Supporting information for

Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides: Synthesis of 2-aroylbenzoate derivatives.

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1 Experimental procedures

1.1 General

Unless otherwise noted, purchased chemicals were used as received without further purification. Solvents were dried according to standard procedures on molecular sieves 4A.[1] $MePh_2SiCO_2H$ (silaCOgen) was prepared as reported previously.[2] DABO boronates **7a** and sodium trihydroxy(4-methoxyphenyl)borate **8a** were prepared according to the previously reported protocol.[3] Flash chromatography was carried out on silica gel 60 (230−400 mesh). NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the solvent residual peak. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dt = double triplet, m = multiplet), coupling constant (J, Hz) and integration. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak ($CDCl_3$: δH 7.26 and δC 77.16; Methanol-d_4: δH 3.31 and δC 49.00; deuterium oxide: δH 4.79; DMSO-d_6 δH 2.51 and δC 39.52). Positive ion electrospray ionization mass spectrometry was conducted on a Thermo Electron LTQ Orbitrap XL spectrometer. The reactions were performed in the previously reported two-chamber system[2] under an argon atmosphere, and a glovebox was employed for weighing out the reagents.

1.2 General procedures

General procedure A: Carbonylative Suzuki Miyaura coupling of 2-bromoiodobenzene 3 with slow addition.

Chamber A: 2-Bromoiodobenzene **3** (50 mg, 1.0 equiv, 0.18 mmol), $PdCl_2$ (0.3 mg, 1 mol%), K_2CO_3 (70 mg, 3 equiv, 0.55 mmol) were dissolved in anisole (1 ml). Chamber B: COgen (107 mg, 2.5 equiv, 0.45 mmol), $Pd(dba)_2$ (12 mg, 5 mol%), tri-*tert*-butylphosphonium tetrafluoroborate (TTBP•HBF_4) (6.3 mg, 5 mol%) and DIPEA (240 mg, 3 equiv) were dissolved in anisole (3 ml). Chamber B was stirred and heated to 80 °C to release CO until gas evolution stops. After release of the CO, both chambers were stirred and heated to 80 °C and a solution of aryl boronic acid **4** (1.2 equiv) in anisole (2 ml) was added slowly (1-2 h) to the reaction mixture in chamber A. The two-chamber system was then placed in an oil bath and stirred at 80 °C for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent.

General procedure B: Carbonylative Suzuki Miuara coupling of 2-bromoiodobenzene 3 with instantaneous addition.

Chamber A: 2-Bromoiodobenzene **3** (50 mg, 1.0 equiv, 0.18 mmol), $PdCl_2$ (0.3 mg, 1 mol%), K_2CO_3 (70 mg, 3 equiv, 0.55 mmol) and aryl boronic acid **4** (1.2 equiv) were dissolved in anisole (3 ml). Chamber B: COgen (107 mg, 2.5 equiv, 0.45 mmol), $Pd(dba)_2$ (12 mg, 5 mol%), TTBP•HBF_4 (6.3 mg, 5 mol%) were added together and dissolved in anisole (3 ml) before DIPEA (240 mg, 3 equiv) was added. Both chambers were stirred and heated at 80°C under tightly closed system for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent.

General procedure C: Carbonylative Suzuki-Miyaura coupling of methyl 2-bromobenzoate 6 with slow addition.

Chamber A: Methyl 2-bromobenzoate **6** (100 mg, 1.0 equiv, 0.47 mmol), PEPPSI-IPr (9.4 mg, 3 mol%), Cs_2CO_3 (450 mg, 3 equiv, 1.4 mmol) were dissolved in anisole (1 ml). Chamber B: COgen (282 mg, 2.5 equiv, 1.2 mmol), $Pd(dba)_2$ (30 mg, 5 mol%), TTBP•HBF_4 (10 mg, 5 mol%) and DIPEA (240 mg, 3 equiv) were dissolved in anisole (3 ml). The reaction mixture in Chamber B was stirred and heated to 80

°C to release CO until gas evolution stops. After release of the CO, both chambers were stirred and heated to 110 °C and a solution of aryl boronic acid **4** (1.5 equiv) in anisole (2 ml) was added slowly (1-2 h) to the reaction mixture in chamber A. The two-chamber system was then placed in an oil bath and stirred at 110 °C for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (7:3) as eluent.

General procedure D: Carbonylative Suzuki-Miyaura coupling of methyl 2-bromobenzoate 6.

Chamber A: Methyl 2-bromobenzoate **6** (1.0 equiv, 0.47 mmol), aryl boronic acid **4** (1.5 equiv), PEPPSI-IPr (3 mol%), Cs_2CO_3 (3 equiv, 1.4 mmol) were dissolved in anisole (3 ml). Chamber B: COgen (282 mg, 2.5 equiv, 1.2 mmol), $Pd(dba)_2$ (30 mg, 5 mol%), TTBP•HBF_4 (10 mg, 5 mol%) were dissolved in anisole (3 ml) before DIPEA (450 mg, 3 equiv) was added. The two-chamber system was then placed in an oil bath and stirred at 110 °C for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane:EtOAc (7:3) as eluent.

General procedure E: Carbonylative Suzuki Miuara coupling of methyl 2-bromobenzoate with DABO boronates or sodium borate salt.

Chamber A: Methyl 2-bromobenzoate **6** (50 mg, 1.0 equiv, 0.23 mmol), $Pd(acac)_2$ (3.5 mg, 5 mol%), CataCXium A•HI (11 mg, 10 mol%), and the DABO boronate **7** or sodium borate salt **8** (1.5 equiv) were dissolved in toluene: H_2O (1:1; 3 ml). Chamber B: COgen (140 mg, 2.5 equiv, 0.58 mmol), $Pd(dba)_2$ (26 mg, 5 mol%), TTBP•HBF_4 (13 mg, 5 mol%) were dissolved in anisole (3 ml) before DIPEA (241 mg, 3 equiv) was added. The two-chamber system was then placed in an oil bath and stirred at 110 °C for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane:EtOAc (7:3) as eluent.

General procedure F: Alkoxy carbonylation of 2-bromobenzophenone derivatives 5 with *n*-BuOH.

Chamber A: 2-bromobenzophenone **5** (1 equiv), $PdCl_2$ (2 mol%), Xantphos (4 mol%), K_2CO_3 (3 equiv) were dissolved in anisole: n-BuOH (1:1; 3 ml). Chamber B: COgen (2.5 equiv), $Pd(dba)_2$ (5 mol%), TTBP•HBF_4 (5 mg, 5 mol%) were dissolved in anisole (3 ml) before DIPEA (3 equiv) was added. The two-chamber system was then placed in an oil bath and stirred under heating for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (7:3).

1.3 Preparation and characterization of 2-bromobenzophenone derivatives 5.

2-*Bromophenyl 4-methoxyphenyl methanone (**5a**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 4-methoxyphenyl boronic acid **4a** (35 mg, 0.21 mmol, 1.2 equiv). Reactions were performed both by the general procedure A or B to provide **5a** (procedure A: 41 mg, 80%; procedure B: 31 mg, 60%) as a colourless solid. Mp 91-93 °C. NMR: δH (400 MHz; $CDCl_3$) 7.79 (2H, d, *J* 8.8), 7.64 (1H, d, *J* 7.9), 7.40 (1H, d, *J* 7.9), 7.33 (2H, t, *J* 7.5), 6.94 (2H, d, *J* 8.8), 3.88 (3H, s). δC (101 MHz, $CDCl_3$) 194.9, 164.6, 141.6, 133.5, 133.1, 131.3, 129.6, 129.2, 127.6, 119.9, 114.4, 56.0. HRMS (ESI): Calcd. for $C_{14}H_{11}O_2{}^{79}BrNa$ $[M+H]^+$ 312.9840; found 312.9827. The spectroscopic data is corresponding to the previously reported in literature.[4]

*2-Bromophenyl 3-methoxyphenyl methanone (**5b**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 3-methoxyphenyl boronic acid **4b** (35 mg, 0.21 mmol, 1.2 equiv). Reactions were performed both by the general procedure A or B to provide **5b** (procedure A: 35 mg, 65%; procedure B: 18 mg, 35%) as a white solid. Mp 85-87 °C. NMR: δH (400 MHz, $CDCl_3$) 7.56 (1H, d, *J* 7.7), 7.36 (1H, s), 7.32 (1H, d, *J* 7.7), 7.26 (3H, t, *J* 7.6), 7.21-7.15 (1H, m), 7.08-7.05 (1H, m), 3.77 (3H, s). δC (101 MHz, $CDCl_3$) 195.8,

160.0, 140.8, 137.6, 133.3, 131.3, 129.7, 129.0, 127.3, 123.6, 120.6, 119.6, 113.8, 55.6. HRMS (ESI): Calcd. for $C_{14}H_{11}O_2{}^{79}BrNa$ $[M+H]^+$ 312.9840; found 312.9827. The spectroscopic data is corresponding to the previously reported in literature.[5]

*2-Bromophenyl 2-methoxyphenyl methanone (**5c**).* 2-Bromoiodobenzene **3** (50 mg) was reacted with (2-methoxyphenyl) boronic acid (35 mg, 0.21 mmol, 1.2 equiv) according to the general procedure A to provide **5c** (31 mg, 60%) as a white solid. Mp 66.3-68 °C. NMR: δH (400 MHz, $CDCl_3$) 7.56-7.52 (1H, m), 7.48-7.44 (1H, m), 7.39 (1H, t, *J* 7.6), 7.27-7.23 (2H, m), 7.19-7.12 (1H, m), 6.91 (1H, t, *J* 7.6), 6.82-6.80 (1H, m), 3.53 (s, 3H). δC (101 MHz, $CDCl_3$) 195.3, 159.5, 142.8, 134.5, 133.1, 131.9, 131.0, 129.4, 127.3, 127.1, 120.8, 119.6, 112.1, 55.9. HRMS (ESI): Calcd. for $C_{14}H_{11}O_2{}^{79}BrNa$ $[M+H]^+$ 312.9840; found 312.9827. The spectroscopic data is corresponding to the previously reported in literature.[5]

*2-Bromophenyl 4-(methylthio)*phenyl methanone (**5d**). 2-Bromoiodobenzene **3** (50 mg) was reacted with (4-(methylthio) phenyl) boronic acid (45 mg, 0.27mmol, 1.5 equiv) according to the general procedure A to provide **5d** (30 mg, 55%) as a white solid. NMR: δH (400 MHz, $CDCl_3$) 7.70 (2H, d, *J* 8.4), 7.63 (1H, d, *J* 7.6), 7.40 (1H, d, *J* 7.6), 7.37-7.27 (2H, m), 7.27-7.20 (2H, m), 2.51 (3H, s). δC (101 MHz, $CDCl_3$) 195.0, 147.3, 140.9, 140.5, 133.3, 132.5, 131.2, 130.7, 129.0, 128.2, 127.4, 125.0, 119.6, 14.8. HRMS (ESI): Calcd. for $C_{14}H_{11}{}^{81}BrOS$ [M+H]+ 308.9727; found 308.9756

*tert-Butyl 2-(2-bromobenzoyl)-1H-pyrrole-1-carboxylate (**5e**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with (1-(tert-butoxycarbonyl)-1H-pyrrol-2-yl)boronic acid **4e** (45 mg, 0.21 mmol, 1.2 equiv) according to the general procedure A to provide **5e** (43 mg, 70%) as a yellow oil. NMR: δH (400 MHz, $CDCl_3$) 7.63 (1H, d, *J* 7.7), 7.48-7.46 (2H, m), 7.38 (2H, t, *J* 7.5), 7.33 (2H, t, *J* 7.5), 6.53-6.52 (1H, m), 6.18 (1H, t, *J* 3.3), 1.56 (9H, s). δC (101 MHz, $CDCl_3$) 184.6, 149.2, 140.9, 134.0, 133.7, 132.1, 130.6, 129.6, 127.5, 125.3, 121.0, 110.9, 85.6, 77.8, 77.7, 77.5, 77.2, 28.0. HRMS (ESI): Calcd. for $C_{16}H_{16}{}^{81}BrNNaO_3$ [M+H]+ 374.0278; found 374.0177.

*tert-Butyl 2-(2-bromobenzoyl)-1H-indole-1-carboxylate (**5f**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with (1-(tert-butoxycarbonyl)-1H-indol-2-yl)boronic acid **4f** (55 mg, 0.21 mmol, 1.5 equiv) according to the general procedure A to provide **5f** (53 mg, 76%) as a yellow oil. NMR: δH (400 MHz, $CDCl_3$) 8.14 (1H, d, *J* 9.2), 7.69-7.67 (1H, m), 7.58-7.56 (2H, m), 7.49-7.45 (1H, m), 7.44-7.36 (2H, m), 7.28 – 7.24 (1H, m), 6.84 (1H, s), 1.58 (9H, s). δC NMR (101 MHz, $CDCl_3$) 186.0, 149.5, 139.7, 139.2, 137.8, 134.0, 132.4, 131.0, 127.9, 127.4, 127.3, 123.5, 122.9, 121.1, 118.7, 115.0, 84.9, 27.9. HRMS (ESI): Calcd. for $C_{20}H_{18}{}^{79}BrNNaO_3$ [M+H]+ 422.0368; found 422.0353.

*Methyl 3-(2-bromobenzoyl)benzoate (**5g**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 3-(methoxycarbonyl)phenyl boronic acid **4g** (38 mg, 0.21 mmol, 1.2 equiv) according to the general procedure A to provide **5g** (22 mg, 40 %) as a colorless oil. NMR: δH (400 MHz, $CDCl_3$) 8.43 (1H, s), 8.27 (1H, d, *J* 7.8), 8.01 (1H, d, *J* 7.8), 7.67 (1H, d, *J* 7.8), 7.57(1H, t, *J* 7.8), 7.47-7.43 (1H, m), 7.41 – 7.36 (2H, m), 3.93 (3H, s). δC (101 MHz, $CDCl_3$) 195.2, 166.3, 140.2, 136.7, 134.5, 134.3, 133.5, 131.7, 131.3, 131.0, 129.3, 129.1, 127.6, 119.7, 52.7. HRMS (ESI): Calcd. for $C_{15}H_{11}O_3{}^{79}BrNa$ [M+H]+; 340.9789 found 340.9757.

*Methyl 2-(2-bromobenzoyl)benzoate (**5h**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 2-(methoxycarbonyl) phenyl boronic acid 4h (35 mg, 0.21 mmol, 1.2 equiv) according to the general procedure A to provide **5h** (33 mg, 58%) as a viscous colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.88-7.86 (1H, m), 7.70-7.68 (1H, m), 7.60-7.57 (2H, m), 7.50-7.48 (1H, m), 7.39-7.36 (1H, m), 7.33-7.31 (2H, m), 3.69 (3H, s). δC (101 MHz, $CDCl_3$) 195.49, 167.58, 140.09, 138.43, 134.68, 132.64, 131.78, 131.27, 131.15, 129.94, 129.57, 127.16, 121.55, 77.48, 77.16, 76.84, 52.72. HRMS (ESI): Calcd. for $C_{15}H_{11}O_3{}^{81}BrNa$ [M+H]+; 342.9769 found 342.9757. The spectroscopic data is corresponding to the previously reported in literature.[6]

*4-(2-Bromobenzoyl)benzonitrile (**5i**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with (4-cyanophenyl) boronic acid **4i** (31 mg, 0.21 mmol, 1.2 equiv). Reactions were performed both by the general procedure A or B to provide **5i** (procedure A: 15 mg, 30%; procedure B: 0 mg, 0%) as a white solid. Mp 113-115

°C. NMR: δH (400 MHz, $CDCl_3$) 7.90 (2H, d, *J* 8.2), 7.77 (2H, d, *J* 8.2), 7.67 (1H, d, *J* 7.8), 87.49 – 7.39 (1H, m), 7.38-7.36 (1H, m). δC (101 MHz, $CDCl_3$) 194.6, 139.6, 139.4, 133.6, 132.6, 132.1, 130.5, 129.4, 127.7, 119.7, 118.0, 116.9. HRMS (ESI): Calcd. for $C_{14}H_8$ ^{79}BrNNaO [M+H]+ 307.9687; found 307.9672. The spectroscopic data is corresponding to the previously reported in literature.[7]

*3-(2-Bromobenzoyl)benzonitrile (**5j**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with (3-cyanophenyl) boronic acid **4j** (31 mg, 0.21 mmol, 1.2 equiv). Reactions were performed following the general procedure A or B to provide **5j** (procedure A: 33 mg, 65%; procedure B: 15 mg, 30%) as a colorless oil. NMR: δH (400 MHz, $CDCl_3$) 8.06 (1H, d, *J* 8.2), 8.03 (1H, s), 7.87 (1H, d, *J* 7.7), 7.68 (1H, d, *J* 7.7), 7.62 (1H, t, *J* 7.8), 7.49-7.40 (2H, m), 7.37-7.35 (1H, m). δC (101 MHz, $CDCl_3$) 194.0, 139.4, 137.2, 136.6, 133.9, 133.8, 133.6, 132.1, 129.9, 129.3, 127.8, 119.6, 117.9, 113.4. HRMS (ESI): Calcd. for $C_{14}H_8$ ^{81}BrNNaO [M+H]+ 309.9666; found 309.9653.

2-Bromophenyl *4-fluorophenyl methanone (**5k**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with (4-fluorophenyl) boronic acid **4k** (30 mg, 0.13mmol, 1.2 equiv), according to the general procedure A to provide **5k** (15 mg, 30%) as a white solid. Mp 51-53 °C. NMR: δH (400 MHz, $CDCl_3$) 7.84 (2H, m), 7.65 (1H, d, *J* 7.8), 7.45-7.41 (1H, m), 7.40-7.30 (2H, m), 7.14 (2H, t, *J* 8.5). δC (101 MHz, $CDCl_3$) 194.5, 166.3 (d, *J* 256.5), 140.6, 133.4, 133.0 (d, *J* 10.1), 132.7 (d, *J* 2.9), 131.4, 129.0, 127.5, 119.6, 116.0 (d, *J* 22.2). HRMS (ESI): Calcd. for $C_{13}H_8$^{79} BrFNaO $[M+H]^+$ 300.9640; found 300.9630. The spectroscopic data is corresponding to the previously reported in literature.[8]

*2-Bromophenyl 3-fluorophenyl methanone (**5l**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 3-fluorophenyl boronic acid **4l** (30 mg, 0.13 mmol, 1.2 equiv), according to the general procedure A to provide **5l** (37 mg, 76%) as a white solid. NMR: δH (400 MHz, $CDCl_3$) 7.66 (1H, d, *J* 7.8), 7.54 (2H, t, *J* 9.7), 7.47-7.42 (2H, m), 7.40-7.34 (2H, m), 7.33-7.28 (1H, m). δC (101 MHz, $CDCl_3$) 194.7, 162.9 (d, *J* 249.5), 140.2, 138.4 (d, *J* 6.1), 133.5, 131.6, 130.5 (d, *J* 8.1), 129.1, 127.5, 126.3 (d, *J* 3.0), 120.9 (d, *J* 22.2), 119.6, 116.7 (d, *J* 22.2). HRMS (ESI): Calcd. for $C_{13}H_8$ ^{79}BrFNaO $[M+H]^+$ 300.9640; found 300.9630.

*2-Bromophenyl 2-fluorophenyl methanone (**5m**)*. 2-Bromoiodobenzene **3** (50 mg) was reacted with 2-fluorophenyl boronic acid 4m (30 mg, 0.13 mmol, 1.2 equiv) according to the general procedure A to provide **5m** (39 mg, 80%) as a white solid. NMR: δH (400 MHz, $CDCl_3$) 7.61 (1H, t, *J* 7.5), 7.47 (1H, d, *J* 7.8), 7.44-7.38 (1H, m), 7.26-7.25 (2H, m), 7.23-7.17 (1H, m), 7.10 (1H, t, *J* 7.6), 6.97-6.92 (1H, m). δC (101 MHz, $CDCl_3$) 192.90, 161.8 (d, *J* 259.6), 141.7, 135.23 (d, *J* 8.1), 133.5, 131.8, 129.4, 127.5, 125.9 (d, *J* 10.1), 124.5 (d, *J* 3.0), 119.5, 116.8 (d, *J* 22.2). HRMS (ESI): Calcd. for $C_{13}H_8$ ^{81}BrFNaO [M+H]+ 302.9620; found 302.9608.

1.4 Preparation and characterization of 2-benzoylbenzoate esters 2 from 2-bromobenzophenones 5 by alkoxycarbonylation.

*Butyl 2-(4-methoxybenzoyl)benzoate (**2a**)*. (2-Bromophenyl)(4-methoxyphenyl)methanone **5a** (40 mg, 0.14 mmol) was transformed to **2a** (28 mg, 65%) according to the general procedure F. NMR: δH (400 MHz, $CDCl_3$) 8.05 (1H, d, *J* 8.8), 7.73 (2H, d, *J* 8.9), 7.63-7.59 (1H, m), 7.56-7.52 (1H, m), 7.36 (1H, d, *J* 8.8), 6.90 (2H, d, *J* 8.9), 4.05 (2H, t, *J* 6.6), 3.85 (3H, s), 1.46-1.39 (2H, m), 1.27-1.18 (3H, m), 0.82 (3H, t, *J* 7.4). δC (101 MHz, $CDCl_3$) 195.82, 166.24, 163.69, 142.06, 132.32, 131.92, 130.41, 130.32, 129.41, 129.38, 127.67, 113.83, 77.48, 77.16, 76.84, 65.53, 55.62, 30.40, 19.21, 13.78. HRMS (ESI): Calcd. for $C_{19}H_{20}NaO_4$ $[M+H]^+$ 335.1259; found 335.1260.

*Butyl 2-(3-methoxybenzoyl)benzoate (**2b**)*. (2-Bromophenyl)(3-methoxyphenyl)methanone **5b** (30 mg, 0.1 mmol) was transformed to **2b** (19 mg, 60%) according to the general procedure F. NMR: δH (400 MHz, $CDCl_3$) 8.06 (1H, d, *J* 7.6), 7.63 (1H, t, *J* 7.5), 7.56 (1H, t, *J* 7.5), 7.44-7.43 (1H, m), 7.39-7.37 (1H, m), 7.30 (1H, t, *J* 7.9), 7.21-7.18 (1H, m), 7.11-7.09 (1H, m), 4.05 (2H, t, *J* 6.6), 3.84 (3H, s), 1.48 – 1.41 (2H, m), 1.28-1.15 (2H, m), 0.83 (3H, t, *J* 7.4). δC (101 MHz, $CDCl_3$) 196.9, 166.1, 159.9, 141.8,

138.6, 132.4, 130.3, 129.7, 129.6, 129.6, 127.8, 122.9, 120.0, 113.1, 77.5, 77.2, 76.8, 65.6, 55.6, 30.4, 19.2, 13.8. HRMS (ESI): Calcd. for $C_{19}H_{20}NaO_4$ $[M+H]^+$ 335.1259; found 335.1260.

*Butyl 2-(4-fluorobenzoyl)benzoate (**2c**)*. (2-Bromophenyl)(4-fluorophenyl)methanone **5k** (15mg, 0.054 mmol), was transformed to **2c** (10 mg, 63%) according to the general procedure F. δH (400 MHz, $CDCl_3$) 8.07 (1H, d, *J* 8.6), 7.81-7.77 (2H, m), 7.66-7.62 (1H, m), 7.59-7.55 (1H, m), 7.37 (1H, d, *J* 8.6), 7.10 (2H, t, *J* 8.6), 4.06 (2H, t, *J* 6.6), 1.49-1.41 (2H, m), 1.27-1.21 (3H, m), 0.84 (3H, t, *J* 7.4). δC (101 MHz, $CDCl_3$) 195.6, 166.0, 165.9 (d, *J* 255.5), 141.6, 133.8, 132.5, 132.2, 132.2 (d, *J* 10.1), 132.1, 130.4, 129.8, 129.4, 127.6, 115.9, 115.7, 77.5, 77.2, 76.8, 65.6, 30.4, 19.2, 13.9, 13.8. HRMS (ESI): Calcd. for $C_{18}H_{17}FNaO_3$ $[M+H]^+$ 323.1059; found 323.1059.

*Butyl 2-(2-fluorobenzoyl)*benzoate (**2d**). (2-Bromophenyl)(4-methoxyphenyl)methanone **5m** (40 mg, 0.47 mmol) was transformed to **2d** (22 mg, 50%) according to the general procedure F. NMR: δH (400 MHz, $CDCl_3$) 8.53 (1H, d, *J* 7.6), 8.38-8.33 (1H, m), 8.12-8.10 (1H, m), 8.07-8.05 (1H, m), 7.89-7.87 (2H, m), 7.77-7.75 (1H, m), 7.69-7.61 (1H, m), 7.60-7.55 (1H, m), 4.62 (2H, t, *J* 6.6), 2.03-1.99 (2H, m), 1.84-1.71 (3H, m), 1.36 (3H, t, *J* 7.4). δC (101 MHz, $CDCl_3$) 193.7, 166.3, 163.2, 161.9 (d, *J* 258.6), 160.7, 143.5, 134.99, 135.0 (d, *J* 9.1), 134.6, 132.3, 131.5, 130.1, 129.7, 127.0, 125.9, 124.3 (d, *J* 4.0), 124.3, 117.0, 116.9 (d, *J* 23.2), 116.8, 65.6, 30.5, 19.2, 13.8. HRMS (ESI): Calcd. for $C_{18}H_{17}FNaO_3$ [M+H]+ 323.1059; found 323.1059.

1.5 Preparation and characterization of 2-benzoylbenzoate esters 2 from 2-bromobenzoates 6 by Suzuki-Miyaura couplings.

*Methyl 2-(4-methoxybenzoyl)benzoate (**2aa**)*. Methyl 2-bromobenzoate **6a** (100 mg for procedure C and D; 50 mg for procedure E) was reacted with 4-methoxyphenyl boronic acid **4a** (105 mg, 1.5 equiv, 0.66 mmol), DABO boronate 2-(4-methoxyphenyl)-1,3,6,2-dioxazaboroane **7a** (82 mg, 1.5 equiv, 0.37 mmol) or sodium trihydroxy(4-methoxyphenyl)borate **8a** (72 mg, 1.5 equiv, 0.37 mmol). Reactions were performed following general procedure C, D or E to provide **2aa** as a colorless oil. Procedure C with **4a**: 100 mg, 80%; procedure D with **4a**: 80 mg, 63%; procedure E with **7a**: 45 mg, 67%; procedure E with **8a**: 44 mg, 65%. NMR: δH (400 MHz, $CDCl_3$) 8.02 (1H, d, *J* 7.6), 7.71 (2H, d, *J* 8.8), 7.61 (1H, t, *J* 7.5), 7.53 (1H, t, *J* 7.5), 7.37 (1H, d, *J* 7.6), 6.89 (2H, d, *J* 8.8), 3.83 (3H, s), 3.63 (3H, s). δC (101 MHz, $CDCl_3$) 195.9, 166.5, 163.6, 142.1, 132.4, 132.3, 131.7, 130.3, 130.2, 129.4, 129.2, 127.8, 113.8, 55.6, 52.3. HRMS (ESI): Calcd. for $C_{16}H_{14}NaO_4$ $[M+H]^+$ 293.0790; found 293.0784. The spectroscopic data is corresponding to the previously reported in literature.[6]

*Methyl 2-(3-methoxybenzoyl) benzoate (**2ab**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 3-methoxyphenyl boronic acid **4b** (105 mg, 1.5 equiv, 0.66 mmol) according to the general procedure C to provide **2ab** (65 mg, 52%) as a colorless oil. NMR: δH (400 MHz, $CDCl_3$) 7.90 (1H, d, *J* 8.7), 7.61-7.46 (1H, m), 7.46-7.33 (1H, m), 7.28 (2H, s), 7.21-7.08 (1H, m), 7.05 (1H, d, *J* 7.7), 6.96 (1H, dd, *J* 8.7, 3.2), 3.70 (3H, s), 3.50 (3H, s). δC (101 MHz, $CDCl_3$) 196.9, 166.5, 159.9, 141.8, 138.6, 132.5, 132.0, 131.2, 130.1, 130.0, 129.7, 129.6, 129.3, 129,0, 127.8, 122.5, 119.8, 113.0, 55.5, 55.3, 52.7, 52.3. HRMS (ESI): Calcd. for $C_{16}H_{14}NaO_4$ $[M+H]^+$ 293.0790; found 293.0784.

*Methyl 2-(2-methoxybenzoyl)benzoate (**2ac**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 2-methoxyphenyl boronic acid **4c** (105 mg, 1.5 equiv, 0.66 mmol) according to the general procedure C to provide **2ac** (93 mg, 74%) as a white solid, Mp 100-103 °C. NMR: δH (400 MHz, $CDCl_3$) 7.87 (1H, d, *J* 8.7), 7.74-7.67 (1H, m), 7.53 (1H, t, *J* 7.5), 7.50-7.42 (2H, m), 7.36 (1H, d, *J* 8.7), 6.99 (1H, t, *J* 7.9), 6.90 (1H, d, *J* 8.3), 3.59 (3H, s), 3.57 (3H, s). δC (101 MHz, $CDCl_3$) 195.7, 167.3, 159.0, 143.8, 134.2, 131.7, 131.6, 129.5, 129.3, 127.5, 127.0, 120.5, 112.2, 77.4, 55.7, 52.1. HRMS (ESI): Calcd. for $C_{16}H_{14}NaO_4$ $[M+H]^+$ 293.0790; found 293.0784.

*Methyl 2-(4-(methylthio)benzoyl) benzoate (**2ad**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 4-(methylthio) phenyl boronic acid (110 mg, 1.5 equiv, 0.65 mmol) according to the general procedure C to provide (101 mg, 76%) as a white solid, Mp 84-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.02 (1H, d, *J* 8.6), 7.64 (2H, d, *J* 8.5), 7.61-7.59 (1H, m), 7.53-7.51 (1H, m), 7.36 (2H, d, *J* 8.6), 7.21(2H, d, *J* 8.5), 3.62 (3H, s), 2.47 (3H, s). δC NMR (101 MHz, $CDCl_3$) 196.1, 166.4, 146.1, 141.8, 133.5, 132.4, 130.1, 129.7, 129.5, 129.1, 127.7, 124.9, 52.3, 14.7. HRMS (ESI): Calcd. for $C_{16}H_{14}NaO_3S$ $[M+H]^+$ 309.0561; found 309.0559.

*Methyl 2-(3-(methoxycarbonyl)benzoyl)benzoate (**2ag**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 3-(methoxycarbonyl)phenyl boronic acid **4g** (125 mg, 1.5 equiv, 0.70 mmol) according to the general procedure C to provide **2ag** (65 mg, 47%) as a colorless oil. NMR: δH (400 MHz, $CDCl_3$) 8.37 (1H, s), 8.23-8.21 (1H, m), 8.07 (1H, d, *J* 8.6), 7.96-7.95 (1H, m), 7.70-7.63 (1H, m), 7.63-7.56 (1H, m), 7.53 (1H, t, *J* 7.8), 7.40 (1H, d, *J* 8.6), 3.90 (3H, s), 3.64 (3H, s). δC (101 MHz, $CDCl_3$) 196.4, 166.4, 141.4, 137.7, 134.0, 133.4, 132.8, 130.8, 130.5, 130.4, 130.0, 129.2, 128.9, 127.8, 52.5, 52.4. HRMS (ESI): Calcd. for $C_{17}H_{14}NaO_5$ $[M+H]^+$ 321.0739; found 321.0730

*Dimethyl 2,2'-carbonyldibenzoate (**2ah**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 2-(methoxycarbonyl)phenyl boronic acid **4h** (125 mg, 1.5 equiv, 0.70 mmol). Reactions were performed both by the general procedure C and D to provide **2ah** as a white solid, Mp 205-207 °C. Procedure C: 103 mg, 75%; procedure D: 36 mg, 26%. NMR: δH (400 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.6), 7.58-7.56 (2H, m), 7.53-7.48 (2H, m), 7.40 (2H, d, *J* 8.6), 3.73 (6H, s). δC (101 MHz, $CDCl_3$) 195.7, 168.3, 138.5, 132.0, 131.4, 131.2, 129.7, 129.4, 128.9, 77.4, 52.6. HRMS (ESI): Calcd. for $C_{17}H_{14}NaO_5$ $[M+H]^+$ 321.0739; found 321.0730.

*Methyl 2-(4-cyanobenzoyl) benzoate (**2ai**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with 4-cyanophenyl boronic acid **4i** (102 mg, 1.5 equiv, 0.7 mmol). Reactions were performed following general procedure C or D to provide **2ai** as a colourless oil. Procedure C: 40 mg, 32%; procedure D: 20 mg, 16%. NMR: δH (400 MHz, $CDCl_3$) 8.08 (1H, d, *J* 8.6), 7.83 (2H, d, *J* 8.6), 7.73 (2H, d, *J* 8.6), 7.69-7.67 (1H, m), 7.64 – 7.60 (1H, m), 7.40 (1H, d, *J* 8.6), 3.67 (3H, s). δC (101 MHz, $CDCl_3$) 195.4, 165.8, 140.6, 140.2, 132.7, 132.2, 130.1, 130.0, 129.2, 128.8, 127.4, 117.8, 116.0, 52.3. HRMS (ESI): Calcd. for $C_{16}H_{11}NNaO_3$ $[M+H]^+$ 288.0637; found 288.0630.

*Methyl 2-(3-cyanobenzoyl) benzoate (**2aj**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with (3-cyanophenyl) boronic acid **4j** (102 mg, 1.5 equiv, 0.7 mmol). Reactions were performed following general procedure C or D to provide **2aj** as a colourless oil. Procedure C: 48 mg, 40%; procedure D: 32 mg, 26%. NMR: δH (400 MHz, $CDCl_3$) 8.10 (1H, d, *J* 8.6), 8.03-7.01 (1H, m), 7.96 (1H, s), 7.83-7.81 (1H, m), 7.70 (1H, t, *J* 7.5), 7.66 – 7.59 (1H, m), 7.58-7.56 (1H, m), 7.38 (1H, d, *J* 8.6), 3.70 (3H, s). δC NMR (101 MHz, $CDCl_3$) 195.5, 166.4, 141.1, 138.6, 136.3, 133.4, 133.3, 133.2, 130.9, 130.6, 130.1, 129.3, 127.9, 118.4, 113.5, 52.9. Calcd. for $C_{16}H_{11}NNaO_3$ $[M+H]^+$ 288.0637; found 288.0630.

*Methyl 2-(4-fluorobenzoyl) benzoate (**2ak**)*. Methyl 2-bromobenzoate **6a** (100 mg for procedure C; 50 mg for procedure E) was reacted with 4-fluorophenyl boronic acid **4k** (100 mg, 1.5 equiv, 0.7 mmol) or 2-(4-fluorophenyl)-1,3,6,2-dioxazaborocane **7k** (73 mg, 1.5 equiv, 0.35 mmol) according to the general procedure C or E to provide **2ak** as a colourless oil. Procedure C: 45 mg, 37%; procedure E: 15 mg, 25%. NMR: δH (400 MHz, $CDCl_3$) 8.05 (1H, d, *J* 8.7), 7.79-7.75 (2H, m), 7.66-7.62 (1H, m), 7.59-7.55 (1H, m), 7.38 (1H, d, *J* 8.7), 7.12-7.07 (2H, m), 3.65 (3H, s). δC (101 MHz, $CDCl_3$) 195.5, 166.4, 165.8 (d, *J* 256.5), 164.4, 141.5, 133.8 (d, *J* 3.0), 132.5, 132.0 (d, *J* 9.1), 130.3, 129.8, 129.2, 127.6, 115.8 (d, *J* 20.2), 52.3. HRMS (ESI): Calcd. for $C_{15}H_{11}FNaO_3$ $[M+H]^+$ 281.0590; found 281.0584. The spectroscopic data is corresponding to the previously reported in literature.[6]

*Methyl 2-(3-fluorobenzoyl) benzoate (**2al**)*. Methyl 2-bromobenzoate **6a** (100 mg) was reacted with (3-fluorophenyl) boronic acid **4l** (100 mg, 1.5 equiv, 0.7 mmol). Reactions were performed following general procedure C or D to provide **2al** as a colorless oil. Procedure C: 70 mg, 58%; procedure D: 51 mg, 43%. NMR: δH (400 MHz, $CDCl_3$) 8.06 (1H, d, *J* 8.7), 7.67-7.63 (1H, m), 7.60-7.56 (1H, m), 7.50-7.44 (2H, m), 7.41-7.35 (2H, m), 7.29-7.21 (1H, m), 3.66 (3H, s). δC (101 MHz, $CDCl_3$) 196.2, 166.6, 163.2 (d, *J* 249.5), 141.8, 139.7 (d, *J* 7.1), 133.0, 130.7, 130.6, 130.3, 129.5, 128.1, 125.5 (d, *J* 3.0), 120.6 (d, *J* 21.6), 116.1 (d, *J* 23.2), 52.7. HRMS (ESI): Calcd. for $C_{15}H_{11}FNaO_3$ $[M+H]^+$ 281.0590; found 281.0584.

*Methyl 2-(2-fluorobenzoyl) benzoate (**2am**).* Methyl 2-bromobenzoate **6a** (100 mg for procedure C and D; 50 mg for procedure E) was reacted with 2-fluorophenyl boronic acid **4m** (100 mg, 1.5 equiv, 0.7 mmol) or 2-(2-fluorophenyl)-1,3,6,2-dioxazaborocane **7m** (73 mg, 1.5 equiv, 0.35 mmol). Reactions were performed following general procedure C, D or E to provide **2am** as a white solid, Mp 56-59 °C. Procedure C: 78 mg, 65%; procedure D: 50 mg, 42%; procedure E: 21 mg, 35%. NMR: δH (400 MHz, $CDCl_3$) 8.02 (1H, d, *J* 8.8), 7.85-7.81 (1H, m), 7.67-7.63 (1H, m), 7.61-7.52 (2H, m), 7.44-7.42 (1H, m), 7.31-7.24 (1H, m), 7.12-7.07 (1H, m), 3.72 (3H, s). δC (101 MHz, $CDCl_3$) 193.8, 166.8, 161.7 (d, *J* 258.6),134.8 (d, *J* 9.1), 132.5, 131.3, 130.00 (d, *J* 19.2), 128.9, 127.2, 125.9 (d, *J* 10.0), 124.3 (d, *J* 4.0), 116.87 (d, *J* 22.2), 52.4. HRMS (ESI): Calcd. for $C_{15}H_{11}FNaO_3$ $[M+H]^+$ 281.0590; found 281.0584.

*Methyl 2-(thiophene-2-carbonyl) benzoate (**2an**)*. Methyl 2-bromobenzoate **6a** (50 mg), was reacted with 2-(thiophen-2-yl)-1,3,6,2-dioxazaborocane **7n** (69 mg, 1.5 equiv, 0.35 mmol) according to the general procedure E to provide **2an** (29 mg, 50%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 8.02 (1H, d, *J* 7.6), 7.65-7.61 (2H, m), 7.58-7.54 (2H, m), 7.45 (1H, d, *J* 7.6), 7.35-7.33 (1H, m), 3.67 (3H, s). δC (101 MHz, $CDCl_3$) 190.7, 166.7, 142.8, 142.2, 133.9, 132.4, 130.3, 129.9, 129.3, 127.8, 127.4, 126.8, 52.4. The spectroscopic data is corresponding to the previously reported in literature.[9]

*Methyl 2-(benzo[b]thiophene-2-carbonyl) benzoate (**2ao**)*. Methyl 2-bromobenzoate **6a** (50 mg), was reacted with 2-(benzo[*b*]thiophen-2-yl)-1,3,6,2-dioxazaborocane **7o** (86 mg, 1.5 equiv, 0.35 mmol) according to the general procedure E to provide **2ao** (55 mg, 75%) as a yellow solid. Mp 78-80 °C. NMR: δH (400 MHz, $CDCl_3$) 7.89 (1H, d, *J* 7.5), 7.68 (1H, d, *J* 8.0), 7.57 (1H, d, *J* 8.0), 7.48-7.45 (2H, m), 7.42 – 7.39 (1H, m), 7.33(1H, d, *J* 7.5), 7.25-7.22 (1H, m), 7.17-7.14 (1H, m), 3.48 (3H, s). δC (101 MHz, $CDCl_3$) 190.7, 166.3, 144.1, 142.8, 140.8, 138.9, 132.4, 131.6, 130.3, 130.1, 129.2, 127.7, 127.5, 126.1, 125.0, 123.0, 52.4. HRMS (ESI): Calcd. for $C_{17}H_{12}NaO_3S$ $[M+H]^+$ 319.0405; found 319.0407.

*Methyl 5-fluoro-2-(4-methoxybenzoyl)benzoate (**2ba**)*. Methyl 2-bromo-5-fluorobenzoate **6b** (50 mg, 0.21 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (48 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2ba** (44 mg, 72%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.72-7.68 (3H, m), 7.44-7.37 (1H, m), 7.33-7.28 (1H, m), 6.92-6.90 (2H, m), 3.85 (3H, s), 3.64 (3H, s). δC (101 MHz, $CDCl_3$) 194.8, 165.5 (d, *J* 3.0), 163.8, 162.8 (d, *J* 251.5), 138.1 (d, *J* 3.0), 131.7, 130.2, 130.0 (d, *J* 8.1), 119.4 (d, *J* 22.2), 117.2 (d, *J* 23.2), 113.9, 77.4, 55.6, 52.6. HRMS (ESI): Calcd. for $C_{16}H_{13}FNaO_4$ $[M+H]^+$ 311.0696; found 311.0695.

*Methyl 4-fluoro-2-(4-methoxybenzoyl)benzoate (**2ca**)*. Methyl 2-bromo-4-fluorobenzoate **6c** (57 mg, 0.24 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (48 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2ca** (35 mg, 50%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 8.08 (1H, dd, *J* 8.7, 5.4), 7.72 (2H, d, *J* 9.0), 7.24-7.19 (1H, m), 7.07 (1H, dd, *J* 8.3, 2.6), 6.92 (2H, d, *J* 9.0), 3.86 (3H, s), 3.64 (3H, s). δC (101 MHz, $CDCl_3$) 194.2, 165.5, 164.9 (d, *J* 257.5), 163.9, 145.1 (d, *J* 7.1), 133.1 (d, *J* 10.1), 131.8, 129.7, 125.2 (d, *J* 3.0), 116.5 (d, *J* 21.2), 115.2 (d, *J* 24.2), 114.0, 55.7, 52.4. HRMS (ESI): Calcd. for $C_{16}H_{13}FNaO_4$ $[M+H]^+$ 311.0696; found 311.0695.

*Methyl 5-chloro-2-(4-methoxybenzoyl)benzoate (**2da**)*. Methyl 2-bromo-5-chlorobenzoate **6d** (50 mg, 0.20 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (45 mg, 1.5 equiv, 0.30 mmol) according to the general procedure E to provide **2da** (30 mg, 50%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 8.01 (1H, d, *J* 2.1), 7.71 (2H, d, *J* 9.0), 7.59 (1H, dd, *J* 8.1, 2.1), 7.33 (1H, d, *J* 8.1), 6.91 (2H, d, *J* 9.0), 3.86 (3H, s), 3.65 (3H, s). δC (101 MHz, $CDCl_3$) 194.8, 165.5, 163.9, 140.4, 135.7, 132.4, 131.8, 131.0, 130.3, 130.1, 129.3, 114.0, 55.6, 52.7. HRMS (ESI): Calcd. for $C_{16}H_{13}ClNaO_4$ $[M+H]^+$ 327.0400; found 327.0401.

*Methyl 4-chloro-2-(4-methoxybenzoyl)benzoate (**2ea**)*. Methyl 2-bromo-4-chlorobenzoate **6e** (50 mg, 0.20 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (46 mg, 1.5 equiv, 0.30 mmol) according to the general procedure E to provide **2ea** (40 mg, 65%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.99 (1H, d, *J* 8.4), 7.72 (2H, d, *J* 9.0), 7.51 (1H, dd, *J* 8.4, 2.0), 7.36 (2H, d, *J* 2.0), 6.92 (2H, d, *J* 9.0), 3.86 (3H, s), 3.65 (3H, s). δC (101 MHz, $CDCl_3$) 194.2, 165.7, 163.9, 143.8, 139.1, 131.8,

131.8, 129.8, 129.6, 127.9, 127.4, 114.0, 55.7, 52.5. HRMS (ESI): Calcd. for $C_{16}H_{13}ClNaO_4$ $[M+H]^+$ 327.0400; found 327.0402.

*Methyl 2-(4-methoxybenzoyl)-5-methylbenzoate (**2fa**)*. Methyl 2-bromo-5-methylbenzoate **6f** (57 mg, 0.19 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (49 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2fa** (50 mg, 71%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.82 (1H, s), 7.72 (2H, d, *J* 9.0), 7.41 (1H, d, *J* 8.4), 7.28 (1H, d, *J* 7.7), 6.89 (2H, d, *J* 9.0), 3.84 (3H, s), 3.60 (3H, s), 2.45 (3H, s). δC (101 MHz, $CDCl_3$) 196.0, 166.9, 163.5, 139.8, 139.2, 132.9, 131.7, 130.6, 129.4, 128.0, 113.8, 77.4, 55.6, 52.2, 21.3. HRMS (ESI): Calcd. for $C_{17}H_{16}NaO_4$ $[M+H]^+$ 307.0900; found 307.0947.

*Methyl 2-(4-methoxybenzoyl)-3-methylbenzoate (**2ga**)*. Methyl 2-bromo-3-methylbenzoate **6g** (59 mg, 0.26 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (49 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2ga** (50 mg, 68%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.92 (1H, d, *J* 8.5), 7.73-7.71 (2H, m), 7.45-7.40 (2H, m), 6.90 (2H, d, *J* 9.1), 3.84 (3H, s), 3.67 (3H, s), 2.17 (3H, s). δC (101 MHz, $CDCl_3$) 197.0, 166.4, 163.7, 141.9, 135.6, 135.0, 131.1, 130.7, 128.6, 128.3, 127.9, 114.0, 77.4, 19.3. HRMS (ESI): Calcd. for $C_{17}H_{16}NaO_4$ $[M+H]^+$ 307.0946; found 307.0945.

*Methyl 4-methoxy-2-(4-methoxybenzoyl) benzoate (**2ha**)*. Methyl 2-bromo-4-methoxybenzoate **6h** (50 mg, 0.20 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (46 mg, 1.5 equiv, 0.30 mmol) according to the general procedure E to provide **2ha** (47 mg, 77%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 8.01 (1H, d, *J* 8.8), 7.73 (2H, d, *J* 9.0), 7.00 (1H, dd, *J* 8.8, 2.6), 6.89 (2H, d, *J* 9.0), 6.83 (1H, d, *J* 2.6), 3.85 (3H, s), 3.84 (3H, s), 3.61 (3H, s). δC (101 MHz, $CDCl_3$) 195.6, 166.0, 163.6, 162.9, 144.6, 132.4, 131.7, 130.2, 120.9, 114.8, 113.9, 112.7, 77.4, 55.8, 55.6, 52.0. HRMS (ESI): Calcd. for $C_{17}H_{16}NaO_5$ $[M+H]^+$ 323.0895; found 323.0894.

*Methyl 2-(4-methoxybenzoyl)-5-methylbenzoate (**2ia**)*. Methyl 2-bromo-4,5-dimethoxybenzoate **6i** (50 mg, 0.18 mmol), was reacted with (4-methoxyphenyl) boronic acid **4a** (40 mg, 1.5 equiv, 0.26 mmol) according to the general procedure E to provide **2ia** (44 mg, 73%) as a white solid, Mp 151-153 °C. NMR: δH (400 MHz, $CDCl_3$) 7.70 (2H, d, *J* 9.0), 7.50 (1H, s), 6.89 (2H, d, *J* 9.0), 6.84 (1H, s), 3.97 (3H, s), 3.90 (3H, s), 3.84 (3H, s), 3.55 (3H, s). δC (101 MHz, $CDCl_3$) 195.6, 166.2, 163.5, 152.3, 149.3, 136.0, 131.5, 130.7, 121.5, 113.8, 112.2, 110.3, 56.3, 55.6, 52.1. HRMS (ESI): Calcd. for $C_{18}H_{18}NaO_6$ $[M+H]^+$ 353.1001; found 353.1001. The spectroscopic data is corresponding to the previously reported in literature.[10]

*Methyl 5-fluoro-2-(2-methoxybenzoyl)benzoate (**2bc**)*. Methyl 2-bromo-5-fluorobenzoate **6b** (50 mg, 0.24 mmol), was reacted with (2-methoxyphenyl) boronic acid **4c** (49 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2bc** (40 mg, 66%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 7.72 (1H, dd, *J* 7.7, 1.8), 7.54 (1H, dd, *J* 8.9, 2.6), 7.51-7.44 (1H, m), 7.42-7.38 (1H, m), 7.25-7.20 (1H, m), 7.02 (1H, t, *J* 7.5), 6.92 (1H, d, *J* 8.4), 3.61 (3H, s), 3.60 (3H, s). δC (101 MHz, $CDCl_3$) 194.6, 166.5, 166.4 (d, *J* 2.0), 162.9 (d, *J* 252.5), 158.9, 139.7 (d, *J* 4.0), 134.4, 132.3 (d, *J* 7.1), 131.5, 130.2 (d, *J* 8.1), 127.0, 120.7, 118.6 (d, *J* 22.2), 116.4 (d, *J* 24.2) , 112.2, 55.7, 52.5. HRMS (ESI): Calcd. for $C_{16}H_{13}FNaO_4$ $[M+H]^+$ 311.0696; found 311.0693.

*Methyl 5-fluoro-2-(2-(methoxycarbonyl)benzoyl)benzoate (**2bh**).* Methyl 2-bromo-5-fluorobenzoate **6b** (50 mg, 0.24 mmol), was reacted with 2-(methoxycarbonyl)phenylboronic acid **4h** (58 mg, 1.5 equiv, 0.32 mmol) according to the general procedure E to provide **2bh** (30 mg, 40%) as a colorless oil. NMR: δH (400 MHz, $CDCl_3$) 7.85 (1H, d, *J* 8.8), 7.61-7.53 (2H, m), 7.44 (1H, dd, *J* 5.9, 2.6), 7.42-7.41 (1H, m), 7.40 (1H, s), 3.78 (3H, s), 3.74 (3H, s). δC (101 MHz, $CDCl_3$) 194.5, 167.9, 167.5 (d, *J* 2.0), 164.1 (d, *J* 255.5) , 138.9, 135.2 (d, *J* 8.1), 134.3 (d, *J* 4.0), 132.6 (d, *J* 9.1), 131.5, 131.4 (d, *J* 27.3), 129.5 (d, *J* 37.4), 117.9, 117.8 (d, *J* 22.2), 116.7 (d, *J* 24.2), 77.4, 53.0, 52.7. HRMS (ESI): Calcd. for $C_{17}H_{13}FNaO_5$ $[M+H]^+$ 339.0645; found 339.0640.

*Methyl 2-(2-naphthoyl)-4-methoxybenzoate (**2hp**)*. Methyl 2-bromo-4-methoxybenzoate **6h** (50 mg, 0.20 mmol), was reacted with 2-napthylboronic acid **4p** (52 mg, 1.5 equiv, 0.30 mmol) according to the general procedure E to provide **2hp** (57 mg, 61%) as a colourless oil. NMR: δH (400 MHz, $CDCl_3$) 8.09-8.07 (2H, m), 8.02 (1H, dd, *J* 8.6, 1.7), 7.93-7.88 (1H, m), 7.86-7.83 (2H, m), 7.60-7.56 (1H, m), 7.53-7.48 (1H, m),7.08 (1H, dd, *J* 8.8, 2.6), 6.93 (1H, d, *J* 2.6), 3.89 (3H, s), 3.57 (3H, s). δC (101 MHz, $CDCl_3$) 197.0, 166.0, 163.0, 144.4, 135.8, 134.7, 132.6, 132.5, 131.6, 129.8, 128.7, 127.9, 126.8, 124.4, 121.1, 115.1, 112.9, 77.4, 55.8, 52.1. HRMS (ESI): Calcd. for $C_{19}H_{14}NaO_4$ $[M+H]^+$ 329.0790; found 329.0790.

2 Additional experimental information

2.1 Two-chamber set-up:

The reactions were performed in the previously reported two-chamber system (Fig 1) under an argon atmosphere.

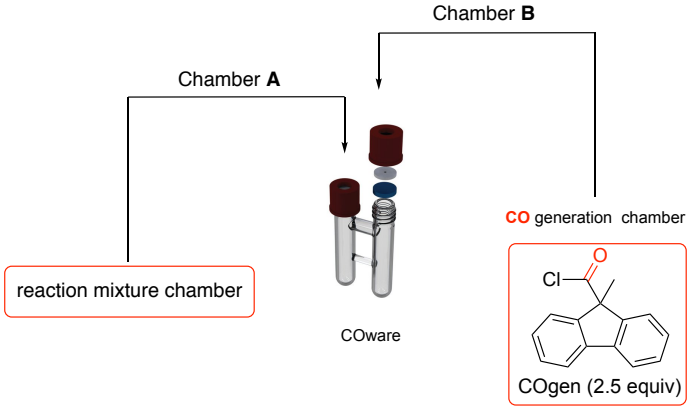
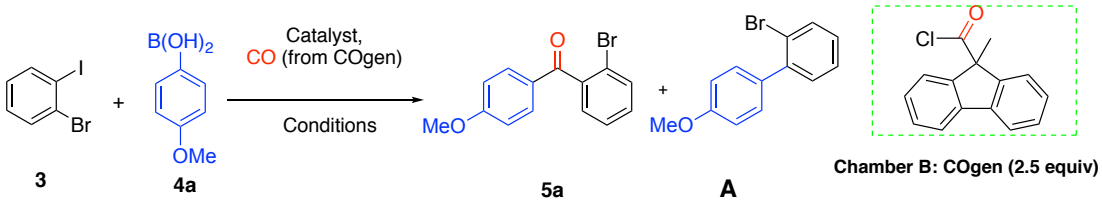


Fig 1. The two-chamber system used in the reactions, and the CO generator (COgen)

2.2 Screening of catalysts and conditions for the Suzuki- Miyaura coupling of 2-bromoiodobenzene 3 with 4-methoxyphenyl boronic acid 4a.



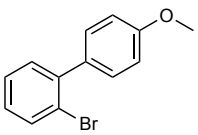
Procedure:

Chamber A: 2-Bromoiodobenzene **3** (50 mg, 1.0 equiv, 0.18 mmol), aryl boronic acid **4a** (1.2 equiv), catalyst and base were dissolved in a solvent (3 ml).

Chamber B: COgen (107 mg, 2.5 equiv, 0.45 mmol), $Pd(dba)_2$ (12 mg, 5 mol%), tri-*tert*-butylphosphonium tetrafluoroborate (TTBP•HBF_4) (6.3 mg, 5 mol%) were dissolved in anisole (3 ml).

DIPEA (240 mg, 3 equiv) was added to chamber B to release CO. The mixture was stirred at 80 °C in a tightly closed system for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent. The ratio (5a: A) has been evaluated based on the crude ^{13}C NMR spectra. The experimental data and the NMR spectra of the byproduct A is shown later.

*Characterization of 2-bromo-4'-methoxy-1,1'-biphenyl **A** (from direct coupling).*



The title compound was isolated as a side product from reactions towards **5a**. NMR: δH (400 MHz, $CDCl_3$) 7.66 (1H, d, *J* 7.8), 7.40-7.31 (4H, m), 7.22-7.13 (1H, m), 6.97

(2H, d, *J* 8.7), 3.87 (3H, s). δC (101 MHz, $CDCl_3$) 159.2, 142.3, 133.7, 133.2, 131.5, 130.7, 128.5, 127.9, 127.5, 123.0, 114.3, 113.5, 77.5, 77.2, 76.8, 55.5, 55.4.

Table ESI-1. Carbonylative Suzuki-Miyaura coupling of 2-bromoiodobenzene **3** with 4-methoxyphenyl boronic acid **4a**.

Entry	Catalyst (mol%)	base	Rxn. time (h)	T (ºC)	Solvent	Addition	Approx. ratio[c] 5a : A	Isol. yield (%)
1	$Pd(PPh_3)_2Cl_2$ (3)	K_2CO_3	20	80	Anisole	normal	0.7 : 1	50
2	$Pd(OAc)_2$ (2)	K_2CO_3	20	80	Anisole	normal	0.1 : 1	10
3	$Pd(dba)_2$ (3)	K_2CO_3	20	80	Anisole	normal	0.5 : 1	35
4	PEPPSI-IPr (3)	Cs_2CO_3	20	80	Chlorobenzene	normal	0.7 : 1	30
5	$PdCl_2$ (3)	K_2CO_3	20	80	Anisole	normal	0.7 : 1	65
6	$PdCl_2$ (1)	K_2CO_3	20	80	Anisole	normal	0.7 : 1	60
7	$PdCl_2$ (1)	K_2CO_3	20	50	Anisole	normal	0.2 : 1	30
8	$PdCl_2$ (1)	K_2CO_3	20	60	Anisole	normal	0.3 : 1	35
9	$PdCl_2$ (1)	K_2CO_3	40	80	Anisole	normal	1 : 1	65
10	$PdCl_2$[b] (1)	K_2CO_3[b]	20	80	Anisole	normal	1 : 0.9	55
11	$PdCl_2$ (1)	K_2CO_3/KI	20	80	Anisole	normal	0.6 : 1	55
12	$PdCl_2$ (1)	Cs_2CO_3	20	80	Anisole	normal	1 : 1	60
13	$PdCl_2$ (1)	K_2CO_3	20	80	Anisole	slow[a]	1 : 0.1	80
14	$PdCl_2$ (1)	K_2CO_3	20	100	Anisole	slow[a]	1 : 0.1	80
15	PEPPSI- IPr (3)	Cs_2CO_3	20	80	Chlorobenzene	slow[a]	1 : 1	60
16	PEPPSI- IPr (3)	Cs_2CO_3	20	120	Chlorobenzene	slow[a]	1 : 1	65

aInstead of dissolving **4a** in chamber A before CO release, a solution of aryl boronic acid **4a** (1.2 equiv) in anisole (2 ml) was added slowly (1-2 h) to the reaction mixture in chamber A after CO release. See General procedure A. b $PdCl_2$ and K_2CO_3 were used as a premix with ratio 1:300. c The ratio (5a : A) is approximately determined using ^{13}C NMR of the crude product mixture.

2.3 Screening of precursors for ex-situ generation of CO.

Procedures:

Chamber A: 2-Bromoiodobenzene **3** (50 mg, 1.0 equiv, 0.18 mmol), $PdCl_2$ (0.3 mg, 1 mol%), K_2CO_3 (70 mg, 3 equiv, 0.55 mmol) were dissolved in a solvent (3 ml). In case of normal addition, the aryl boronic acid **4a** (1.2 equiv) was added to the mixture before CO generation was started. In case of slow addition, the aryl boronic acid **4a** (1.2 equiv) was dissolved in anisole (2 ml) and added after CO generation over a period of 1-2 hours.

Chamber B for entry 1 and 2: Fe-tetraphenylporphyrin (6 mg), $TBABF_4$ (1.1g), DMF (30 ml), and tetrafluoroethylene (2 ml) were introduced to chamber B. Electrodes were mounted and the COware was sealed tightly with the screw caps fitted with teflon-coated silicon seals.

The reaction mixture in chamber A was bubbled through with CO_2 for 10-15 min until saturation. The ElectroWare[4] was set up using galvanostatic configuration. The electrodes were connected and the electrolysis began, while both reaction chambers were stirring. Chamber B kept stirring at room temperature, while the other chamber A was placed in a preheated hotplate at 80 °C for 18 h. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent.[11]

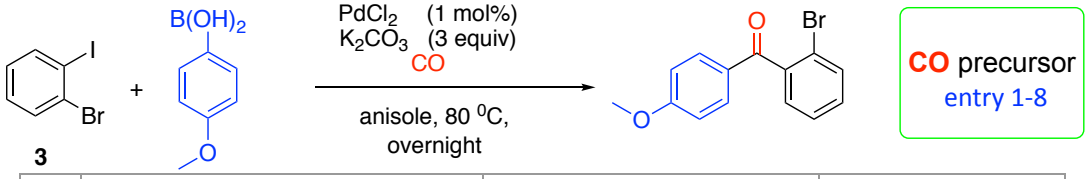
Chamber B for entry 3 and 4: COgen (107 mg, 2.5 equiv, 0.45 mmol), $Pd(dba)_2$ (12 mg, 5 mol%), tri-*tert*-butylphosphonium tetrafluoroborate (TTBP•HBF_4) (6.3 mg, 5 mol%) and DIPEA (240 mg, 3 equiv) were dissolved in anisole (3 ml).

The mixture was stirred at 80 °C in a tightly closed system for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent.

For entry 5 and 6: To a two necked round bottomed flask degassed and charged with aqueous solution of NaOH (2 M, 20 ml), a balloon was fitted via 5 ml syringe cylinder at one neck. The syringe cylinder was filled with $CaCl_2$ as a drying agent, that was kept in place by cotton wool pads at both sides. Through the other neck oxalyl chloride was added slowly with a syringe to the basic solution. The evolved gas was collected in the balloon. The CO balloon was transferred to the reaction mixture vial (chamber A). The mixture was stirred at 80 °C in a tightly closed system for 20 hours. The reaction mixture was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane: EtOAc (8:2) as eluent.[12]

Chamber B for entry 7 and 8: Sulfuric acid (1.5 mmol) was introduced before the two-chamber system was tightened and heated at 80 °C. Then formic acid was added slowly to chamber B. The reaction mixture was allowed to stir at 80 °C for 18h.[13]

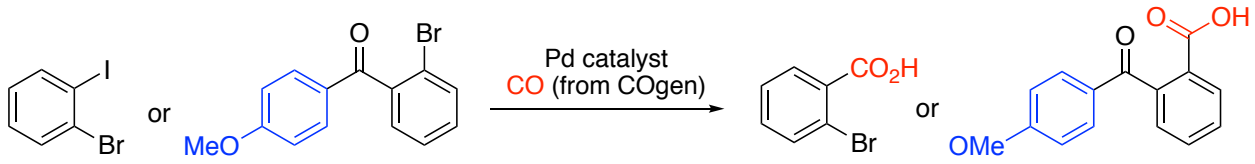
Table ESI-2. Screening of CO precursors.



3

no	CO source	Addition of boronic acid	Isolated yield (%)
1	CO_2 reduction	Normal	29
2	CO_2 reduction	Slow addition	30
3	COgen	Normal	60
4	COgen	Slow addition	80
5	Oxalyl chloride+ NaOH (aq)	Normal (ballon)	60
6	Oxalyl chloride + NaOH (aq)	Slow addition (ballon)	60
7	Formic acid+ H_2SO_4 (1.2 mmol)	Normal (ballon)	10
8	Formic acid+ H_2SO_4 (1.2 mmol)	In situ	0

2.4 Attempts to hydroxycarbonylate 2-bromoiodobenzene 3 or 2-bromobenzophenone 5a



3 **5a**

Procedures:

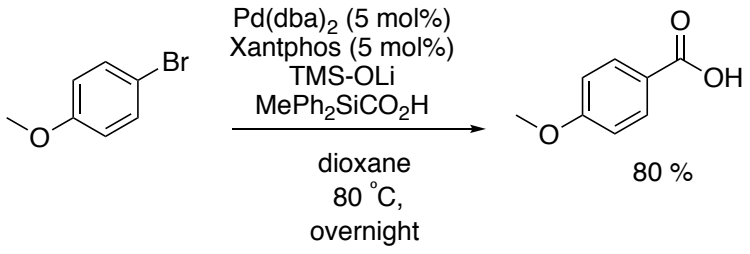
In a dry and clean 8 ml vial equipped with a stirring bar, the aryl halide (1 equiv.), $MePh_2SiCOOH$ (64 mg, 1.5 equiv), base (2-3 equiv.), palladium precursor and ligand were dissolved in 3 ml dioxane. The vial was tightly sealed with a screw cap. The reaction was allowed to stir for overnight at 40 °C. The crude mixture was then poured into water (30 ml) and diluted with DCM before pH was adjusted to 10.

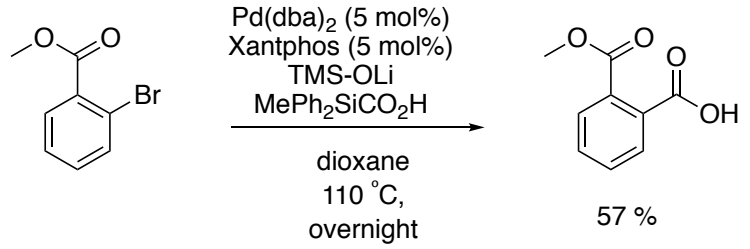
The aqueous phase was washed with DCM several times. The combined aqueous phase was acidified to pH 2-3 using HCl (4M) and then washed with DCM for several times. The combined organic phase was then dried over $MgSO_4$, filtered by suction and concentrated *in vacuo* to leave the product as colorless solid.

Table ESI-3. Screening of catalyst and conditions for hydroxycarbonylation of **3** or **5a**.

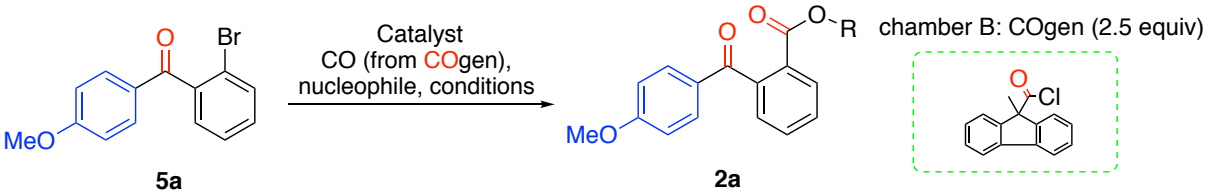
Entry	Subst.	Pd source (mol%)	Ligand (mol%)	Base	Carboxylate source	Solvent	eq. CO	T (°C)	Isol. yield %
4	3	$Pd(dba)_2$ (5)	-	TMSOLi	$MePh_2SiCO_2H$	dioxane	2.5	110	-
6	3	$Pd(dba)_2$ (5)	Xantphos (5)	TMSOK	$MePh_2SiCO_2H$	toluene	1.5	60	traces
7	3	$Pd(dba)_2$ (5)	Xantphos (5)	TMSOK	$MePh_2SiCO_2H$	dioxane	1.5	60	60
8	5a	$Pd(dba)_2$ (5)	Xantphos (5)	TMSOLi	$MePh_2SiCO_2H$	dioxane	1.5	80	-
9	5a	$Pd(dba)_2$ (5)	Xantphos (5)	TMSOLi	$MePh_2SiCO_2H$	dioxane	1.5	115	-
10	5a	$Pd(dba)_2$ (5)	PPh_3 (10)	TMSOLi	$MePh_2SiCO_2H$	dioxane	2.5	110	-

The following control experiments were performed to establish that the procedure gives the wanted carboxylation product for standard substrates.





2.5 Screening for catalysts and conditions for the alkoxycarbonylation of 2-bromobenzophenone 5a



Procedure:

ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.

Chamber A: 2-Bromophenyl-4-methoxyphenylmethanone **5a** (1.0 equiv, 0.47 mmol), Pd precursor and base (3 equiv) were dissolved in solvent (2 ml). The nucleophile (2 equiv) was added to the reaction mixture.

Chamber B: COgen (2.5 equiv), $Pd(dba)_2$ (5 mol%), TTBP•HBF_4 (5 mol%) were dissolved in anisole (3 ml) before DIPEA (3 equiv) was added. The mixture was stirred with heating in a tightly closed system for 20-24 hours.

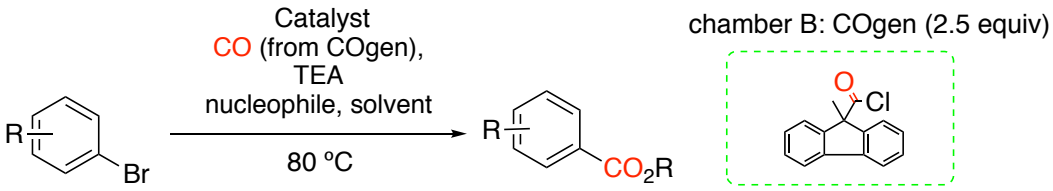
The reaction mixture in chamber A was filtered through celite and concentrated on a rotavapor. The crude was purified by column chromatography with pentane : EtOAc (7:3) as eluent.

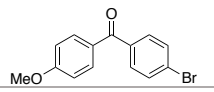
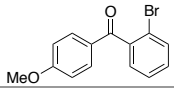
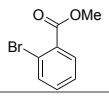
Table ESI-4. Screening for conditions for alkoxycarbonylation on the 2-bromobenzophenone.

Entry	Pd source (mol%)	Ligand (mol%)	Nucl.	Base	Solvent	T (ºC)	Isol. yield (%)
1	dppf($PdCl_2$) (10)		H_2O	TEA	H_2O: THF (1:4)	120	-*
2	dppf($PdCl_2$) (10)	Dppf (20)	iPrOH	TEA	DMF	80	11
3	dppf($PdCl_2$) (10)	Dppf (20)	*n*BuOH	TEA	DMF	80	-*
4	$Pd(OAc)_2$ (2)	Xantphos (4)	iPrOH	TEA	TEA	80	15
5	$Pd(OAc)_2$ (2)	Xantphos (4)	*n*BuOH	TEA	TEA	80	11
6	$Pd(OAc)_2$ (2)	Xantphos (4)	MeOH	TEA	Dioxane	110	5
7	dppf($PdCl_2$) (10)	Dppf (20)	MeOH	TEA	DMF	80	-*
8	$Pd(dba)_2$ (5)	Dippf (5)	EtONa	-	THF	80	-*
9	PEPPSI-IPr (3)		*n*BuOH	Cs_2CO_3	Chlorobenzene	80	-*
10	PEPPSI (5)	IMes (10)	*n*BuOH	Cs_2CO_3	Chlorobenzene	110	-*
11	$Pd(PPh_3)_2Cl_2$ (5)	IMes (10)	*n*BuOH	Cs_2CO_3	Heptane	120	-*
12	$PdCl_2$ (2)	Xantphos (2)	*n*BuOH	K_2CO_3	Anisole	110	65

* Only starting material or the corresponding biphenyl were detected.

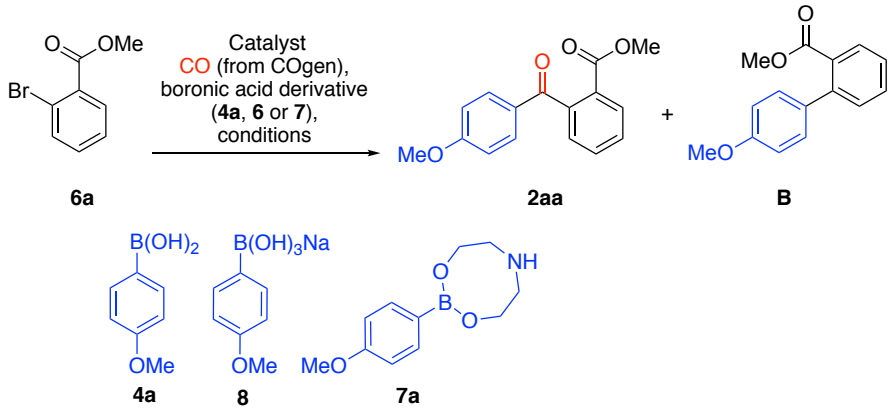
Table ESI-5. Control experiments for alkoxycarbonylation with 4-bromobenzophenone.



Entry	Substrate	Pd source (mol%)	Ligand (mol%)	Nucl.	Base	Solvent	Isol. yield (%)
1		$Pd(OAc)_2$ (2)	Xantphos (4)	*n*BuOH	TEA	TEA	99
2		dppfPdCl_2 (10)	Dppf (20)	iPrOH	TEA	DMF	97
3		$Pd(OAc)_2$ (2)	Xantphos (4)	*n*BuOH	TEA	TEA	11
4		dppfPdCl_2 (10)	Dppf (20)	iPrOH	TEA	DMF	11
5		$Pd(dba)_2$ (5)	Dippf (5)	*t*BuONa	-	THF	60

2.6 Screening for catalysts and conditions for the carbonylative Suzuki-Miyaura coupling of methyl 2-bromobenzoate 6a

Table ESI-6. Optimization of reaction conditions for the palladium catalyzed carbonylative Suzuki-Miyaura coupling of methyl-2-bromobenzoate **6a**.

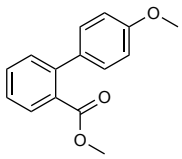


Entry	Pd-source (mol%)	Ligand (mol%)	Nuc.	base	solvent	T (°C)	addition	Ratio[d] 2aa: B	Isol. yield (%)
1[a]	$Pd(acac)_2$. (5)	CataCXium A•HI (10)	**8**	-	Toluene: H_2O (10:1)	80	normal	1 : 0.45	65[a]
2[a]	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	Toluene: H_2O (10:1)	95	normal	1 : 0.3	67[a]
3	$Pd(acac)_2$ (5)	CataCXium A (10)	**4a**	K_2CO_3	Toluene: H_2O (10:1)	100	normal	-	30
4[a]	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	DMSO	90	normal	-	traces[a]
5[a]	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	DMF: H_2O (10:1)	90	normal	-	-*,[a]
6	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	Toluene: H_2O: MeOH (10:1:1)	90	slow	-	traces
7	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	Toluene: H_2O: TBAB (1:1:0.5)	95	slow	-	traces
8[a]	$Pd(acac)_2$ (5)	CataCXium A•HI (10)	**7a**	-	Dioxane: H_2O (10:1)	95	normal	-	-*,[a]
9[b]	$PdCl_2$ (1)		**4a**	K_2CO_3	Anisole	110	normal	-	-*,[b]
10[b]	$Pd(OAc)_2$ (5)	CataCXium A (10)	**4a**	K_2CO_3	Toluene: H_2O (10:1)	110	normal	-	-*,[b]
11[b]	$Pd(PPh)_3Cl_2$ (10)		**4a**	K_2CO_3	Anisole	110	normal	0.2 : 1	20[b]
12[b]	$Pd(OAc)_2$ (5)	Xantphos (5)	**4a**	Cs_2CO_3	Toluene	80	normal	0.3 : 1	20[b]
13[c]	Xantphos G2 (5)		**4a**	K_2CO_3	Anisole	100	slow	-	traces[c]
14[b]	$Pd(OAc)_2$ (5)	CataCXium A (10)	**4a**	K_2CO_3	Dioxane	100	normal	-	traces[b]
15[b]	$PdCl_2$ (2)	Xantphos (4)	**4a**	K_2CO_3	Toluene	100	normal	-	-*,[b]
16[b]	PEPPSI-IPr (3)		**4a**	Cs_2CO_3	Chlorobenzene	80	normal	1 : 0.5	60[b]
17[c]	PEPPSI-IPr (3)		**4a**	Cs_2CO_3	Chlorobenzene	110	slow	1 : 0.15	80[c]

18[c]	PEPPSI-IPr (3)		**4a**	Cs_2CO_3	Anisole	110	slow	1 : 0.15	80[c]
19[b]	PEPPSI-Allyl (3)		**4a**	Cs_2CO_3	Anisole	110	normal	1: 0.6	50[b]
20[b]	$Ni(COD)_2$	dcype	**4a**	Cs_2CO_3	Toluene	110	normal	-	-*,[b]

a Following general procedure E. b Following general procedure D. c Following general procedure C. d The ratio (2aa : B) was determined using ^{13}C NMR of the crudes. *Only starting material or the corresponding biphenyl B were detected.

*Characterization of methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate **B**.*



The title compound was isolated as a side product from reactions towards **2aa**. NMR: δH (400 MHz, $CDCl_3$) 7.70 (1H, d, *J* 8.2), 7.41 (1H, t, *J* 8.3), 7.29 (2H, d, *J* 7.3), 7.16 (2H, d, *J* 8.8), 6.85 (2H, d, *J* 8.8), 3.75 (3H, s), 3.58 (3H, s). δC (101 MHz, $CDCl_3$) 169.5, 159.1, 142.1, 133.7, 131.3, 131.0, 130.8, 129.8, 129.6, 126.9, 113.7, 77.5, 77.2, 76.8, 55.4, 52.1.

3 References

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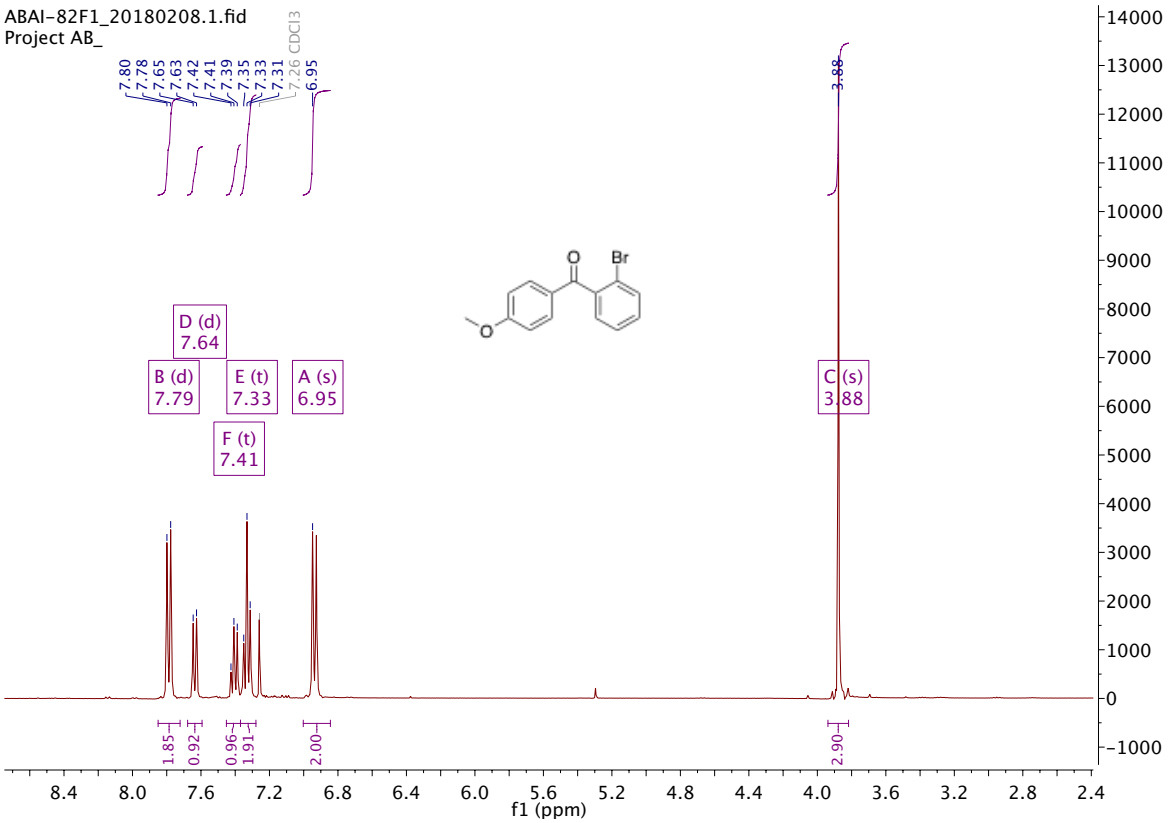
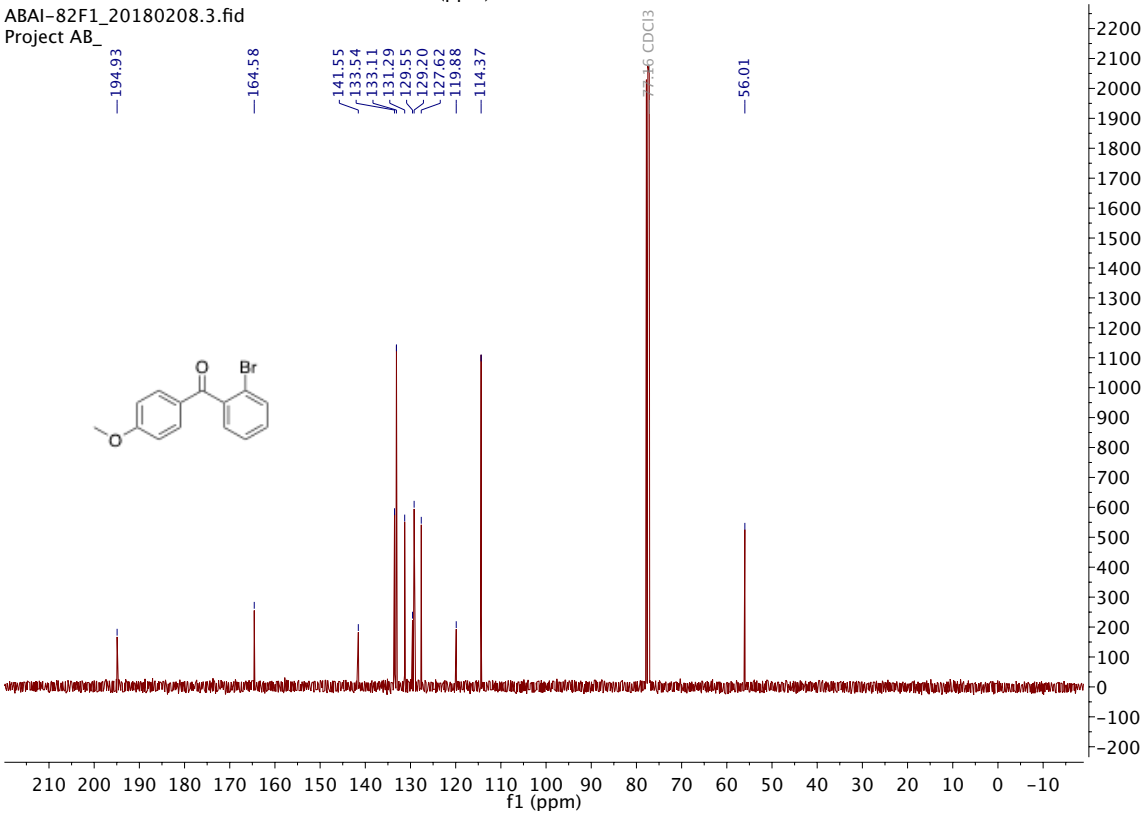
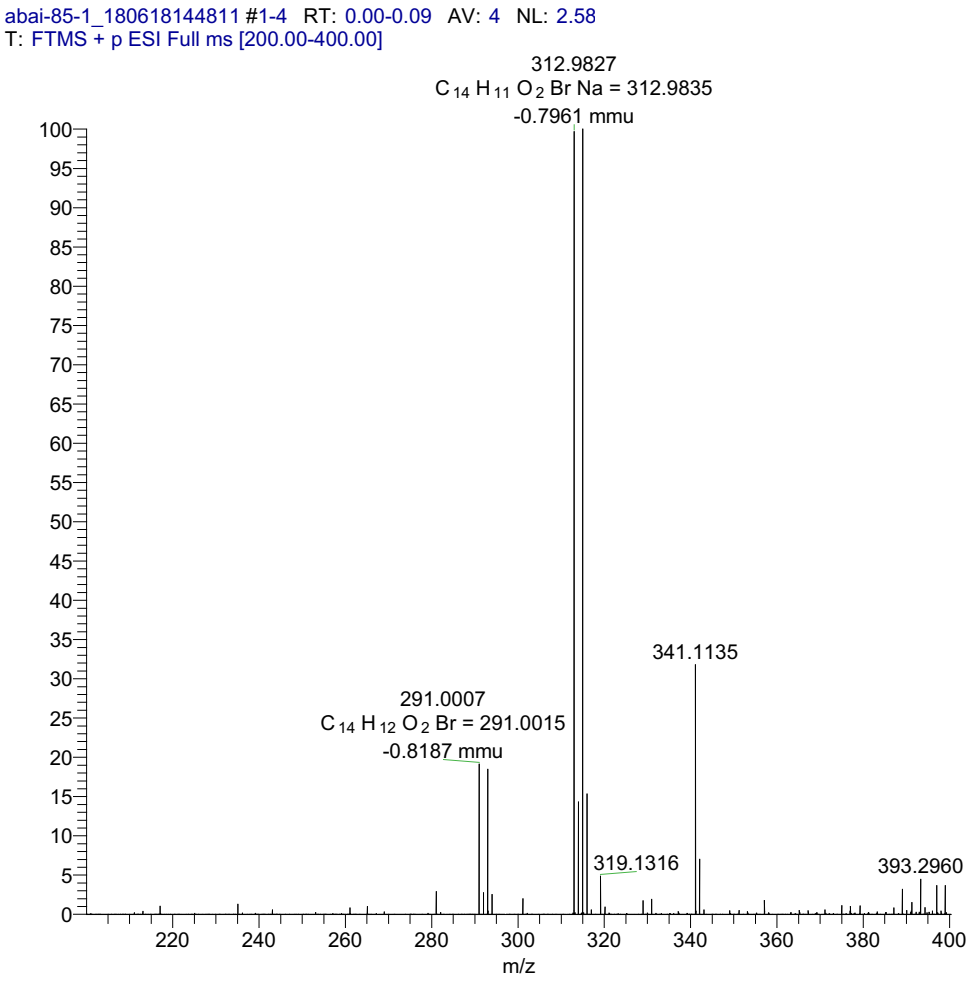
4 Spectra

4.1 Spectra for diaryl ketones 5

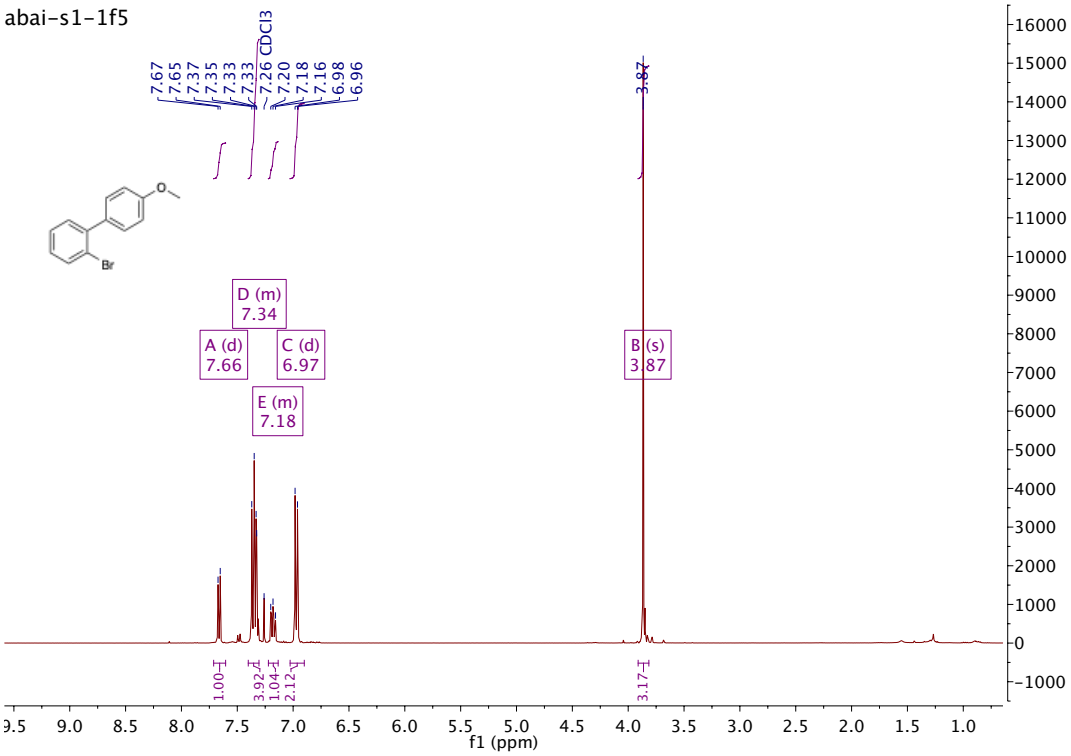
2-Bromophenyl 4-methoxyphenyl methanone ***5a****.*

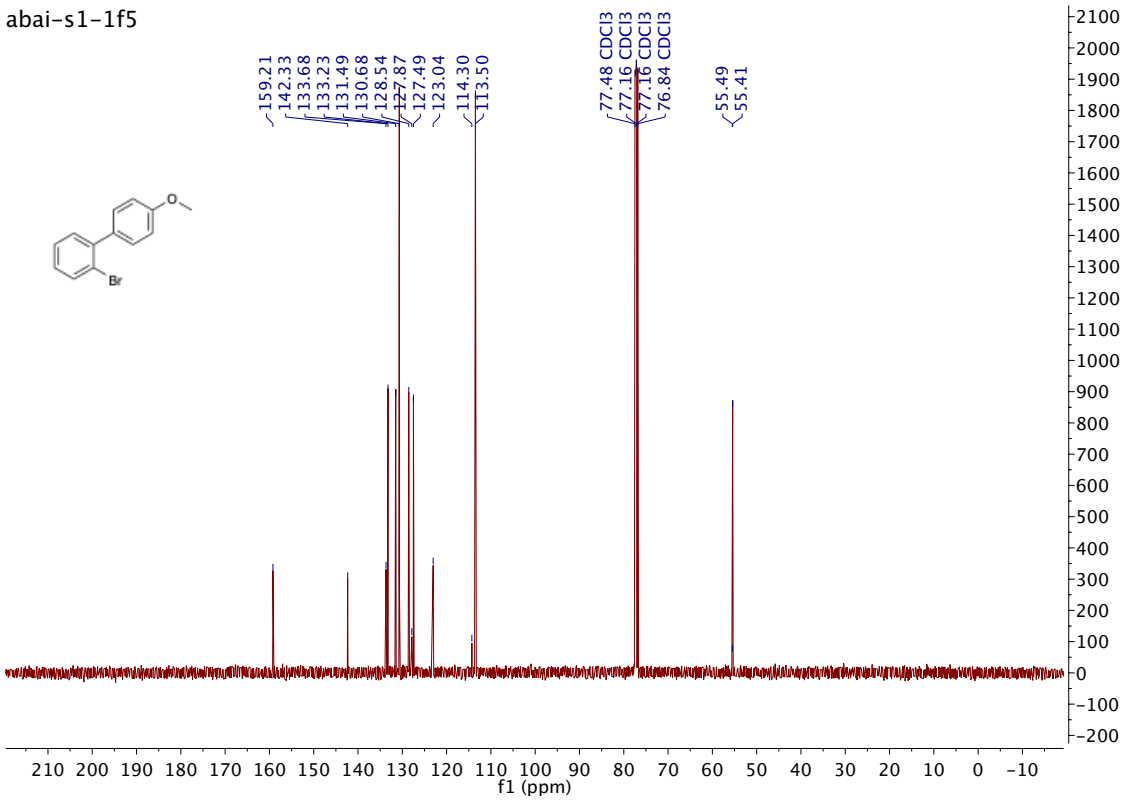




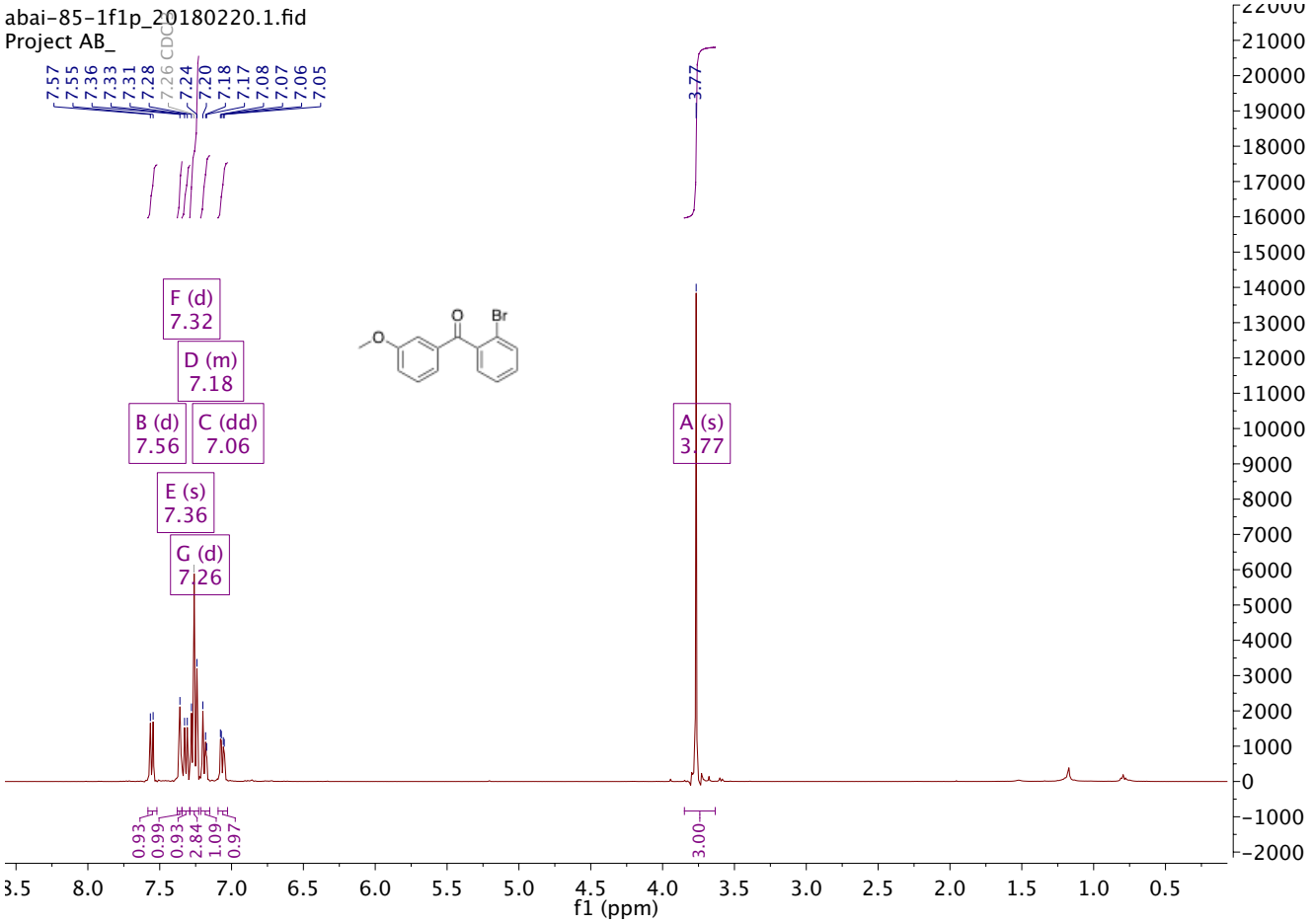


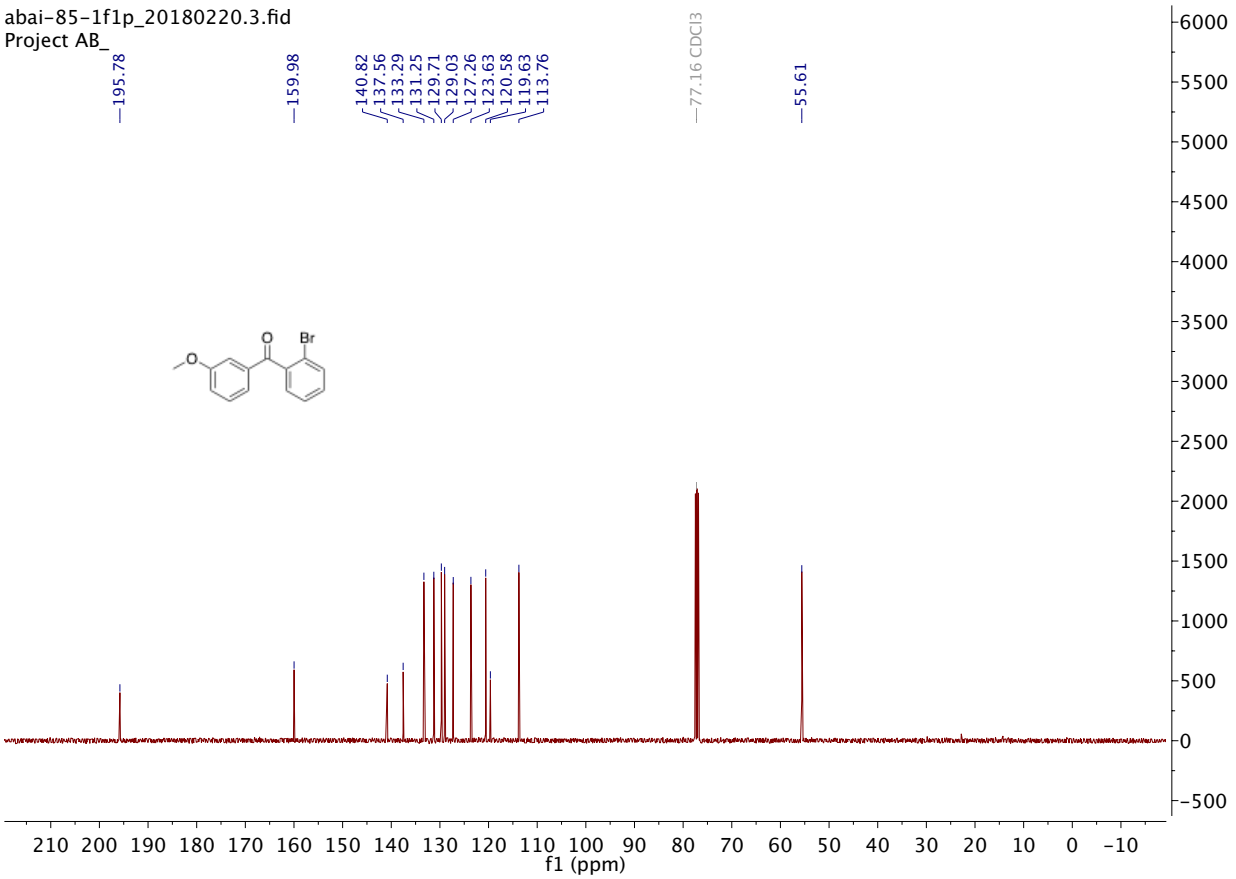
2-bromo-4'-methoxy-1,1'-biphenyl ***A*** *(from direct coupling)*





2-Bromophenyl 3-methoxyphenyl methanone ***5b***





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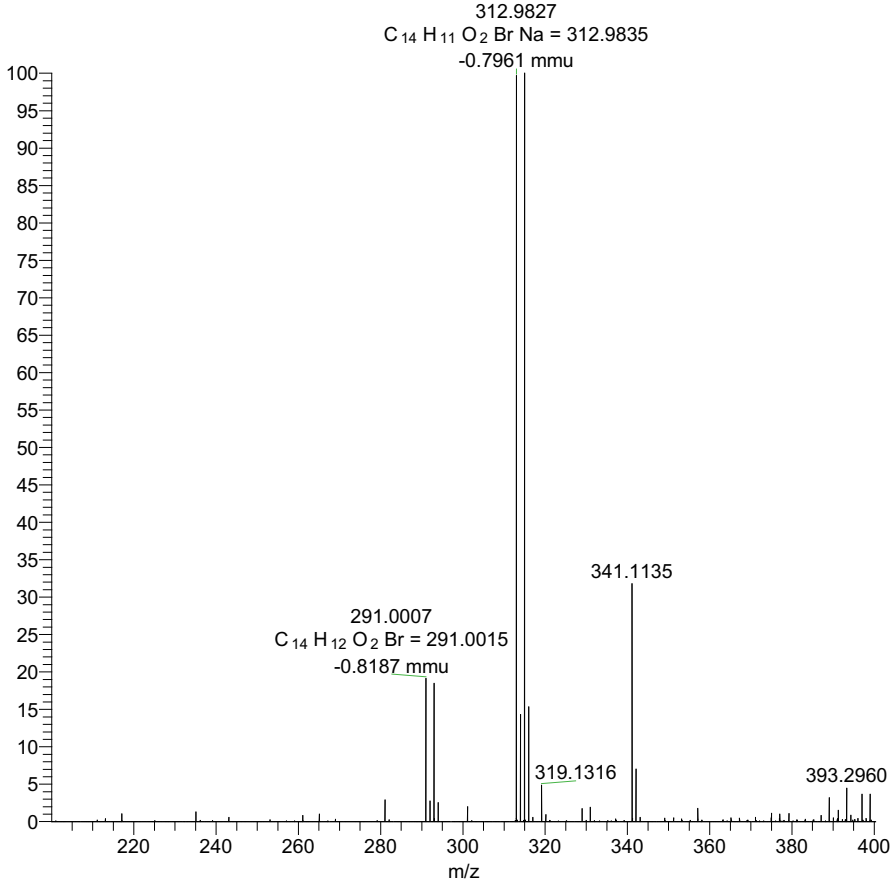
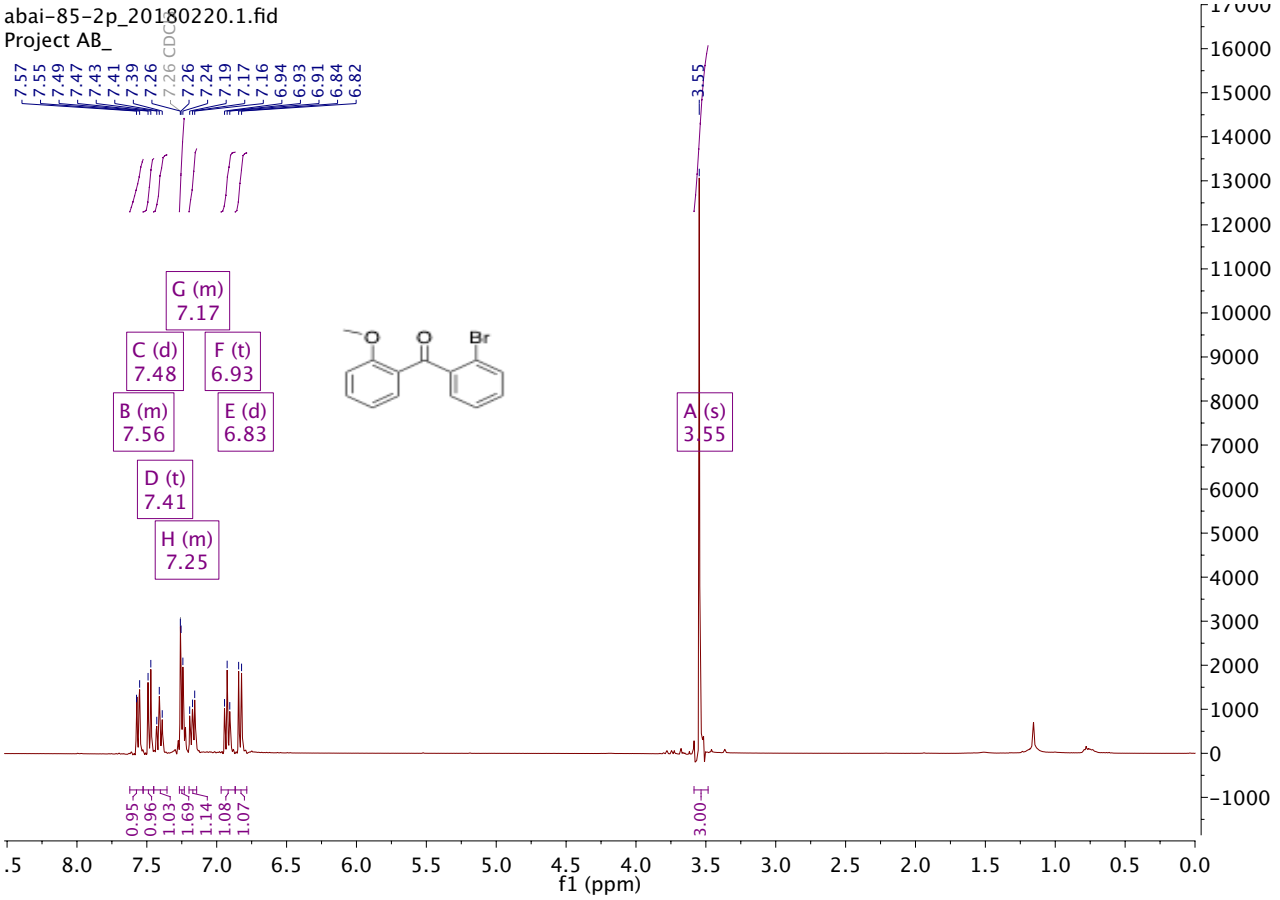
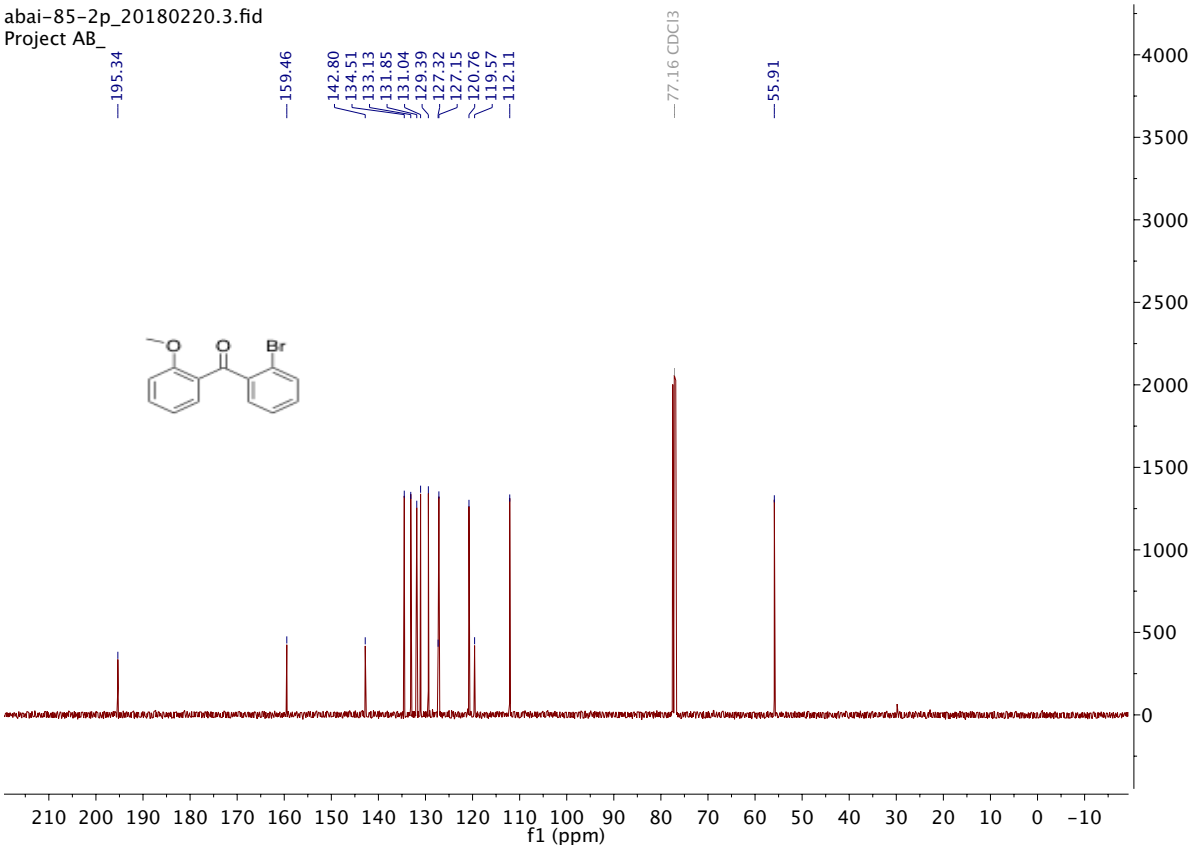
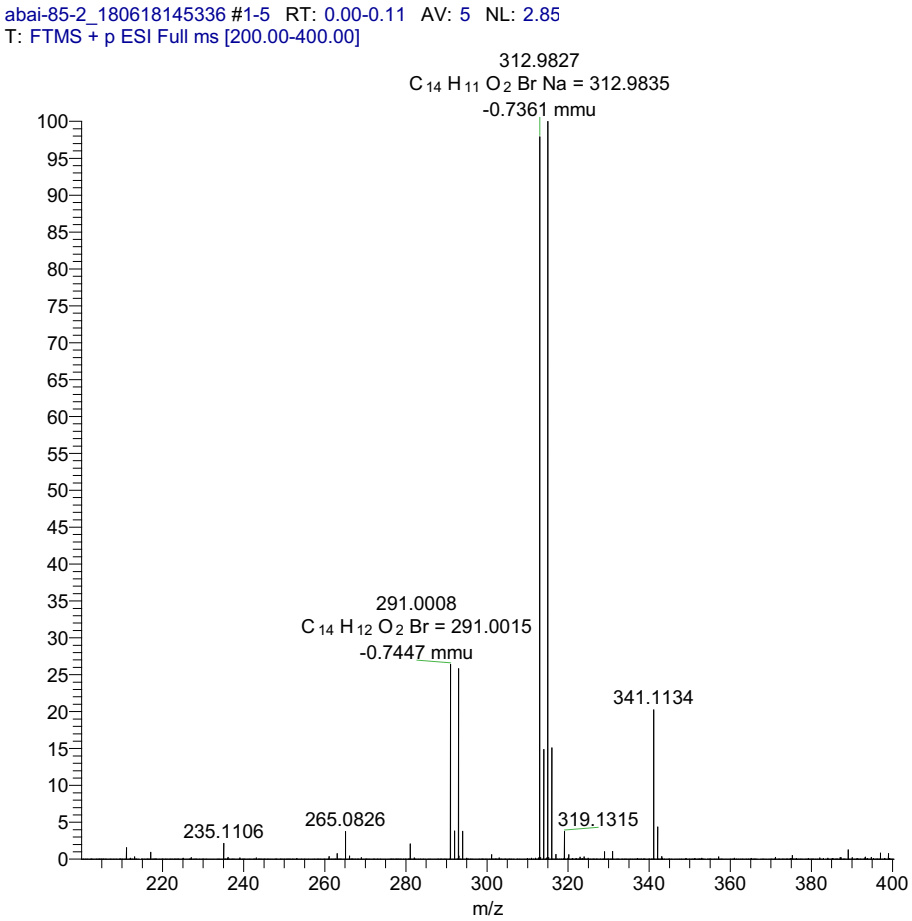


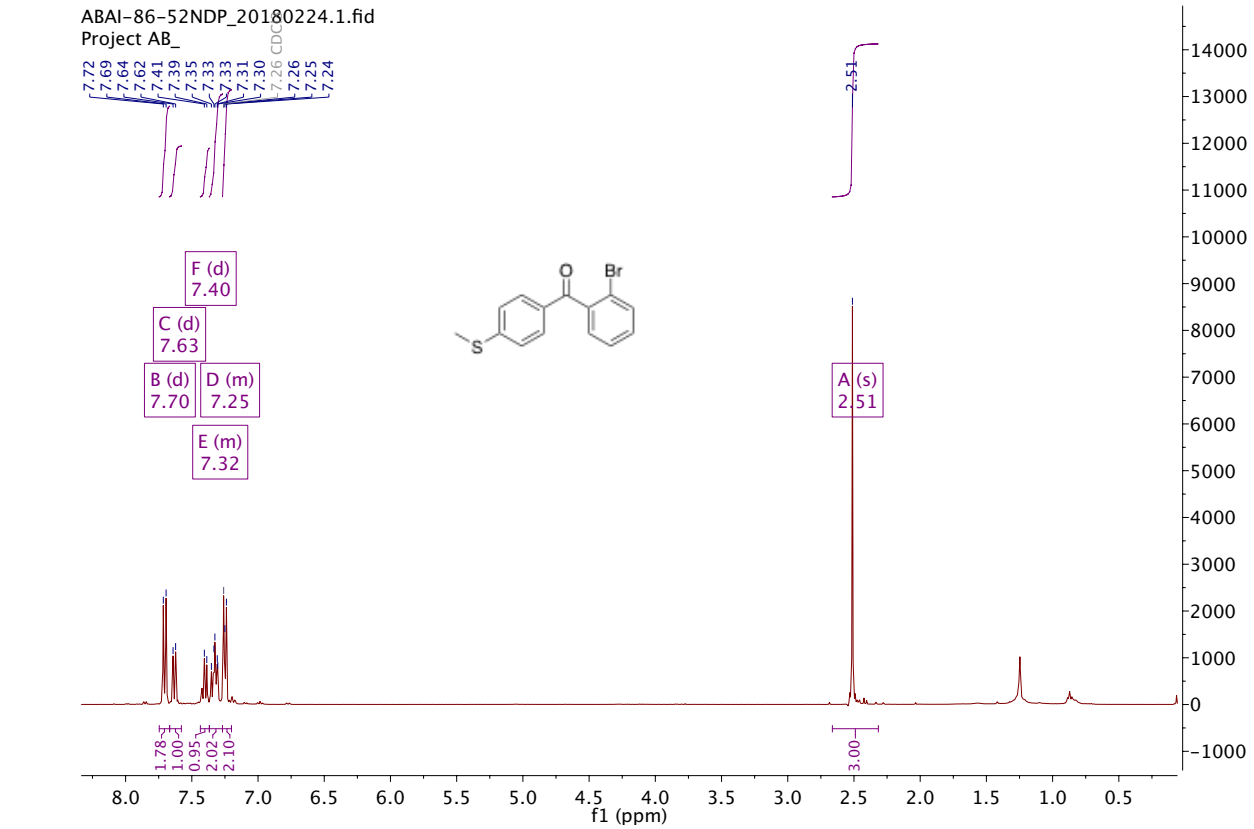
2-Bromophenyl 2-methoxyphenyl methanone ***5c***

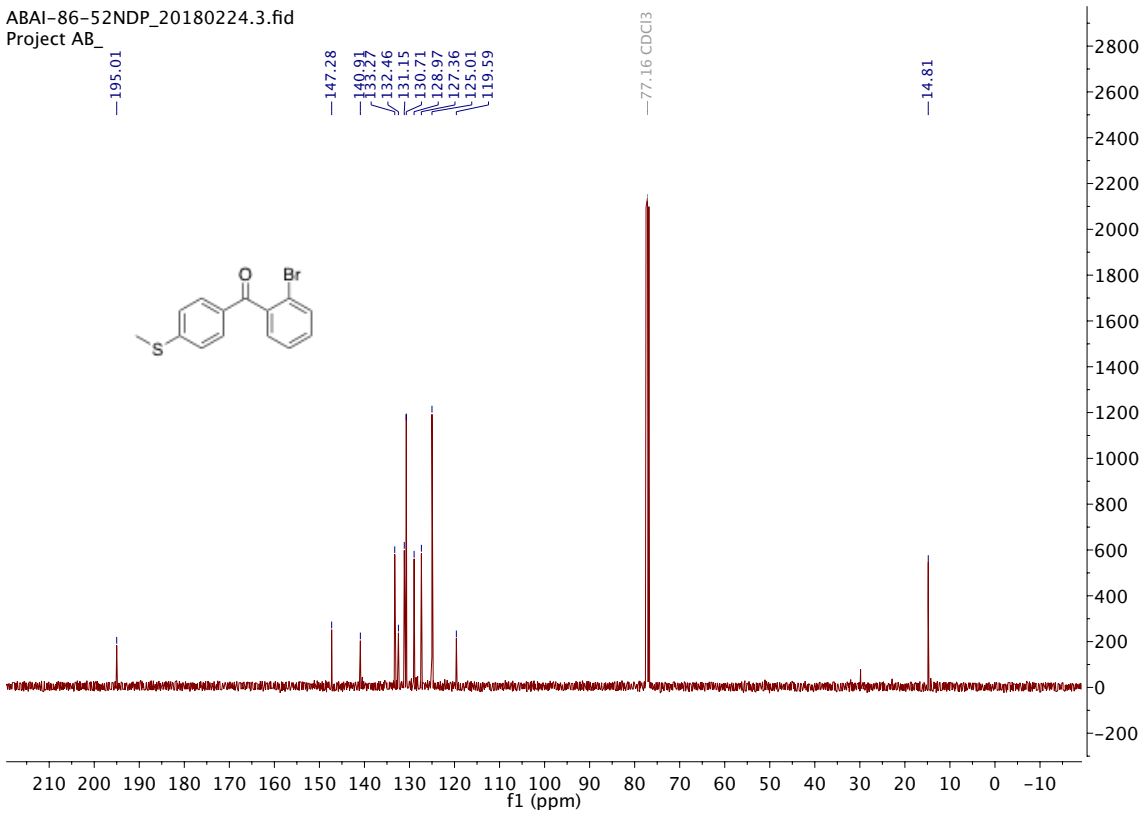






2-Bromophenyl 4-(methylthio)phenyl methanone ***5d***

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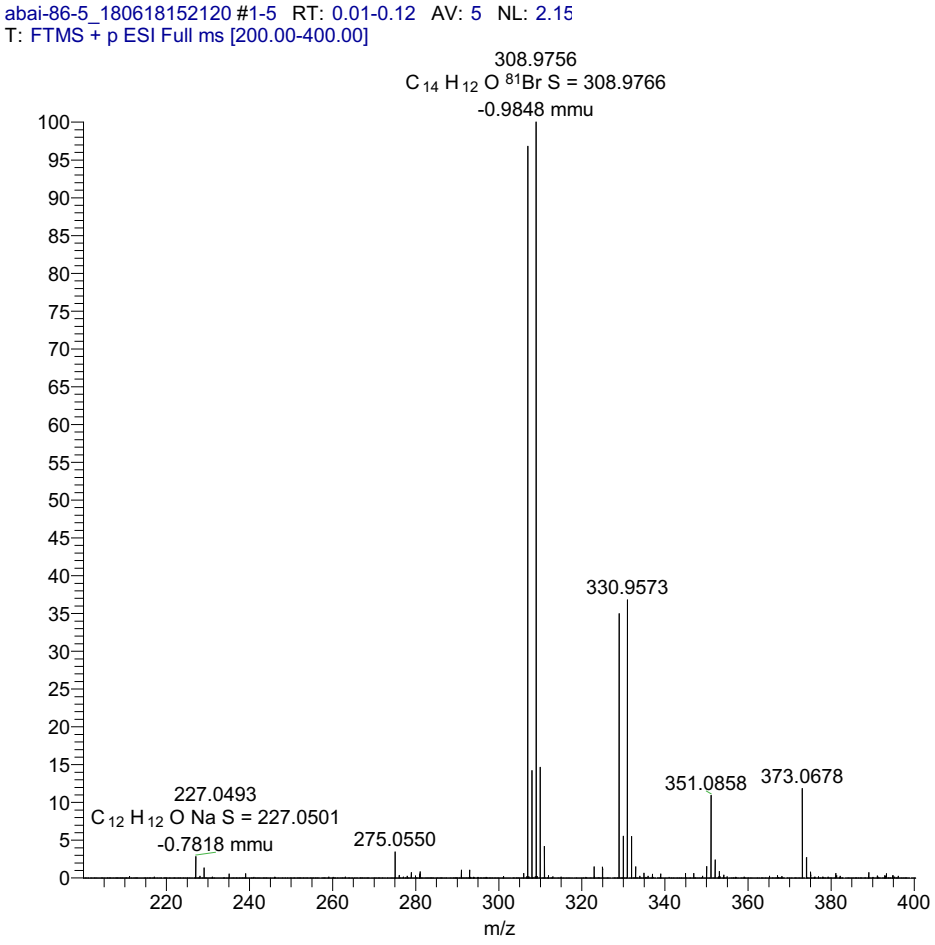
O
Br
S
f1 (ppm)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-0.9848 mmu
330.9573
351.0858
373.0678
227.0493
C 12 H 12 O Na S = 227.0501
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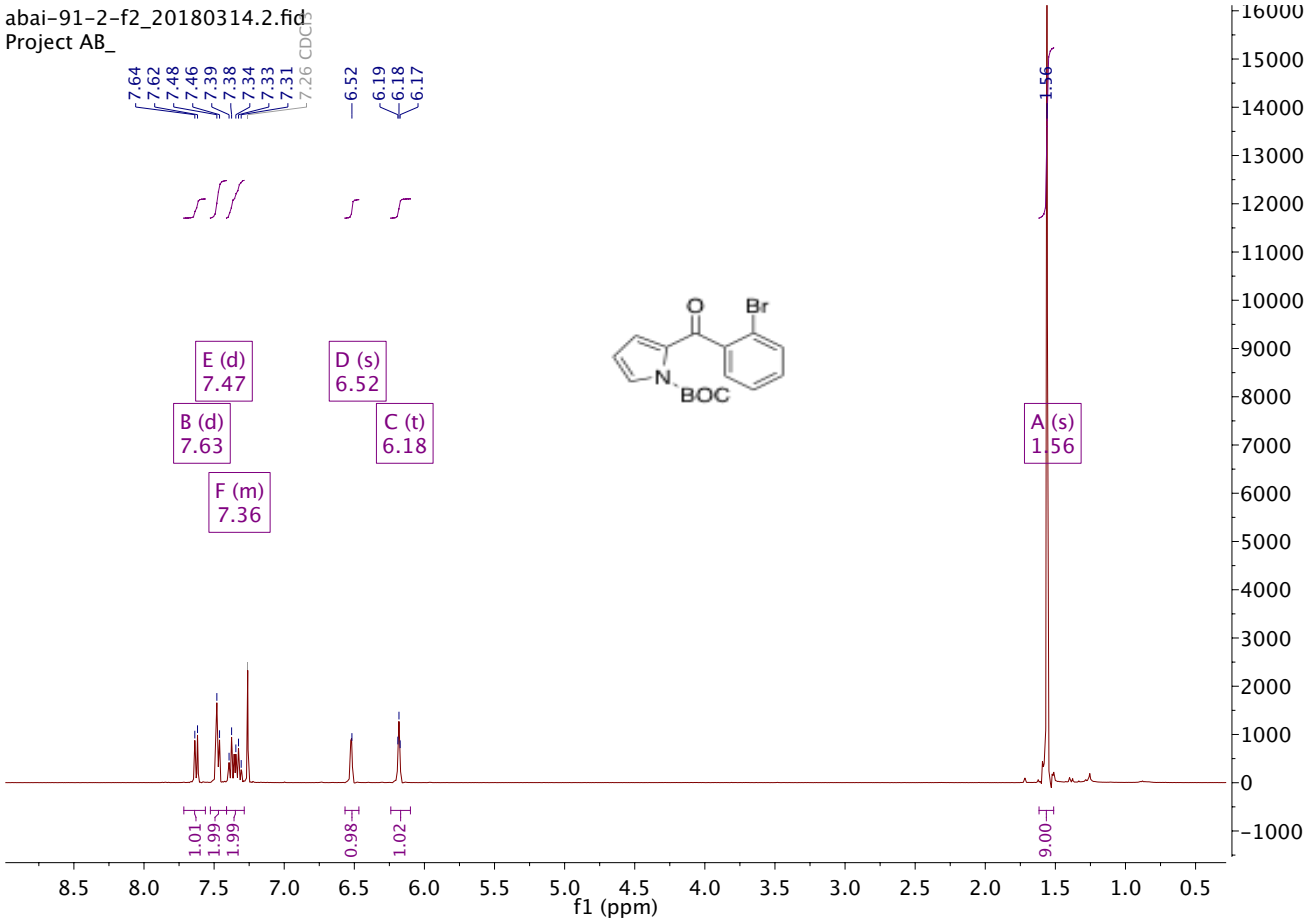
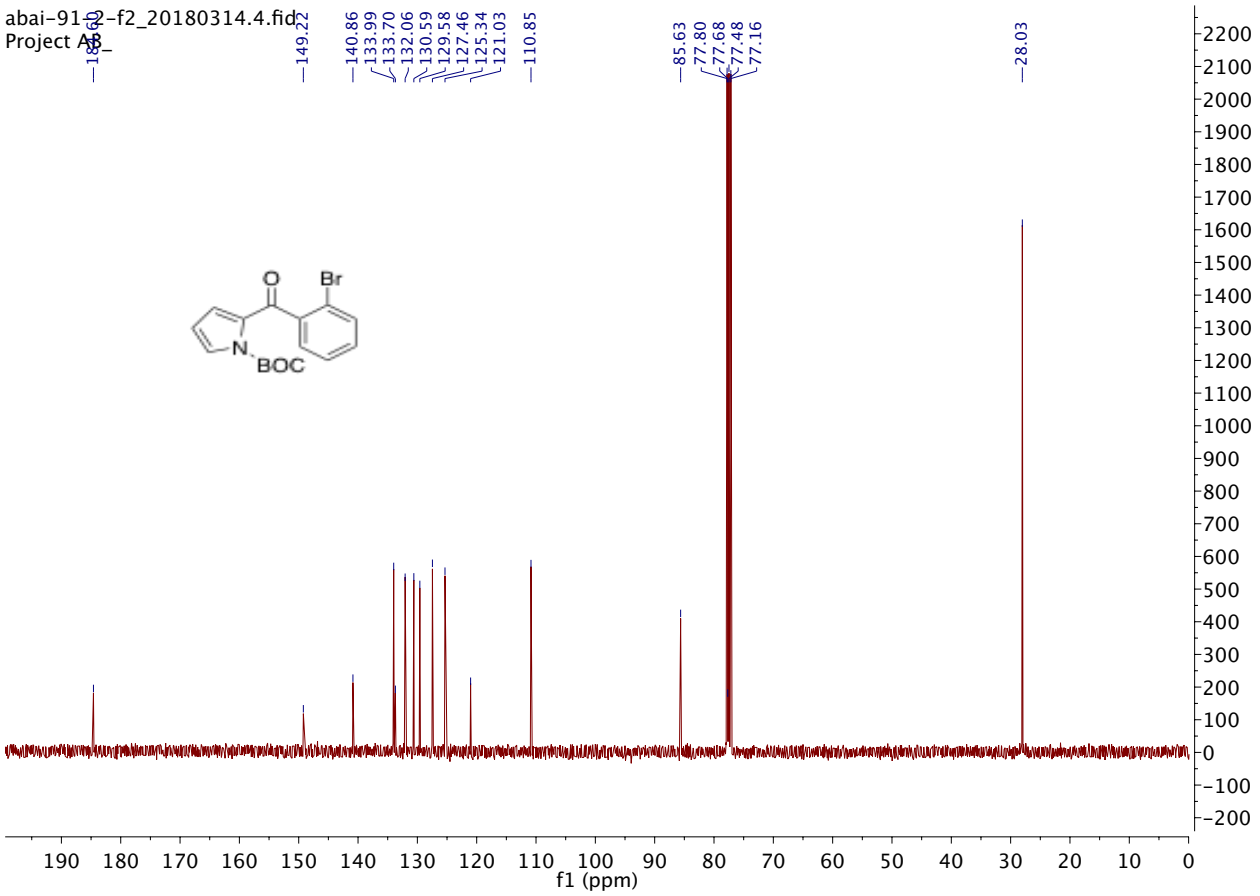
275.0550
m/z

tert-Butyl 2-(2-bromobenzoyl)-1H-pyrrole-1-carboxylate ***5e***

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127.46
125.34
121.03
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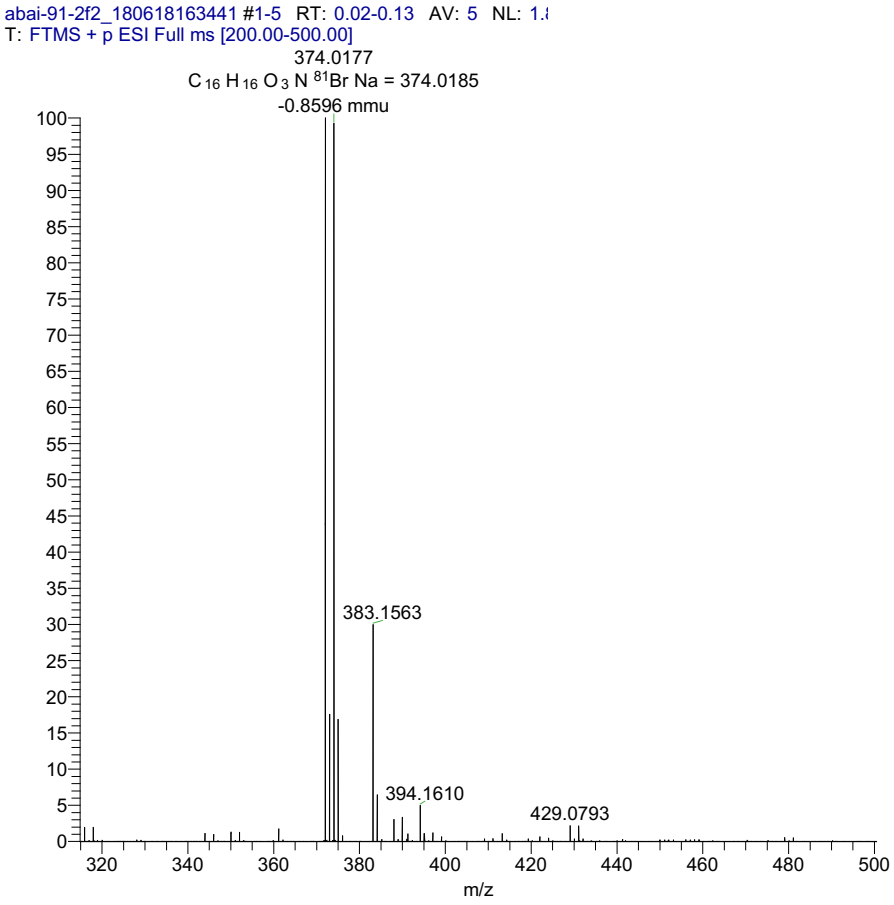
85.63
77.80
77.68
77.48
77.16
28.03
O
Br
N
BOC
f1 (ppm)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C16 H16 O3 N 81Br Na = 374.0185
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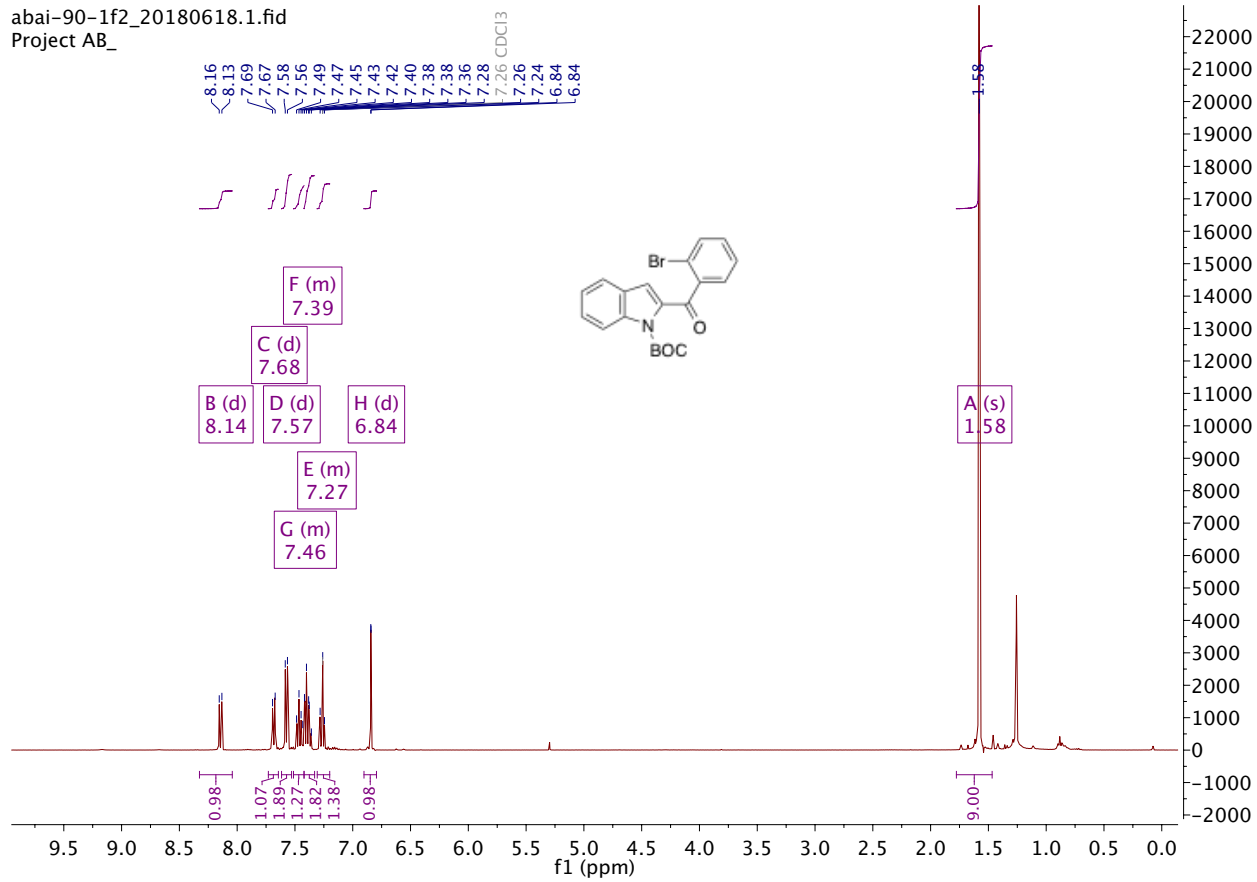
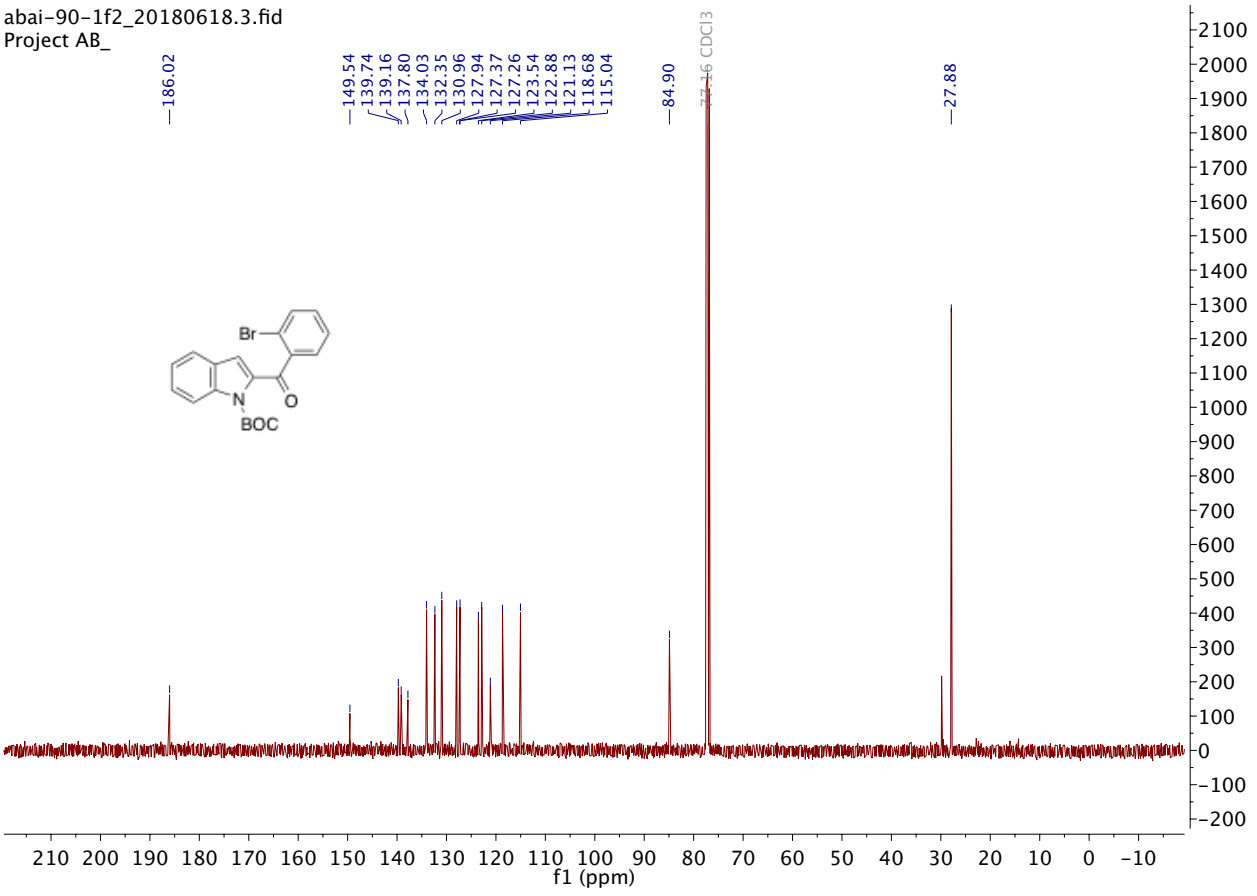
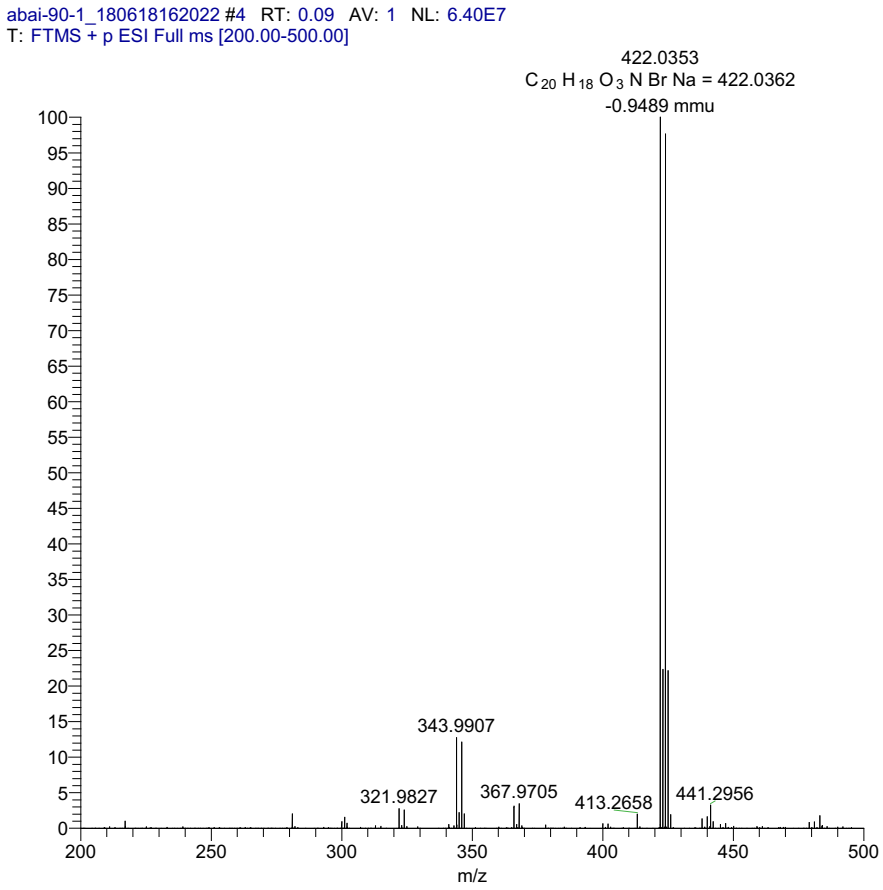
383.1563
394.1610
429.0793
m/z

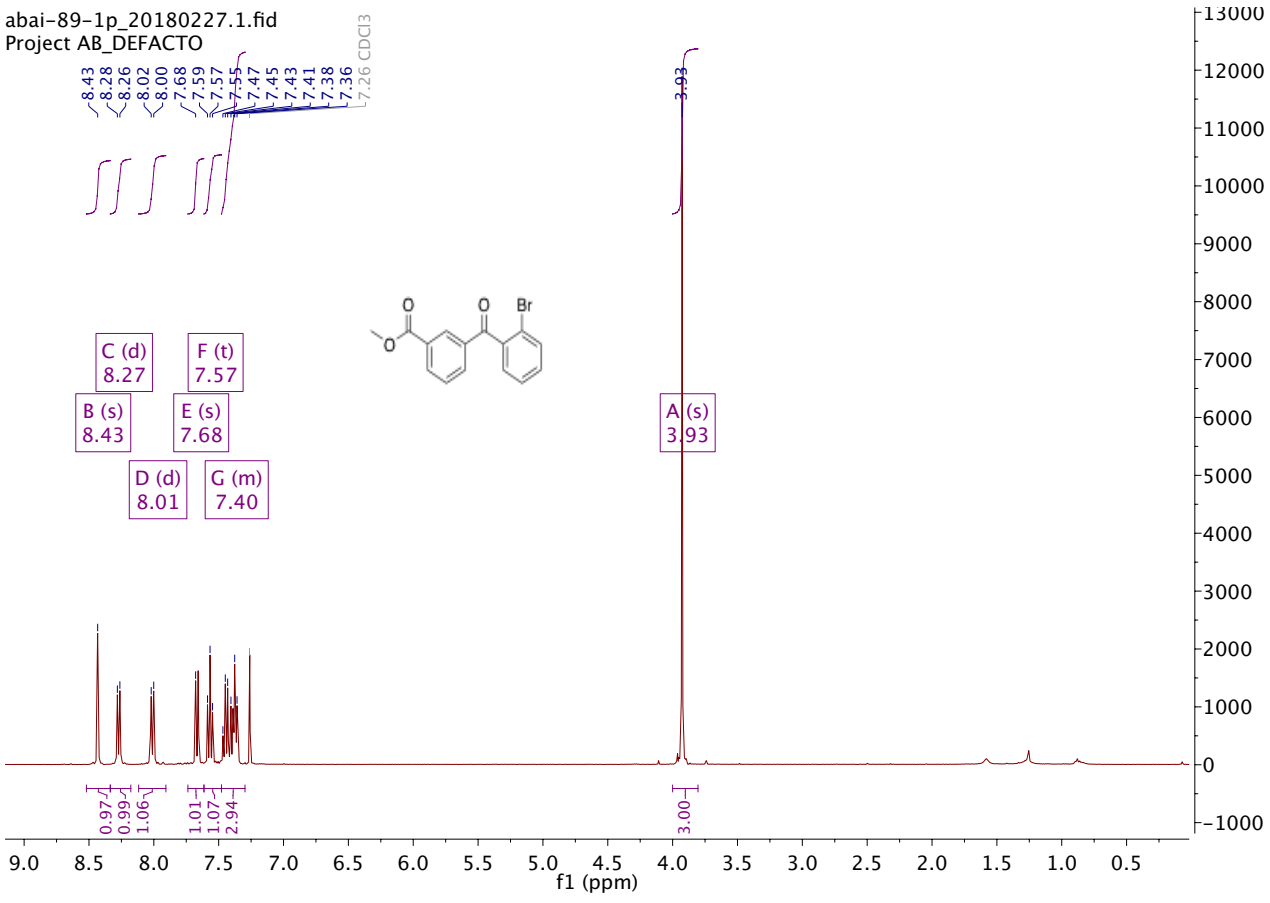
tert-butyl 2-(2-bromobenzoyl)-1H-indole-1-carboxylate ***5f***

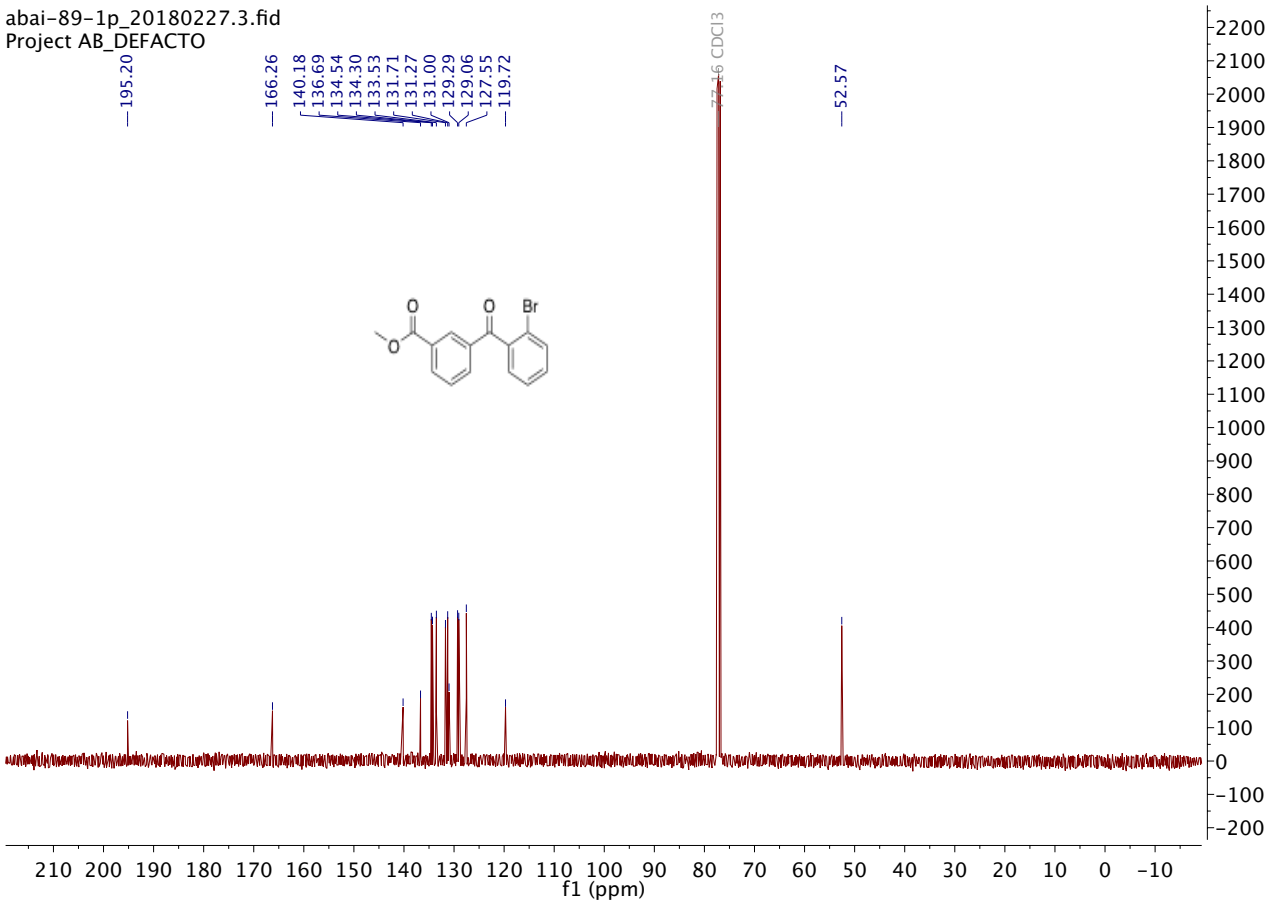






Methyl 3-(2-bromobenzoyl)benzoate ***5g***





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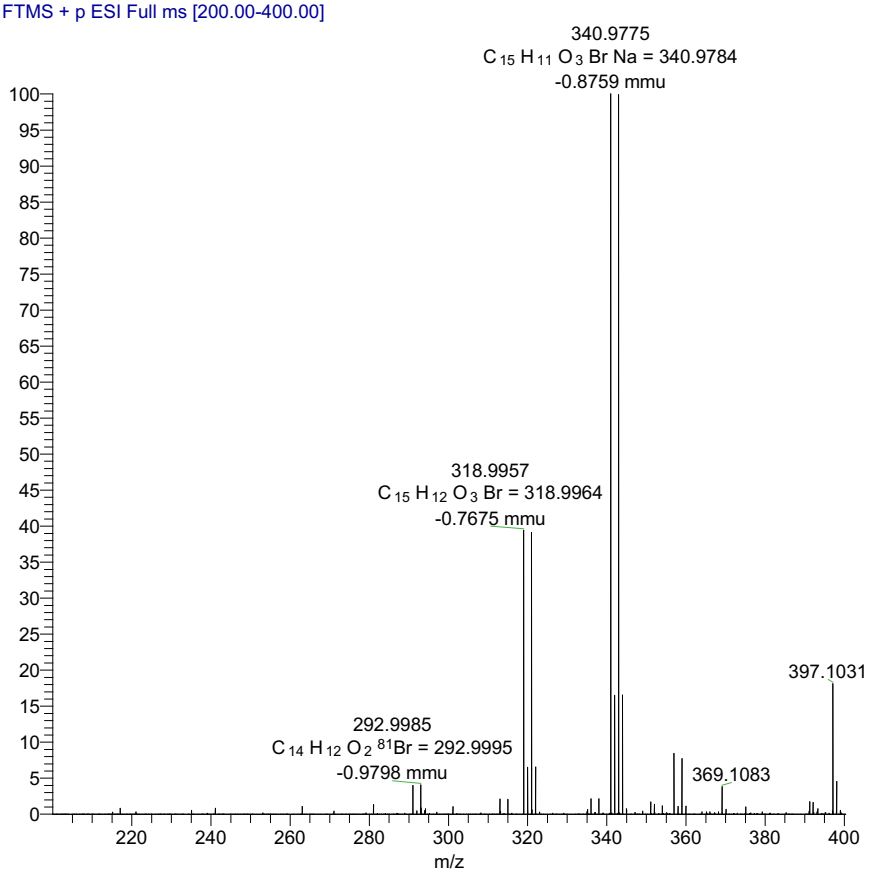
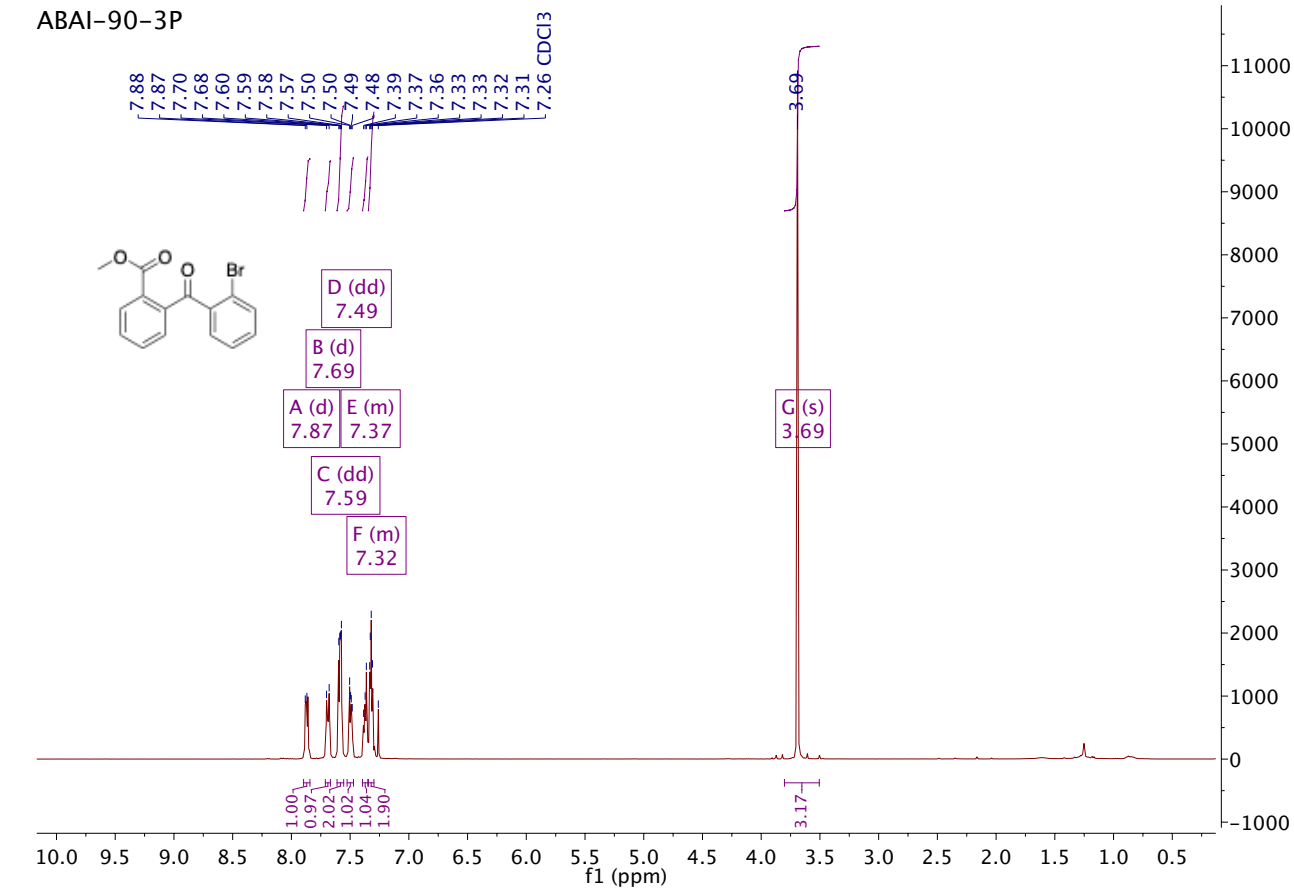
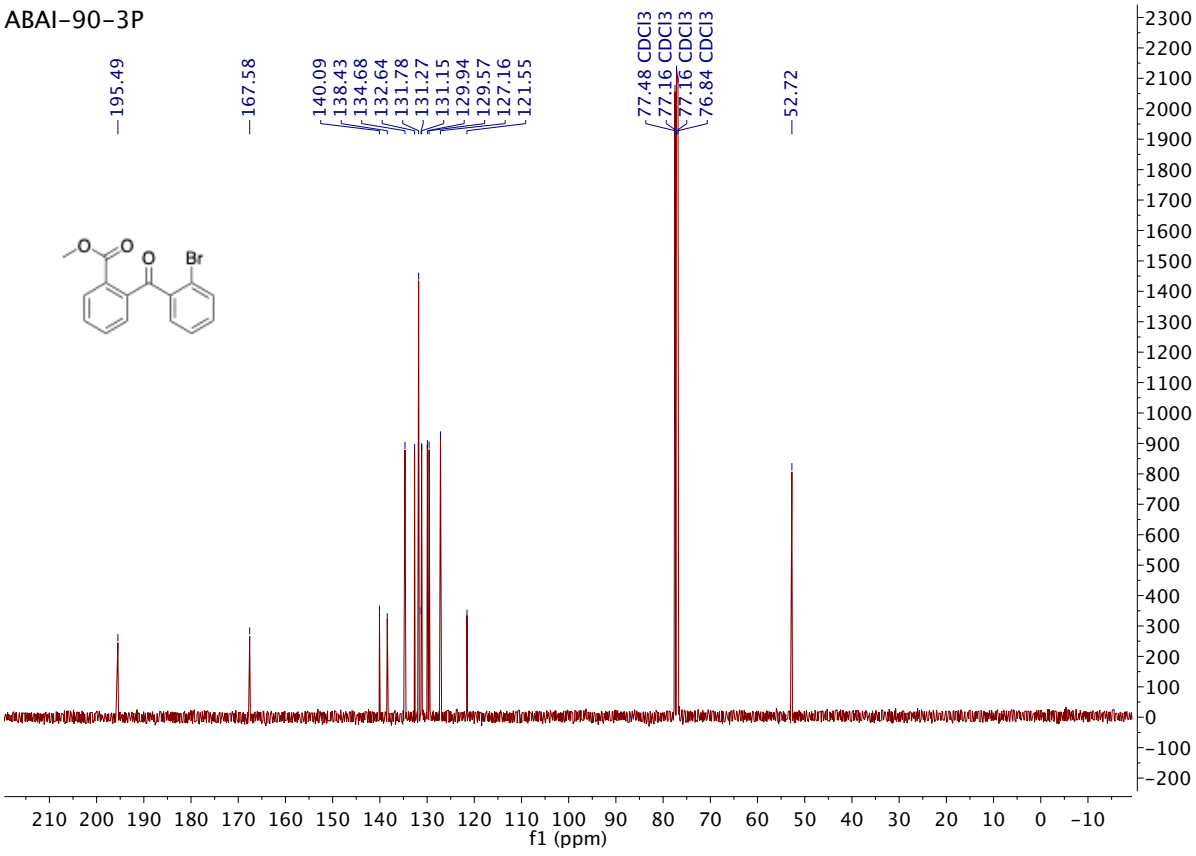
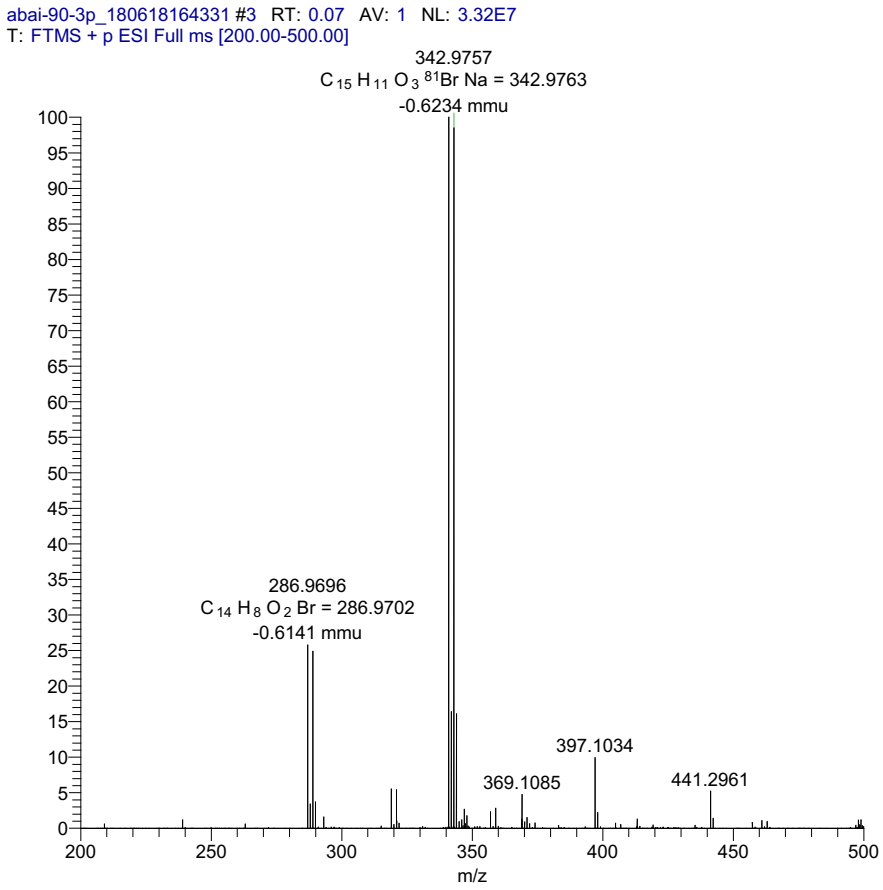
T: FTMS + p ESI Full ms [200.00-400.00]



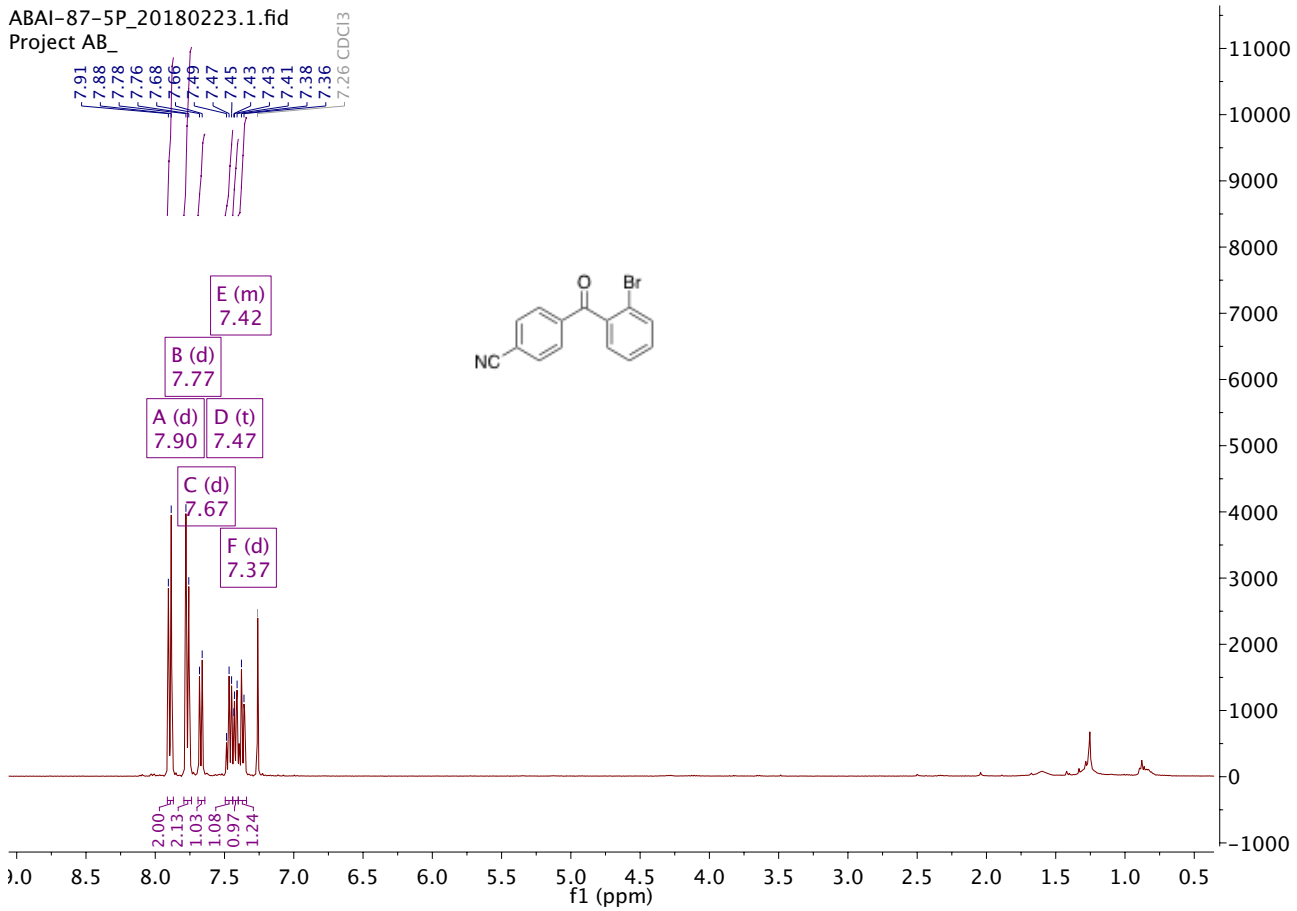
Methyl 2-(2-bromobenzoyl)benzoate ***5h***

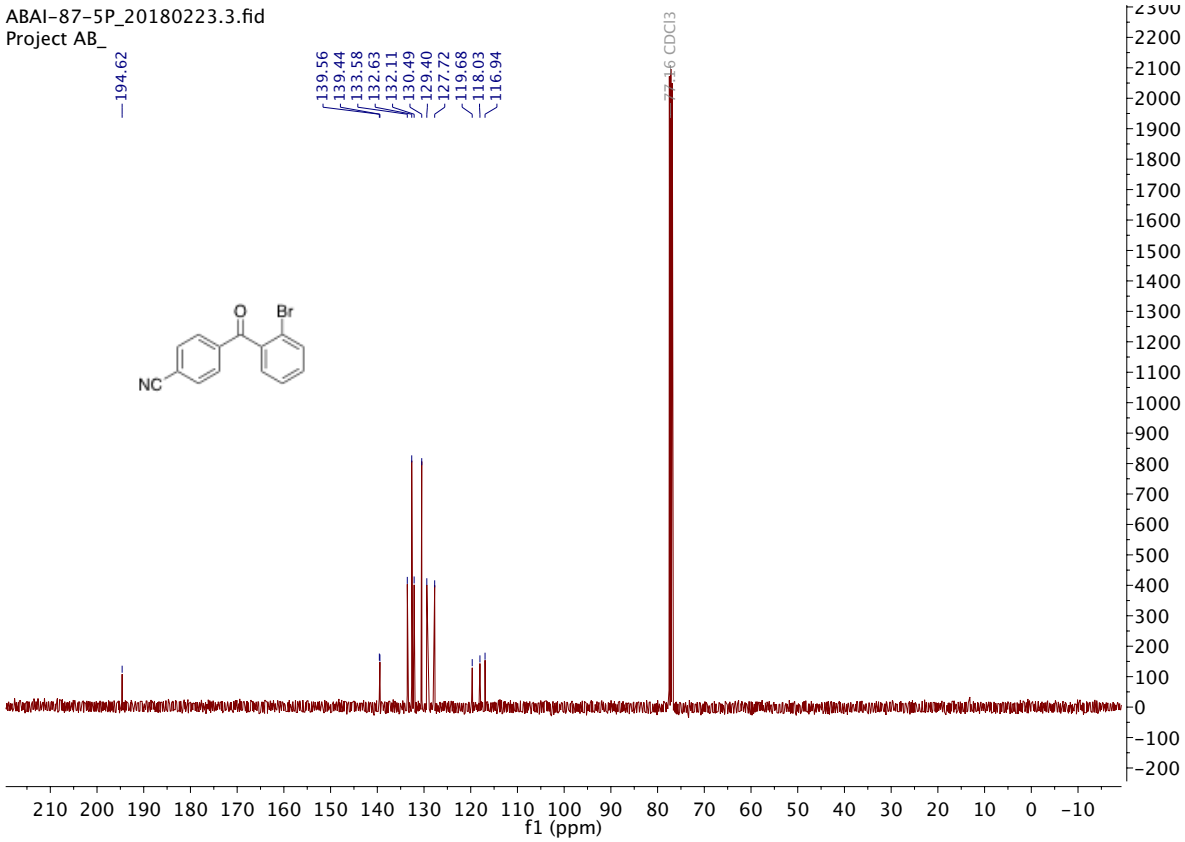






4-(2-Bromobenzoyl)benzonitrile ***5i***

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139.44
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132.63
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129.40
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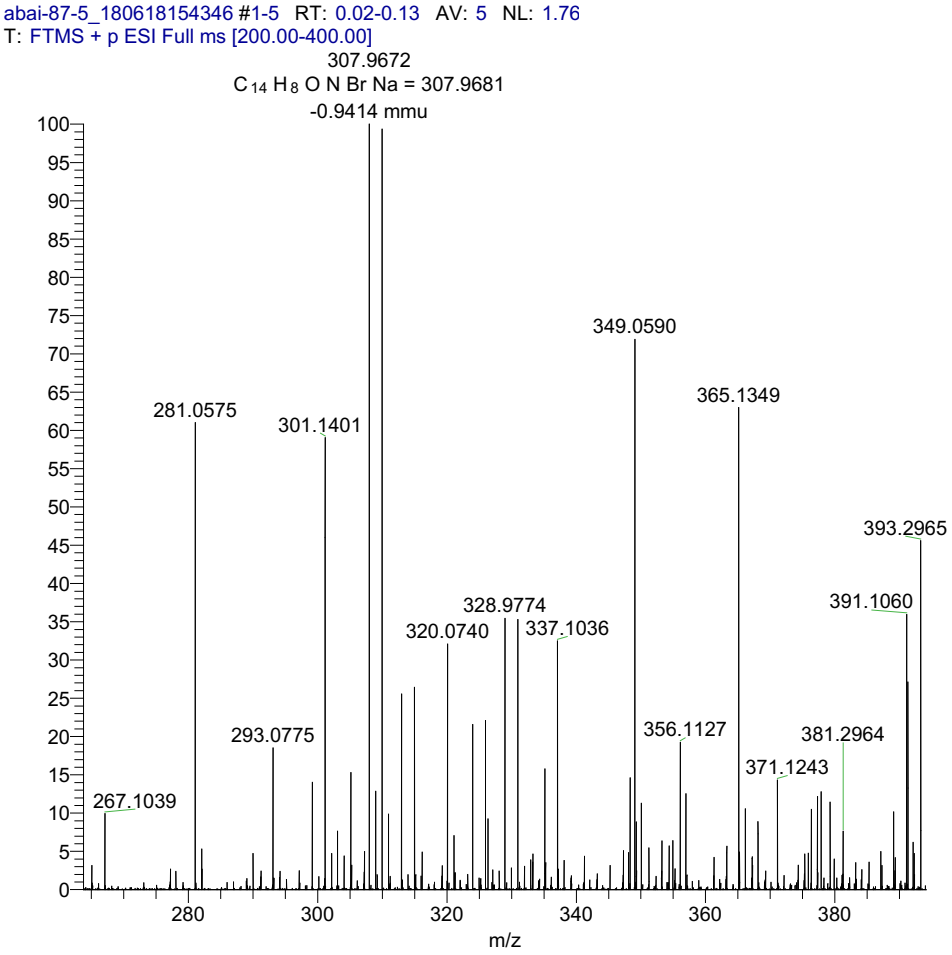
119.68
118.03
116.94
77.16 CDCl3
O
Br
NC
f1 (ppm)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T: FTMS + p ESI Full ms [200.00-400.00]
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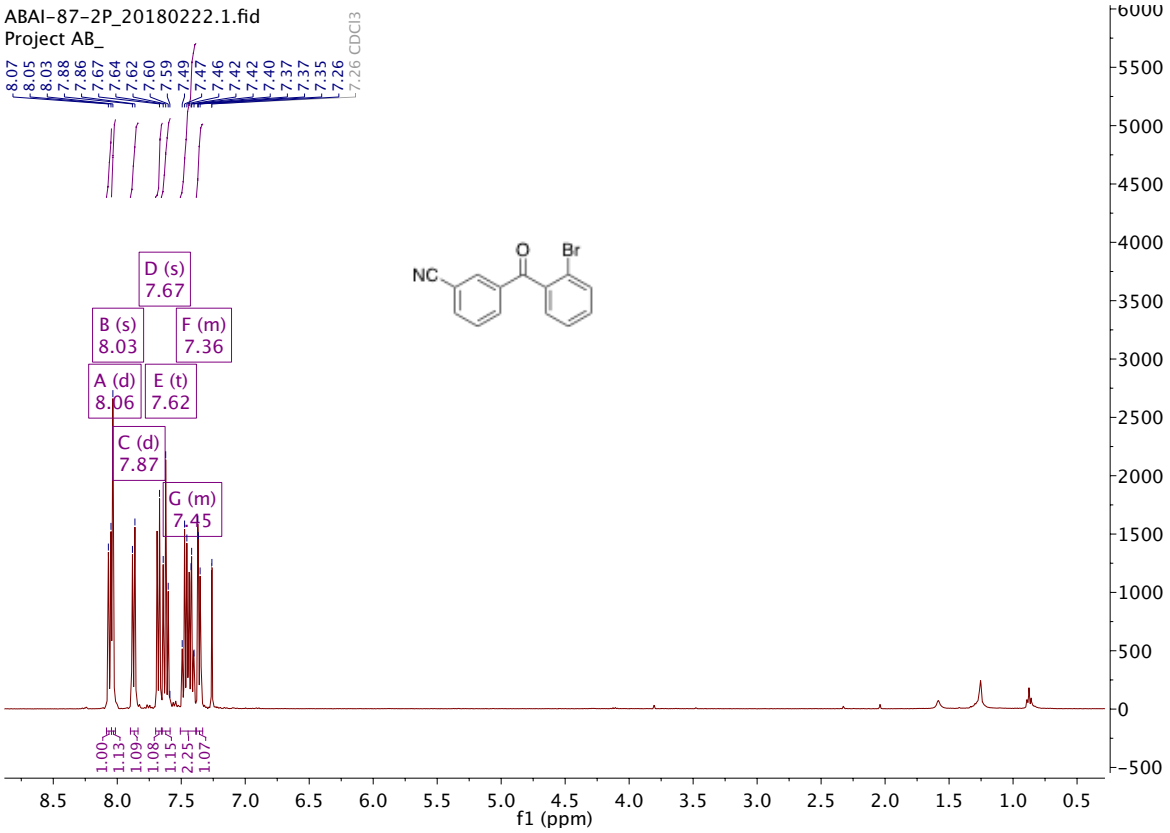
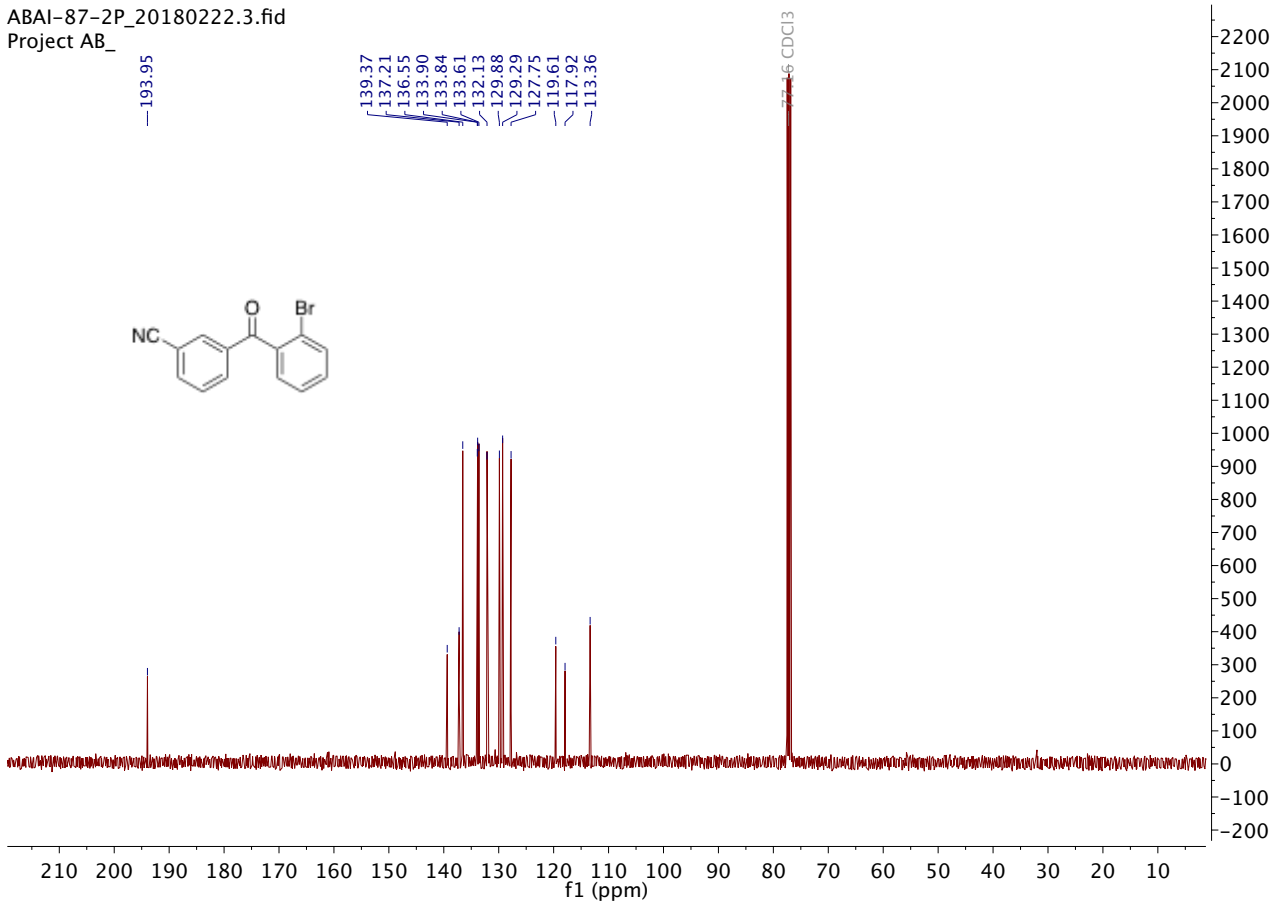
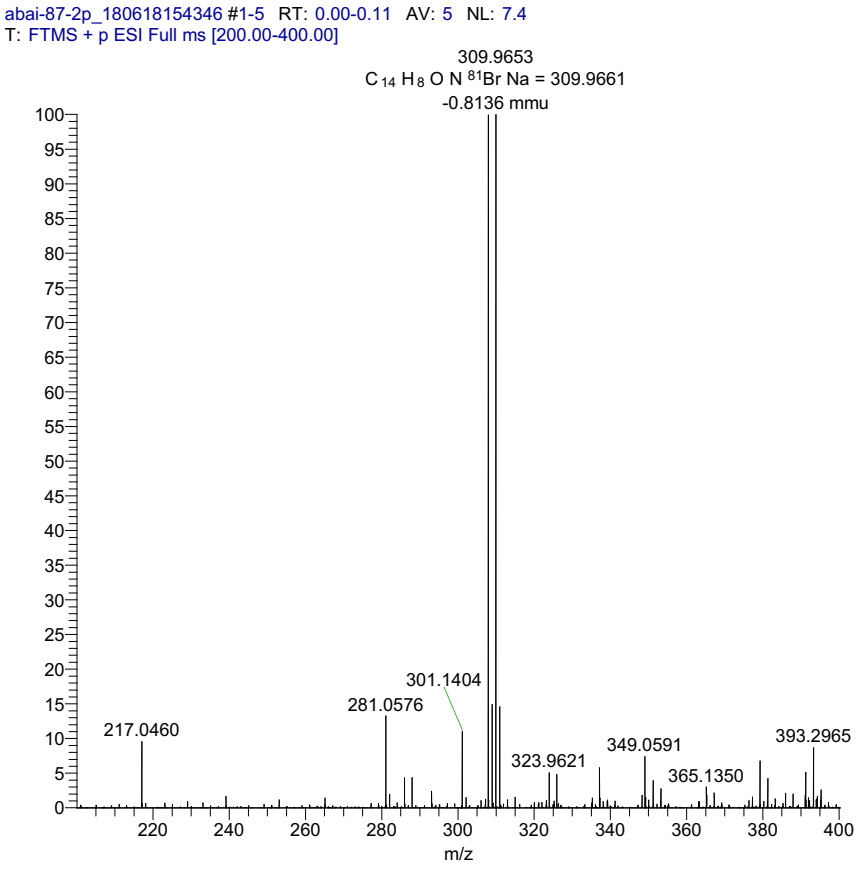
349.0590
365.1349
281.0575
301.1401
393.2965
391.1060
328.9774
320.0740
337.1036
293.0775
356.1127
381.2964
371.1243
267.1039
m/z

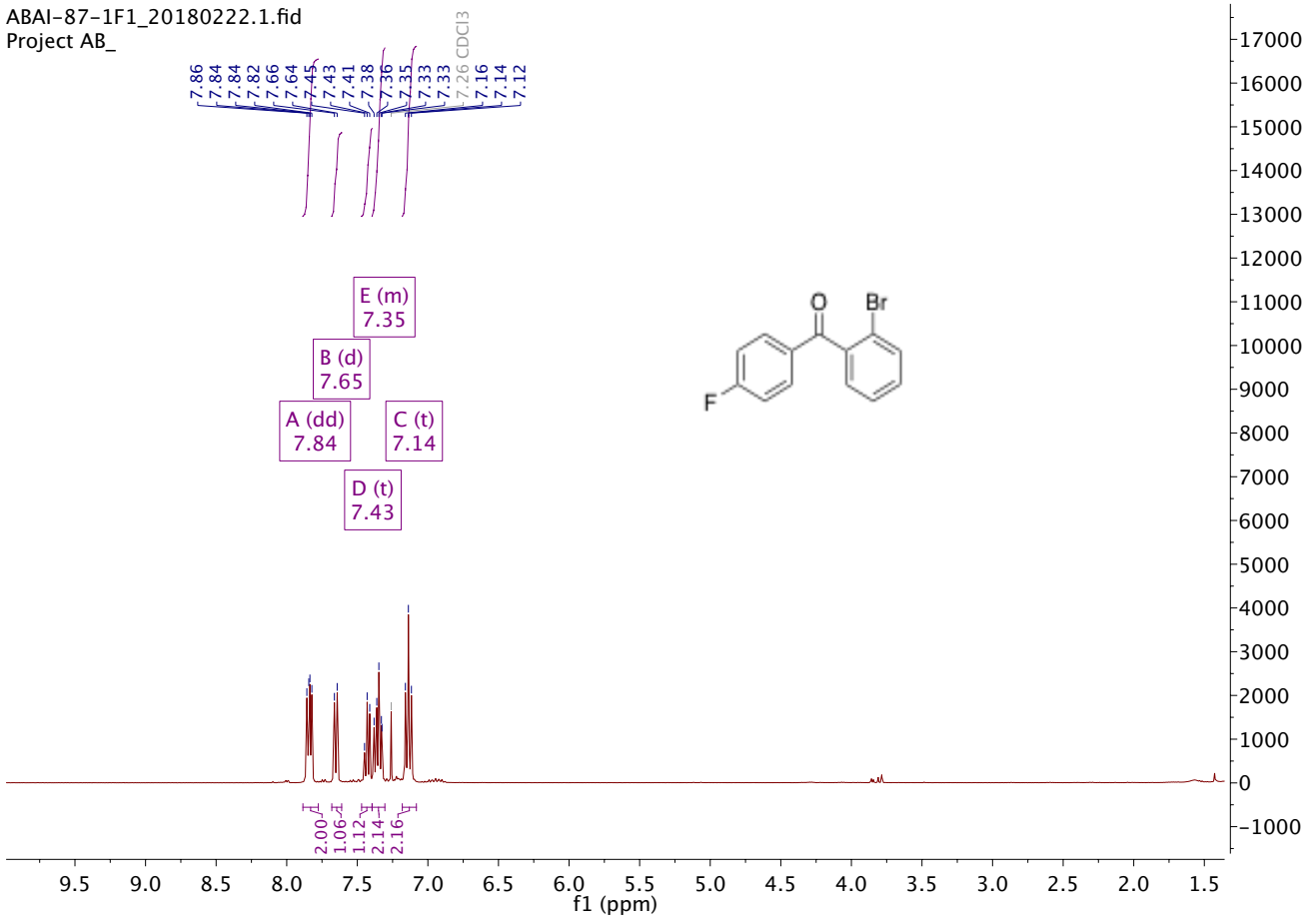
3-(2-Bromobenzoyl)benzonitrile ***5j***

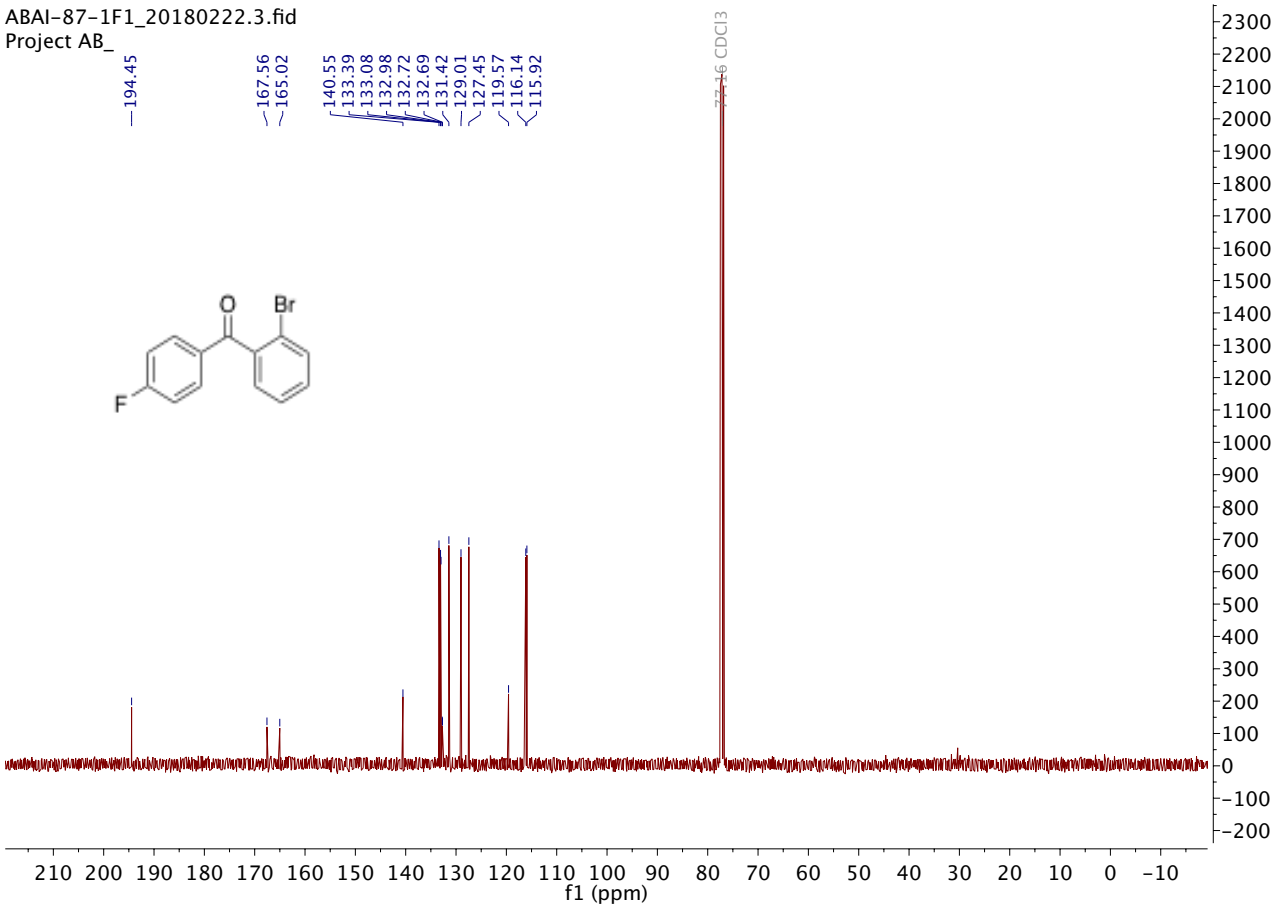






2-Bromophenyl 4-fluorophenyl methanone ***5k***

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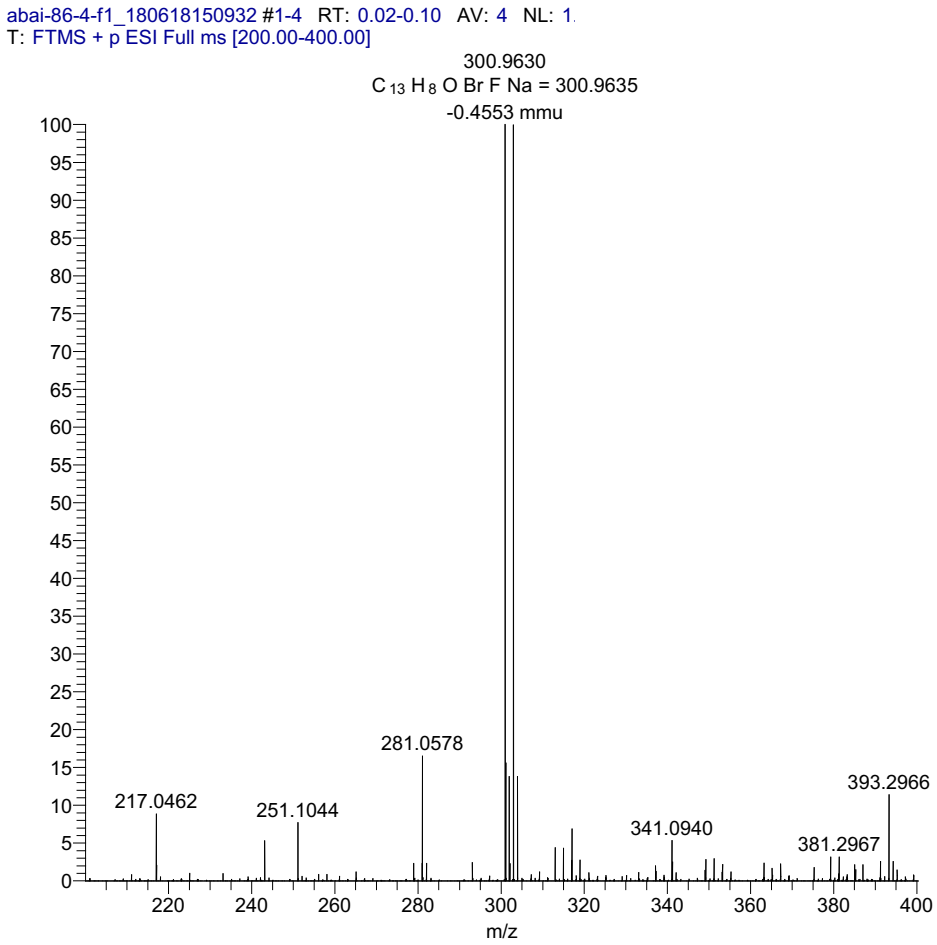
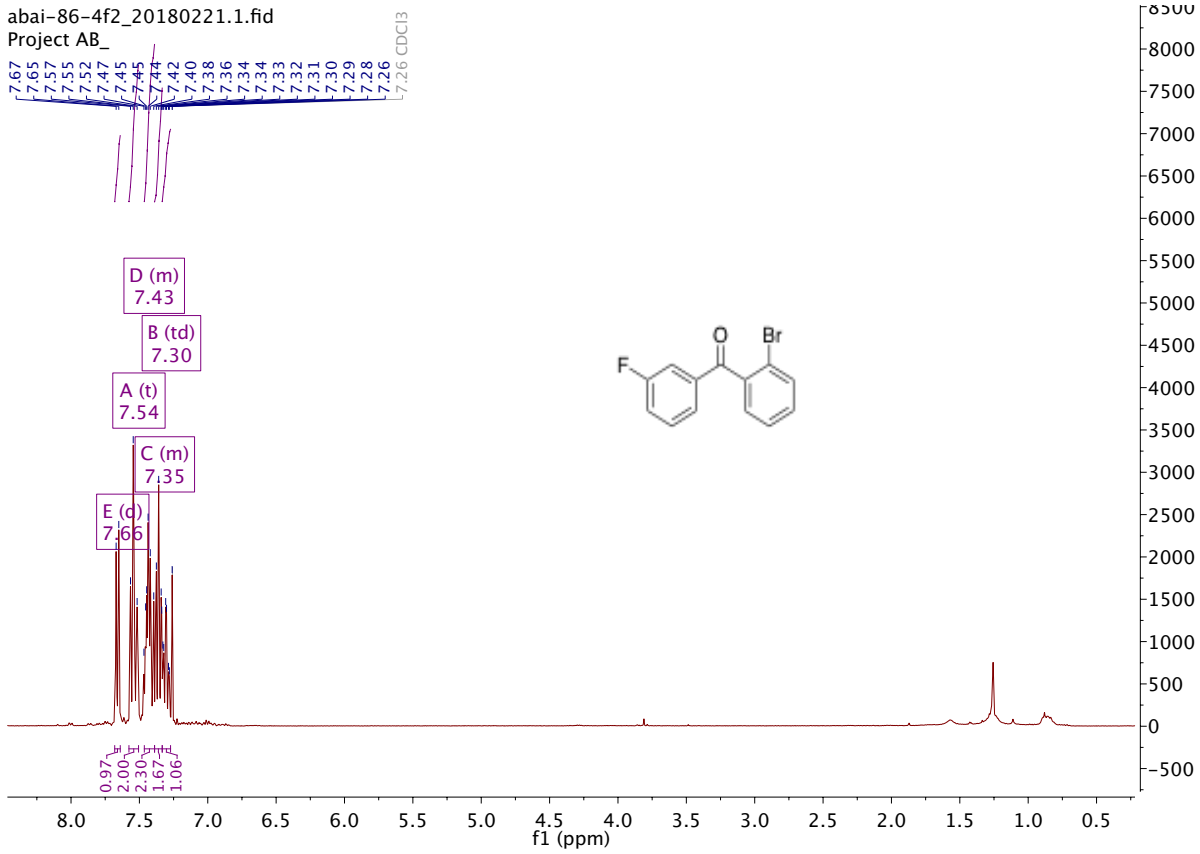
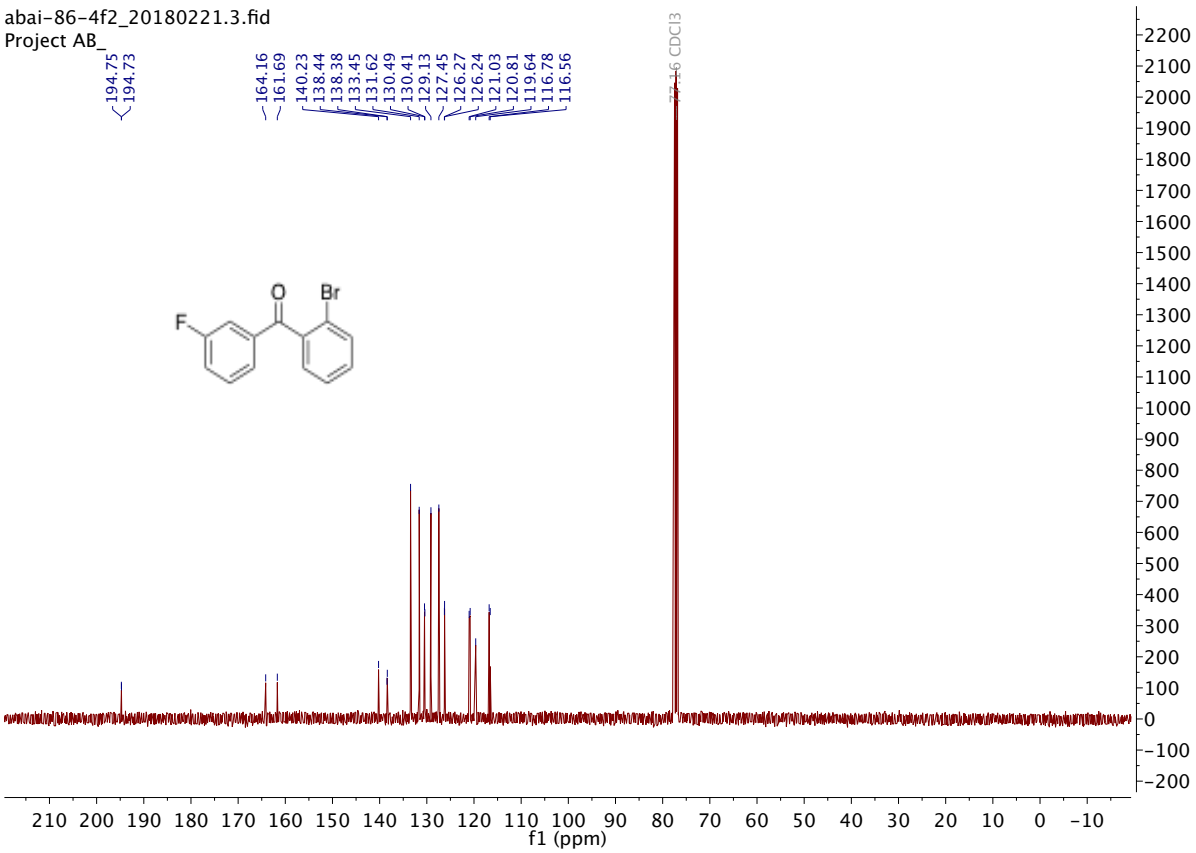
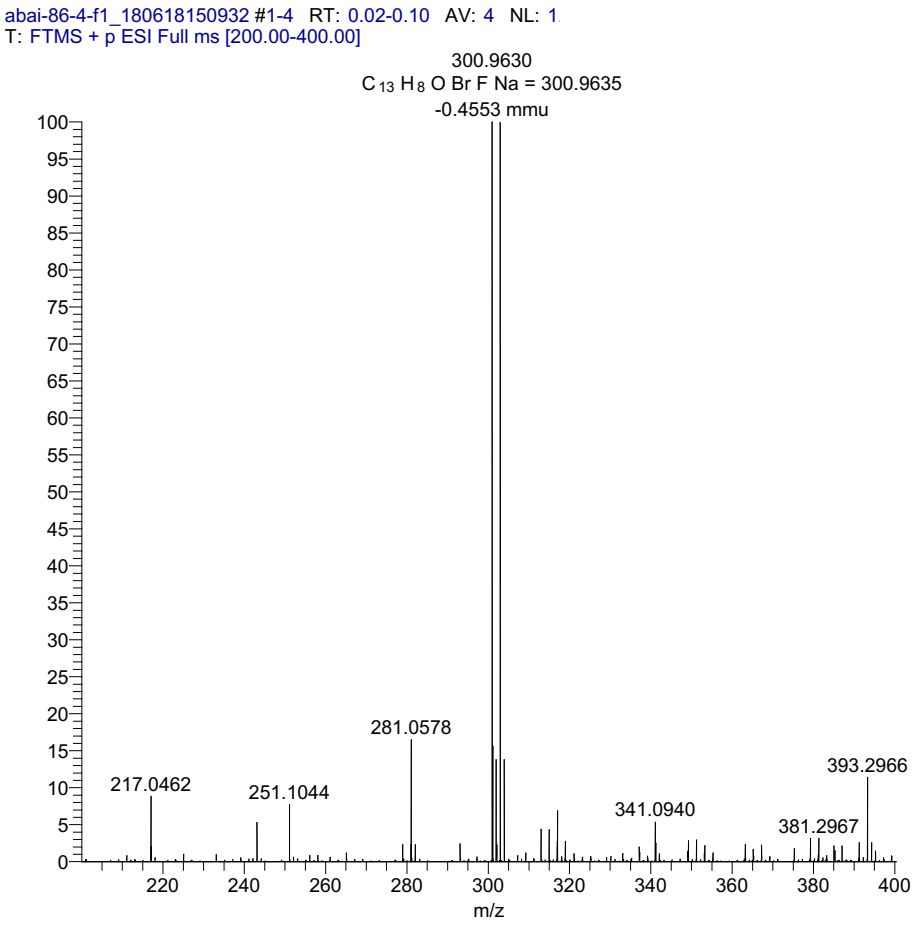
116.14
115.92
77.16 CDCl3
O
Br
F
f1 (ppm)



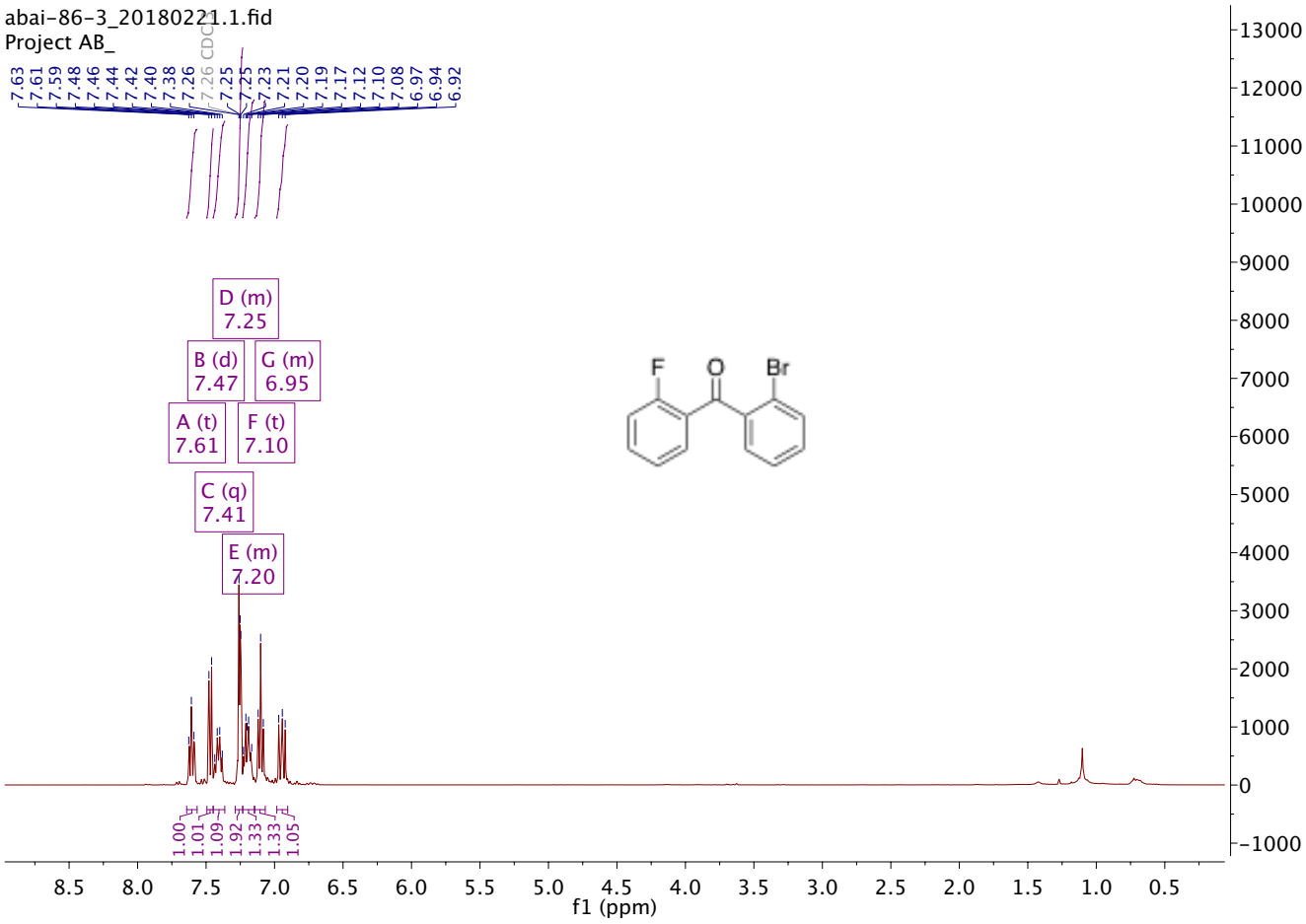
*2-**b**romophenyl 3-fluorophenyl methanone **5l***

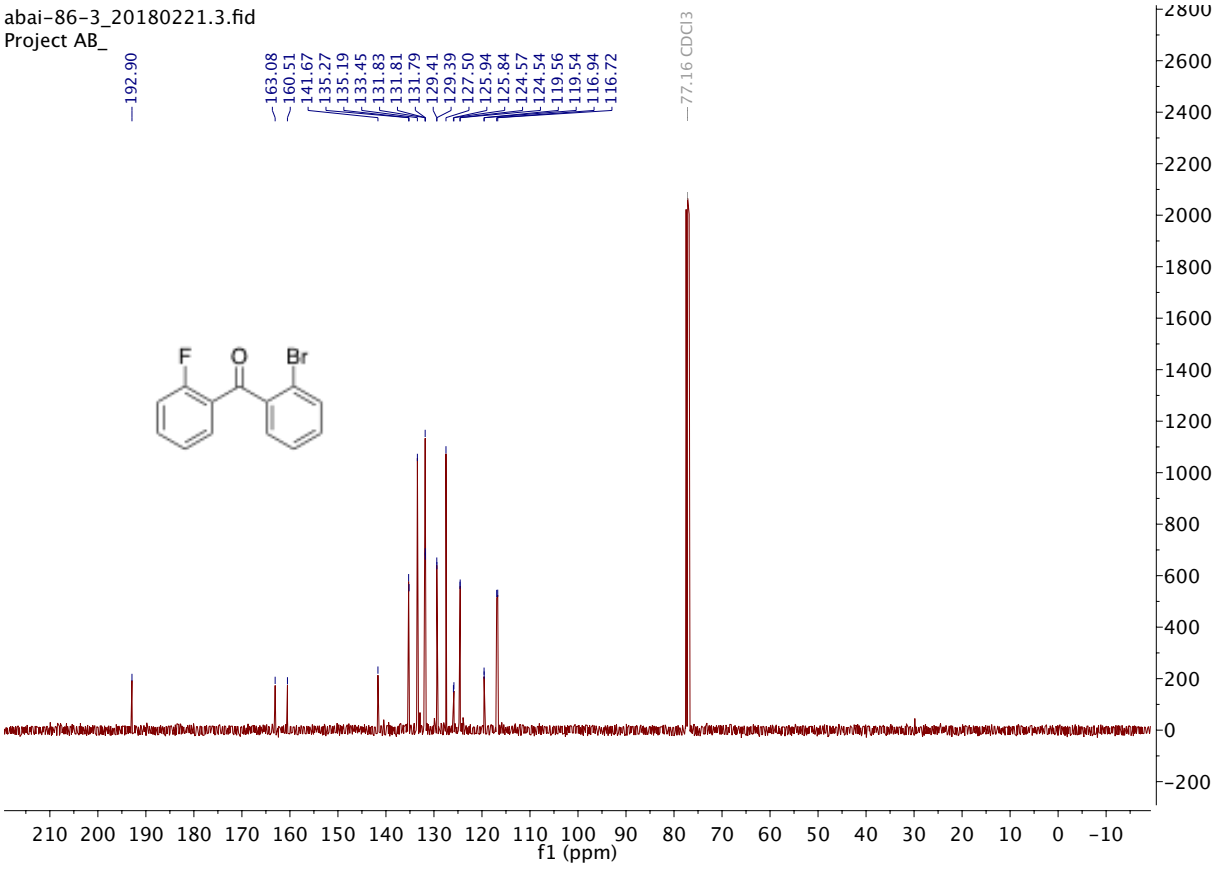



abai-86-4f2_20180221.3.fid
Project AB_
194.75
194.73
164.16
161.69
140.23
138.44
138.38
133.45
131.62
130.49
130.41
129.13
127.45
126.27
126.24
121.03
120.81
119.64
116.78
116.56
77.46 CDCl3
O
Br
F
f1 (ppm)

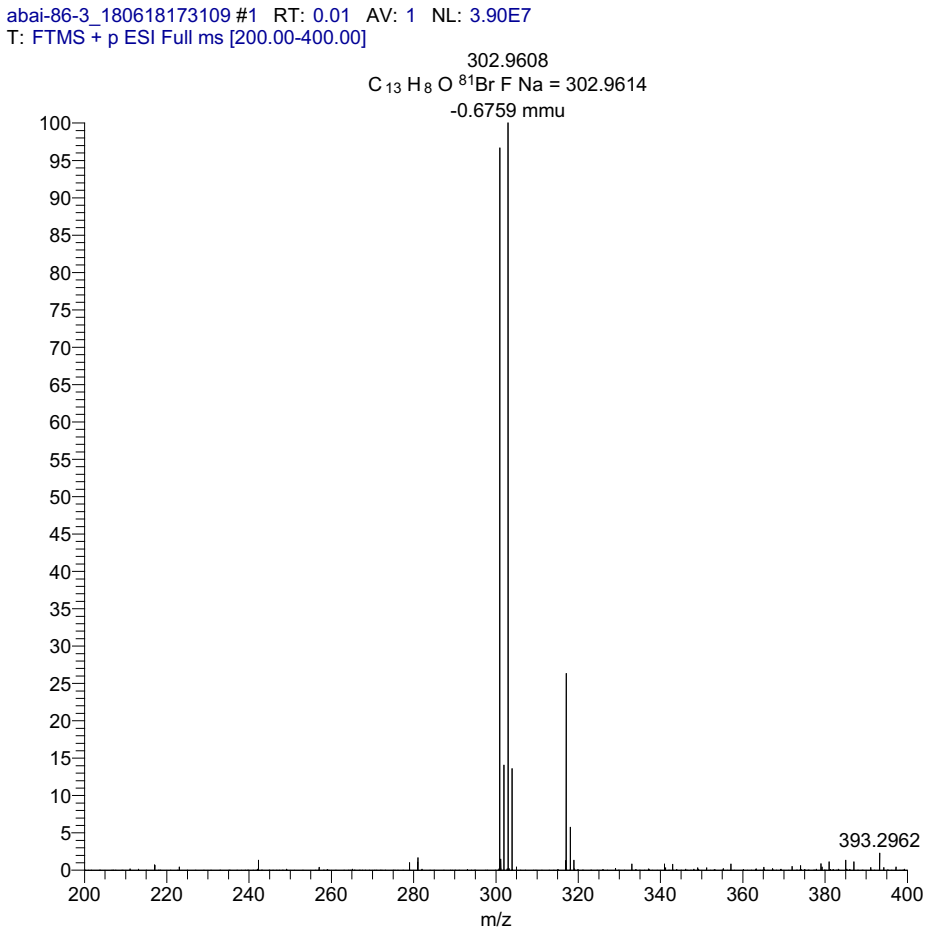

abai-86-4-f1_180618150932 #1-4 RT: 0.02-0.10 AV: 4 NL: 1
T: FTMS + p ESI Full ms [200.00-400.00]
300.9630
C 13 H 8 O Br F Na = 300.9635
-0.4553 mmu
281.0578
217.0462
251.1044
341.0940
381.2967
393.2966
m/z

2-Bromophenyl 2-fluorophenyl methanone ***5m***



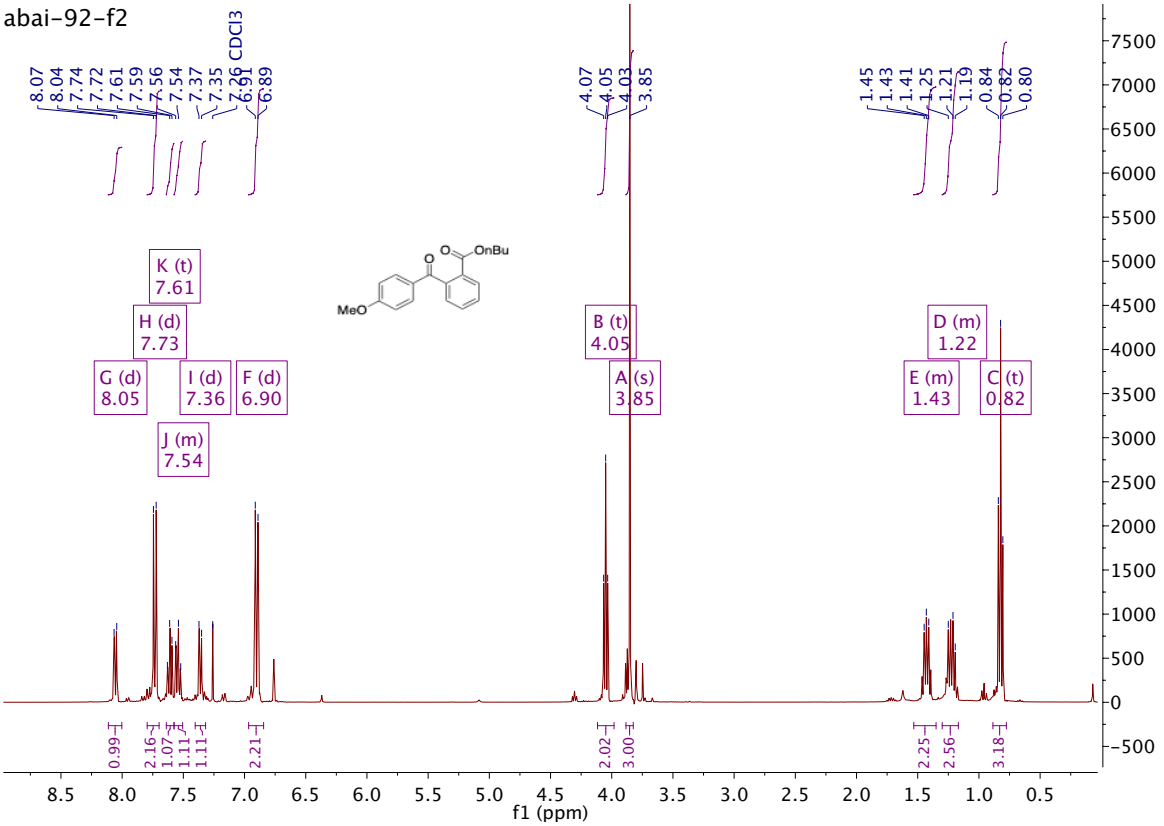


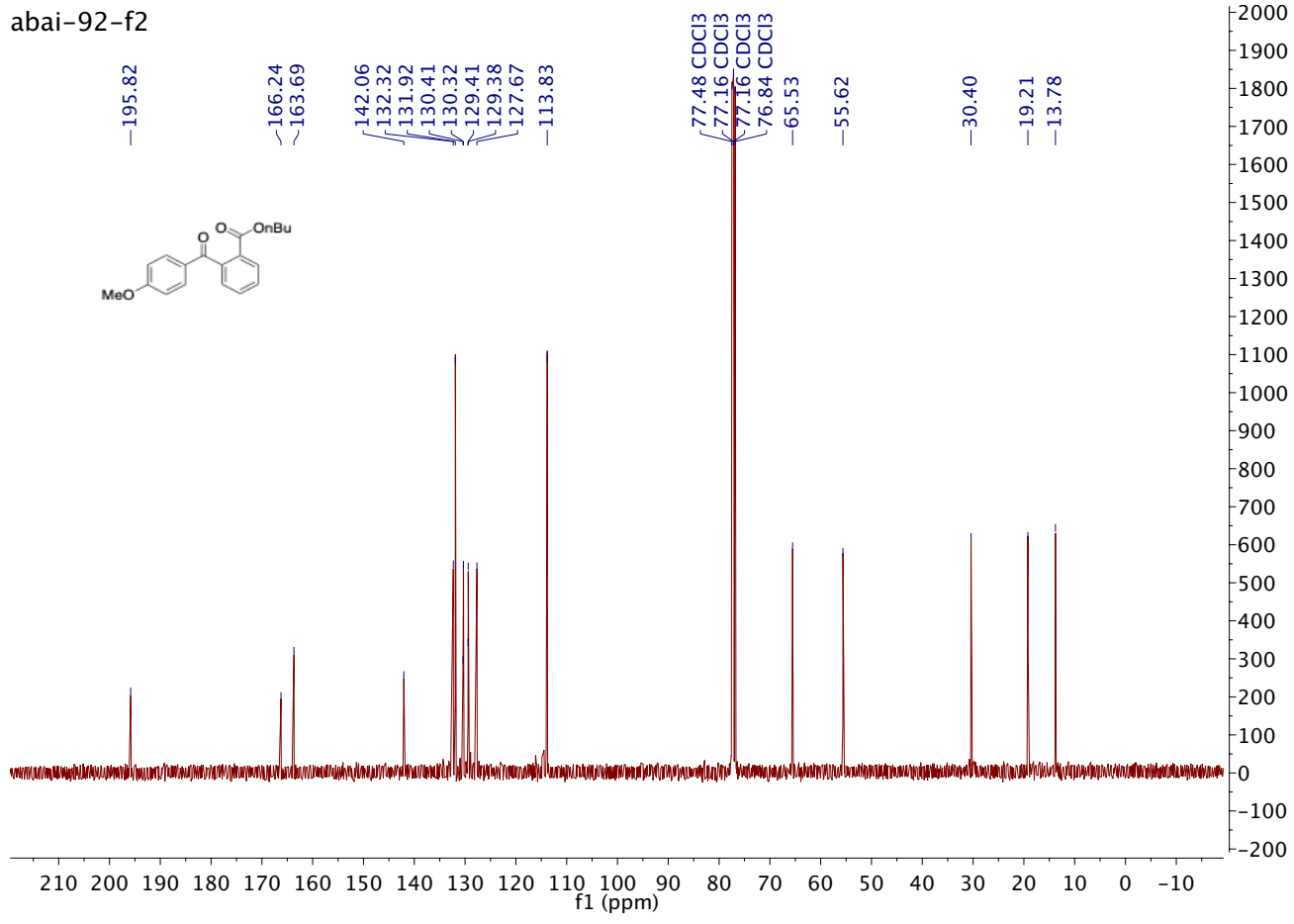
ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.

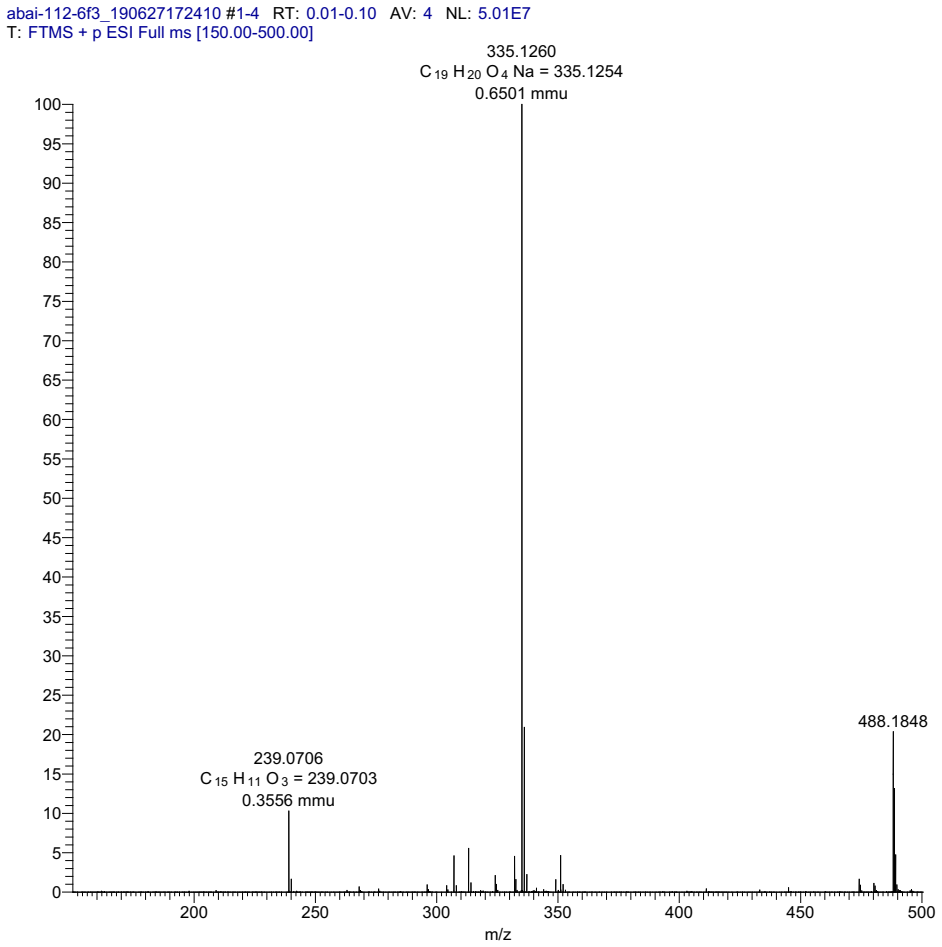


4.2 Spectra for butyl 2-benzoylbenzoate esters 2

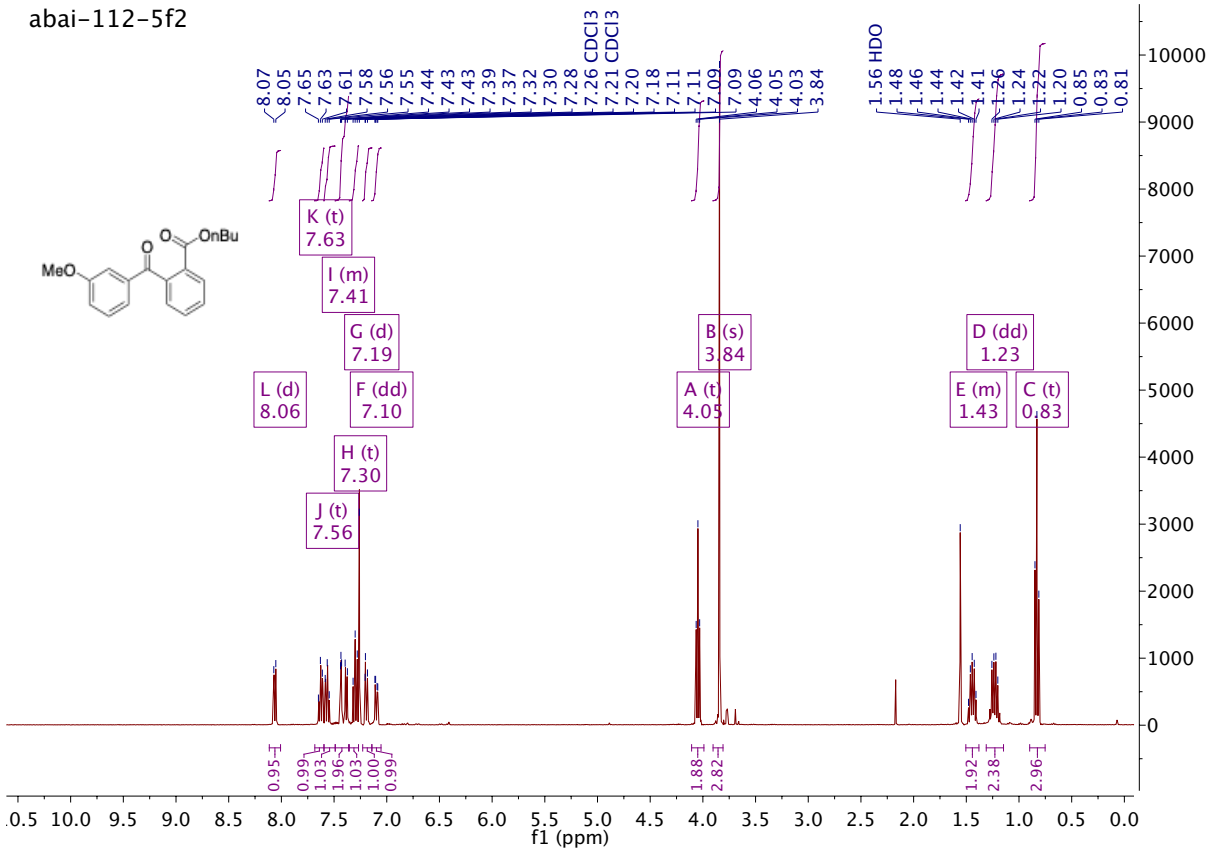
Butyl 2-(4-methoxybenzoyl)benzoate ***2a***

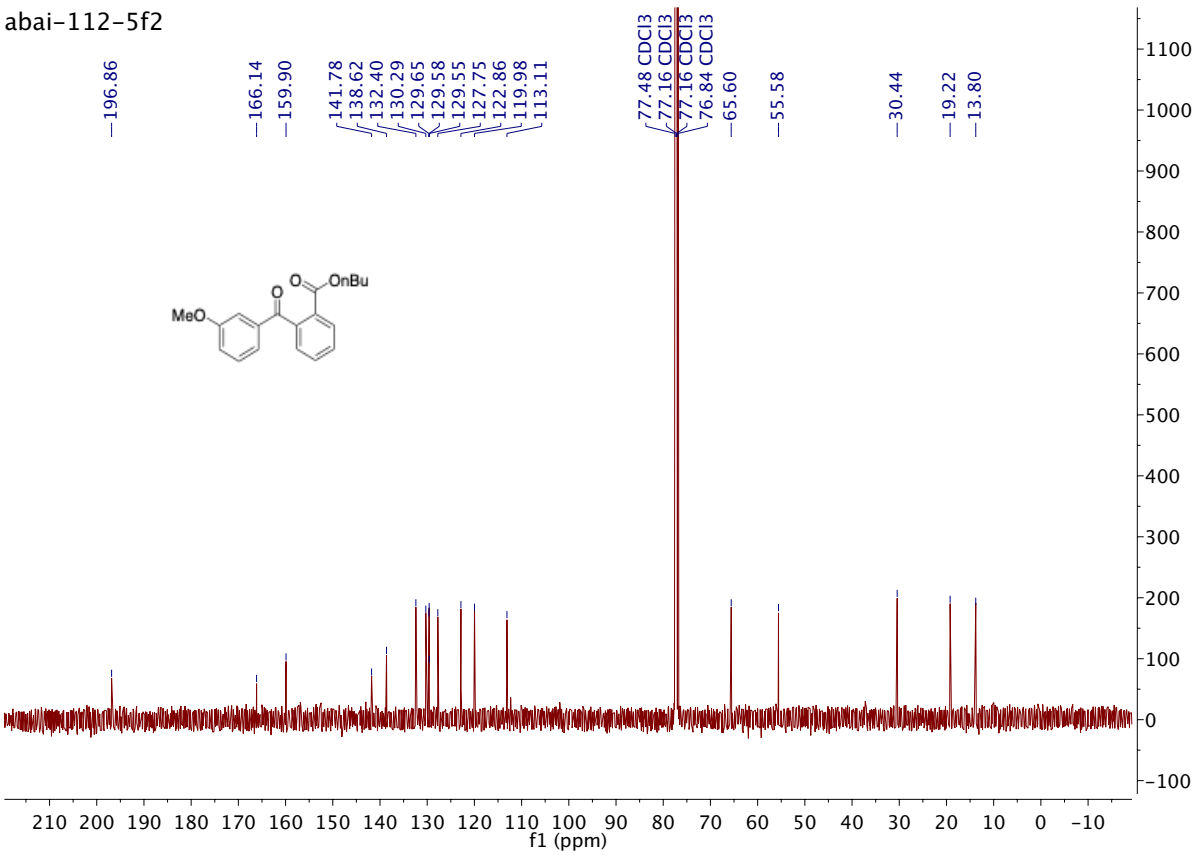


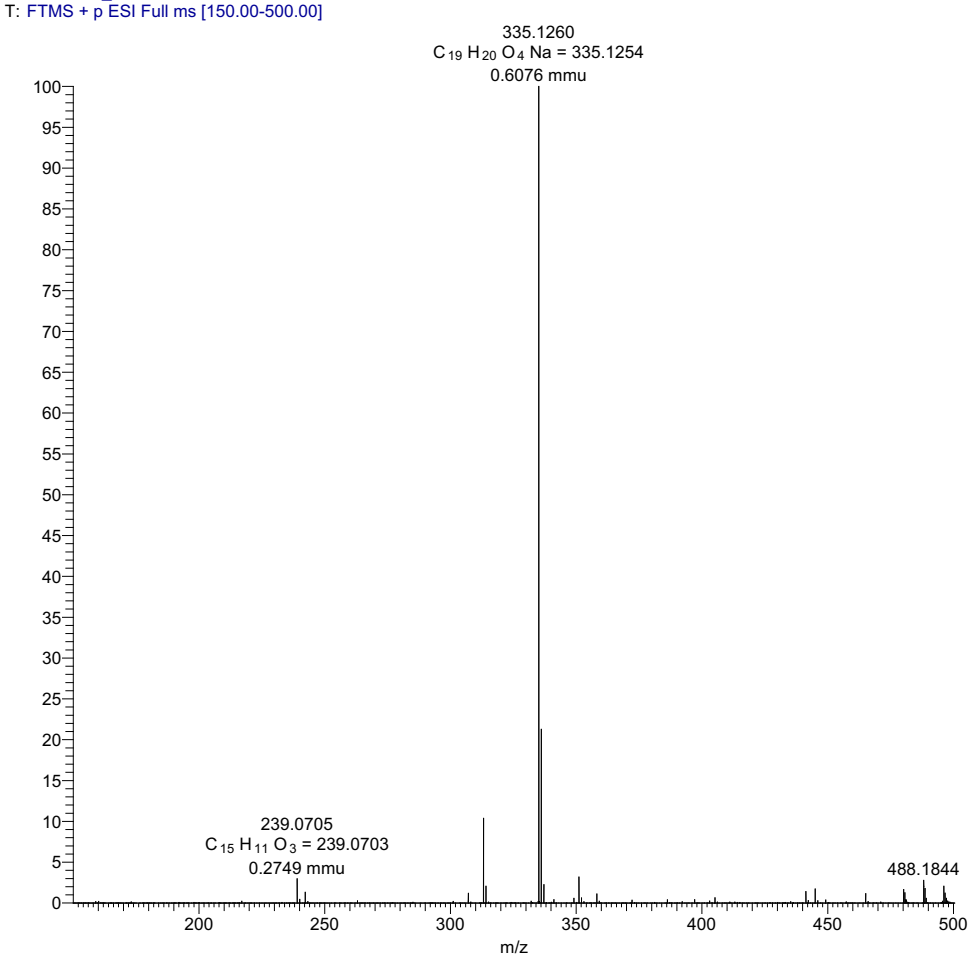




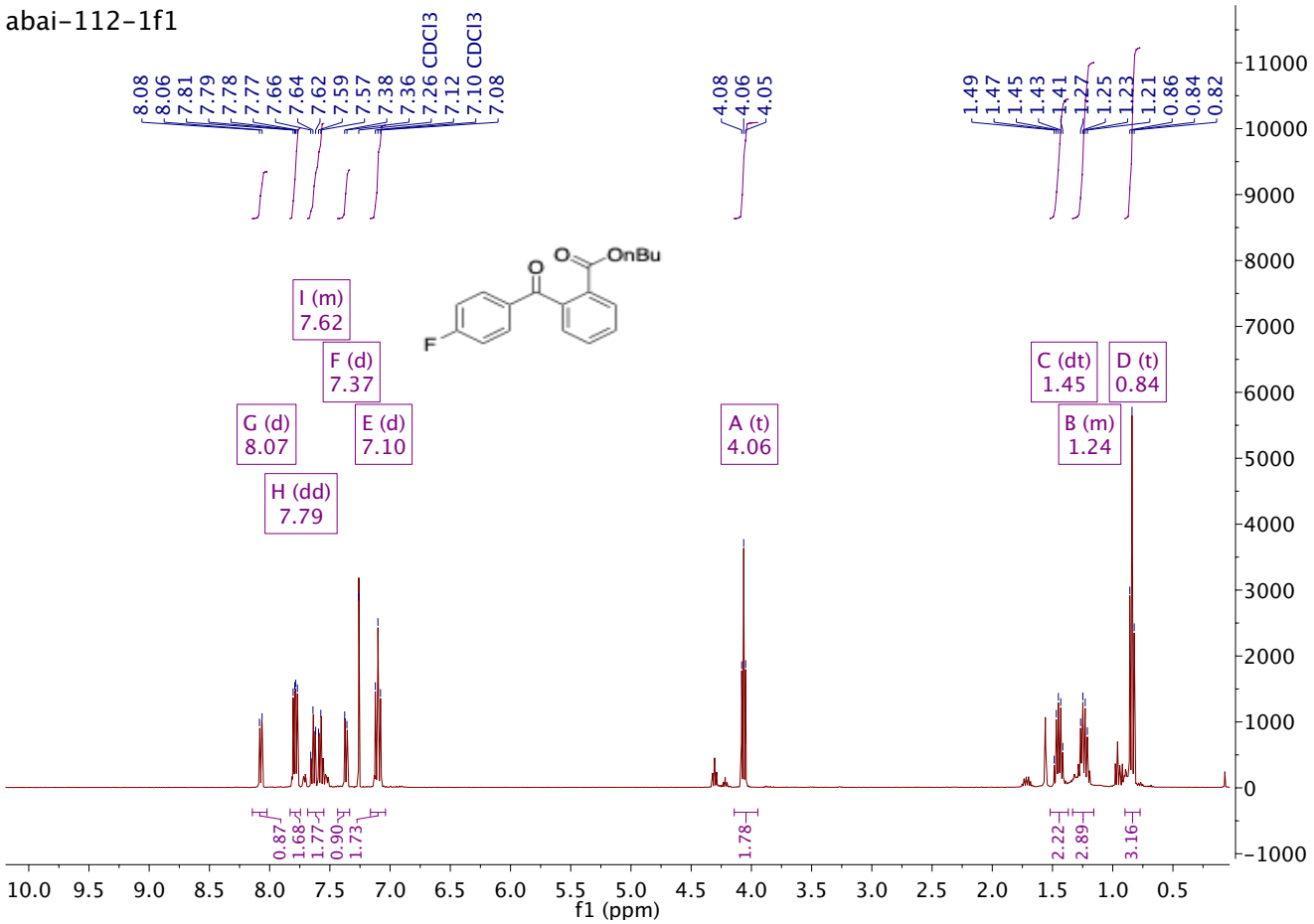
Butyl 2-(3-methoxybenzoyl)benzoate ***2b***

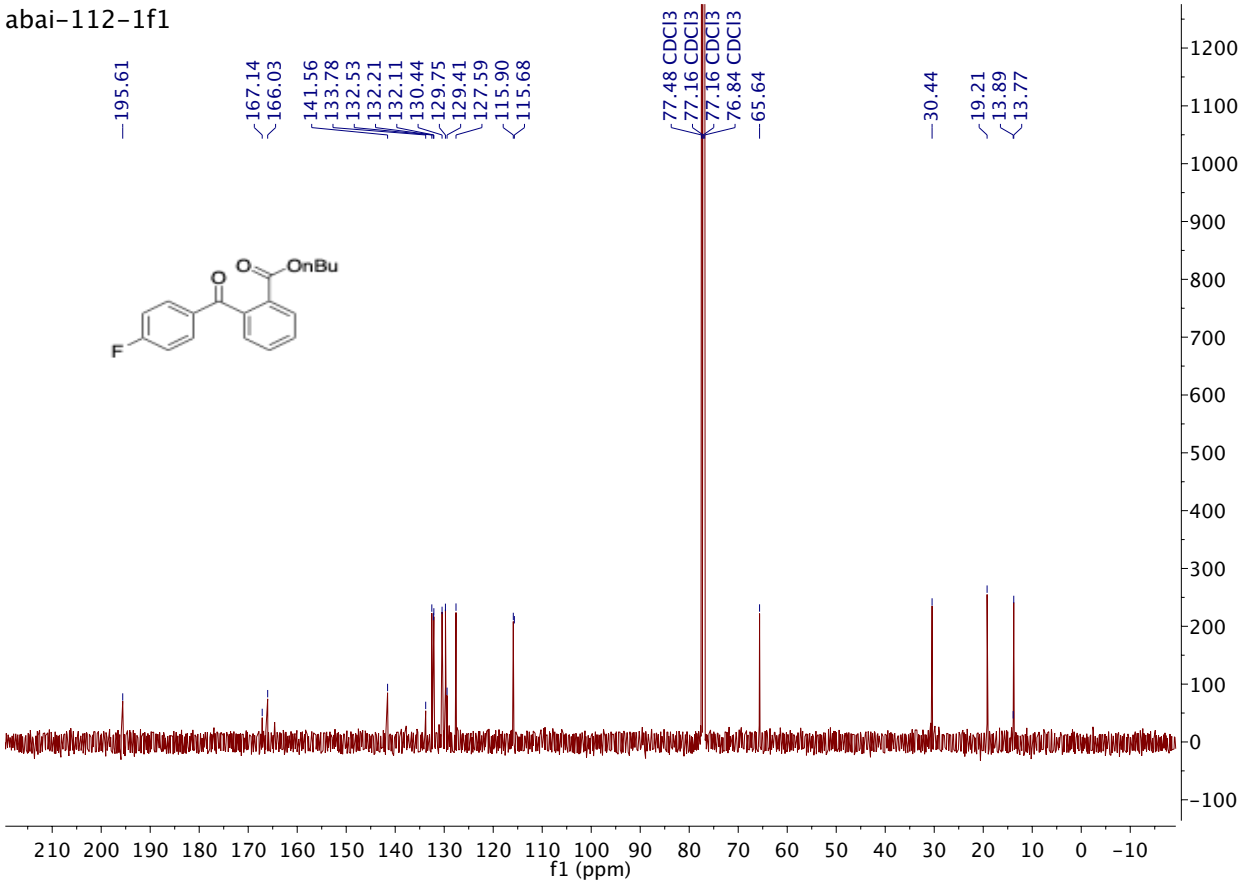


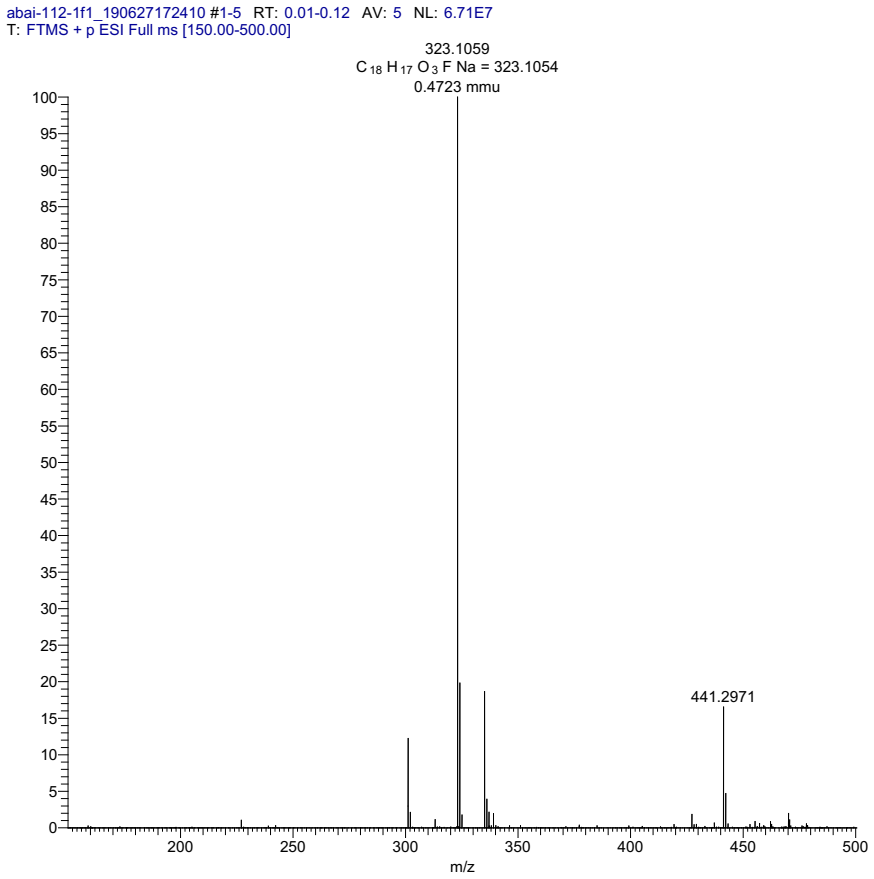

abai-112-5f2
196.86
166.14
159.90
141.78
138.62
132.40
130.29
129.65
129.58
129.55
127.75
122.86
119.98
113.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.60
55.58
30.44
19.22
13.80
MeO
O
O
OnBu
f1 (ppm)


abai-112-5f2_190627172410 #1-5 RT: 0.00-0.11 AV: 5 NL: 4.27E7
T: FTMS + p ESI Full ms [150.00-500.00]
335.1260
C19 H20 O4 Na = 335.1254
0.6076 mmu
239.0705
C15 H11 O3 = 239.0703
0.2749 mmu
488.1844
m/z

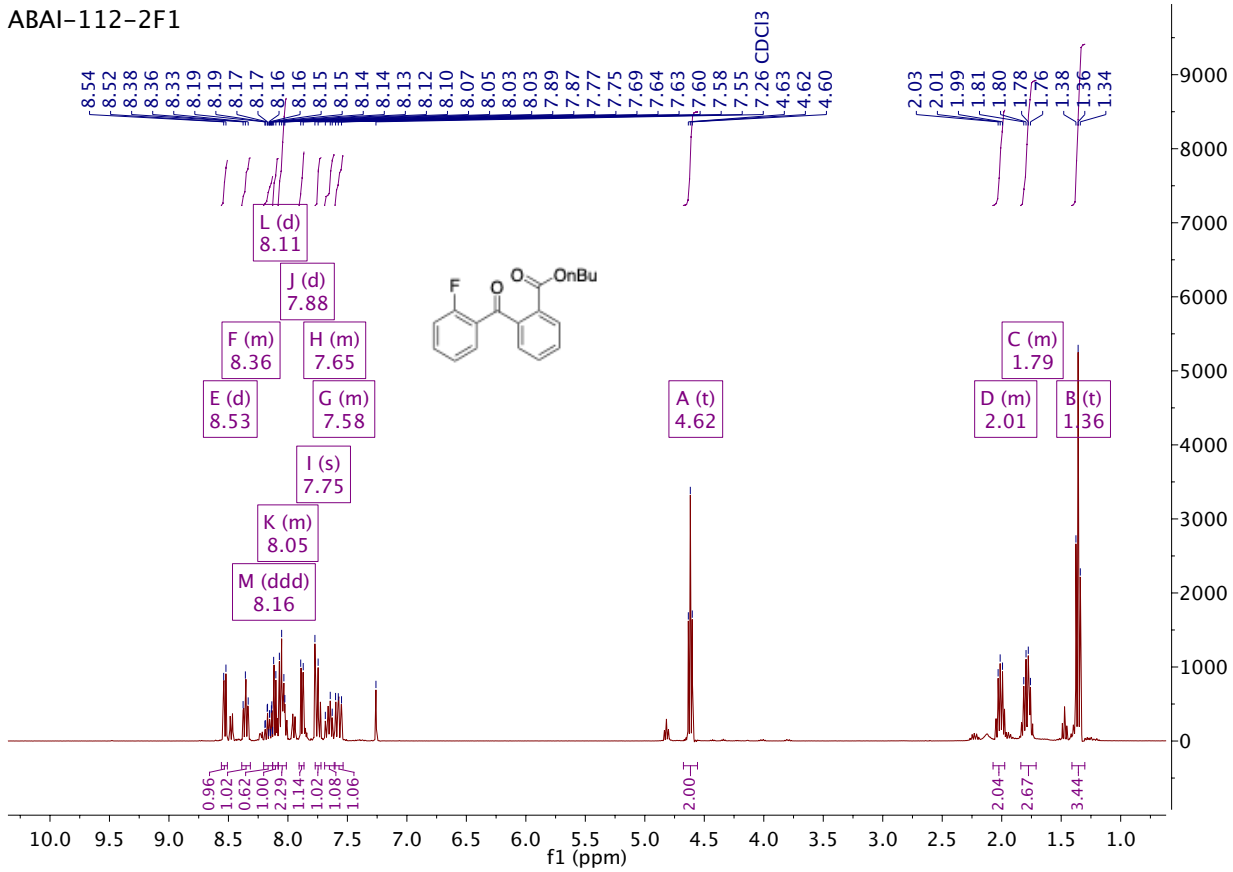
Butyl 2-(4-fluorobenzoyl)benzoate ***2c***



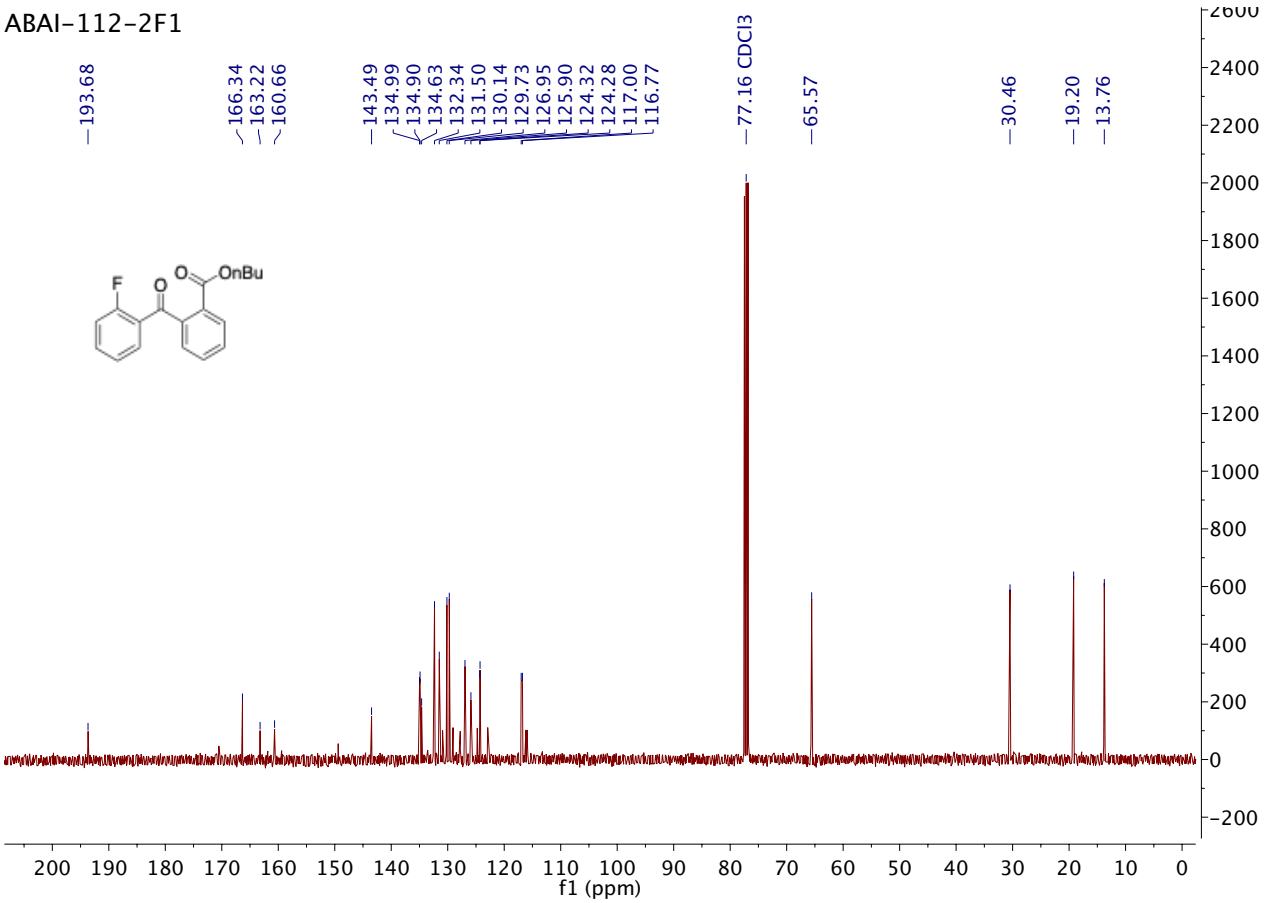


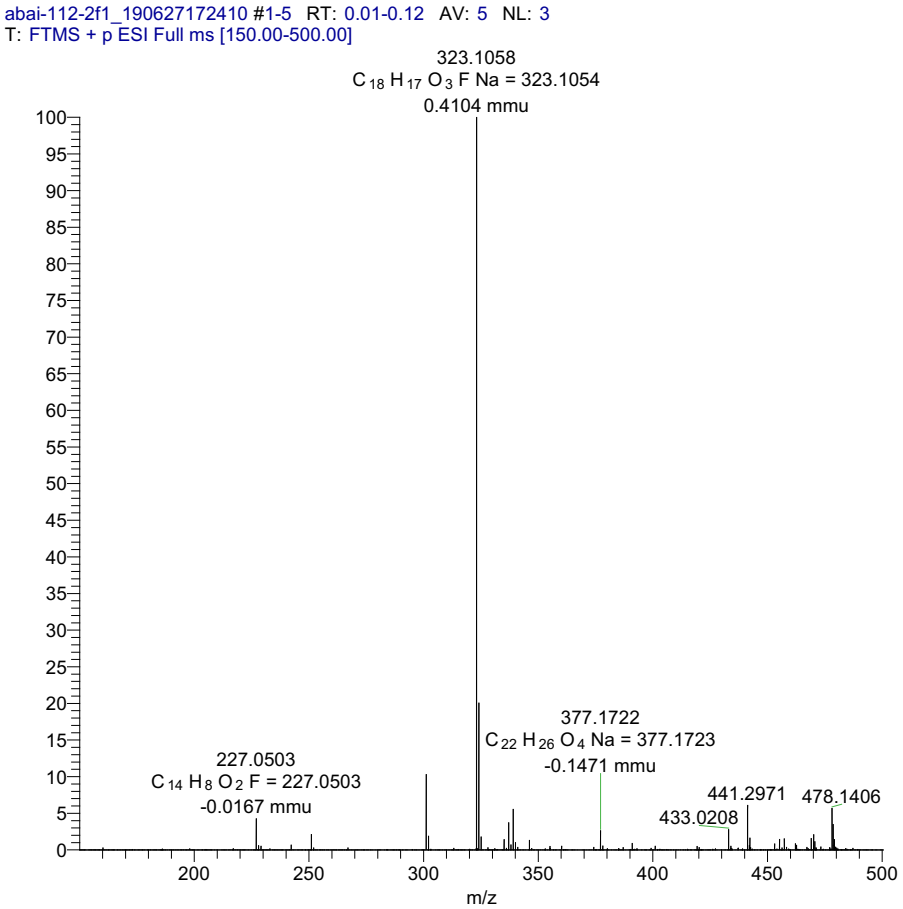


Butyl 2-(2-fluorobenzoyl)benzoate ***2d***



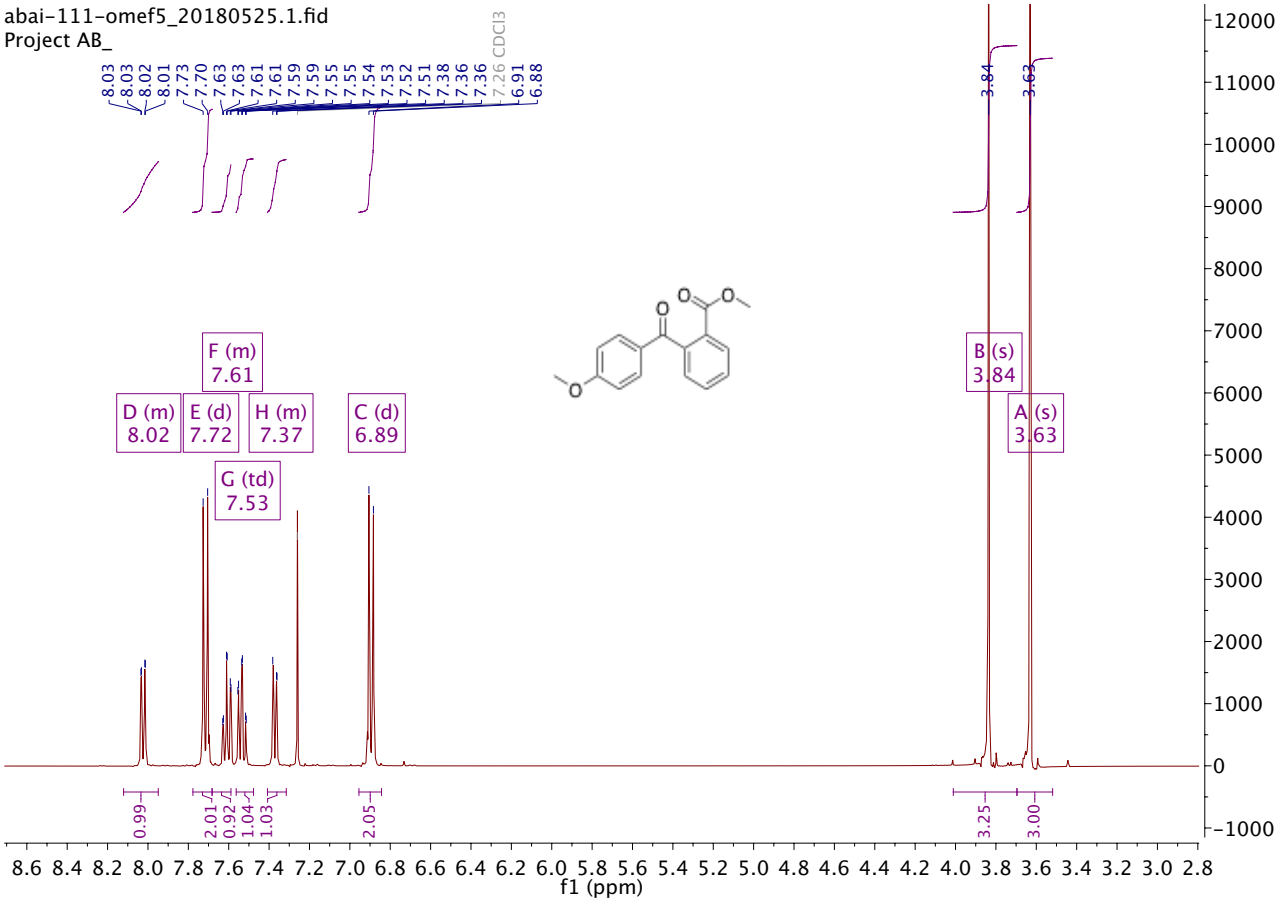
ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.

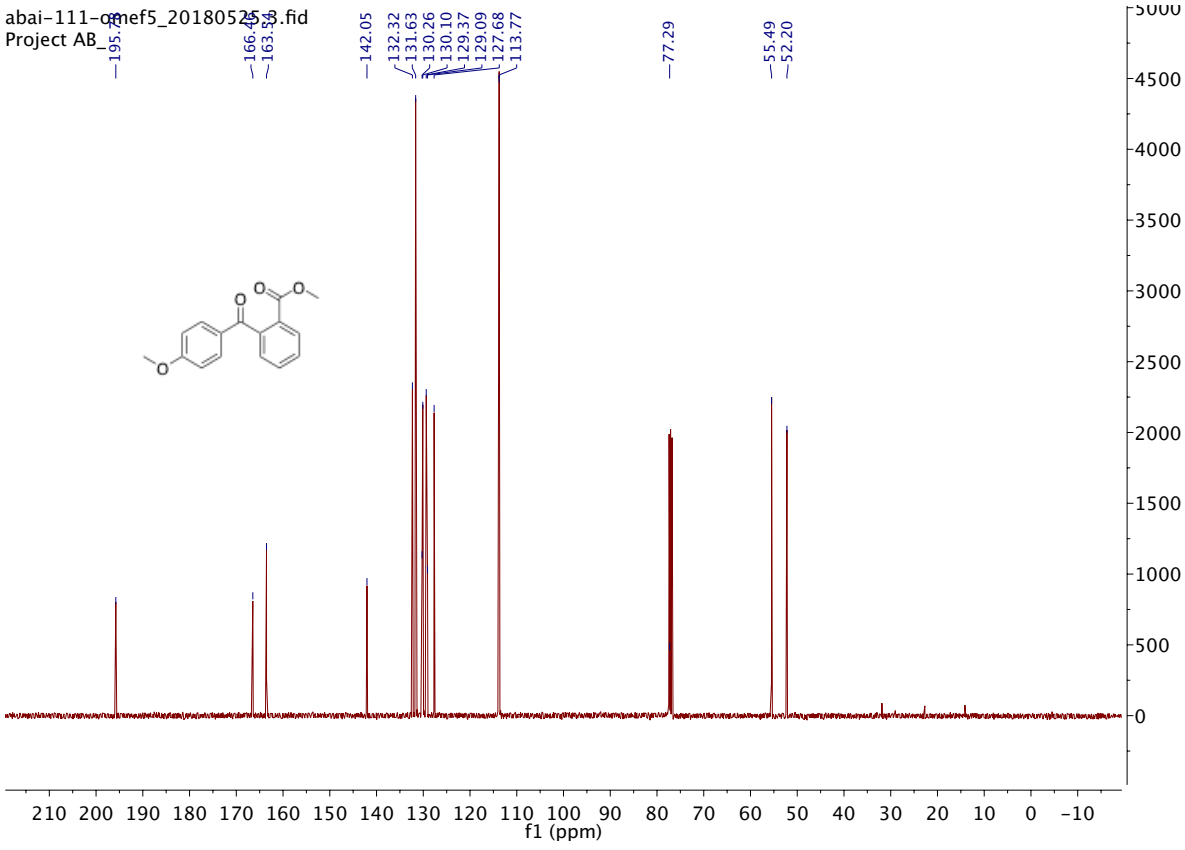


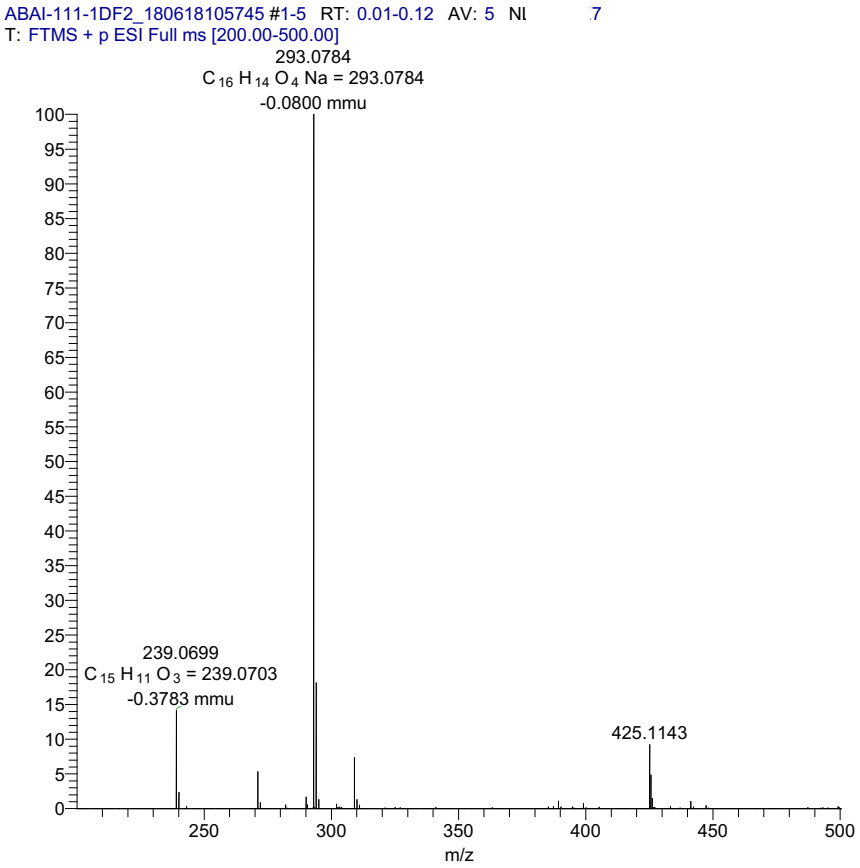


4.3 Spectra for methyl 2-benzoylbenzoate esters 2

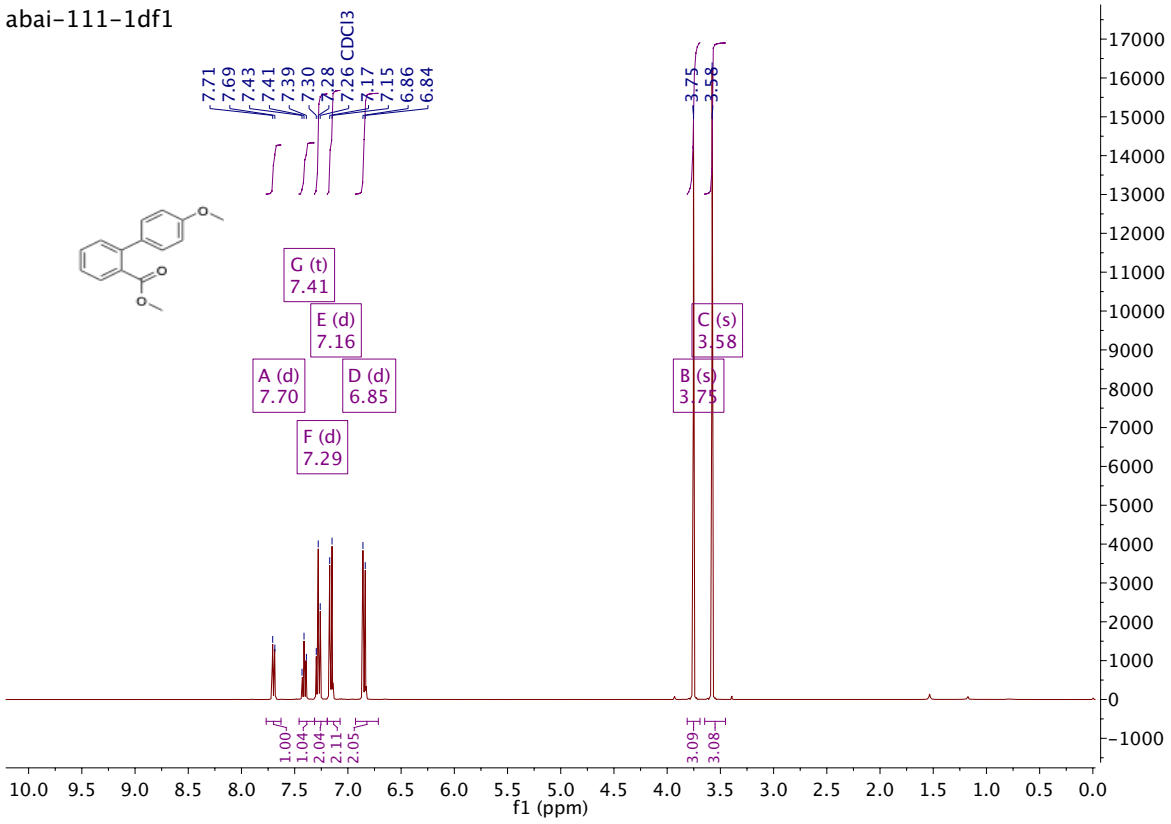
Methyl 2-(4-methoxybenzoyl)benzoate ***2aa***

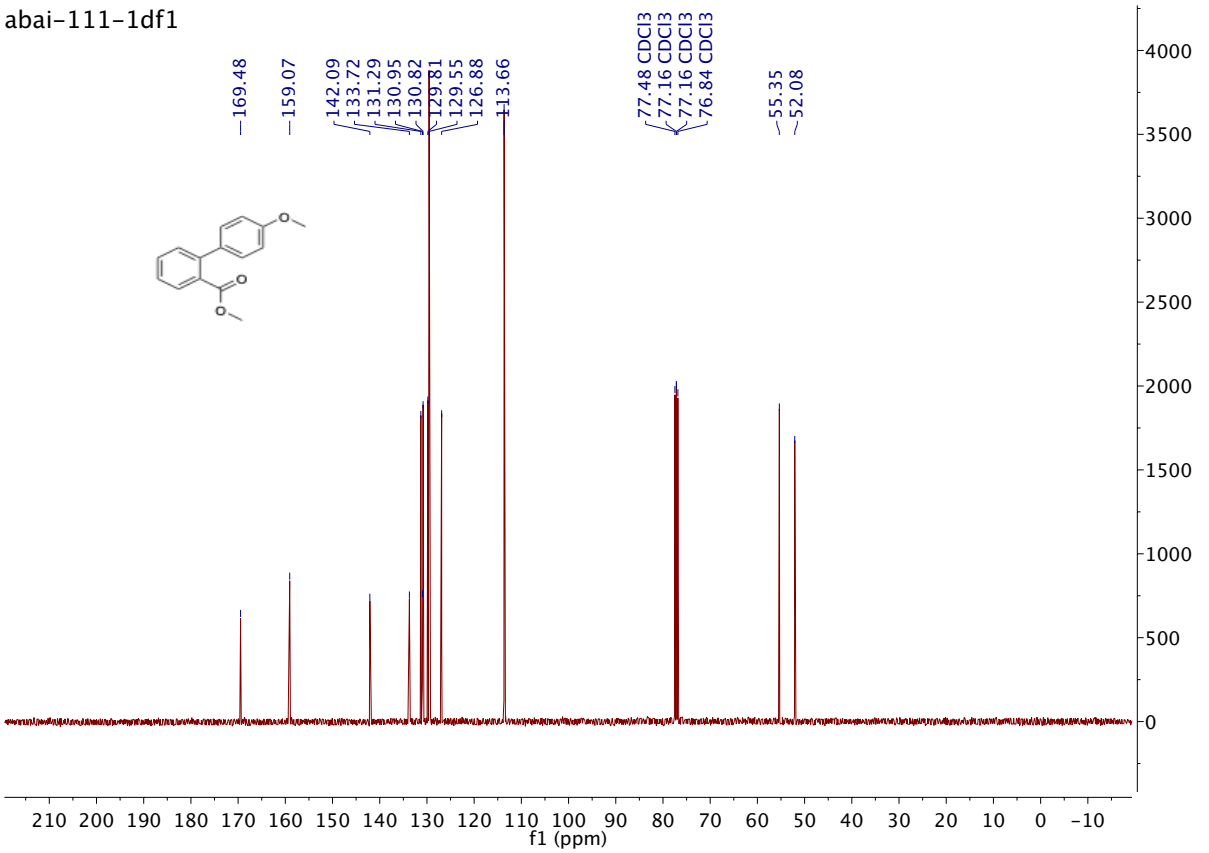




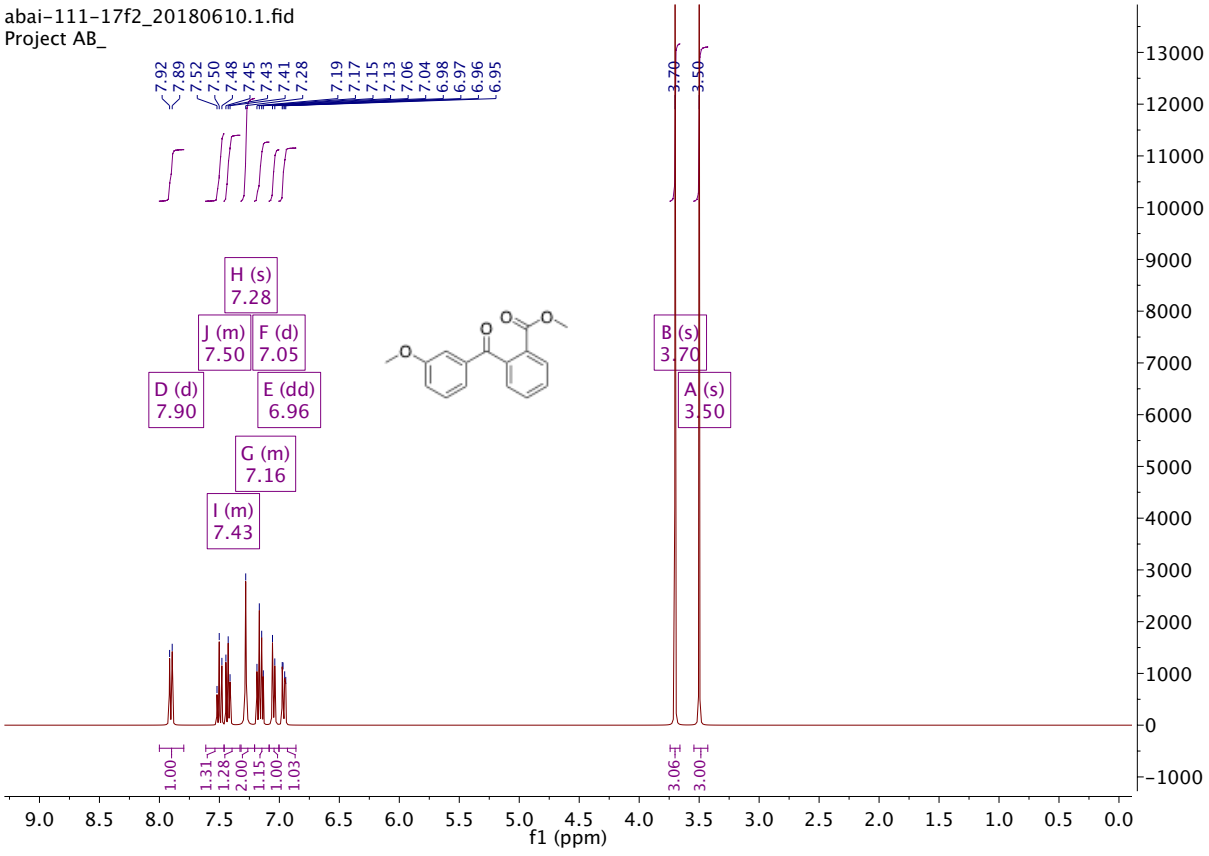


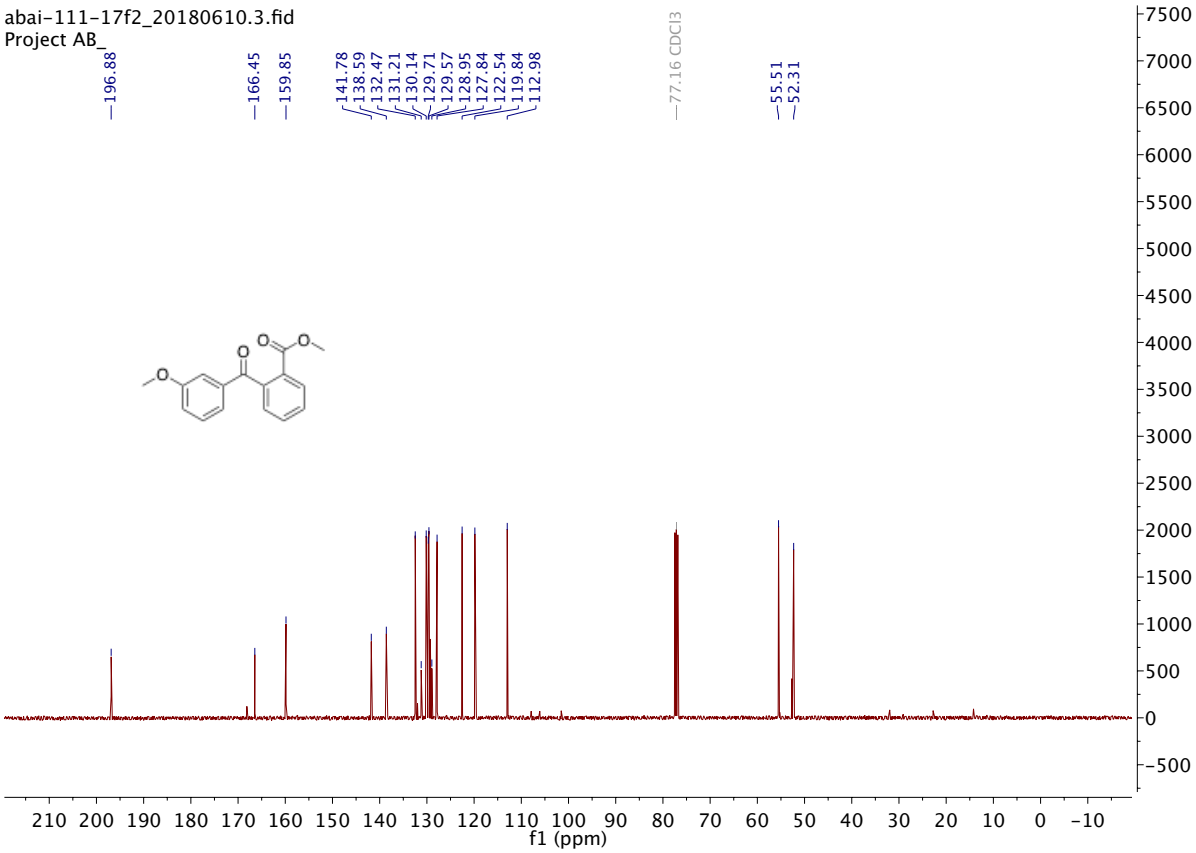
*methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate **B** (from direct coupling).*

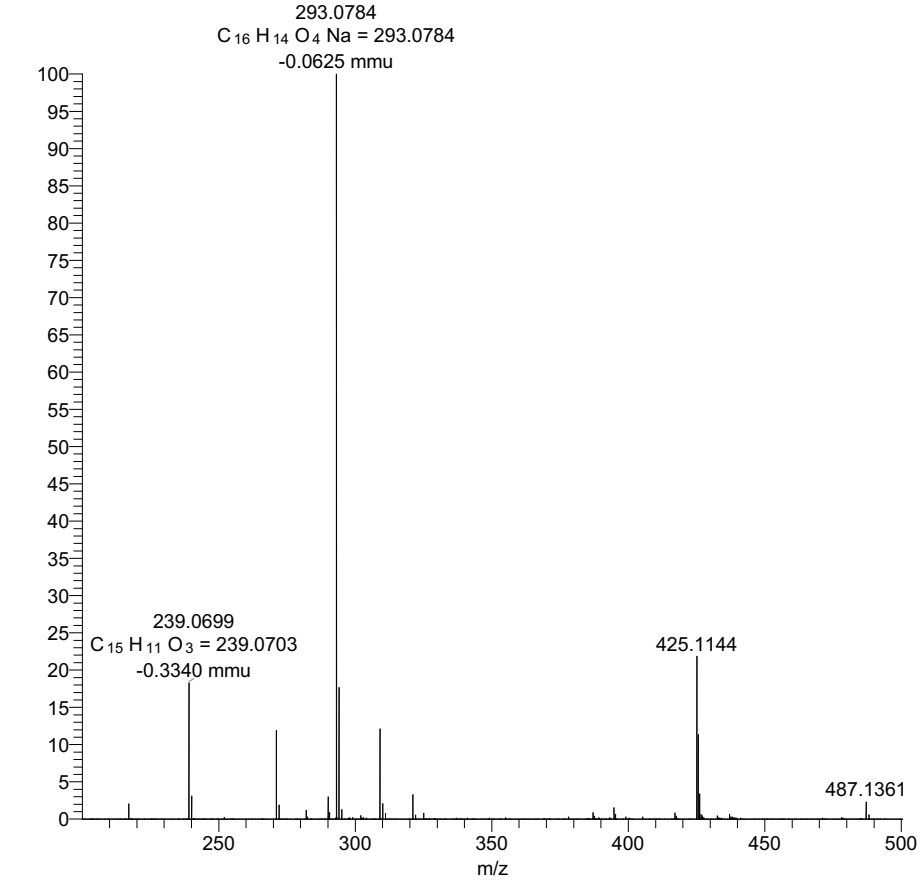




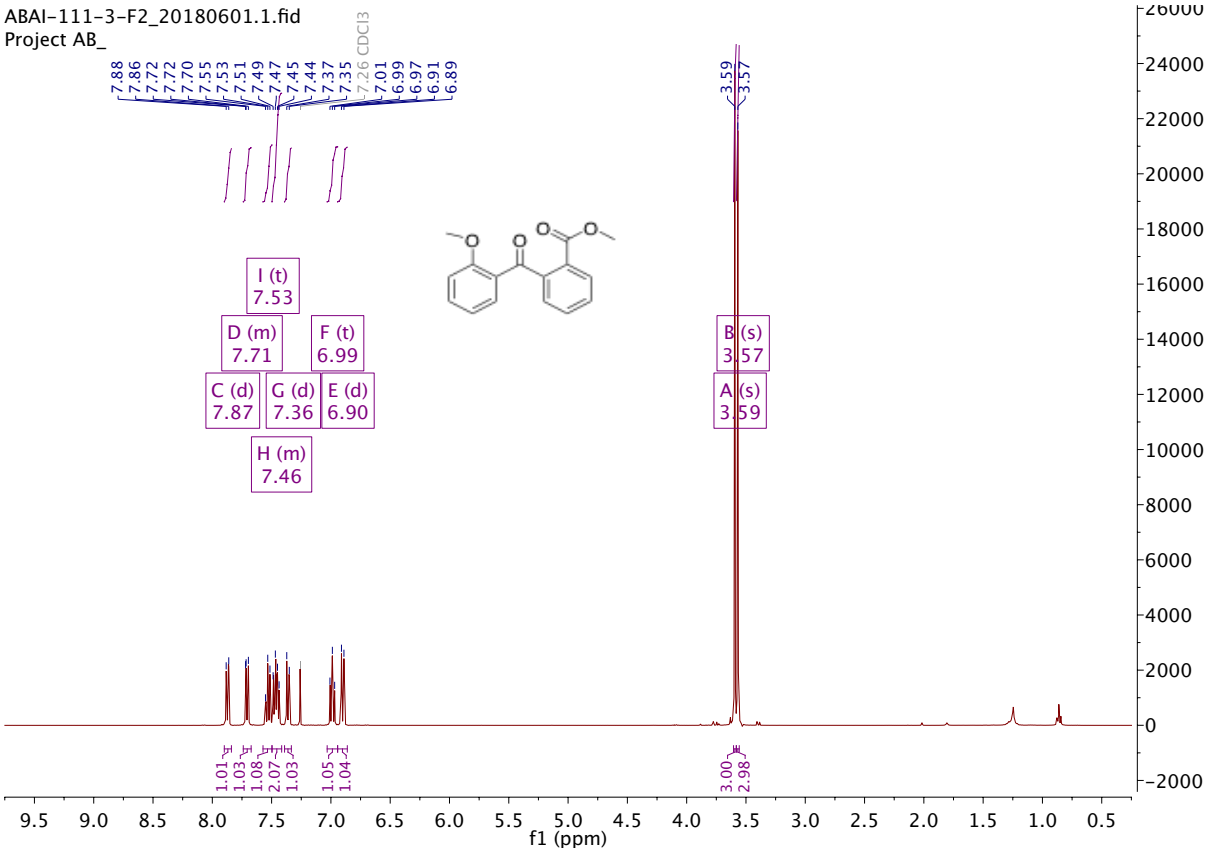
Methyl 2-(3-methoxybenzoyl) benzoate ***2ab***

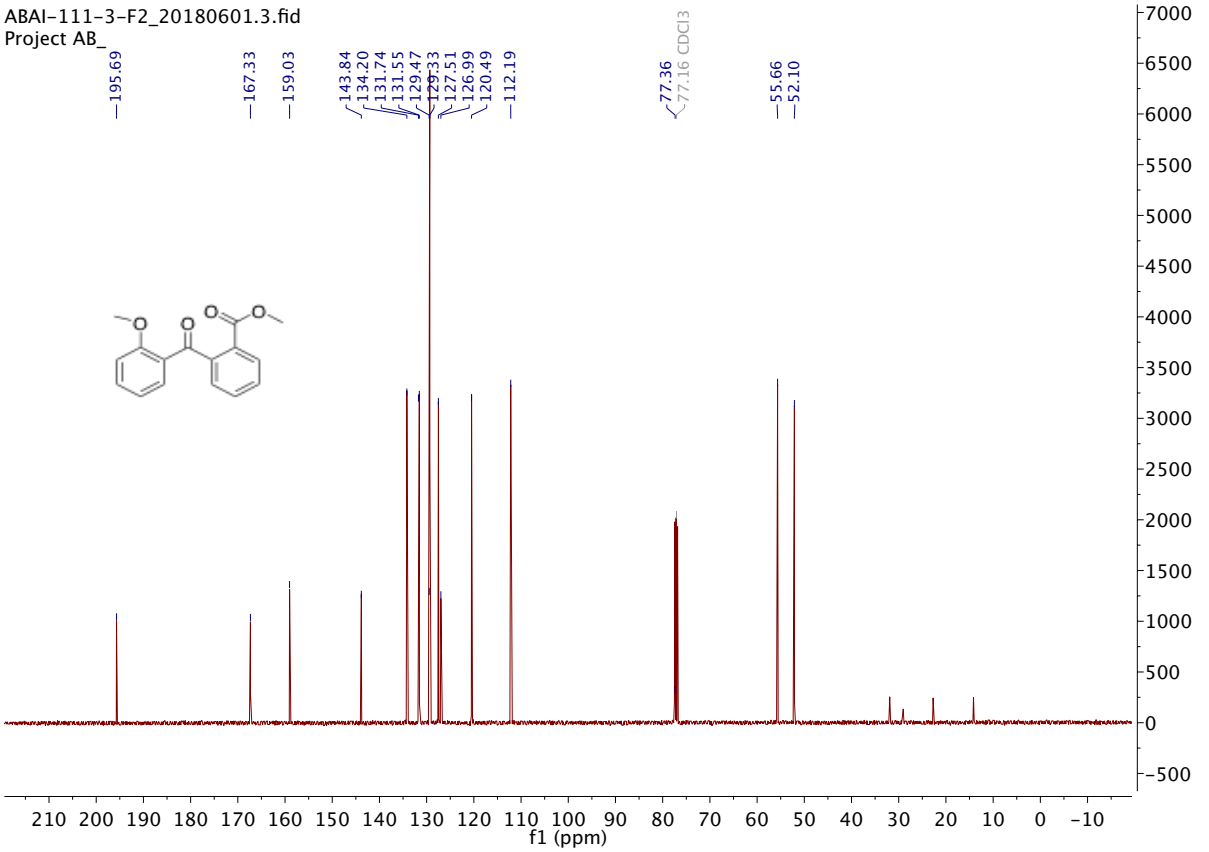


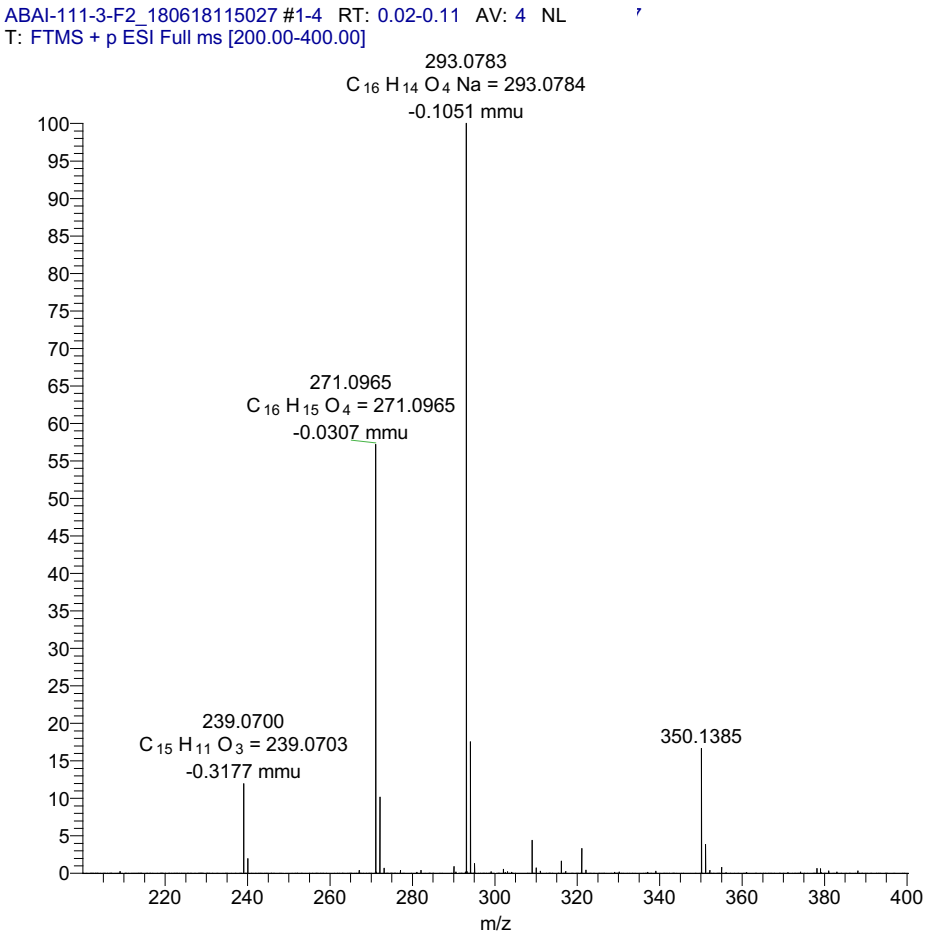

abai-111-17f2_20180610.3.fid
Project AB_
196.88
166.45
159.85
141.78
138.59
132.47
131.21
130.14
129.71
129.57
128.95
127.84
122.54
119.84
112.98
77.16 CDCl3
55.51
52.31
f1 (ppm)


ABAI-111-17-F2 #1-4 RT: 0.02-0.11 AV: 4 NL: 6.66E7
T: FTMS + p ESI Full ms [200.00-500.00]
293.0784
C16 H14 O4 Na = 293.0784
-0.0625 mmu
239.0699
C15 H11 O3 = 239.0703
-0.3340 mmu
425.1144
487.1361
m/z

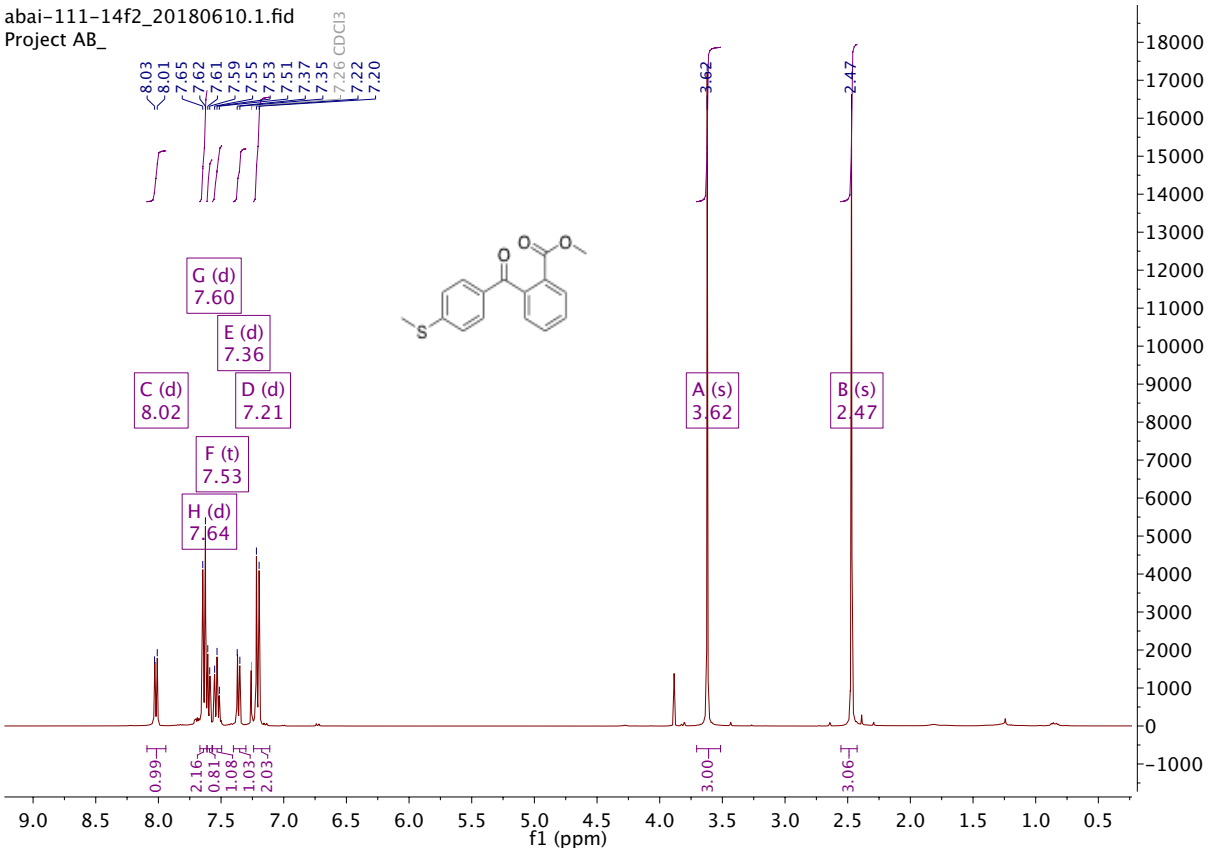
Methyl 2-(2-methoxybenzoyl)benzoate ***2ac***

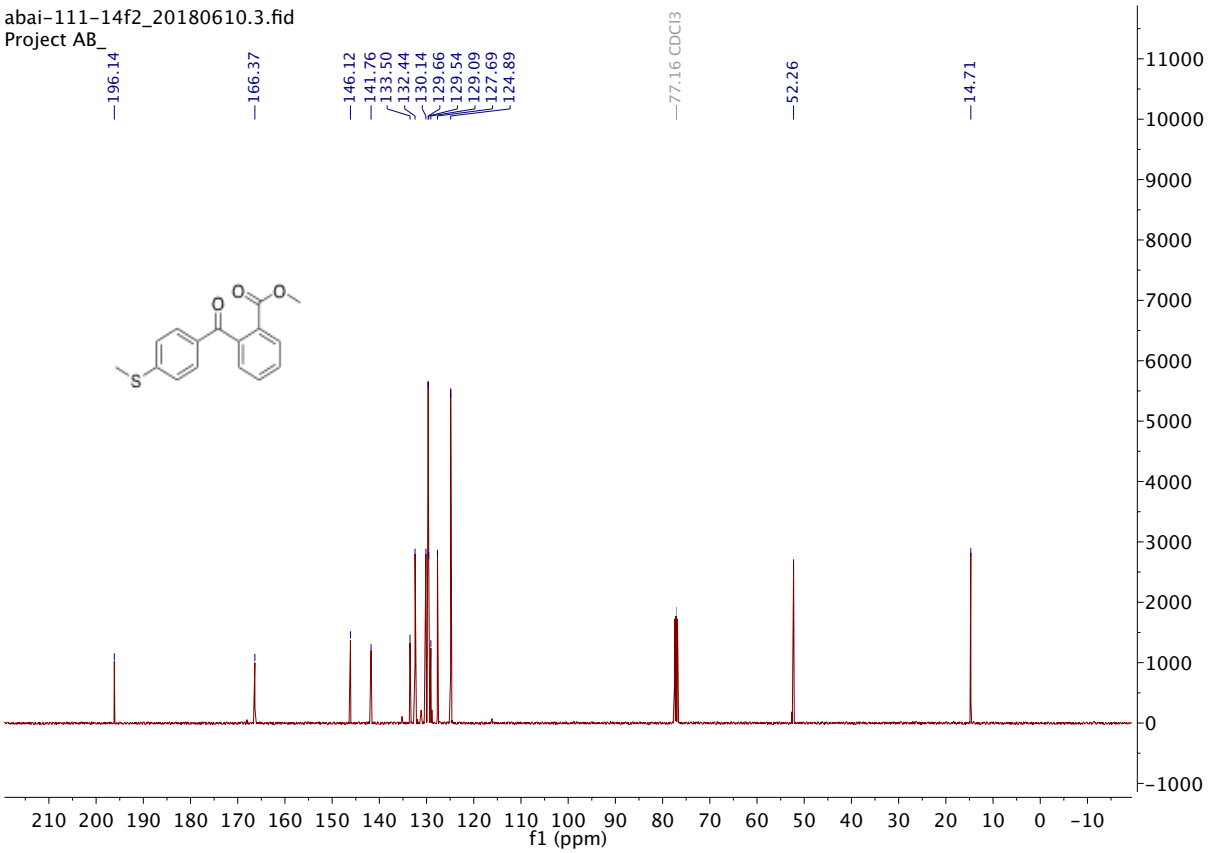


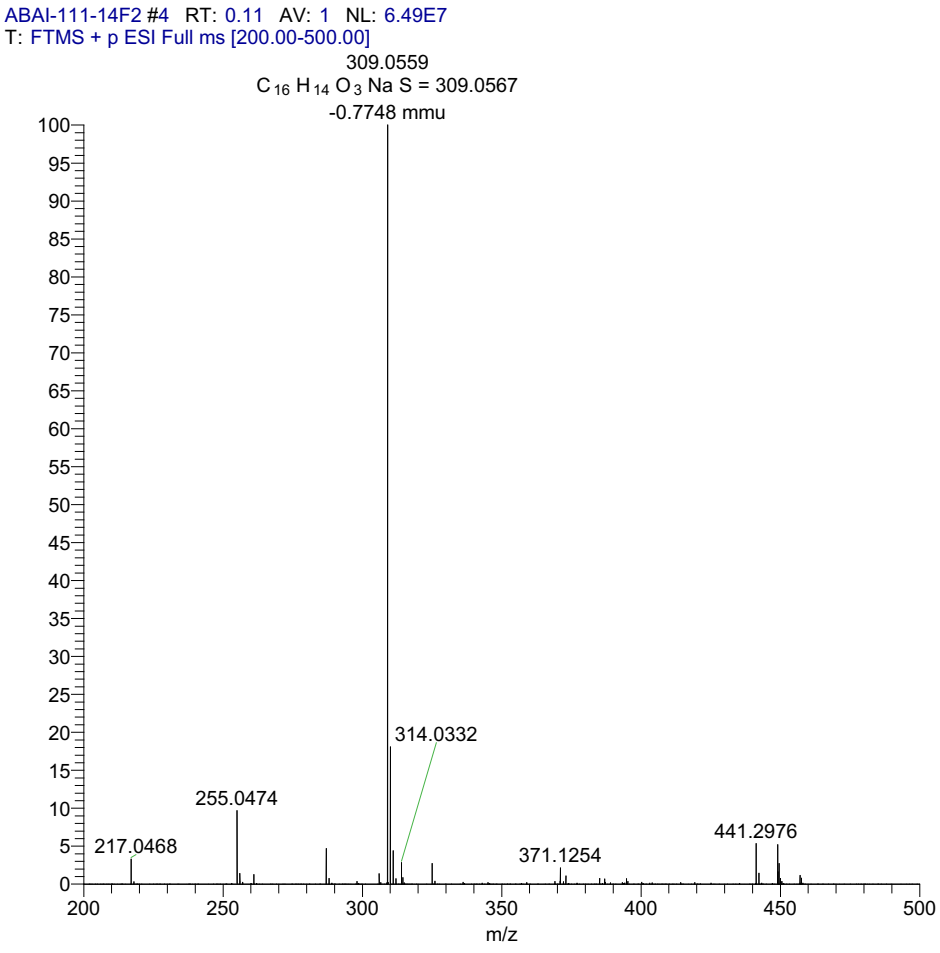




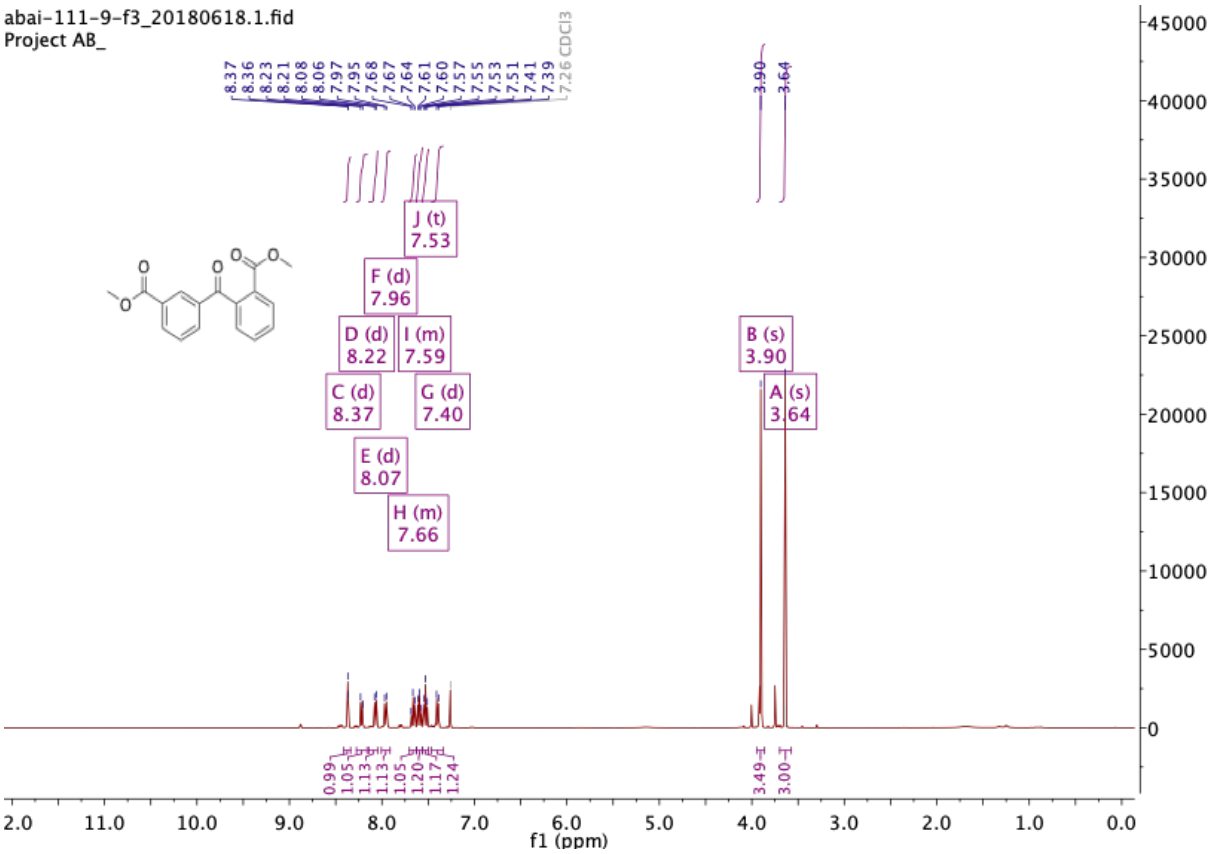
Methyl 2-(4-(methylthio)benzoyl) benzoate ***2ad***

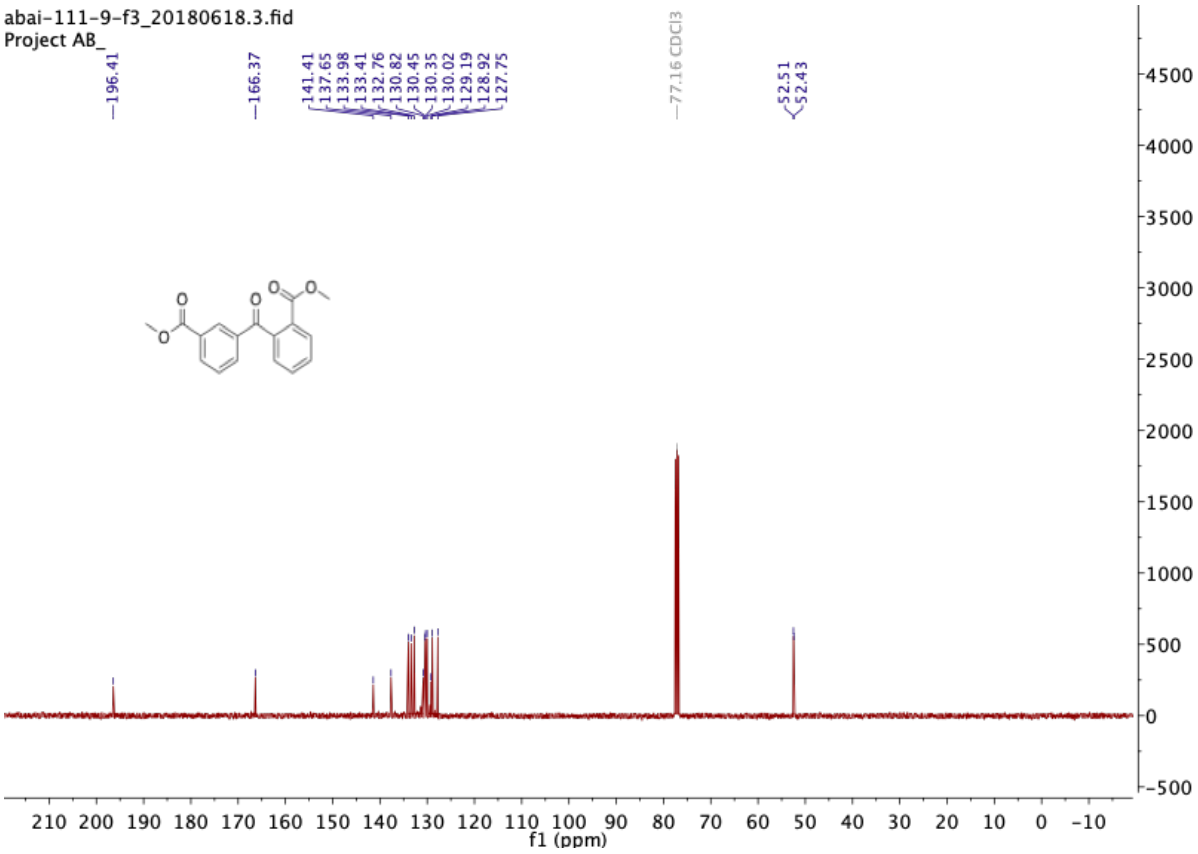


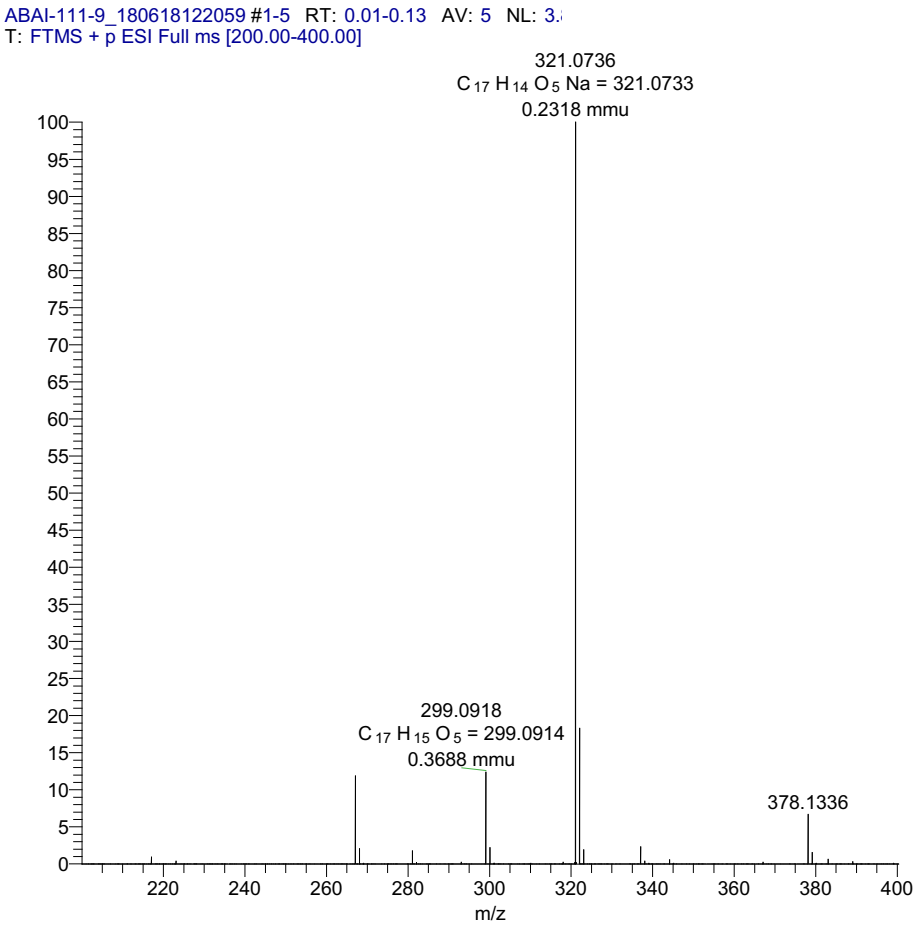

abai-111-14f2_20180610.3.fid
Project AB_
196.14
166.37
146.12
141.76
133.50
132.44
130.14
129.66
129.54
129.09
127.69
124.89
77.16 CDCl3
52.26
14.71
O
O
O
S
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ABAI-111-14F2 #4 RT: 0.11 AV: 1 NL: 6.49E7
T: FTMS + p ESI Full ms [200.00-500.00]
309.0559
C16 H14 O3 Na S = 309.0567
-0.7748 mmu
314.0332
255.0474
217.0468
371.1254
441.2976
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
200
250
300
350
400
450
500
m/z

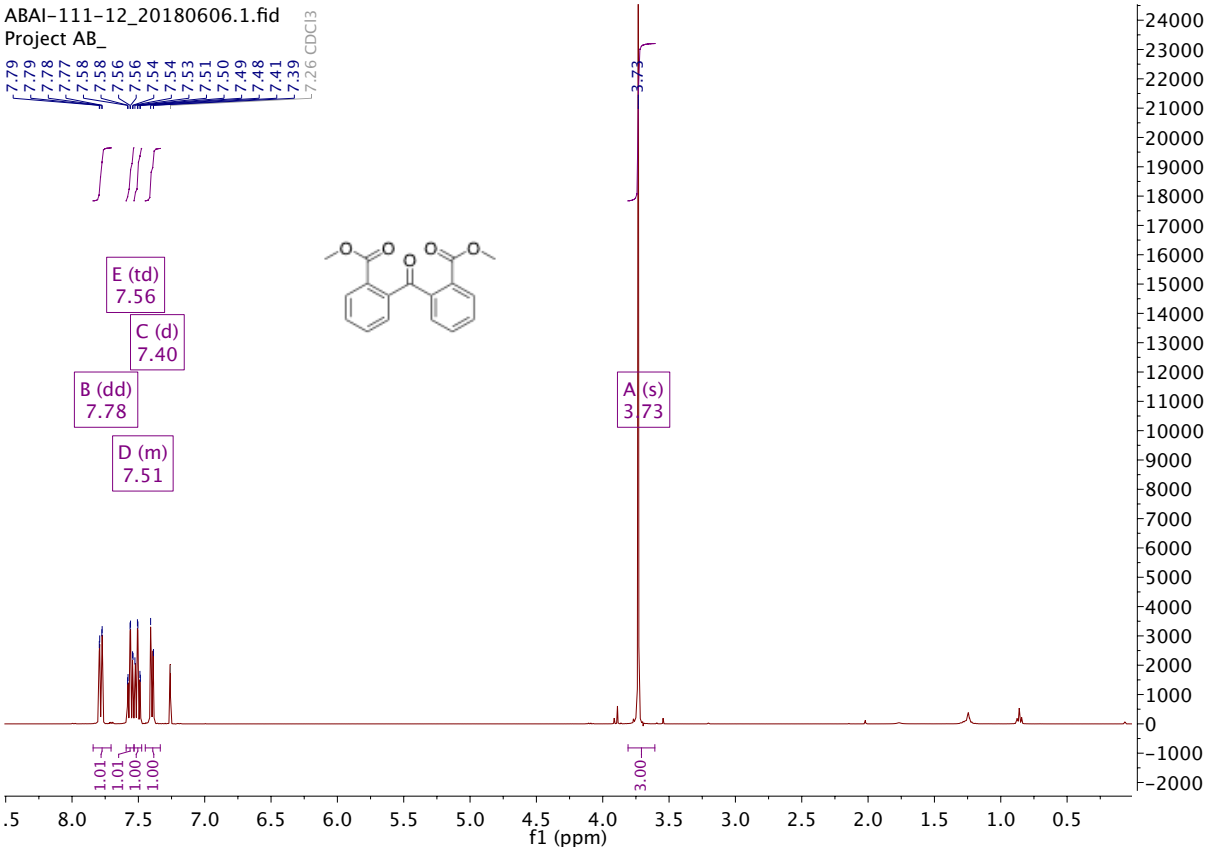
Methyl 2-(3-(methoxycarbonyl)benzoyl)benzoate ***2ag***

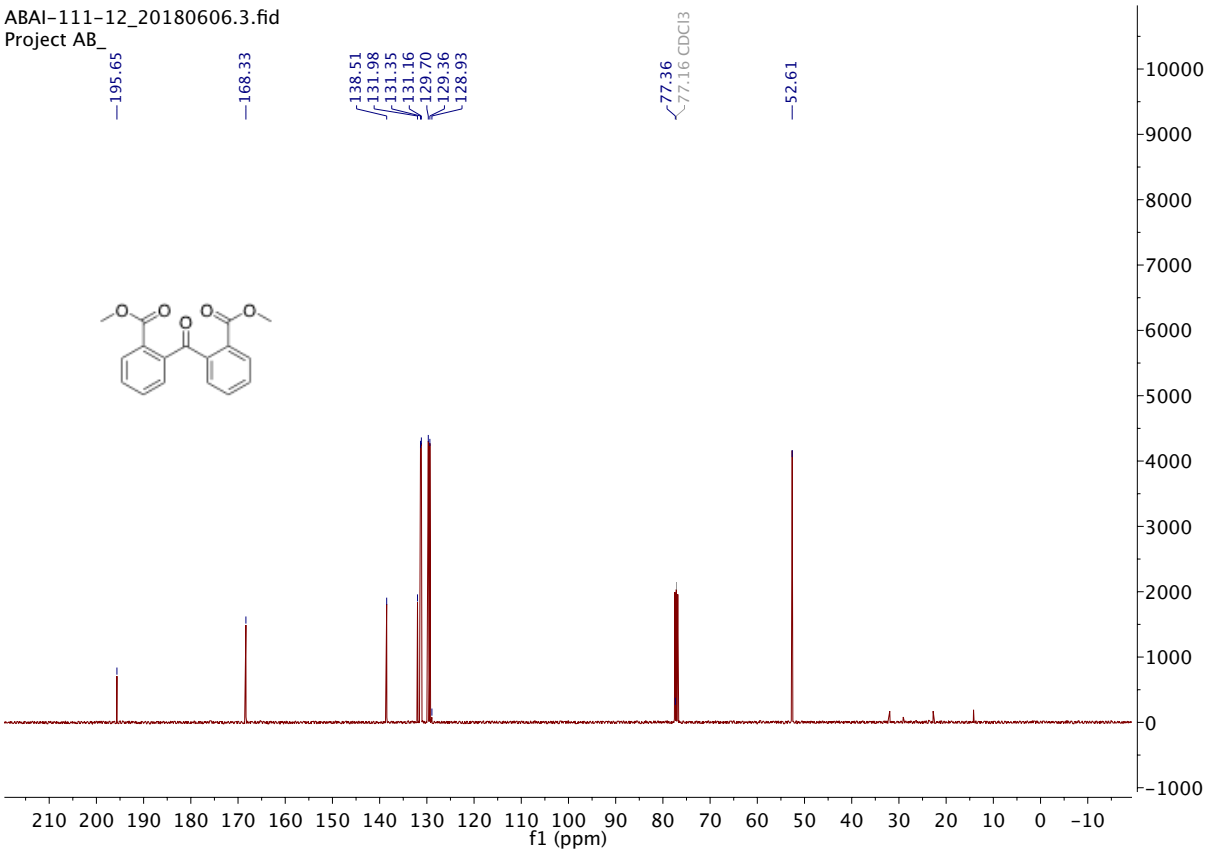




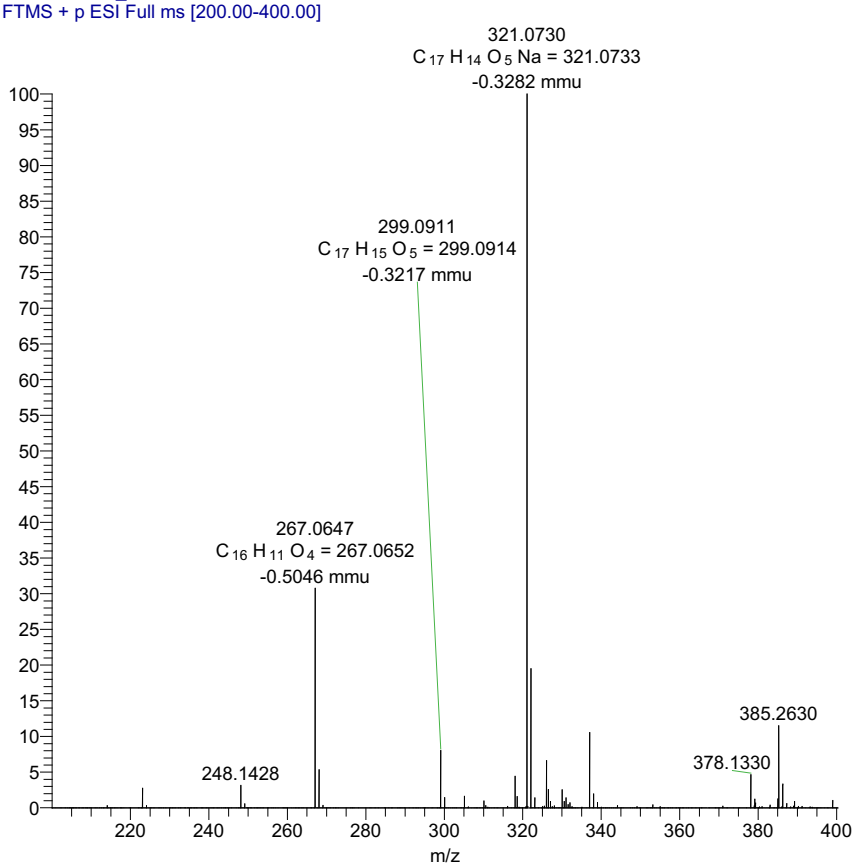


Dimethyl 2,2'-carbonyldibenzoate ***2ah***

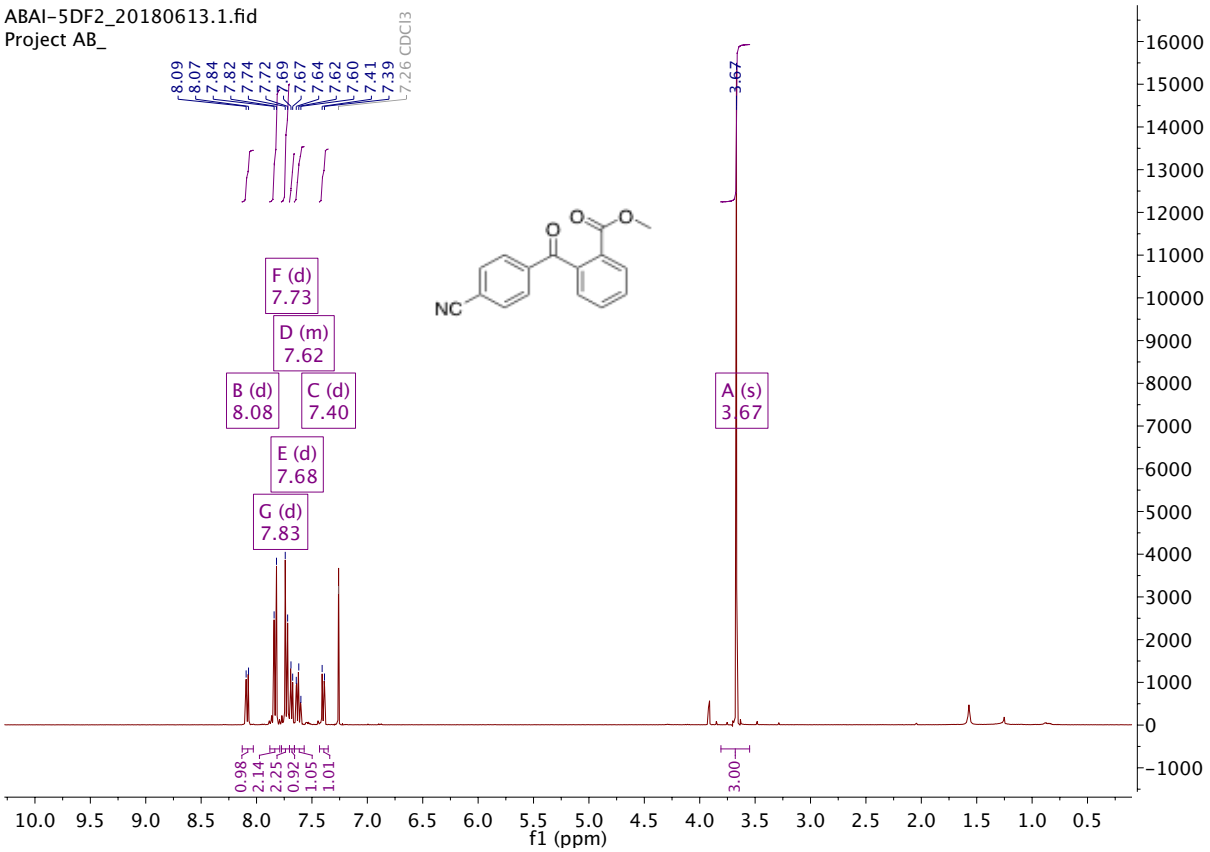


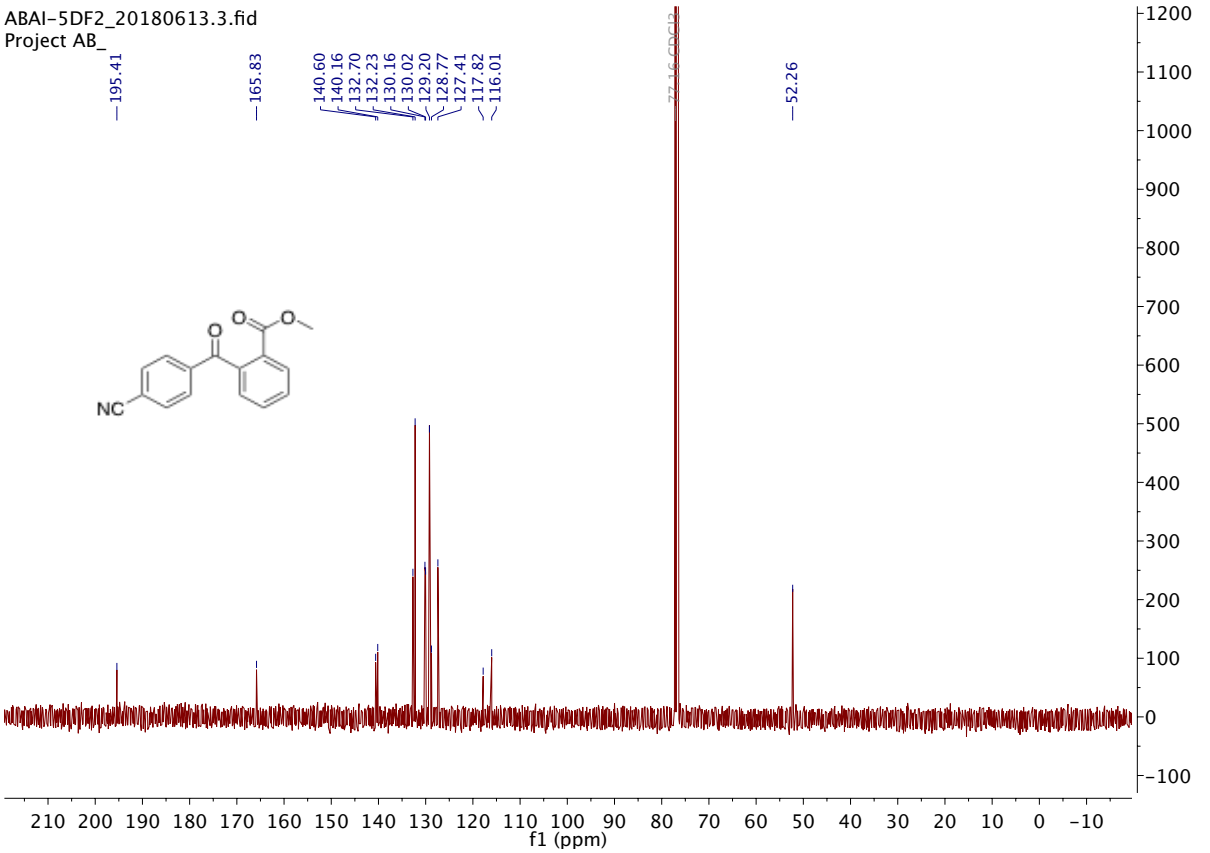


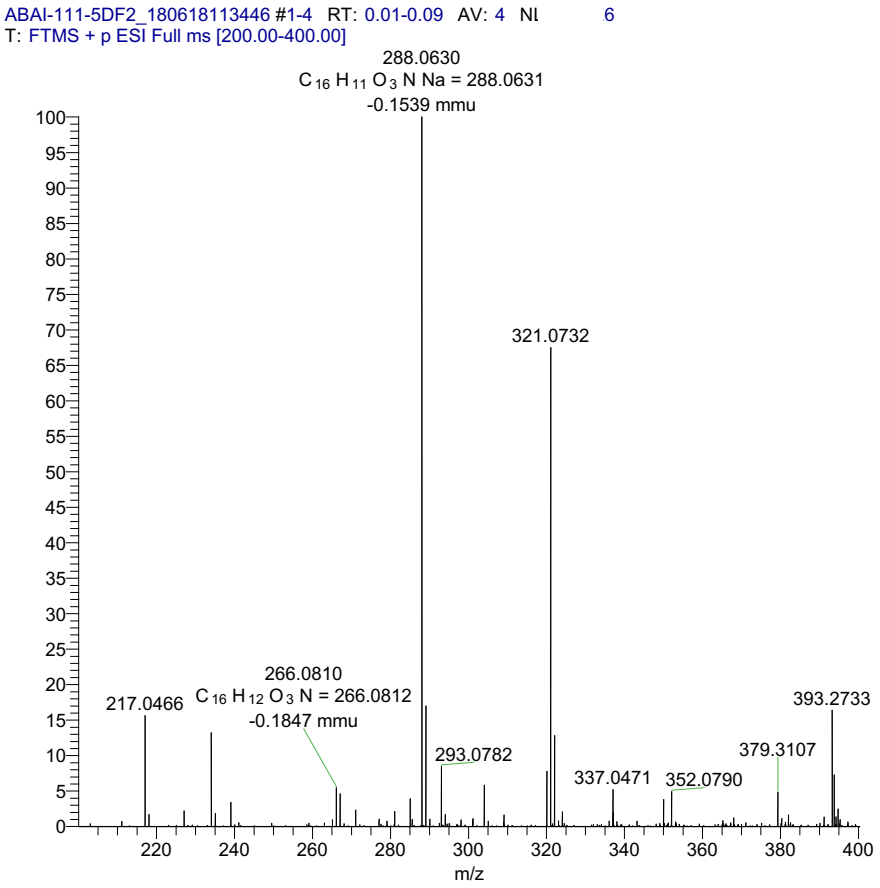
ABAI-111-7D-F2_180618115027 #1-4 RT: 0.02-0.11 AV: 4 N E7
T: FTMS + p ESI Full ms [200.00-400.00]



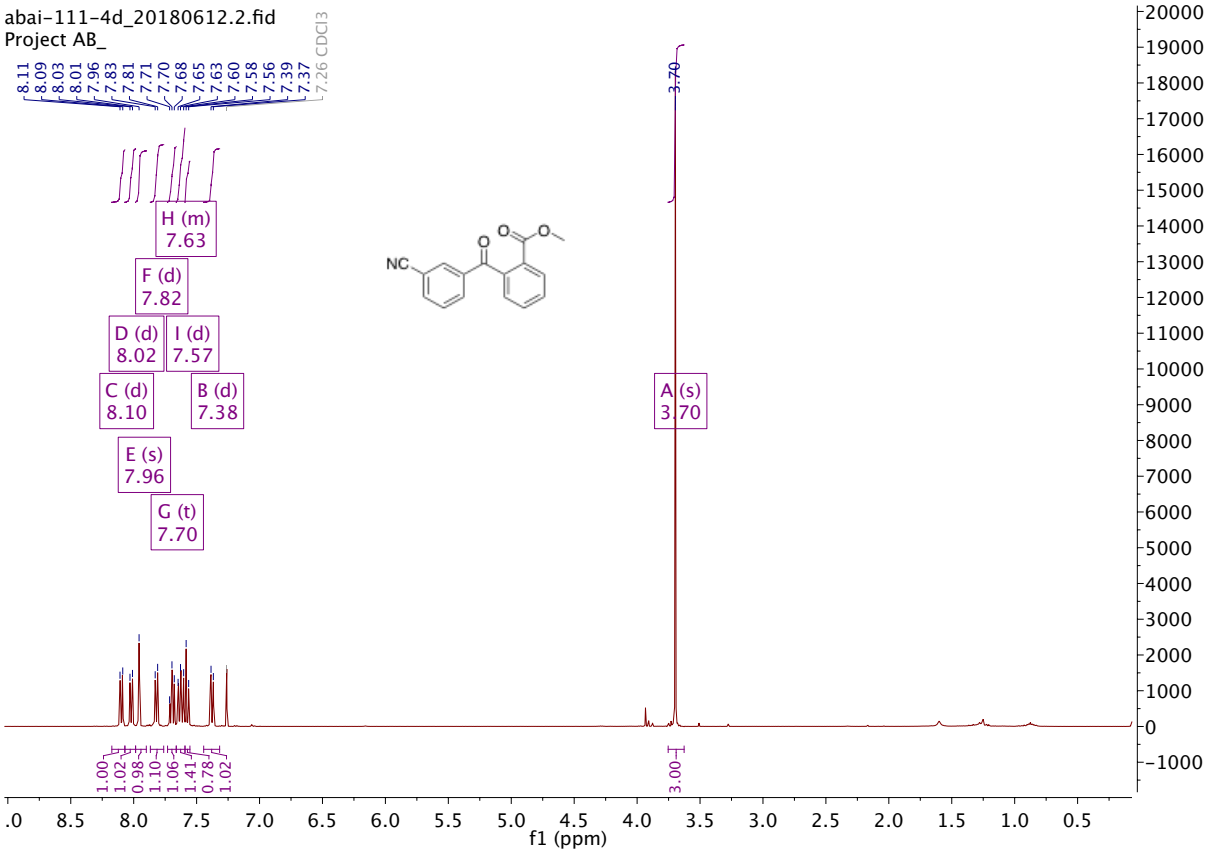
Methyl 2-(4-cyanobenzoyl) benzoate ***2ai***



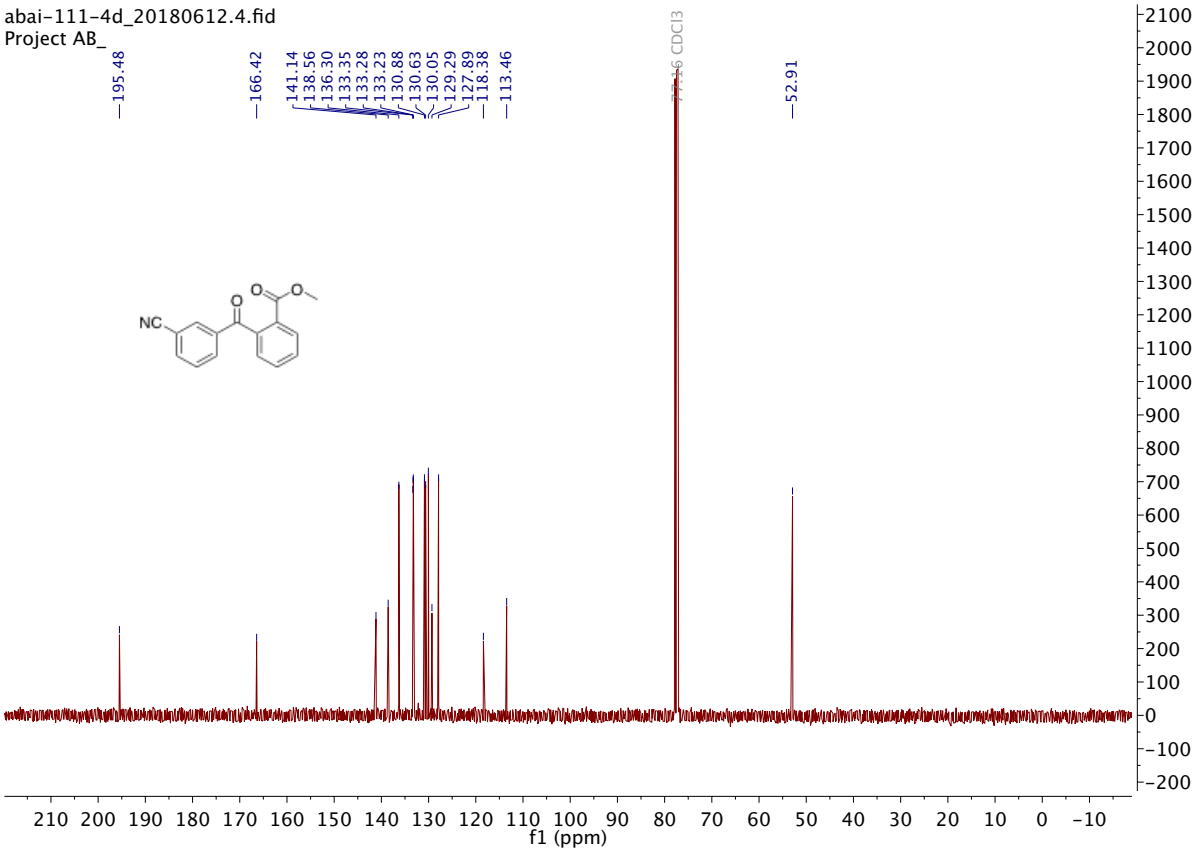


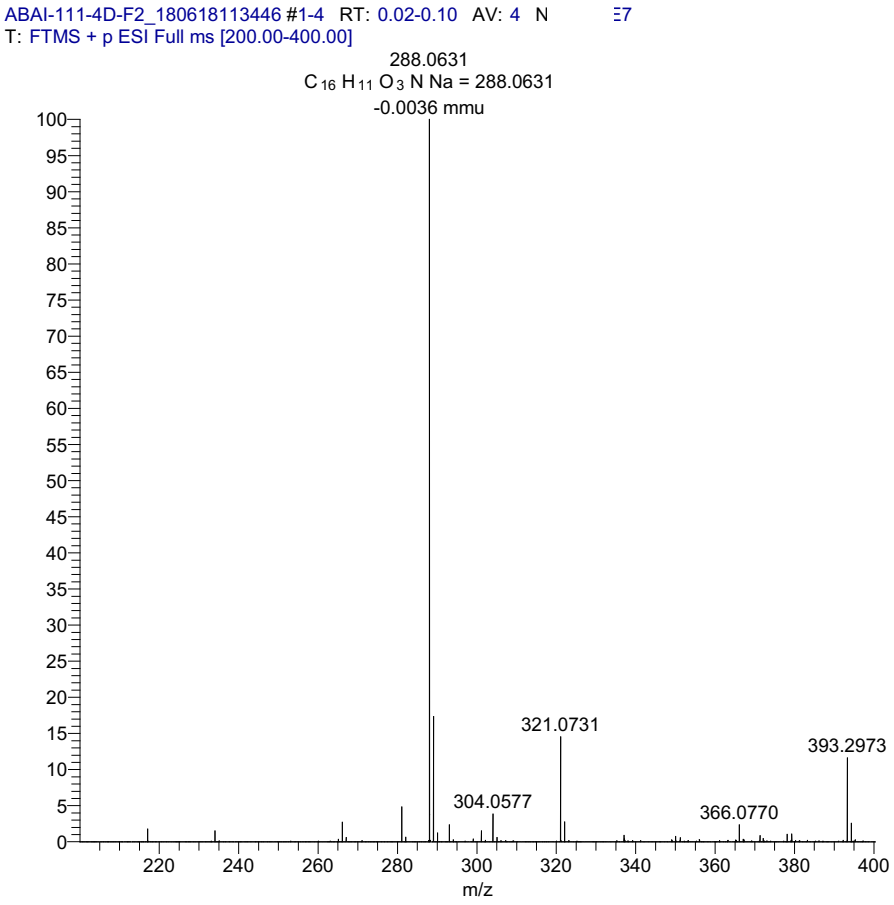


Methyl 2-(3-cyanobenzoyl) benzoate ***2aj***

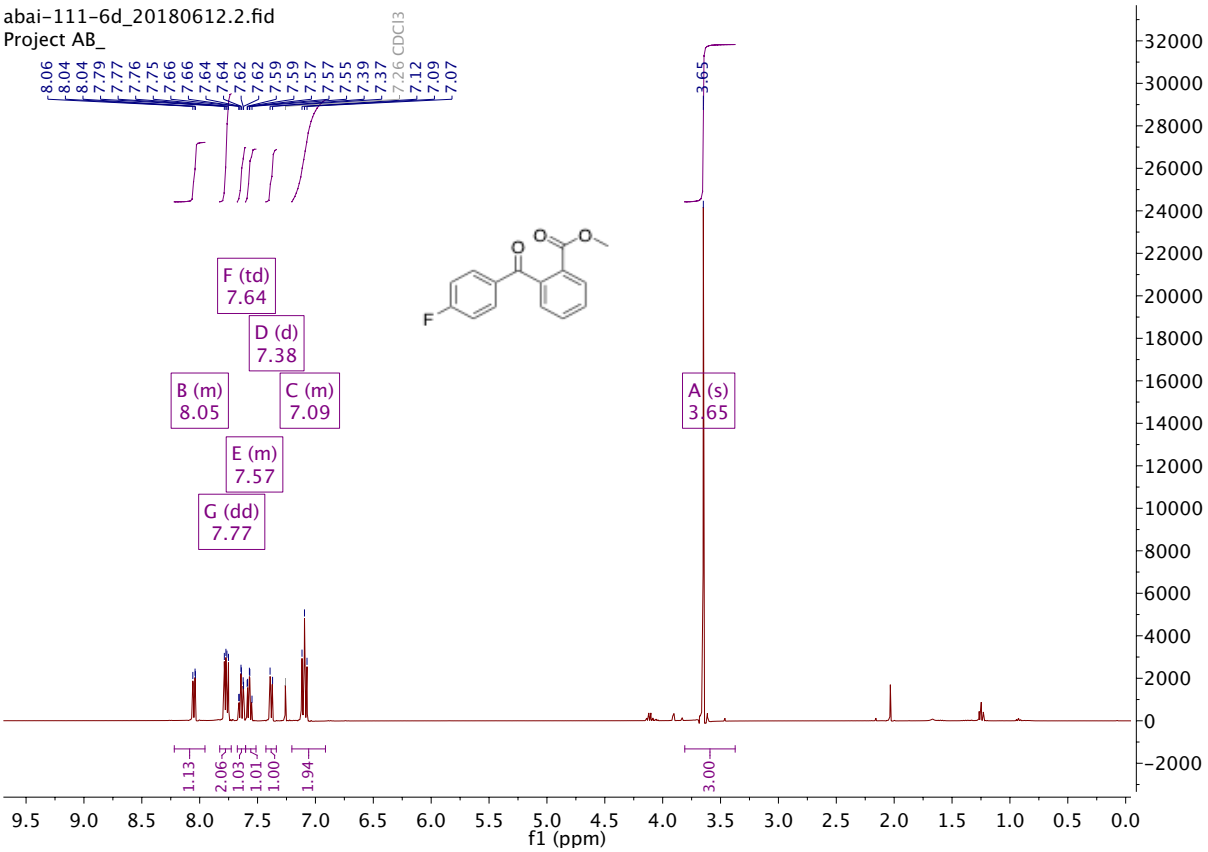


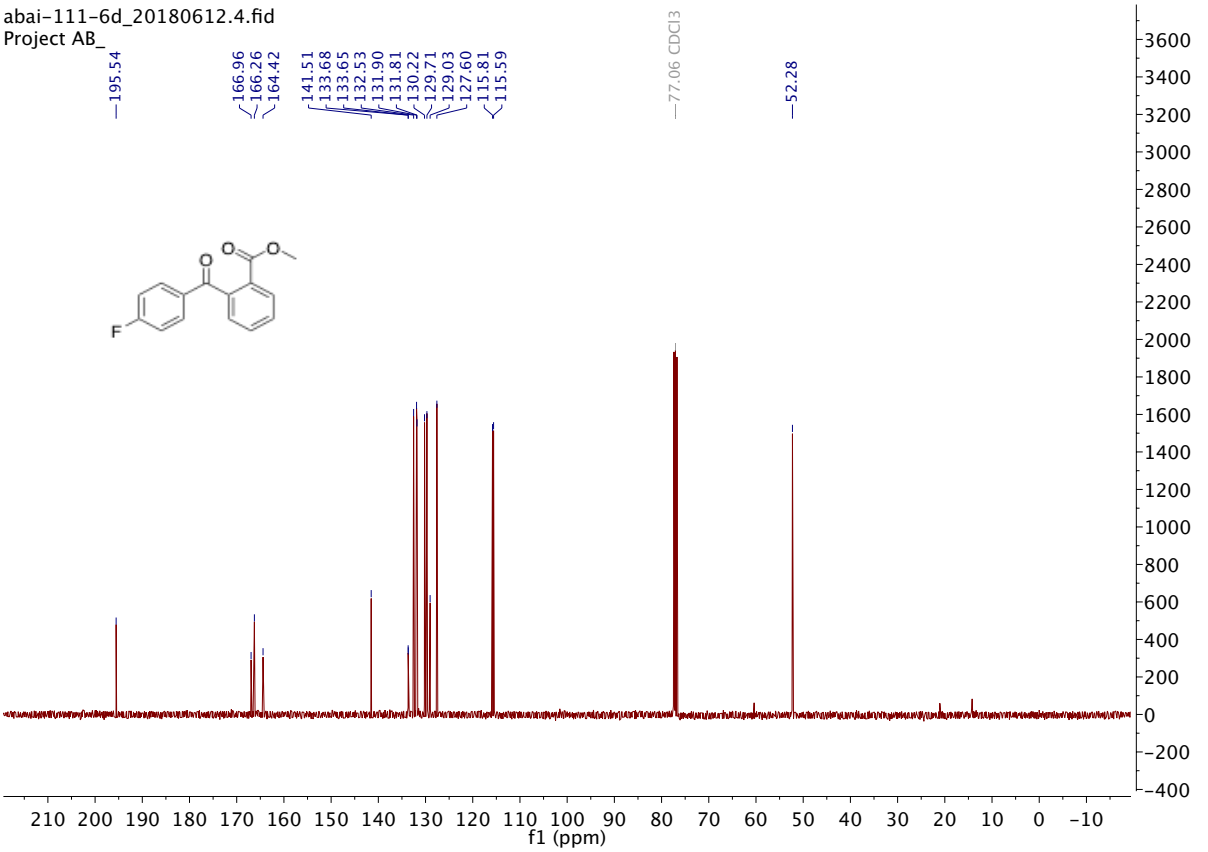
ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.

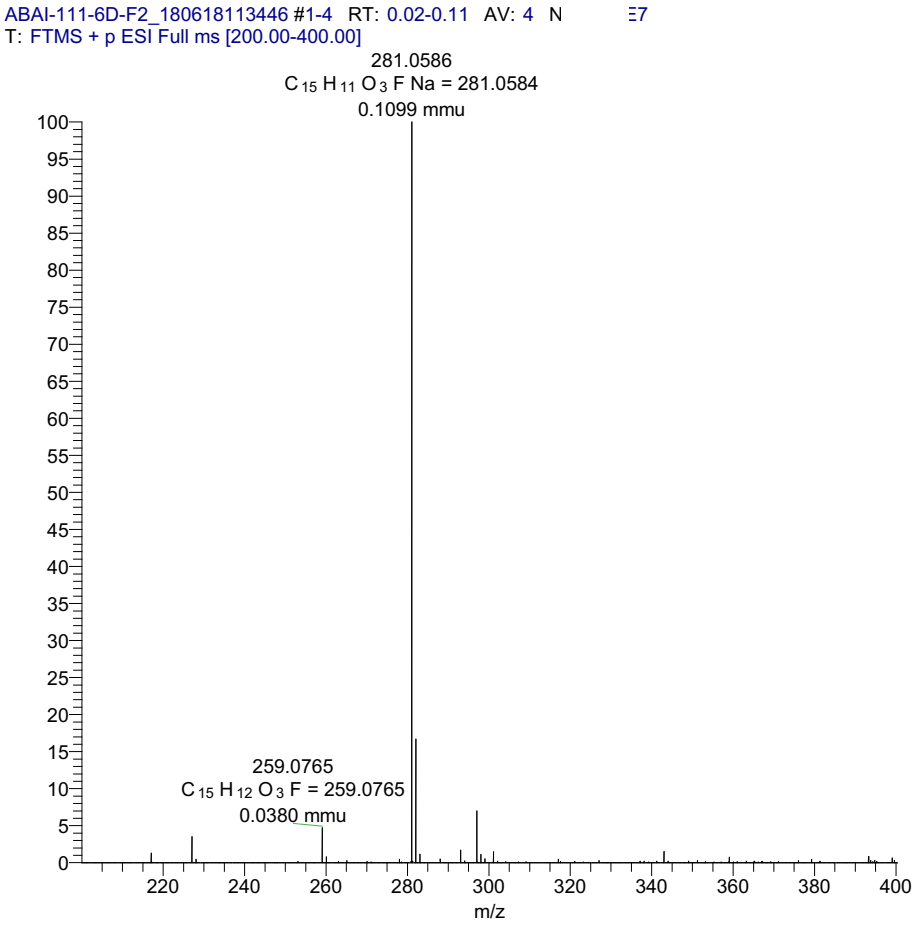




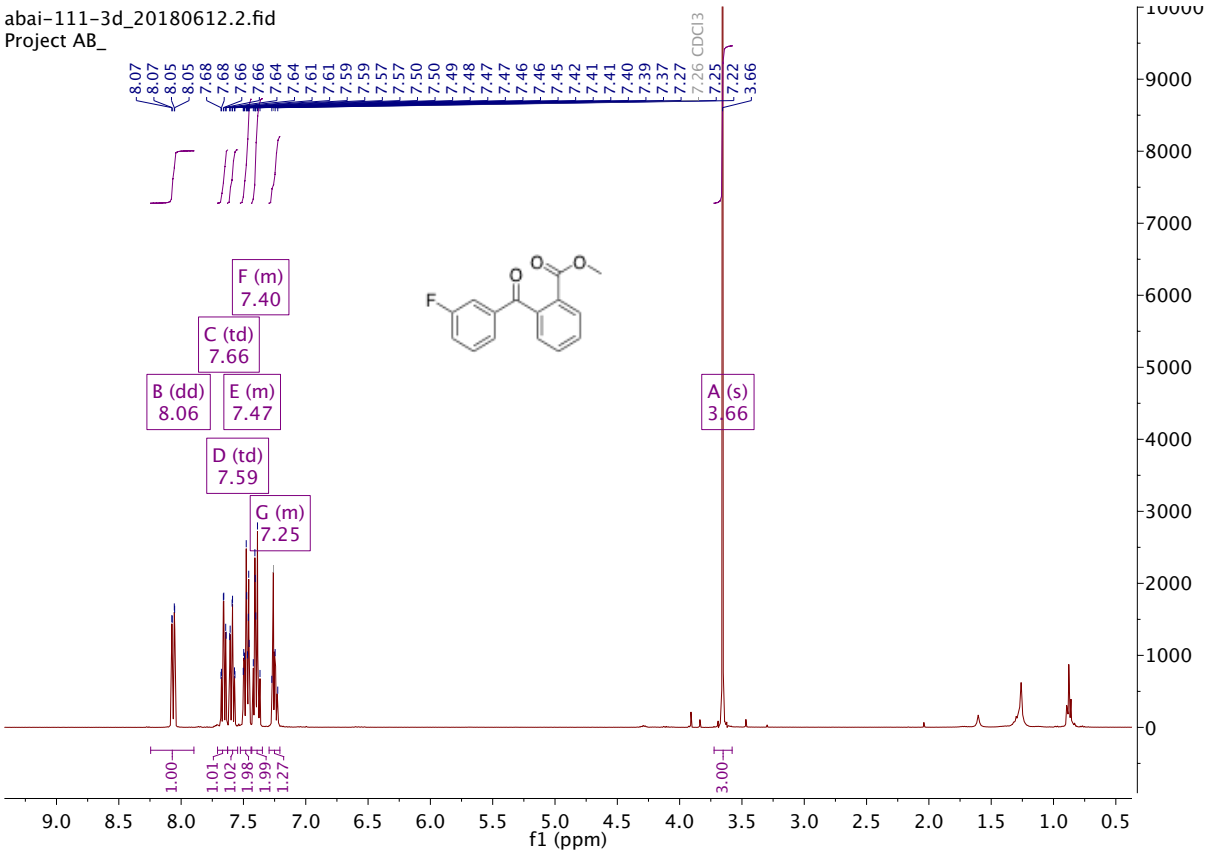
Methyl 2-(4-fluorobenzoyl) benzoate ***2ak***

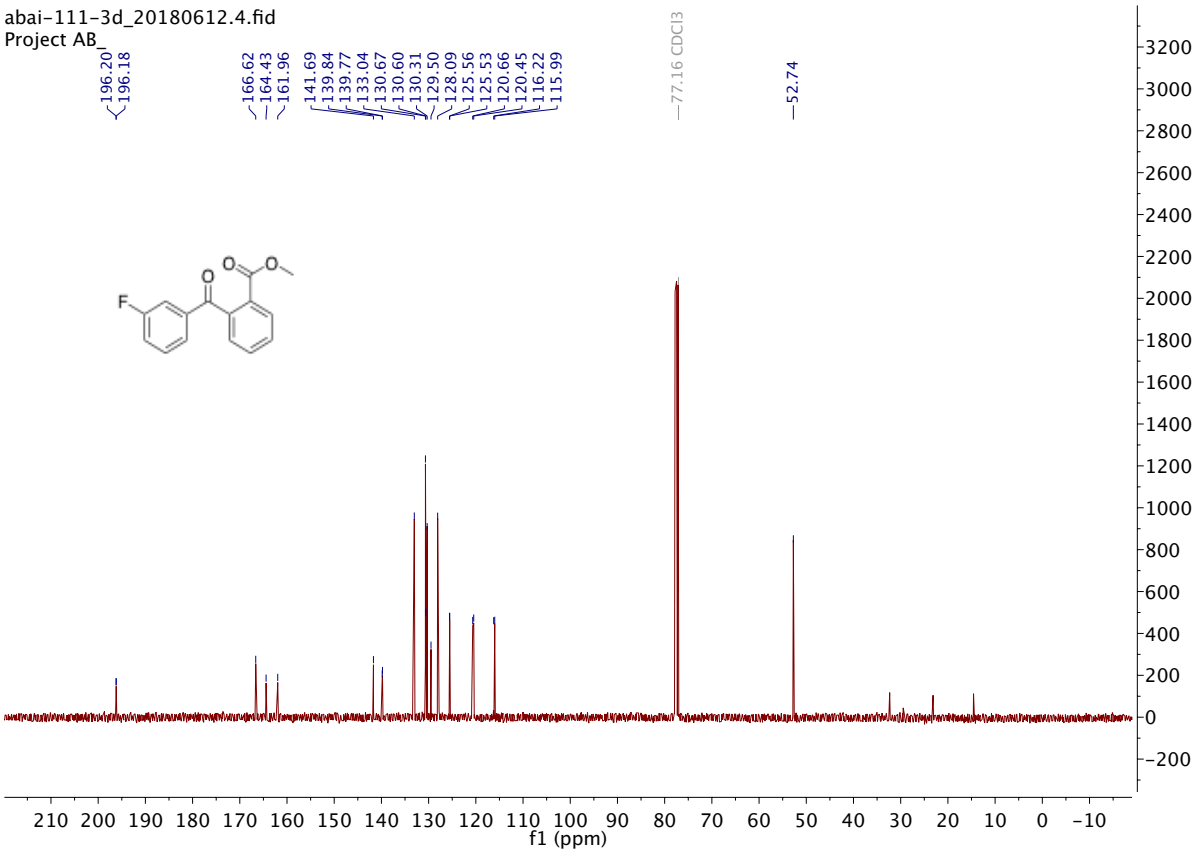


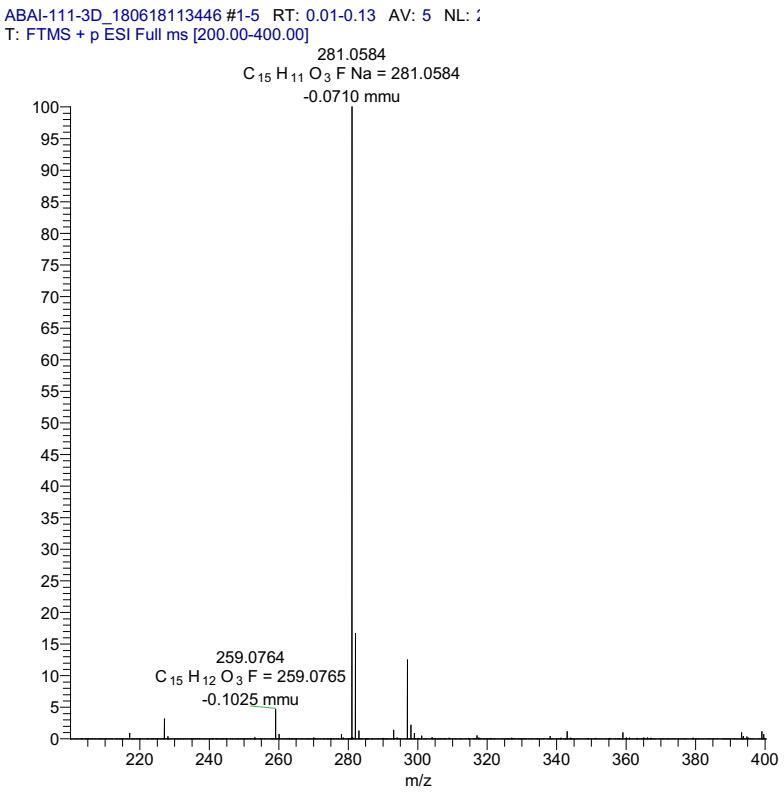




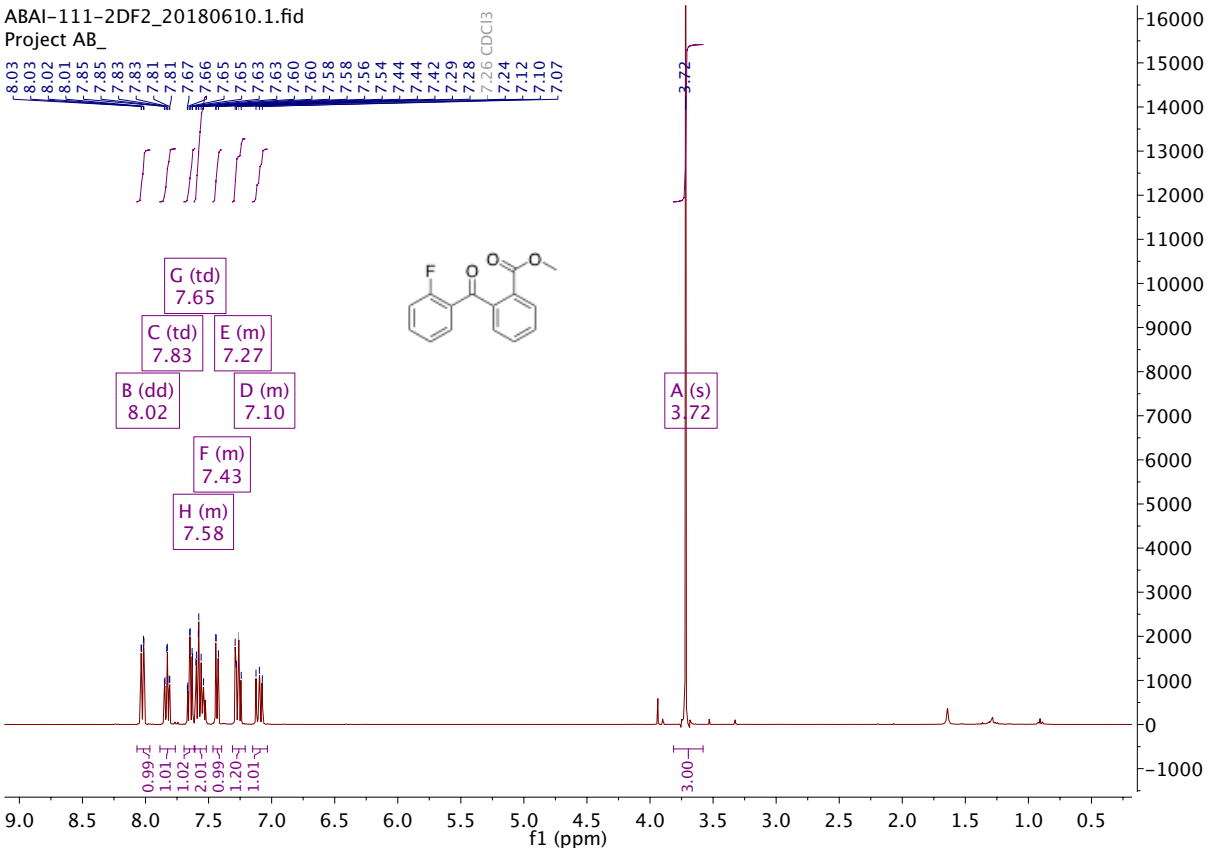
Methyl 2-(3-fluorobenzoyl) benzoate ***2al***

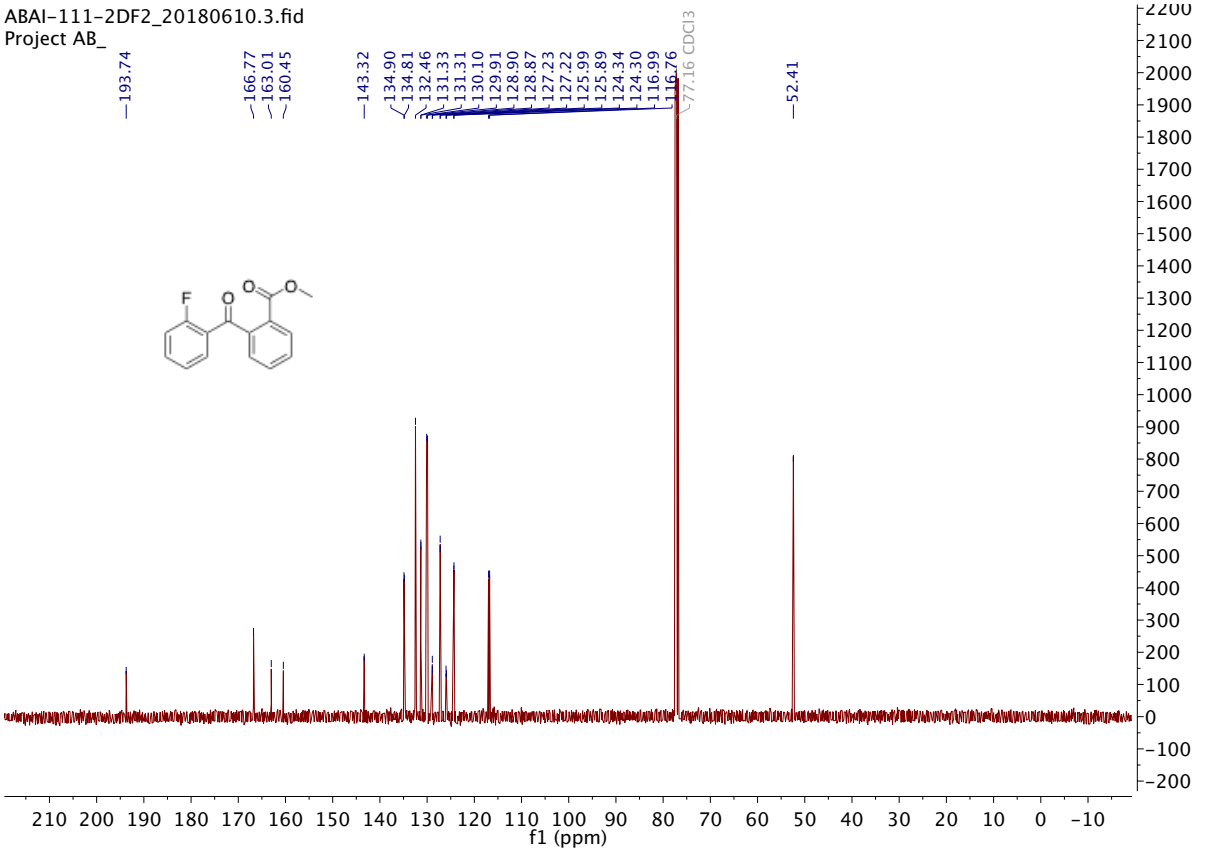


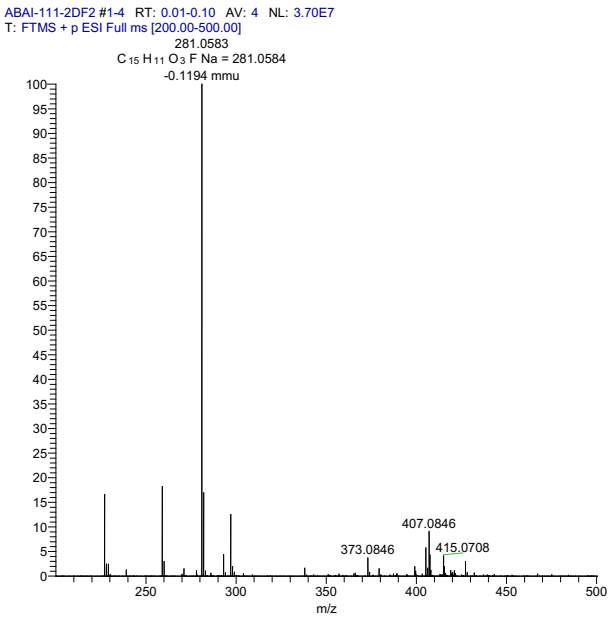

abai-111-3d_20180612.4.fid
Project AB_
196.20
196.18
166.62
164.43
161.96
141.69
139.84
139.77
133.04
130.67
130.60
130.31
129.50
128.09
125.56
125.53
120.66
120.45
116.22
115.99
77.16 CDCl3
52.74
F
O
O
O
f1 (ppm)


ABAI-111-3D_180618113446 #1-5 RT: 0.01-0.13 AV: 5 NL:
T: FTMS + p ESI Full ms [200.00-400.00]
281.0584
C15 H11 O3 F Na = 281.0584
-0.0710 mmu
259.0764
C15 H12 O3 F = 259.0765
-0.1025 mmu
m/z

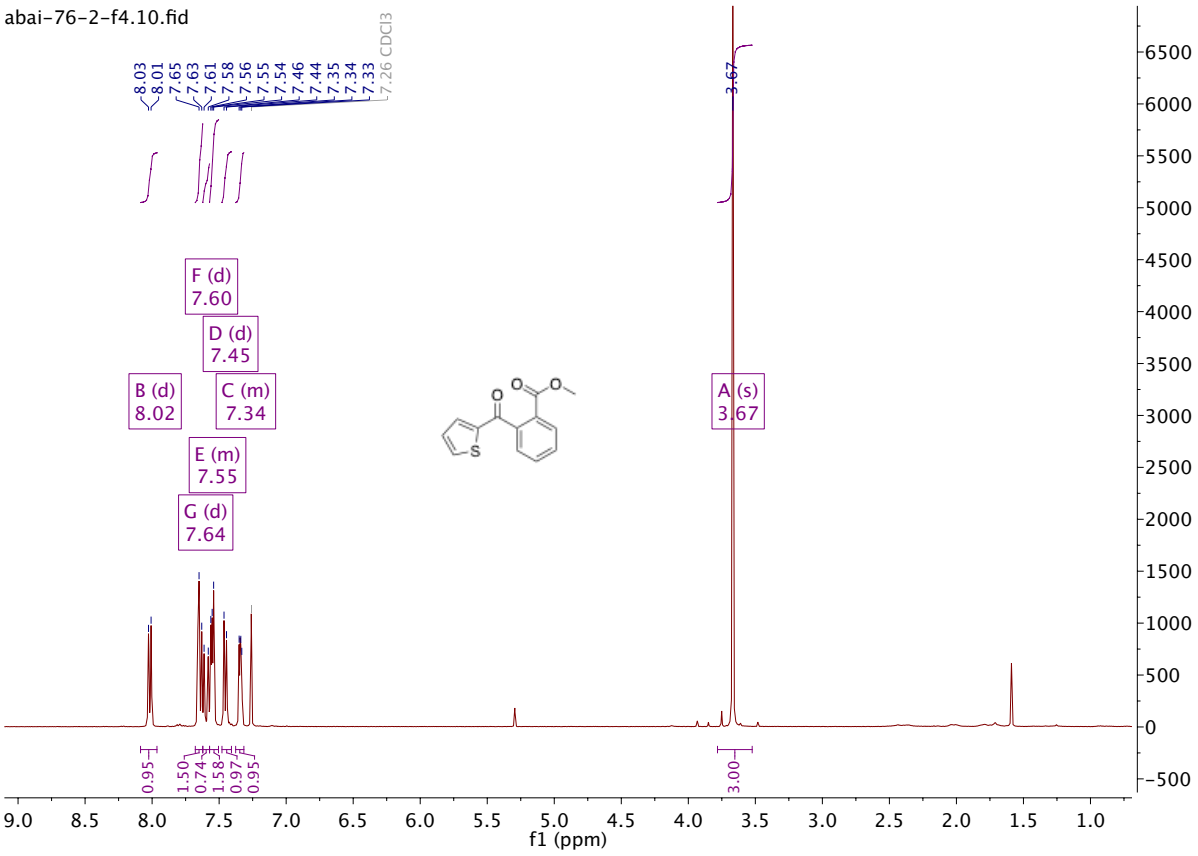
Methyl 2-(2-fluorobenzoyl) benzoate ***2am***

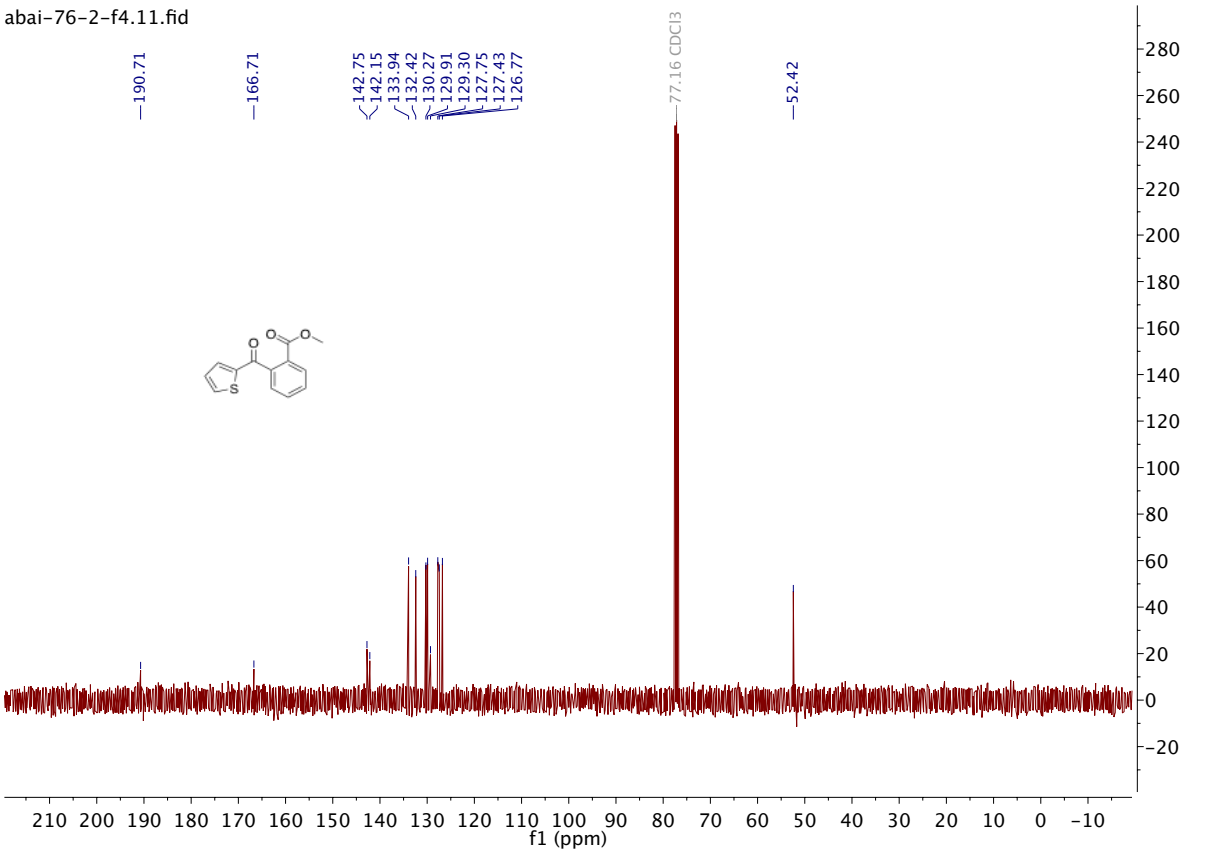




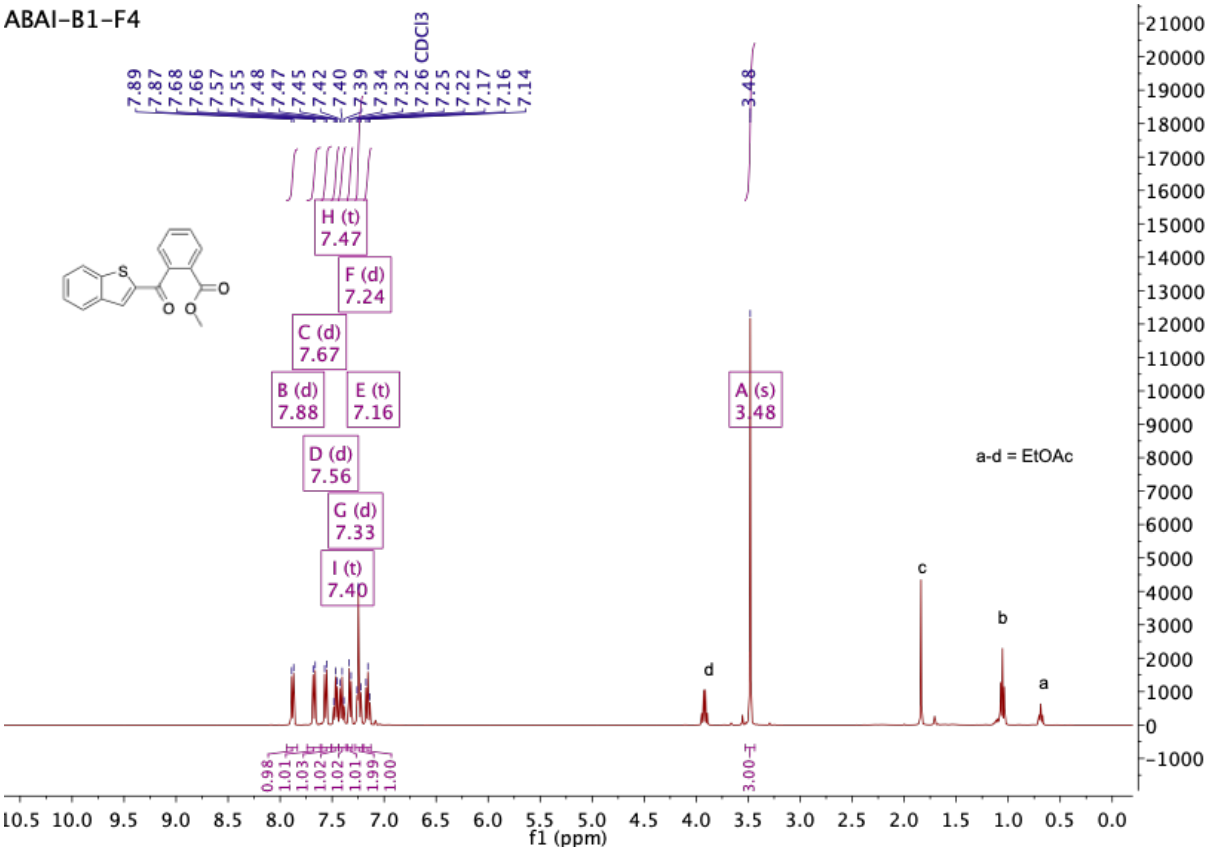


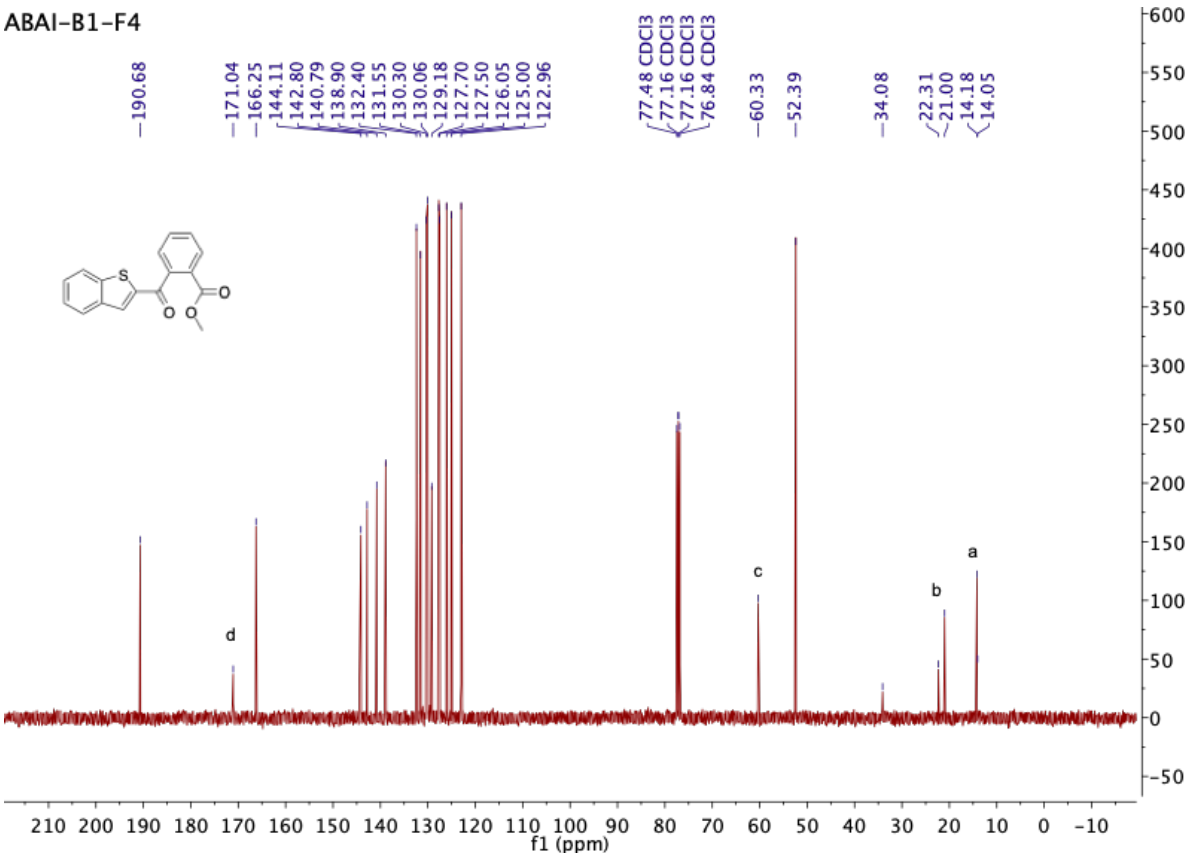
Methyl 2-(thiophene-2-carbonyl) benzoate ***2an***



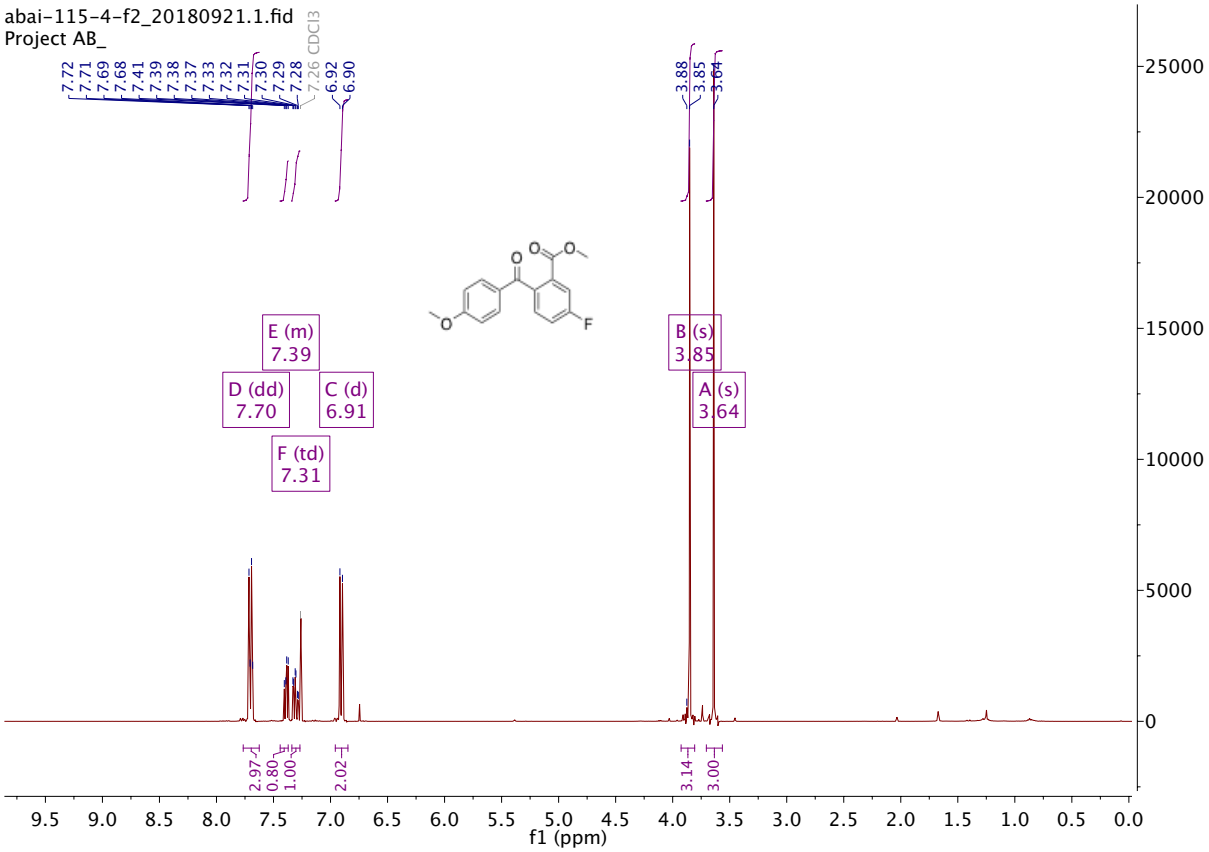


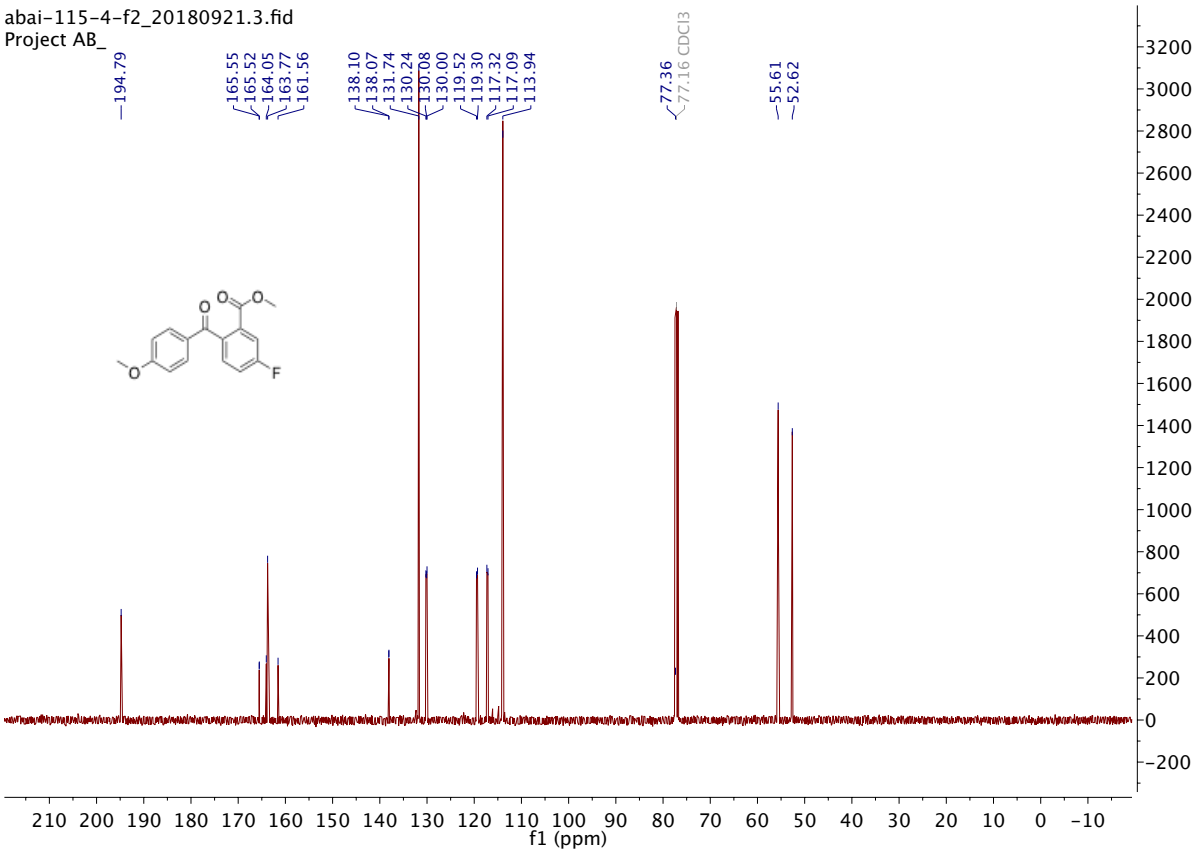
Methyl 2-(benzo[b]thiophene-2-carbonyl) benzoate ***2ao***

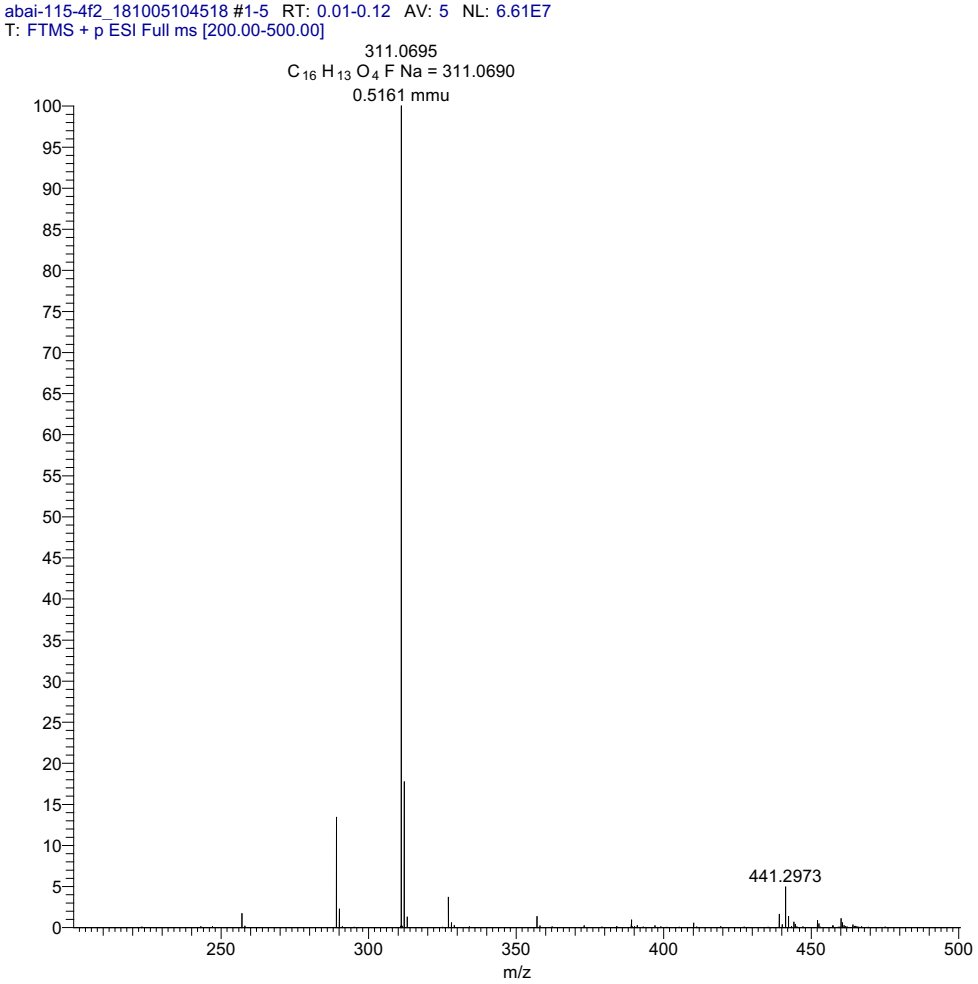




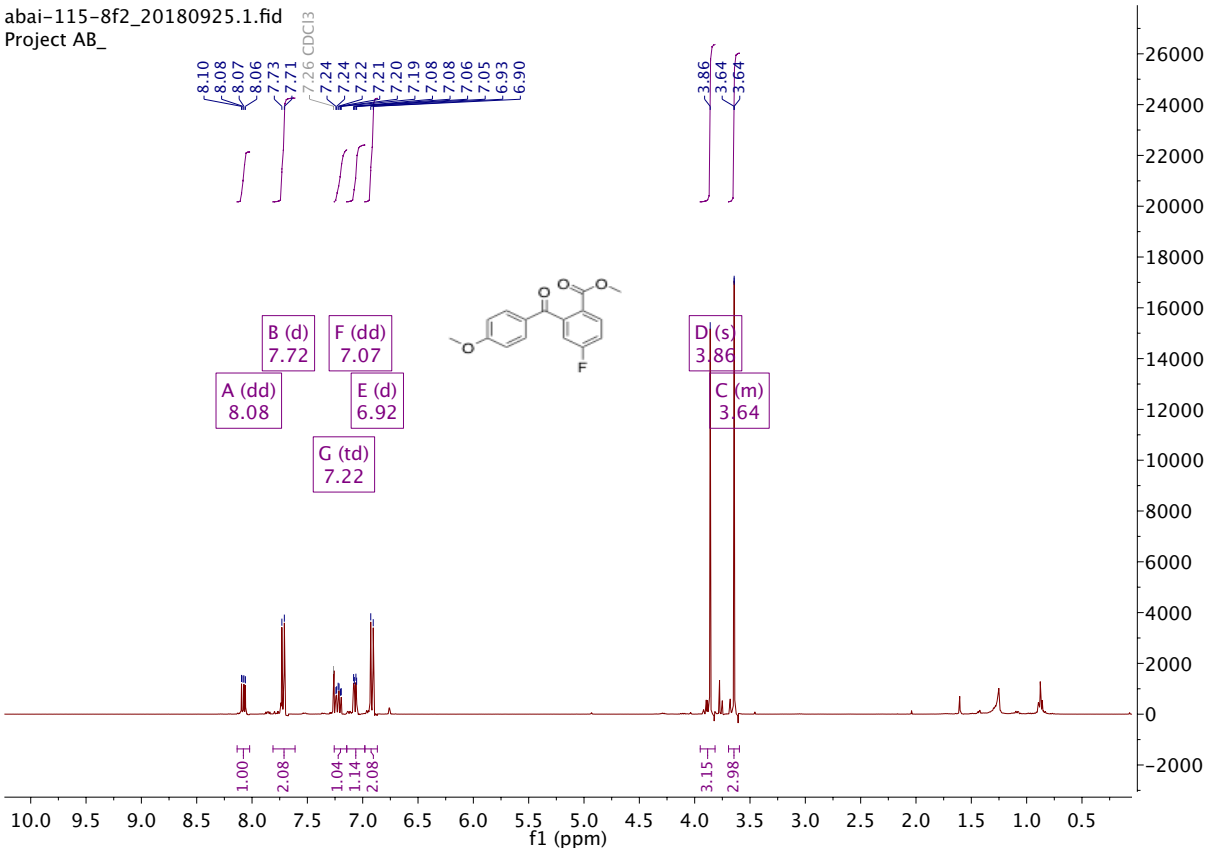
Methyl 5-fluoro-2-(4-methoxybenzoyl)benzoate ***2ba***

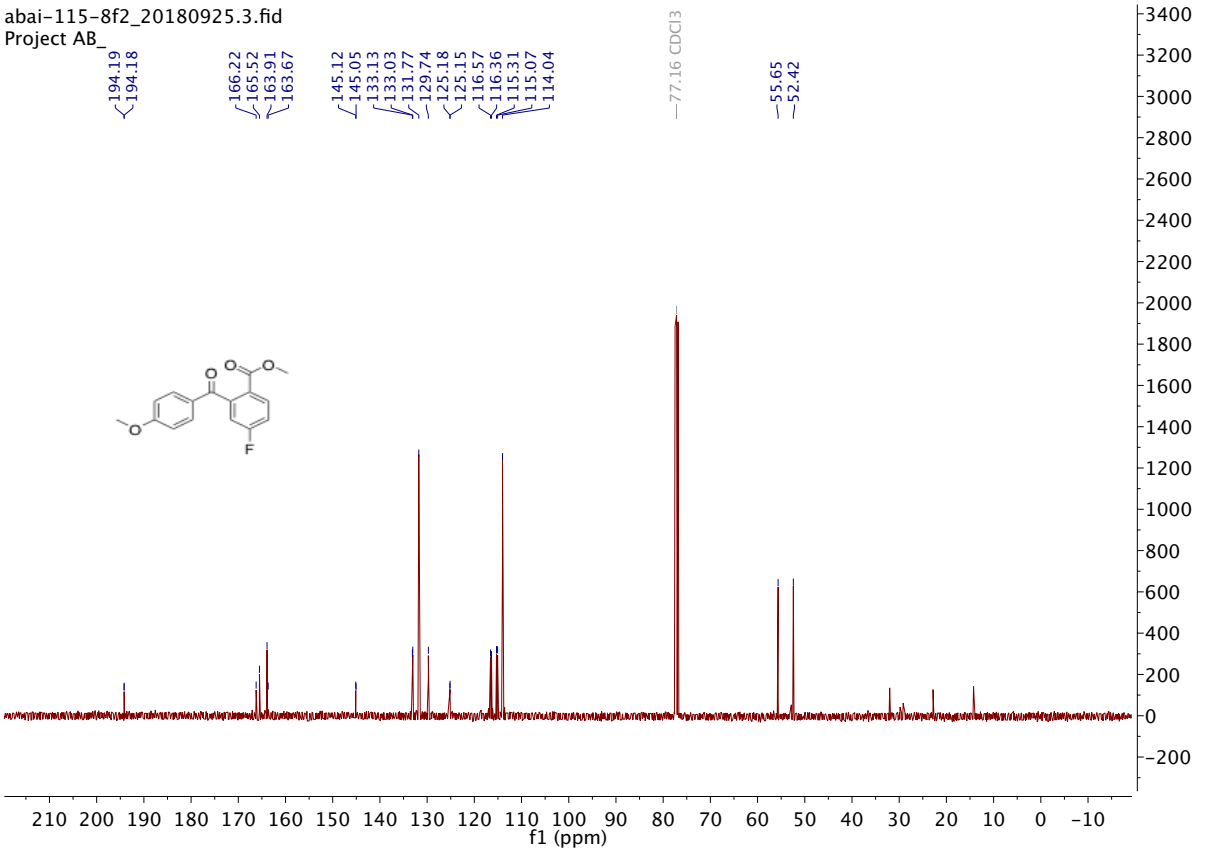



abai-115-4-f2_20180921.3.fid
Project AB_
194.79
165.55
165.52
164.05
163.77
161.56
138.10
138.07
131.74
130.24
130.08
130.00
119.52
119.30
117.32
117.09
113.94
77.36
77.16 CDCl3
55.61
52.62
f1 (ppm)

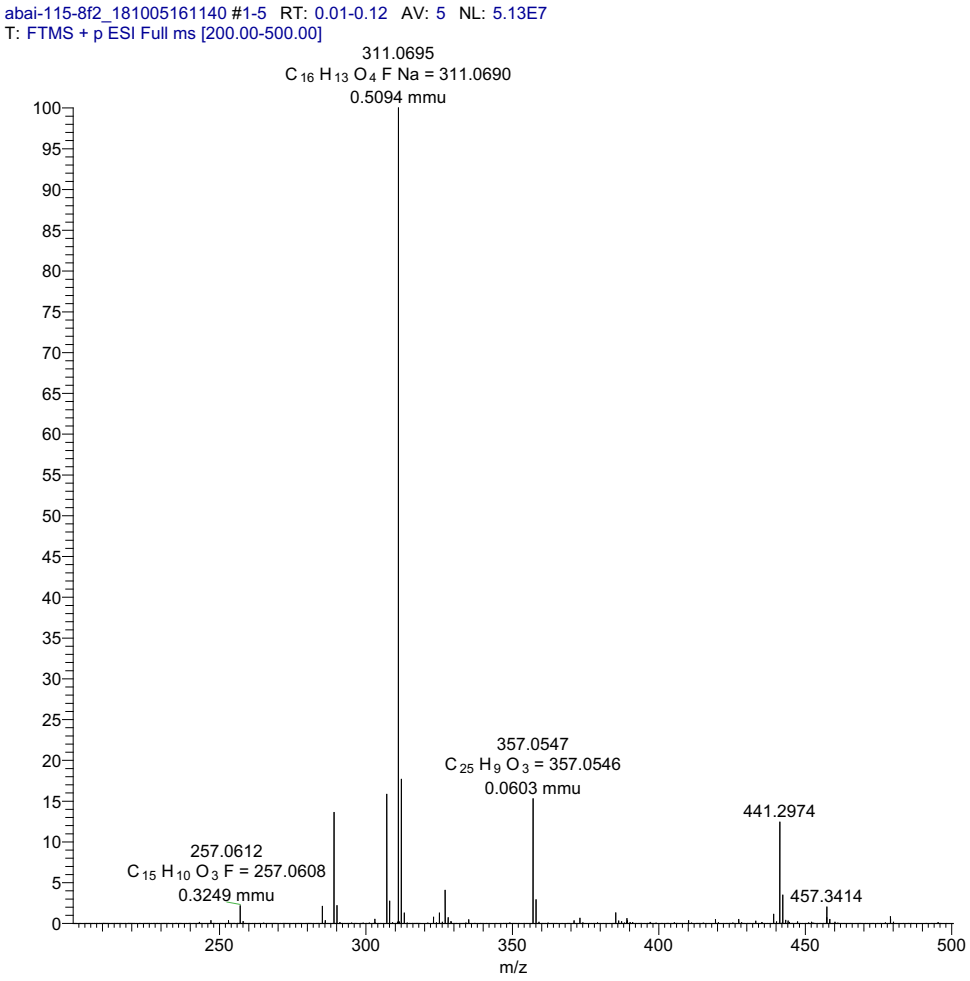

abai-115-4f2_181005104518 #1-5 RT: 0.01-0.12 AV: 5 NL: 6.61E7
T: FTMS + p ESI Full ms [200.00-500.00]
311.0695
C16 H13 O4 F Na = 311.0690
0.5161 mmu
441.2973
m/z

Methyl 4-fluoro-2-(4-methoxybenzoyl)benzoate ***2ca***

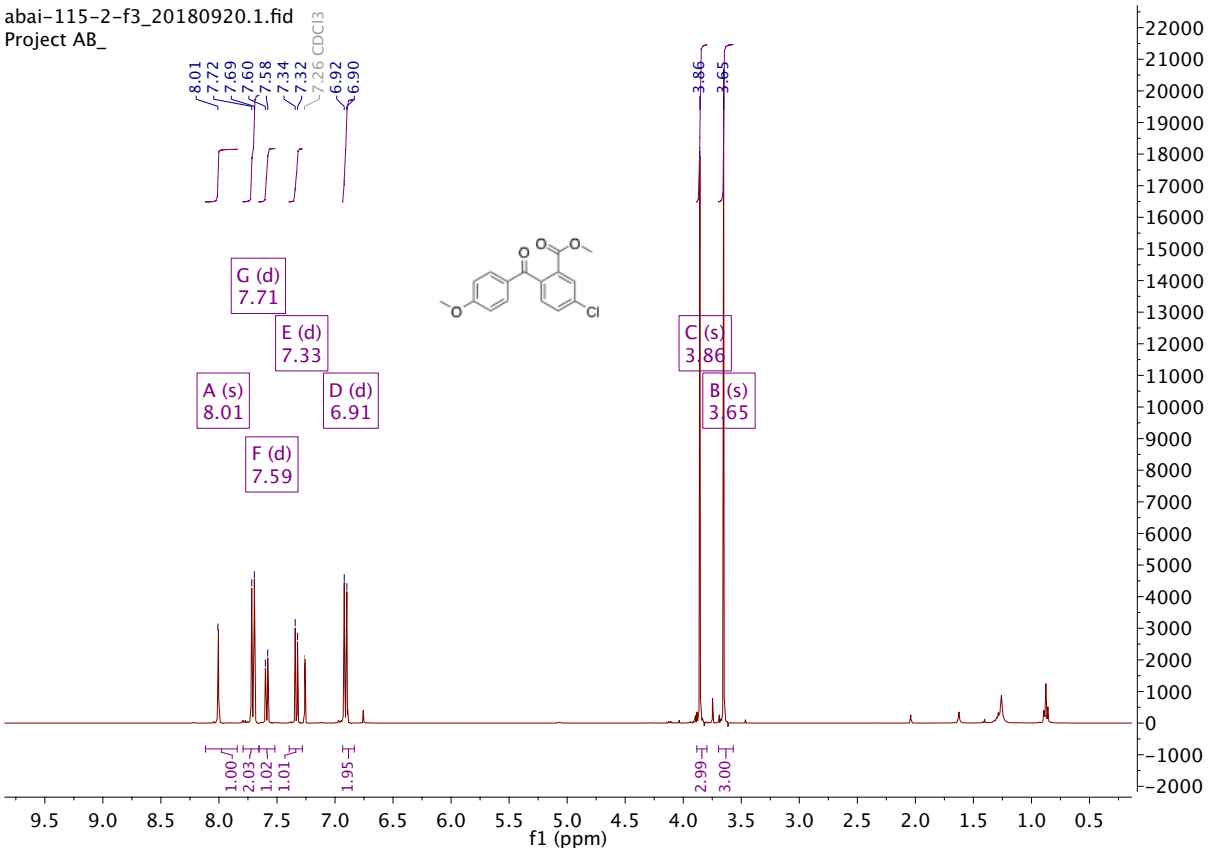


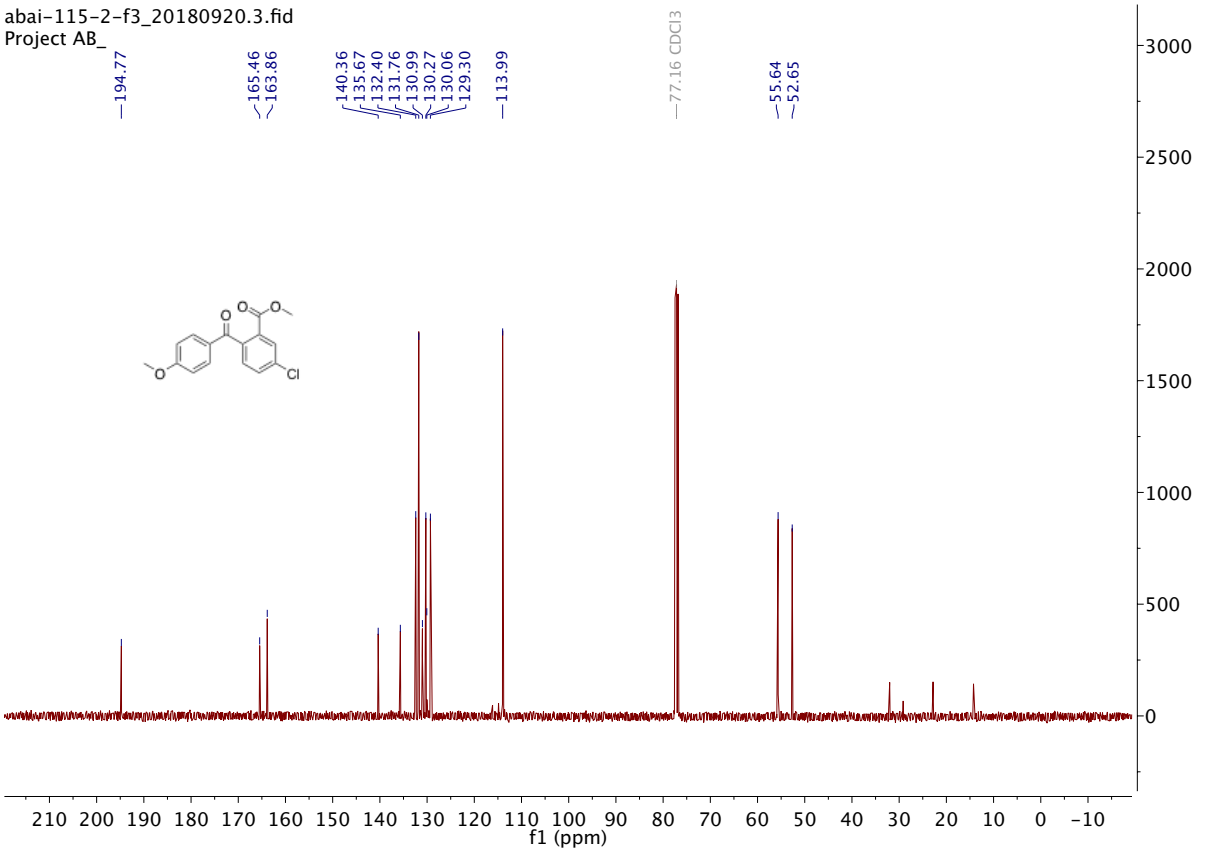


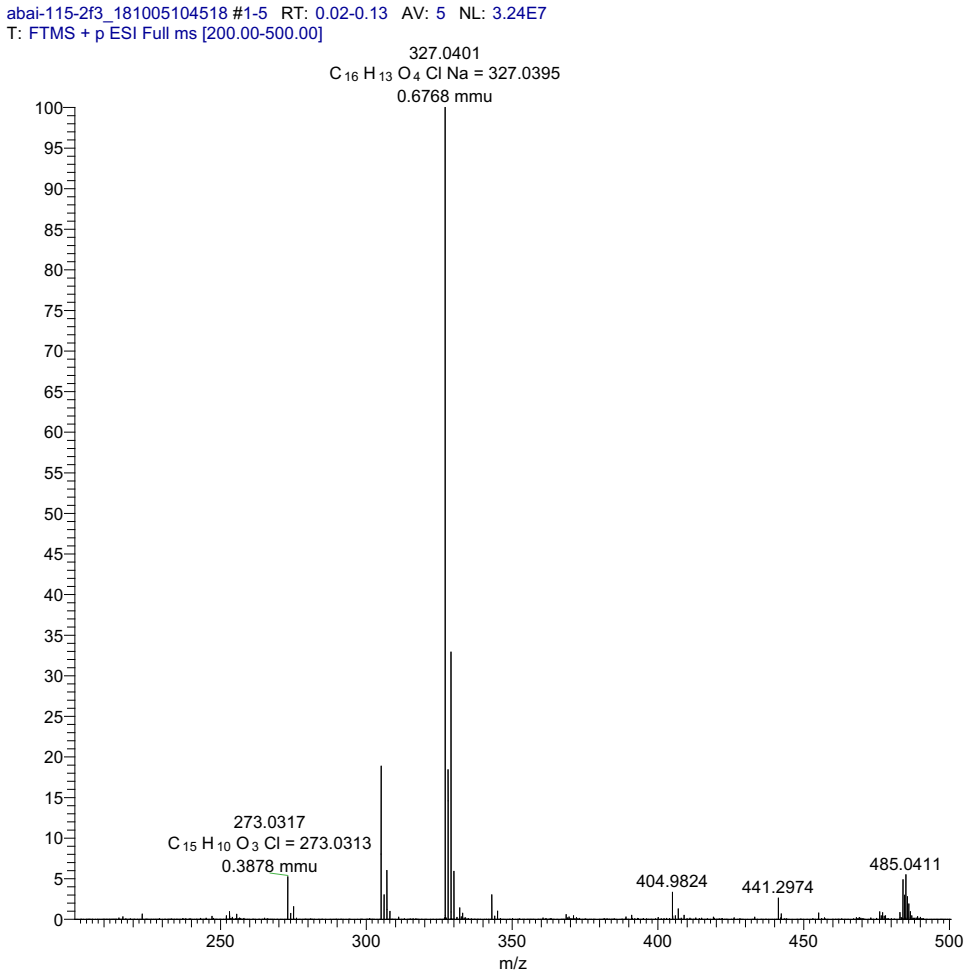
ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.



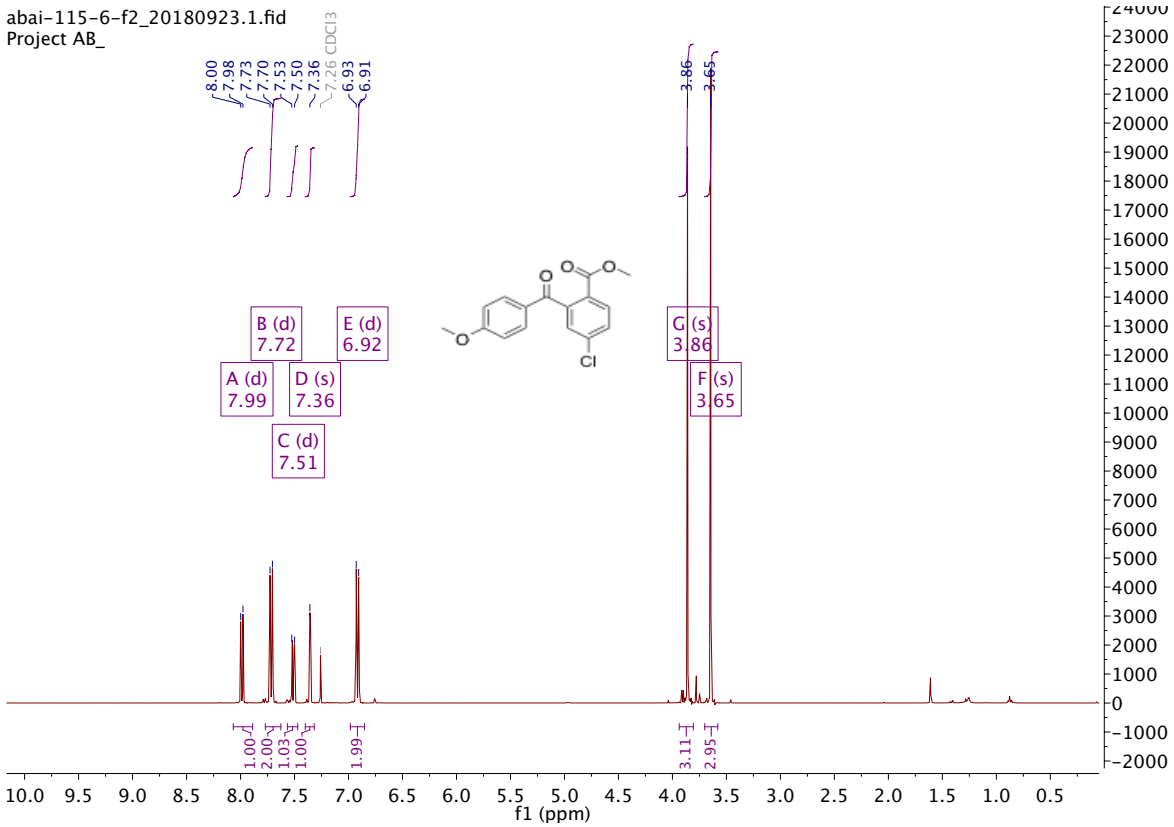
Methyl 5-chloro-2-(4-methoxybenzoyl)benzoate ***2da***

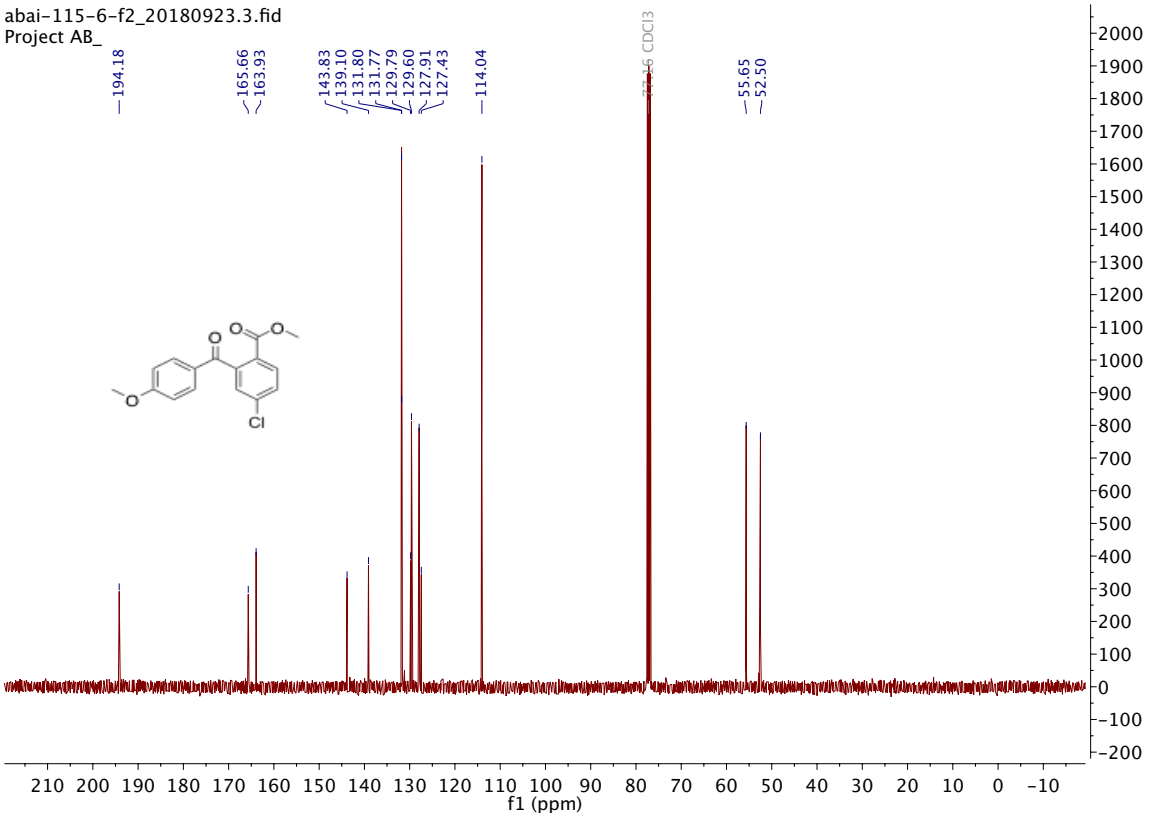


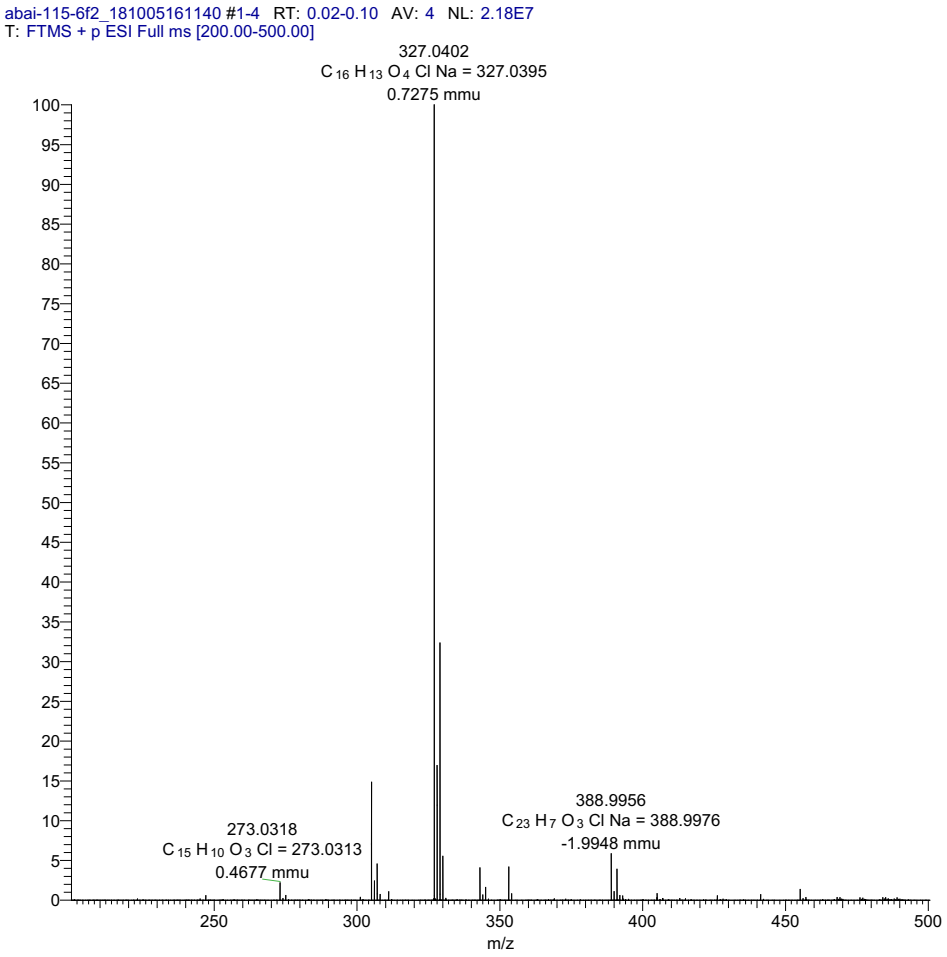




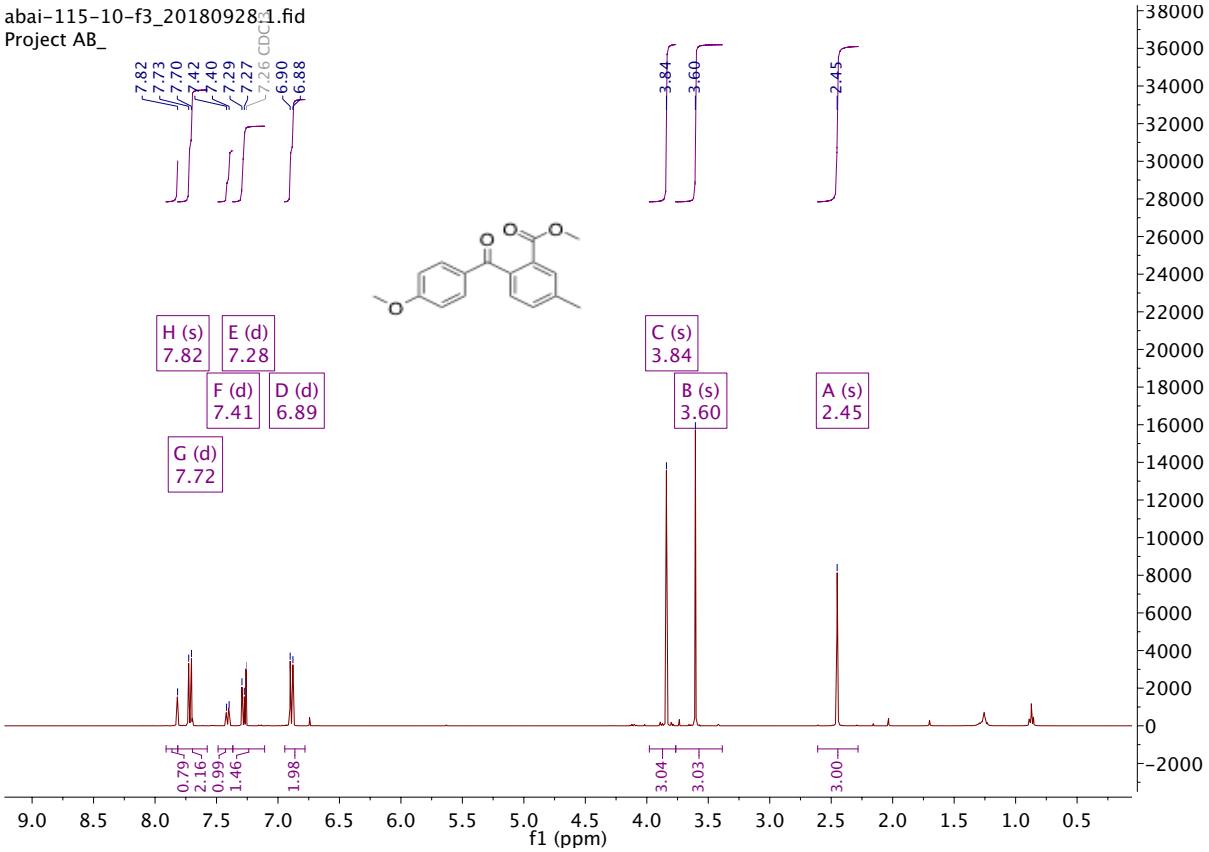
Methyl 4-chloro-2-(4-methoxybenzoyl)benzoate ***2ea***

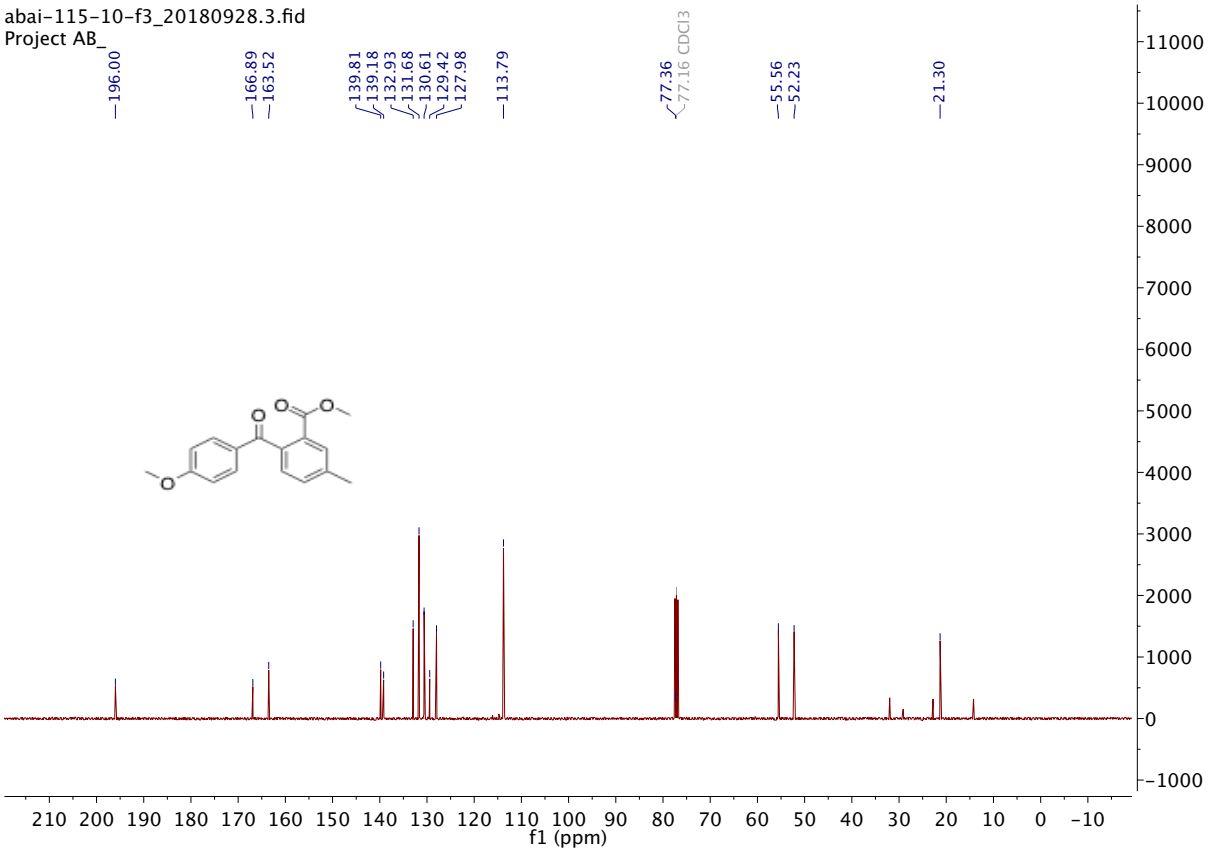


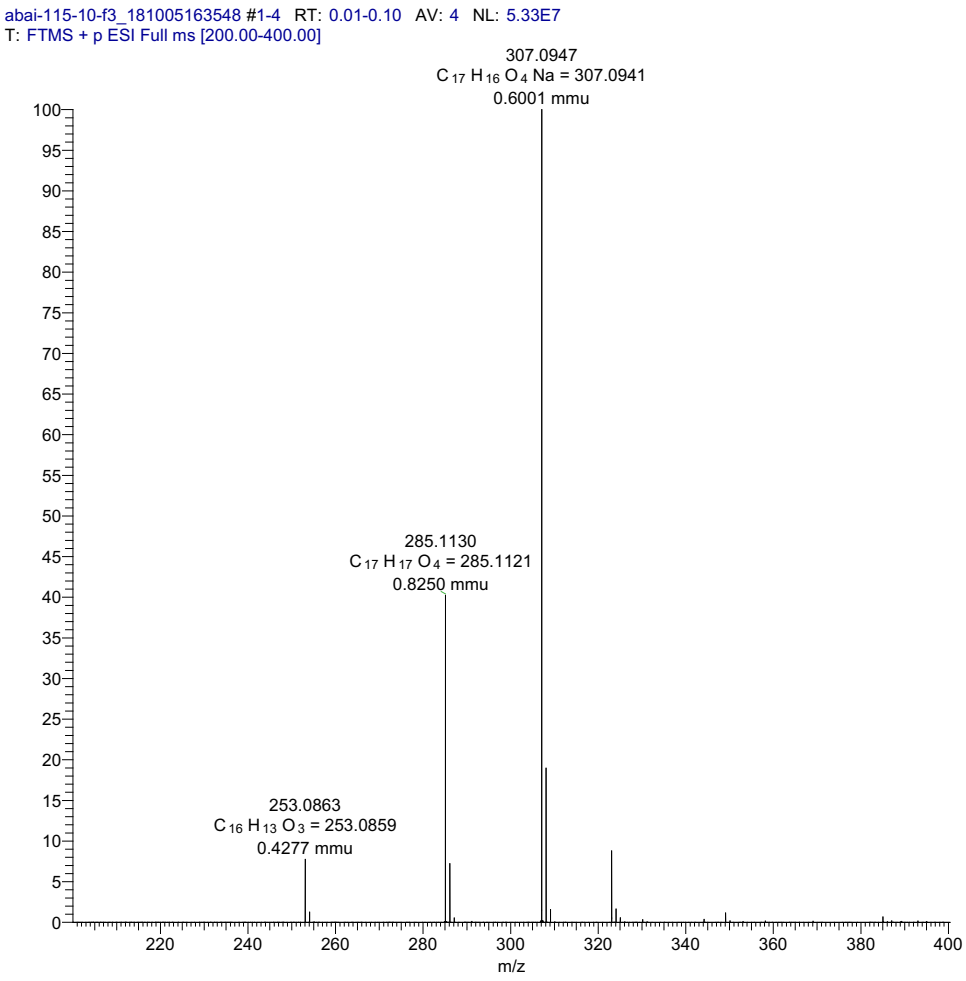

abai-115-6-f2_20180923.3.fid
Project AB_
194.18
165.66
163.93
143.83
139.10
131.80
131.77
129.79
129.60
127.91
127.43
114.04
77.16 CDCl3
55.65
52.50
O
O
O
O
Cl
f1 (ppm)


abai-115-6f2_181005161140 #1-4 RT: 0.02-0.10 AV: 4 NL: 2.18E7
T: FTMS + p ESI Full ms [200.00-500.00]
327.0402
C16 H13 O4 Cl Na = 327.0395
0.7275 mmu
273.0318
C15 H10 O3 Cl = 273.0313
0.4677 mmu
388.9956
C23 H7 O3 Cl Na = 388.9976
-1.9948 mmu
m/z

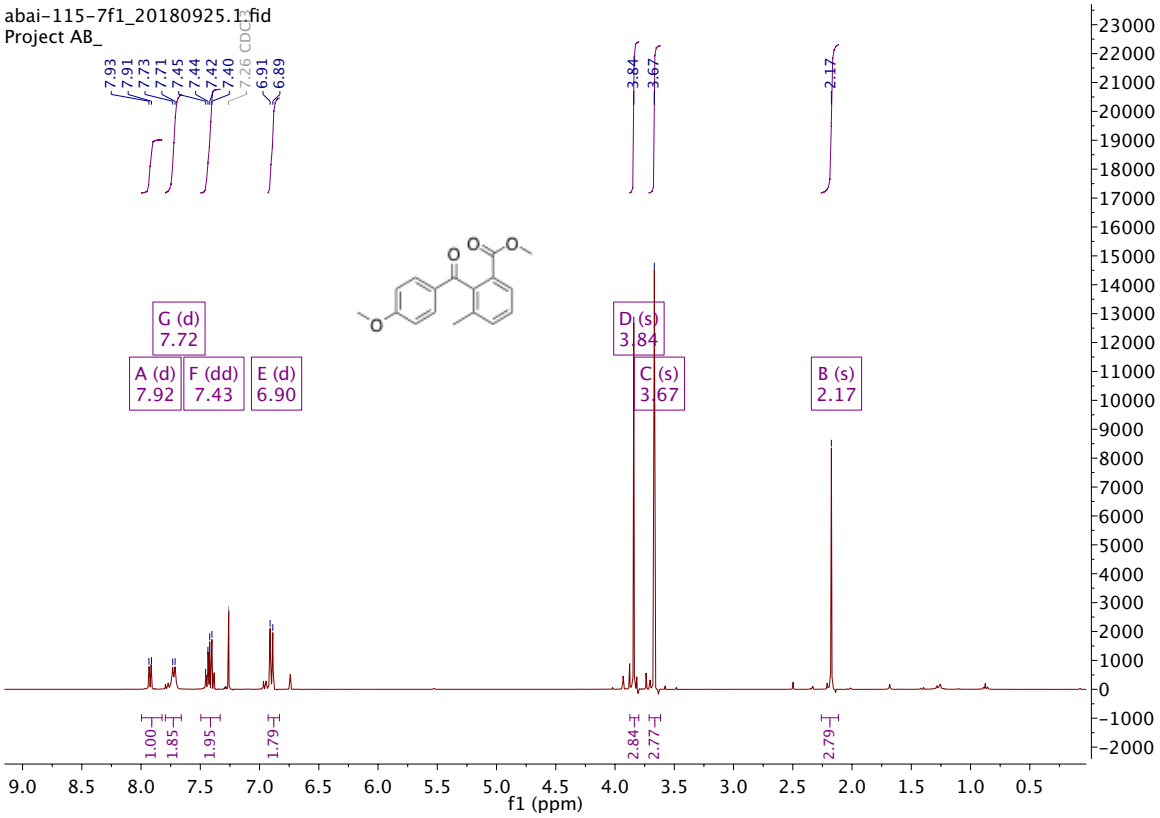
Methyl 2-(4-methoxybenzoyl)-5-methylbenzoate ***2fa***

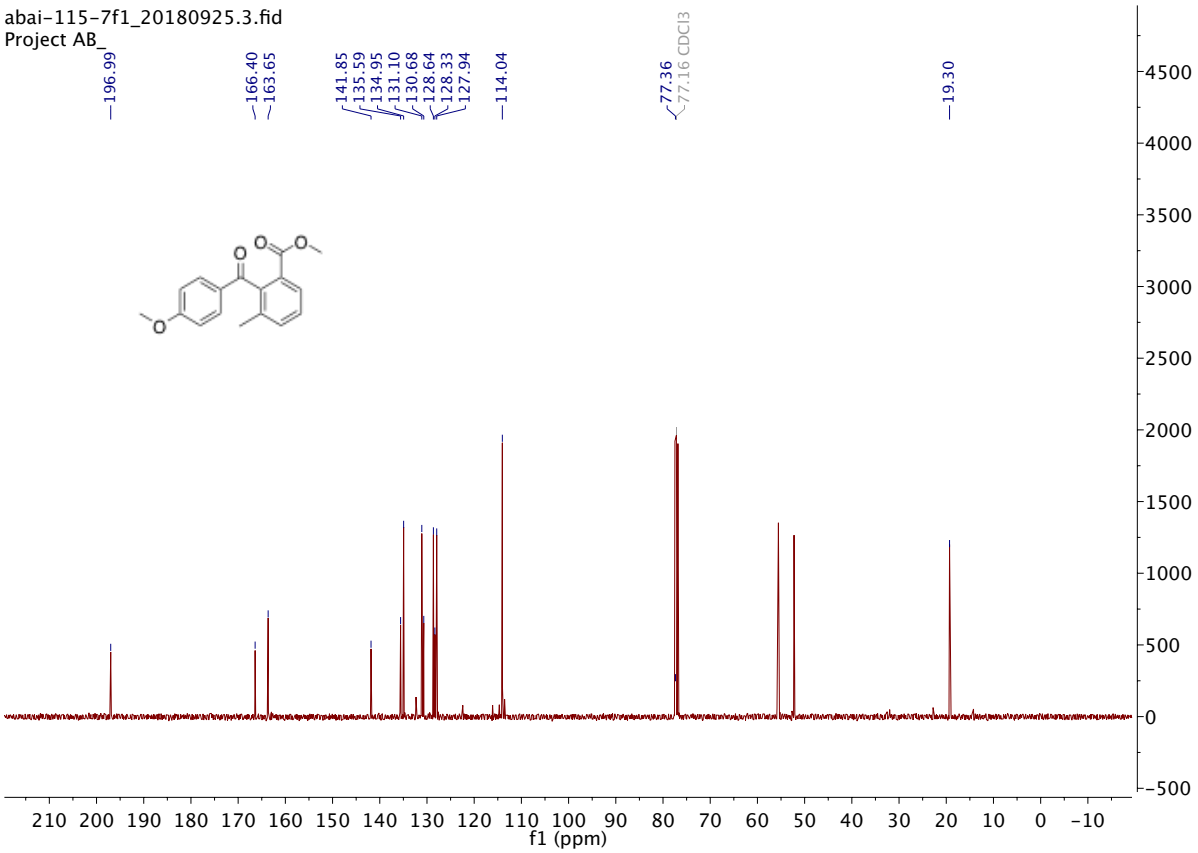


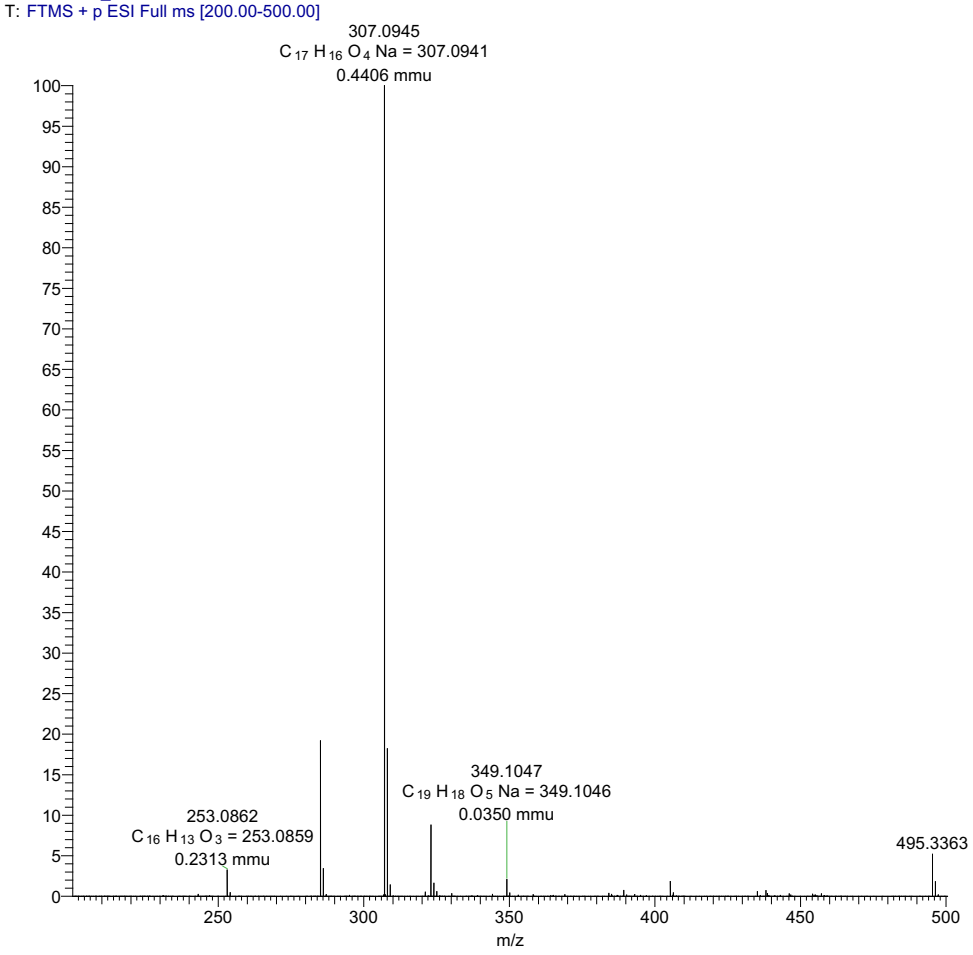




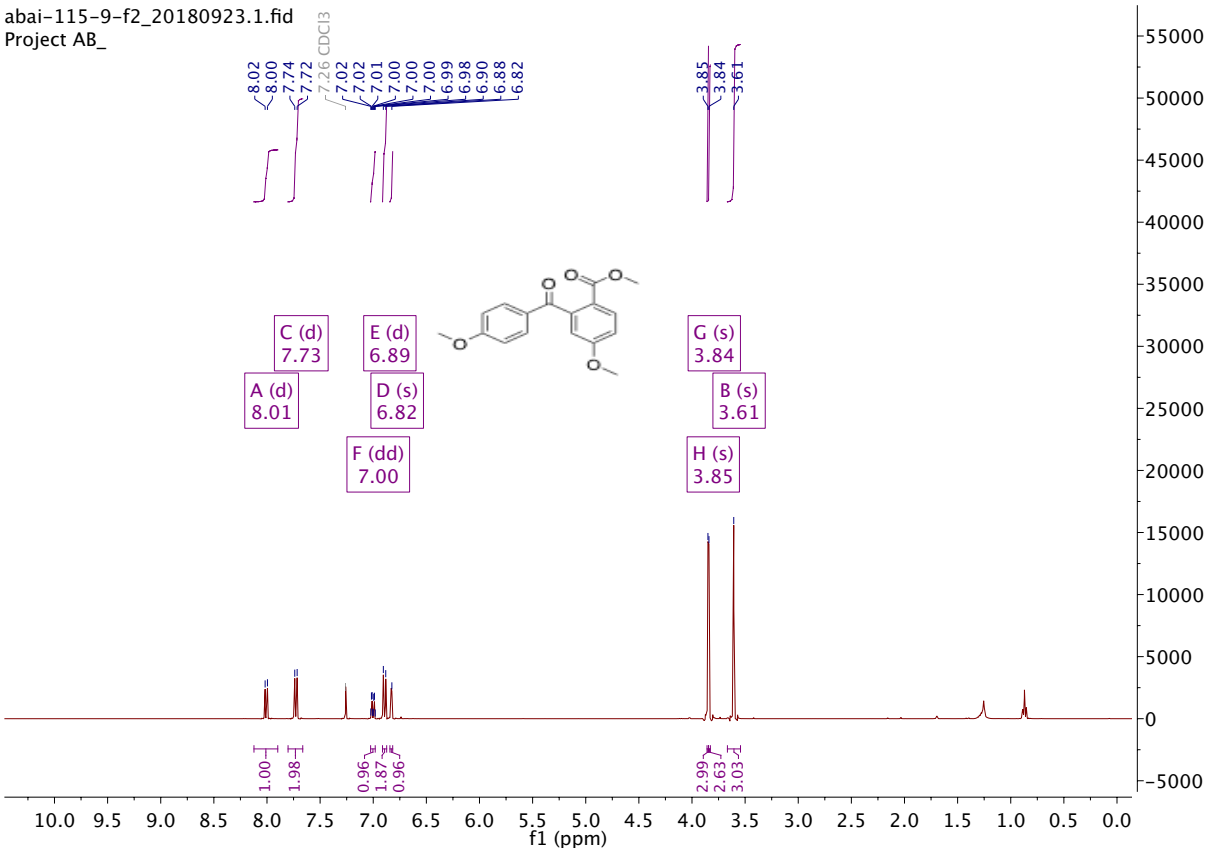
Methyl 2-(4-methoxybenzoyl)-3-methylbenzoate ***2ga***

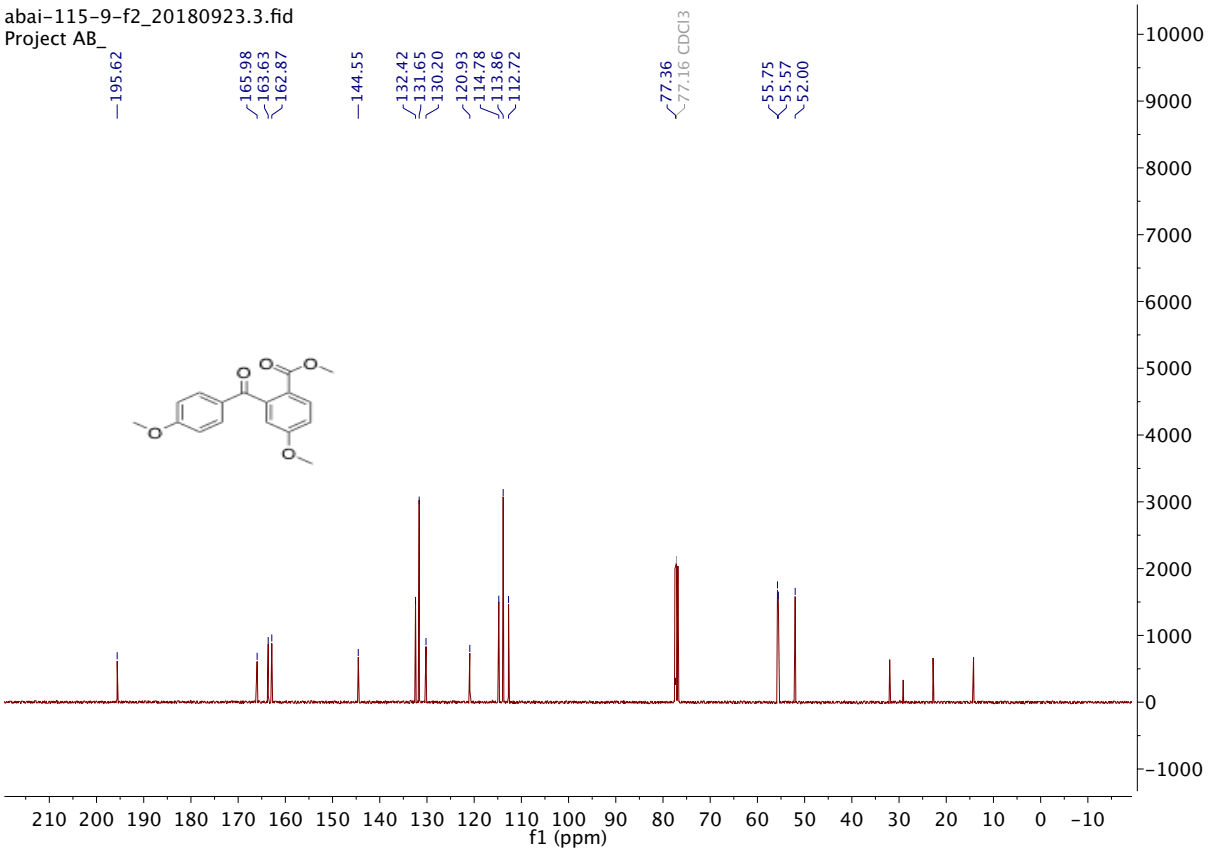


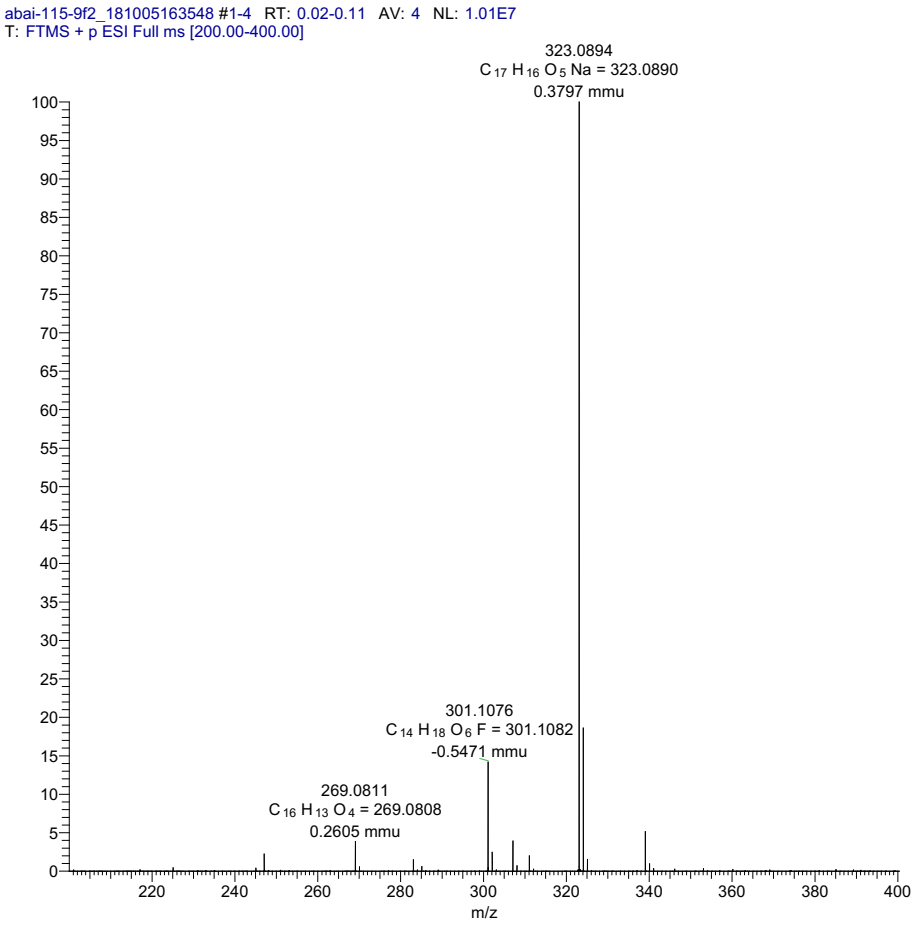

abai-115-7f1_20180925.3.fid
Project AB_
196.99
166.40
163.65
141.85
135.59
134.95
131.10
130.68
128.64
128.33
127.94
114.04
77.36
77.16 CDCl3
19.30
f1 (ppm)


abai-115-7f1_181005161140 #1-5 RT: 0.01-0.12 AV: 5 NL: 6.95E7
T: FTMS + p ESI Full ms [200.00-500.00]
307.0945
C17 H16 O4 Na = 307.0941
0.4406 mmu
349.1047
C19 H18 O5 Na = 349.1046
0.0350 mmu
253.0862
C16 H13 O3 = 253.0859
0.2313 mmu
495.3363
m/z

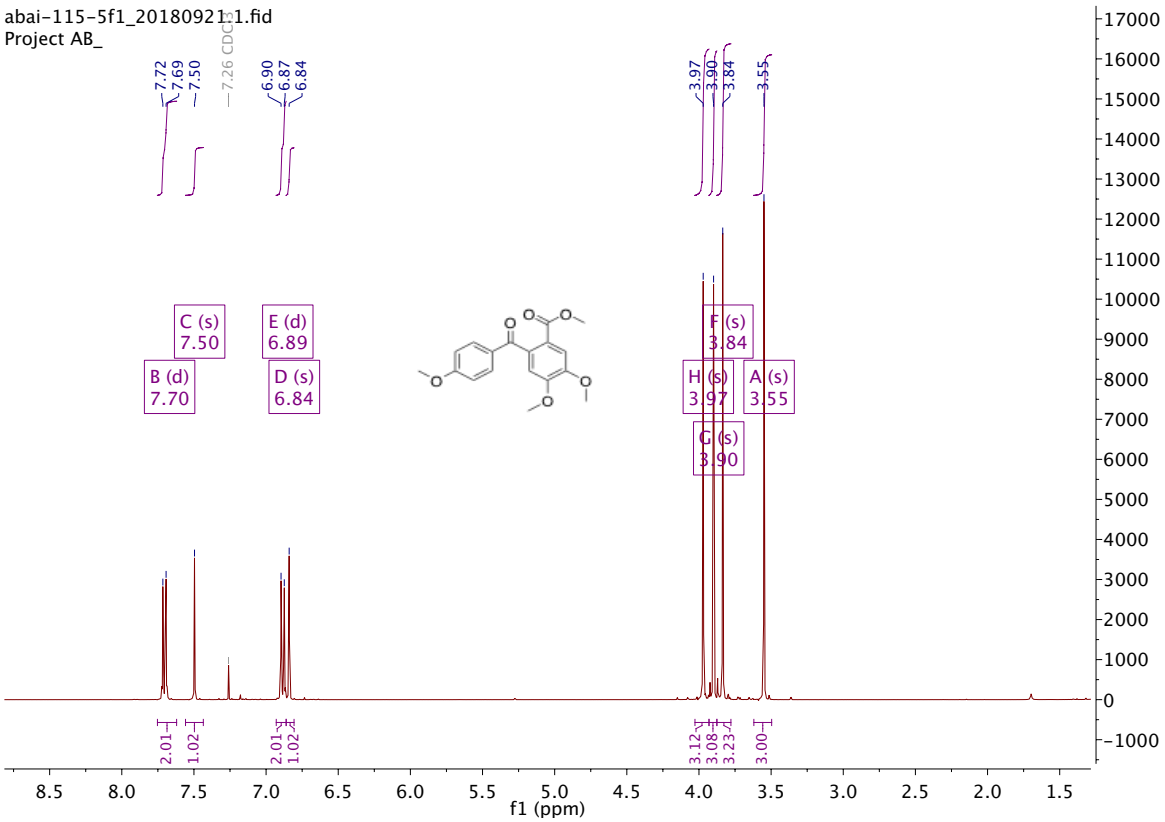
Methyl 4-methoxy-2-(4-methoxybenzoyl) benzoate ***2ha***

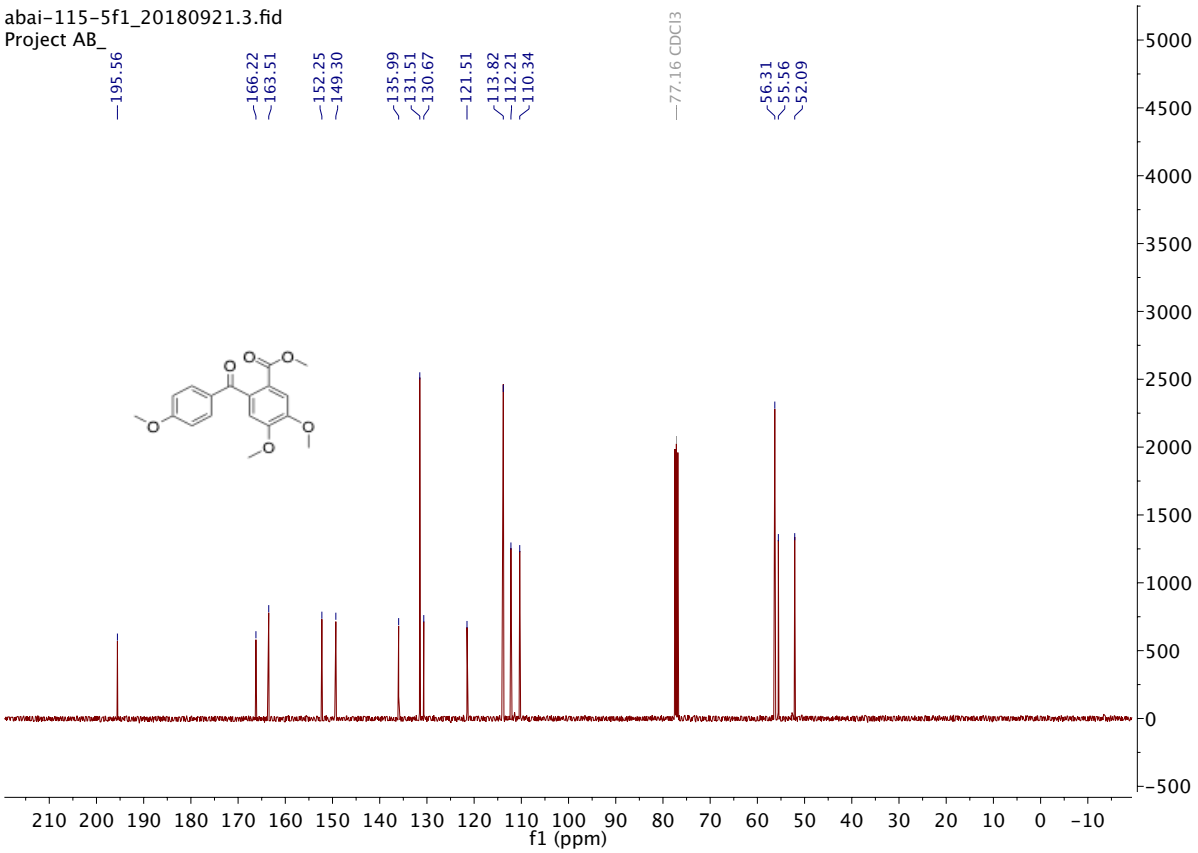


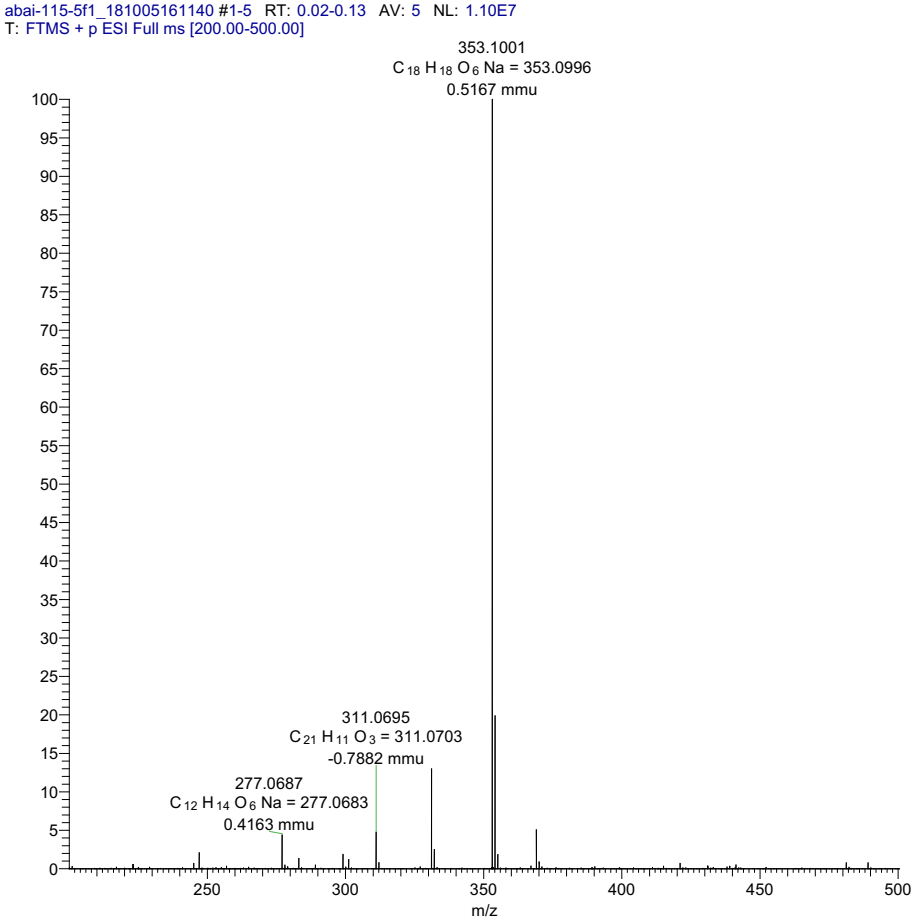




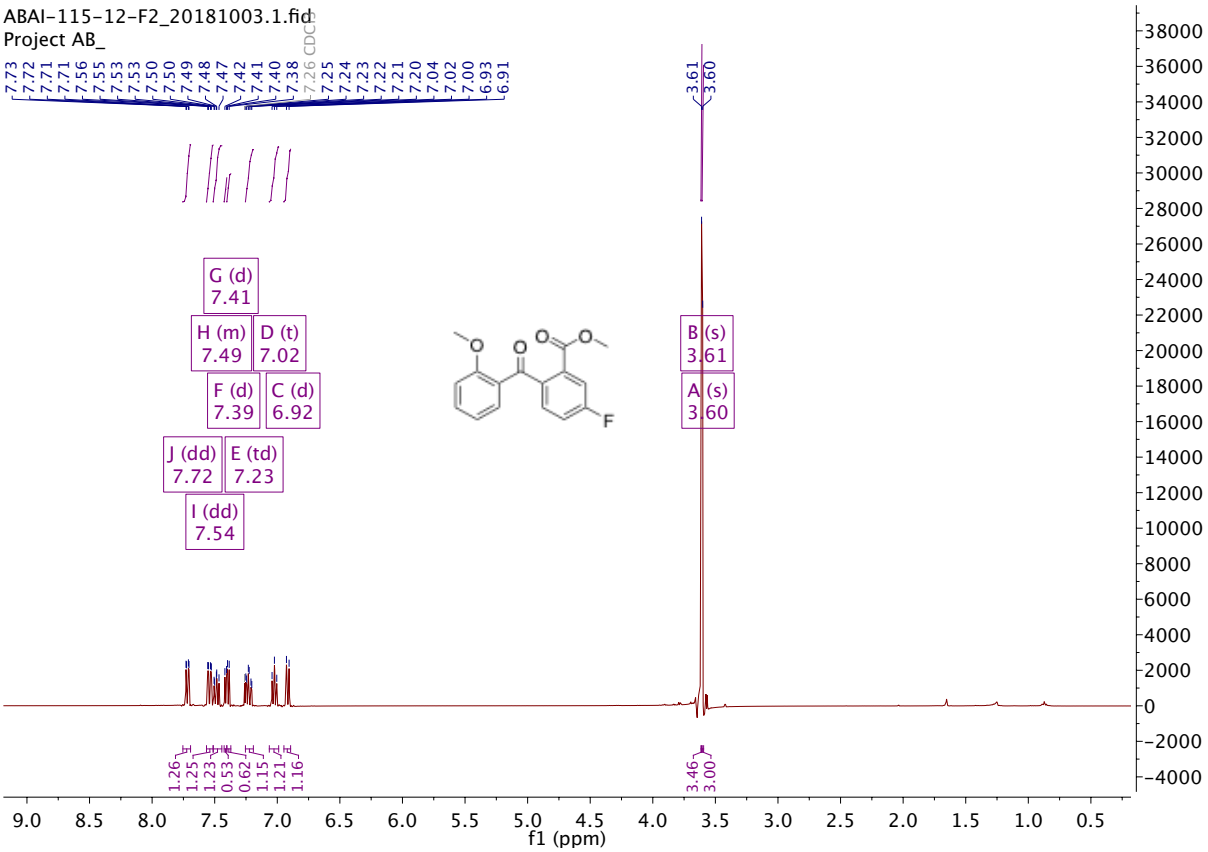
Methyl 2-(4-methoxybenzoyl)-5-methylbenzoate ***2ia***

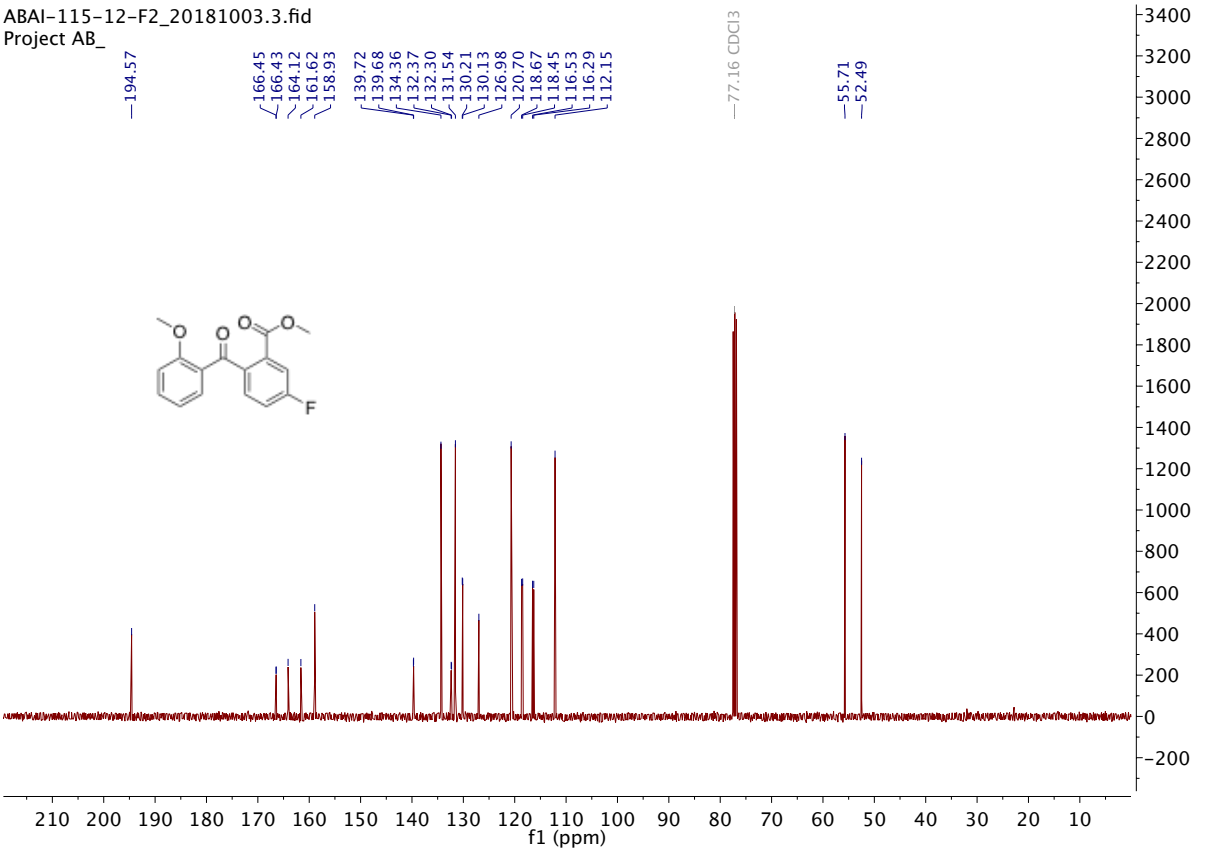


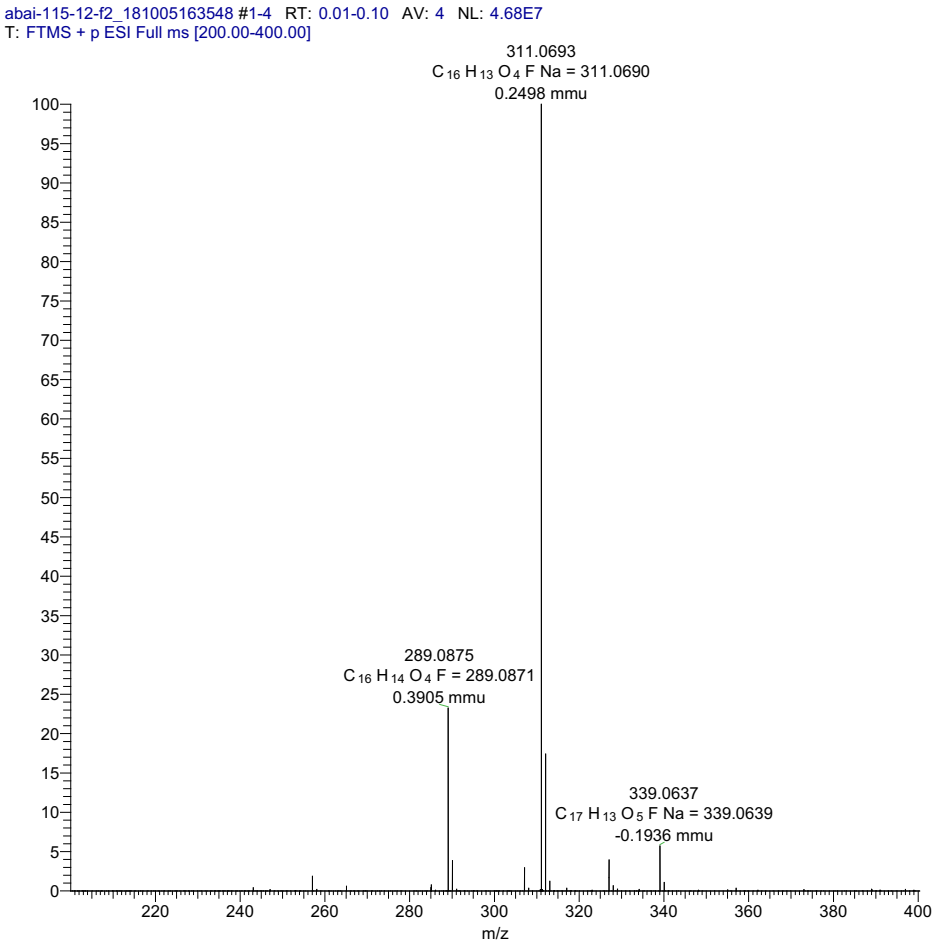

abai-115-5f1_20180921.3.fid
Project AB_
195.56
166.22
163.51
152.25
149.30
135.99
131.51
130.67
121.51
113.82
112.21
110.34
77.16 CDCl3
56.31
55.56
52.09
f1 (ppm)


abai-115-5f1_181005161140 #1-5 RT: 0.02-0.13 AV: 5 NL: 1.10E7
T: FTMS + p ESI Full ms [200.00-500.00]
353.1001
C18 H18 O6 Na = 353.0996
0.5167 mmu
311.0695
C21 H11 O3 = 311.0703
-0.7882 mmu
277.0687
C12 H14 O6 Na = 277.0683
0.4163 mmu
m/z

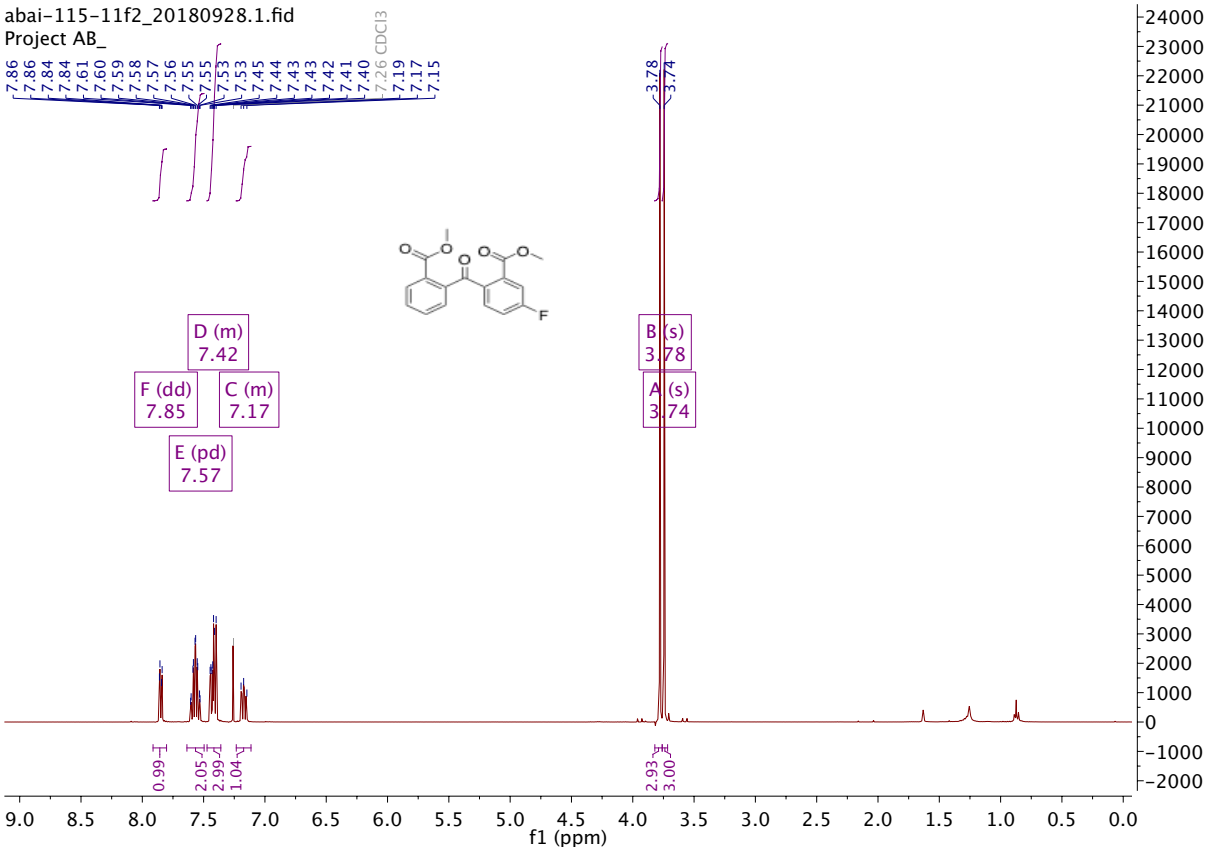
Methyl 5-fluoro-2-(2-methoxybenzoyl)benzoate ***2bc***

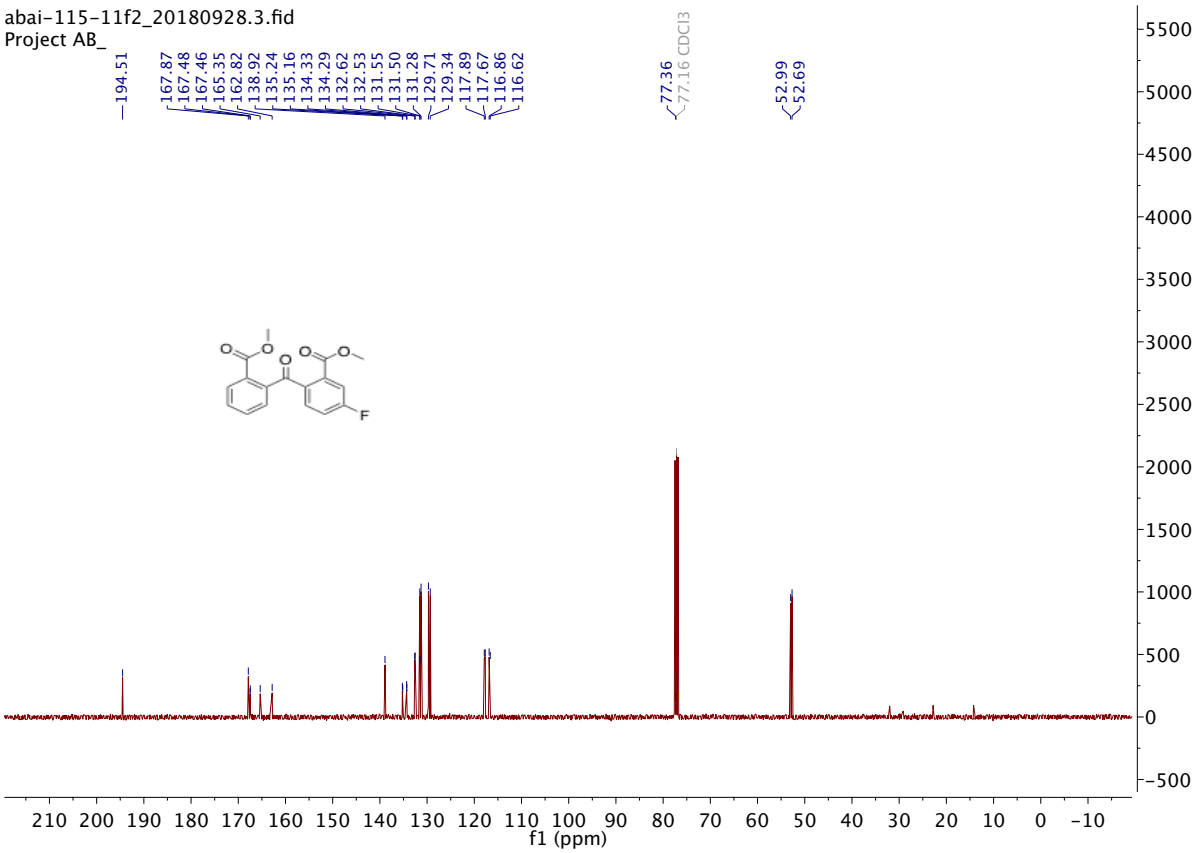


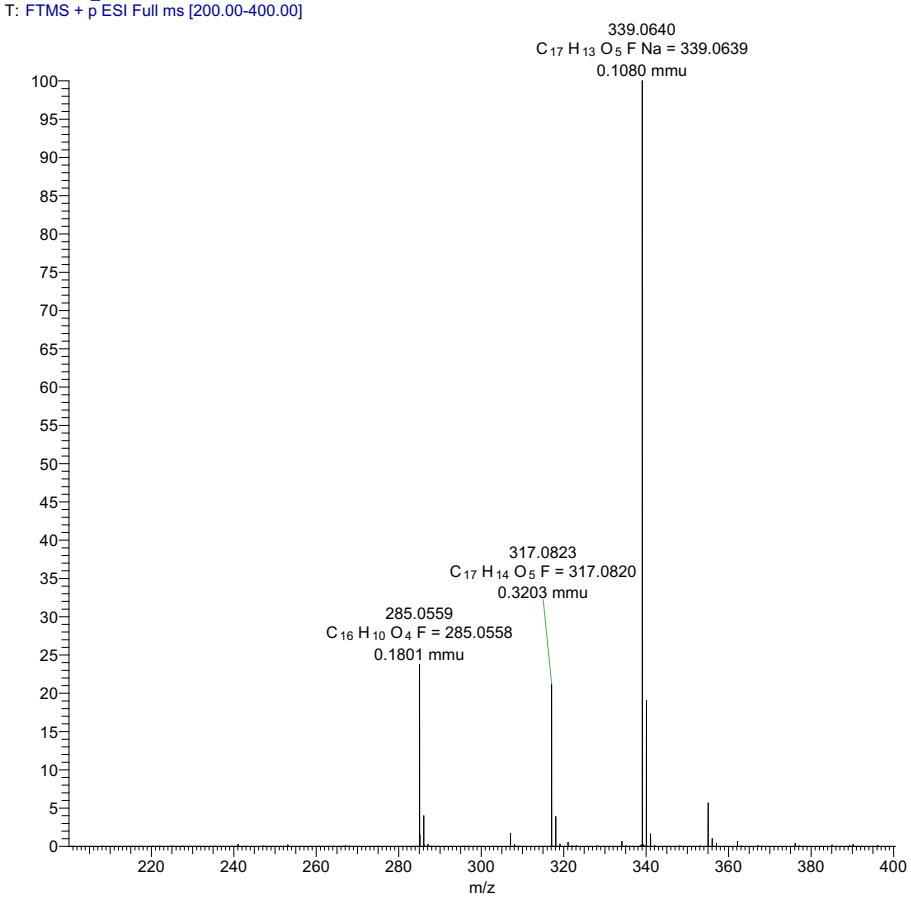




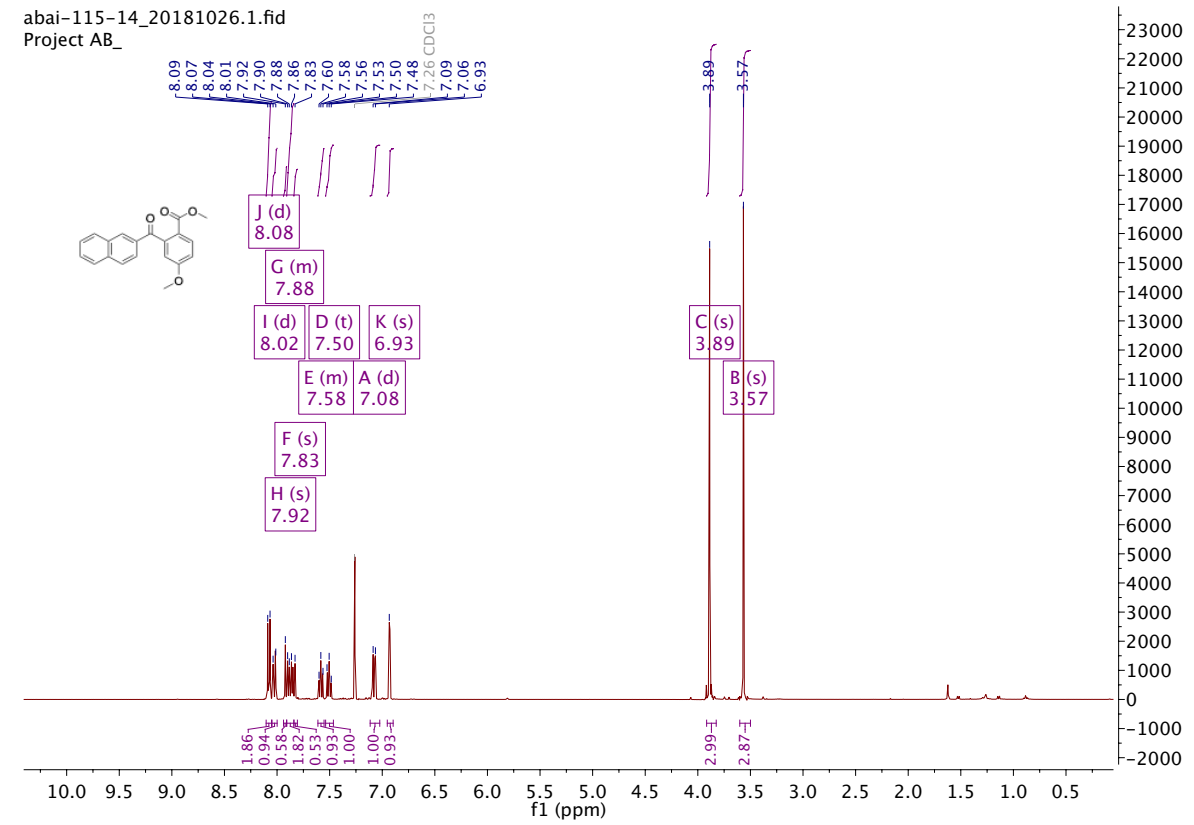
Methyl 5-fluoro-2-(2-(methoxycarbonyl)benzoyl)benzoate ***2bh***

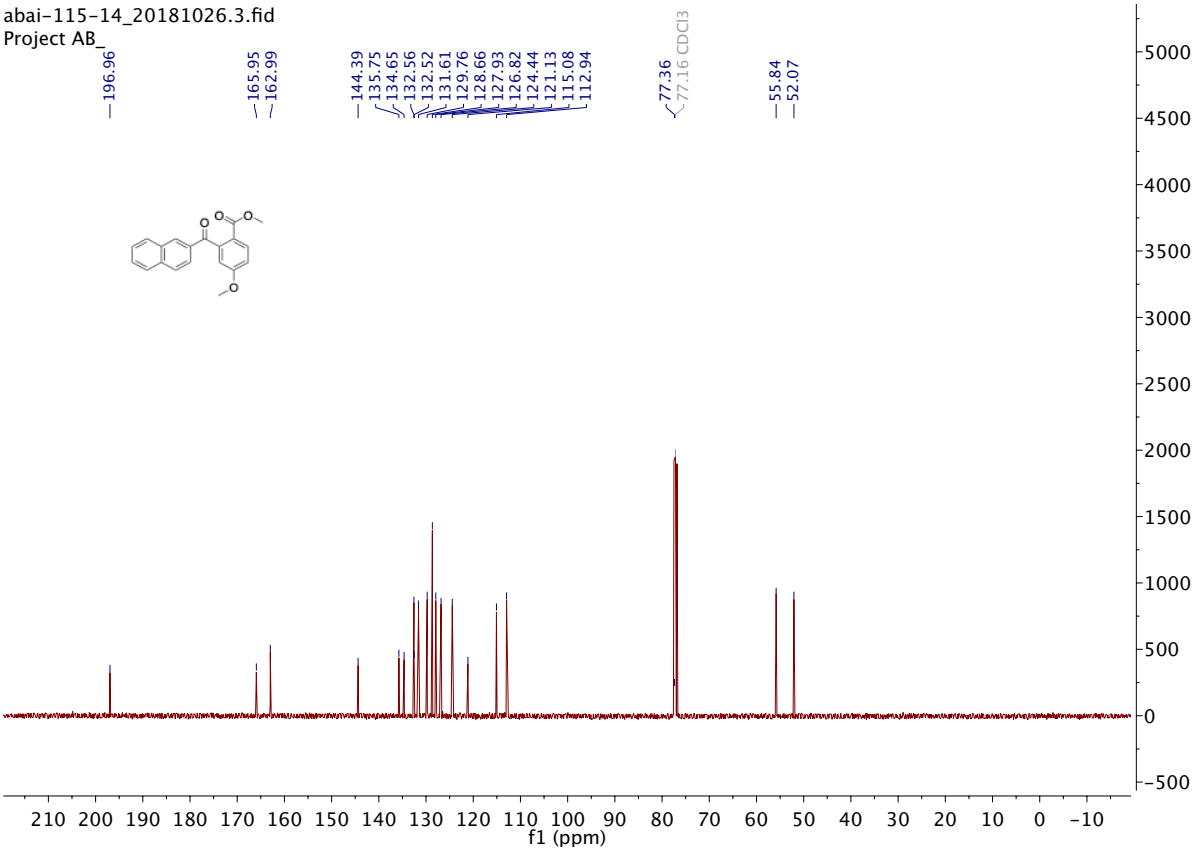



abai-115-11f2_20180928.3.fid
Project AB_
194.51
167.87
167.48
167.46
165.35
162.82
138.92
135.24
135.16
134.33
134.29
132.62
132.53
131.55
131.50
131.28
129.71
129.34
117.89
117.67
116.86
116.62
77.36
77.16 CDCl3
52.99
52.69
F
f1 (ppm)

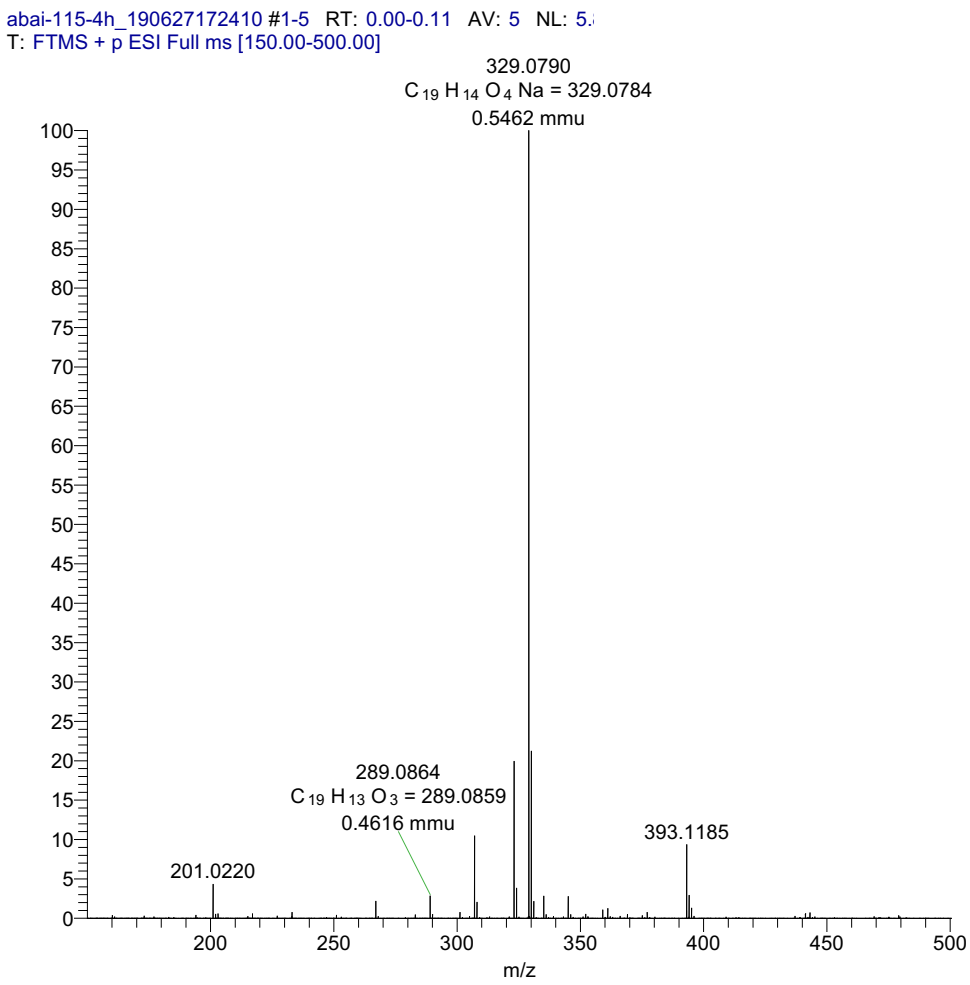

abai-115-11_181005163548 #1-4 RT: 0.02-0.11 AV: 4 NL: 3.76E7
T: FTMS + p ESI Full ms [200.00-400.00]
339.0640
C17 H13 O5 F Na = 339.0639
0.1080 mmu
317.0823
C17 H14 O5 F = 317.0820
0.3203 mmu
285.0559
C16 H10 O4 F = 285.0558
0.1801 mmu
m/z

Methyl 2-(2-naphthoyl)-4-methoxybenzoate ***2hp***

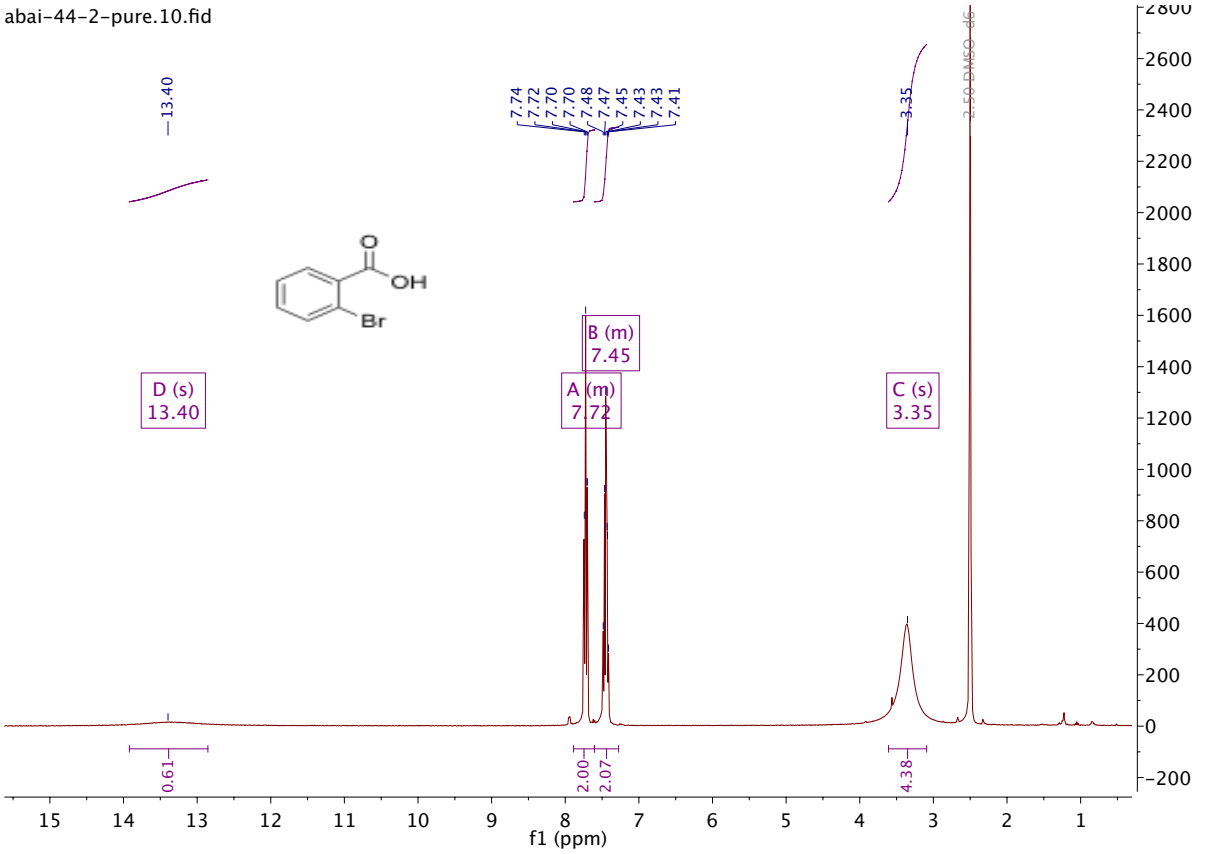


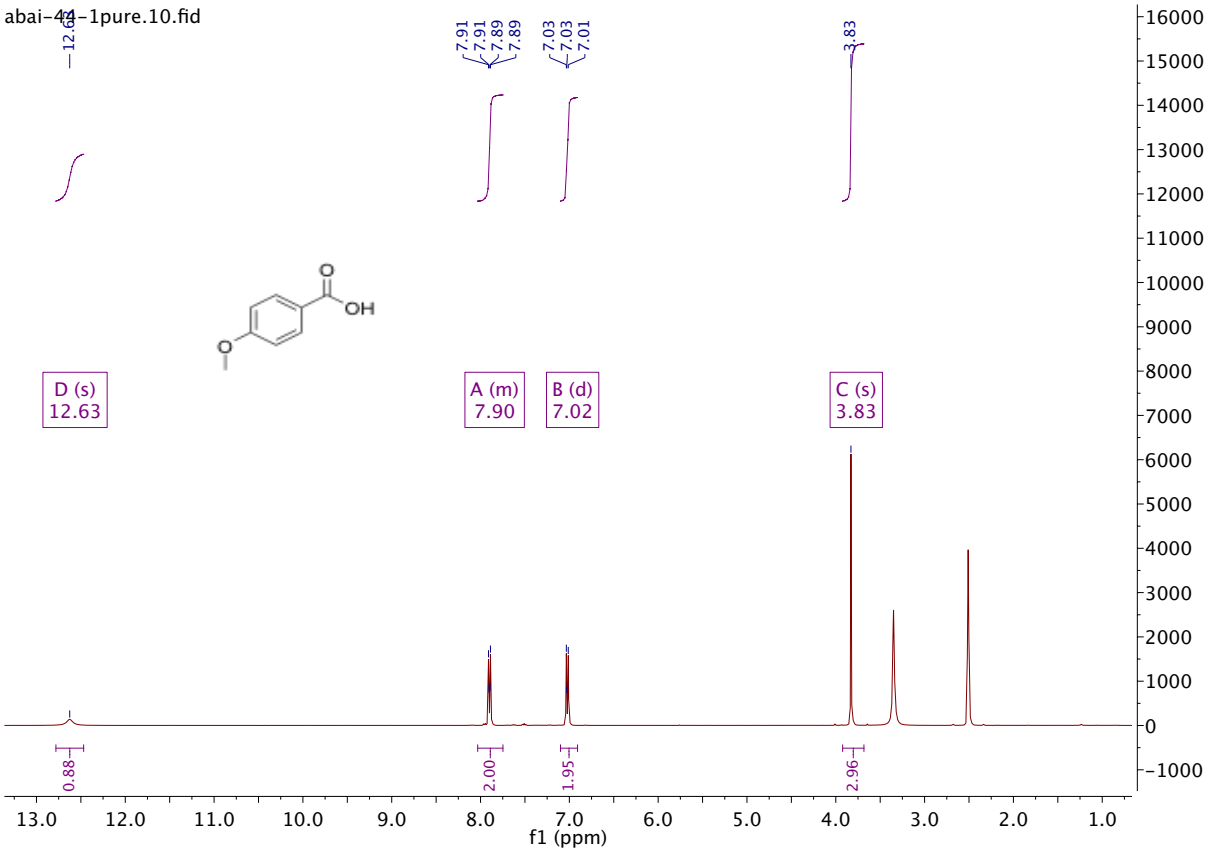


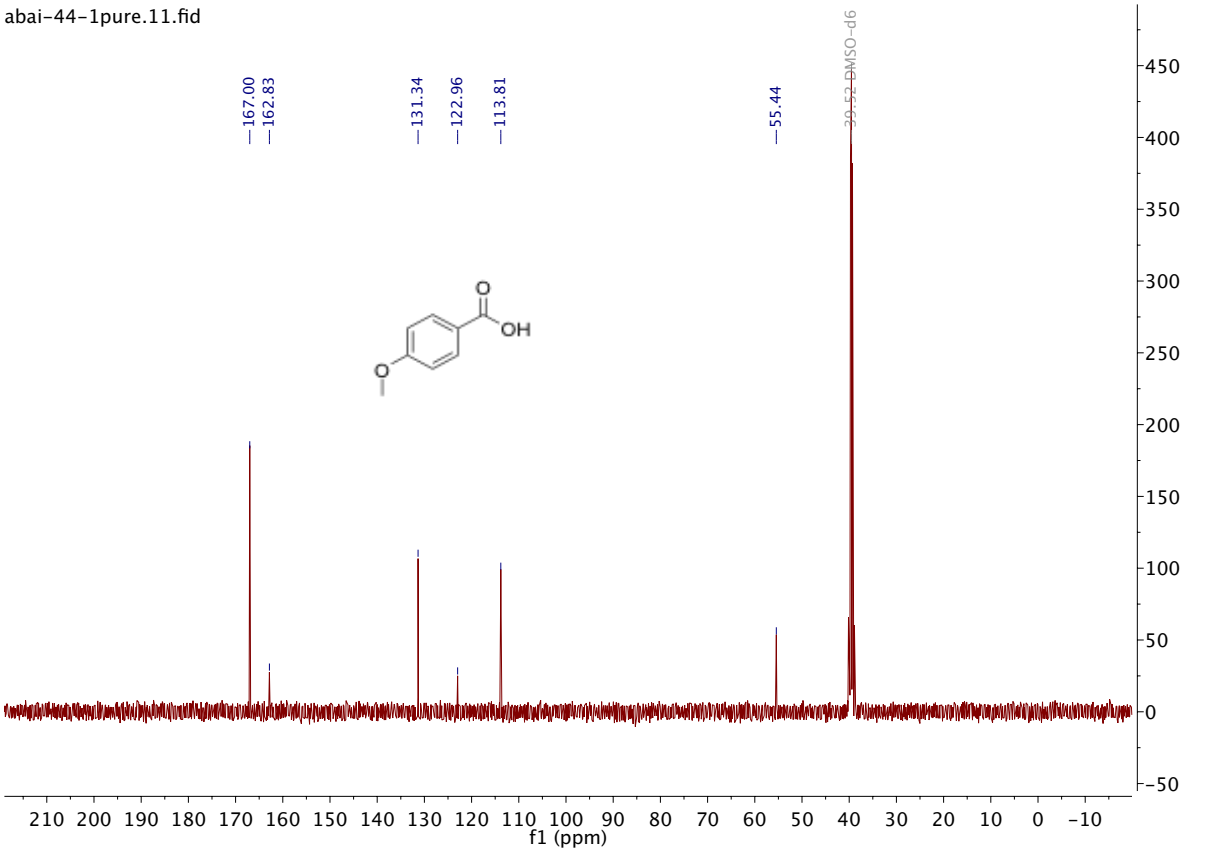
ESI : Carbonylative Suzuki-Miyaura couplings of sterically hindered aryl halides.

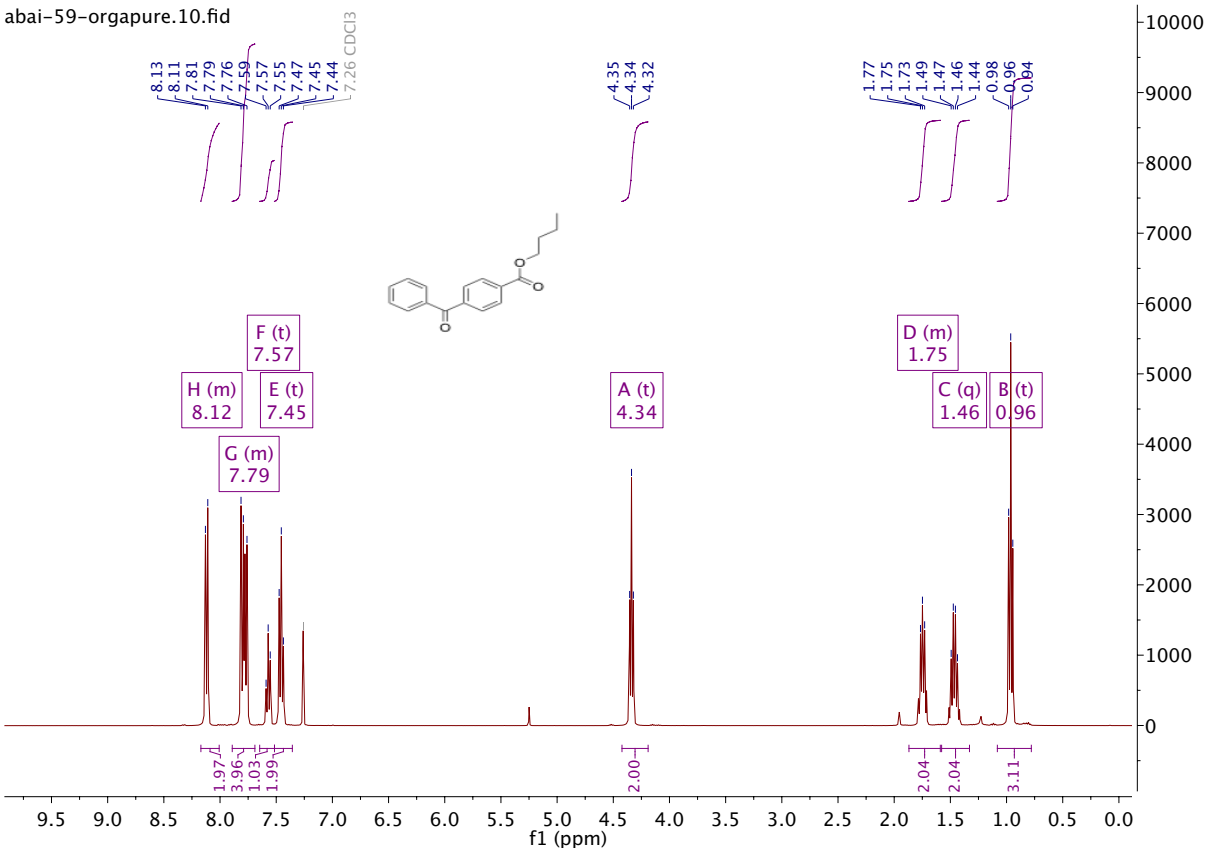


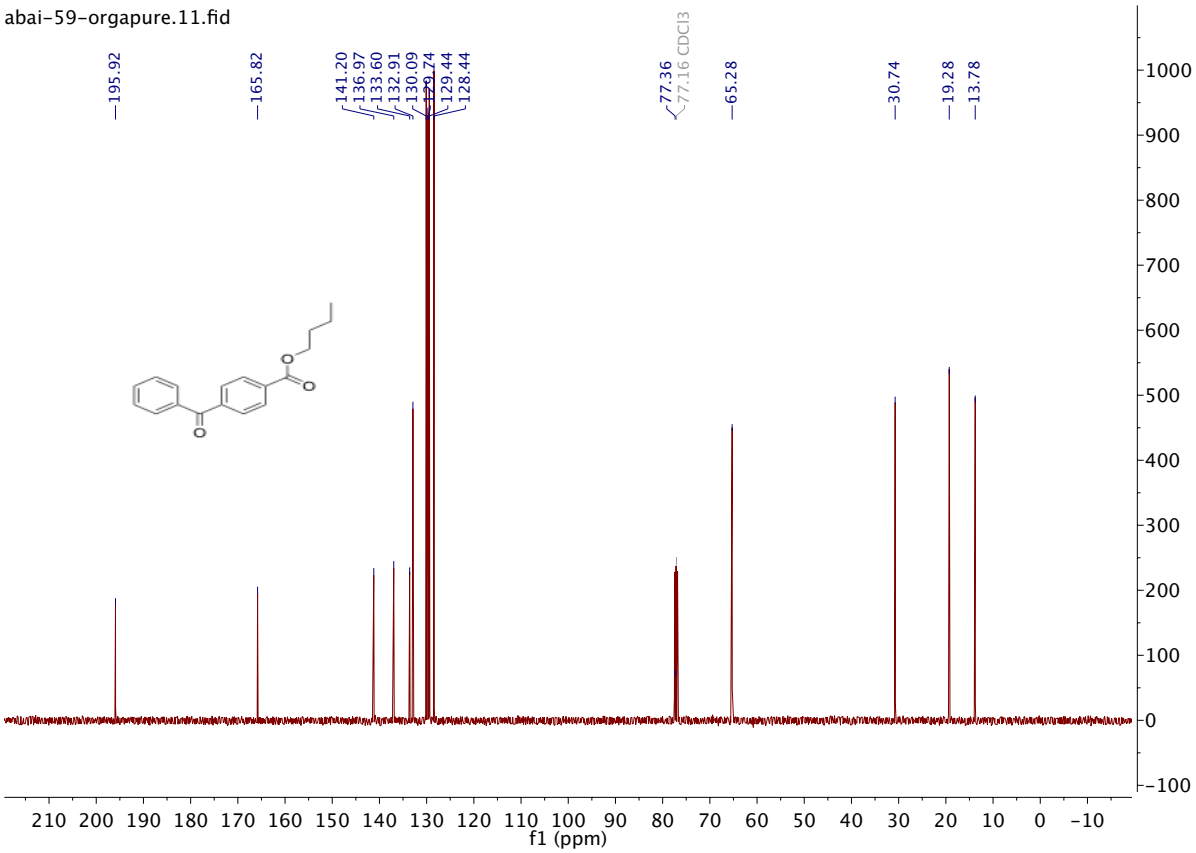
4.4 Spectra for products from control experiments for hydrocarbonylations (section 1.4).






abai-44-1pure.11.fid
167.00
162.83
131.34
122.96
113.81
55.44
39.52 DMSO-d6
OH
O
f1 (ppm)


abai-59-orgapure.10.fid
8.13
8.11
7.81
7.79
7.76
7.59
7.57
7.55
7.47
7.45
7.44
7.26 CDCl3
4.35
4.34
4.32
1.77
1.75
1.73
1.49
1.47
1.46
1.44
0.98
0.96
0.94
F (t) 7.57
H (m) 8.12
E (t) 7.45
G (m) 7.79
A (t) 4.34
D (m) 1.75
C (q) 1.46
B (t) 0.96
1.97
3.96
1.03
1.99
2.00
2.04
2.04
3.11
f1 (ppm)


abai-59-orgapure.11.fid
195.92
165.82
141.20
136.97
133.60
132.91
130.09
129.74
129.44
128.44
77.36
77.16 CDCl3
65.28
30.74
19.28
13.78
f1 (ppm)