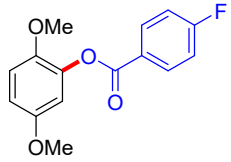
2,5-Dimethoxyphenyl benzoate[1] **(3).** White solid, 47.2 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 6.97 – 6.93 (m, 1H), 6.81 – 6.76 (m, 2H), 3.78 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 153.9, 145.7, 140.6, 133.6, 130.4, 129.5, 128.6, 113.6, 111.7, 109.6, 56.8, 56.0. IR (neat, cm^{-1}): 3442, 2964, 1747, 759. HRMS m/z $[M + Na]^+$ calcd 281.0784, obsd 281.0785.



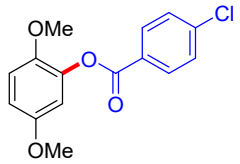
2,5-Dimethoxyphenyl 4-methylbenzoate (4). White solid, 43.5 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.33 – 7.29 (m, 2H), 6.97 – 6.91 (m, 1H), 6.80 – 6.75 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 153.9, 145.7, 144.4, 140.7, 130.5, 129.4, 126.7, 113.6, 111.6, 109.7, 56.8, 55.9, 21.9. IR (neat, cm^{-1}): 3439, 2958, 1745, 776. HRMS m/z $[M + Na]^+$ calcd 295.0941, obsd 295.0940.



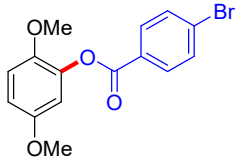
2,5-Dimethoxyphenyl 4-pentylbenzoate (5). Colorless oil, 56.7 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 7.33 – 7.29 (m, 2H), 6.97 – 6.92 (m, 1H), 6.80 – 6.75 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.73 – 2.67 (m, 2H), 1.66 (p, J = 7.5 Hz, 2H), 1.39 – 1.30 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 153.9, 149.4, 145.7, 140.7, 130.5, 128.7, 126.9, 113.6, 111.6, 109.7, 56.8, 55.9, 36.2, 31.6, 31.0, 22.6, 14.2. IR (neat, cm^{-1}): 3446, 2955, 1748, 758. HRMS m/z $[M + Na]^+$ calcd 351.1567, obsd 351.1566.



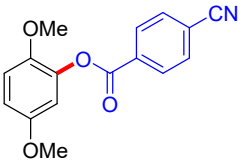
2,5-Dimethoxyphenyl 4-fluorobenzoate (6). White solid, 39.3 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.19 (m, 2H), 7.21 – 7.14 (m, 2H), 6.95 (d, J = 8.8 Hz, 1H), 6.82 – 6.74 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (d, J = 254.7 Hz), 163.8, 153.9, 145.6, 140.4, 133.1 (d, J = 9.4 Hz), 125.7 (d, J = 2.9 Hz), 115.9 (d, J = 22.0 Hz), 113.6, 111.7, 109.6, 56.7, 56.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.65. IR (neat, cm^{-1}): 3442, 2948, 1742, 778. HRMS m/z $[M + Na]^+$ calcd 299.0690, obsd 299.0693.



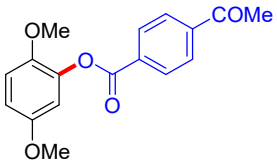
2,5-Dimethoxyphenyl 4-chlorobenzoate (7). White solid, 38.2 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 2H), 7.51 – 7.46 (m, 2H), 6.95 (d, J = 8.8 Hz, 1H), 6.79 (dd, J = 8.8, 3.0 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 153.9, 145.5, 140.3, 140.2, 131.8, 129.0, 127.9, 113.6, 111.8, 109.6, 56.7, 56.0. IR (neat, cm^{-1}): 3438, 2952, 1746, 765. HRMS m/z $[M + Na]^+$ calcd 315.0395, obsd 315.0396.



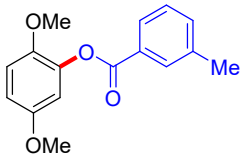
2,5-Dimethoxyphenyl 4-bromobenzoate (8). White solid, 42.4 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.67 – 7.62 (m, 2H), 6.94 (d, J = 8.8 Hz, 1H), 6.79 (dd, J = 8.8, 3.0 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 153.9, 145.5, 140.3, 132.0, 131.9, 128.9, 128.4, 113.6, 111.8, 109.5, 56.7, 56.0. IR (neat, cm^{-1}): 3444, 2948, 1740, 768. HRMS m/z $[M + Na]^+$ calcd 358.9889, 360.9869, obsd 358.9889, 360.9865.



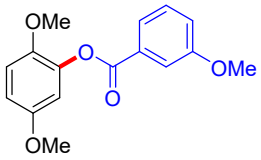
2,5-Dimethoxyphenyl 4-cyanobenzoate (9). White solid, 40.1 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 2H), 7.84 – 7.77 (m, 2H), 6.95 (d, J = 8.9 Hz, 1H), 6.80 (dd, J = 8.9, 3.0 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 153.8, 145.3, 140.0, 133.3, 132.4, 130.9, 118.0, 117.0, 113.5, 111.9, 109.4, 56.6, 55.9. IR (neat, cm^{-1}): 3442, 2948, 2225, 1740, 768. HRMS m/z $[M + Na]^+$ calcd 306.0737, obsd 306.0739.



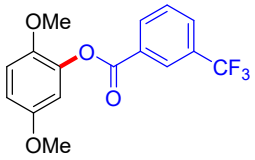
2,5-Dimethoxyphenyl 4-acetylbenzoate (10). White solid, 50.2 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 2H), 8.09 – 8.04 (m, 2H), 6.95 (d, J = 8.6 Hz, 1H), 6.83 – 6.74 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 163.9, 153.9, 145.4, 140.7, 140.3, 133.2, 130.7, 128.4, 113.6, 111.8, 109.5, 56.7, 55.9, 27.1. IR (neat, cm^{-1}): 3449, 2953, 1744, 1646, 768. HRMS m/z $[M + Na]^+$ calcd 323.0890, obsd 323.0890.



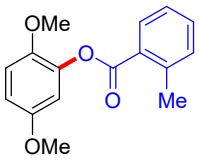
2,5-Dimethoxyphenyl 3-methylbenzoate (11). Light yellow oil, 42.3 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.46 – 7.37 (m, 2H), 6.97 – 6.92 (m, 1H), 6.81 – 6.75 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 153.9, 145.7, 140.6, 138.5, 134.4, 130.9, 129.3, 128.6, 127.6, 113.6, 111.7, 109.6, 56.7, 55.9, 21.4. IR (neat, cm^{-1}): 3453, 2948, 1738, 753. HRMS m/z $[M + Na]^+$ calcd 295.0941, obsd 295.0939.



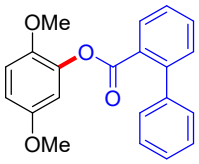
2,5-Dimethoxyphenyl 3-methoxybenzoate (12). Colorless oil, 47.5 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, J = 7.7, 1.2 Hz, 1H), 7.72 (dd, J = 2.7, 1.5 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.18 (ddd, J = 8.2, 2.7, 1.2 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.78 (d, J = 8.2 Hz, 2H), 3.88 (s, 3H), 3.78 (2s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 159.7, 153.9, 145.6, 140.6, 130.7, 129.7, 122.9, 120.3, 114.6, 113.6, 111.7, 109.6, 56.7, 55.9, 55.6. IR (neat, cm^{-1}): 3449, 2953, 1744, 775. HRMS m/z $[M + Na]^+$ calcd 311.0890, obsd 311.0891.



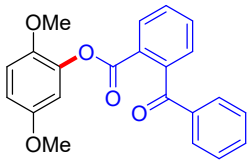
2,5-Dimethoxyphenyl 3-(trifluoromethyl)benzoate (13). Light yellow solid, 44.5 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 1.7 Hz, 1H), 8.40 (dt, J = 8.0, 1.7 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.66 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 8.9 Hz, 1H), 6.84 – 6.75 (m, 2H), 3.78 (2s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 153.9, 145.5, 140.2, 133.6, 131.4 (q, J = 33.1 Hz), 130.4, 130.1 (q, J = 3.6 Hz), 129.4, 127.3 (q, J = 3.8 Hz), 123.76 (q, J = 272.5 Hz), 113.6, 111.9, 109.5, 56.6, 56.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75. IR (neat, cm^{-1}): 3443, 2946, 1743, 785. HRMS m/z [M + Na]$^+$ calcd 349.0658, obsd 349.0657.



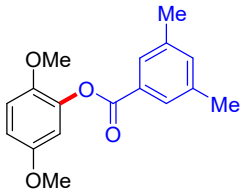
2,5-Dimethoxyphenyl 2-methylbenzoate (14). Light yellow oil, 40.5 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 6.96 (dt, J = 9.2, 1.5 Hz, 1H), 6.81 – 6.76 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 153.9, 145.7, 141.3, 140.6, 132.7, 131.9, 131.4, 128.7, 126.0, 113.6, 111.5, 109.7, 56.7, 55.9, 21.9. IR (neat, cm^{-1}): 3439, 2948, 1746, 773. HRMS m/z $[M + Na]^+$ calcd 295.0941, obsd 295.0942.



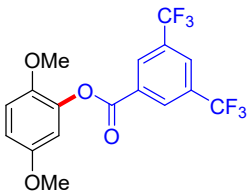
2,5-Dimethoxyphenyl [1,1'-biphenyl]-2-carboxylate (15). White solid, 47.6 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 (td, *J* = 7.7, 1.4 Hz, 1H), 7.52 – 7.35 (m, 7H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.35 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 153.7, 145.6, 143.0, 141.2, 140.2, 131.8, 131.0, 130.4, 130.2, 128.9, 128.2, 127.5, 127.4, 113.4, 111.6, 109.0, 56.6, 55.9. IR (neat, cm^{-1}): 3443, 2952, 1741, 778. HRMS m/z $[M + Na]^+$ calcd 357.1097, obsd 357.1097.



2,5-Dimethoxyphenyl 2-benzoylbenzoate (16). White solid, 52.8 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.71 (td, *J* = 7.5, 1.4 Hz, 1H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.48 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.43 (dd, *J* = 8.3, 7.1 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.28 (d, *J* = 3.0 Hz, 1H), 3.66 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.9, 153.6, 145.4, 142.3, 139.9, 137.3, 133.2, 133.1, 130.9, 129.8, 129.6, 128.6, 128.4, 128.1, 113.6, 112.0, 108.8, 56.6, 55.9. IR (neat, cm^{-1}): 3448, 2942, 1746, 1652, 768. HRMS m/z $[M + Na]^+$ calcd 385.1046, obsd 385.1045.

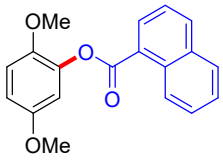


2,5-Dimethoxyphenyl 3,5-dimethylbenzoate (17). Yellow oil, 50.6 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.30 – 7.23 (m, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.82 – 6.73 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 153.9, 145.7, 140.6, 138.3, 135.3, 129.2, 128.1 (2C), 113.6, 111.6, 109.6, 56.7, 55.9, 21.3. IR (neat, cm^{-1}): 3443, 2945, 1742, 765. HRMS m/z $[M + Na]^+$ calcd 309.1097, obsd 309.1095.

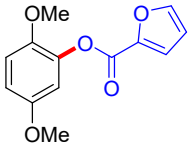


2,5-Dimethoxyphenyl 3,5-bis(trifluoromethyl)benzoate (18). White solid, 67.2 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.63 (m, 2H), 8.14 (s, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.83 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 3.79 (2s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 153.9, 145.2, 139.8, 132.5 (q, *J* = 34.2 Hz), 131.7, 130.5 (q, *J* = 3.9 Hz), 127.0 (q, *J* = 3.6 Hz), 123.0 (q, 272.3 Hz), 113.5, 112.2, 109.4, 56.6, 56.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93. IR (neat,

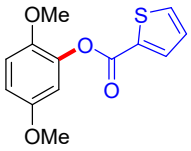
cm^{-1}): 3439, 2940, 1740, 773. HRMS m/z [M + Na]$^+$ calcd 417.0532, obsd 417.0527.



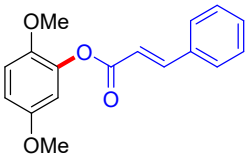
2,5-Dimethoxyphenyl 1-naphthoate (19). White solid, 40.3 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (dq, *J* = 8.6, 0.9 Hz, 1H), 8.48 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.10 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.64 (ddd, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.60 – 7.54 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.86 – 6.79 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 154.0, 145.7, 140.7, 134.2, 134.0, 131.8, 131.4, 128.7, 128.2, 126.5, 126.1, 126.0, 124.7, 113.6, 111.7, 109.8, 56.8, 56.0. IR (neat, cm^{-1}): 3445, 2945, 1748, 776. HRMS m/z [M + Na]$^+$ calcd 331.0941, obsd 331.0940.



2,5-Dimethoxyphenyl furan-2-carboxylate (20). White solid, 43.2 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.39 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.93 (dd, *J* = 8.5, 0.8 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.59 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 153.8, 147.2, 145.6, 143.9, 139.6, 119.7, 113.6, 112.3, 111.9, 109.6, 56.7, 55.9. IR (neat, cm^{-1}): 3448, 2941, 1741, 765. HRMS m/z [M + Na]$^+$ calcd 271.0577, obsd 271.0576.

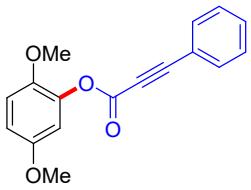


2,5-Dimethoxyphenyl thiophene-2-carboxylate (21). White solid, 45.3 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.78 (dd, *J* = 7.4, 2.7 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 153.8, 145.7, 140.1, 134.9, 133.5, 132.7, 128.1, 113.7, 111.9, 109.6, 56.8, 55.9. IR (neat, cm^{-1}): 3443, 2935, 1738, 755. HRMS m/z [M + Na]$^+$ calcd 287.0349, obsd 287.0351.

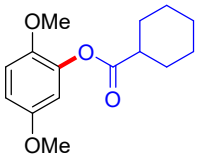


2,5-Dimethoxyphenyl cinnamate[2] **(22).** Light yellow solid, 51.5 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.46 – 7.38 (m, 3H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.77 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 153.9, 146.8, 145.6, 140.4, 134.3, 130.8,

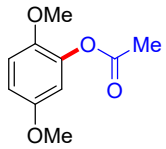
129.1, 128.4, 117.0, 113.5, 111.6, 109.6, 56.7, 55.9. IR (neat, cm^{-1}): 3438, 2937, 1742, 1667, 756. HRMS m/z $[M + Na]^+$ calcd 307.0941, obsd 307.0941.



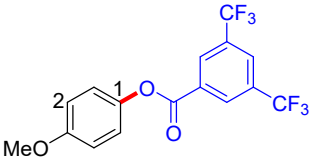
2,5-Dimethoxyphenyl 3-phenylpropiolate (23). Light yellow solid, 52.3 mg, 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 – 7.37 (m, 2H), 6.94 (d, J = 8.9 Hz, 1H), 6.79 (dd, J = 8.9, 3.1 Hz, 1H), 6.75 (d, J = 3.1 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 151.9, 145.3, 139.4, 133.3, 131.1, 128.7, 119.4, 113.5, 112.2, 109.3, 88.7, 80.2, 56.6, 55.9. IR (neat, cm^{-1}): 3443, 2945, 2230, 1748, 763. HRMS m/z $[M + Na]^+$ calcd 305.0784, obsd 305.0784.



2,5-Dimethoxyphenyl cyclohexanecarboxylate (24). Colorless oil, 32.1 mg, 61% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 9.0 Hz, 1H), 6.72 (dd, J = 9.0, 3.0 Hz, 1H), 6.61 (d, J = 3.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.59 (tt, J = 11.1, 3.7 Hz, 1H), 2.12 – 2.03 (m, 2H), 1.82 (dt, J = 12.5, 3.7 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.43 – 1.26 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 153.9, 145.5, 140.7, 113.6, 111.3, 109.6, 56.8, 55.9, 43.1, 29.2, 25.9, 25.5. IR (neat, cm^{-1}): 3456, 2944, 1742, 773. HRMS m/z $[M + Na]^+$ calcd 287.1254, obsd 287.1254.

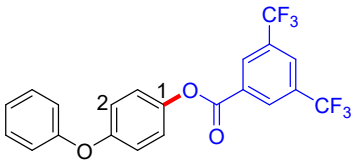


2,5-Dimethoxyphenyl acetate[3] **(25).** Yellow oil, 20.8 mg, 53% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 9.0 Hz, 1H), 6.74 (dd, J = 9.0, 3.0 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 153.8, 145.4, 140.3, 113.4, 111.5, 109.6, 56.6, 55.9, 20.8. IR (neat, cm^{-1}): 3443, 2932, 1738, 753. HRMS m/z $[M + Na]^+$ calcd 219.0628, obsd 219.0624.

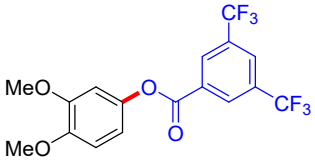


4-Methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (26). Two regioisomers (**C1**:**C2** = 1.5:1) were formed as determined by ^1H NMR analysis of the crude reaction mixture. Colorless oil, 47.8 mg, 66% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.62 (m, 2H), 8.16 – 8.11 (m, 1H), 7.30 (ddd, J = 8.3, 7.5, 1.7 Hz, 0.6H), 7.20 – 7.12 (m, 1.4H), 7.07 – 6.94 (m, 2H), 3.84 (s, 1.2H), 3.83 (s, 1.8H).

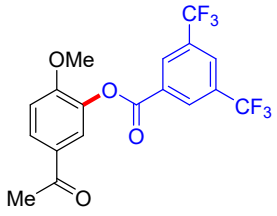
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 162.3, 157.9, 151.1, 143.9, 139.4, 132.8 (q, *J* = 34.2 Hz), 132.5 (q, *J* = 34.3 Hz), 131.8, 130.5 (q, *J* = 3.9 Hz), 130.4 (q, *J* = 3.8 Hz), 127.7, 127.0 (q, *J* = 3.6 Hz), 126.9 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.3 Hz), 123.0 (q, *J* = 272.2 Hz), 122.7, 122.3, 121.0, 114.8, 112.7, 56.0, 55.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91, -62.92. IR (neat, cm^{-1}): 3446, 3438, 2943, 2932, 1744, 1738, 766, 753. HRMS m/z $[M + H]^+$ calcd 365.0607, obsd 365.0603.



4-Phenoxyphenyl 3,5-bis(trifluoromethyl)benzoate (27). Two regioisomers (**C1**:**C2** = 1.6:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture.White solid, 72.3 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.64 (m, 0.76H), 8.45 – 8.40 (m, 1.24H), 8.18 – 8.13 (m, 0.38H), 8.10 – 8.05 (m, 0.62H), 7.41 – 7.34 (m, 0.76H), 7.33 – 7.02 (m, 7H), 7.00 – 6.95 (m, 1.24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 162.1, 157.0, 156.9, 155.7, 148.3, 145.7, 141.5, 132.6 (q, *J* = 34.2 Hz), 132.5, 132.4 (q, *J* = 34.2 Hz), 132.2, 131.9, 131.4, 130.4 (q, *J* = 3.9 Hz), 130.0, 129.9, 127.8, 127.1 (q, *J* = 3.6 Hz), 127.0 (q, *J* = 3.6 Hz), 124.4, 123.8, 123.7, 123.6, 123.4 (q, *J* = 272.3 Hz), 123.1 (q, *J* = 272.2 Hz), 122.7, 121.0, 119.7, 119.2, 118.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93, -62.94. IR (neat, cm^{-1}): 3446, 3420, 2935, 2928, 1736, 1731, 775, 764. HRMS m/z $[M + H]^+$ calcd 427.0763, obsd 427.0766.

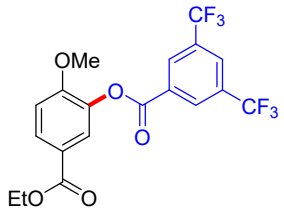


3,4-Dimethoxyphenyl 3,5-bis(trifluoromethyl)benzoate (28). White solid, 47.6 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.62 (m, 2H), 8.16 – 8.13 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.82 – 6.76 (m, 2H), 3.92 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 149.7, 147.5, 144.0, 132.6 (q, *J* = 34.3 Hz), 132.0, 130.4 (q, *J* = 3.9 Hz), 127.0 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 272.9 Hz), 112.8, 111.3, 105.5, 56.3, 56.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.92. IR (neat, cm^{-1}): 3433, 2935, 1743, 775, 764. HRMS m/z $[M + Na]^+$ calcd 417.0532, obsd 417.0535.

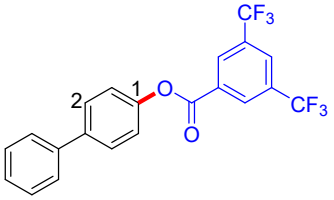


5-Acetyl-2-methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (29). White solid, 45.2 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.6 Hz, 2H), 8.16 (tt, *J* = 1.6, 0.9 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 162.1, 155.1, 139.3, 132.6 (q, *J* = 34.2 Hz), 131.4, 130.7, 130.5 (q, *J* = 3.9 Hz), 128.9, 127.2 (q, *J* = 3.7 Hz), 123.1, 122.9 (q, *J* = 272.9 Hz), 111.9, 56.4, 26.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93. IR (neat, cm^{-1}): 3438, 2943, 1738, 1645, 776, 763. HRMS

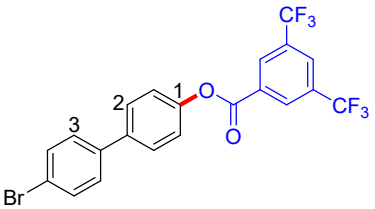
m/z [M + Na]$^+$ calcd 429.0532, obsd 429.0531.



Ethyl 3-((3,5-bis(trifluoromethyl)benzoyl)oxy)-4-methoxybenzoate (30). White solid, 46.2 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.6 Hz, 2H), 8.17 – 8.13 (m, 1H), 8.03 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.87 (d, *J* = 2.1 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 162.0, 154.9, 139.0, 132.6 (q, *J* = 34.1 Hz), 131.5, 130.5 (q, *J* = 3.3 Hz), 129.9, 127.2 (q, *J* = 3.6 Hz), 124.3, 123.6, 122.9 (q, *J* = 272.9 Hz), 111.9, 61.2, 56.3, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93. IR (neat, cm^{-1}): 3443, 3435, 2943, 2938, 1738, 1725, 776, 763. HRMS m/z [M + Na]$^+$ calcd 459.0638, obsd 459.0637.

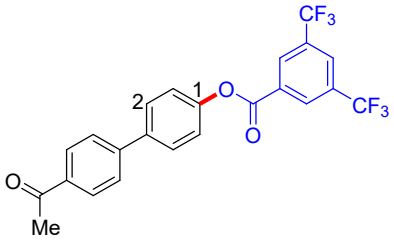


[1,1'-Biphenyl]-4-yl 3,5-bis(trifluoromethyl)benzoate (31). Two regioisomers (**C1**:**C2** = 2:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 70.3 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.56 (m, 2H), 8.36 – 8.30 (m, 1H), 8.09 – 8.05 (m, 1H), 8.00 – 7.95 (m, 0.5H), 7.61 – 7.56 (m, 2H), 7.53 – 7.49 (m, 2H), 7.41 – 7.33 (m, 4H), 7.32 – 7.17 (m, 5H), 7.16 (s, 0.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 162.5, 149.8, 147.5, 140.2, 139.9, 137.2, 135.0, 132.6 (q, *J* = 34.2 Hz), 132.4 (q, *J* = 34.2 Hz), 131.9, 131.8, 131.3, 130.4 (q, *J* = 3.6 Hz), 130.2 (q, *J* = 3.6 Hz), 129.0, 129.0, 128.9, 128.6, 128.5, 127.9, 127.7, 127.3, 127.2 (q, *J* = 3.6 Hz), 127.1, 127.0 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 272.9 Hz), 122.9 (q, *J* = 272.9 Hz), 122.6, 121.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91, -62.99. IR (neat, cm^{-1}): 3443, 3438, 2937, 2929, 1743, 1732, 785, 776. HRMS m/z [M + Na]$^+$ calcd 433.0634, obsd 433.0635.

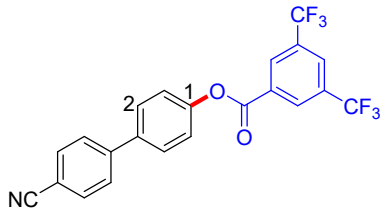


4'-Bromo-[1,1'-biphenyl]-4-yl 3,5-bis(trifluoromethyl)benzoate (32). Three regioisomers (**C1**:**C2**:**C3** = 7.5:3:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 82.8 mg, 85% yield. **C1** + **C2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.66 (m, 2H), 8.47 – 8.43 (m, 0.8H), 8.18 – 8.15 (m, 1H), 8.12 – 8.09 (m, 0.4H), 7.66 – 7.62 (m, 2H), 7.61 – 7.56 (m, 2H), 7.51 – 7.38 (m, 4.2H), 7.35 – 7.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.4, 150.1, 147.4, 139.1, 138.7, 136.1, 133.9, 132.7 (q, *J* = 34.2 Hz), 132.6 (q, *J* = 34.2 Hz), 132.1,

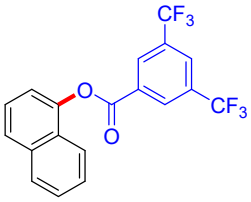
131.8, 131.8, 131.5, 131.1, 130.6, 130.4 (q, J = 4.0 Hz), 130.2 (q, J = 4.0 Hz), 129.3, 128.9, 128.4, 127.3, 127.2 (q, J = 3.6 Hz), 127.1 (q, J = 3.6 Hz), 124.3, 122.4 (q, J = 272.3 Hz), 122.0, 121.9 (q, J = 272.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.92, -62.98. **C3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.38 (m, 2H), 8.08 (s, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 147.9, 136.2, 134.1, 132.7, 132.3, 131.3, 130.3, 128.8, 128.7, 128.2, 126.0, 124.2, 121.5.(The signal-to-noise ratio is too low, and the coupling between C and F is not obvious.) ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02. IR (neat, cm^{-1}): 3438, 3422, 2937, 2929, 1741, 1732, 1728, 775, 756, 743. HRMS m/z $[M + Na]^+$ calcd 510.9739, 512.9719, obsd 510.9738, 512.9718.



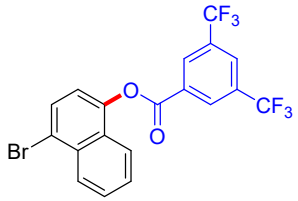
4'-Acetyl-[1,1'-biphenyl]-4-yl 3,5-bis(trifluoromethyl)benzoate (33). Two regioisomers (**C1**:**C2** = 4.2:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 65.3 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.40 (m, 2.48H), 8.11 – 8.07 (m, 1.24H), 7.99 (dd, J = 8.0, 1.7 Hz, 0.48H), 7.97 – 7.93 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 (d, J = 1.7 Hz, 0.48H), 7.52 – 7.48 (m, 2H), 7.46 – 7.44 (m, 1H), 7.43 – 7.39 (m, 0.48H), 7.39 – 7.34 (m, 1.48H), 2.67 (s, 0.72H), 2.58 (s, 3H). **C1**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 162.4, 147.4, 136.4, 133.9, 132.6 (q, J = 34.2 Hz), 131.1, 130.2 (q, J = 3.7 Hz), 129.7, 129.2, 128.6, 127.3, 127.2 (q, J = 3.6 Hz), 122.8, 122.7 (q, J = 272.3 Hz), 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99, -63.01. IR (neat, cm^{-1}): 3443, 3432, 2945, 2932, 1741, 1738, 1645, 1638, 767, 743. HRMS m/z $[M + Na]^+$ calcd 475.0739, obsd 475.0731.



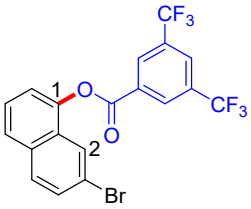
4'-Cyano-[1,1'-biphenyl]-4-yl 3,5-bis(trifluoromethyl)benzoate (34). Two regioisomers (**C1**:**C2** = 1.25:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 52.5 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.65 (m, 2H), 8.45 – 8.40 (m, 1.6H), 8.19 – 8.15 (m, 1H), 8.13 – 8.09 (m, 0.8H), 7.79 – 7.73 (m, 2.4H), 7.73 – 7.69 (m, 3H), 7.69 – 7.63 (m, 2.8H), 7.58 – 7.51 (m, 2.8H), 7.48 – 7.44 (m, 1.6H), 7.39 – 7.35 (m, 1.8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.3, 151.0, 150.8, 147.3, 144.6, 144.4, 142.0, 141.2, 137.8,132.9, 132.6 (q, J = 34.2 Hz), 132.5 (q, J = 34.2 Hz), 132.4, 131.0, 130.4 (q, J = 3.8 Hz), 130.2 (q, J = 3.8 Hz), 129.7, 128.8, 128.0, 127.9, 127.4, 127.2 (q, J = 3.7 Hz), 123.0, 122.6 (q, J = 272.3 Hz), 122.3, 122.0 (q, J = 273.2 Hz), 111.9, 111.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.92, -62.99. IR (neat, cm^{-1}): 3455, 3446, 2943, 2932, 2230, 2224, 1743, 1733, 753, 742. HRMS m/z $[M + Na]^+$ calcd 458.0586, obsd 458.0587.



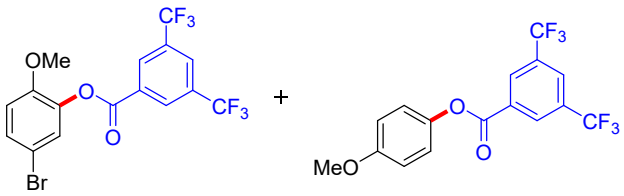
Naphthalen-1-yl 3,5-bis(trifluoromethyl)benzoate (35). White solid, 68.3 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.75 (m, 2H), 8.25 – 8.19 (m, 1H), 7.97 – 7.92 (m, 1H), 7.86 (dd, *J* = 8.8, 4.0 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.39 (dd, *J* = 7.5, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 146.4, 134.9, 132.8 (q, *J* = 34.3 Hz), 131.8, 130.5 (d, *J* = 3.8 Hz), 128.4, 127.3 (q, *J* = 3.7 Hz), 127.0, 127.0, 126.9, 126.6, 125.6, 123.0 (q, *J* = 273.1 Hz), 120.9, 118.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.89. IR (neat, cm^{-1}): 3432, 2928, 1732, 776, 742. HRMS m/z $[M + Na]^+$ calcd 407.0477, obsd 407.0476.



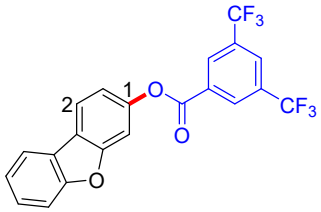
4-Bromonaphthalen-1-yl 3,5-bis(trifluoromethyl)benzoate (36). White solid, 59.3 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.75 (m, 2H), 8.31 (dt, *J* = 8.6, 0.9 Hz, 1H), 8.23 – 8.20 (m, 1H), 7.89 – 7.84 (m, 2H), 7.68 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 146.0, 133.1, 132.9 (q, *J* = 34.1 Hz), 131.4, 130.5 (q, *J* = 4.0 Hz), 129.4, 128.3, 128.0, 127.8 (2C), 127.5 (q, *J* = 3.6 Hz), 122.9 (q, *J* = 273.1 Hz), 121.4, 120.9, 118.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.89. IR (neat, cm^{-1}): 3442, 2934, 1744, 758, 743. HRMS m/z $[M + Na]^+$ calcd 484.9582, 486.9562, obsd 484.9585, 486.9563.



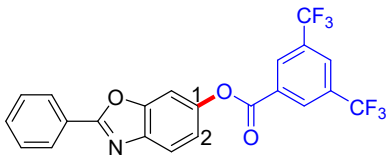
7-Bromonaphthalen-1-yl 3,5-bis(trifluoromethyl)benzoate (37). Two regioisomers (**C1**:**C2** = 1.2:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 53.8 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.74 (m, 2H), 8.25 – 8.20 (m, 1H), 8.12 – 7.90 (m, 1H), 7.83 – 7.78 (m, 1H), 7.76 – 7.67 (m, 1.6H), 7.65 – 7.53 (m, 2H), 7.39 (dd, *J* = 7.6, 1.0 Hz, 0.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (2C), 161.7, 146.5, 145.4, 144.0, 135.9, 133.7, 133.3, 132.9 (d, *J* = 33.9 Hz), 132.8 (d, *J* = 33.9 Hz), 131.5, 131.4, 131.1, 130.7 (q, *J* = 3.9 Hz), 130.6 (q, *J* = 3.9 Hz), 130.5, 130.4, 130.1, 129.6, 128.4, 128.1, 127.9 (2C), 127.6 (q, *J* = 3.6 Hz), 127.5 (q, *J* = 3.6 Hz), 127.2, 126.6 (q, *J* = 273.2 Hz), 124.0 (q, *J* = 273.2 Hz), 121.0, 119.4, 118.7, 113.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.87, -62.89. IR (neat, cm^{-1}): 3442, 3438, 2940, 2934, 1744, 1738, 758, 743. HRMS m/z $[M + Na]^+$ calcd 484.9582, 486.9562, obsd 484.9583, 486.9561.



5-Bromo-2-methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (38) + 4-methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (39). The mixture of **38** and **39** (1:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. Colorless oil, 53.5 mg, 33% yield of **38**, 33% yield of **39**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.60 (m, 2H), 8.16 – 8.12 (m, 1H), 7.41 (dd, *J* = 8.8, 2.4 Hz, 0.5H), 7.33 (d, *J* = 2.4 Hz, 0.5H), 7.18 – 7.12 (m, 1H), 6.98 – 6.94 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 0.5H), 3.84 (s, 1.5H), 3.82 (s, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 161.9, 157.9, 150.5, 143.9, 139.9, 132.9, 132.6 (d, *J* = 34.2 Hz), 132.5 (d, *J* = 34.2 Hz), 132.0, 131.3, 130.6 (q, *J* = 3.8 Hz), 130.5, 130.4 (q, *J* = 3.8 Hz), 127.2 (q, *J* = 3.6 Hz), 127.0 (q, *J* = 3.6 Hz), 126.0, 122.9 (q, *J* = 273.2 Hz), 122.8 (q, *J* = 273.2 Hz), 122.3, 118.0, 114.8, 113.9, 112.2, 56.2, 55.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93, -62.94. IR (neat, cm^{-1}): 3443, 3432, 2944, 2934, 1744, 1743, 758, 743. HRMS m/z $[M + Na]^+$ calcd 464.9531, 466.9511, (**38**); 387.0427, (**39**), obsd 464.9530, 466.9510; 387.0426.

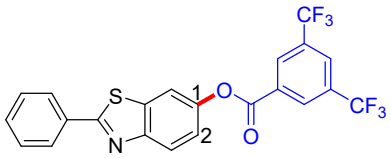


Dibenzo[b,d]furan-3-yl 3,5-bis(trifluoromethyl)benzoate (40). Two regioisomers (**C1**:**C2** = 1.1:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. White solid, 70.2 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.81 (m, 1.8H), 8.72 – 8.69 (m, 2H), 8.27 – 8.24 (m, 0.9H), 8.20 – 8.17 (m, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.98 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.67 – 7.64 (m, 0.9H), 7.62 (dt, *J* = 4.0, 0.8 Hz, 0.9H), 7.60 (dt, *J* = 4.0, 0.9 Hz, 1H), 7.59 – 7.54 (m, 1.8H), 7.53 – 7.47 (m, 2.8H), 7.39 (td, *J* = 7.5, 1.1 Hz, 1H), 7.31 – 7.23 (m, 2.9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 162.2, 157.5, 157.1, 156.4, 156.2, 149.5, 144.9, 133.0 (q, *J* = 34.3 Hz), 132.7 (d, *J* = 34.3 Hz), 131.8, 131.5, 130.5 (q, *J* = 3.1 Hz), 130.4 (d, *J* = 3.1 Hz), 127.9, 127.7, 127.6 (q, *J* = 3.6 Hz), 127.5, 127.2 (q, *J* = 3.6 Hz), 123.4, 123.3, 122.7 (q, *J* = 273.2 Hz), 122.4 (q, *J* = 273.2 Hz), 122.0, 121.2, 120.8, 117.5, 116.5, 116.0, 112.0, 111.9, 110.3, 105.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.89, -62.91. IR (neat, cm^{-1}): 3441, 3428, 2942, 2928, 1740, 1738, 763, 755. HRMS m/z $[M + Na]^+$ calcd 447.0426, obsd 447.0425.



2-Phenylbenzo[d]oxazol-6-yl 3,5-bis(trifluoromethyl)benzoate (41). Two regioisomers (**C1**:**C2** = 16:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. **C1** were separated by chromatography. White solid, 56.3 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71

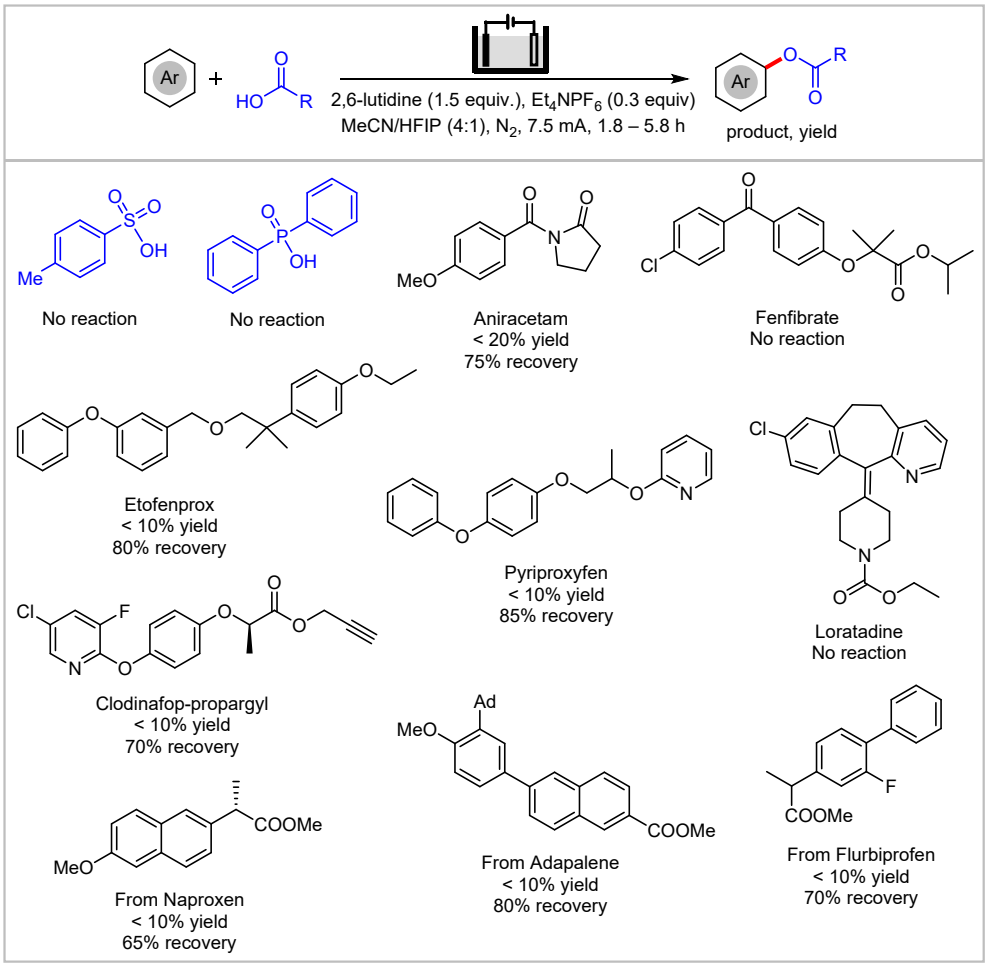
– 8.67 (m, 2H), 8.28 – 8.24 (m, 2H), 8.19 – 8.16 (m, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.25 (dd, J = 8.6, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 162.9, 150.8, 147.7, 140.7, 132.7 (q, J = 34.2 Hz), 132.0, 131.7, 130.5 (q, J = 3.6 Hz), 129.2, 127.8, 127.3 (q, J = 3.9 Hz), 126.9, 122.9 (q, J = 273.0 Hz), 120.4, 118.5, 104.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91. IR (neat, cm^{-1}): 3435, 2934, 2234, 1744, 763, 755. HRMS m/z [M + Na]$^+$ calcd 474.0535, obsd 474.0536.



2-Phenylbenzo[d]thiazol-6-yl 3,5-bis(trifluoromethyl)benzoate (42). Two regioisomers (**C1**:**C2** = 10:1) were formed as determined by ^{1}H NMR analysis of the crude reaction mixture. **C1** were separated by chromatography. White solid, 54.3 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.67 (m, 2H), 8.19 – 8.16 (m, 1H), 8.14 (d, J = 8.9 Hz, 1H), 8.12 – 8.08 (m, 2H), 7.83 (d, J = 2.4 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.37 (dd, J = 8.9, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 162.8, 152.6, 147.8, 136.0, 133.4, 132.7 (q, J = 34.2 Hz), 131.7, 131.4, 130.4 (q, J = 3.0 Hz), 129.3, 127.7, 127.3 (q, J = 3.9 Hz), 124.1, 122.8 (q, J = 273.2 Hz) 120.6, 114.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91. IR (neat, cm^{-1}): 3433, 2929, 2241, 1742, 761, 753. HRMS m/z [M + Na]$^+$ calcd 490.0307, obsd 490.0308.

V. Unsuccessful Substrates

Scheme S1. Unsuccessful examples.



Reaction conditions: RVC anode, Pt plate cathode, arene (0.2 mmol), acid (0.3 mmol), 2,6-lutidine (1.5 equiv.), Et_4NPF_6 (0.3 equiv.), MeCN (4 mL), HFIP (1 mL), constant current (7.5 mA), 1.8-5.8 h, undivided cell, rt, under N_2.

VI. Mechanistic Studies

1. Detection of crude reaction

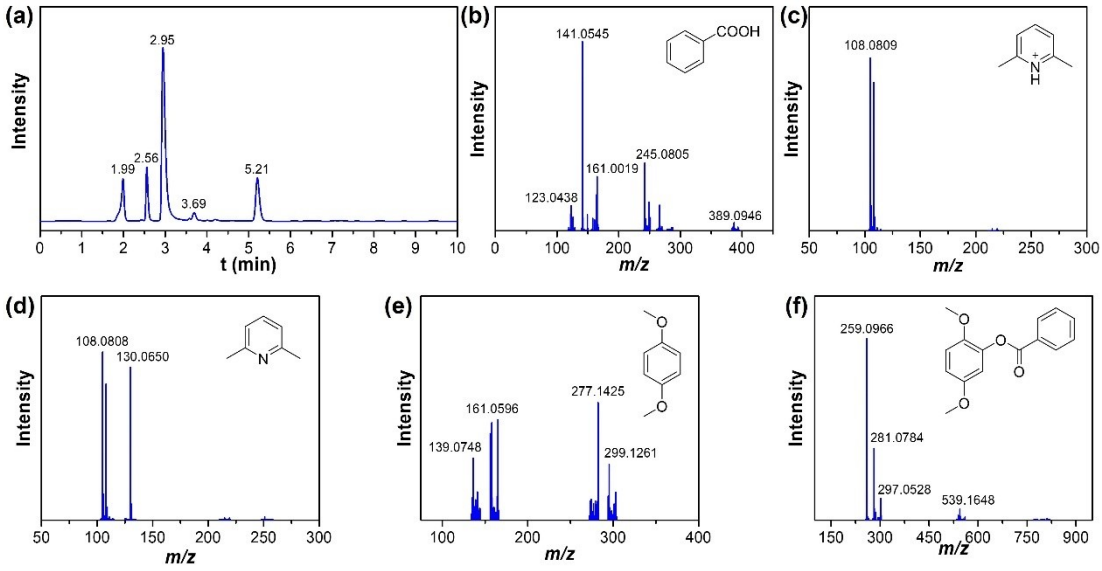


Figure S2. LC–MS data for the crude reaction under standard conditions.

The crude reaction of **1** and **2** was detected by LC-MS under standard conditions. As shown in Figure S2a, there are five peaks with peak times of 1.99, 2.56, 2.95, 3.69, and 5.21 min in the liquid chromatogram, which correspond to compounds benzoic acid, 2,6-dimethylpyridin-1-ium, 2,6-dimethylpyridine, 1,4-dimethoxybenzene, and 2,5-dimethoxyphenyl benzoate, respectively.

Table S1: benzoic acid (Figure S2b)

m/z	123.0438	141.0545	161.0019	245.0805	389.0946
species	$M + H^+$	$M + Na^+$	$M + K^+$	$2M + H^+$	$3M + Na^+$

Table S2: 2,6-dimethylpyridin-1-ium (Figure S2c)

m/z	108.0809
species	M

Table S3: 2,6-dimethylpyridine (Figure S2d)

m/z	108.0809	130.0650
species	$M + H^+$	$M + Na^+$

Table S4: 1,4-dimethoxybenzene (Figure S2e)

m/z	139.0748	161.0596	277.1425	299.1261
species	$M + H^+$	$M + Na^+$	$2M + H^+$	$2M + Na^+$

Table S5: 2,5-dimethoxyphenyl benzoate (Figure S2f)

m/z	259.0966	281.0784	297.0524	539.1648
species	$M + H^+$	$M + Na^+$	$M + K^+$	$2M + Na^+$

2. Cyclic voltammetry studies

The cyclic voltammograms were recorded at rt using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate was 100 mV/s.

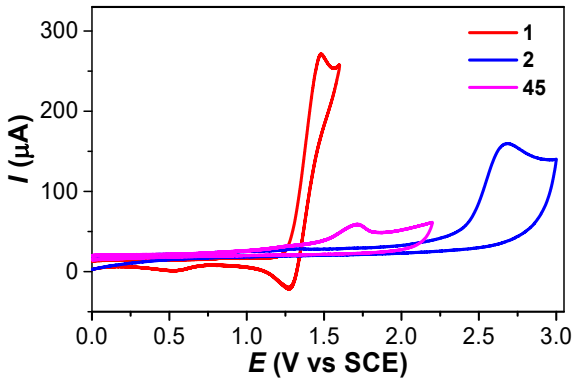


Figure S3. Cyclic voltammograms of compound **1**, **2** and **45** in MeCN with 0.1 M nBu$_4$NPF$_6$. Red line: 1 (10 mM), $E_{p/2}$ = 1.37 V; blue line: **2** (10 mM), $E_{p/2}$ = 2.55 V; magenta line: **45** (10 mM), $E_{p/2}$ = 1.60 V.

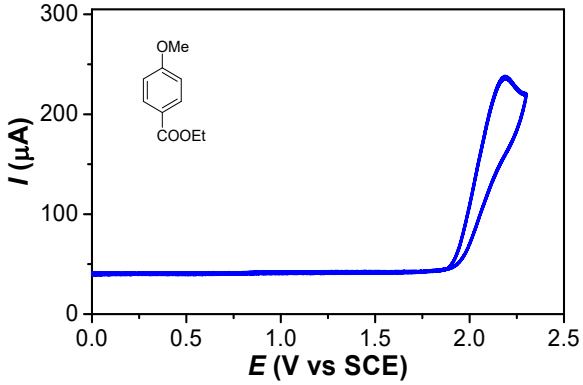
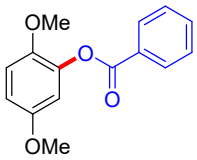


Figure S4. Cyclic voltammograms of compound ethyl 4-methoxybenzoate (10 mM) in MeCN with 0.1 M nBu$_4$NPF$_6$, $E_{p/2}$ = 2.05 V.

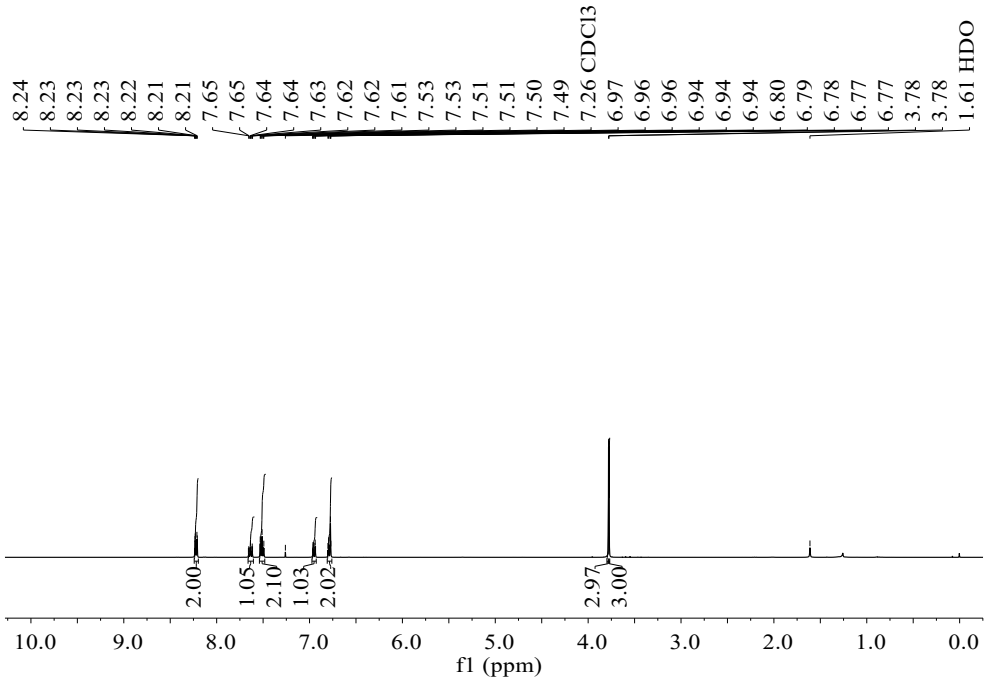
VII. References

1. H. Rao, P. Wang and C. J. Li, *Eur. J. Org. Chem.*, 2012, 6503-6507.
2. Y. J. Liang, Y. Y. Gao, H. B. Han, L. Li and L. Liu, *Org. Biomol. Chem.*, 2024, **22**, 5101-5104.
3. T. A. Hong Nguyen and D. R. Hou, *Org. Lett.*, 2021, **23**, 8127-8131.

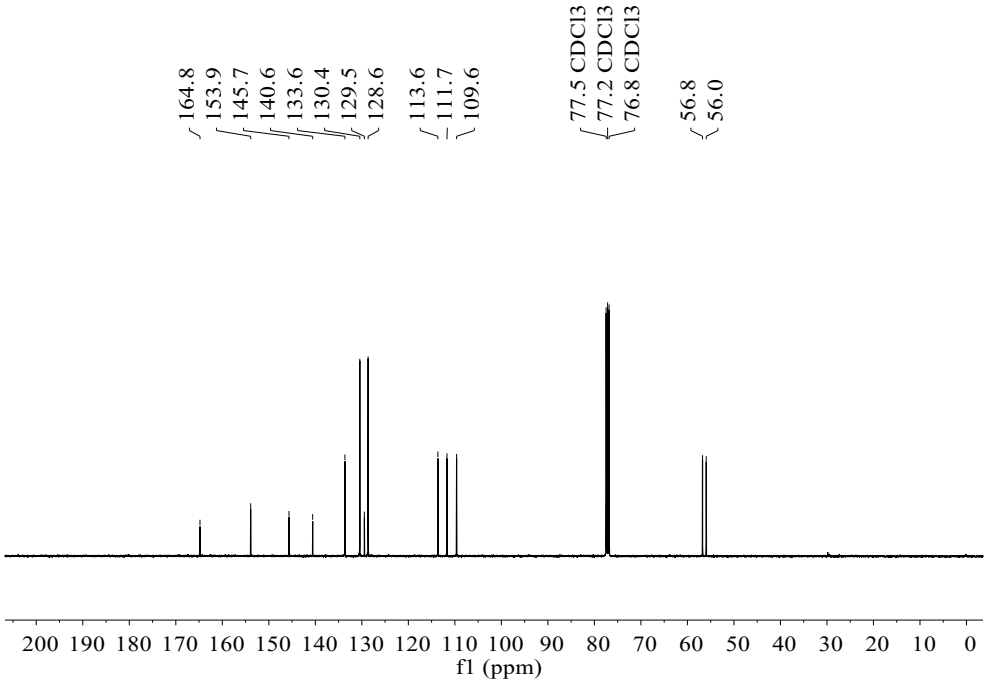
VIII. NMR Spectra

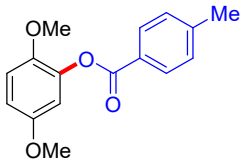


Compound **3**, ^{1}H NMR (400 MHz, $CDCl_3$)

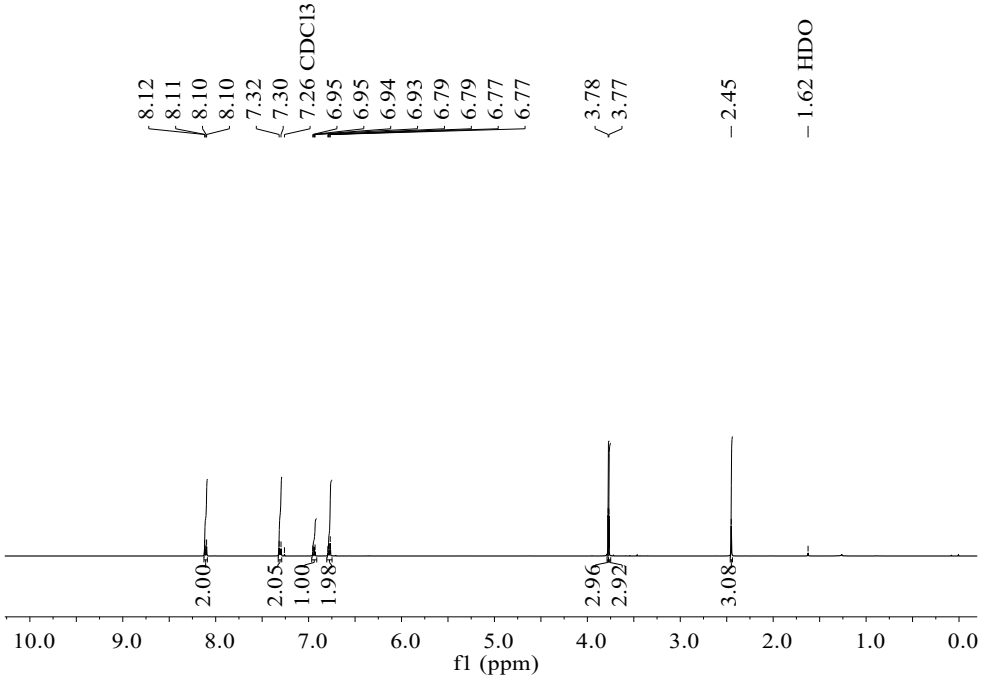


Compound **3**, ^{13}C NMR (101 MHz, $CDCl_3$)

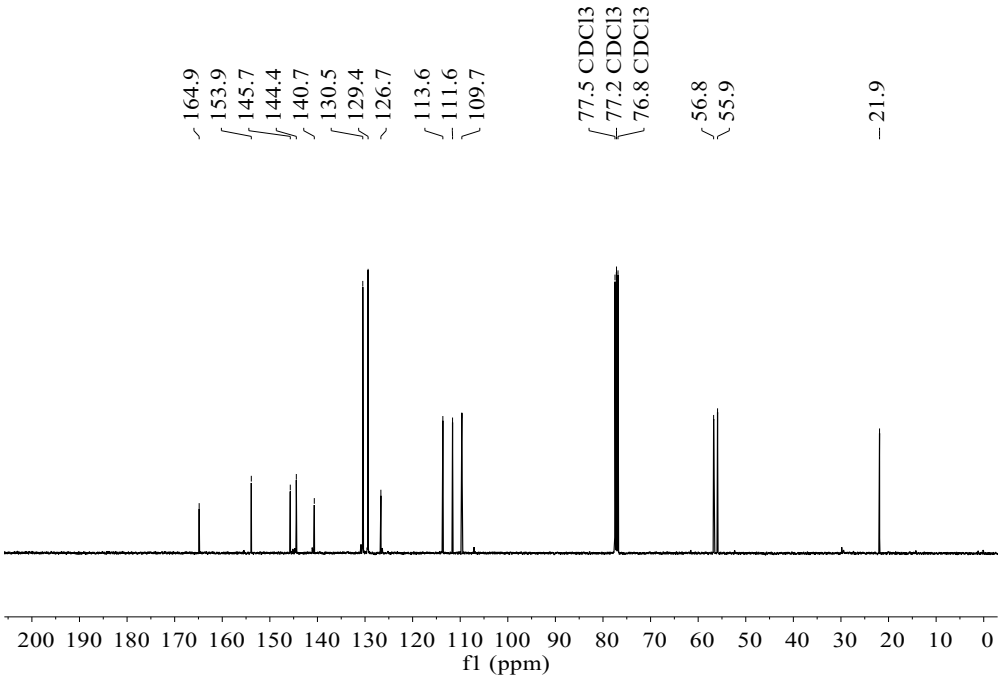


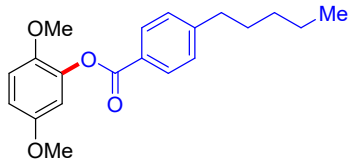


Compound **4**, ^{1}H NMR (400 MHz, $CDCl_3$)

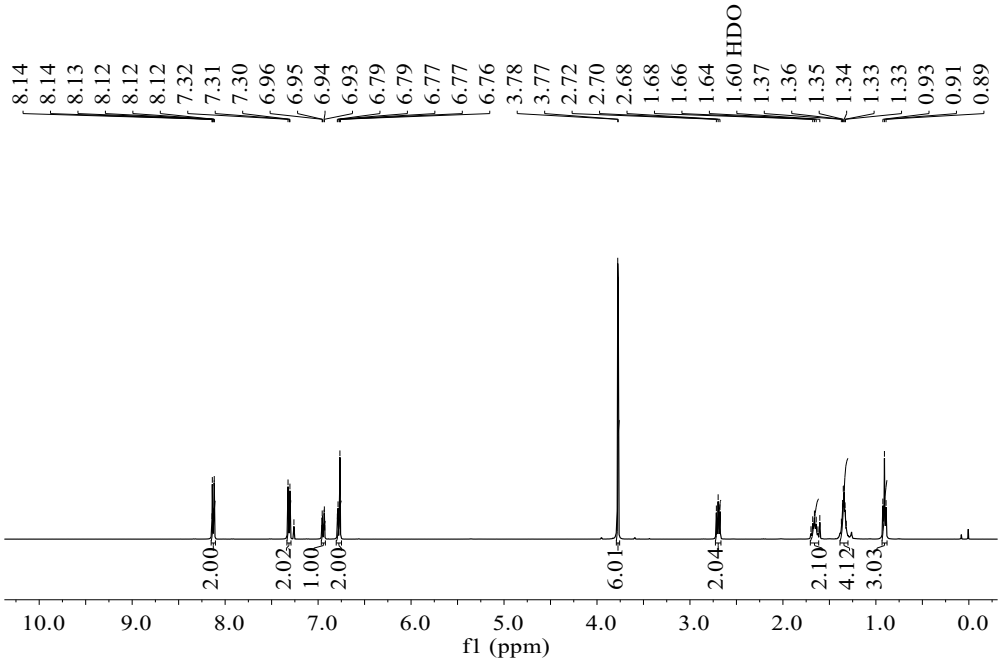


Compound **4**, ^{13}C NMR (101 MHz, $CDCl_3$)

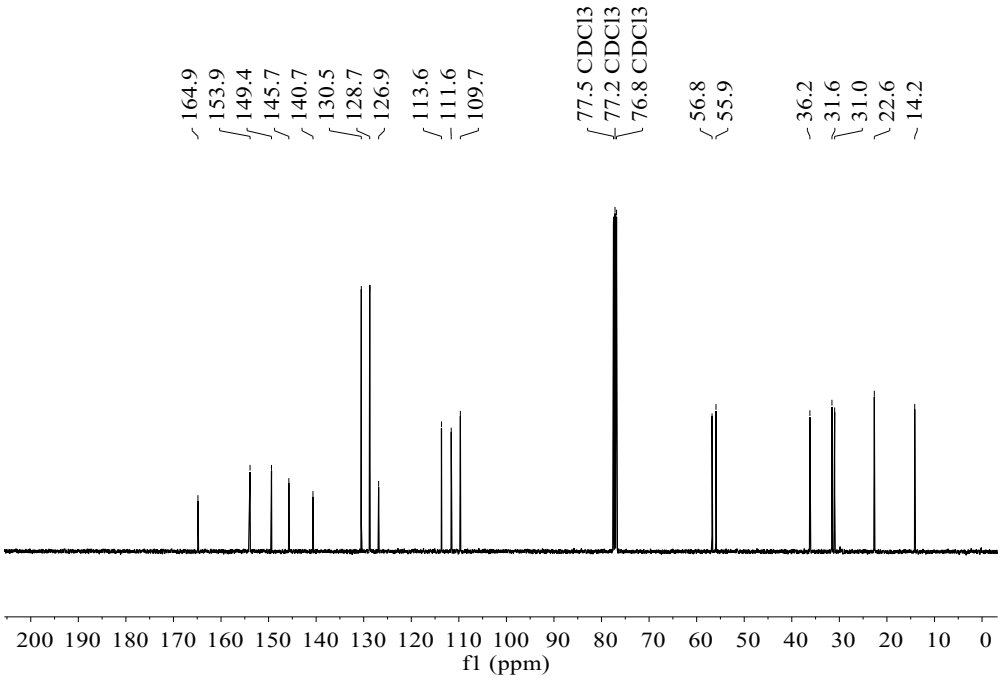


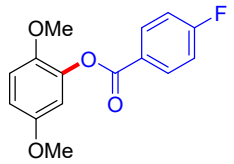


Compound **5**, ^{1}H NMR (400 MHz, $CDCl_3$)

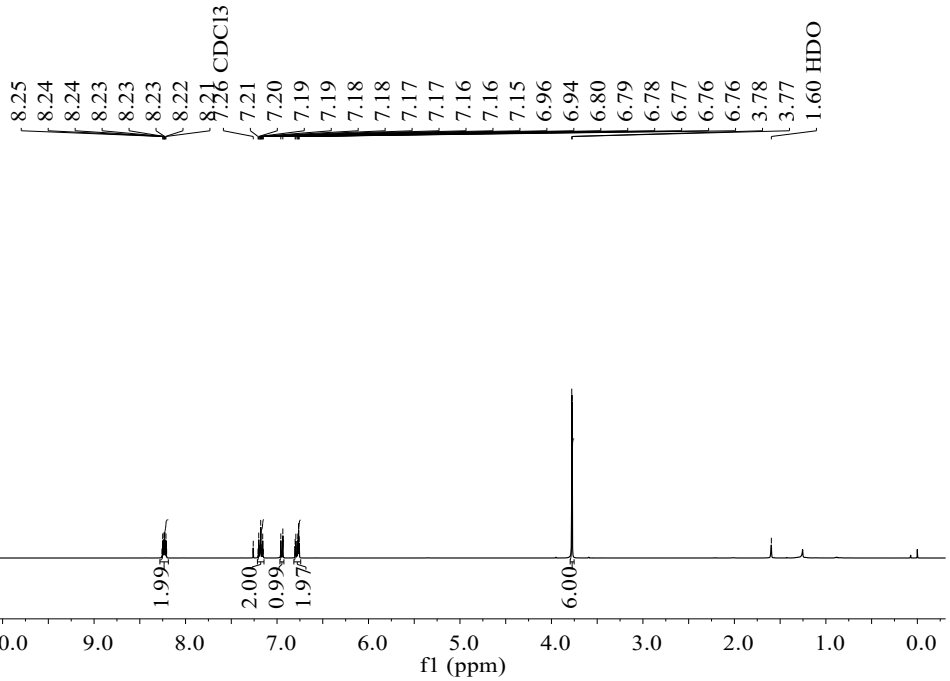


Compound **5**, ^{13}C NMR (101 MHz, $CDCl_3$)

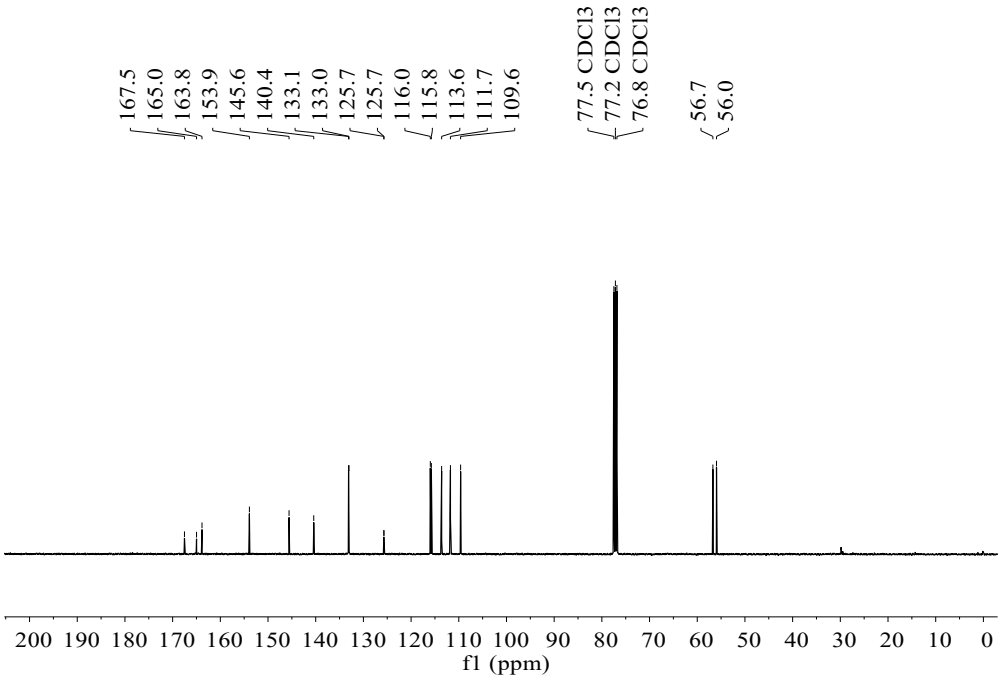




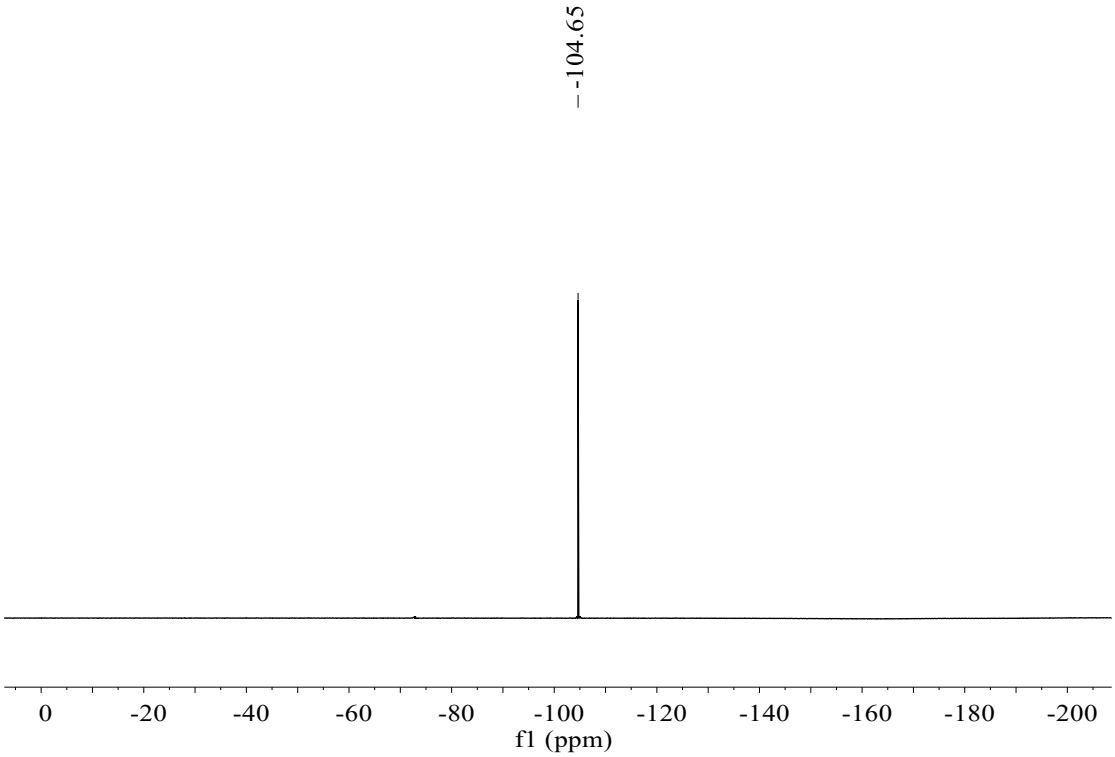
Compound **6**, ^{1}H NMR (400 MHz, $CDCl_3$)

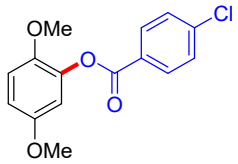


Compound **6**, ^{13}C NMR (101 MHz, $CDCl_3$)

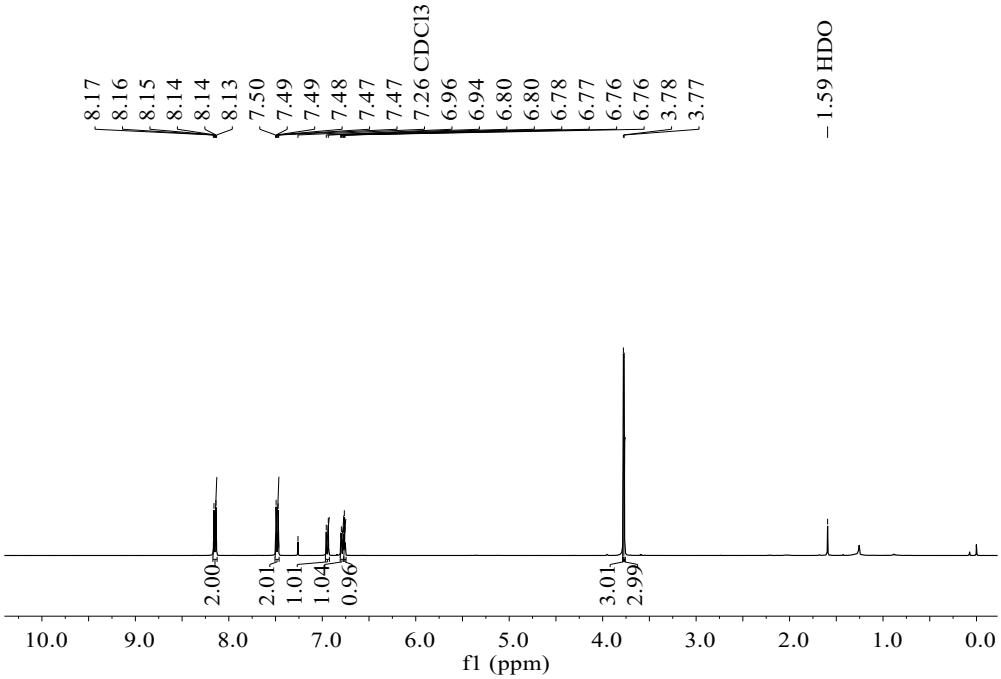


Compound **6**, ^{19}F NMR (376 MHz, $CDCl_3$)

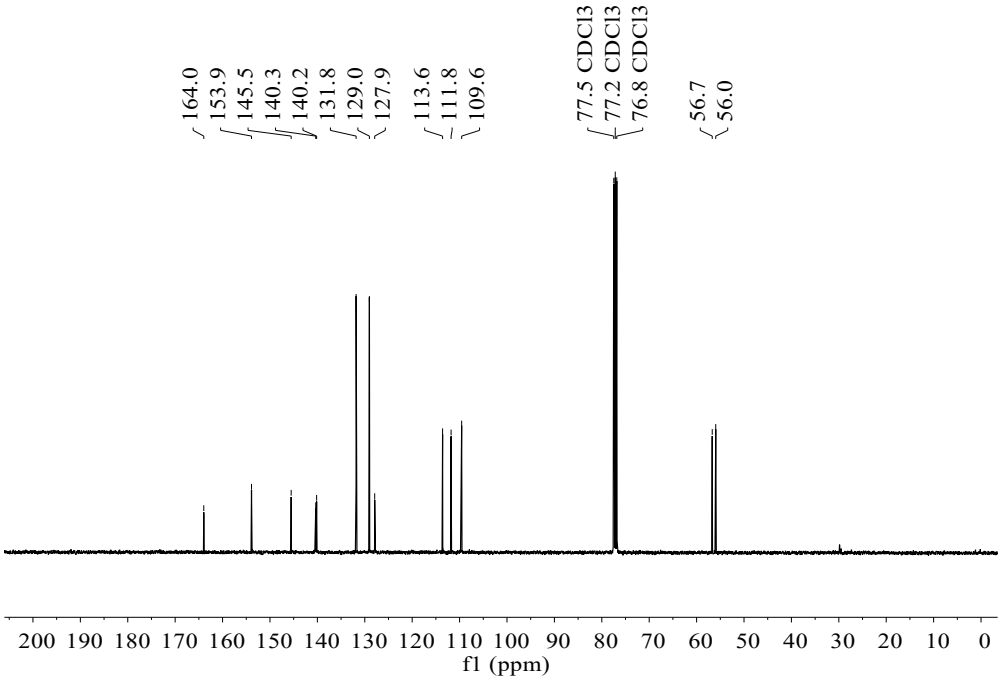


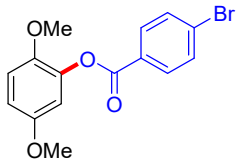


Compound **7**, ^{1}H NMR (400 MHz, $CDCl_3$)

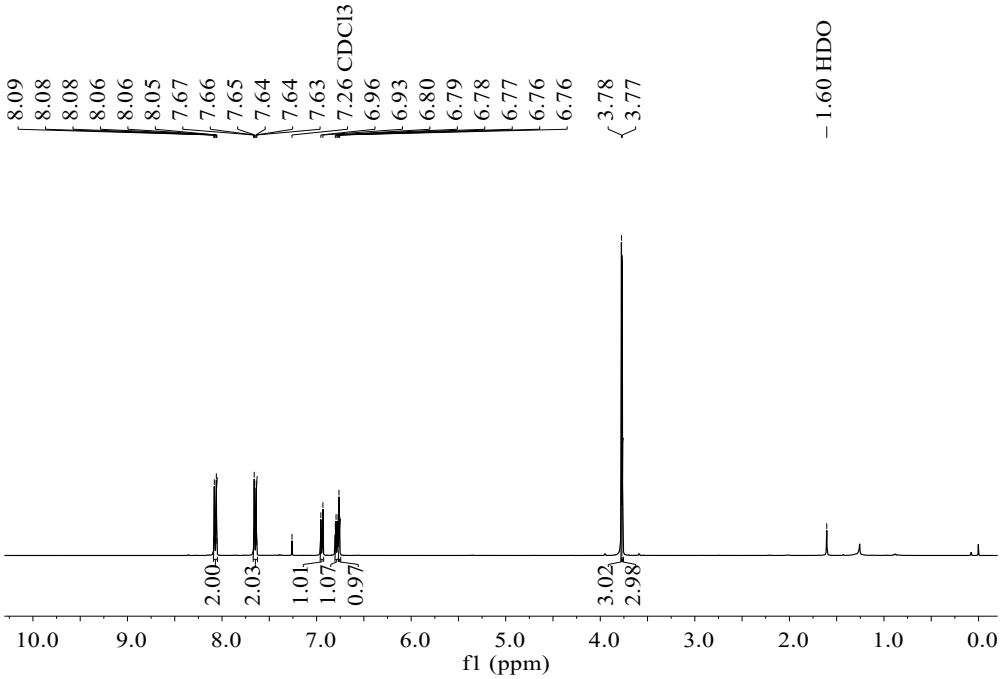


Compound **7**, ^{13}C NMR (101 MHz, $CDCl_3$)

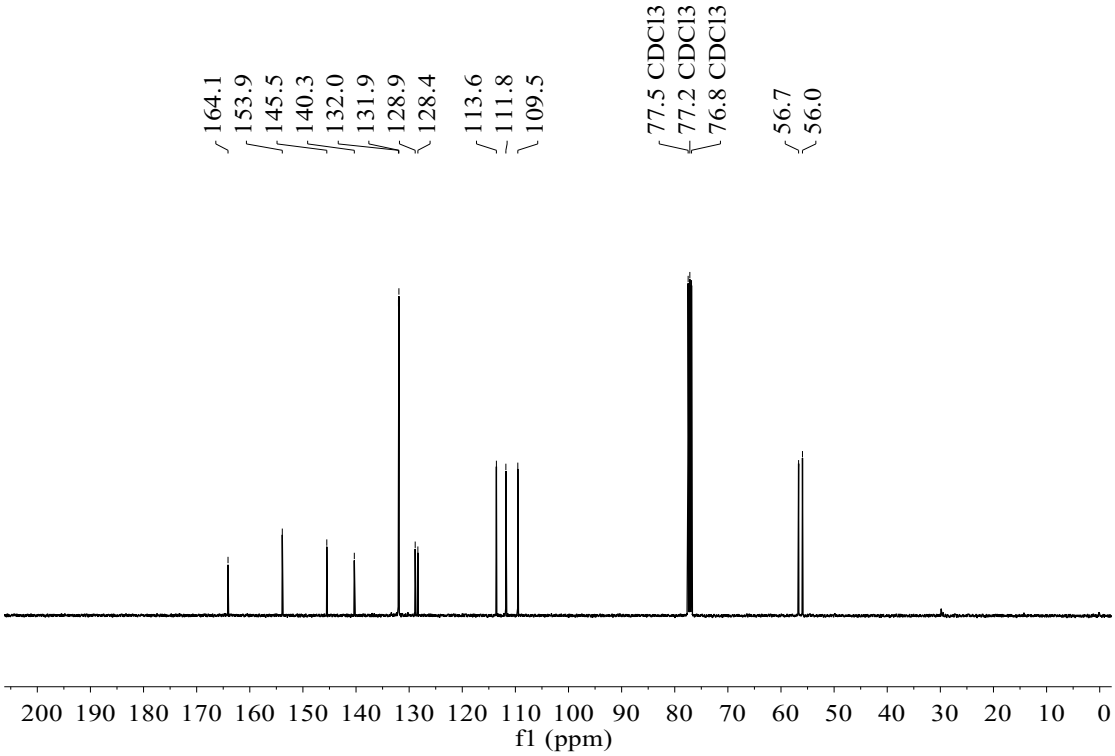


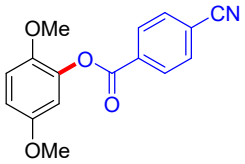


Compound **8**, ^{1}H NMR (400 MHz, $CDCl_3$)

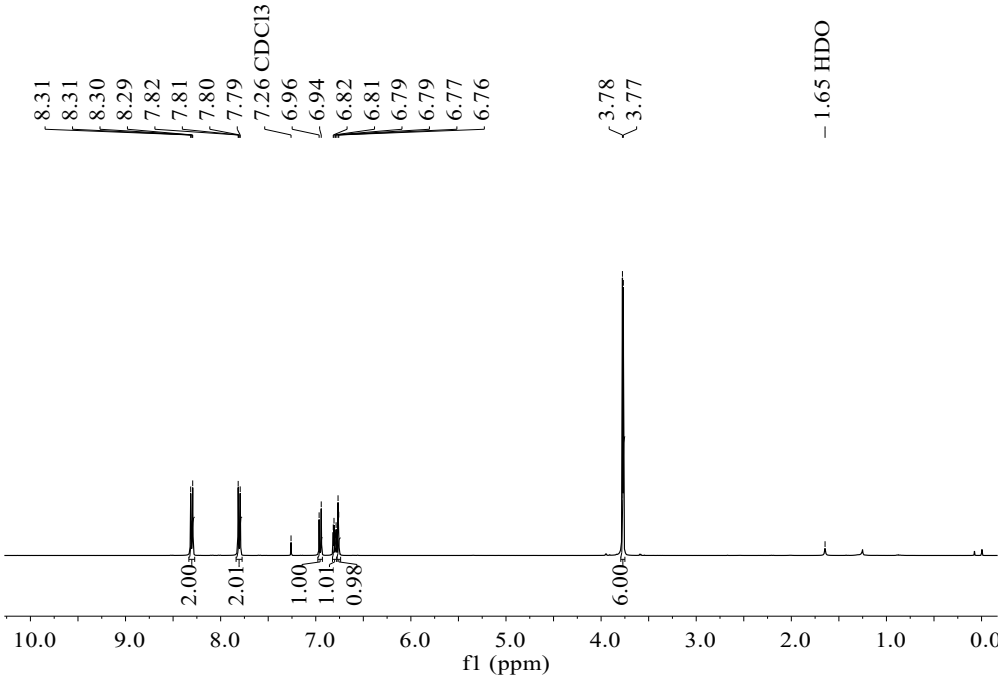


Compound **8**, ^{13}C NMR (101 MHz, $CDCl_3$)

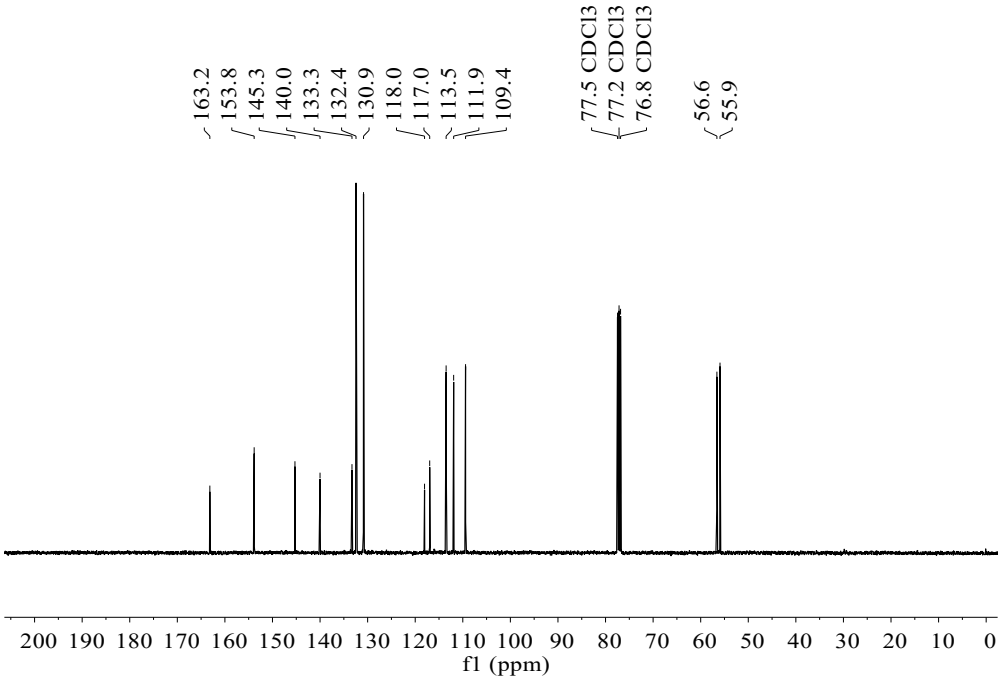


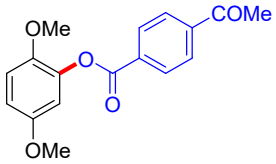


Compound **9**, ^{1}H NMR (400 MHz, $CDCl_3$)

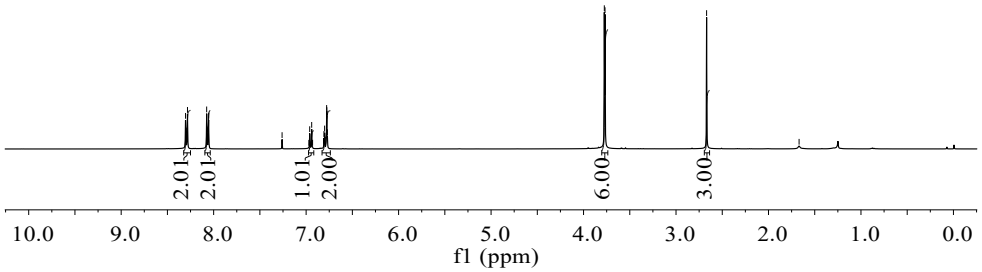


Compound **9**, ^{13}C NMR (101 MHz, $CDCl_3$)

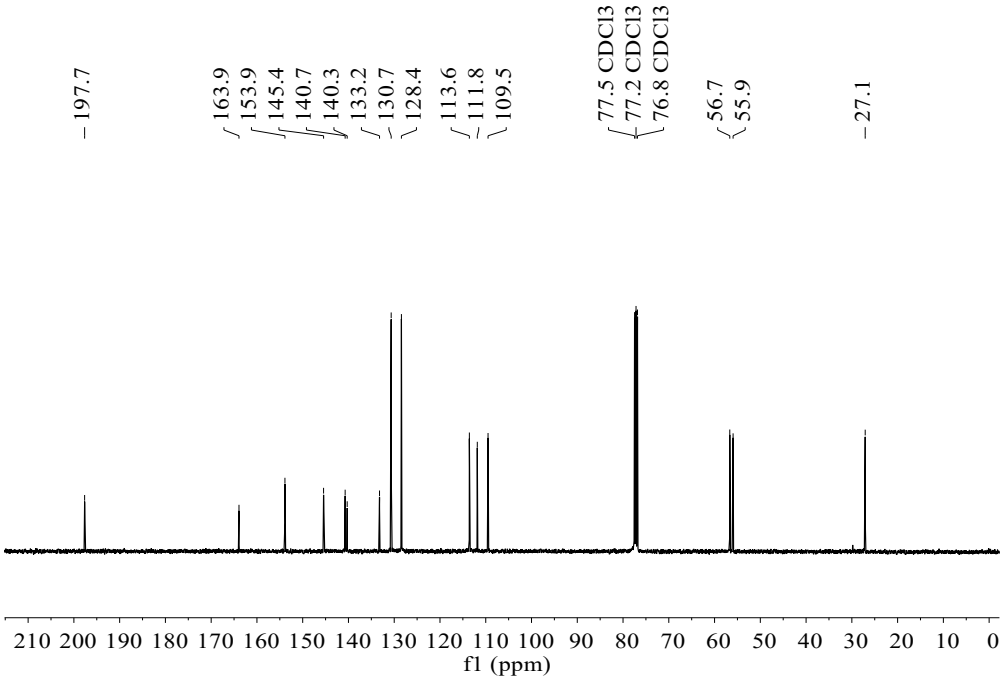


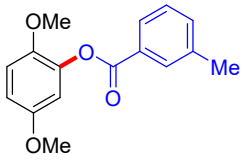


Compound **10**, ^{1}H NMR (400 MHz, $CDCl_3$)

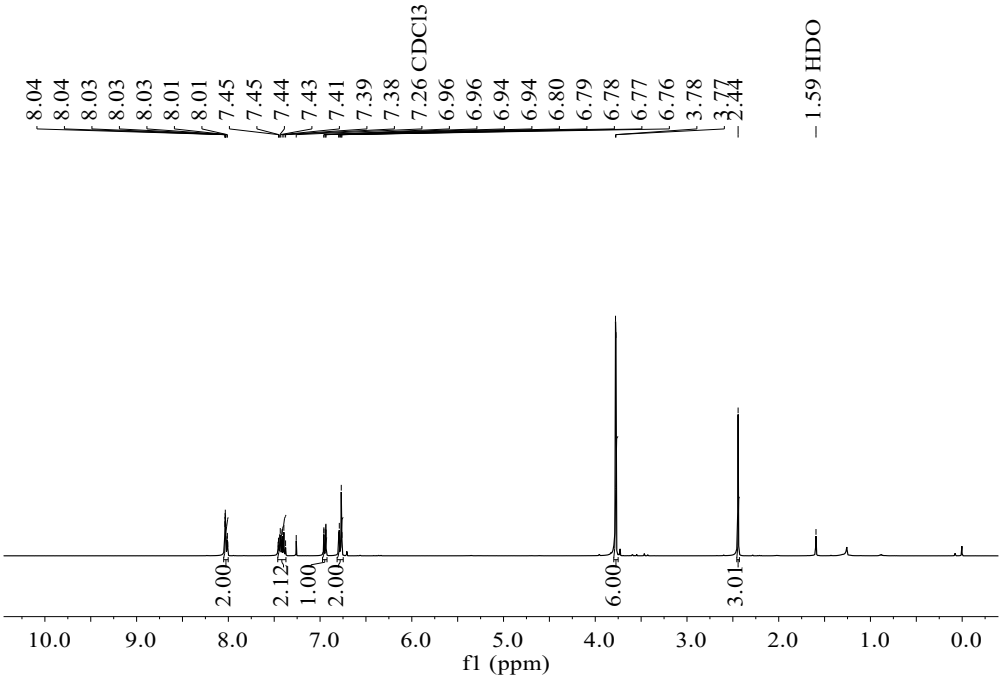


Compound **10**, ^{13}C NMR (101 MHz, $CDCl_3$)

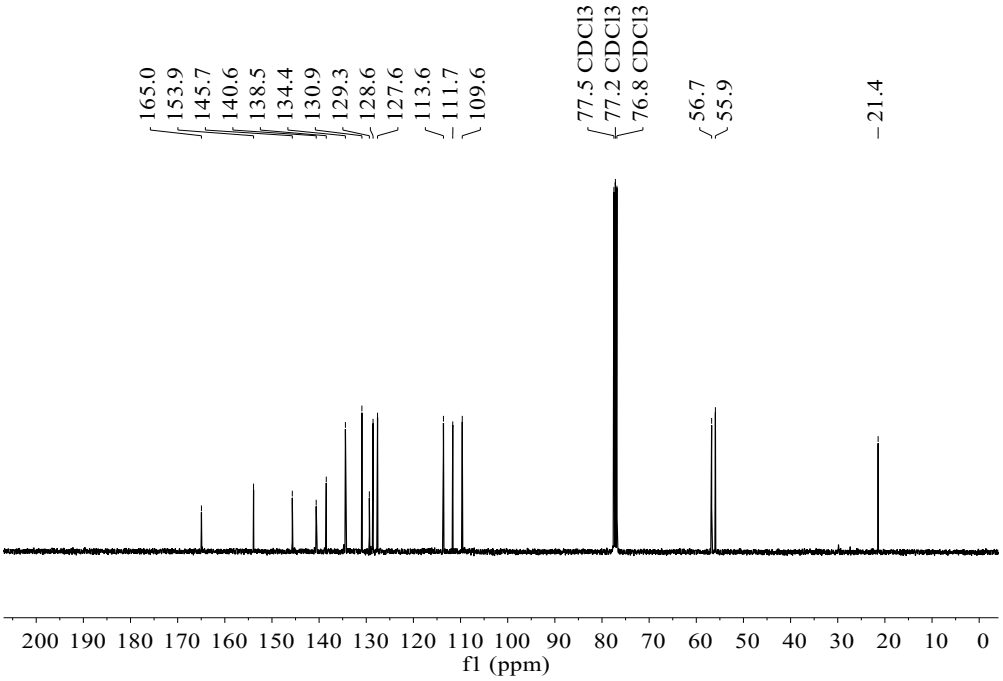


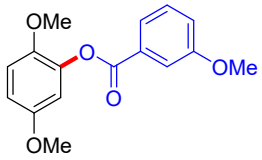


Compound **11**, ^{1}H NMR (400 MHz, $CDCl_3$)

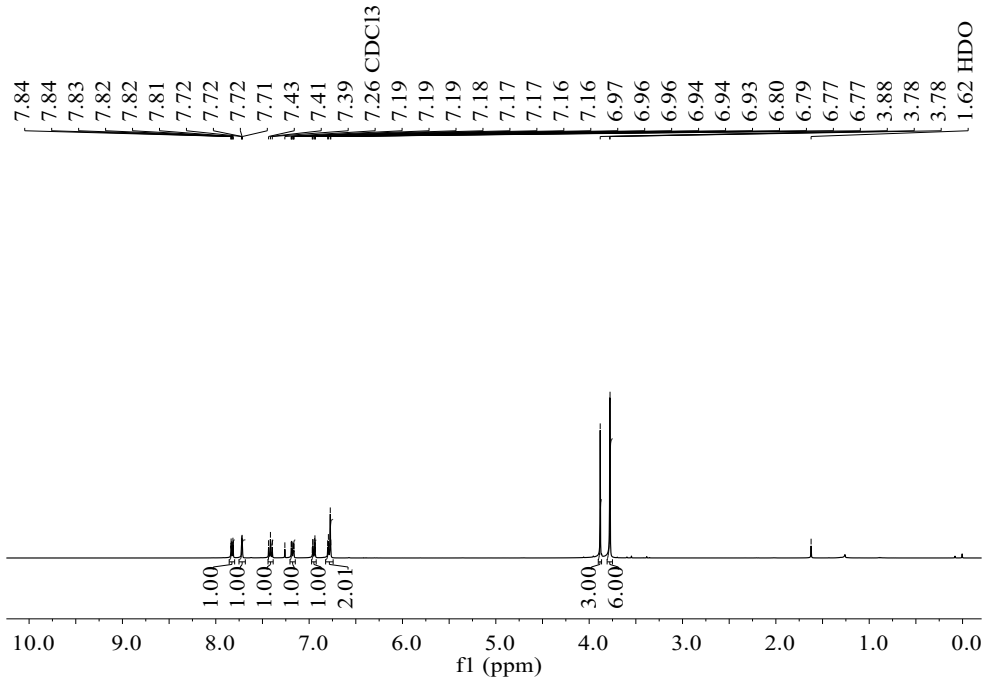


Compound **11**, ^{13}C NMR (101 MHz, $CDCl_3$)

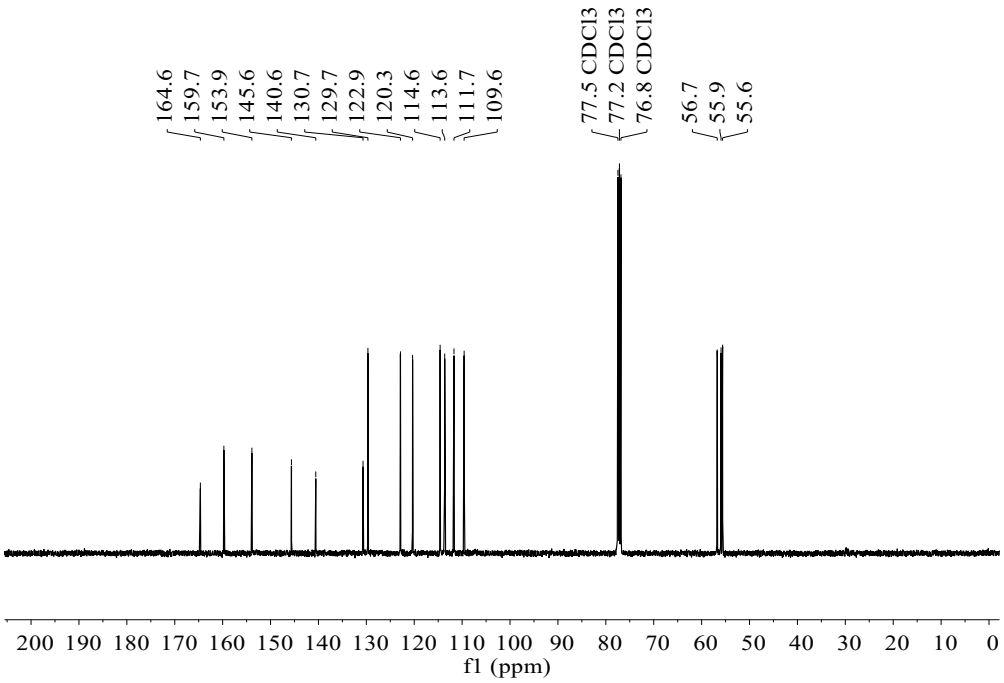


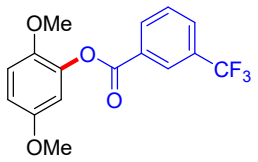


Compound **12**, ^{1}H NMR (400 MHz, $CDCl_3$)

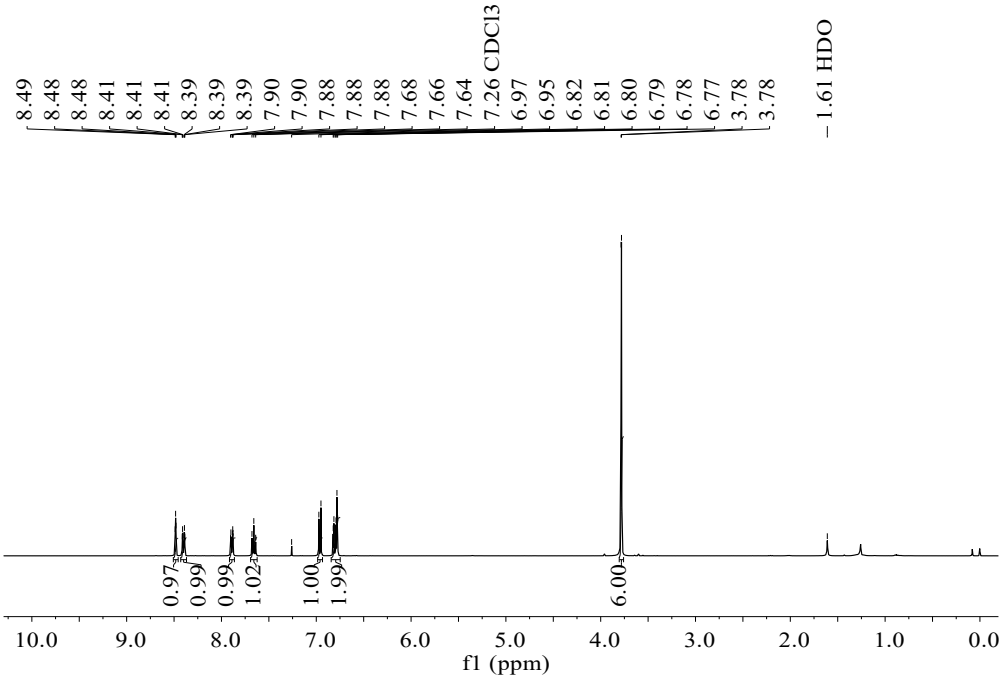


Compound **12**, ^{13}C NMR (101 MHz, $CDCl_3$)

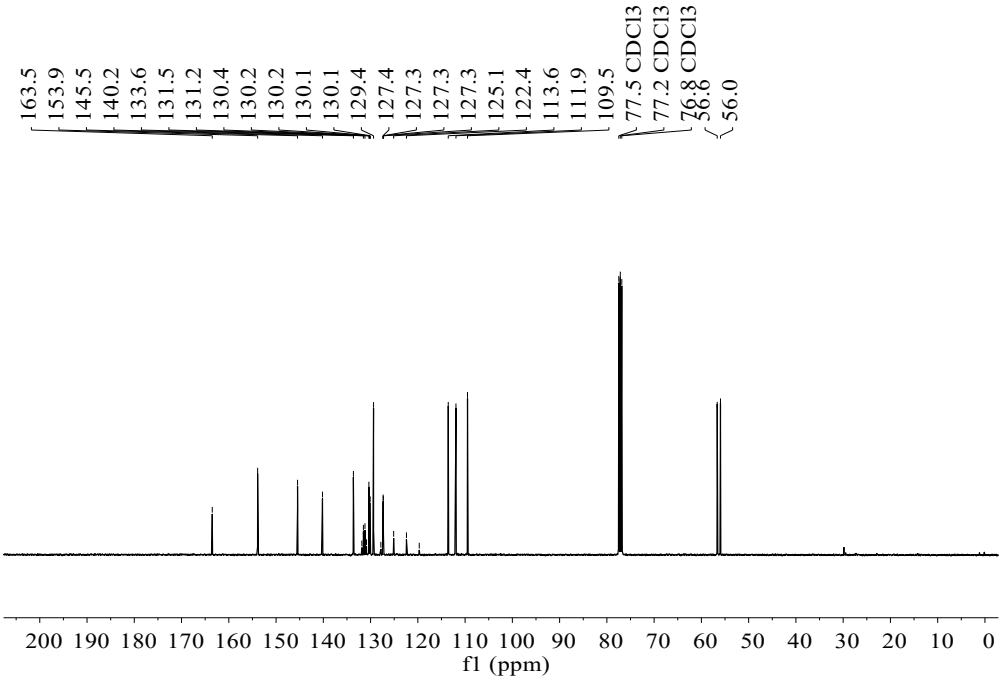




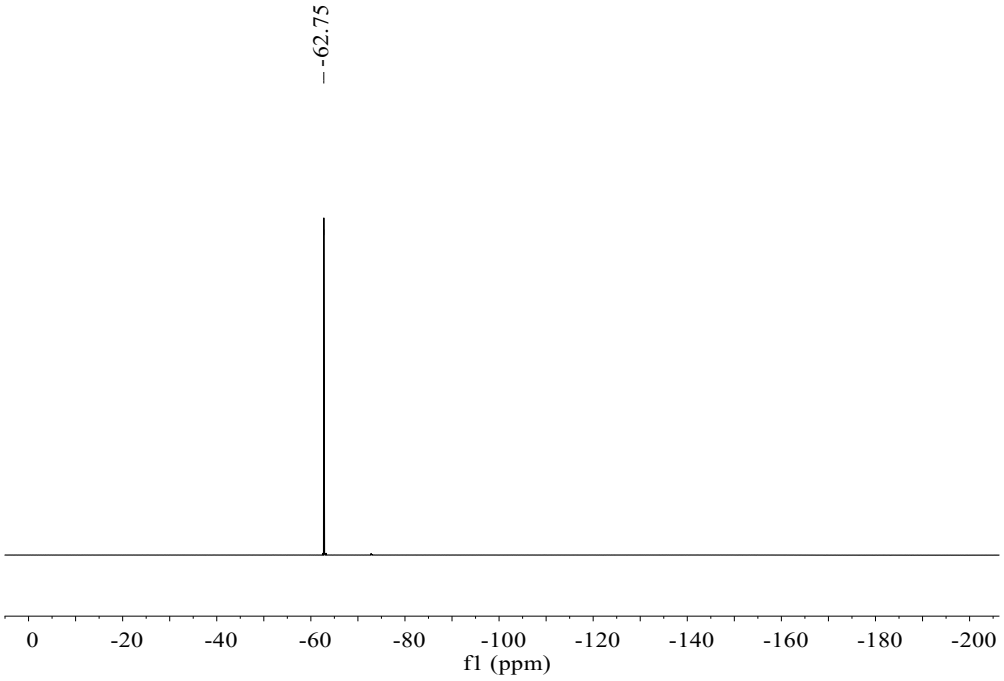
Compound **13**, ^{1}H NMR (400 MHz, $CDCl_3$)

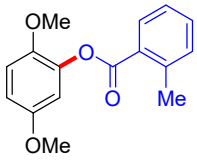


Compound **13**, ^{13}C NMR (101 MHz, $CDCl_3$)

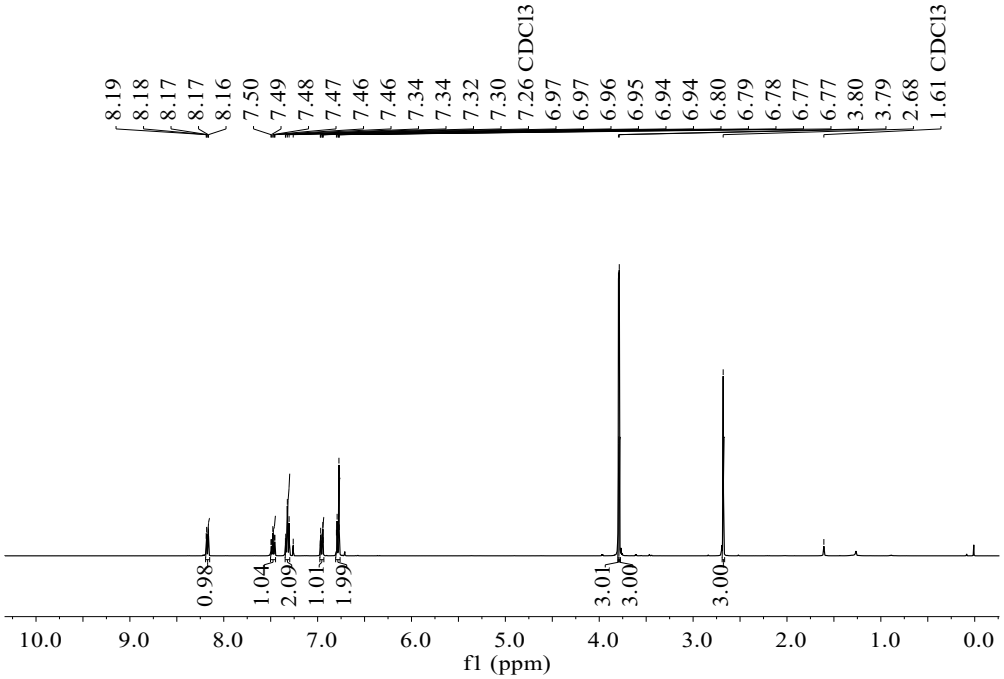


Compound **13**, ^{19}F NMR (376 MHz, $CDCl_3$)

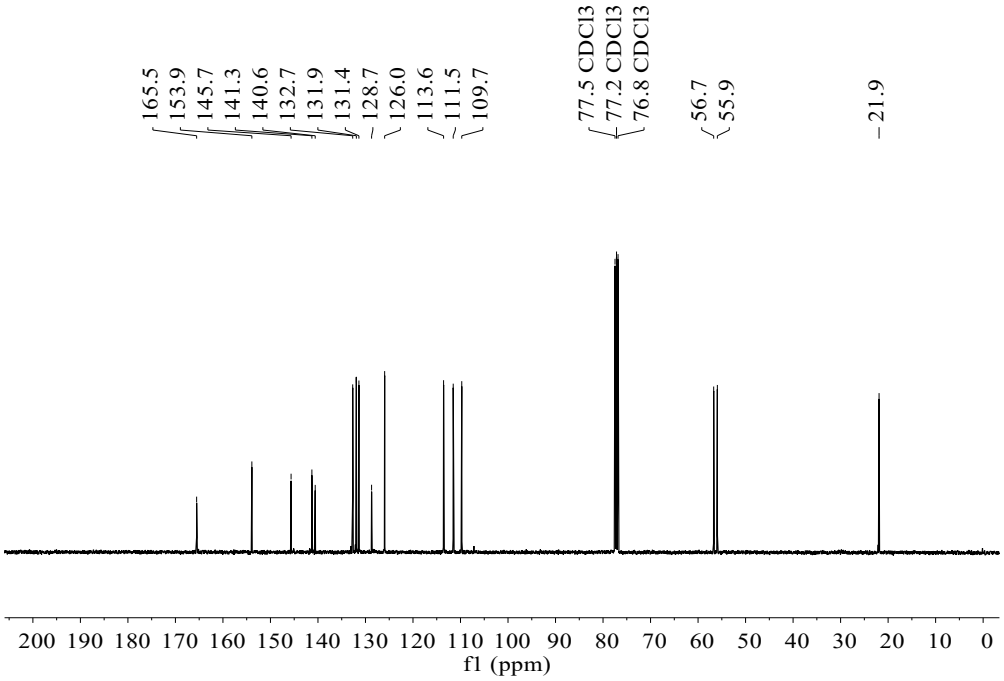


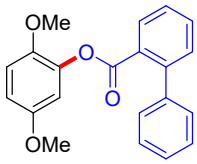


Compound **14**, ^{1}H NMR (400 MHz, $CDCl_3$)

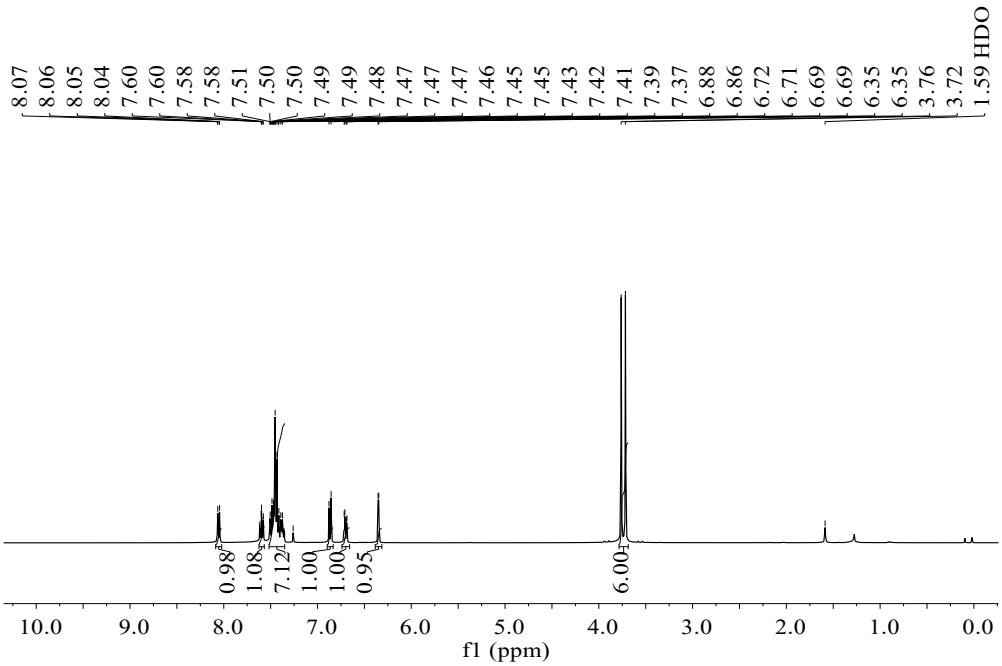


Compound **14**, ^{13}C NMR (101 MHz, $CDCl_3$)

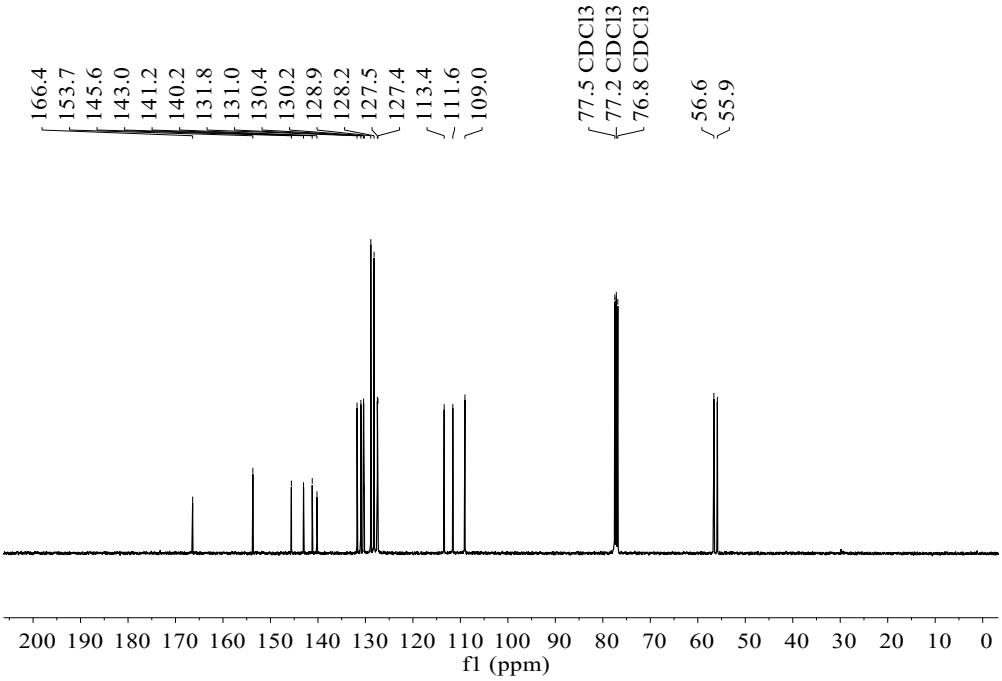


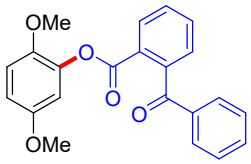


Compound **15**, ^{1}H NMR (400 MHz, $CDCl_3$)

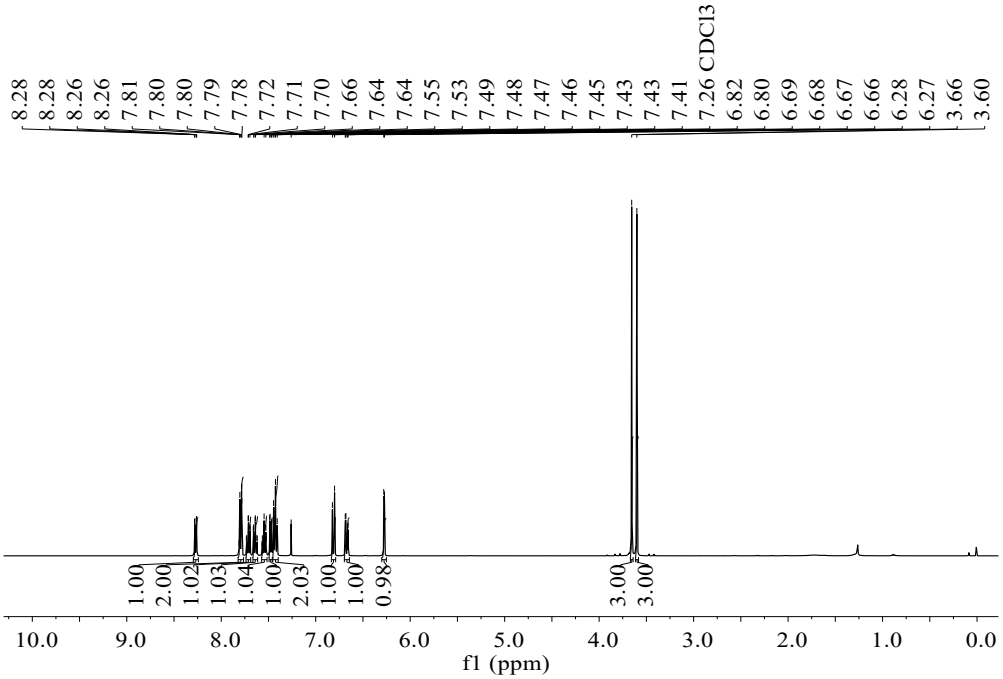


Compound **15**, ^{13}C NMR (101 MHz, $CDCl_3$)

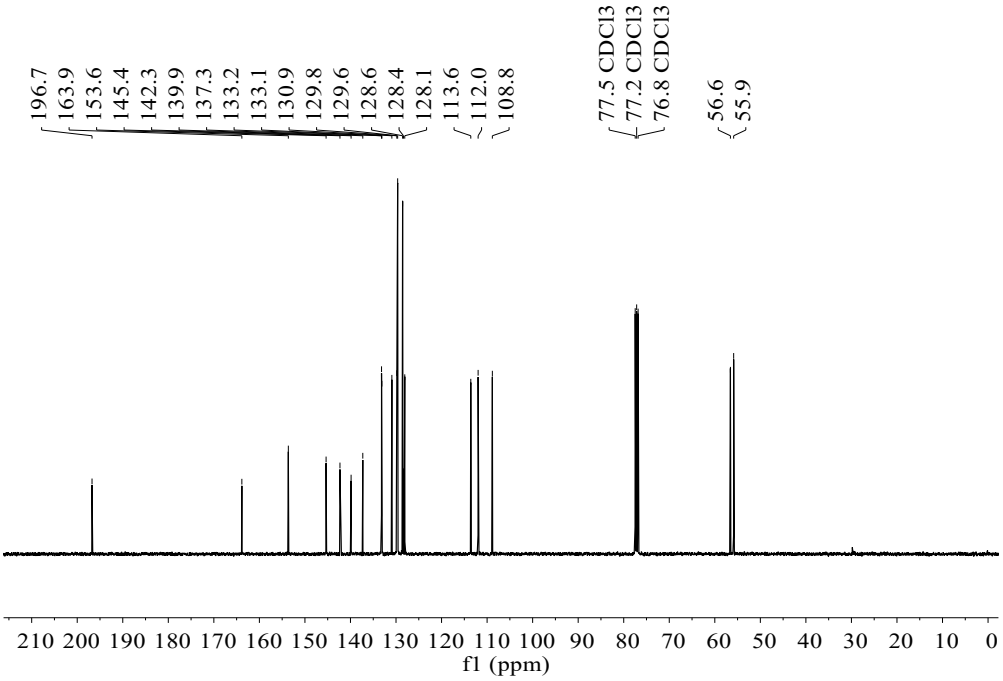


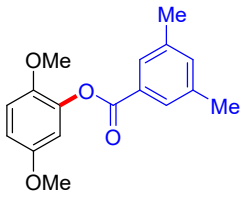


Compound **16**, ^{1}H NMR (400 MHz, $CDCl_3$)

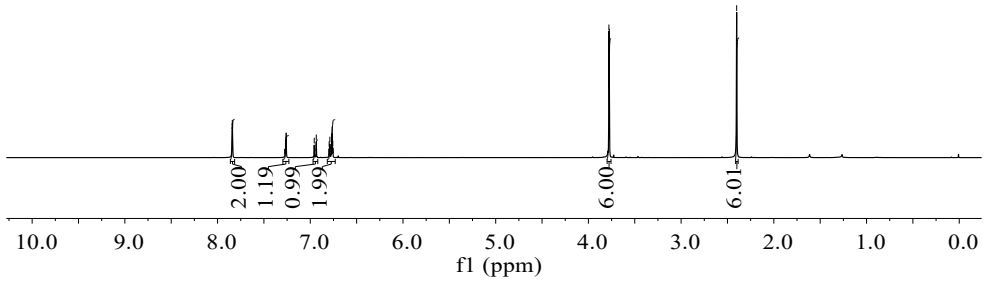


Compound **16**, ^{13}C NMR (101 MHz, $CDCl_3$)

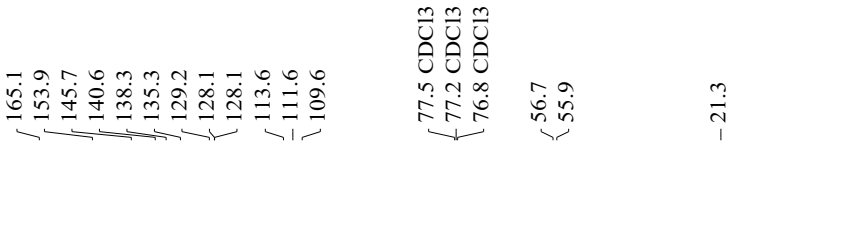


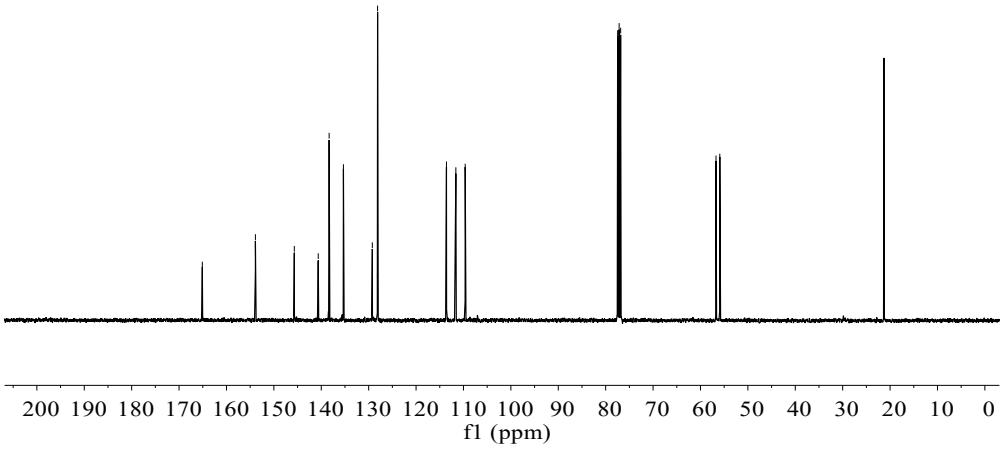


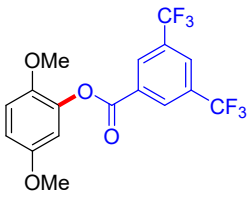
Compound **17**, ^{1}H NMR (400 MHz, $CDCl_3$)



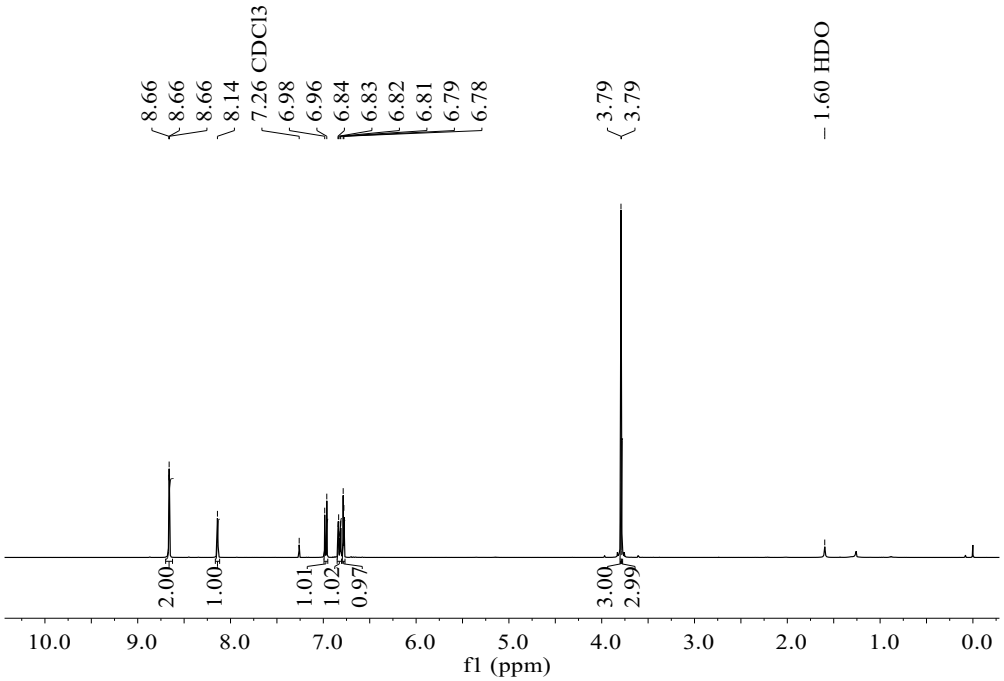
Compound **17**, ^{13}C NMR (101 MHz, $CDCl_3$)



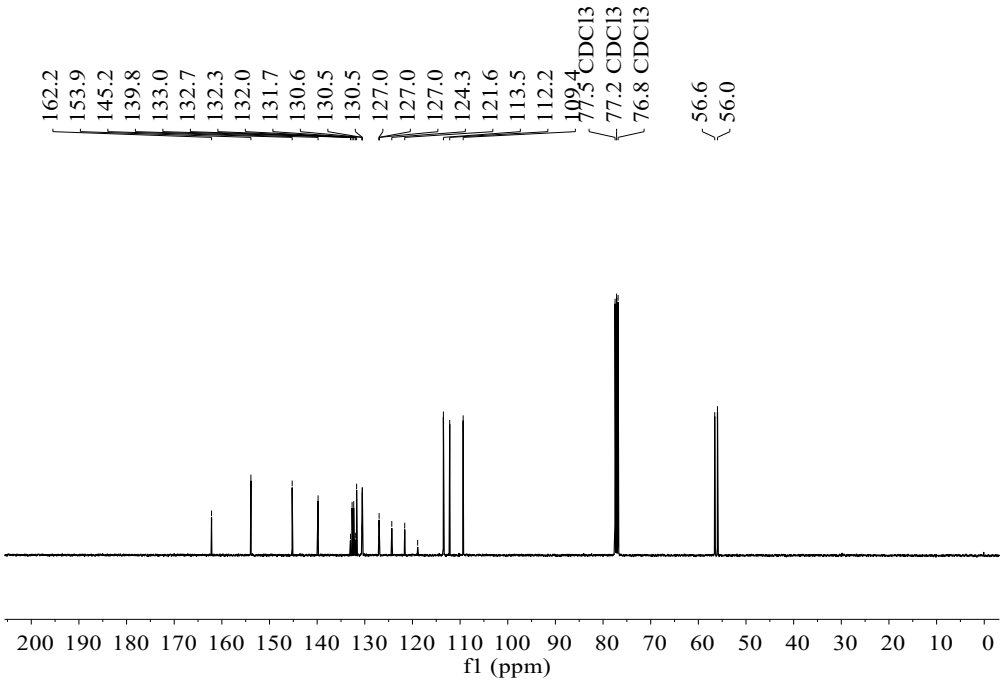




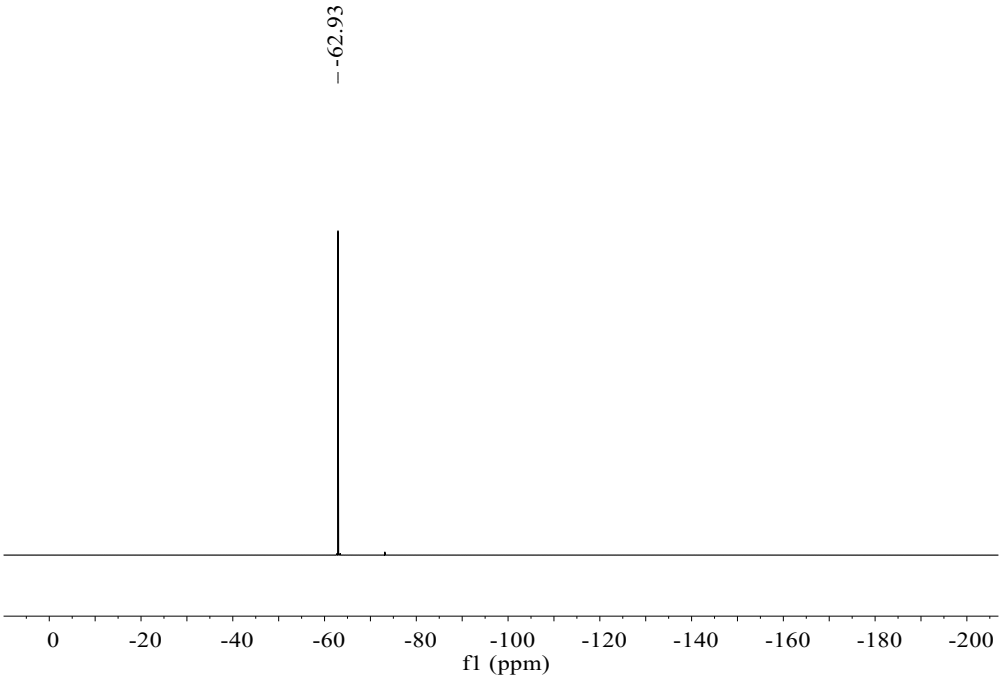
Compound **18**, ^{1}H NMR (400 MHz, $CDCl_3$)

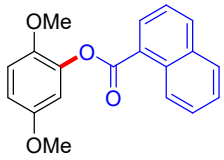


Compound **18**, ^{13}C NMR (101 MHz, $CDCl_3$)

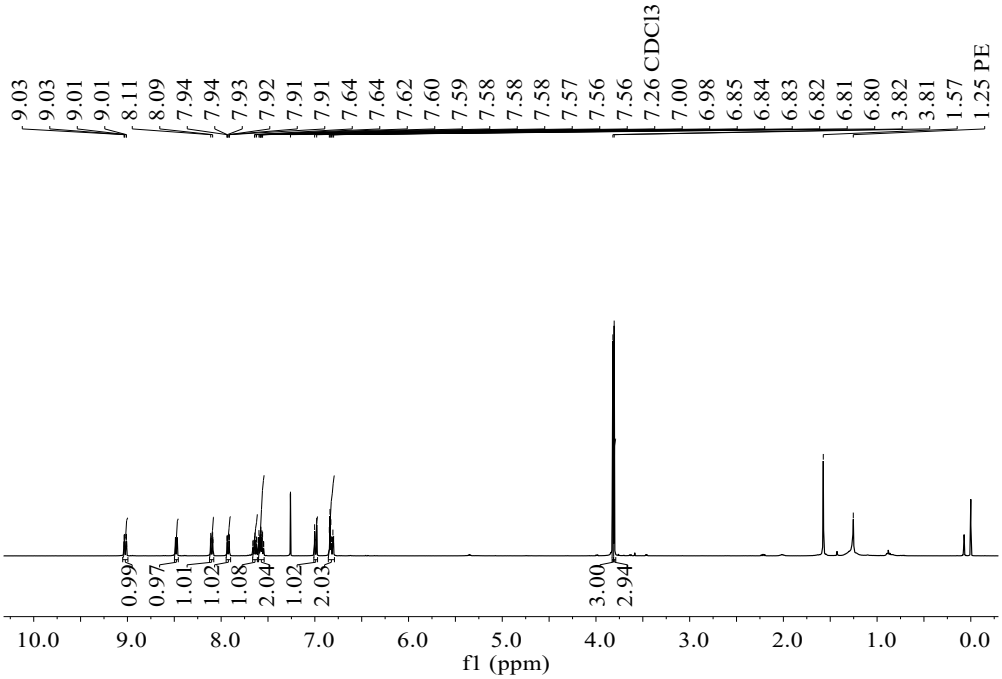


Compound **18**, ^{19}F NMR (376 MHz, $CDCl_3$)

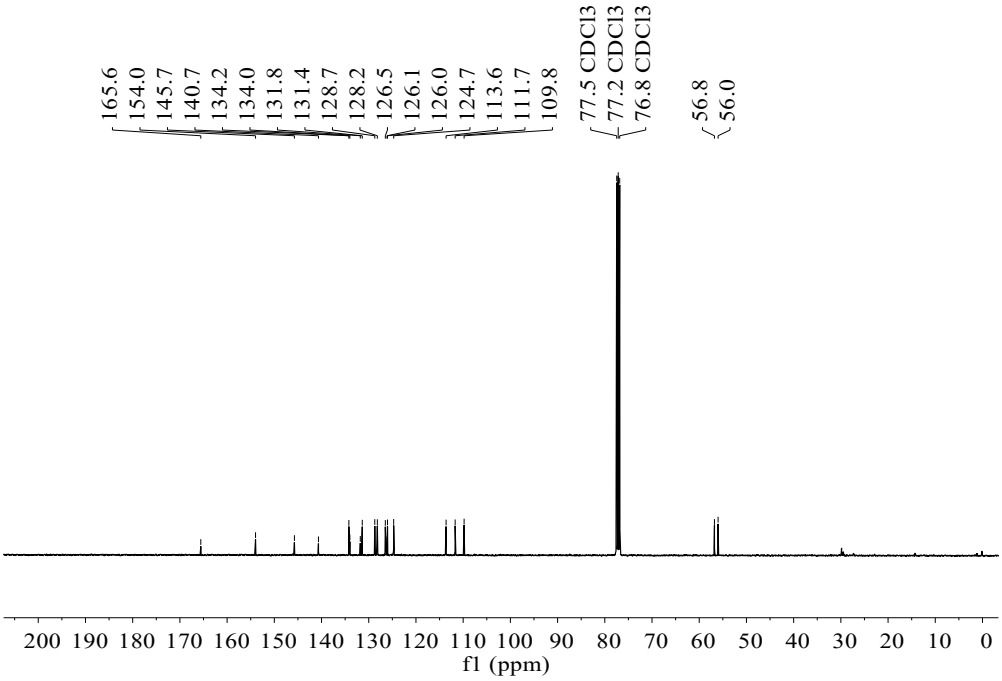


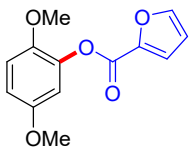


Compound **19**, ^{1}H NMR (400 MHz, $CDCl_3$)

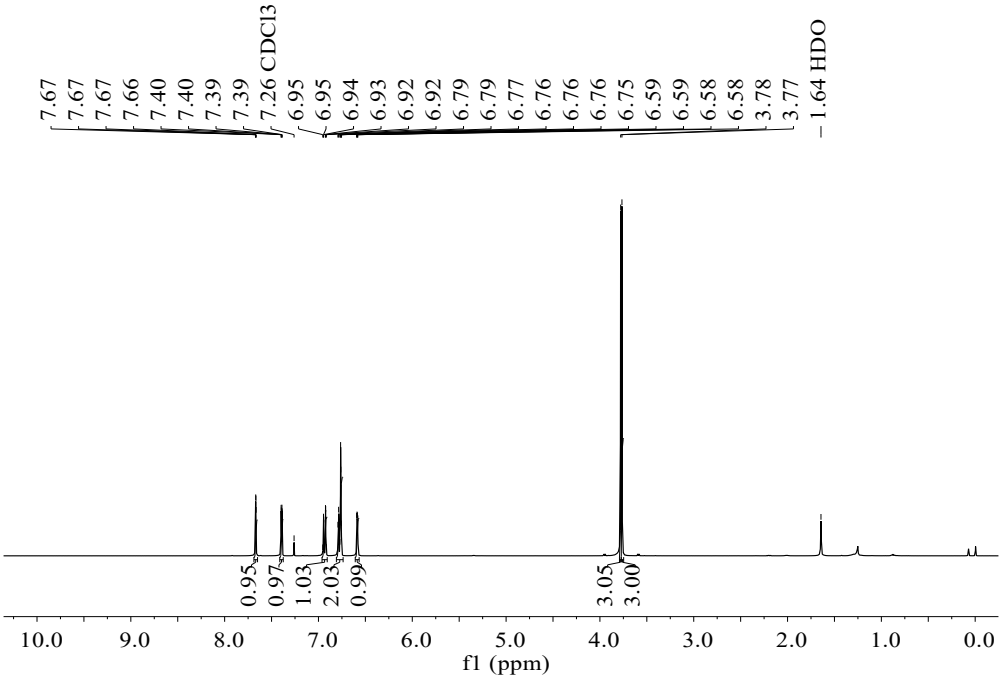


Compound **19**, ^{13}C NMR (101 MHz, $CDCl_3$)

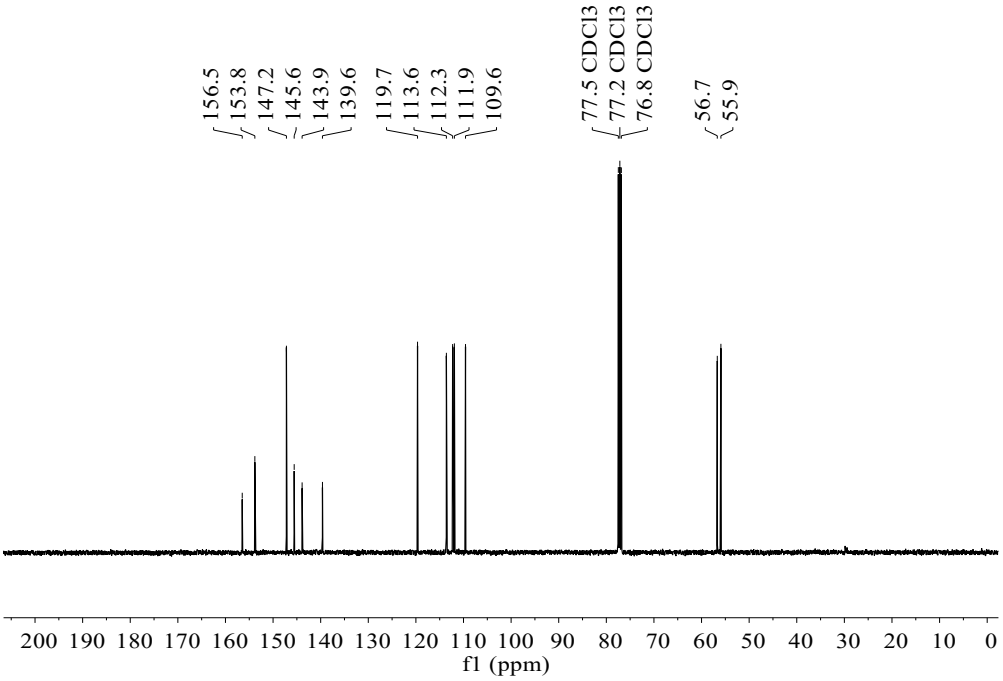


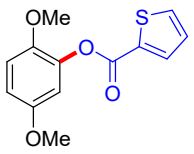


Compound **20**, ^{1}H NMR (400 MHz, $CDCl_3$)

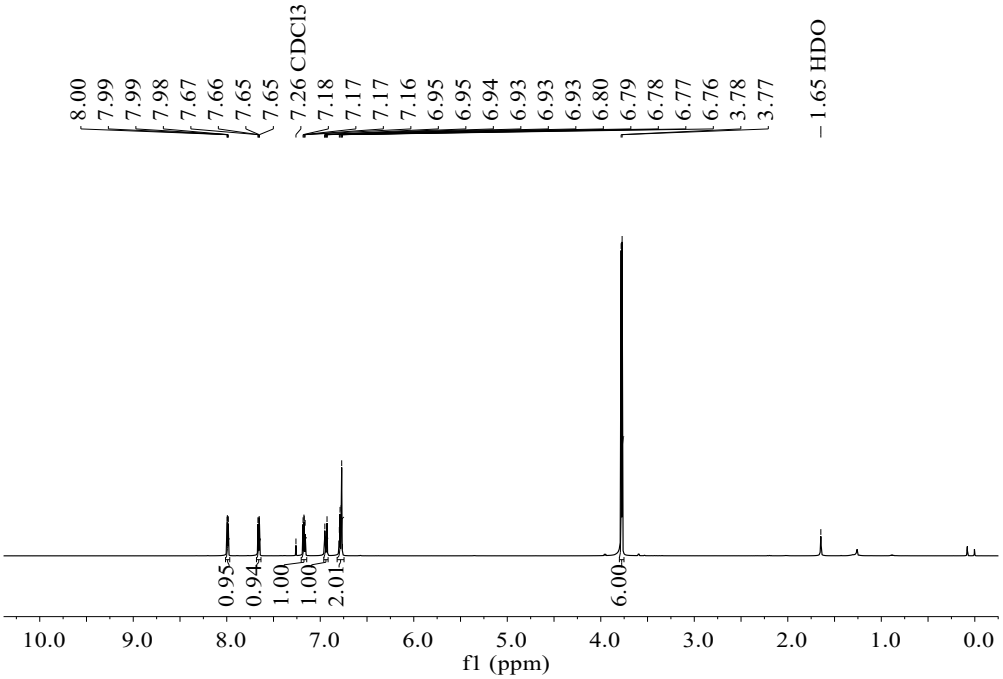


Compound **20**, ^{13}C NMR (101 MHz, $CDCl_3$)

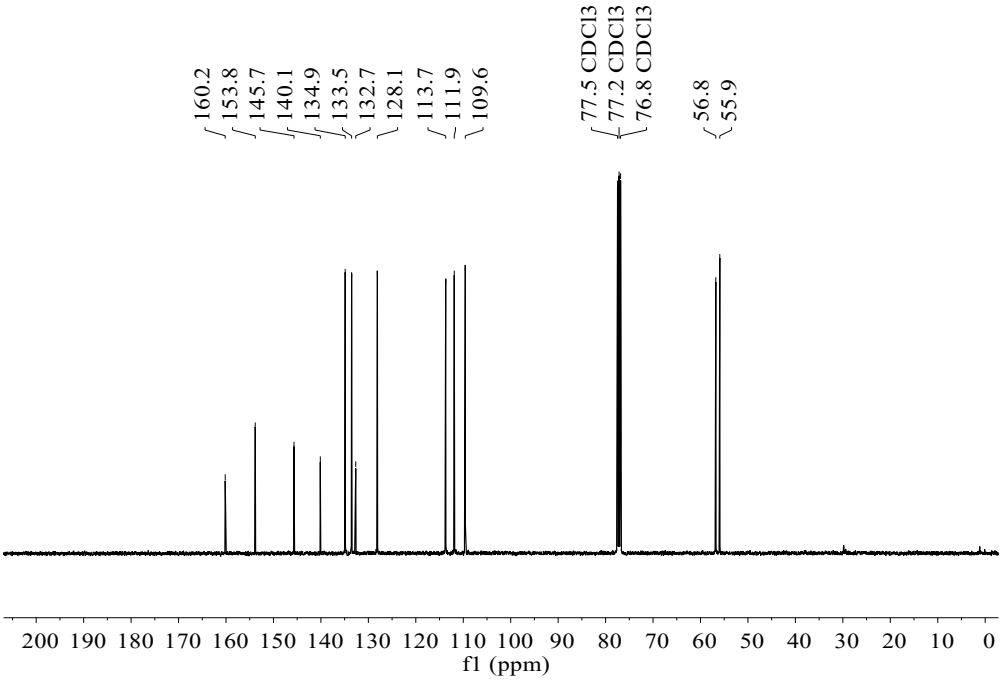


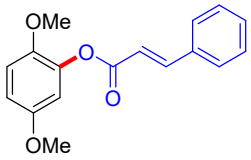


Compound **21**, ^{1}H NMR (400 MHz, $CDCl_3$)

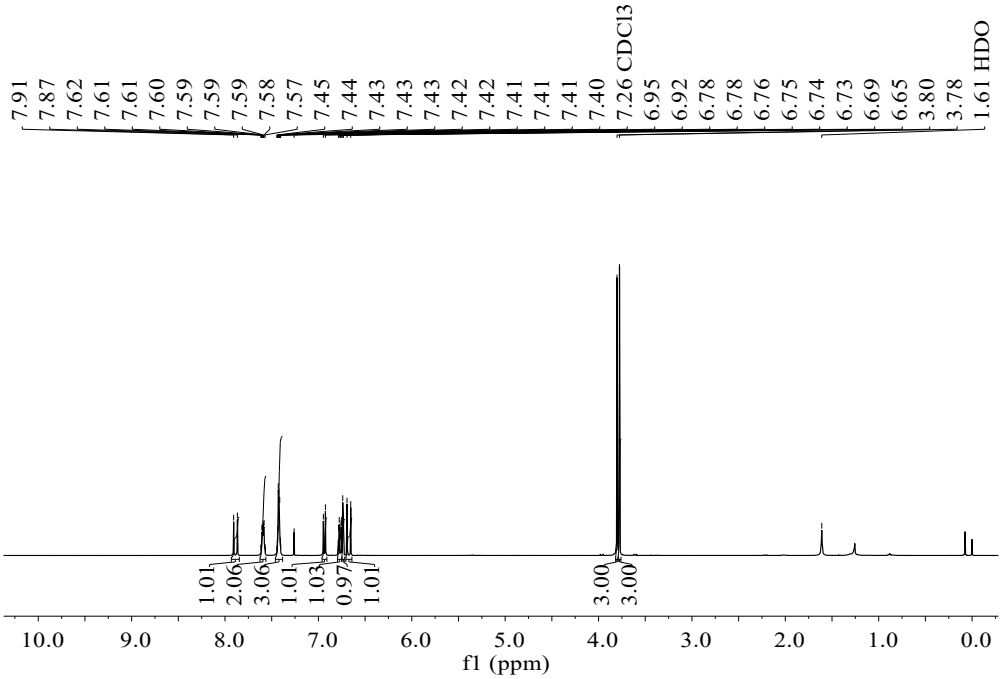


Compound **21**, ^{13}C NMR (101 MHz, $CDCl_3$)

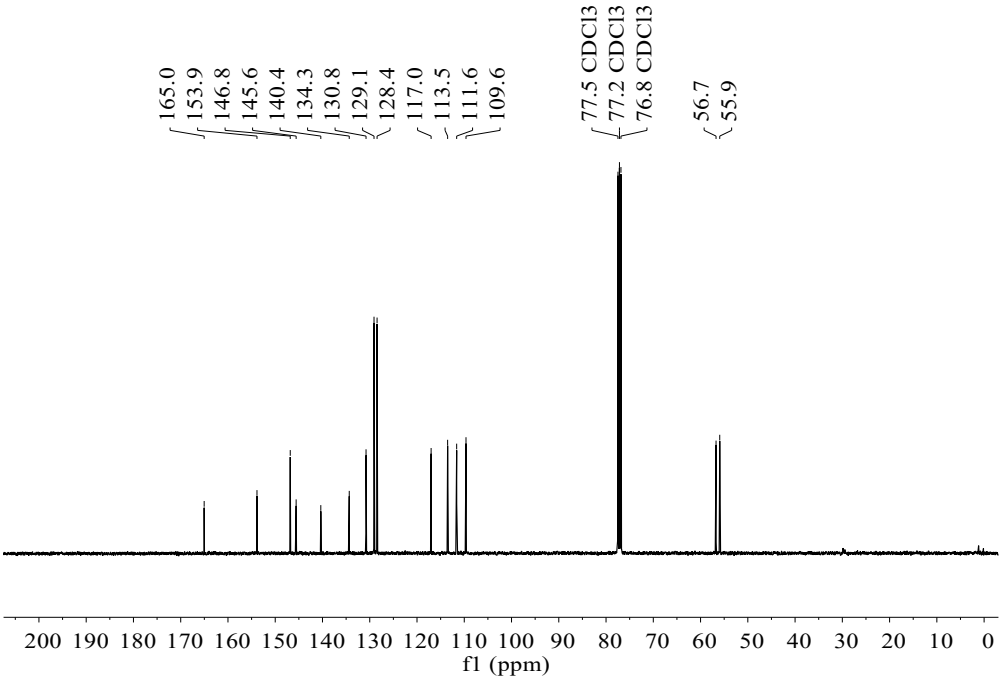


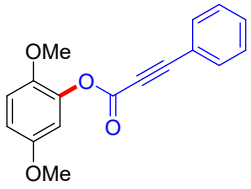


Compound **22**, ^{1}H NMR (400 MHz, $CDCl_3$)

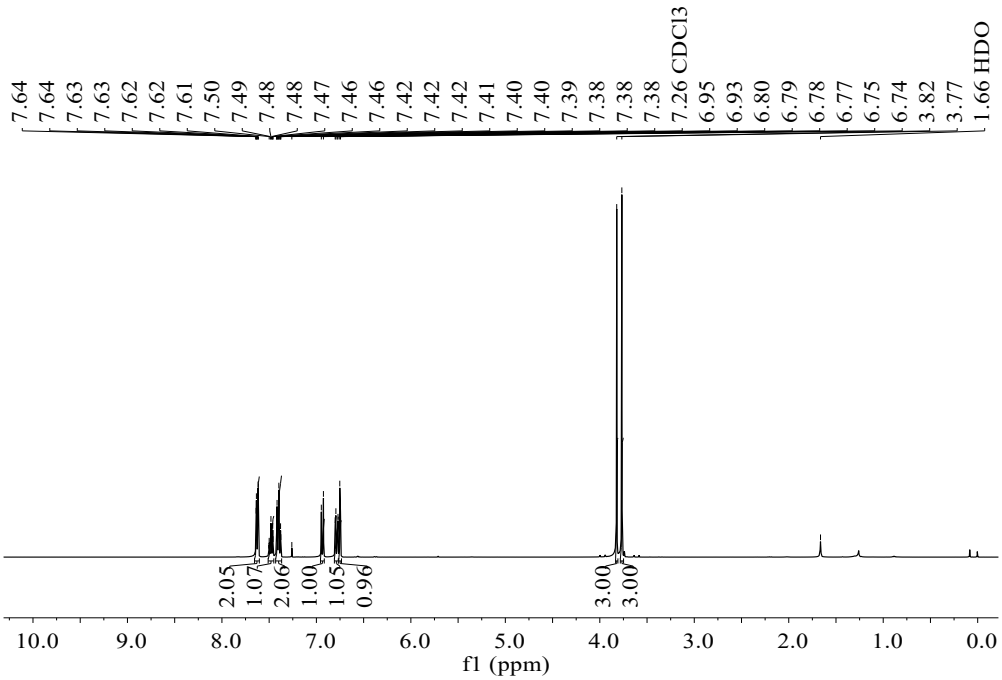


Compound **22**, ^{13}C NMR (101 MHz, $CDCl_3$)

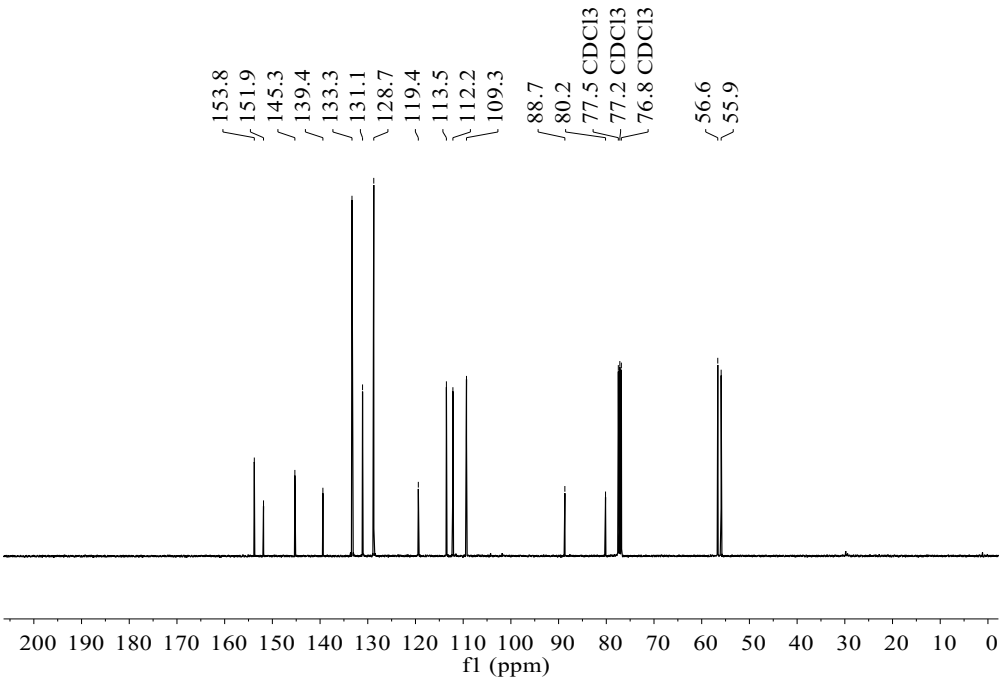


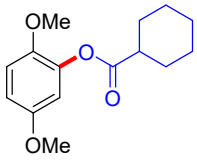


Compound **23**, ^{1}H NMR (400 MHz, $CDCl_3$)

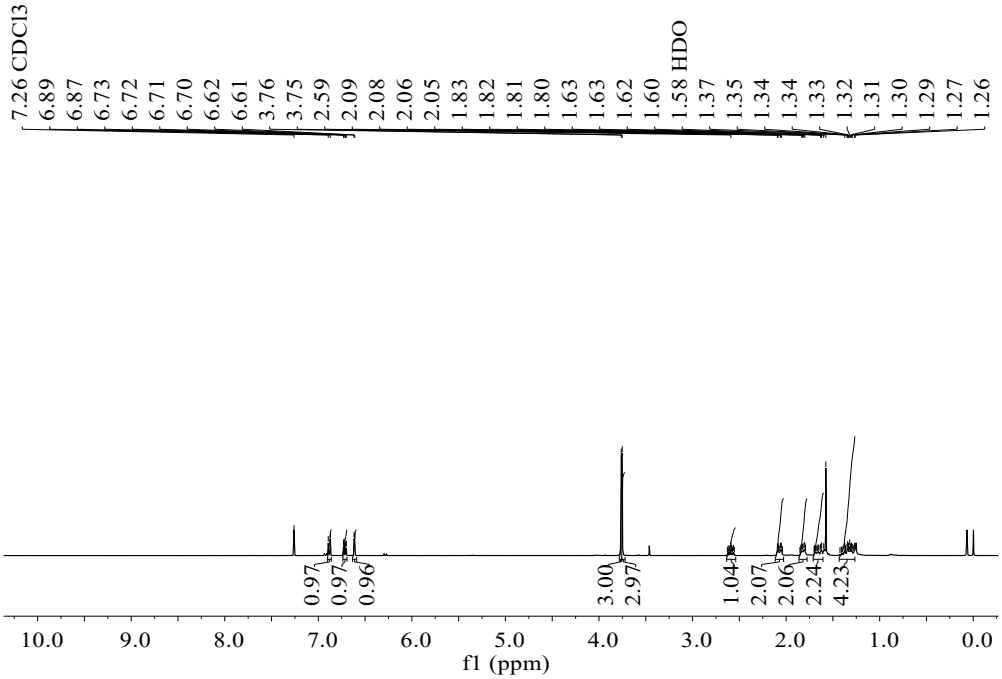


Compound **23**, ^{13}C NMR (101 MHz, $CDCl_3$)

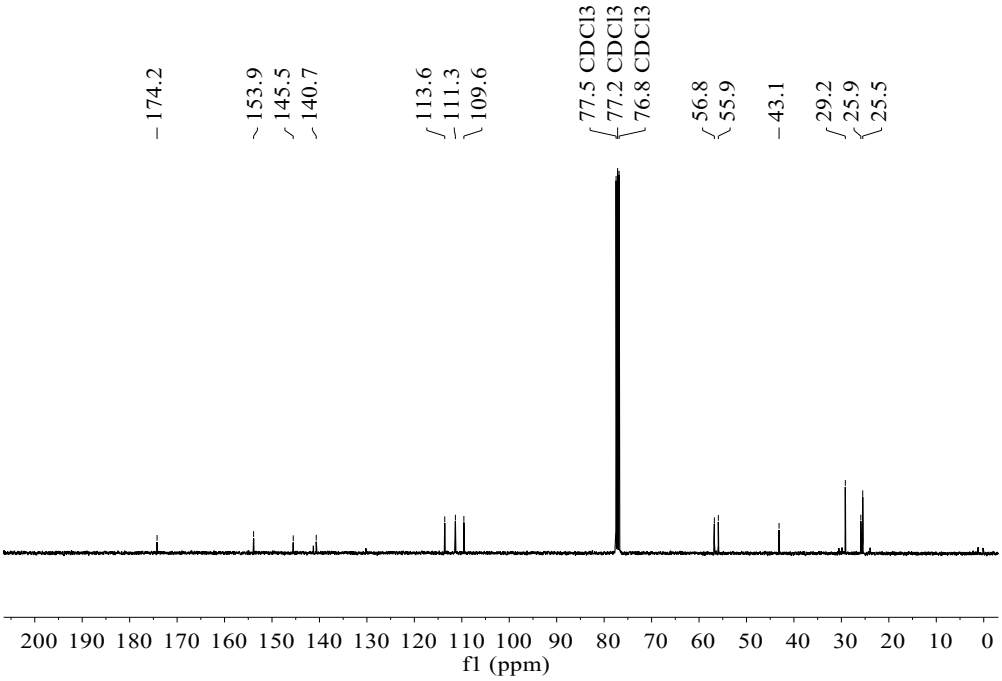


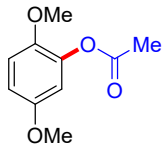


Compound **24**, ^{1}H NMR (400 MHz, $CDCl_3$)

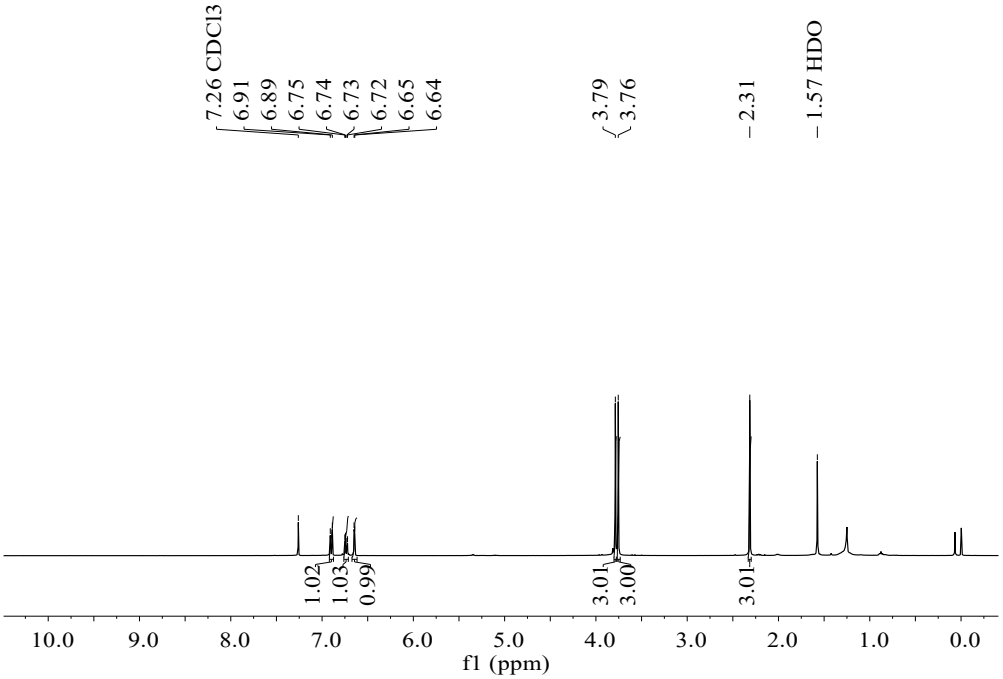


Compound **24**, ^{13}C NMR (101 MHz, $CDCl_3$)

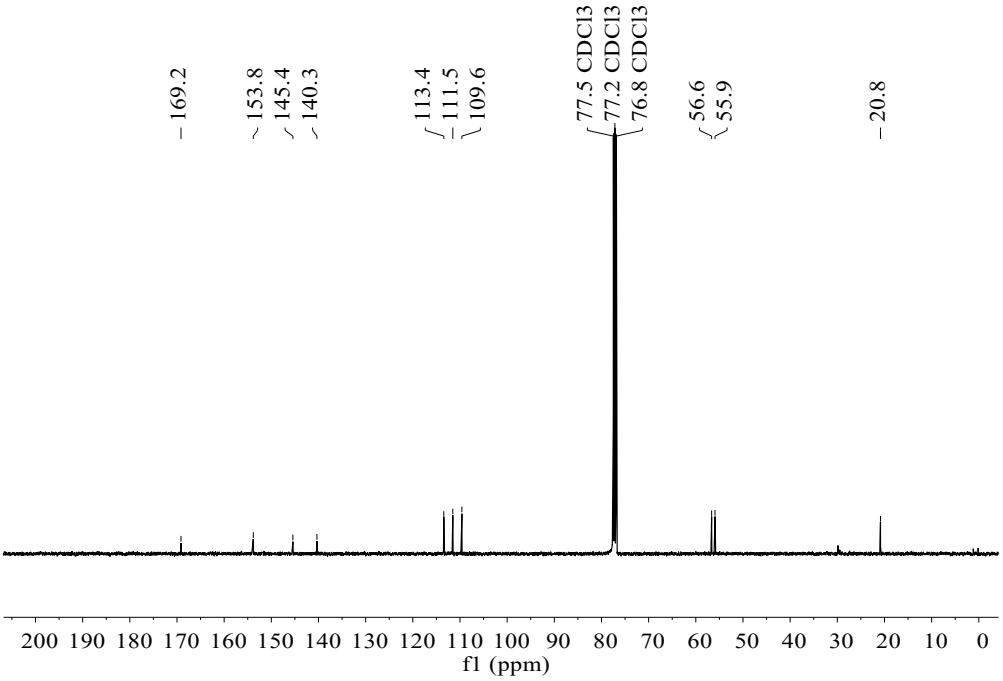


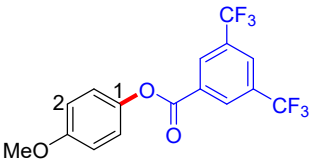


Compound **25**, ^{1}H NMR (400 MHz, $CDCl_3$)

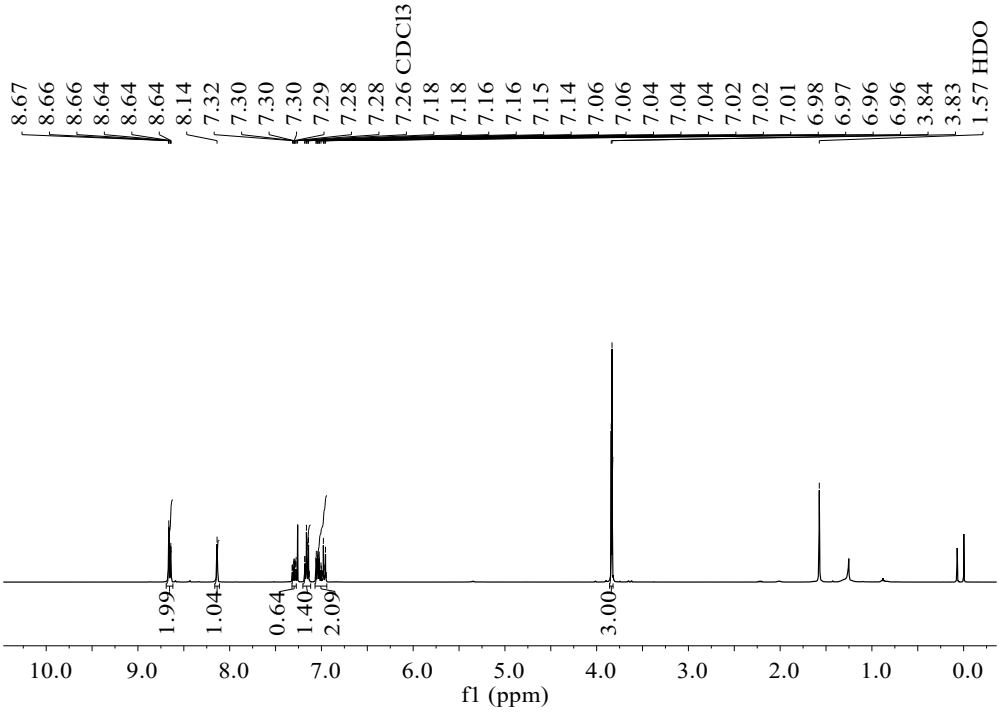


Compound **25**, ^{13}C NMR (101 MHz, $CDCl_3$)

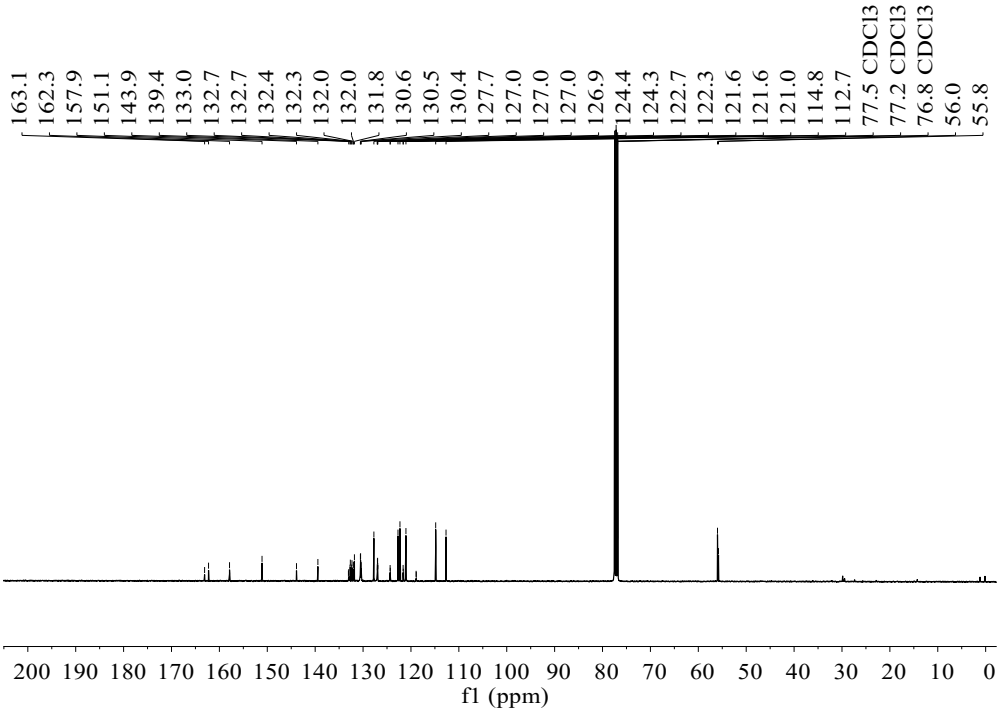




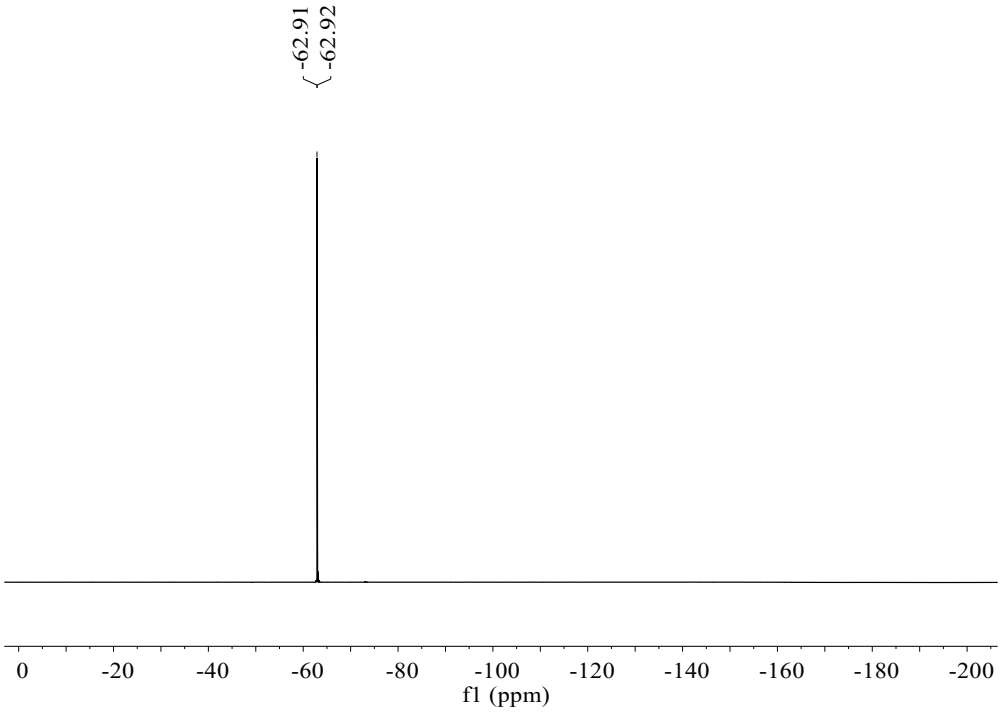
Compound **26** (C1:C2 = 1.5 :1), ^{1}H NMR (400 MHz, $CDCl_3$)

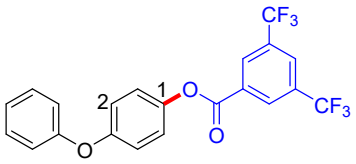


Compound **26** (C1:C2 = 1.5 :1), ^{13}C NMR (101 MHz, $CDCl_3$)

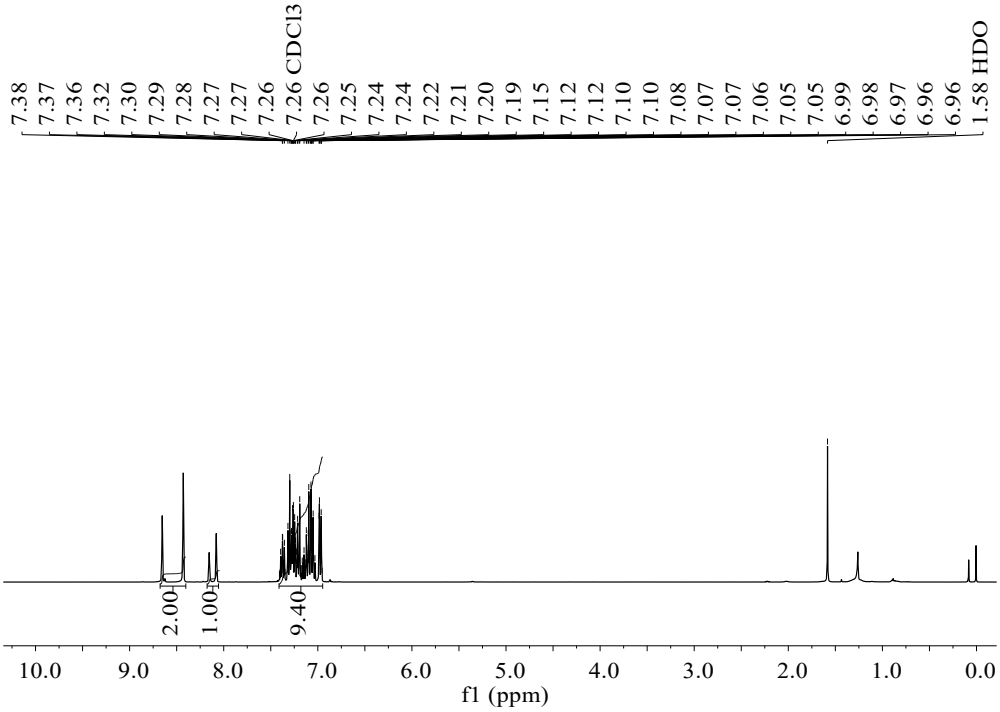


Compound **26** (C1:C2 = 1.5 :1), ^{19}F NMR (376 MHz, $CDCl_3$)

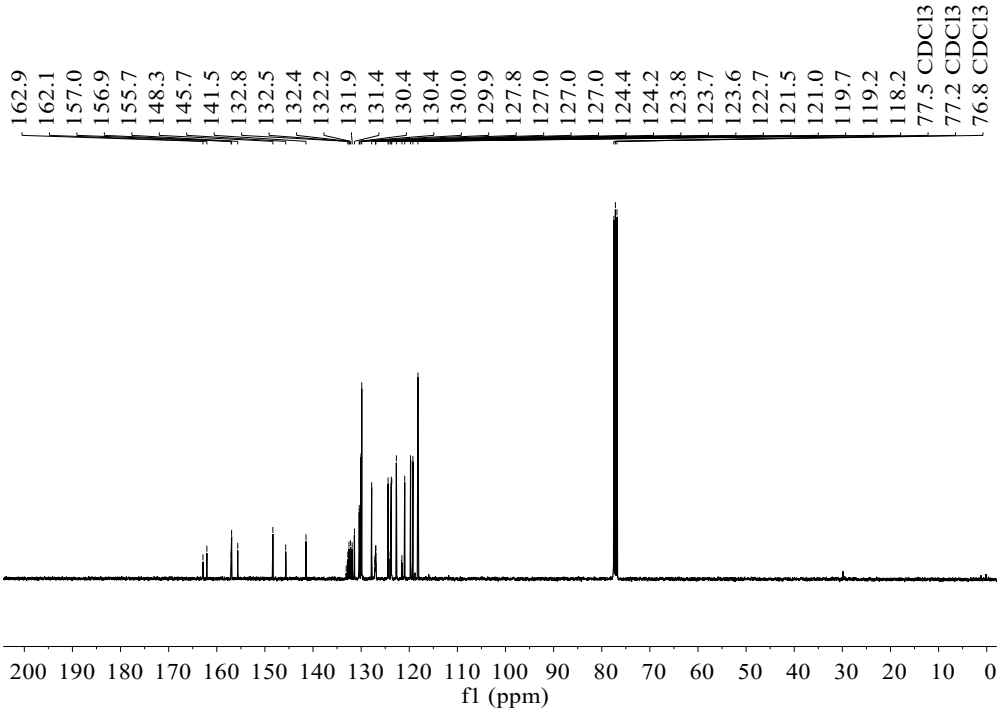




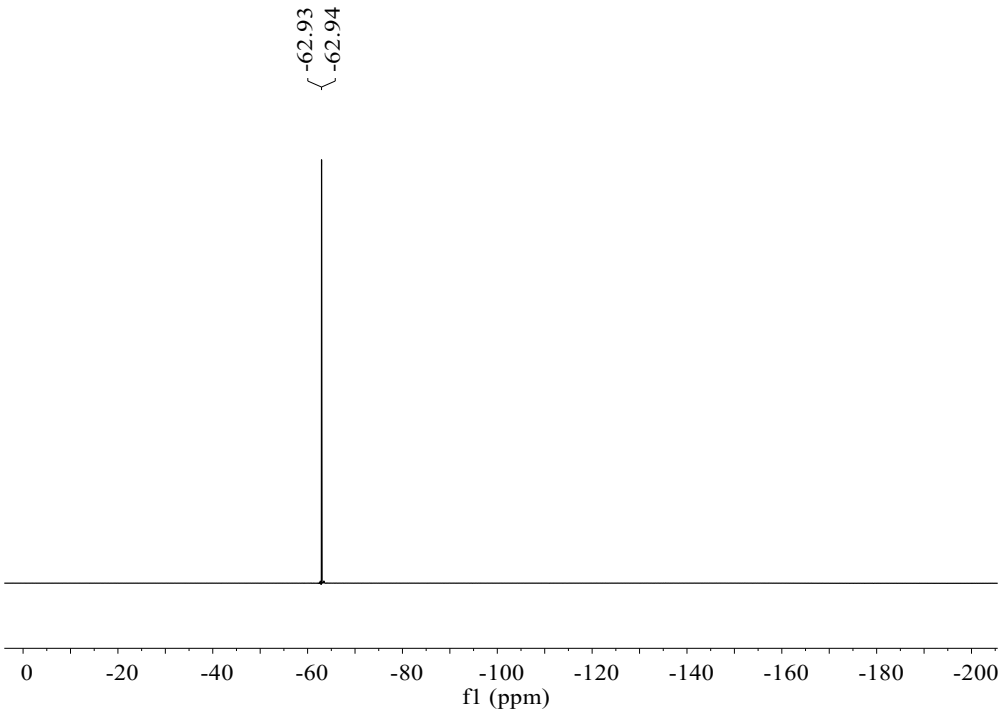
Compound **27** (C1:C2 = 1.6 :1), ^{1}H NMR (400 MHz, $CDCl_3$)

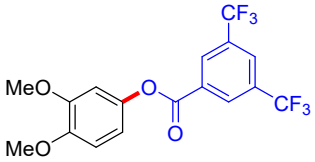


Compound **27** (C1:C2 = 1.6 :1), ^{13}C NMR (101 MHz, $CDCl_3$)

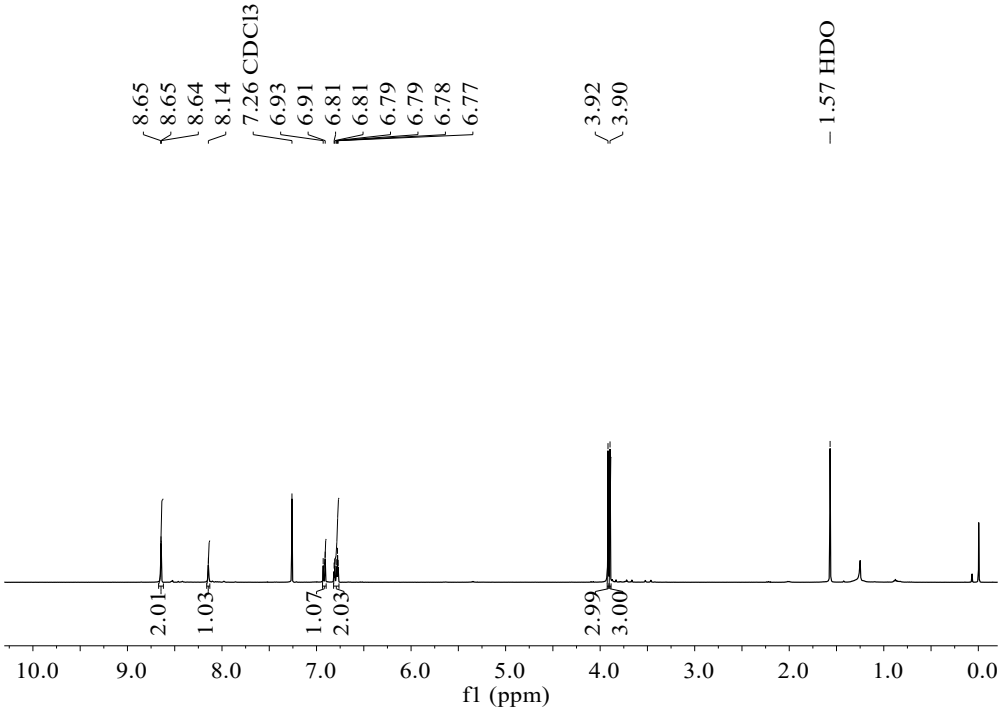


Compound **27** (C1:C2 = 1.6 :1), ^{19}F NMR (376 MHz, $CDCl_3$)

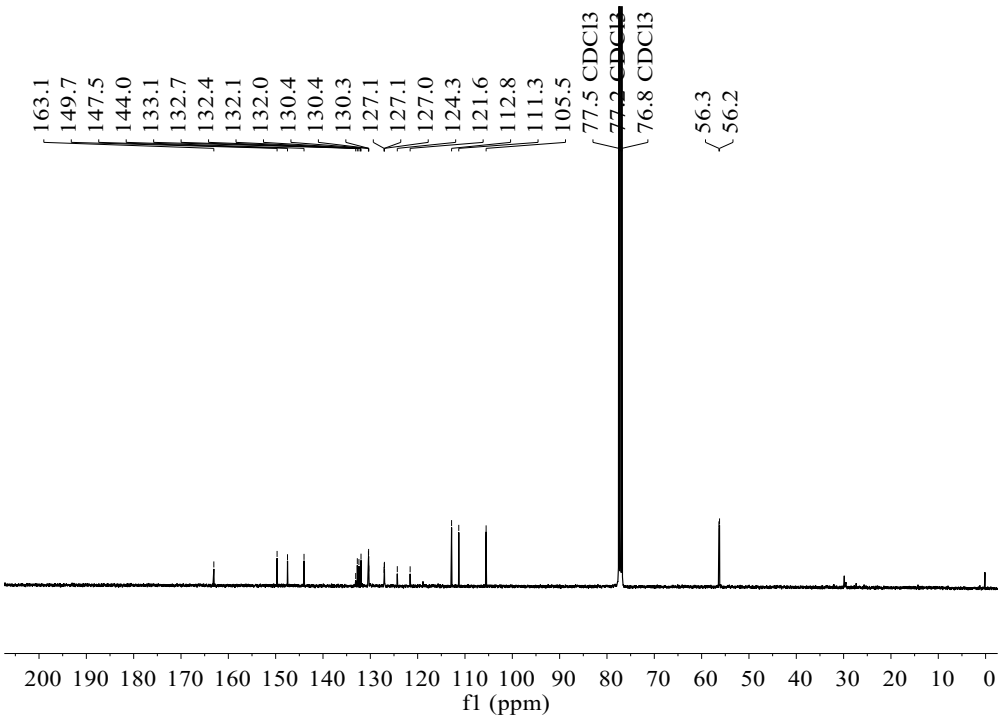




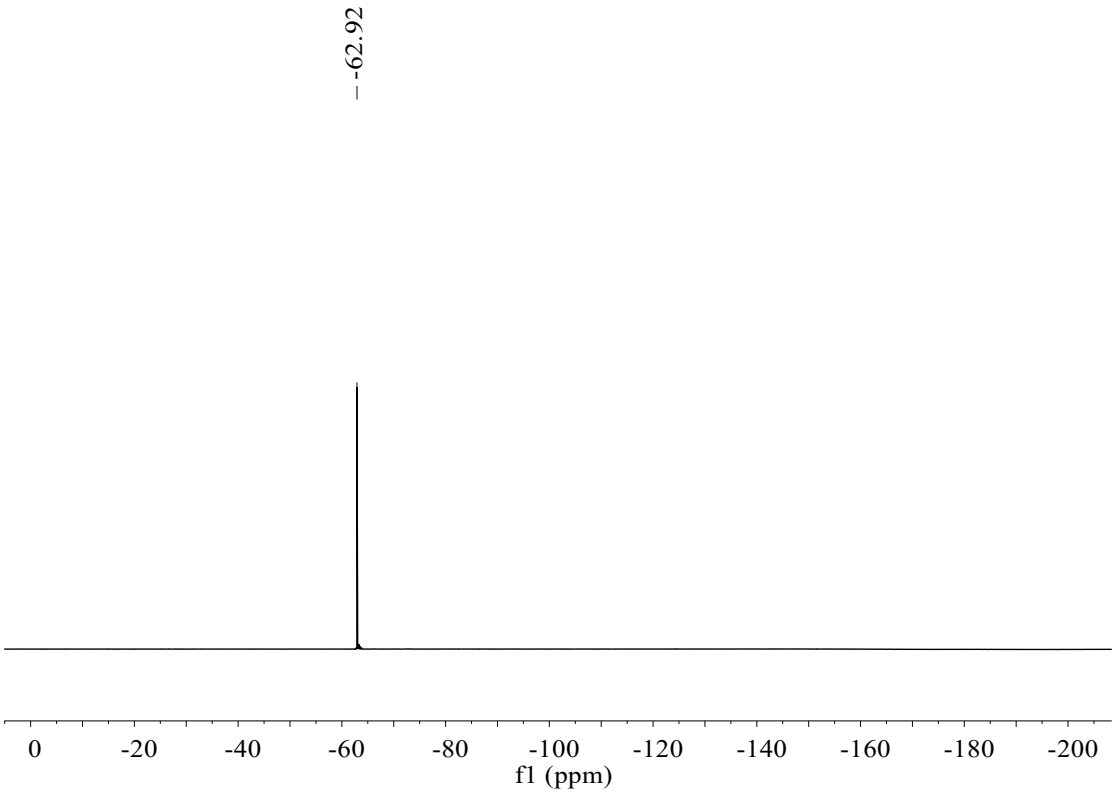
Compound **28**, ^{1}H NMR (400 MHz, $CDCl_3$)

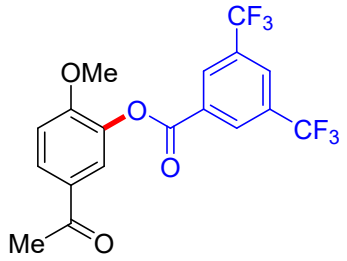


Compound **28**, ^{13}C NMR (101 MHz, $CDCl_3$)

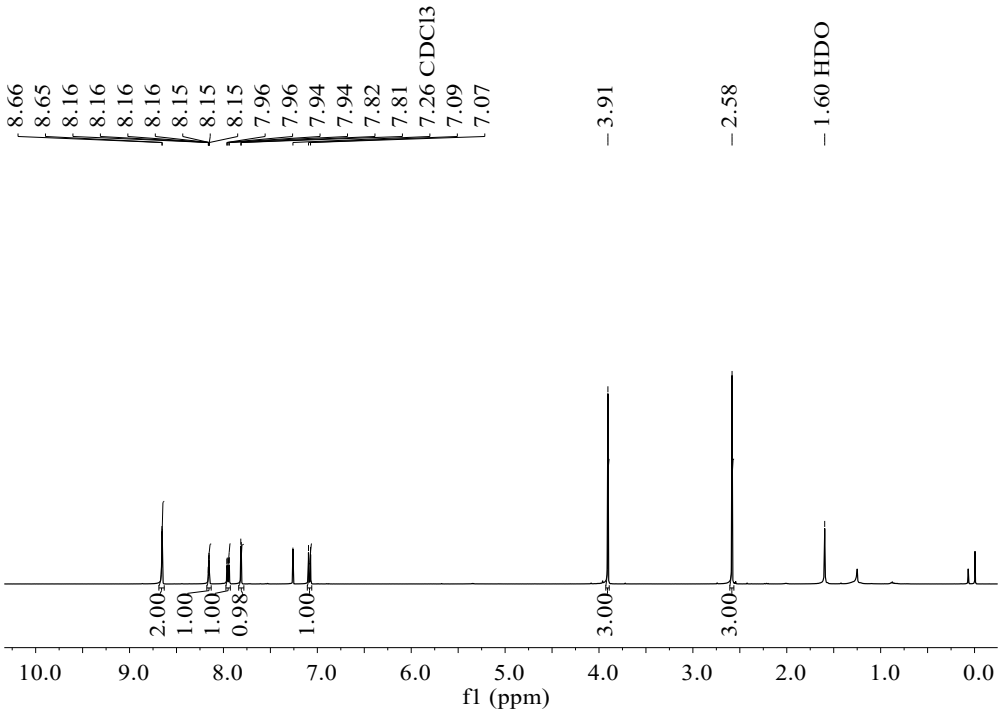


Compound **28**, ^{19}F NMR (376 MHz, $CDCl_3$)

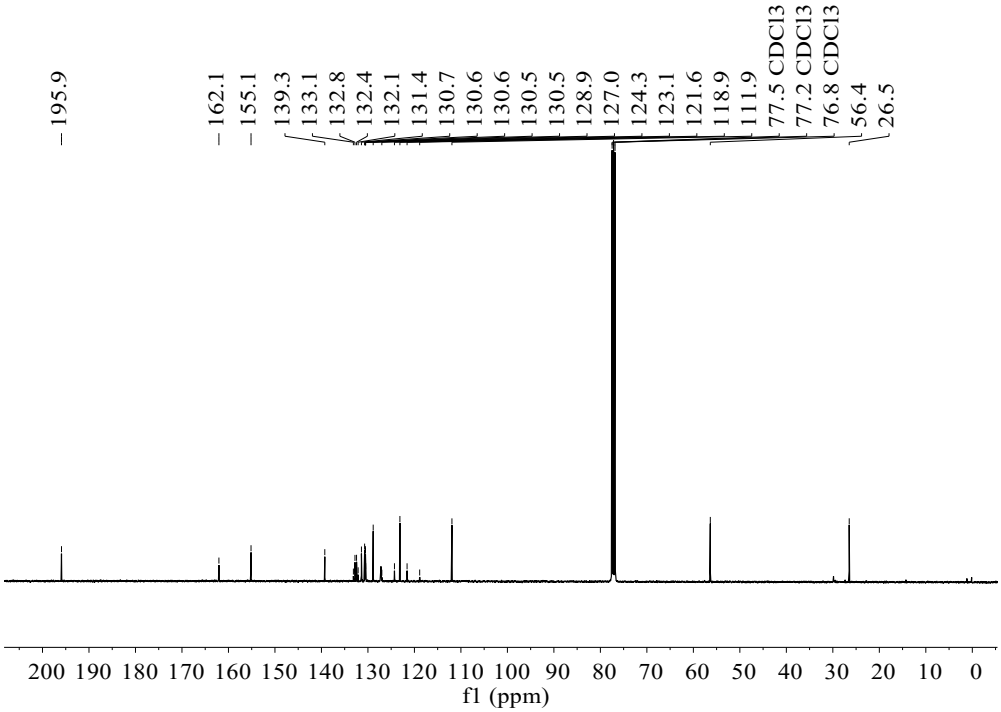




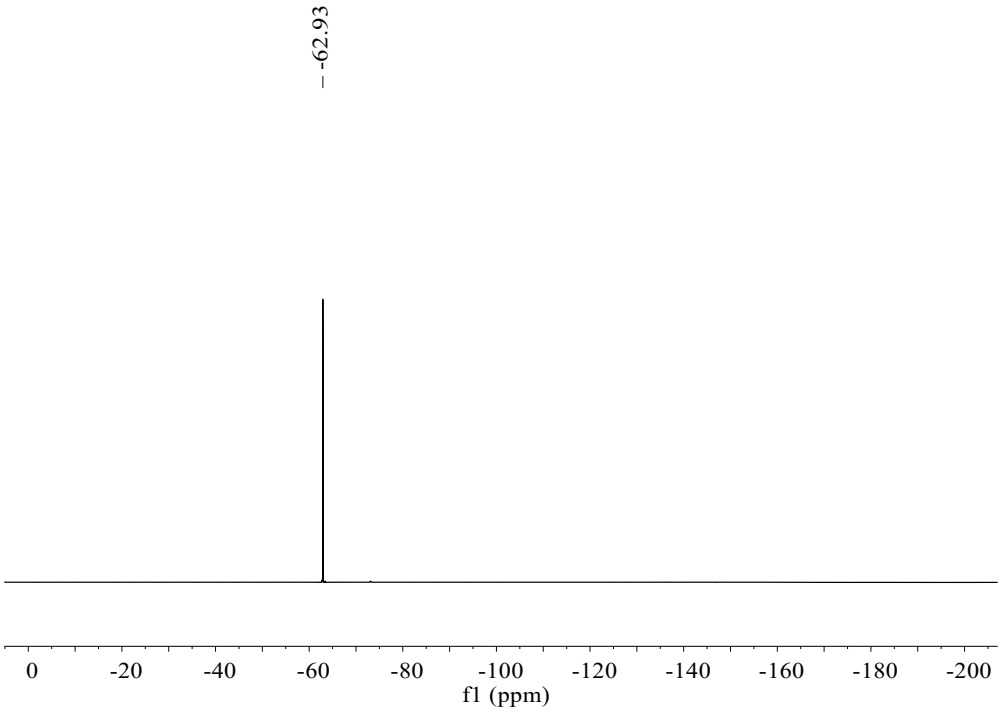
Compound **29**, ^{1}H NMR (400 MHz, $CDCl_3$)

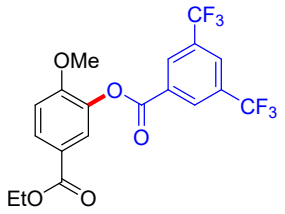


Compound **29**, ^{13}C NMR (101 MHz, $CDCl_3$)

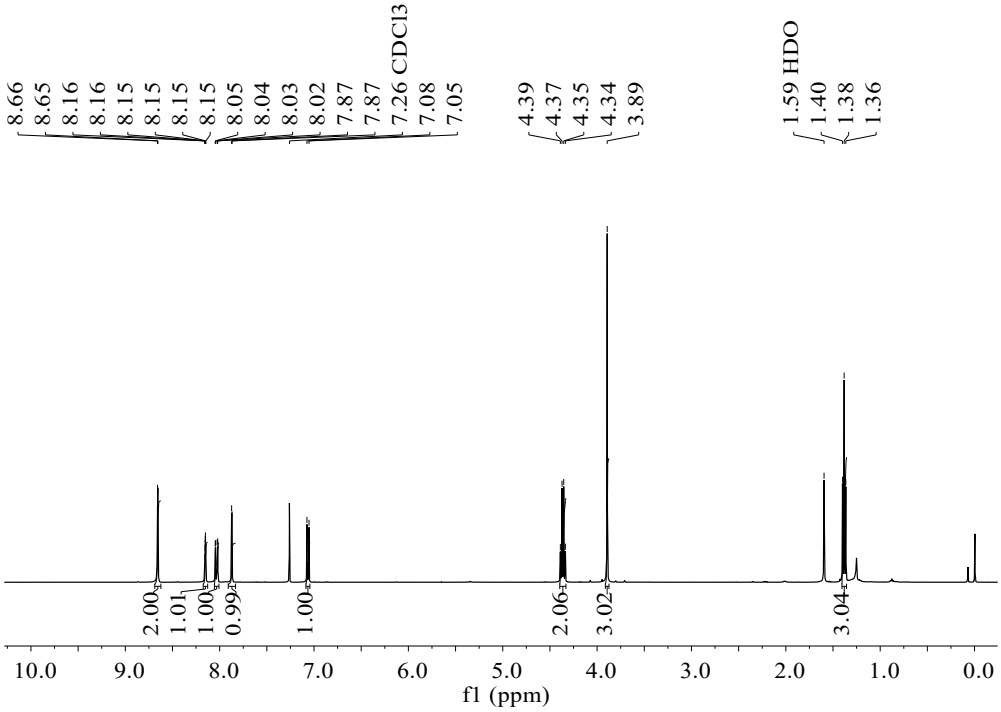


Compound **29**, ^{19}F NMR (376 MHz, $CDCl_3$)

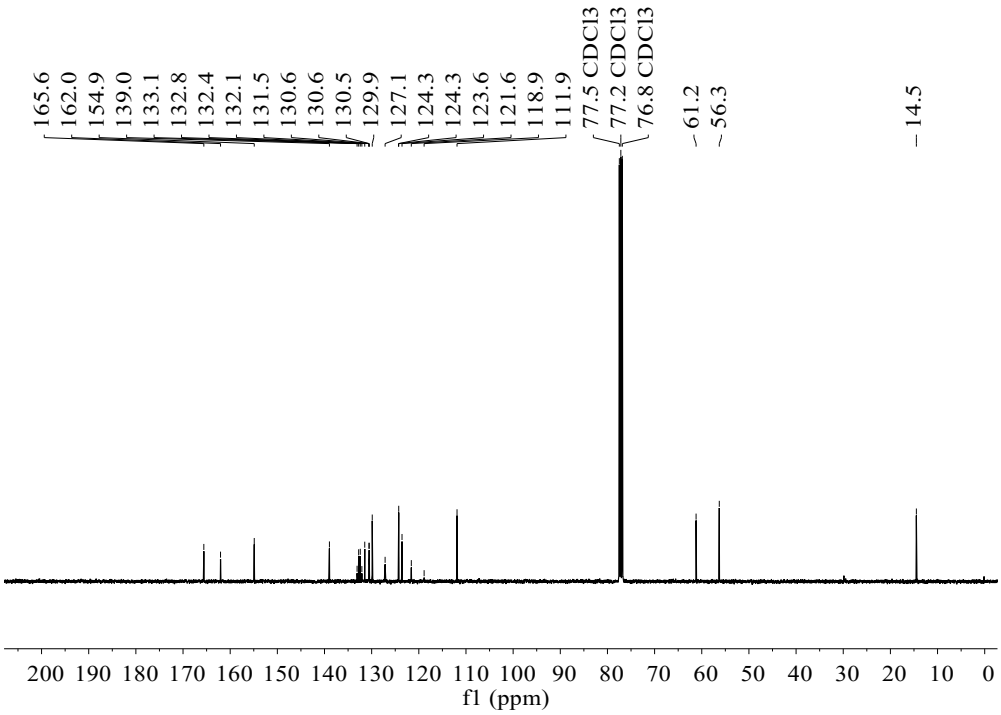




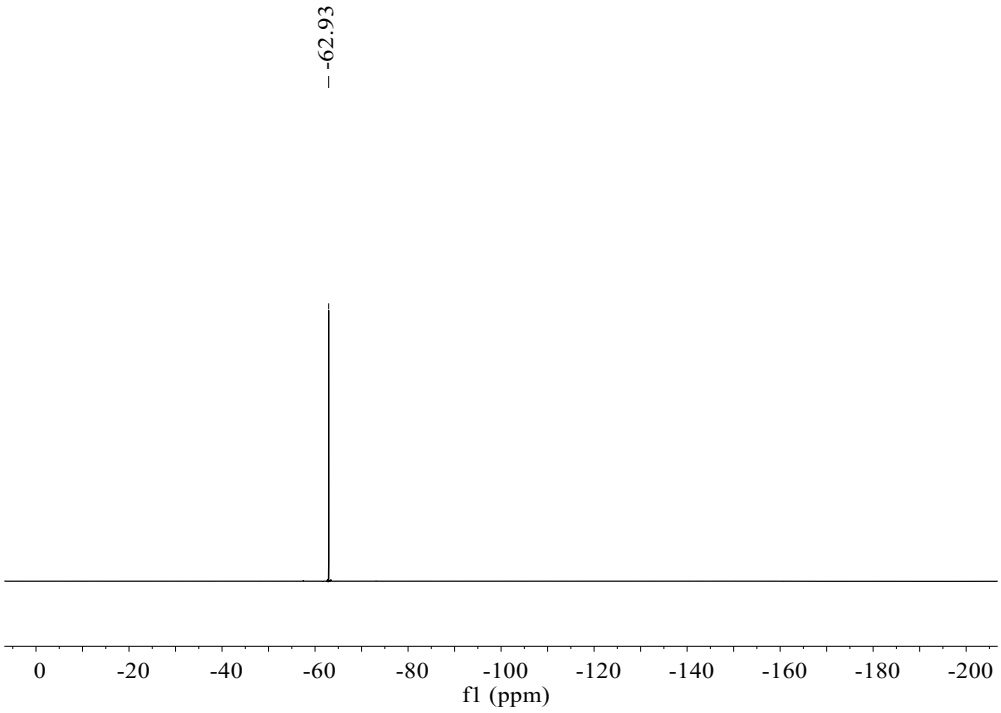
Compound **30**, ^{1}H NMR (400 MHz, $CDCl_3$)

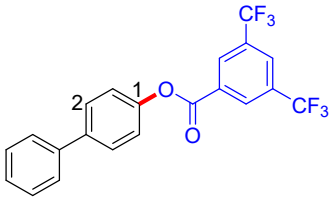


Compound **30**, ^{13}C NMR (101 MHz, $CDCl_3$)

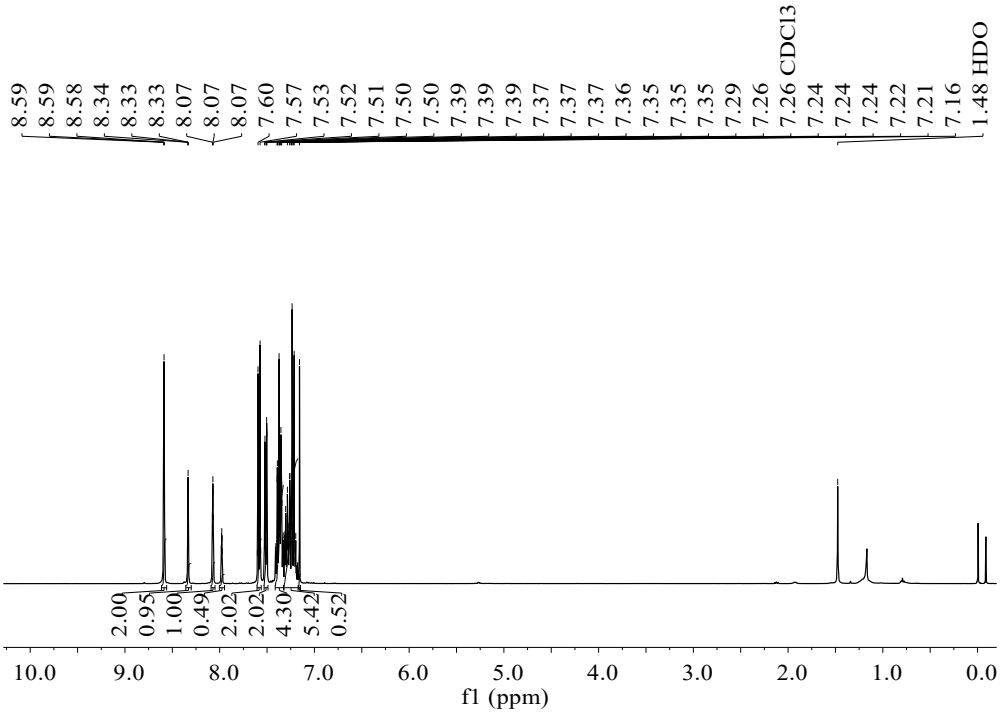


Compound **30**, ^{19}F NMR (376 MHz, $CDCl_3$)

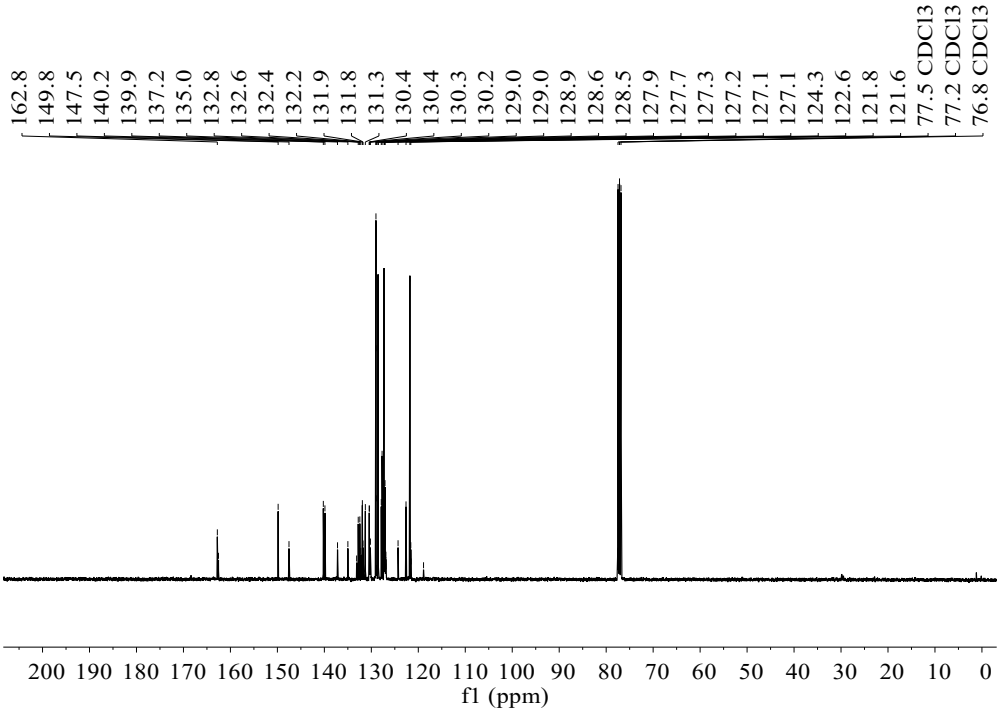




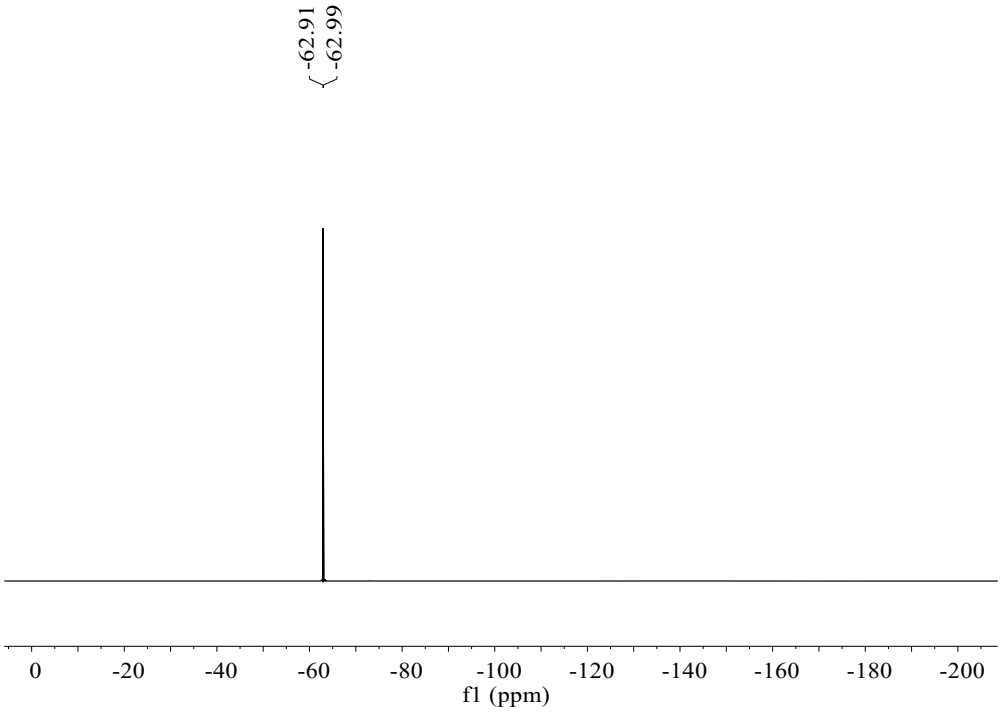
Compound **31** (C1:C2 = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$)

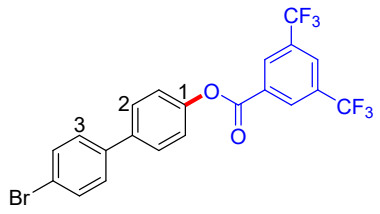


Compound **31** (C1:C2 = 2:1), ^{13}C NMR (101 MHz, $CDCl_3$)

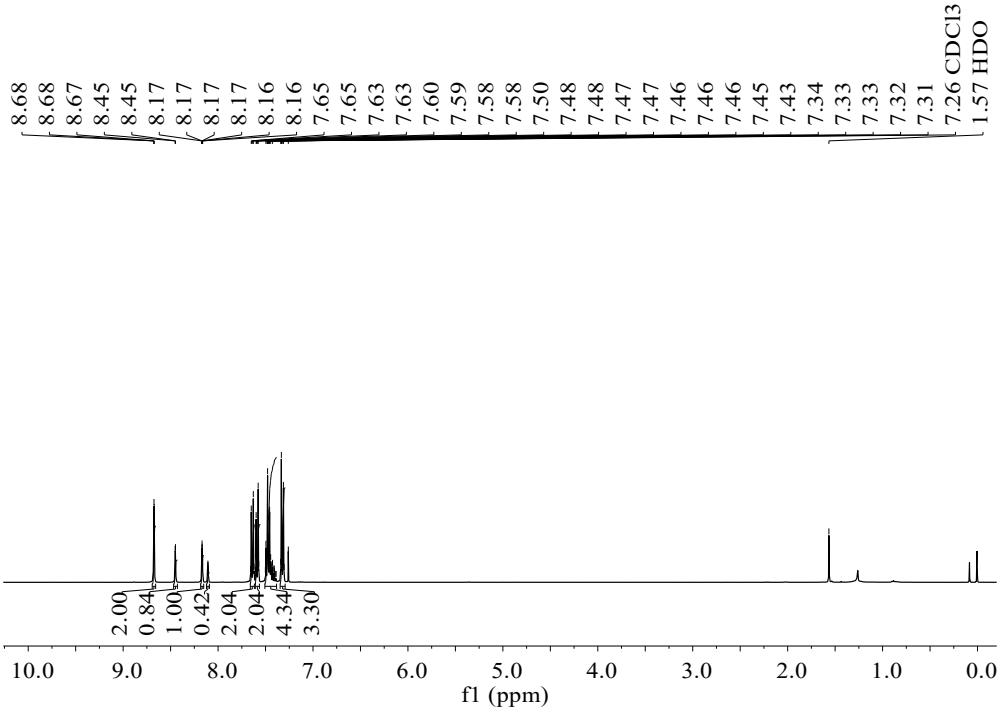


Compound **31** (C1:C2 = 2:1), ^{19}F NMR (376 MHz, $CDCl_3$)

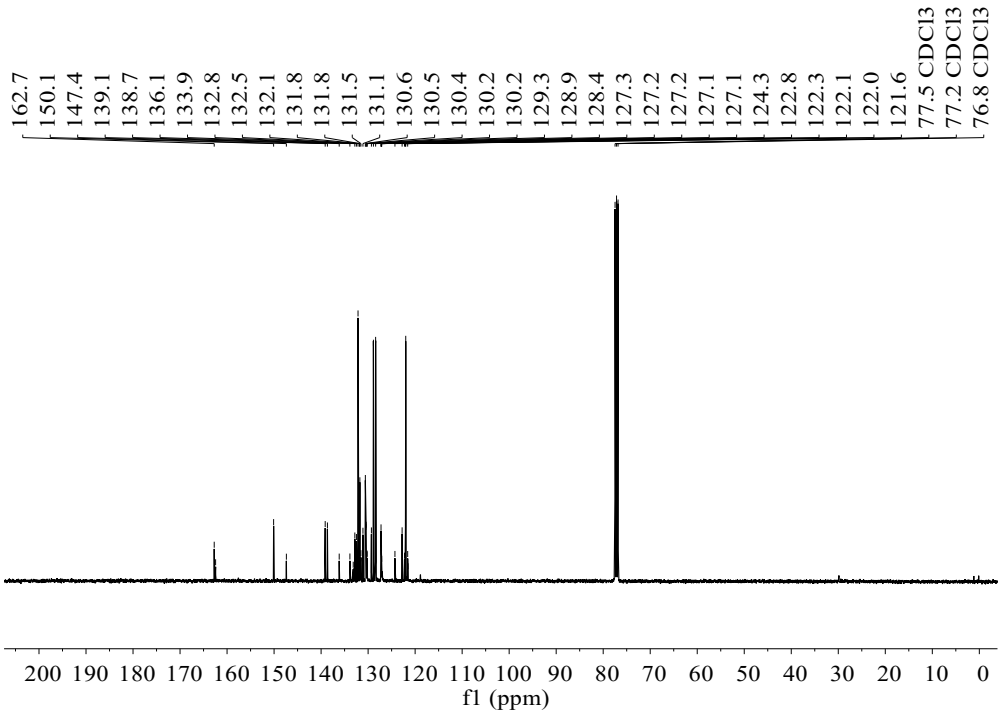




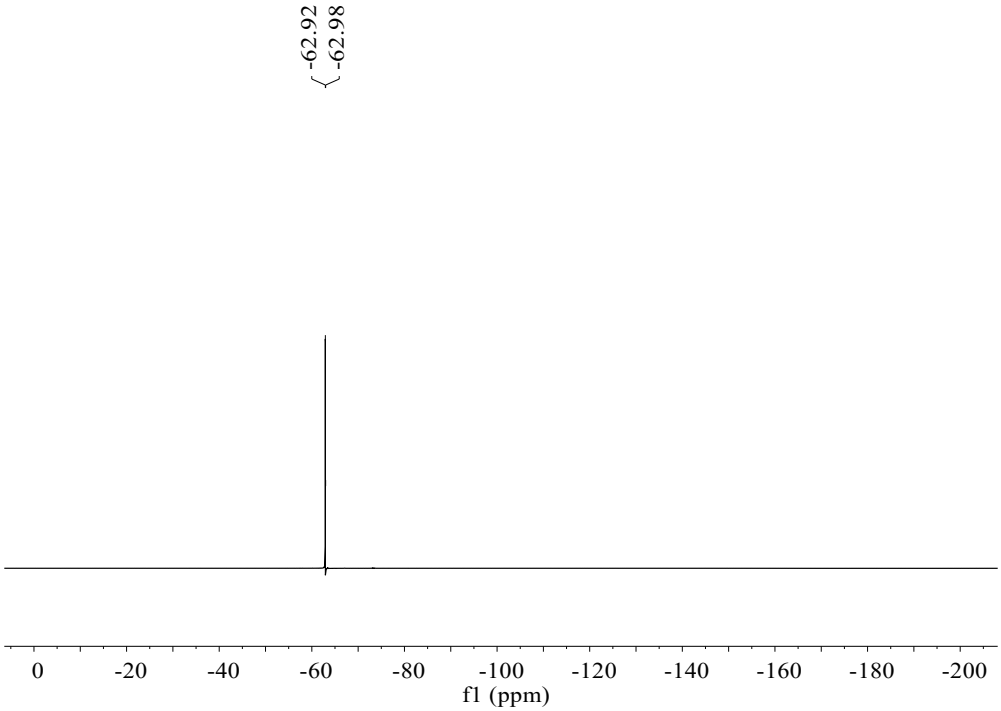
Compound **32** (C1:C2 = 2.5:1), ^{1}H NMR (400 MHz, $CDCl_3$)

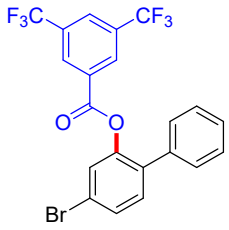


Compound **32** (C1:C2 = 2.5:1), ^{13}C NMR (101 MHz, $CDCl_3$)

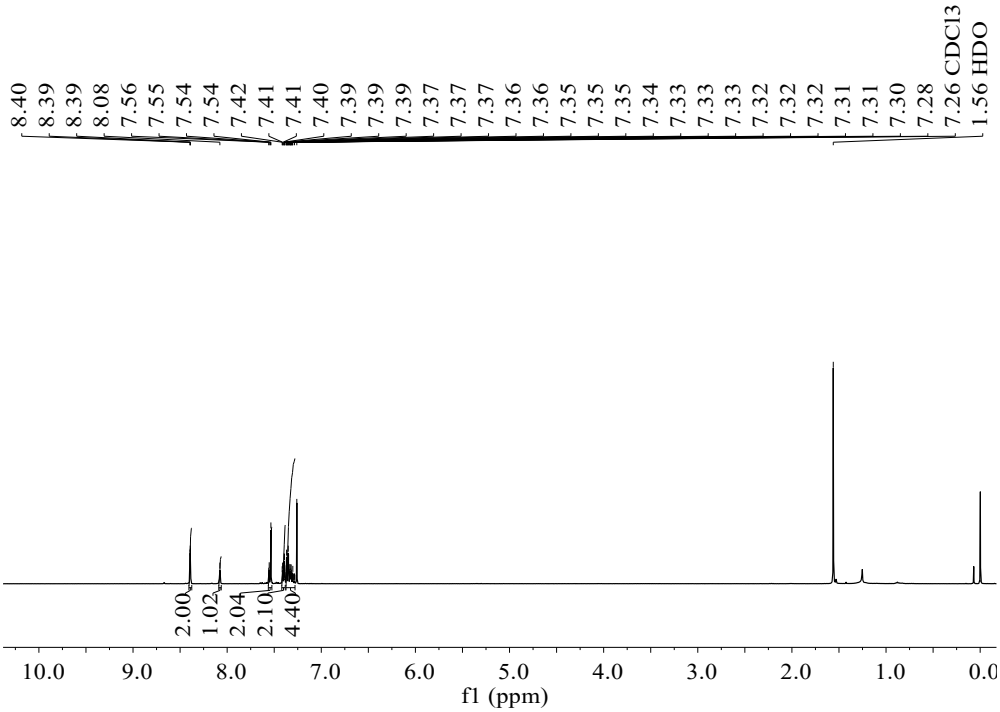


Compound **32** (C1:C2 = 2.5:1), ^{19}F NMR (376 MHz, $CDCl_3$)

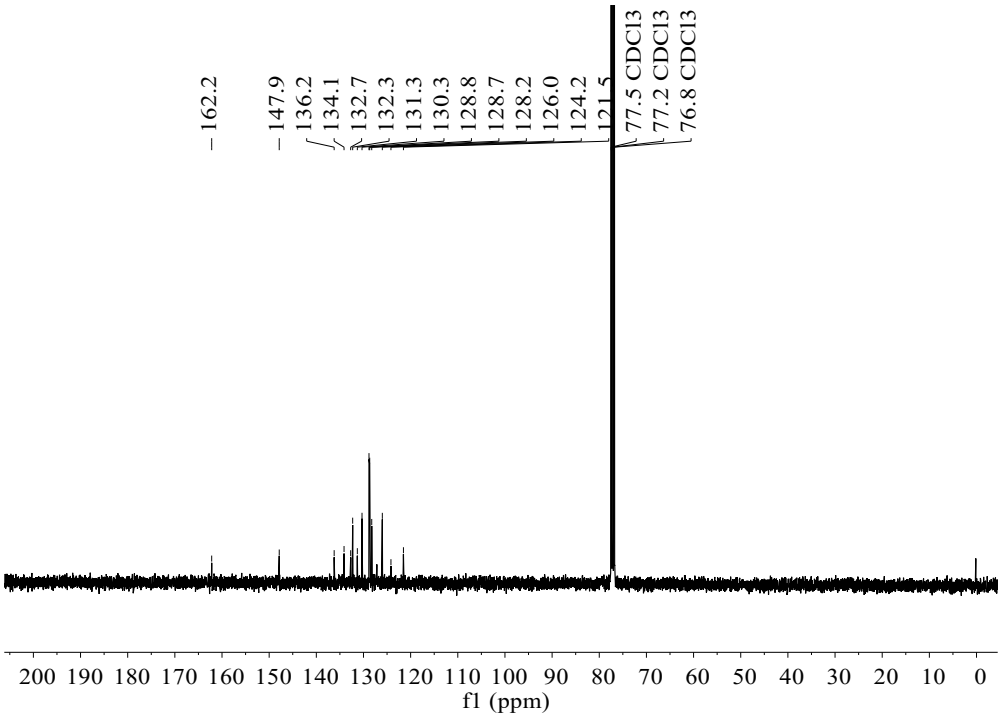




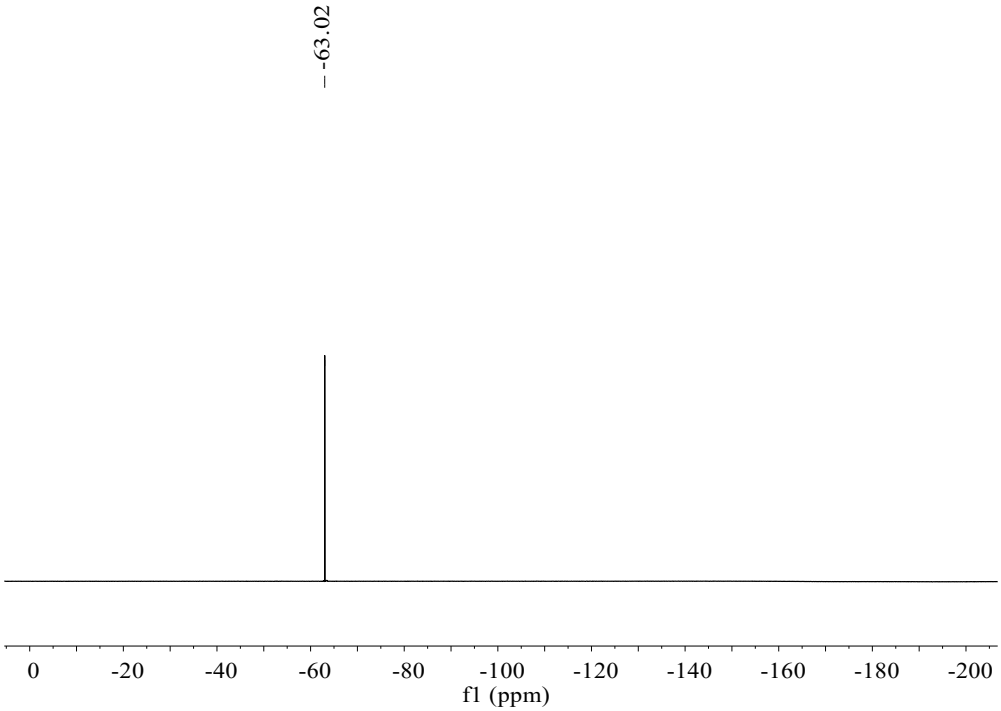
Compound **32** (C3), ^{1}H NMR (400 MHz, $CDCl_3$)

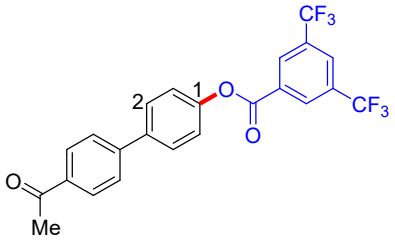


Compound **32** (C3), ^{13}C NMR (101 MHz, $CDCl_3$)

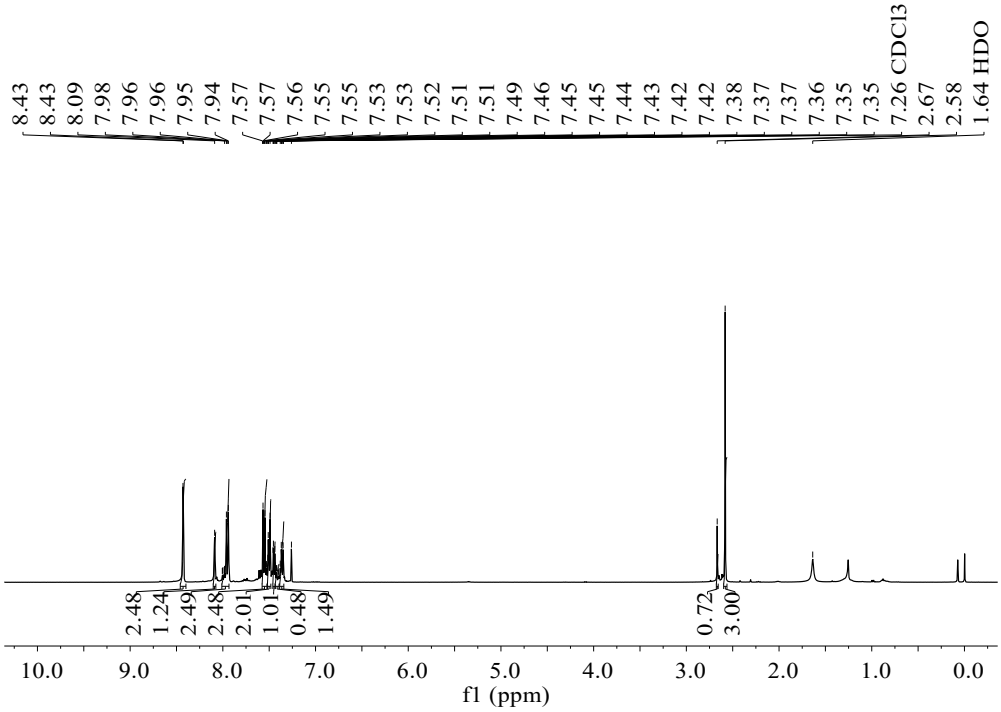


Compound **32** (C3), ^{19}F NMR (376 MHz, $CDCl_3$)

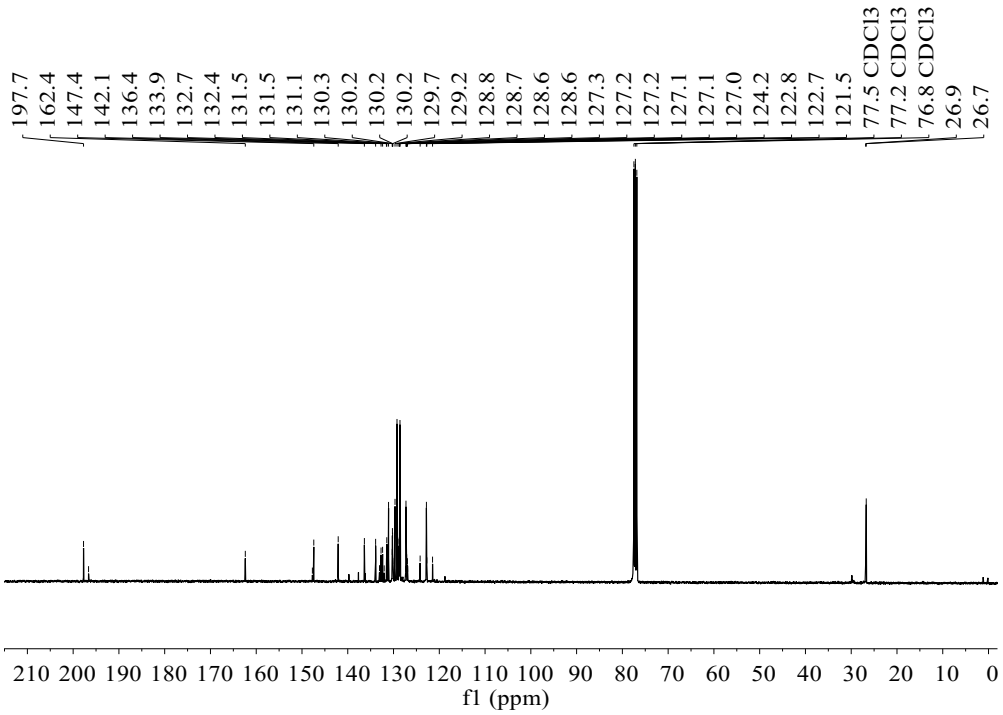




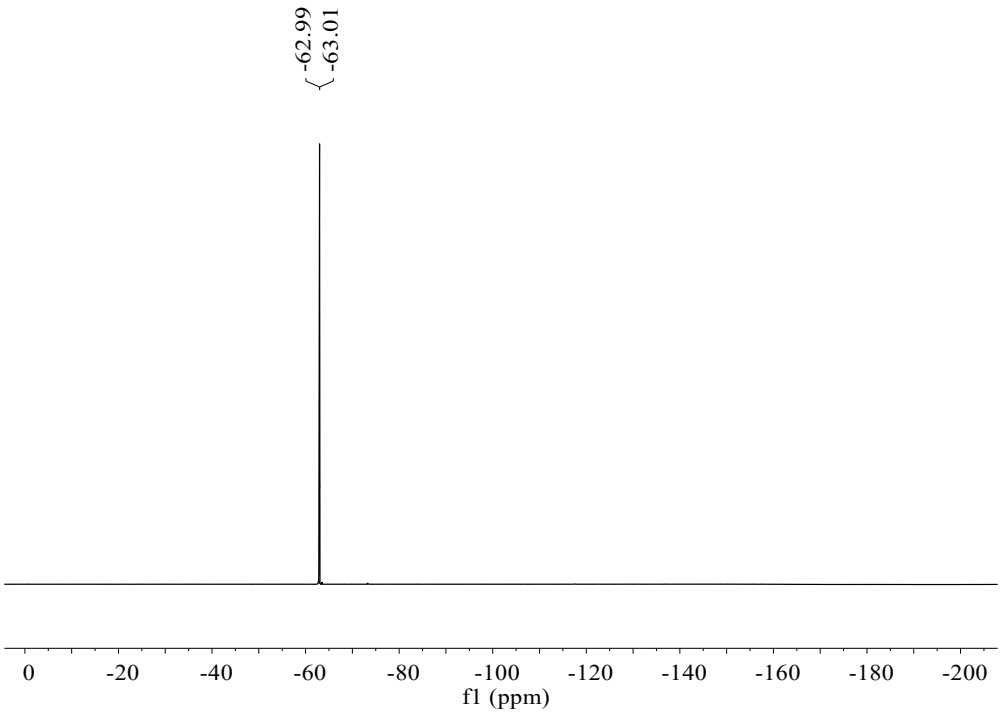
Compound **33** (C1:C2 = 4.2:1), ^{1}H NMR (400 MHz, $CDCl_3$)

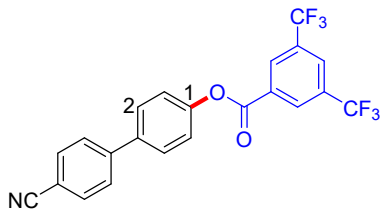


Compound **33** (C1:C2 = 4.2:1), ^{13}C NMR (101 MHz, $CDCl_3$)

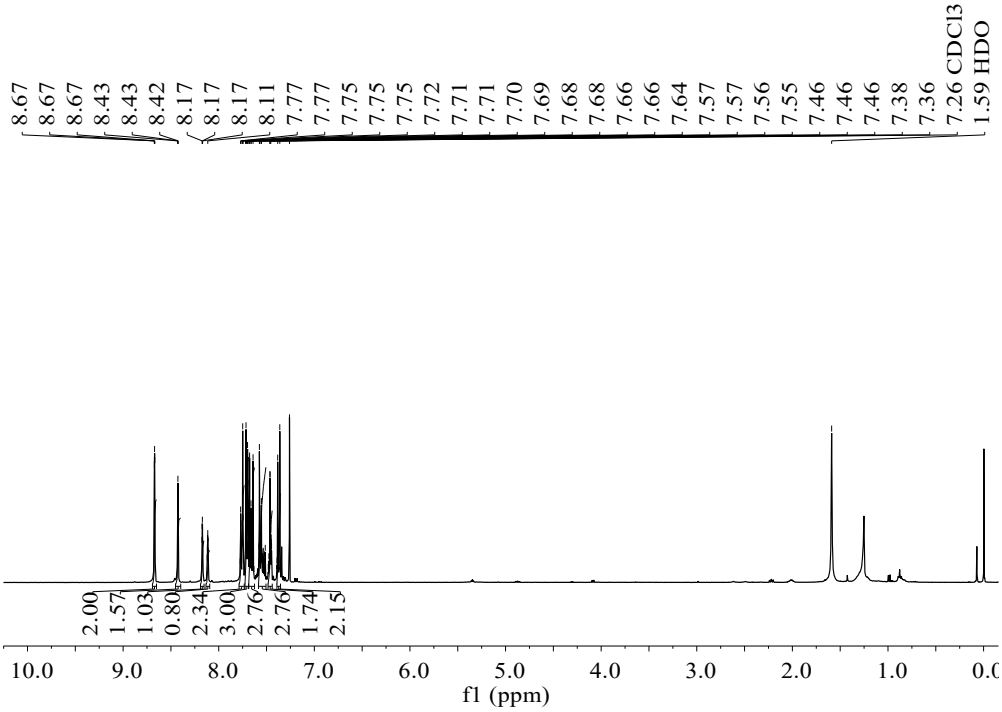


Compound **33** (C1:C2 = 4.2:1), ^{19}F NMR (376 MHz, $CDCl_3$)

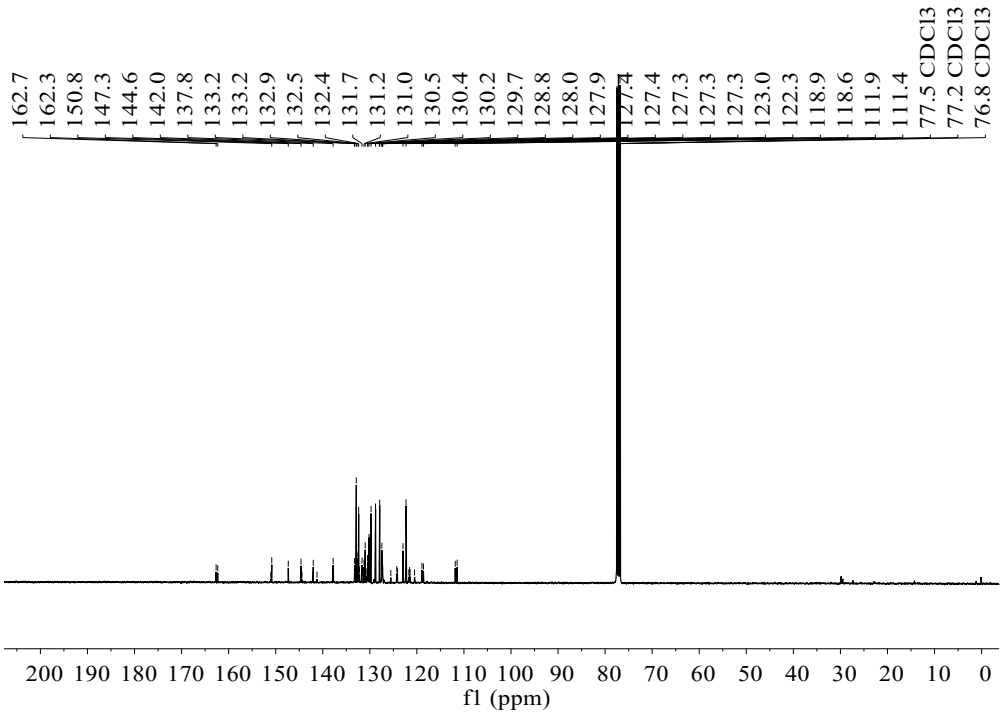




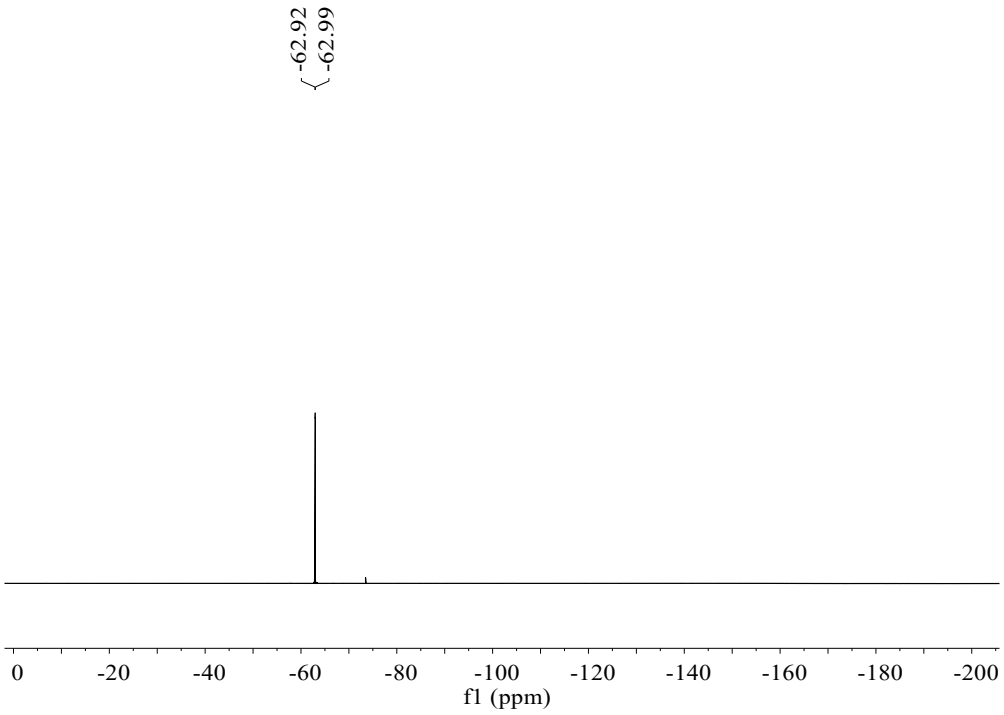
Compound **34** (C1:C2 = 1.25:1), ^{1}H NMR (400 MHz, $CDCl_3$)

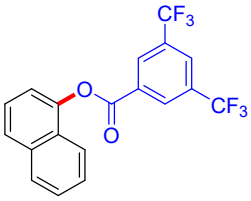


Compound **34** (C1:C2 = 1.25:1), ^{13}C NMR (101 MHz, $CDCl_3$)

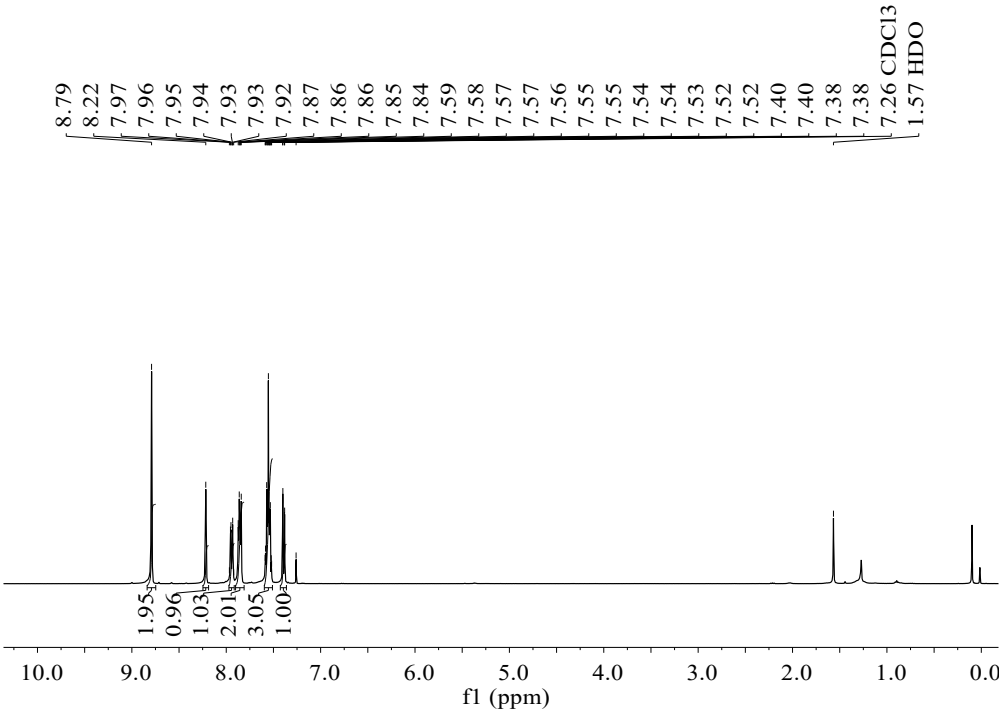


Compound **34** (C1:C2 = 1.25:1), ^{19}F NMR (376 MHz, $CDCl_3$)

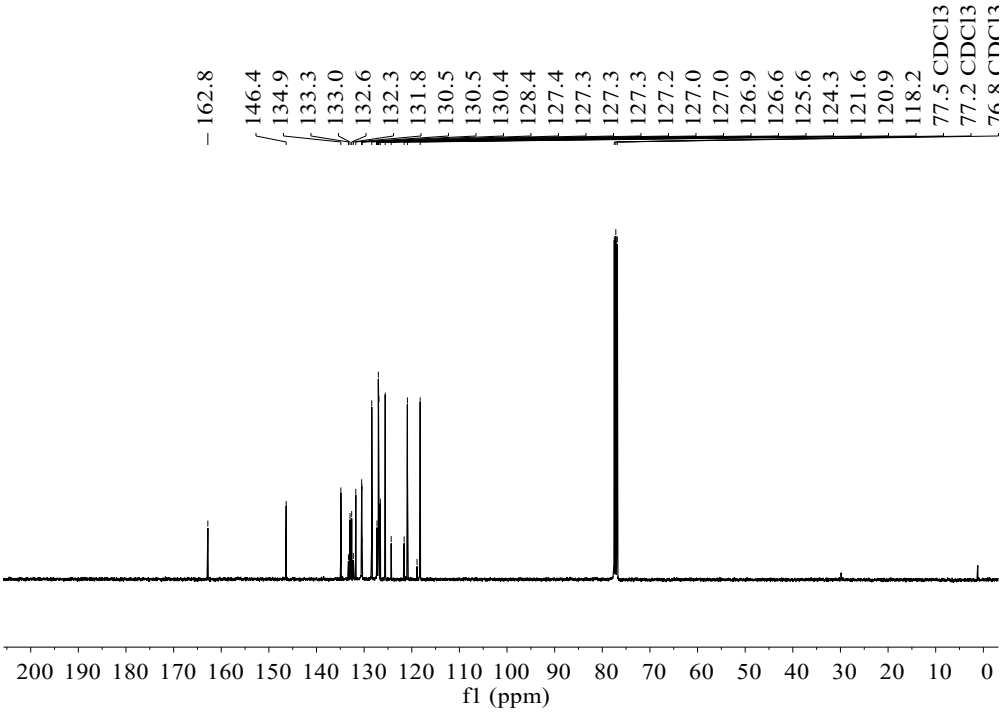




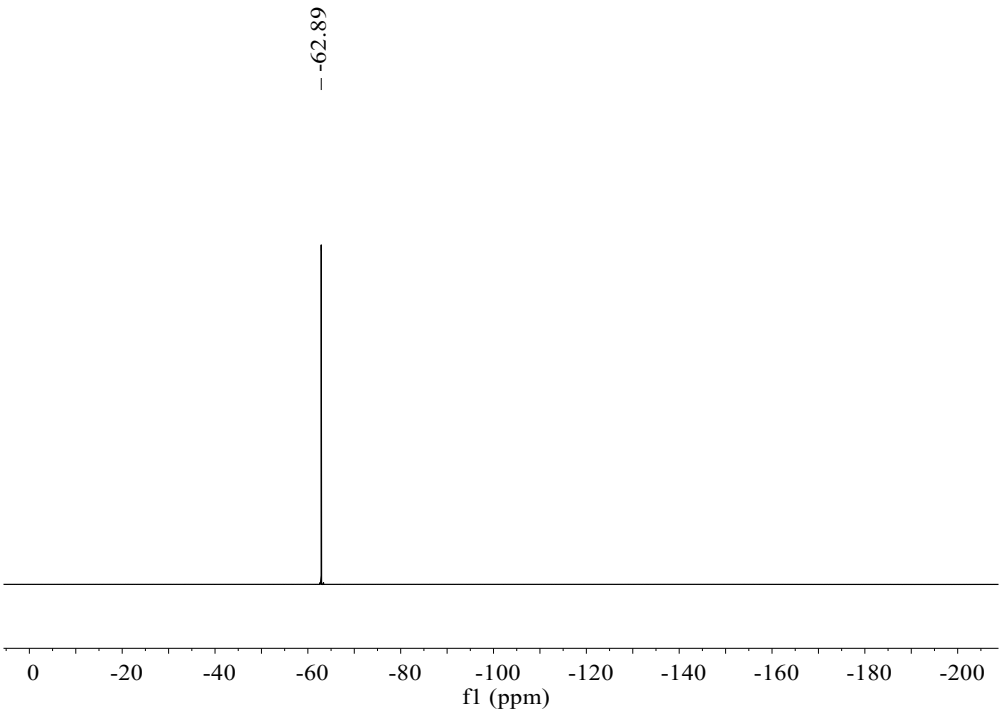
Compound **35**, ^{1}H NMR (400 MHz, $CDCl_3$)

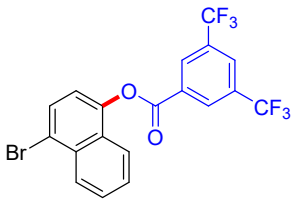


Compound **35**, ^{13}C NMR (101 MHz, $CDCl_3$)

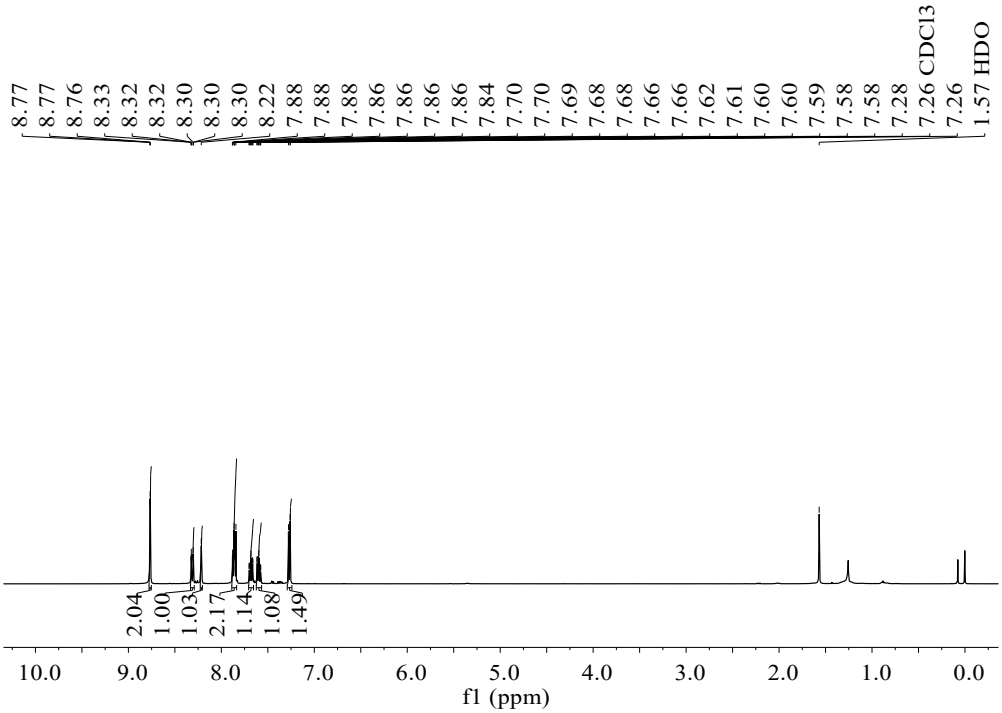


Compound **35**, ^{19}F NMR (376 MHz, $CDCl_3$)

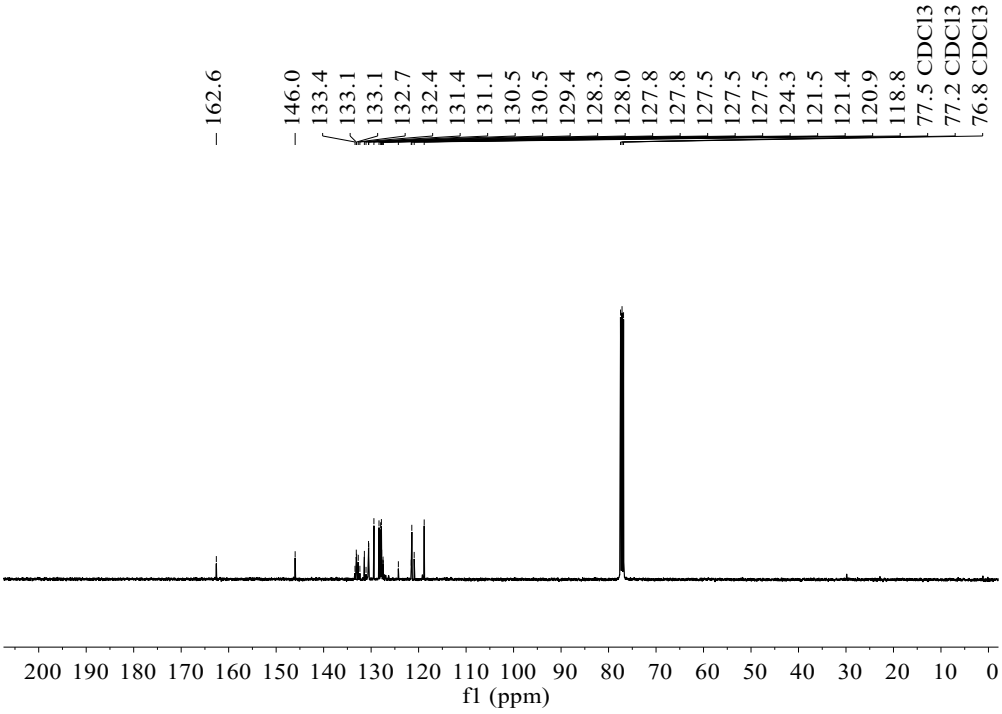




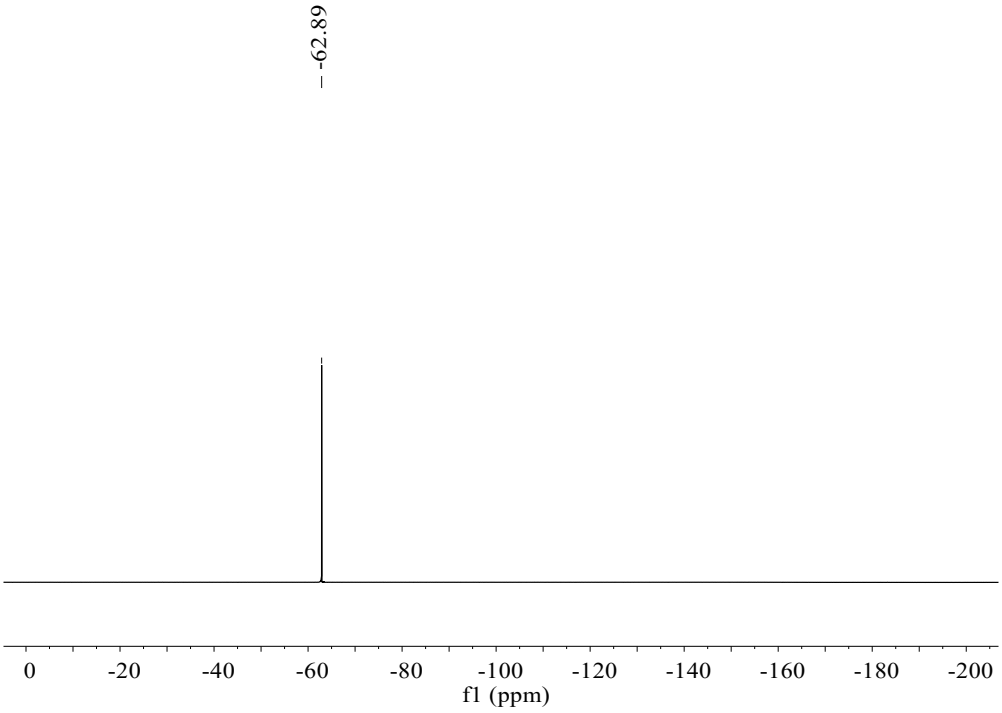
Compound **36**, ^{1}H NMR (400 MHz, $CDCl_3$)

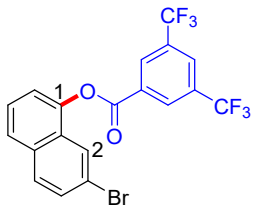


Compound **36**, ^{13}C NMR (101 MHz, $CDCl_3$)

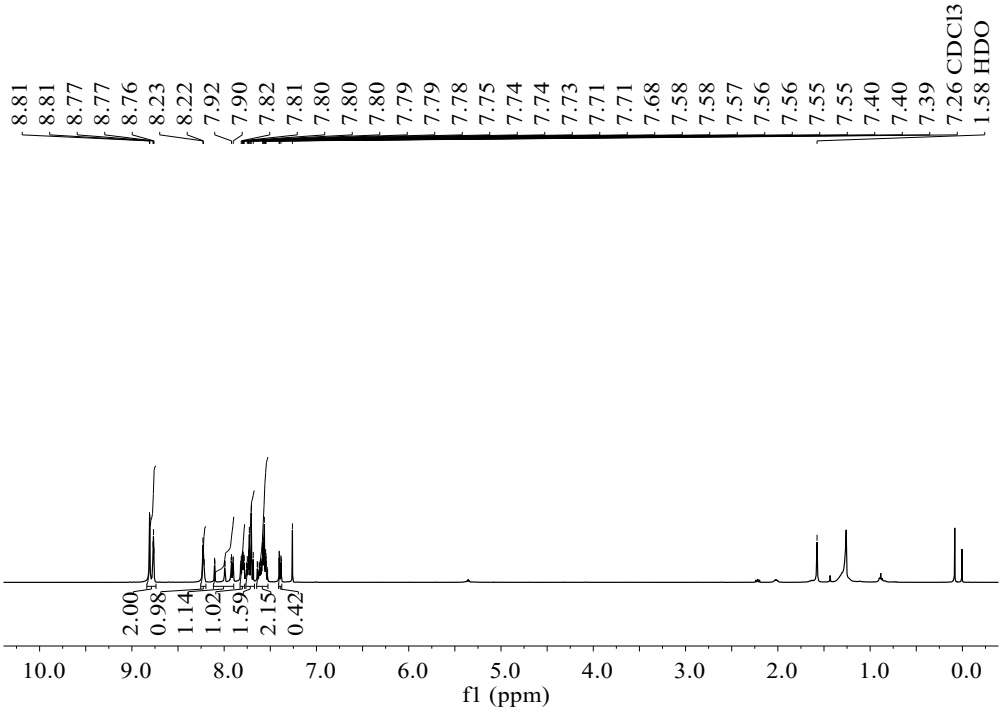


Compound **36**, ^{19}F NMR (376 MHz, $CDCl_3$)

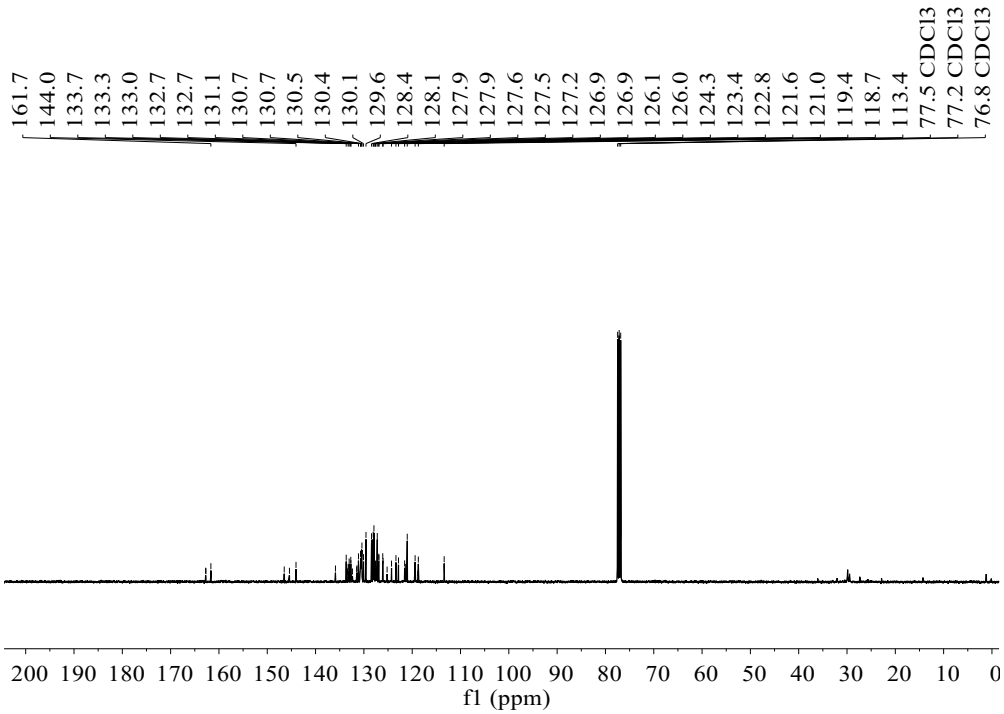




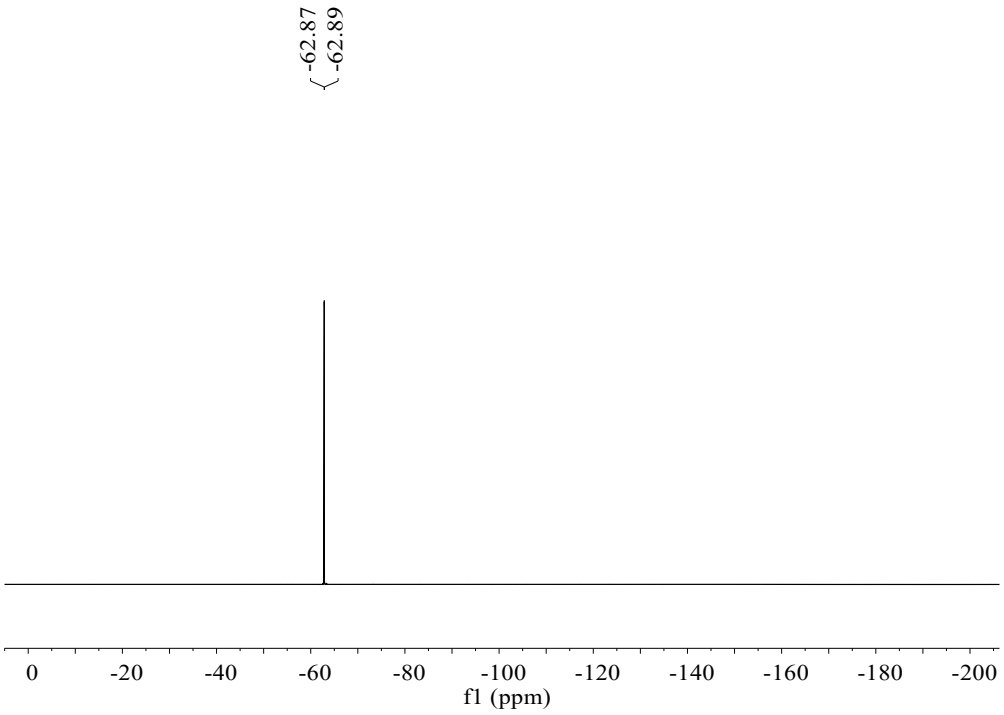
Compound **37** (C1:C2 = 1.2:1), ^{1}H NMR (400 MHz, $CDCl_3$)

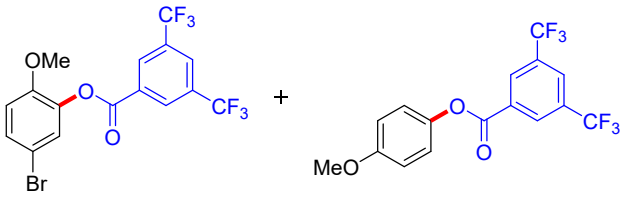


Compound **37** (C1:C2 = 1.2:1), ^{13}C NMR (101 MHz, $CDCl_3$)

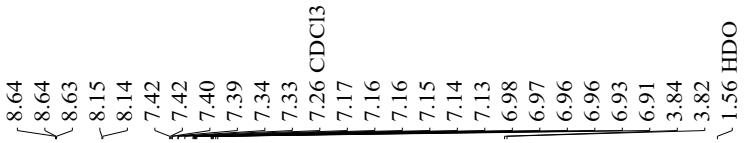


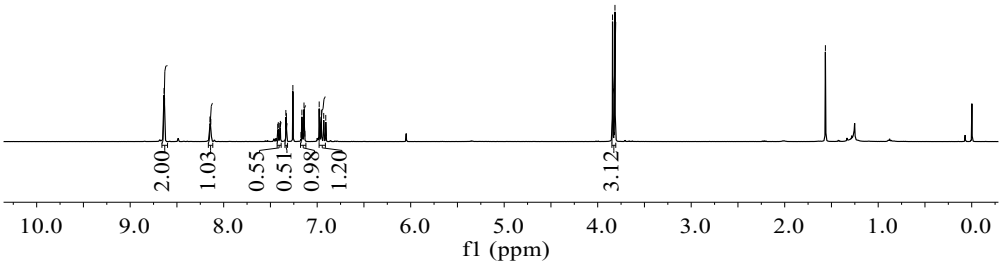
Compound **37** (C1:C2 = 1.2:1), ^{19}F NMR (376 MHz, $CDCl_3$)



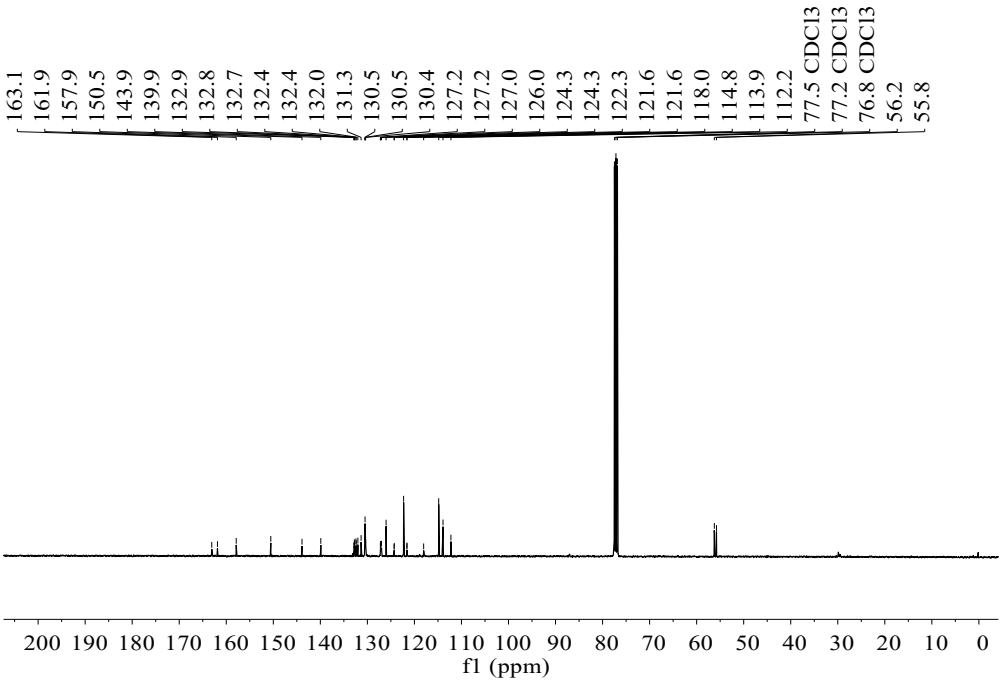


Compound **38** + **39** (1:1), ^{1}H NMR (400 MHz, $CDCl_3$)

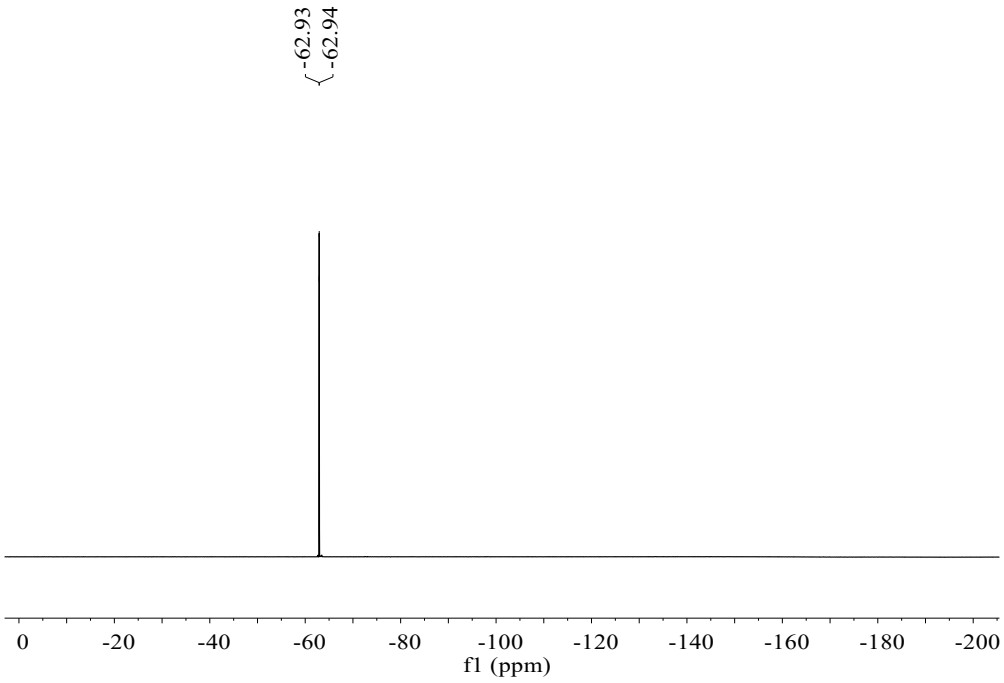


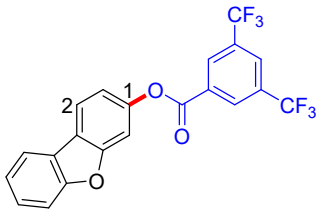


Compound **38** + **39** (1:1), ^{13}C NMR (101 MHz, $CDCl_3$)

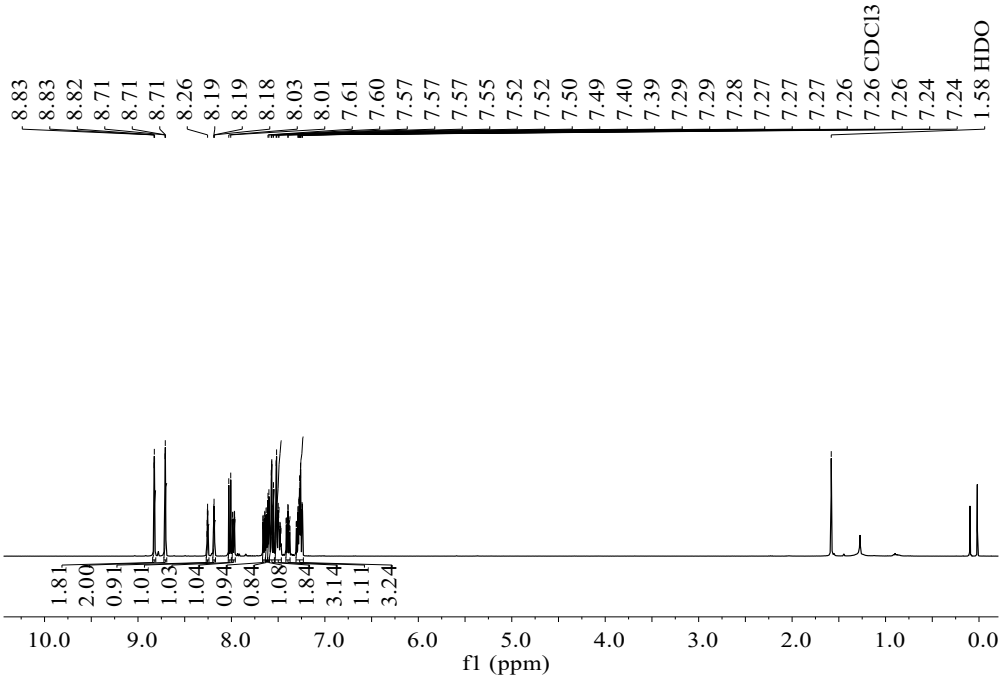


Compound **38** + **39** (1:1), ^{19}F NMR (376 MHz, $CDCl_3$)

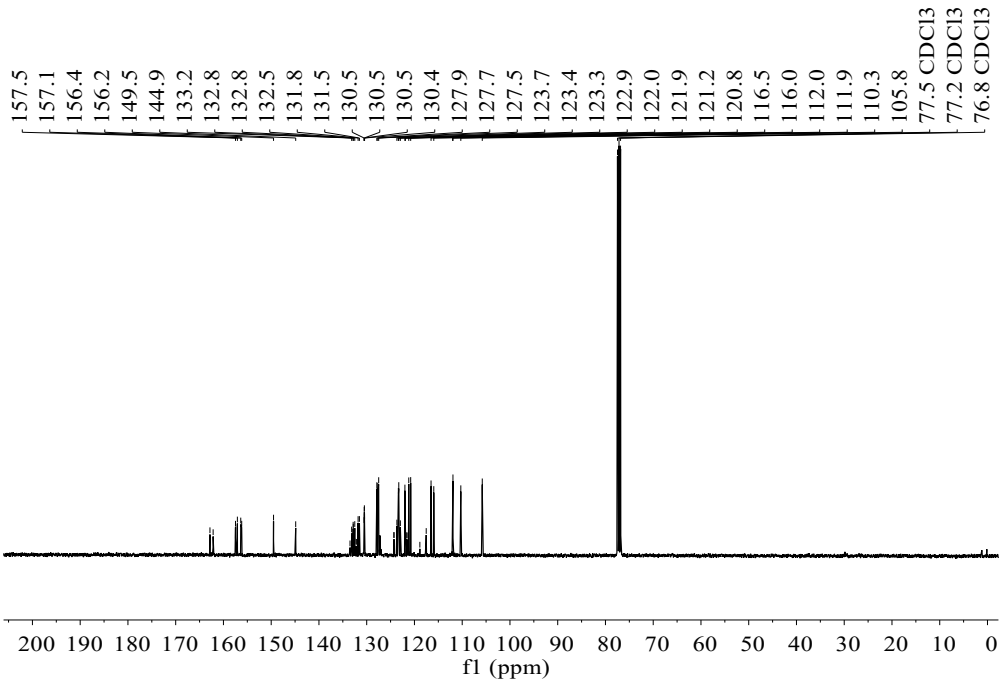




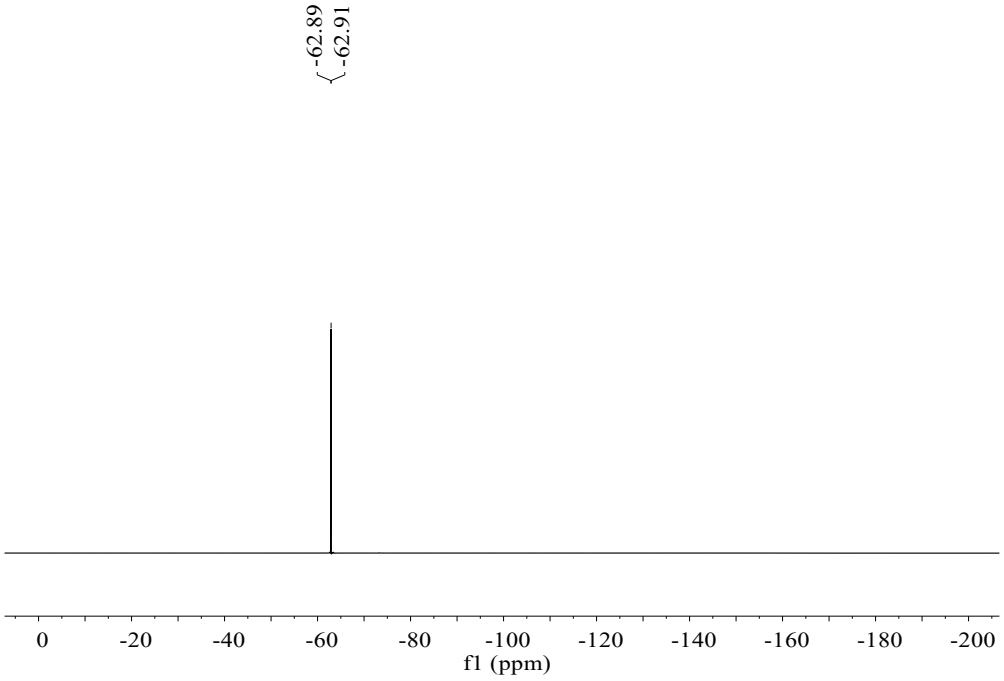
Compound **40** (C1:C2 = 1.2:1), ^{1}H NMR (400 MHz, $CDCl_3$)

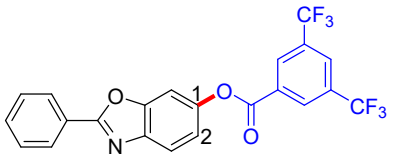


Compound **40** (C1:C2 = 1.2:1), ^{13}C NMR (101 MHz, $CDCl_3$)

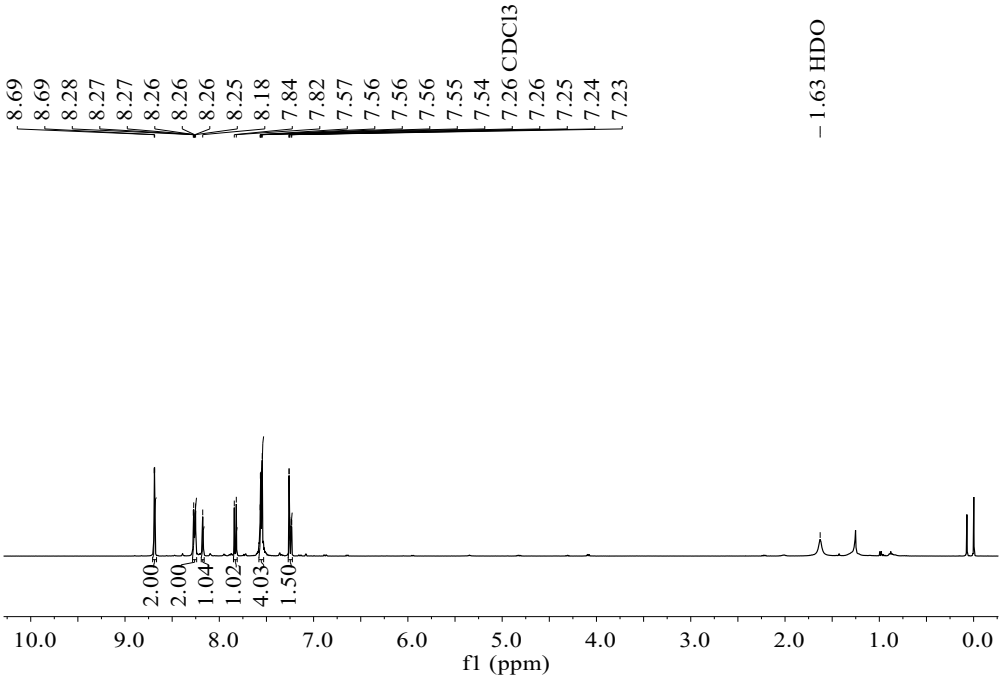


Compound **40** (C1:C2 = 1.2:1), ^{19}F NMR (376 MHz, $CDCl_3$)

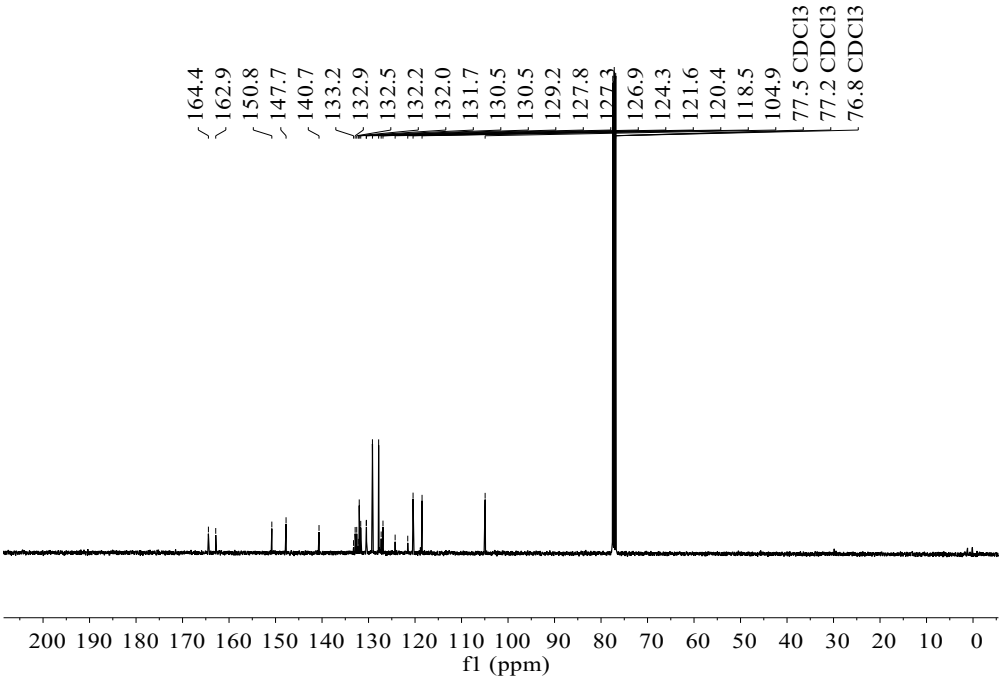




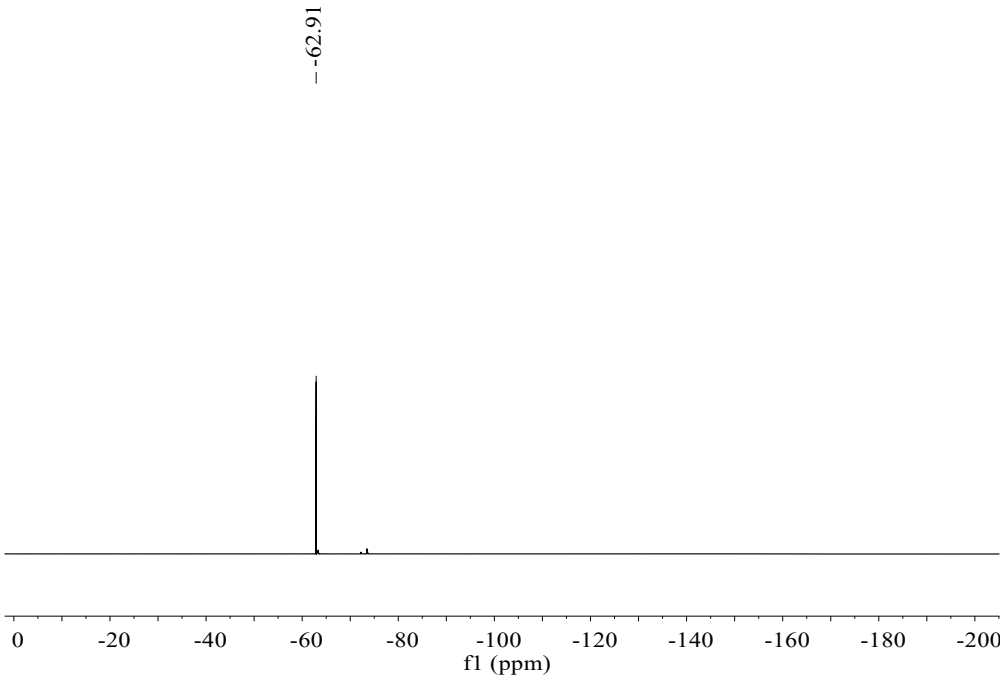
Compound **41** (C1), ^{1}H NMR (400 MHz, $CDCl_3$)

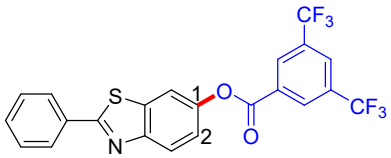


Compound **41** (C1), ^{13}C NMR (101 MHz, $CDCl_3$)

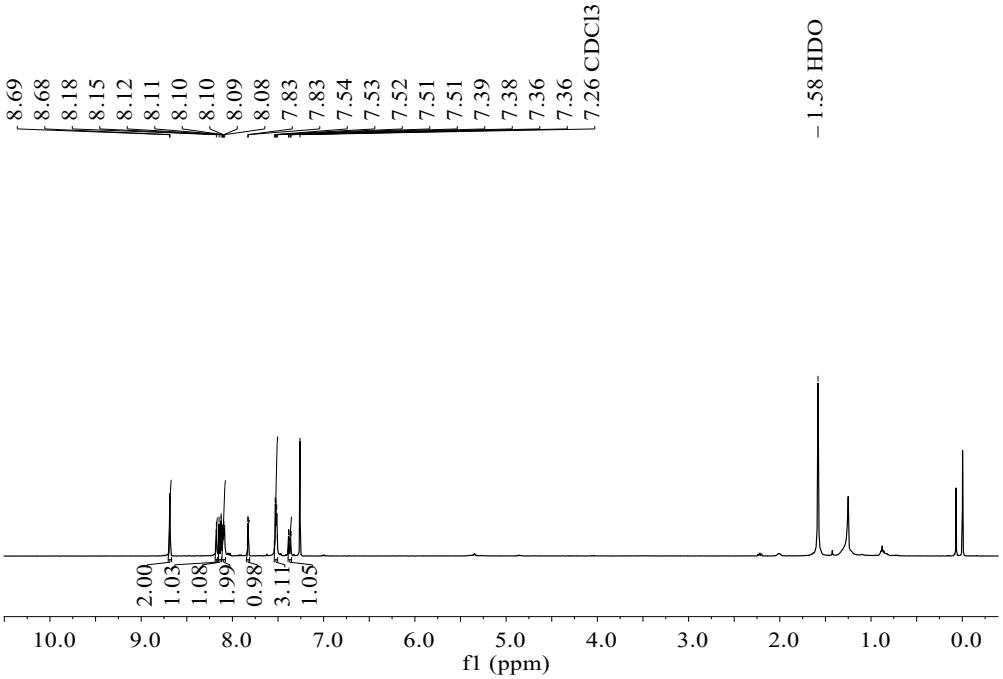


Compound **41** (C1), ^{19}F NMR (376 MHz, $CDCl_3$)

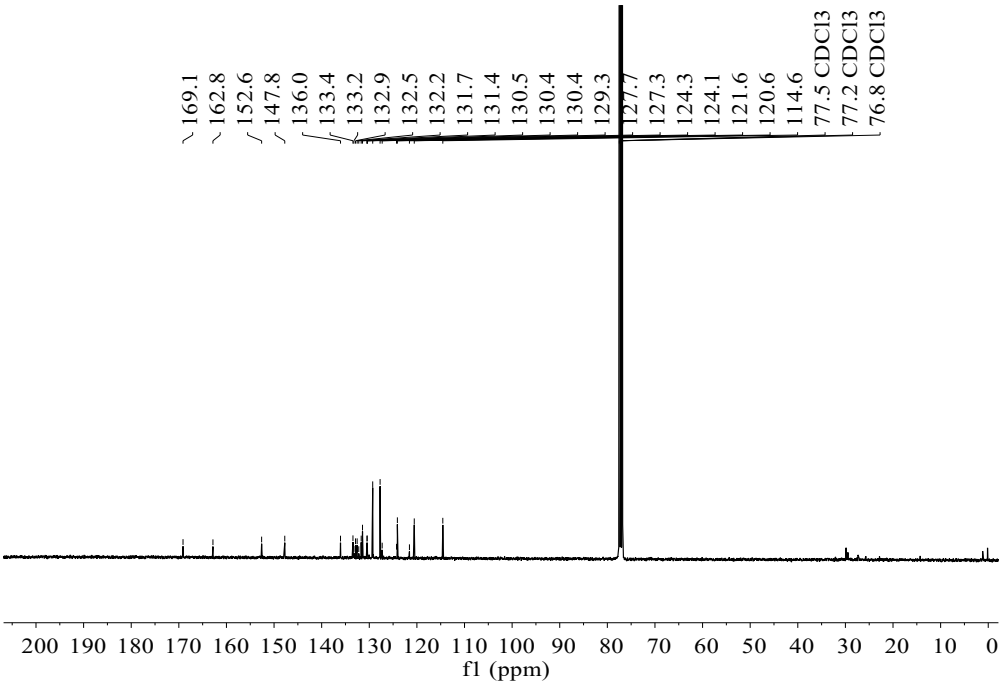




Compound **42** (C1), ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **42** (C1), ^{13}C NMR (101 MHz, $CDCl_3$)



Compound **42** (C1), ^{19}F NMR (376 MHz, $CDCl_3$)