Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Non-symmetrical Diarylcarboxylic Acids via Rhodium(I)-catalyzed Regiospecific Cross-dehydrogenation Coupling of Aromatic Acids: Twofolds Direct C–H Bond Activations in Water

Hailong Zhang, Guo-Jun Deng, Shiguang Li, Chao-Jun Li and Hang Gong**

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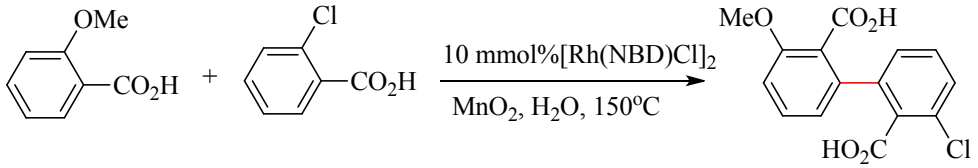
1. General information

Preparative thin-layer chromatography was performed for product purification using Sorbent Silica Gel 60 F254 TLC plates and visualized with ultraviolet light. Petroleum ether and ethyl acetate was used as eluents. IR spectra were recorded on a New Fourier transform infrared spectroscopy. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a 400 MHz, 100 MHz and 377 MHz NMR spectrometer respectively. Spectrometer as solutions in $CDCl_3$ unless otherwise stated. HRMS were made by means of ESI. Melting points (mp) were measured on micro melting point apparatus and uncorrected. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were carried out in a sealed tube under an atmosphere of air. Unless otherwise noted, all reagents were purchased as reagent grade and were used without further purification.

2. Selected optimization results



1a 1b 1c

Entry	1a(equiv.)	1b(equiv.)	MnO_2(equiv.)	H_2O(mL)	Yield(%)
1	1	3	3	2	65
2	1	3	3	0.5	61
3	1	3	3	1	68
4	1	3	5	1	70
5	1	5	5	1	65

[a]Conditions: $[Rh(NBD)Cl]_2$ (10 mmol%), Air, 150 °C under air atmosphere for 24 h.[b]Isolated yields.

3. Experimental procedure

A typical experimental procedure is as follows:

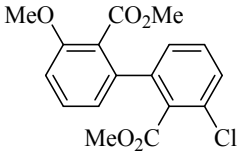
A solution of an aromatic acid **A** (0.1 mmol), aromatic acid **B** (0.3 mmol), $[Rh(nbd)Cl]_2$ (4.6 mg, 0.01 mmol), and activated MnO_2 (purchased from Aldrich and used as received, 45 mg, 0.5 mmol) in distilled water (1.0 mL) was stirred in a sealed tube under an atmosphere of air at 150 °C for 24 h. The reaction mixture was then cooled to room temperature and acidified by dilute HCl to pH<3, and then the solvent was evaporated *in vacuo*. The residue was dissolved in THF and filtered through a 1-inch plug of silica gel to remove the salts. Afterward, the solvent was evaporated *in vacuo*. The residue was dissolved in 1 mL acetone, and 0.5 mmol CH_3I and 1.0 mmol K_2CO_3 were added to react at 60 °C for 24h. The pure product was obtained by preparative thin-layer chromatography on silica gel with petroleum ether and ethyl acetate as eluent.

Gram-scale synthesis of compound 3-methoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylic acid (18d)

A solution of 2-methoxybenzoic acid (1 g, 6.6 mmol) and 2-methylbenzoic acid(2.7g, 19.7 mmol), $[Rh(nbd)Cl]_2$ (6.9 mg, 0.015 mmol, 0.2 mol%), and MnO_2 (32.9 g, 21.6 mmol, 5 equiv.) in distilled water (5 mL) was stirred in a sealed tube at 150 °C for 72 h under an atmosphere of air. The reaction mixture was then cooled to room temperature and acidified by dilute HCl to PH<3, and then the solvent was evaporated in vacuo. The residue was purified by preparative chromatography using gradient eluent (hexane and ethyl acetate containing 0.3 % formic acid). After the solvent was evaporated under vacuo, pure product was obtained in 71 % yield (1330 mg).

4. Characterization data for CDC products

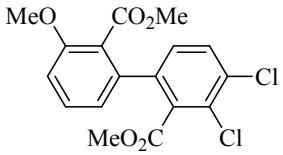
(**3a**) Dimethyl 3-chloro-3'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 70%; Mp 105-106 °C; IR (ATR) 2946, 2845, 1741, 1723, 1586, 1443, 1259, 1185, 1136, 1031, 953, 832, 791, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 3H), 7.21 (d, J = 6.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 3.88 (s, 3H), 3.65 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 166.85, 156.50, 139.50, 138.28, 133.10, 131.16, 130.32, 129.80, 128.77, 127.95,

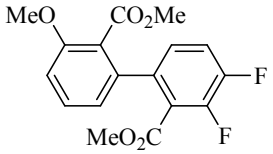
123.08, 121.59, 110.66, 55.99, 52.35, 52.11; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}ClNaO_5$ 357.0500, found [M+Na] 357.0497.

(**3b**) Dimethyl 3,4-dichloro-3'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



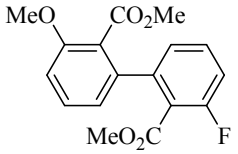
Colorless oil; Yield 76%; IR (ATR) 2925, 2851, 1732, 1650, 1582, 1462, 1385, 1261, 1096, 1038, 967, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.65 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.30, 166.15, 156.70, 137.62, 137.32, 135.15, 132.73, 130.45, 130.41, 129.49, 128.87, 123.26, 121.74, 111.13, 56.08, 52.58, 52.24; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}Cl_2O_5$ 369.0291, found [M+H] 369.0292.

(**3c**) Dimethyl 3,4-difluoro-3'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



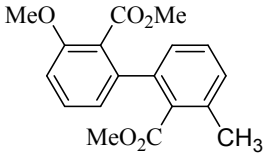
Colorless solid; Yield 70%; Mp 96-98 °C; IR (ATR) 2953, 2848, 1746, 1722, 1577, 1505, 1465, 1439, 1258, 1185, 1058, 992, 837, 800, 728, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.40, 164.07 (d, *J* = 3.0 Hz), 156.47, 151.12 (d, *J* = 12.9 Hz), 148.64 (d, *J* = 12.5 Hz), 146.87 (d, *J* = 12.7 Hz), 137.99, 135.73 (d, *J* = 5.0 Hz), 130.31, 125.78 (d, *J* = 5.8 Hz), 123.08 (d, *J* = 8.4 Hz), 121.74, 118.32 (d, *J* = 16.9 Hz), 110.70, 56.00, 52.56, 52.11; ^{19}F NMR (377 MHz, CDCl3) δ -137.25 (s), -137.86 (s); HRMS (ESI) *m/z* calcd for $C_{17}H_{14}F_2NaO_5$ 359.0702, found [M+Na] 359.0702.

(**3d**) Dimethyl 3-fluoro-3'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



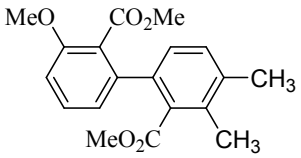
Colorless solid; Yield 75%; Mp 69-70 °C; IR (ATR) 2947, 2918, 2848, 1741, 1725, 1574, 1458, 1260, 1184, 1108, 1058, 832, 792, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.15–7.08 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.66 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 165.21, 161.13, 158.61, 156.45, 140.88 (d, *J* = 2.1 Hz), 138.76, 131.12 (d, *J* = 9.1 Hz), 130.26, 125.60 (d, *J* = 3.3 Hz), 122.85, 121.62, 115.36 (d, *J* =17.6 Hz), 110.53, 55.99, 52.31, 52.05; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.68; HRMS (ESI) *m/z* calcd for $C_{17}H_{16}FO_5$ 318.0976, found [M+H] 319.0976.

(**3e**) Dimethyl 3-methoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



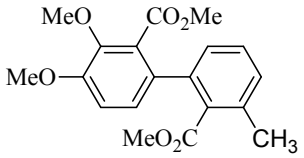
Colorless oil; Yield 82%; IR (ATR) 2949, 2840, 1724, 1575, 1459, 1437, 1259, 1104, 1068, 967, 765, 666 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H),7.20 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.59 (s, 3H), 3.56 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.43, 167.75, 156.34, 140.20, 138.16, 135.83, 132.97, 129.97, 129.71, 128.89, 127.07, 123.18, 121.82, 110.07, 55.98, 51.95, 51.71, 20.02; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}KO_5$ 353.0786, found [M+K] 353.0786.

(**3f**) Dimethyl 3'-methoxy-3,4-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate



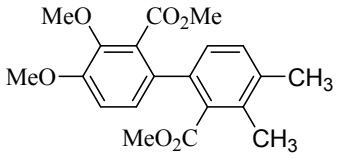
Colorless solid; Yield 82%; Mp 94-96 °C; IR (ATR) 2951, 2923, 1729, 1719, 1579, 1459, 1254, 1137, 1053, 998, 828, 742, 702, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6 Hz, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.61 (s, 3H), 3.56 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.08, 167.93, 156.31, 140.04, 136.69, 135.31, 133.71, 130.27, 129.90, 129.88, 126.79, 123.36, 122.00, 109.91, 55.99, 51.97, 51.74, 20.12, 16.86; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NaO_5$ 351.1203, found [M+Na] 351.1200.

(**3g**) Dimethyl 3,4-dimethoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



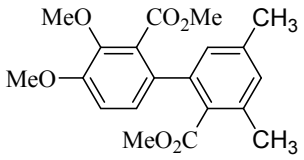
Colorless solid; Yield 91%; Mp 100-103 °C; IR (ATR) 2917, 2849, 1731, 1602, 1568, 1496, 1457, 1436, 1261, 1105, 1054, 795, 743, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19-7.23 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 2H), 3.84 (d, *J* = 4.0 Hz, 6H), 3.52 (d, *J* = 12.8 Hz, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.62, 167.31, 151.90, 146.05, 137.77, 135.63, 133.31, 131.46, 129.41, 128.81, 127.37, 125.32, 112.75, 109.94, 61.68, 55.89, 51.96, 51.71, 19.98; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NaO_6$ 367.1152, found [M+Na] 367.1149.

(**3h**) Dimethyl 3,4-dimethoxy-3',4'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 78%; Mp 152-154 °C; IR (ATR) 2917, 2848, 1731, 1473, 1434, 1274, 1140, 1051, 939, 822, 743, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.92-6.97 (m, 2H), 3.90 (d, *J* = 4.0 Hz, 6H), 3.60 (d, *J* = 22.4 Hz, 6H), 2.27 (d, *J* = 20.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.31, 167.48, 151.84, 146.13, 136.41, 135.07, 133.99, 133.39, 131.40, 130.23, 129.05, 127.11, 125.53, 112.71, 61.68, 55.93, 52.01, 51.78, 20.11, 16.83; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}O_6$ 359.1489, found [M+H] 359.1487.

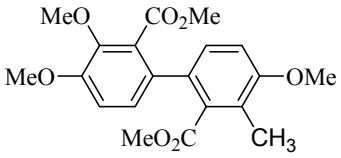
(**3i**) Dimethyl 3,4-dimethoxy-3',5'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 77%; Mp 121-123 °C; IR (ATR) 2941, 2849, 1728, 1600, 1497, 1435, 1261, 1142, 1081, 1056, 932, 872, 834, 741, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.92-6.94 (m, 3H), 3.90 (s, 6H), 3.63 (s, 3H), 3.56 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.75, 167.46, 151.83, 146.09,

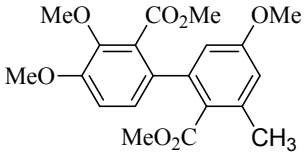
139.03, 138.18, 135.96, 131.87, 130.37, 130.33, 128.74, 128.18, 125.32, 112.87, 61.71, 55.93, 51.97, 51.67, 21.18, 20.12; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}O_6$ 359.1489, found [M+H] 359.1487.

(**3j**) Dimethyl 3,4,4'-trimethoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



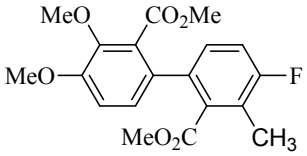
Colorless solid; Yield 45%; Mp 156-158 °C; IR (ATR) 2951, 2359, 1728, 1595, 1475, 1436, 1270, 1244, 1144, 1052, 823, 745, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 1H), 6.94 (q, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.90 (d, *J* = 3.3 Hz, 6H), 3.85 (s, 3H), 3.64 (s, 3H), 3.58 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.58, 167.61, 156.89, 151.75, 145.99, 134.96, 131.15, 129.36, 129.25, 128.21, 125.73, 124.14, 112.77, 110.36, 61.68, 55.92, 55.64, 52.06, 51.83, 13.17; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}O_7$ 375.1438, found [M+H] 375.1441.

(**3k**) Dimethyl 3,4,5'-trimethoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



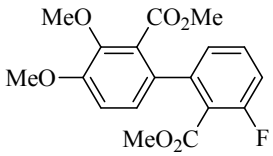
Colorless solid; Yield 57%; Mp 139-141 °C; IR (ATR) 2922, 2850, 2359, 1729, 1598, 1456, 1259, 1204, 1130, 1029, 824, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.64 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 2.0 Hz, 6H), 3.79 (s, 3H), 3.65 (s, 3H), 3.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.58, 167.61, 156.89, 151.75, 145.99, 134.96, 131.21, 129.36, 129.25, 128.21, 125.73, 124.14, 112.77, 110.36, 61.68, 55.92, 55.64, 52.06, 51.83, 13.17; HRMS (ESI) *m/z* calcd for $C_{20}H_{22}NaO_7$ 397.1258, found [M+ Na] 397.1250.

(**3l**) Dimethyl 4-fluoro-3',4'-dimethoxy-3-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



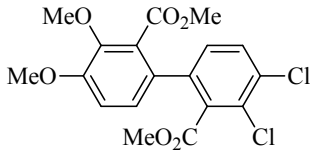
Colorless solid; Yield 60%; Mp 99-101 °C; IR (ATR) 2950, 2848, 1738, 1731, 1574, 1694, 1568, 1416, 1258, 1030, 818, 742, 673 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.02 (m, 2H), 6.96–6.91 (m, 2H), 3.90 (d, *J* = 1.6 Hz, 6H), 3.63 (s, 3H), 3.59 (s, 3H), 2.28 (d, *J* = 2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.46, 167.27, 161.55, 159.11, 152.11, 146.23, 135.55, 133.61, 130.51, 128.94 (d, *J* = 10.3 Hz), 125.52, 122.94 (d, *J* = 18.8 Hz), 115.77, 115.66 (d, *J* = 22.9 Hz), 61.70, 55.93, 52.05, 51.98, 11.95, 11.90; ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.97 (s); HRMS (ESI) *m/z* calcd for $C_{19}H_{19}FNaO_6$ 385.1058, found [M+Na] 385.1058.

(**3m**) Dimethyl 3'-fluoro-3,4-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



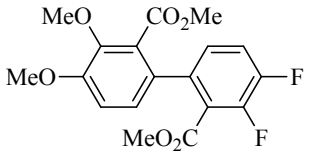
Colorless solid; Yield 73%; Mp 119-121 °C; IR (ATR) 2917, 2848, 1733, 1600, 1567, 1499, 1457, 1261, 1142, 1081, 1056, 932, 872, 834, 741, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.14–7.06 (m, 2H), 6.97 (s, 2H), 3.91 (s, 6H), 3.67 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.09, 165.40, 161.09, 158.58, 152.38, 146.30, 140.65, 131.00 (d, *J* = 9.1 Hz), 130.05 (d, *J* = 2.4 Hz), 128.69, 125.67 (d, *J* = 71.4 Hz), 121.56 (d, *J* =15.4 Hz), 121.48, 115.11 (d, *J* = 21.7 Hz), 113.04, 61.73, 55.94, 52.32, 52.08; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.99 (s); HRMS (ESI) *m/z* calcd for $C_{18}H_{17}FNaO_6$ 371.0901, found [M+ Na] 371.0900.

(**3n**) Dimethyl 3,4-dichloro-3',4'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



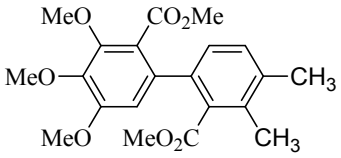
Colorless solid; Yield 52%; Mp 135-137 °C; IR (ATR) 2923, 2359, 1733, 1458, 1262, 1241, 1146, 1113, 1047, 1008, 824, 742, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.99–6.94 (m, 2H), 3.91 (s, 6H), 3.66 (d, *J* = 3.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 166.37, 152.78, 137.50, 135.35, 132.54, 130.35, 129.30, 128.91, 128.57, 125.54, 118.97, 112.94, 109.98, 61.75, 55.95, 52.58, 52.23; HRMS (ESI) *m/z* calcd for $C_{18}H_{17}Cl_2O_6$ 399.0397, found [M+ H] 399.0396.

(**3o**) Dimethyl 3,4-difluoro-3',4'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



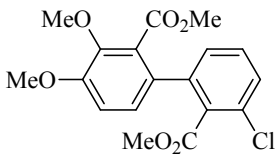
Colorless solid; Yield 60%; Mp 86-87 °C; IR (ATR) 2360, 2341, 1733, 1723, 1481, 1292, 1275, 1146, 1054, 1033, 817, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 1H), 7.03 (m, 1H), 6.95 (m, 2H), 3.91 (d, *J* = 2.8 Hz, 6H), 3.67 (d, *J* = 20.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.04, 164.27 (d, *J* = 2.9 Hz), 152.49, 149.31 (d, *J* = 13.4 Hz), 148.53 (d, *J* = 10.9 Hz), 146.78 (d, *J* = 13.1 Hz), 146.28, 135.53 (d, *J* = 4.0 Hz), 128.99 (d, *J* = 46.5 Hz), 126.22 (t, *J* = 4.8 Hz), 125.48, 123.45 (d, *J* = 11.8 Hz), 118.25 (d, *J* = 16.9 Hz), 113.02, 61.71, 55.93, 52.58, 52.17; ^{19}F NMR (377 MHz, $CDCl_3$) δ -137.63 (s), -138.13 (s); HRMS (ESI) *m/z* calcd for $C_{18}H_{16}F_2KO_6$ 405.0547, found [M+ K] 405.0534.

(**3p**) Dimethyl 3,4,5-trimethoxy-3',4'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless oil; Yield 75%; IR (ATR) 2941, 2850, 1735, 1719, 1594, 1459, 1278, 1048, 929, 801, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 3.60 (d, *J* = 3.6 Hz, 6H), 2.31 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.25, 167.29, 153.83, 151.40, 141.20, 136.63, 135.61, 135.11, 133.72, 133.54, 130.30, 126.82, 121.31, 109.28, 61.94, 60.96, 56.09, 51.93, 51.84, 20.11, 16.81; HRMS (ESI) *m/z* calcd for $C_{21}H_{25}O_7$ 389.1595, found [M+H] 389.1591.

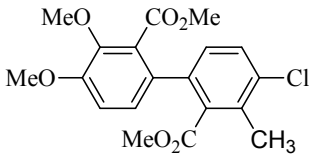
(**3q**) Dimethyl 3'-chloro-3,4-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 52%; Mp 118-120 °C; IR (ATR) 2941, 2839, 2359, 1731, 1717, 1593, 1490, 1426, 1278, 1259, 1097, 1012, 823, 732, 682 cm^{-1}; ^{1}H NMR (400 MHz,

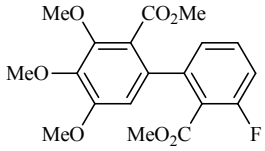
$CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.98 (q, *J* = 8.4 Hz, 2H), 3.91 (d, *J* = 2 Hz, 6H), 3.66 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.09, 167.05, 152.55, 146.32, 139.41, 133.43, 131.09, 129.76, 129.60, 128.92, 128.59, 128.38, 125.48, 112.94, 61.76, 55.94, 52.36, 52.15; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}ClO_6$ 365.0786, found [M+ H] 365.0783.

(**3r**) Dimethyl 4-chloro-3',4'-dimethoxy-3-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



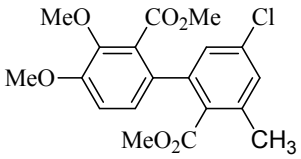
Colorless solid; Yield 55%; Mp 126-128 °C; IR (ATR) 2940, 2849, 1733, 1722, 1548, 1498, 1434, 1393, 1249, 1098, 1020, 830, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.94 (s, 2H), 3.90 (d, *J* = 2.4 Hz, 6H), 3.64 (s, 3H), 3.59 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.88, 167.15, 152.28, 146.31, 136.16, 135.56, 134.32, 133.22, 130.18, 129.52, 128.96, 128.52, 125.42, 112.90, 61.70, 55.94, 52.08, 52.03, 17.52; HRMS (ESI) *m/z* calcd for $C_{19}H_{19}ClNaO_6$ 401.0762, found [M+Na] 401.0760.

(**3s**) Dimethyl 3'-fluoro-3,4,5-trimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



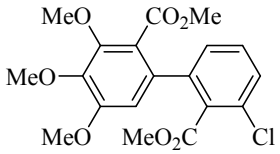
Colorless oil; Yield 66%; IR (ATR) 2927, 2849, 1725, 1611, 1566, 1450, 1399, 1351, 1264, 1146, 1108, 1044, 987, 815, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.38 (m, 1H), 7.16–7.08 (m, 2H), 6.57 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.86 (s, 3H), 3.70 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.88, 165.35, 160.86, 154.13, 151.57, 158.47, 141.38 (d, *J* = 64.4 Hz), 133.83, 131.07 (d, *J* = 9.0 Hz), 125.65 (d, *J* = 3.3 Hz), 121.21 (d, *J* = 43.8 Hz), 115.27 (d, *J* = 24.9 Hz), 108.94, 62.00, 61.00, 56.16, 52.41, 52.02; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.01 (s); HRMS (ESI) *m/z* calcd for $C_{19}H_{19}FNaO_7$ 401.1007, found [M+Na] 401.1007.

(**3t**) Dimethyl 5'-chloro-3,4-dimethoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



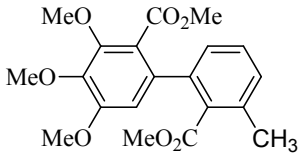
Colorless solid; Yield 35%; Mp 123-125 °C; IR (ATR) 2951, 2362, 1734, 1603, 1497, 1435, 1249, 1100, 1052, 1013, 939, 847, 730, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8 Hz, 1H), 6.94 (s, 2H), 3.90 (s, 6H), 3.62 (d, *J* = 21.2 Hz, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.94, 167.19, 152.27, 146.26, 136.14, 135.52, 134.32, 133.24, 130.04, 129.54, 128.93, 128.50, 125.42, 112.85, 61.73, 55.93, 52.14, 52.09, 17.56; HRMS (ESI) *m/z* calcd for $C_{19}H_{19}ClNaO_6$ 401.7062, found [M+ Na] 401.7052.

(**3u**) Dimethyl 3'-chloro-3,4,5-trimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 54%; Mp 74-75 °C; IR (ATR) 2949, 2359, 1729, 1557, 1434, 1347, 1256, 1137, 1034, 916, 718, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.00 – 3.81 (m, 9H), 3.68 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 166.79, 154.11, 151.75, 141.87, 139.88, 133.40, 133.12, 131.08, 129.80, 128.71, 128.05, 121.17, 109.19, 62.00, 60.98, 56.16, 52.40, 52.01; HRMS (ESI) *m/z* calcd for $C_{19}H_{19}ClNaO_7$ 417.0712, found [M+Na] 417.0708.

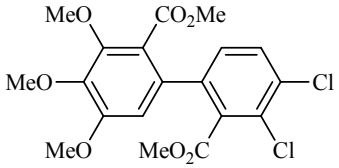
(**3v**) Dimethyl 3,4,5-trimethoxy-3'-methyl-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless oil; Yield 60%; IR (ATR) 2945, 2846, 1723, 1568, 1496, 1429, 1397, 1347, 1265, 1219, 1107, 1027, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.84 (s, 3H), 3.60 (d, *J* = 6.0 Hz, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.62, 167.18, 153.93, 151.47, 141.29, 138.37, 135.71, 135.26, 133.02,

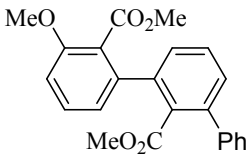
129.63, 128.99, 127.08, 121.14, 109.05, 77.36, 77.04, 76.72, 61.98, 60.99, 56.12, 51.94, 51.85, 19.98; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}O_7$ 375.1438, found [M+H] 375.1442.

(**3w**) Dimethyl 3',4'-dichloro-3,4,5-trimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



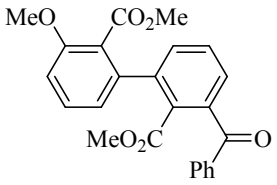
Colorless solid; Yield 44%; Mp 90-92 °C; IR (ATR) 2941, 2849, 1732, 1721, 1589, 1393, 1343, 1280, 1097, 1022, 831, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 3.93 (d, *J* = 14.6 Hz, 6H), 3.84 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H), -0.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.72, 166.30, 154.35, 151.91, 142.05, 137.93, 134.99, 132.69, 132.42, 130.40, 129.44, 128.97, 121.13, 109.22, 62.01, 60.99, 56.18, 52.64, 52.14; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}Cl_2NaO_7$ 451.0322, found [M+Na] 451.0324.

(**3x**) Dimethyl 3-methoxy-[1,1':3',1''-terphenyl]-2,2'-dicarboxylate



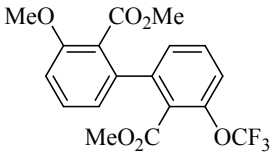
Colorless solid; Yield 57%; Mp 142-143 °C; IR (ATR) 2948, 2839, 1724, 1574, 1435, 1110, 1087, 1063, 829, 797, 701, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 3H), 7.37–7.24 (m, 4H), 6.93 (dd, *J* = 14.0, 8.4 Hz, 2H), 3.89 (s, 3H), 3.59 (s, 3H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.14, 167.71, 156.52, 140.64, 140.48, 139.80, 138.41, 132.71, 130.10, 129.26, 128.93, 128.63, 128.36, 128.30, 127.50, 123.26, 122.04, 110.38, 56.02, 51.99, 51.68; HRMS (ESI) *m/z* calcd for $C_{23}H_{24}NO_5$ 394.1649, found [$M+NH_4$] 394.1632.

(**3y**) Dimethyl 3'-benzoyl-3-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate



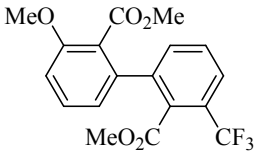
Colorless solid; Yield 41%; Mp 155-156 °C; IR (ATR) 3007, 2949, 1729, 1671, 1577, 1451, 1255, 1118, 1051, 964, 873, 762, 725, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.60–7.37 (m, 7H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.58 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.32, 167.54, 167.26, 156.47, 140.00, 139.58, 139.50, 136.94, 133.17, 132.49, 131.79, 130.30, 129.76, 129.55, 128.49, 128.25, 122.84, 121.88, 110.47, 56.03, 51.99; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}O_6$ 405.1333, found [M+H] 405.1330.

(**3z**) Dimethyl 3-methoxy-3'-(trifluoromethoxy)-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 50%; Mp 96-98 °C; IR (ATR) 2964, 2842, 1728, 1577, 1463, 1431, 1289, 1212, 1150, 1117, 1060, 880, 786, 717, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.65 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.31, 165.41, 156.64, 146.09 (d, *J* = 1.7 Hz), 140.57, 138.34, 130.37 (d, *J* = 2.5 Hz), 128.23, 127.16, , 123.00, 121.75, 120.41 (q, *J* = 257.2 Hz), 119.92, 110.95, 56.06, 52.32, 51.98; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.22 (s); HRMS (ESI) *m/z* calcd for $C_{18}H_{15}F_3NaO_6$ 407.0713, found [M+ Na] 407.0721.

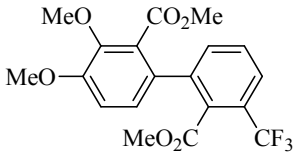
(**3za**) Dimethyl 3-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2,2'-dicarboxylate



Colorless solid; Yield 67%; Mp 84-86 °C; IR (ATR) 2958, 2845, 1734, 1720, 1580, 1431, 1288, 1139, 1123, 1066, 1031, 822, 791, 731, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 1H), 7.56–7.48 (m, 2H), 7.40–7.36 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 3.62 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.24, 167.03, 156.73, 139.16, 138.15, 133.34, 131.59, 130.34, 129.00, 127.78 (q, *J* = 31.9 Hz), 125.48 (q, *J* = 4.6 Hz), 123.42 (q, *J* = 272.1

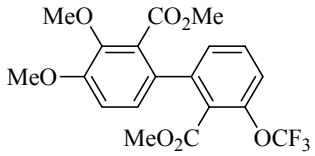
Hz), 123.30, 121.93, 111.05, 56.07, 52.45, 52.00; ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.72, HRMS (ESI) *m/z* calcd for $C_{18}H_{16}F_3O_5$ 369.0944, found [M+ H] 369.0941.

(**3zb**) Dimethyl 3,4-dimethoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2,2'-dicarboxylate



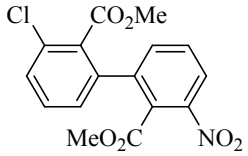
Colorless solid; Yield 54%; Mp 108-109 °C; IR (ATR) 2952, 2843, 1793, 1735, 1599, 1458, 1430, 1295, 1124, 1014, 802, 744, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.56–7.46 (m, 2H), 7.02–6.92 (m, 2H), 3.92 (s, 6H), 3.61 (d, *J* = 14 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.26 (d, *J* = 3.6 Hz), 166.88 (d, *J* = 2.4 Hz), 152.69, 146.56, 138.94, 133.76, 131.86, 129.29 (d, *J* = 1.9 Hz), 128.93 (t, *J* = 2.9 Hz), 127.65 (q, *J* = 34.0 Hz), 125.67, 125.27 (d, *J* = 4.4 Hz), 123.48 (q, *J* = 278.4 Hz), 114.83, 112.95, 61.73, 55.94, 52.44, 52.01; ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.76 (s); HRMS (ESI) *m/z* calcd for $C_{19}H_{18}F_3O_6$ 399.1050, found [M+H] 399.1053.

(**3zc**) Dimethyl3,4-dimethoxy-3'-(trifluoromethoxy)-[1,1'-biphenyl]-2,2'-dicarboxylate



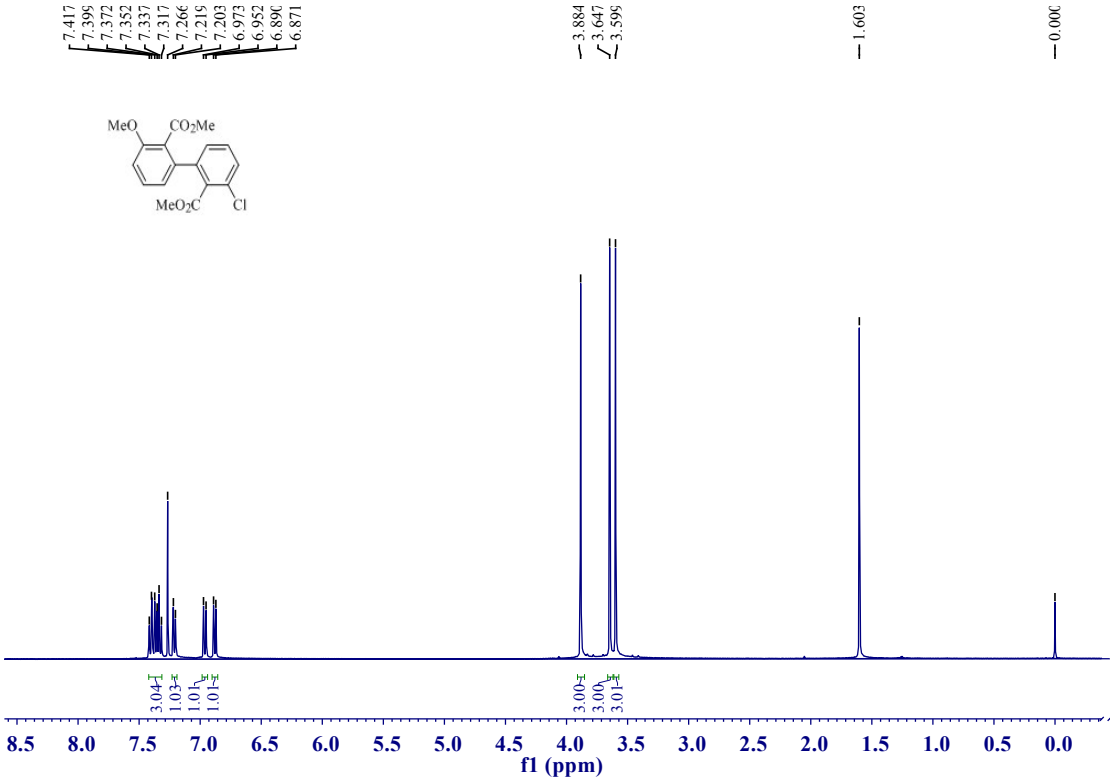
Colorless solid; Yield 39%; Mp 64-65 °C; IR (ATR) 2922, 2359, 1739, 1608, 1461, 1243, 1168, 1051, 1034, 960, 826, 799, 744, 643 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 6H), 3.66 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.94, 165.63, 152.58, 146.45, 146.00, 140.34, 130.24, 129.59, 128.77, 128.59, 127.44, 125.44, 120.37 (q, *J* = 256.2 Hz), 119.64, 113.05, 61.75, 55.94, 52.32, 52.02; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.22 (s); HRMS (ESI) *m/z* calcd for $C_{19}H_{18}F_3O_7$ 415.0999, found [M+H] 415.0993.

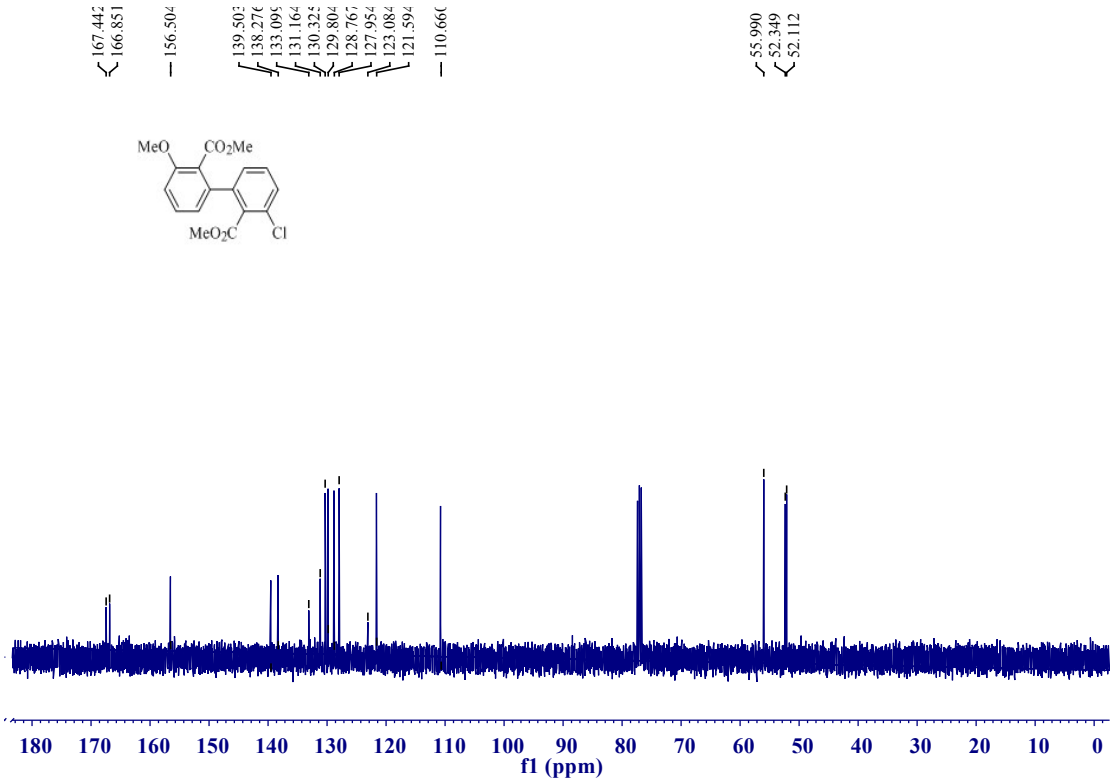
(**3zd**) Dimethyl 3-chloro-3'-nitro-[1,1'-biphenyl]-2,2'-dicarboxylate

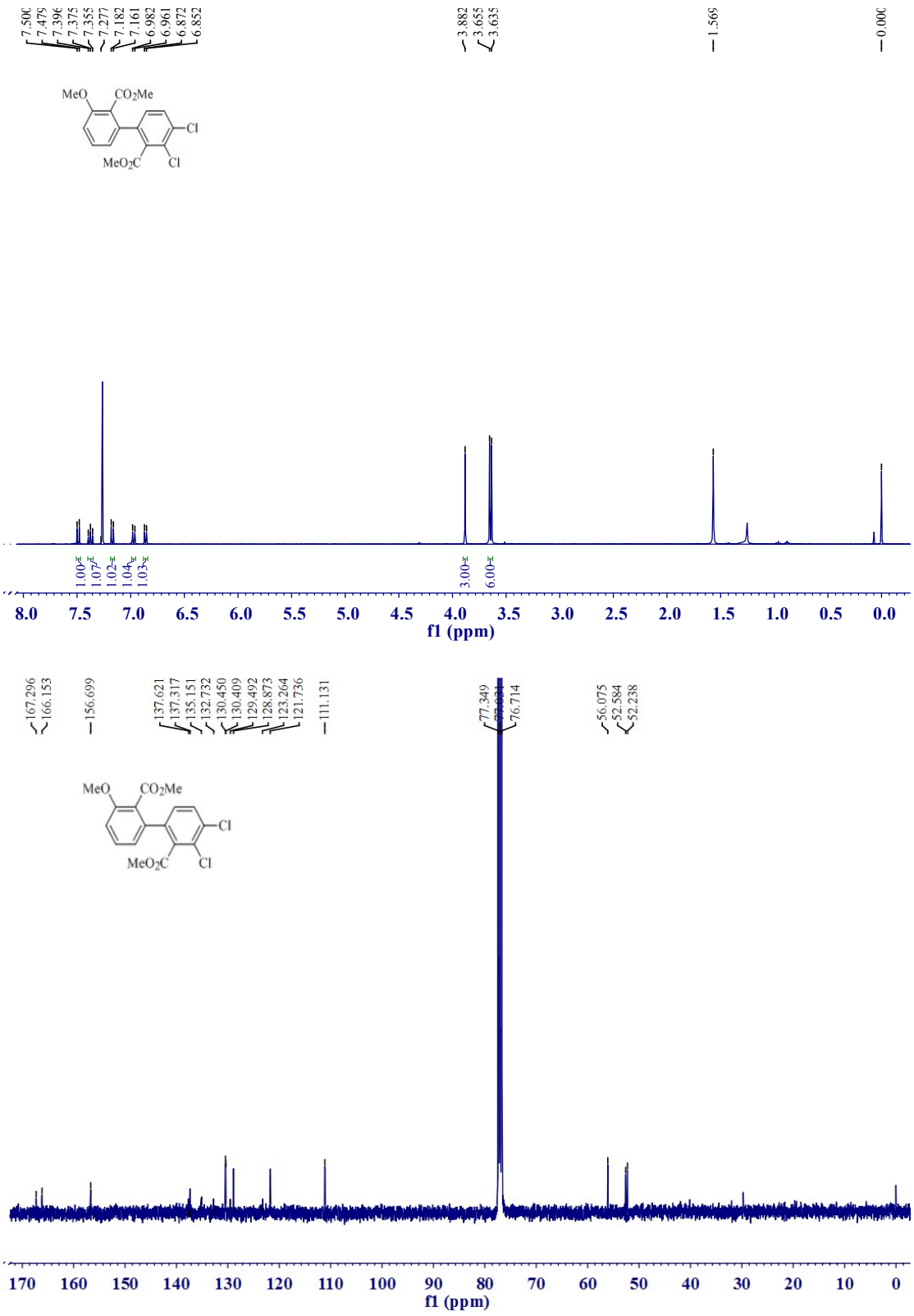


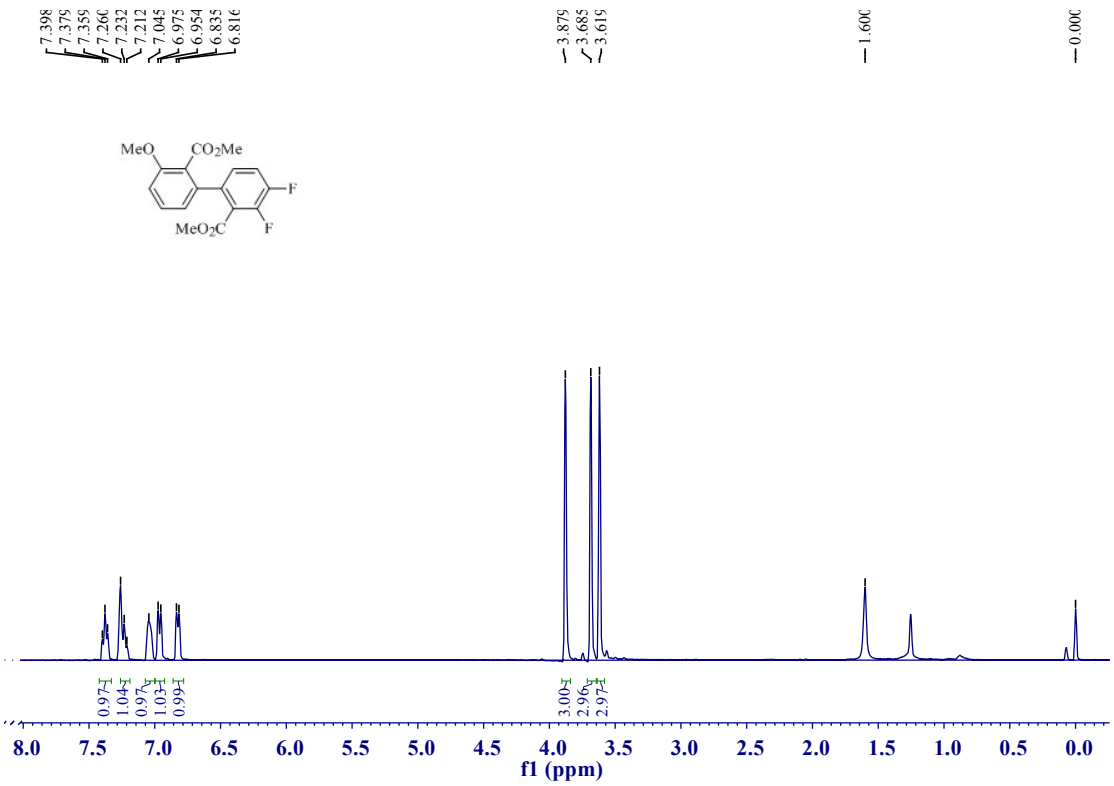
Colorless solid; Yield 45%; Mp 93-95 °C; IR (ATR) 2958, 2363, 1736, 1719, 1531, 1422, 1360, 1276, 1119, 1061, 952, 182, 696, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.60 (m, 1H), 7.50 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.24 (m, 1H), 3.69 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.23, 165.38, 146.39, 139.03, 137.20, 135.55, 133.25, 131.81, 130.06, 129.55, 129.16, 128.40, 123.99, 53.03, 52.46; HRMS (ESI) *m/z* calcd for $C_{16}H_{12}ClNNaO_6$ 372.0245, found [M+Na] 372.0248.

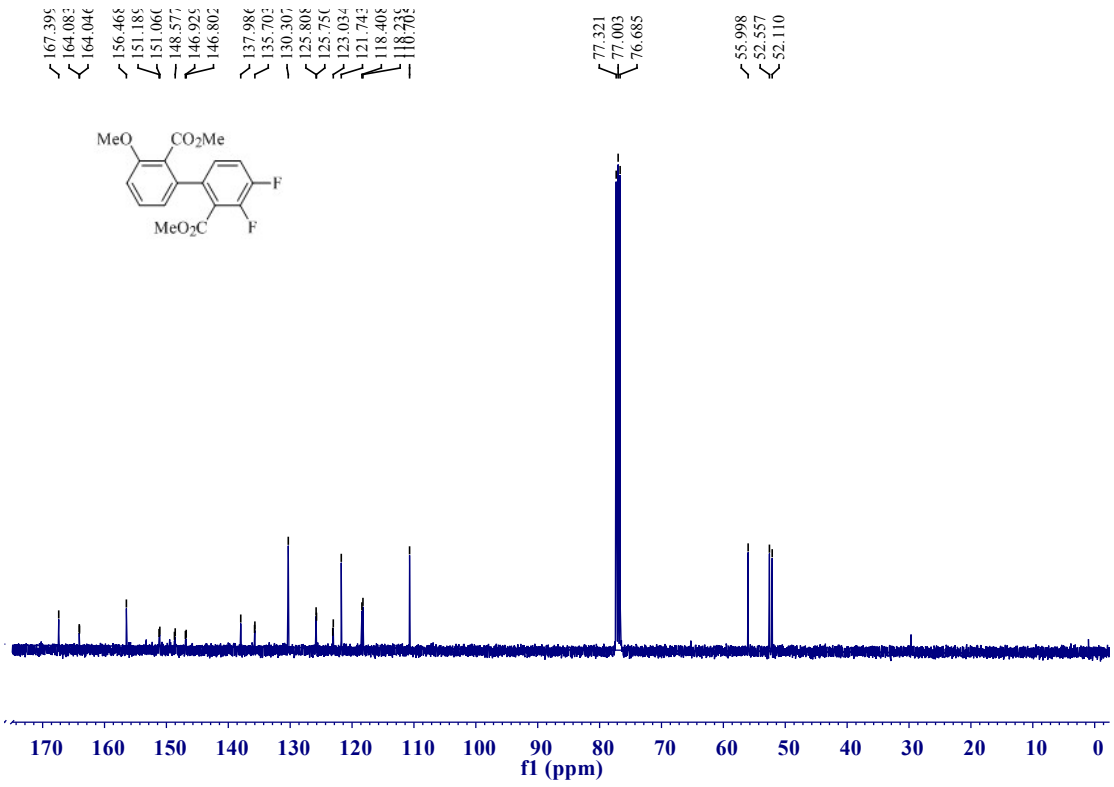
5. Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra.

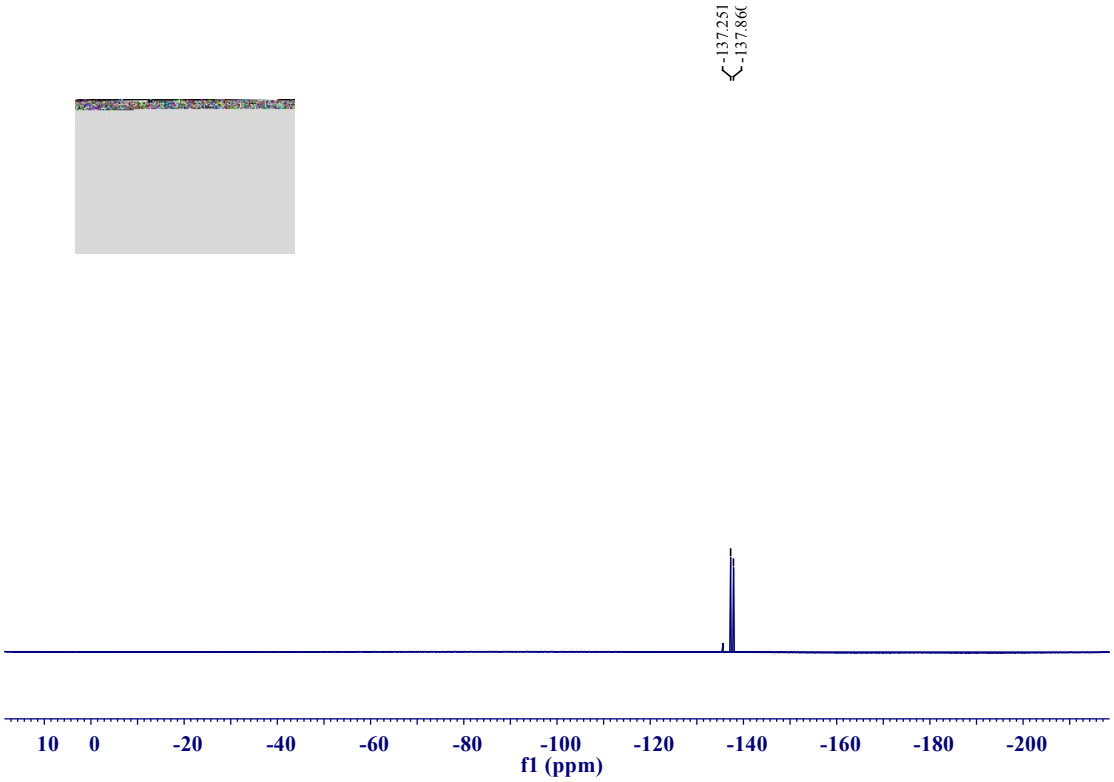


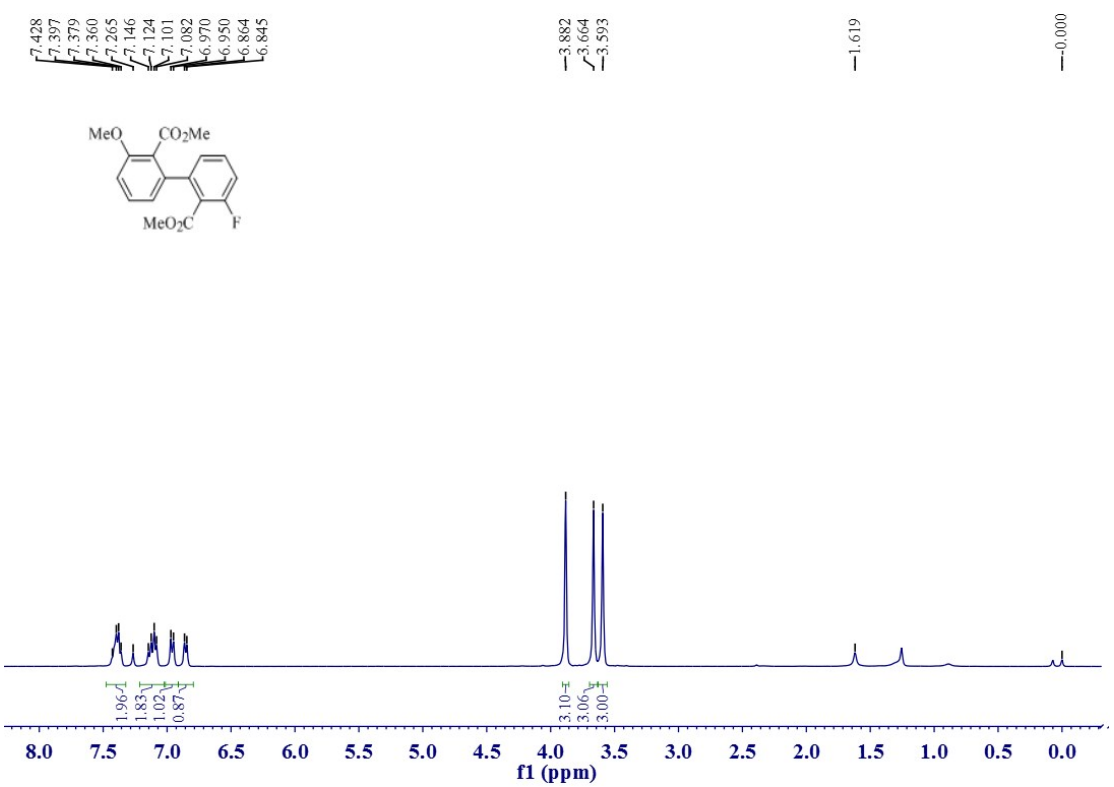


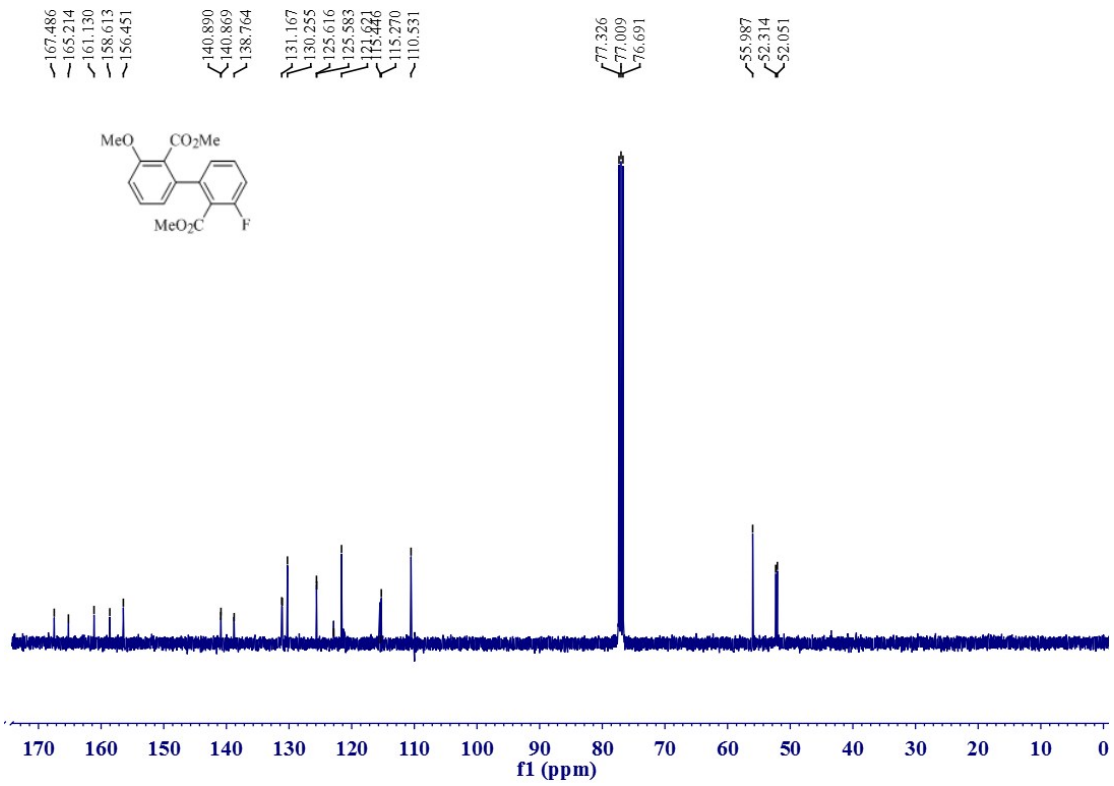

7.500
7.479
7.396
7.375
7.355
7.277
7.182
7.161
6.982
6.961
6.872
6.852
3.882
3.655
3.635
1.569
0.000
MeO
CO2Me
Cl
MeO2C
Cl
1.00
1.07
1.02
1.04
1.03
3.00
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
167.296
166.153
156.699
137.621
137.317
135.151
132.732
130.450
130.409
129.492
128.873
123.264
121.736
111.131
77.349
77.031
76.714
56.075
52.584
52.238
MeO
CO2Me
Cl
MeO2C
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

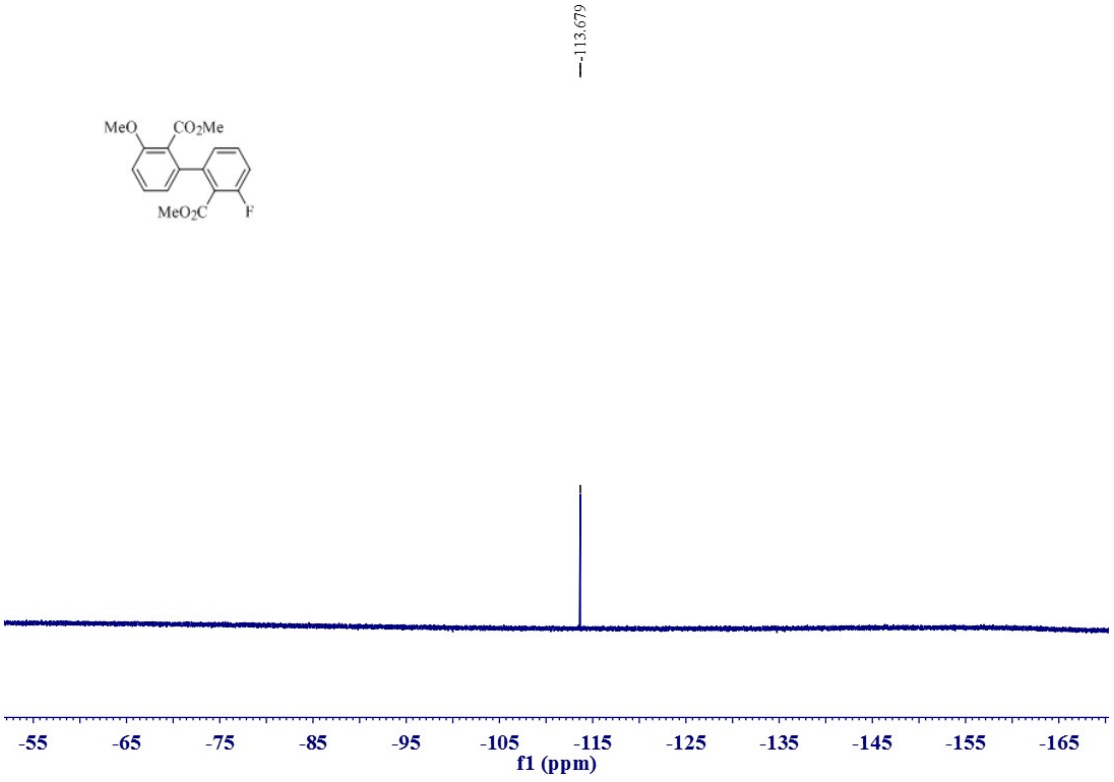

MeO
CO2Me
F
MeO2C
F
f1 (ppm)

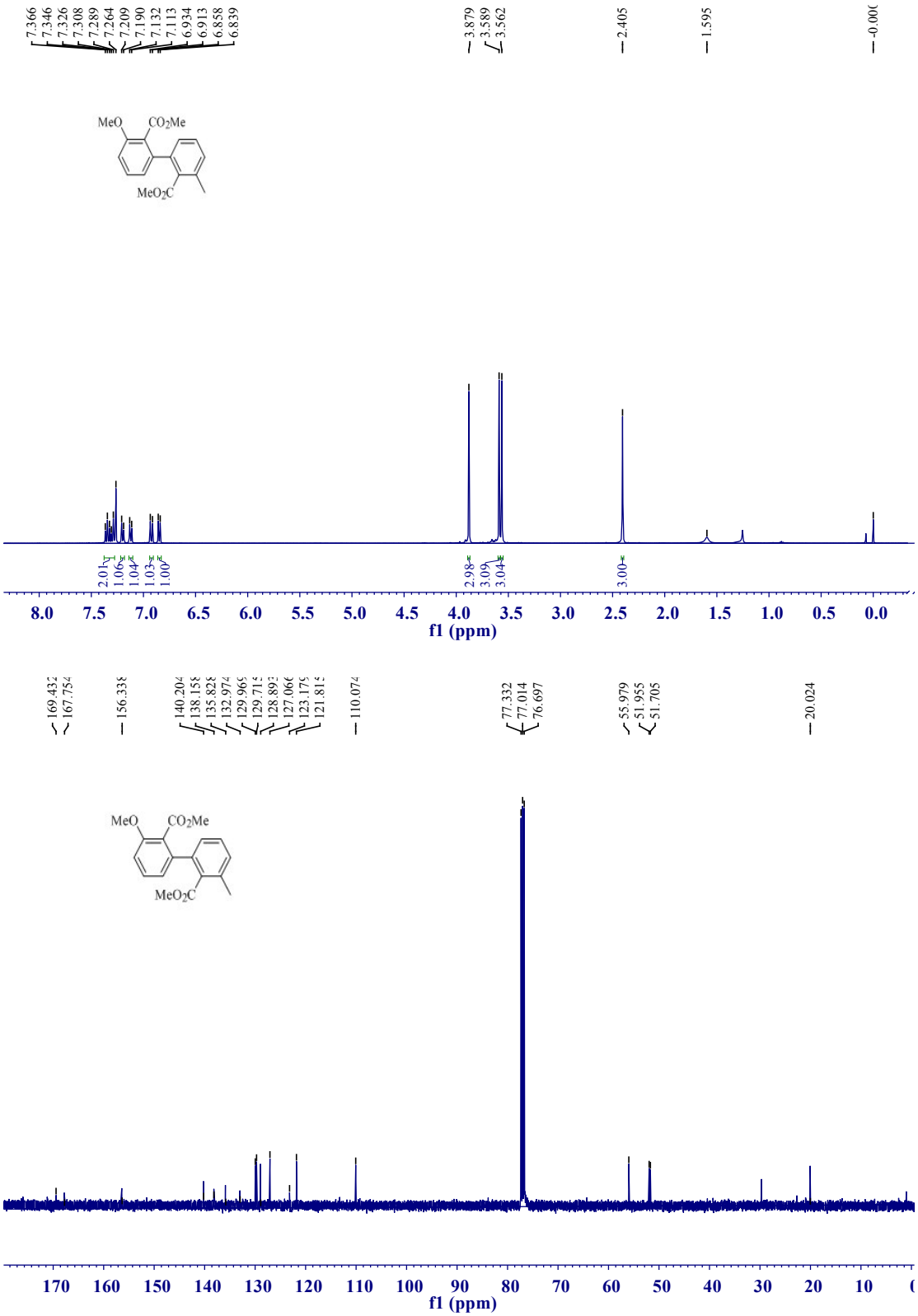

MeO
CO2Me
F
MeO2C
F
f1 (ppm)

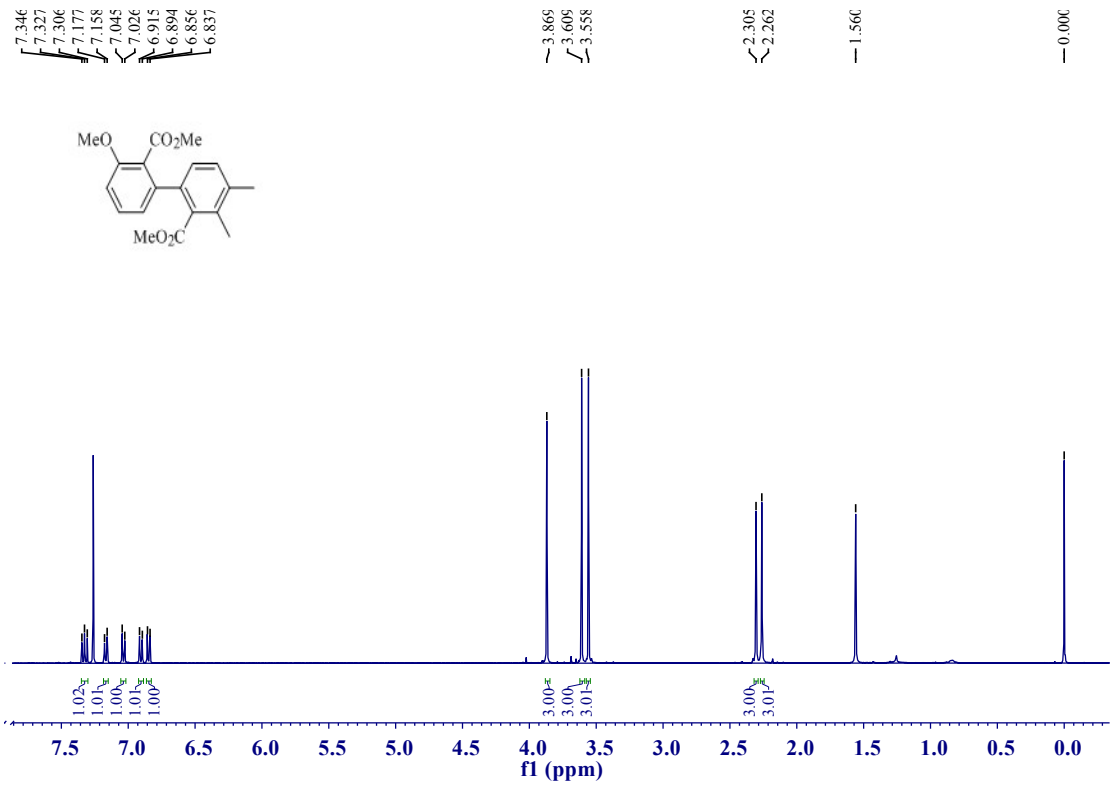

-137.251
-137.866
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

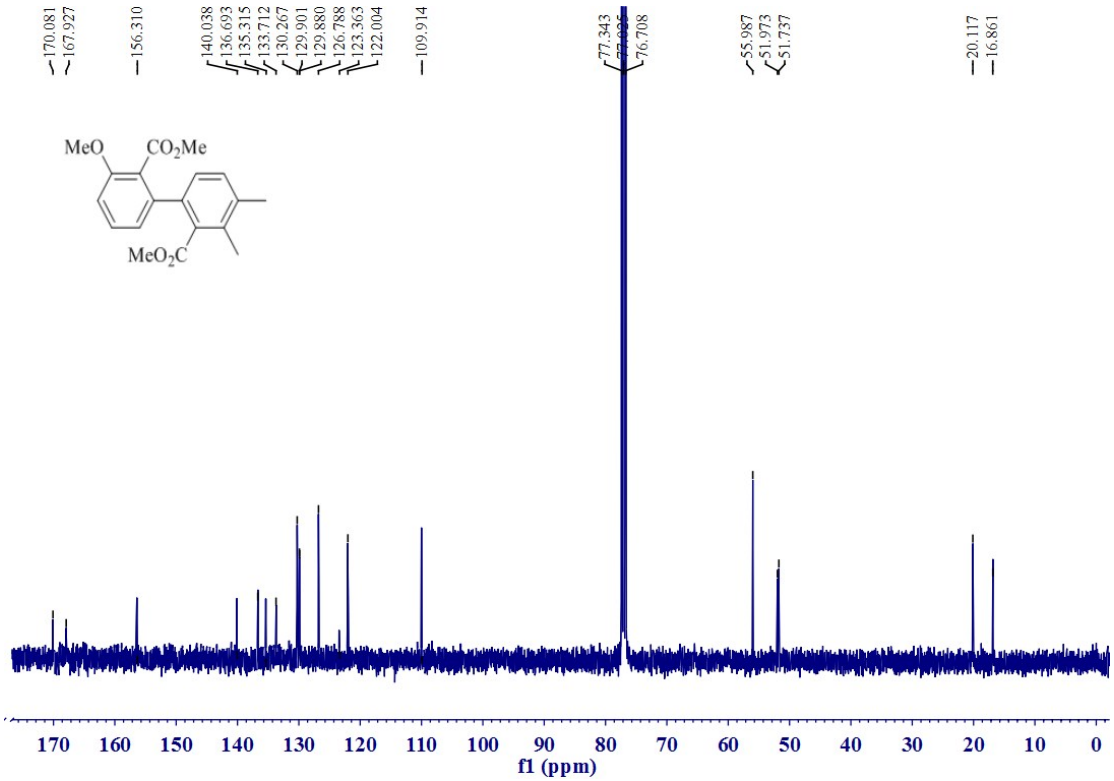

7.428
7.397
7.379
7.360
7.265
7.146
7.124
7.101
7.082
6.970
6.950
6.864
6.845
3.882
3.664
3.593
1.619
0.000
MeO
CO2Me
MeO2C
F
1.96
1.83
1.02
0.87
3.10
3.06
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

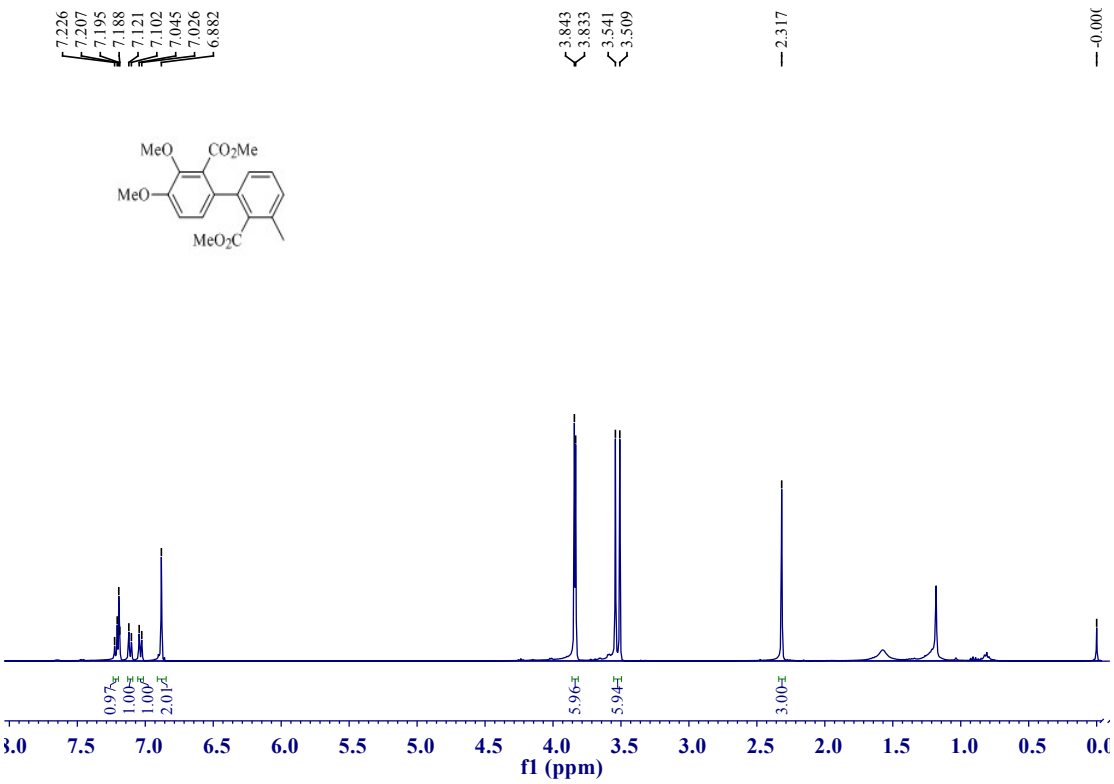

167.486
165.214
161.130
158.613
156.451
140.890
140.869
138.764
131.167
130.255
125.616
125.583
121.621
115.446
115.270
110.531
77.326
77.009
76.691
55.987
52.314
52.051
MeO
CO2Me
MeO2C
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

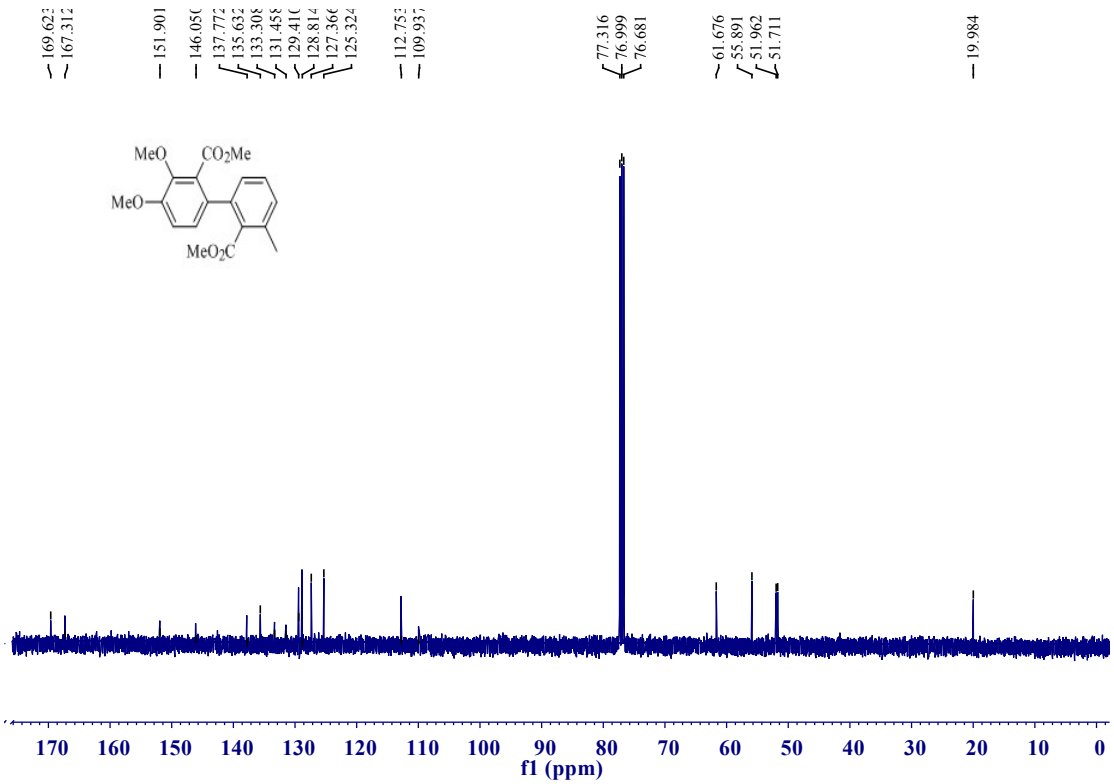

-113.679
MeO
CO2Me
MeO2C
F
-55 -65 -75 -85 -95 -105 -115 -125 -135 -145 -155 -165
f1 (ppm)


7.366
7.346
7.326
7.308
7.289
7.264
7.209
7.190
7.132
7.113
6.934
6.913
6.858
6.839
3.879
3.589
3.562
2.405
1.595
MeO
CO2Me
MeO2C
2.01
1.06
1.04
1.03
1.00
2.98
3.09
3.04
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
169.432
167.754
156.338
140.204
138.158
135.828
132.974
129.965
129.715
128.893
127.066
123.175
121.815
110.074
77.332
77.014
76.697
55.979
51.955
51.705
20.024
MeO
CO2Me
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


MeO
CO2Me
MeO2C
f1 (ppm)


MeO
CO2Me
MeO2C
f1 (ppm)


7.226
7.207
7.195
7.188
7.121
7.102
7.045
7.026
6.882
3.843
3.833
3.541
3.509
2.317
MeO
CO2Me
MeO
MeO2C
0.97
1.00
1.00
2.01
5.96
5.94
3.00
f1 (ppm)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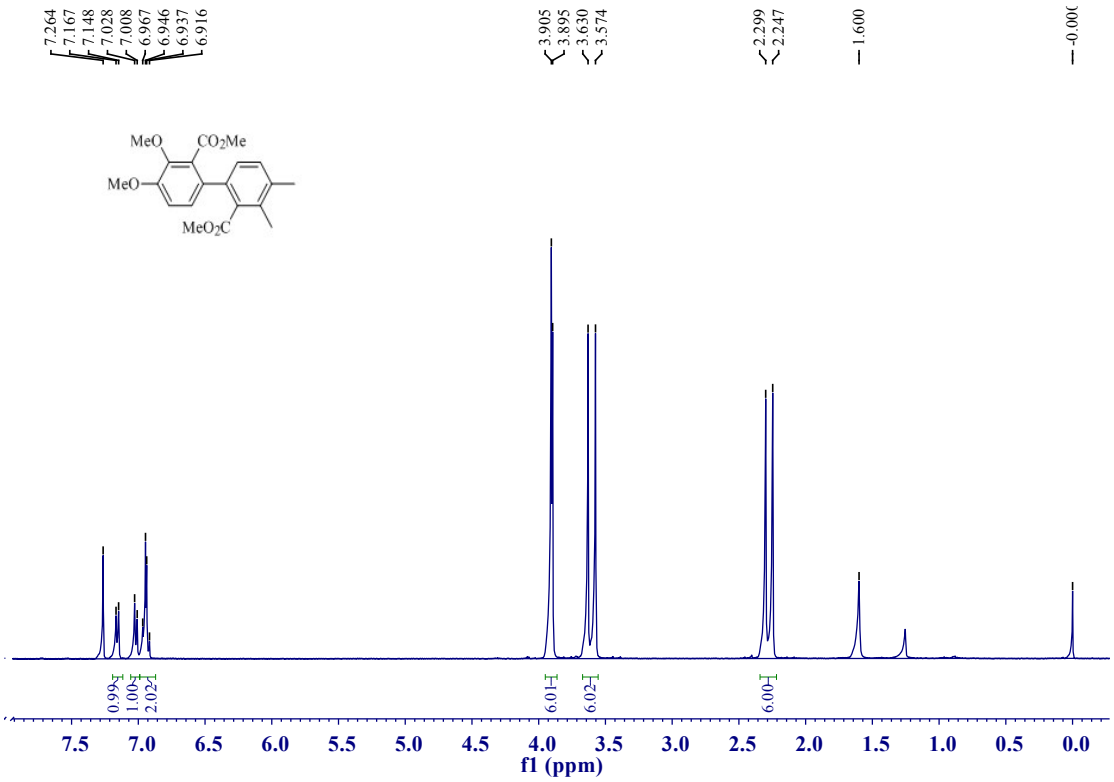
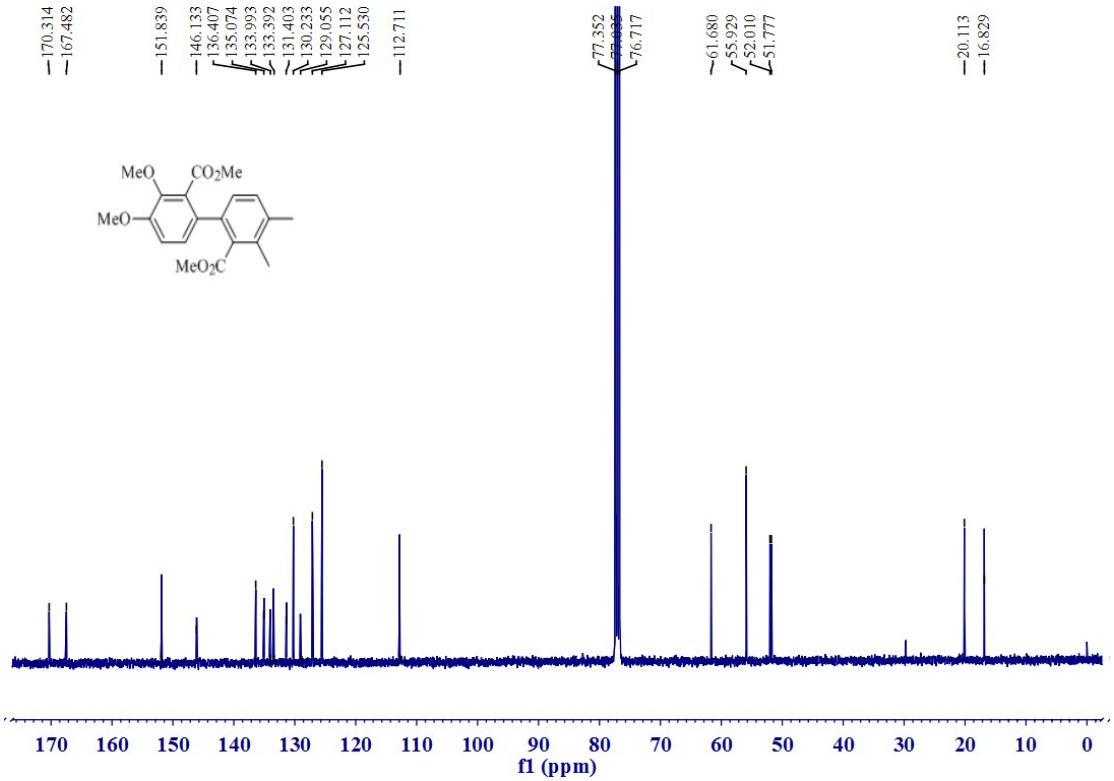
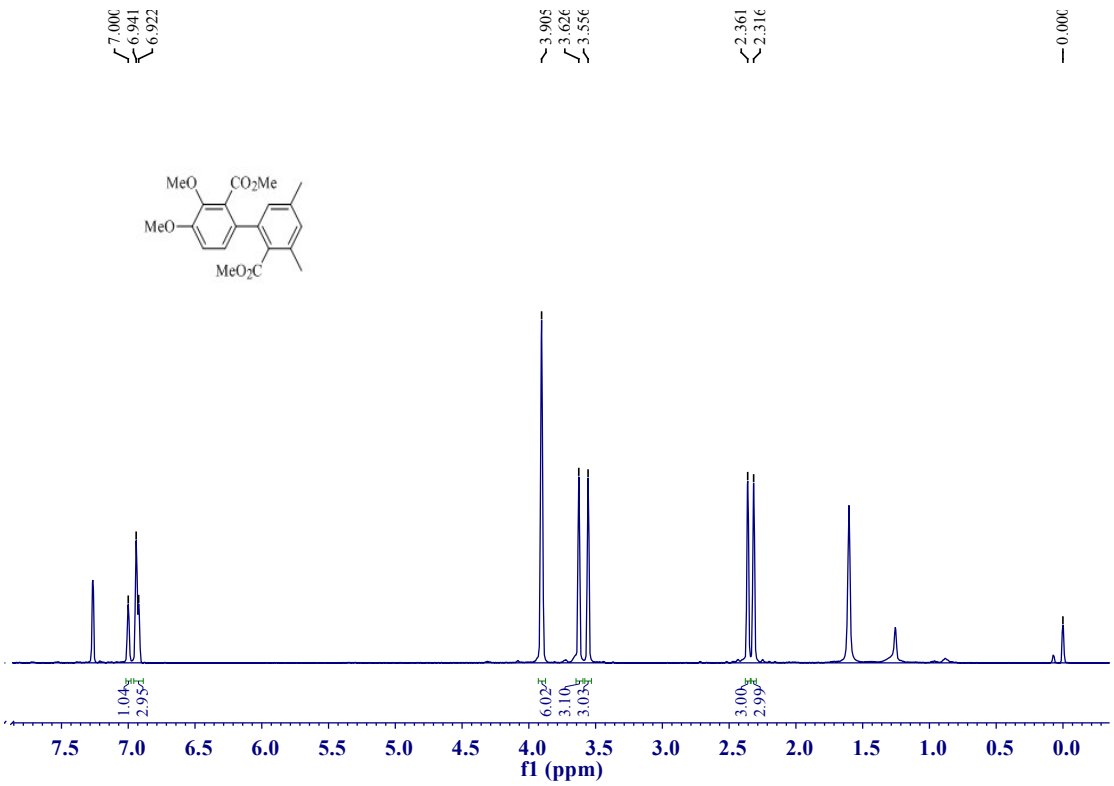
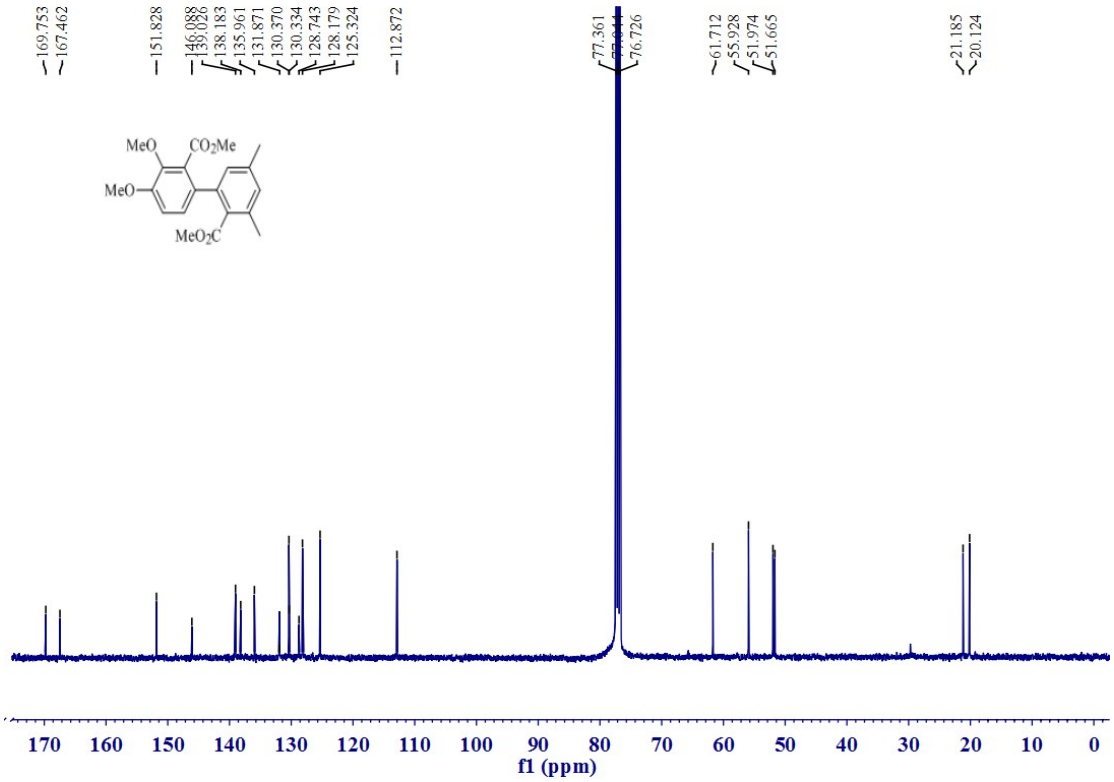
167.312
151.901
146.050
137.772
135.632
133.308
131.458
129.410
128.814
127.366
125.324
112.753
109.935
77.316
76.999
76.681
61.676
55.891
51.962
51.711
19.984
MeO
CO2Me
MeO
MeO2C
f1 (ppm)


7.264
7.167
7.148
7.028
7.008
6.967
6.946
6.937
6.916
3.905
3.895
3.630
3.574
2.299
2.247
1.600
MeO
CO2Me
MeO
MeO2C
0.99
1.00
2.02
6.01
6.02
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.314
167.482
151.839
146.133
136.407
135.074
133.993
133.392
131.403
130.233
129.055
127.112
125.530
112.711
77.352
77.035
76.717
61.680
55.929
52.010
51.777
20.113
16.829
MeO
CO2Me
MeO
MeO2C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.000
6.941
6.922
3.905
3.626
3.556
2.361
2.316
0.000
MeO
CO2Me
MeO
MeO2C
1.04
2.95
6.02
3.10
3.03
3.00
2.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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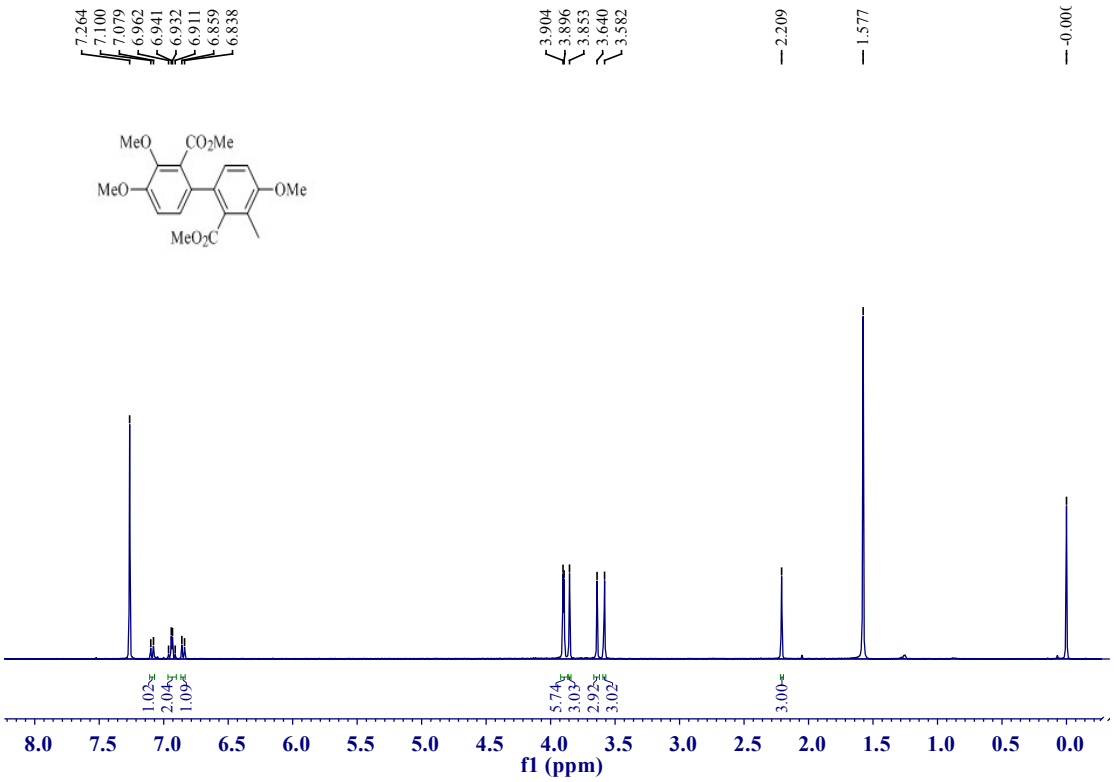
151.828
146.088
139.026
138.183
135.961
131.871
130.370
130.334
128.743
128.179
125.324
112.872
77.361
77.044
76.726
61.712
55.928
51.974
51.665
21.185
20.124
MeO
CO2Me
MeO
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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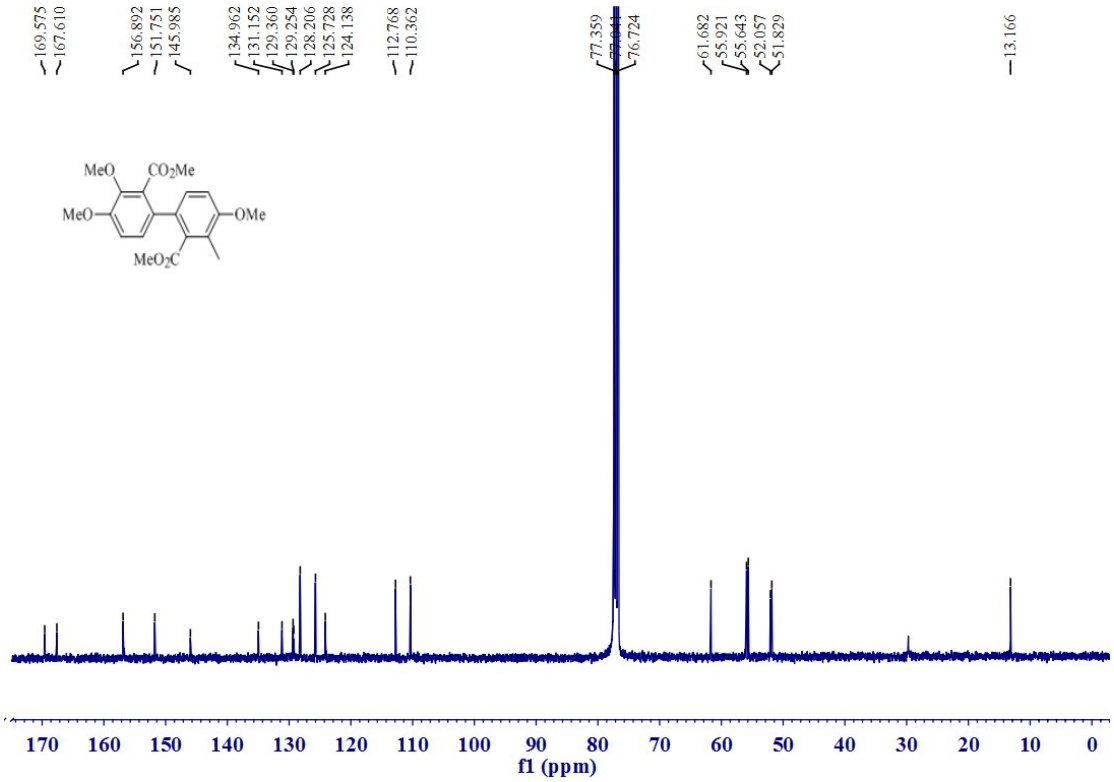
7.100
7.079
6.962
6.941
6.932
6.911
6.859
6.838
3.904
3.896
3.853
3.640
3.582
2.209
1.577
MeO
CO2Me
MeO
OMe
MeO2C
1.02
2.04
1.09
5.74
3.03
2.92
3.02
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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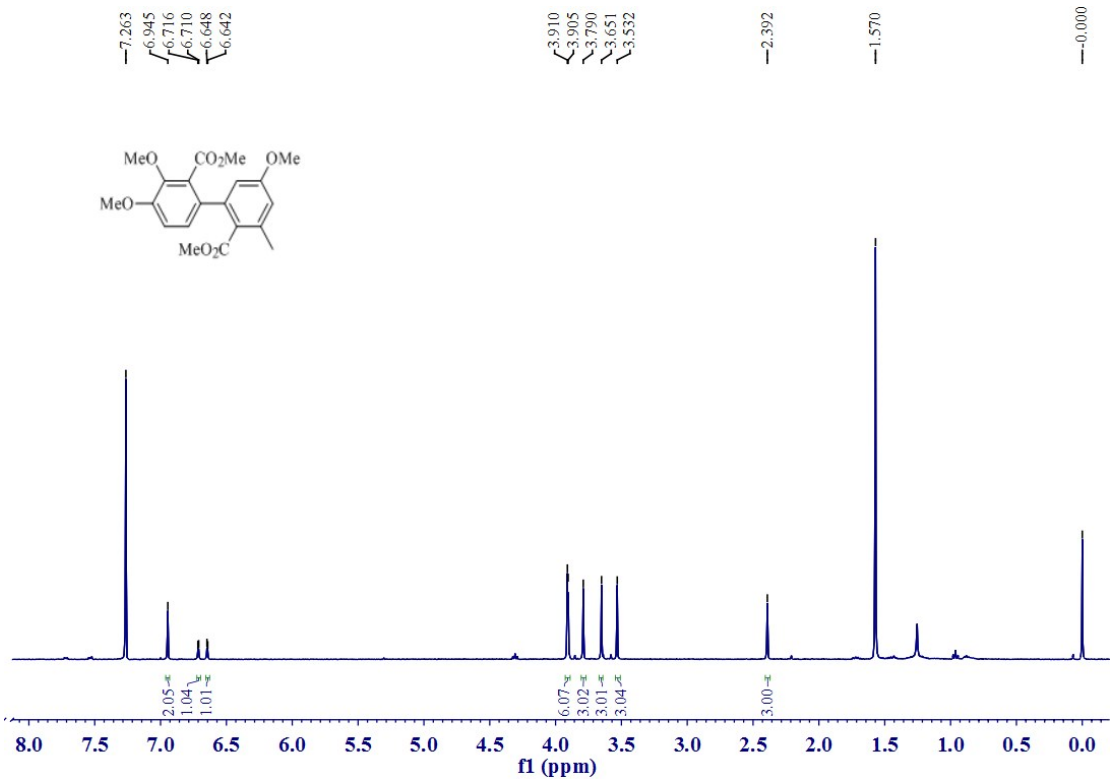
167.610
156.892
151.751
145.985
134.962
131.152
129.360
129.254
128.206
125.728
124.138
112.768
110.362
77.359
76.724
61.682
55.921
55.643
52.057
51.829
13.166
MeO
CO2Me
MeO
OMe
MeO2C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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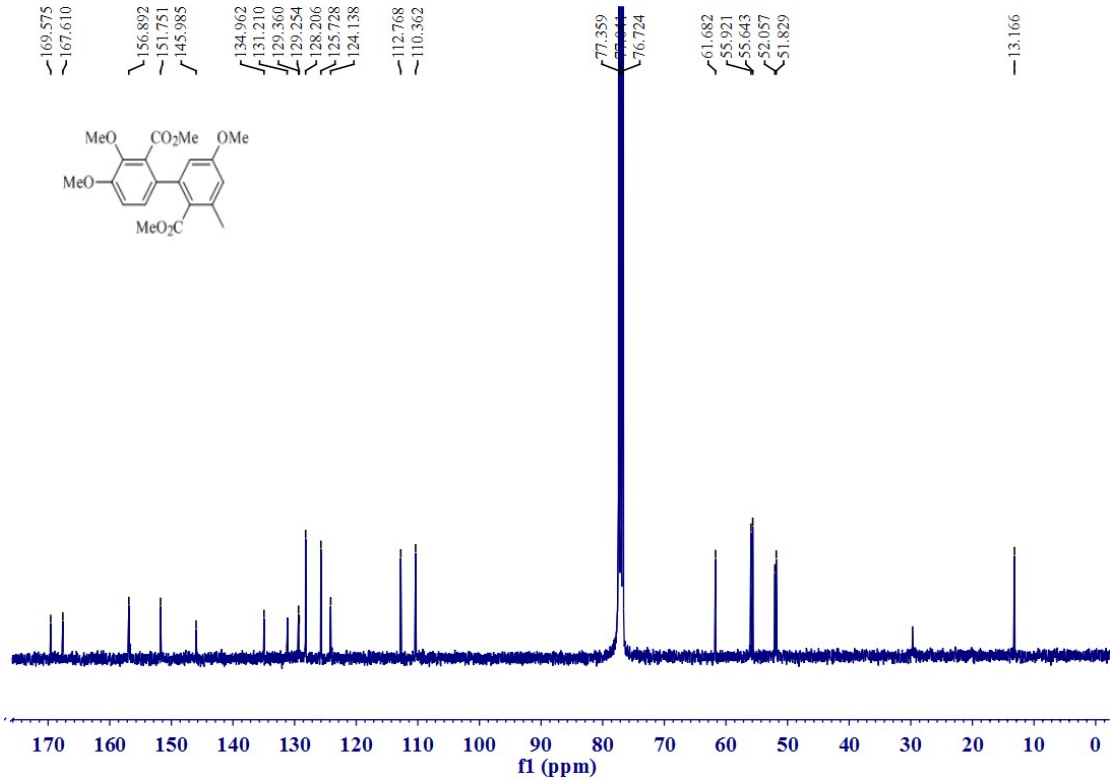
6.710
6.648
6.642
3.910
3.905
3.790
3.651
3.532
2.392
1.570
0.000
MeO
CO2Me
OMe
MeO
MeO2C
2.05
1.04
1.01
6.07
3.02
3.01
3.04
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.575
167.610
156.892
151.751
145.985
134.962
131.210
129.360
129.254
128.206
125.728
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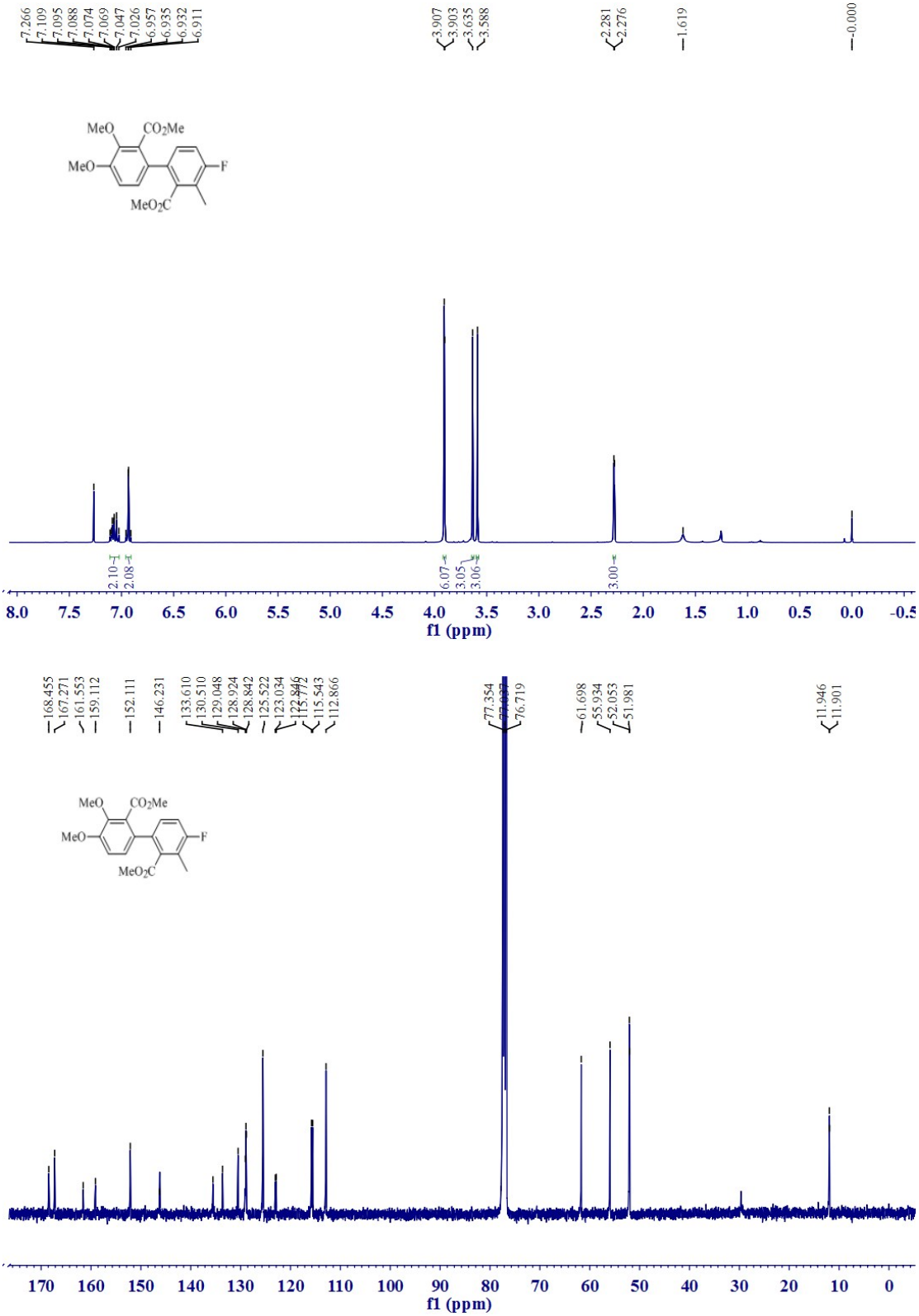
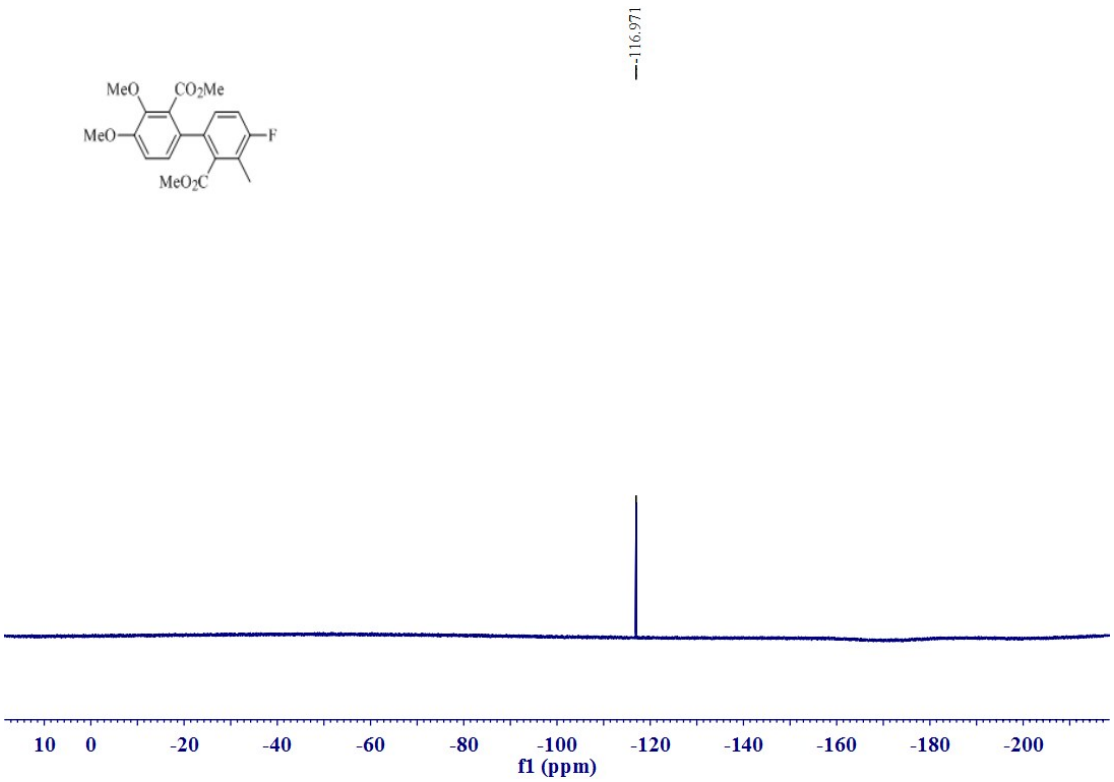
112.768
110.362
77.359
76.724
61.682
55.921
55.643
52.057
51.829
13.166
MeO
CO2Me
OMe
MeO
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.266
7.109
7.095
7.088
7.074
7.069
7.047
7.026
6.957
6.935
6.932
6.911
3.907
3.903
3.635
3.588
2.281
2.276
1.619
-0.000
MeO
CO2Me
MeO
F
MeO2C
2.10
2.08
6.07
3.05
3.06
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
168.455
167.271
161.553
159.112
152.111
146.231
133.610
130.510
129.048
128.924
128.842
125.522
123.034
115.772
115.543
112.866
77.354
76.719
61.698
55.934
52.053
51.981
11.946
11.901
MeO
CO2Me
MeO
F
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

MeO
CO2Me
MeO
F
MeO2C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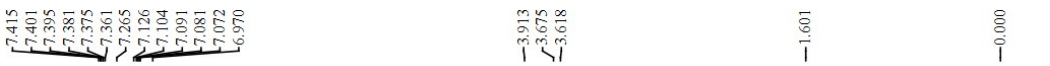
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.375
7.361
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7.126
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7.091
7.081
7.072
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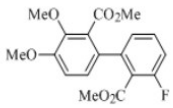
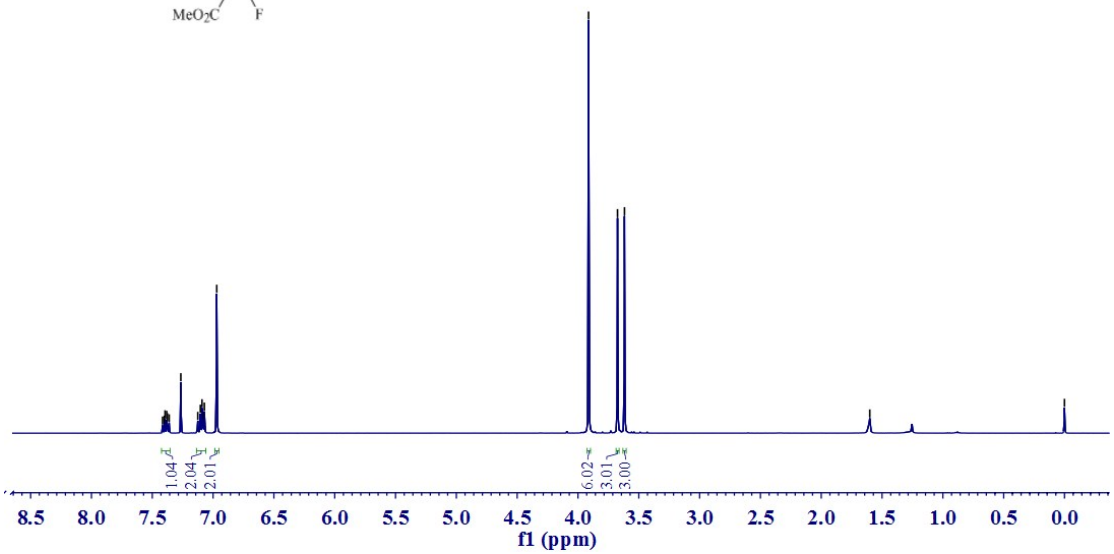
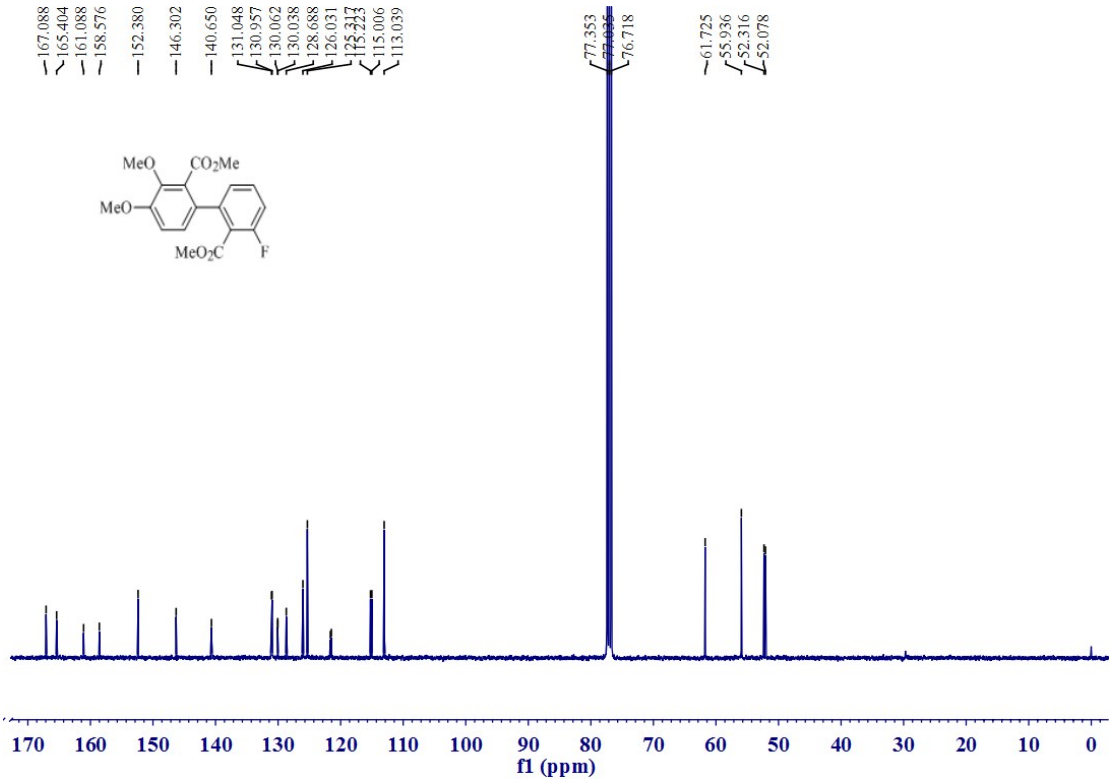
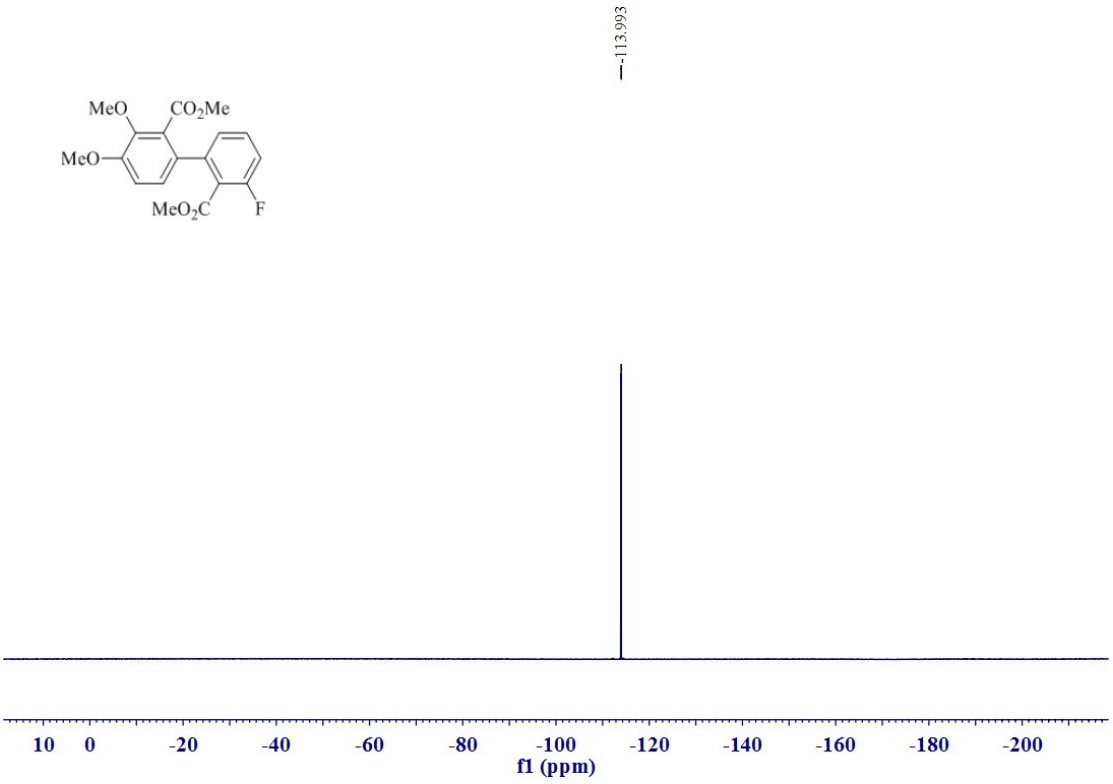
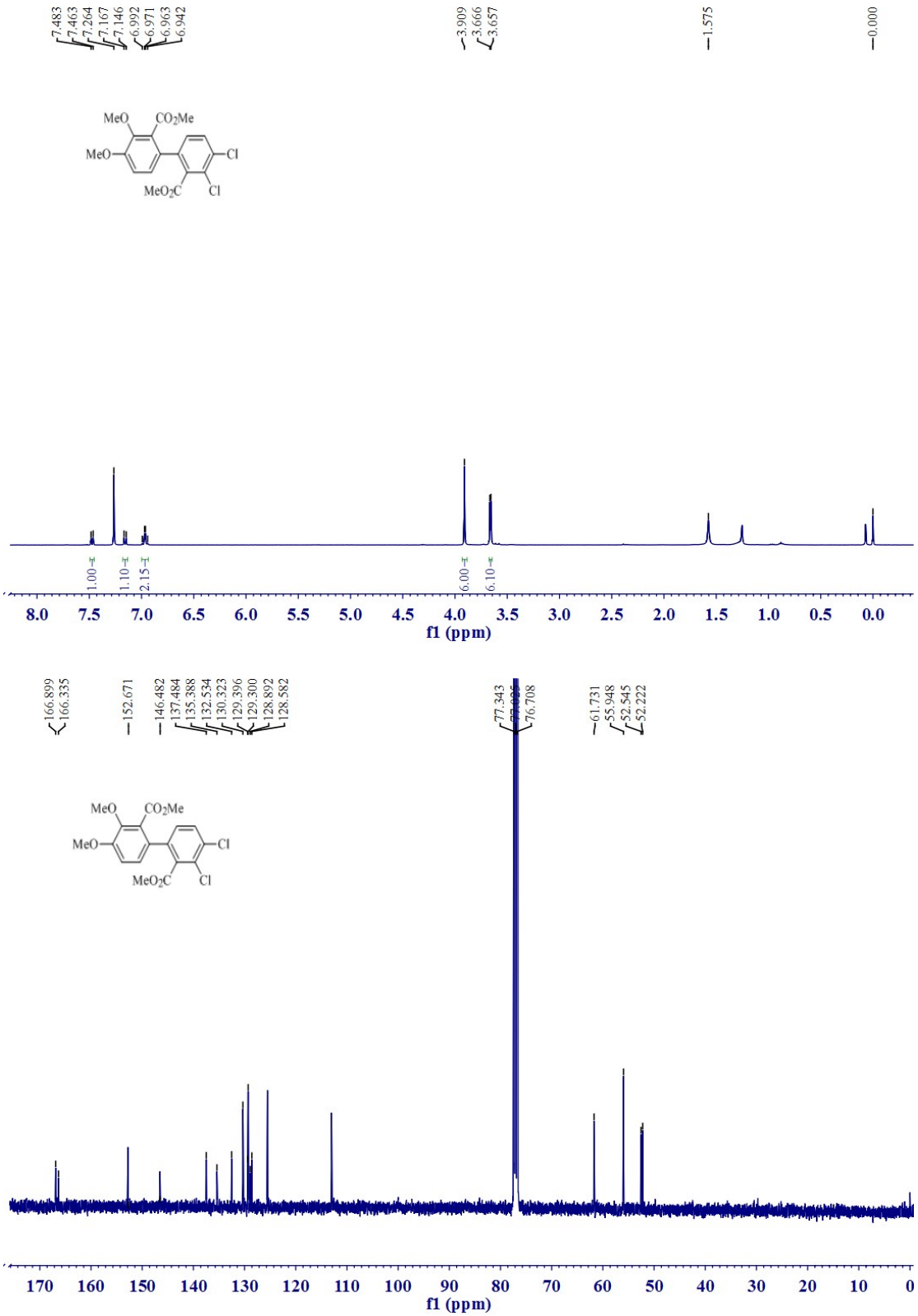
3.913
3.675
3.618
1.601
0.000

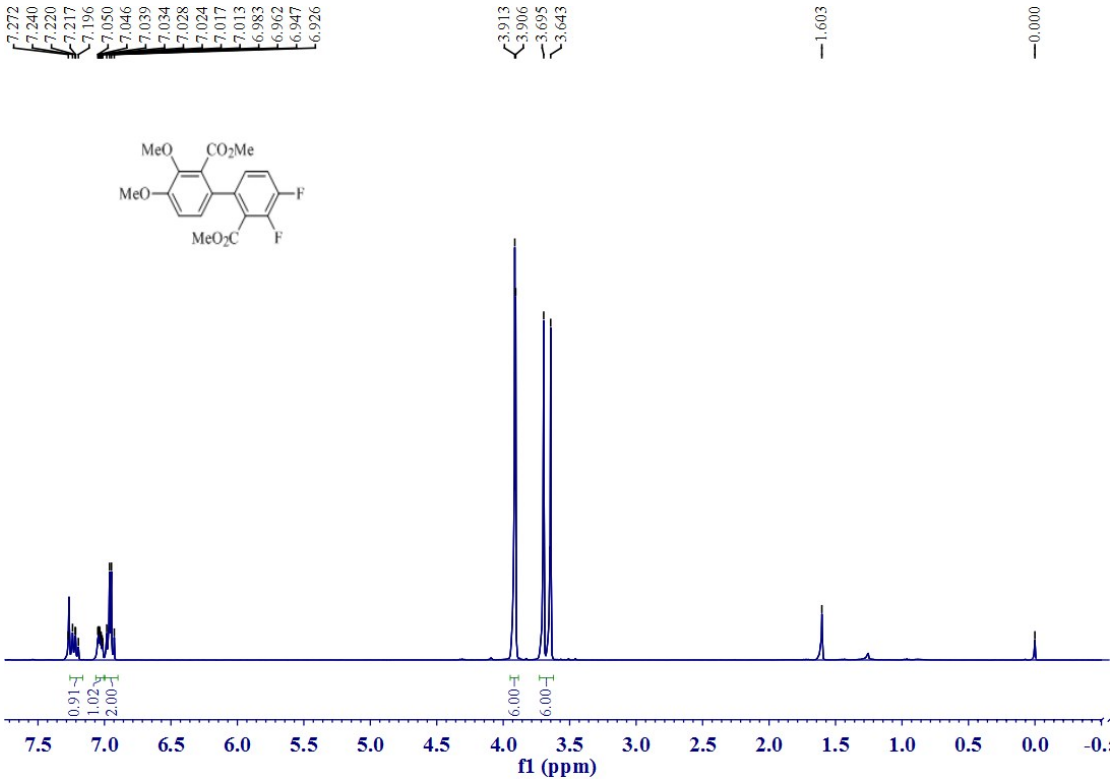

MeO
CO2Me
MeO
MeO2C
F

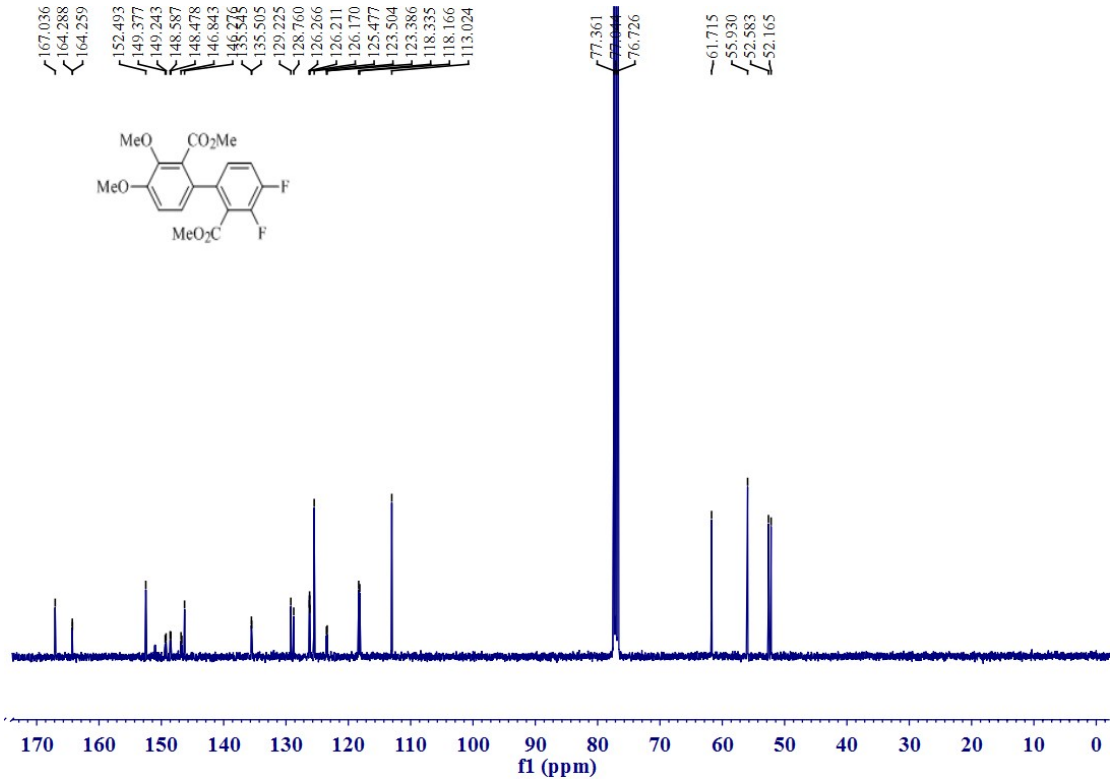

1.04
2.04
2.01
6.02
3.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

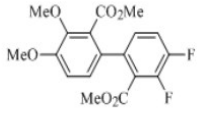

167.088
165.404
161.088
158.576
152.380
146.302
140.650
131.048
130.957
130.062
130.038
128.688
126.031
115.006
113.039
77.353
76.718
61.725
55.936
52.316
52.078
MeO
CO2Me
MeO
MeO2C
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-113.993
MeO
CO2Me
MeO
MeO2C
F
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

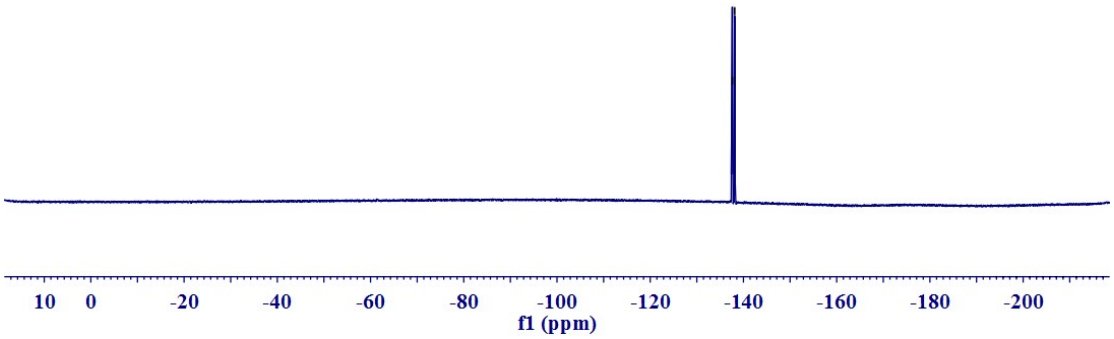

7.483
7.463
7.264
7.167
7.146
6.992
6.971
6.963
6.942
3.909
3.666
3.657
1.575
0.000
MeO
CO2Me
MeO
Cl
MeO2C
Cl
1.00
1.10
2.15
6.00
6.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
166.899
166.335
152.671
146.482
137.484
135.388
132.534
130.323
129.396
129.300
128.892
128.582
77.343
76.708
61.731
55.948
52.545
52.222
MeO
CO2Me
MeO
Cl
MeO2C
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.272
7.240
7.220
7.217
7.196
7.050
7.046
7.039
7.034
7.028
7.024
7.017
7.013
6.983
6.962
6.947
6.926
3.913
3.906
3.695
3.643
1.603
0.000
MeO
CO2Me
MeO
F
MeO2C
F
0.91
1.02
2.00
6.00
6.00
f1 (ppm)

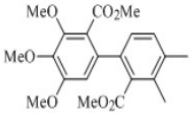

167.036
164.288
164.259
152.493
149.377
149.243
148.587
148.478
146.843
135.505
129.225
128.760
126.266
126.211
126.170
125.477
123.504
123.386
118.335
118.166
113.024
77.361
76.726
61.715
55.930
52.583
52.165
MeO
CO2Me
MeO
F
MeO2C
F
f1 (ppm)

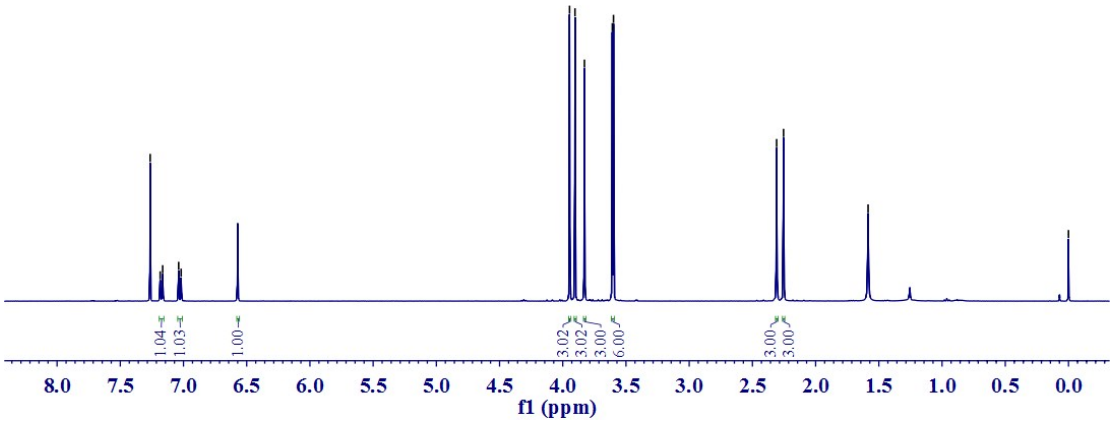


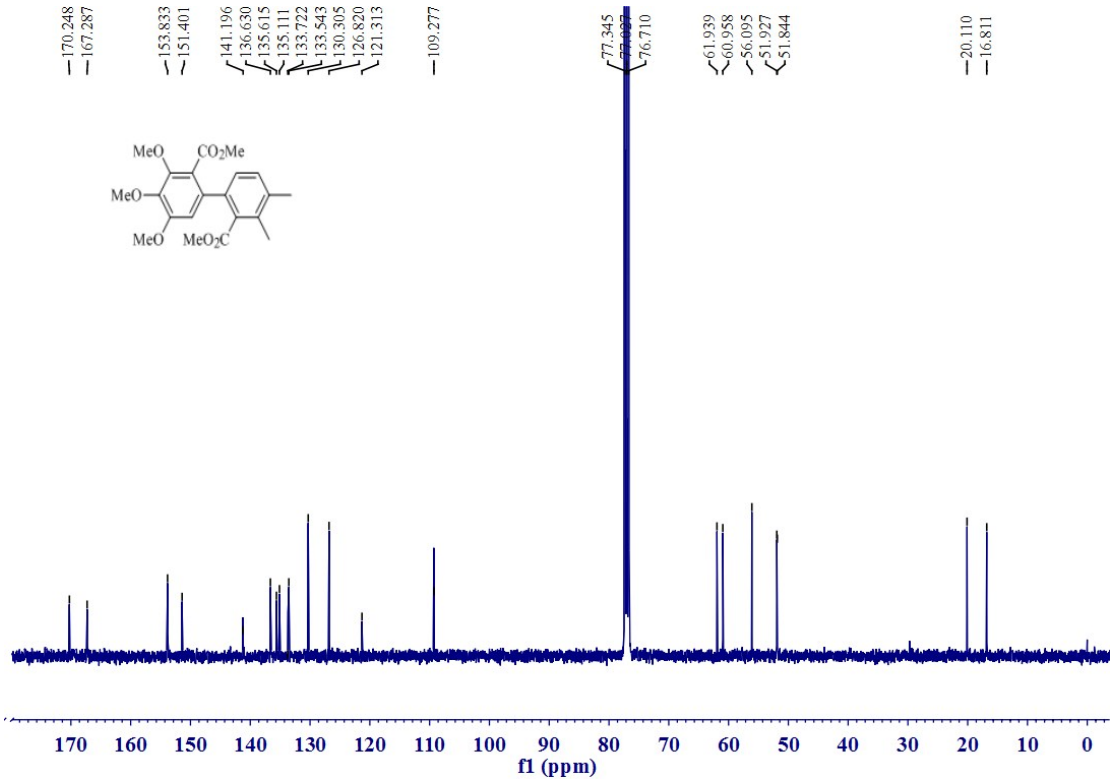
-137.631
-138.128

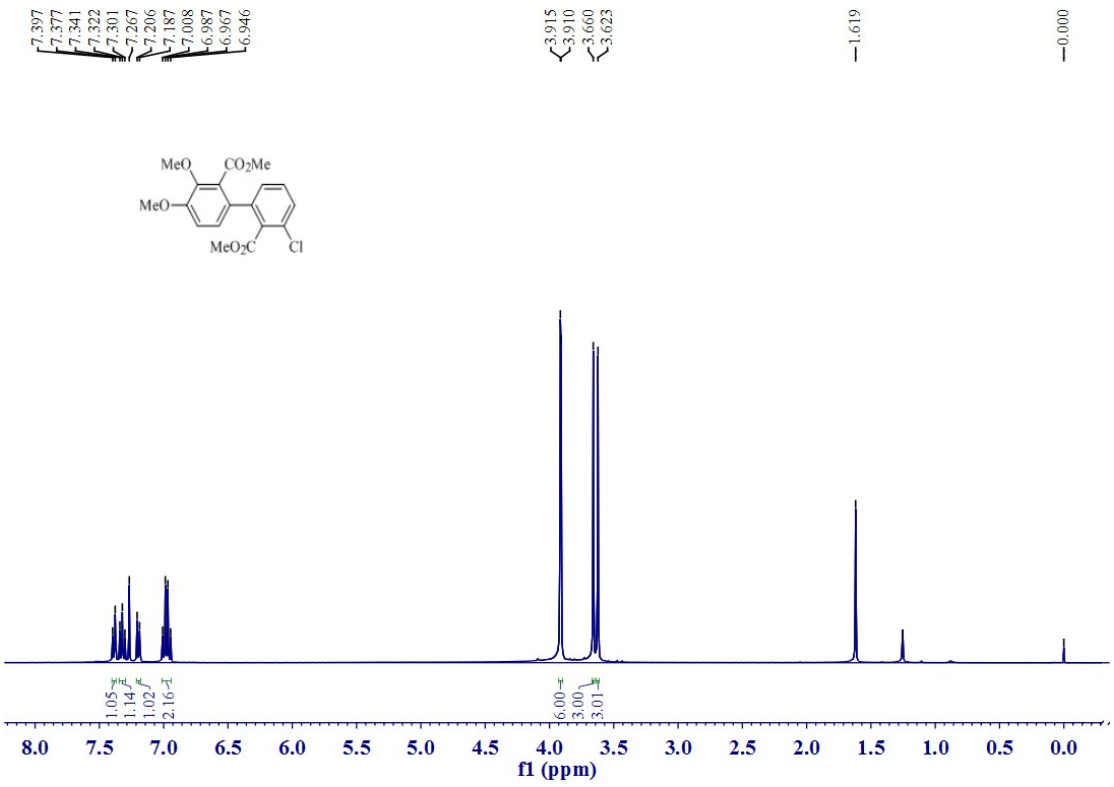


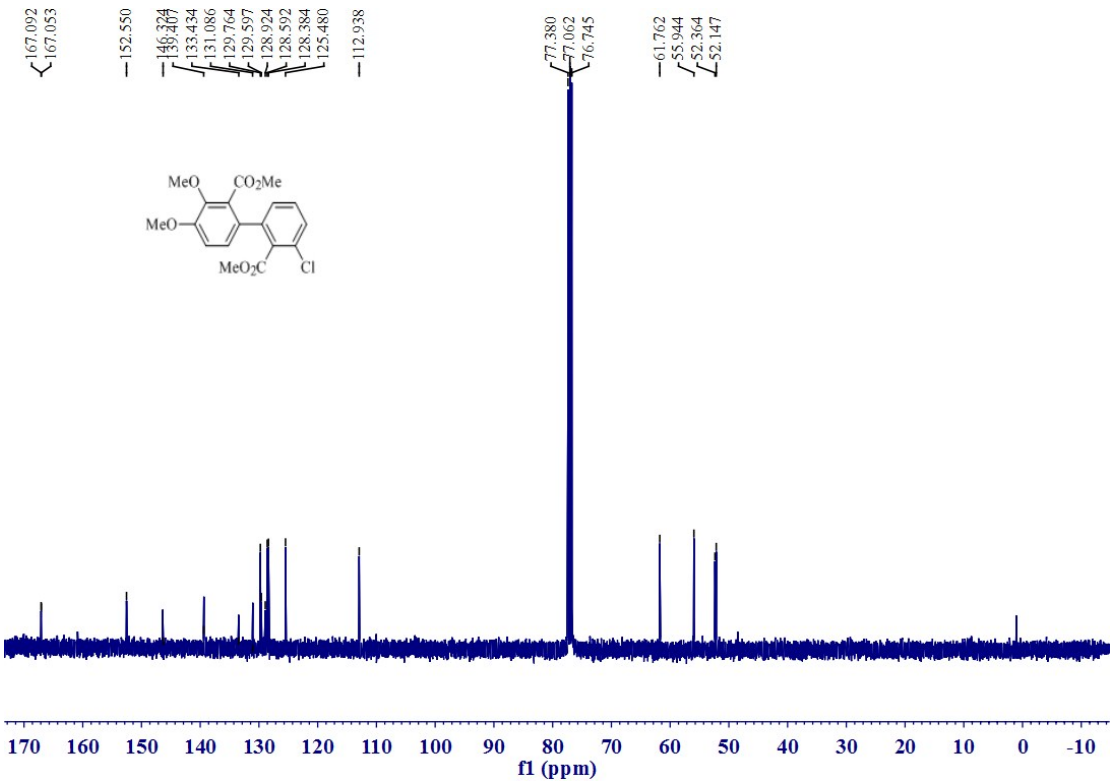
7.263
7.184
7.165
7.038
7.019
3.946
3.903
3.829
3.608
3.599
2.309
2.254
1.585
0.000

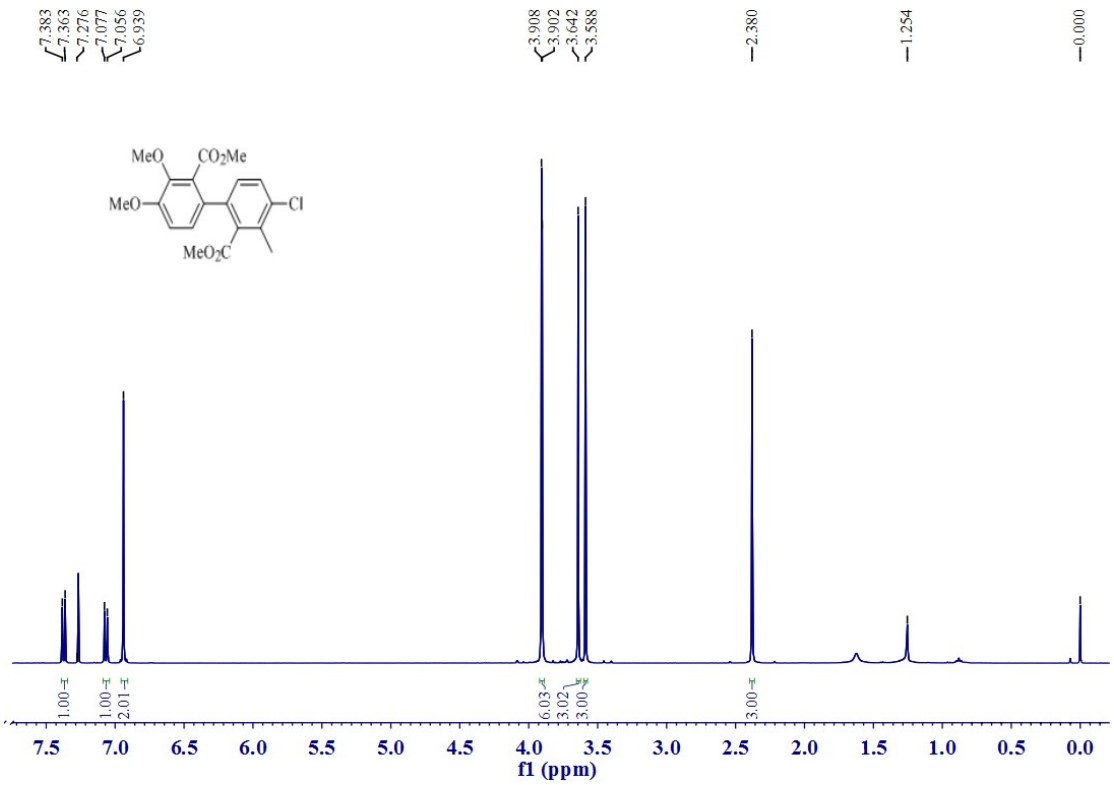


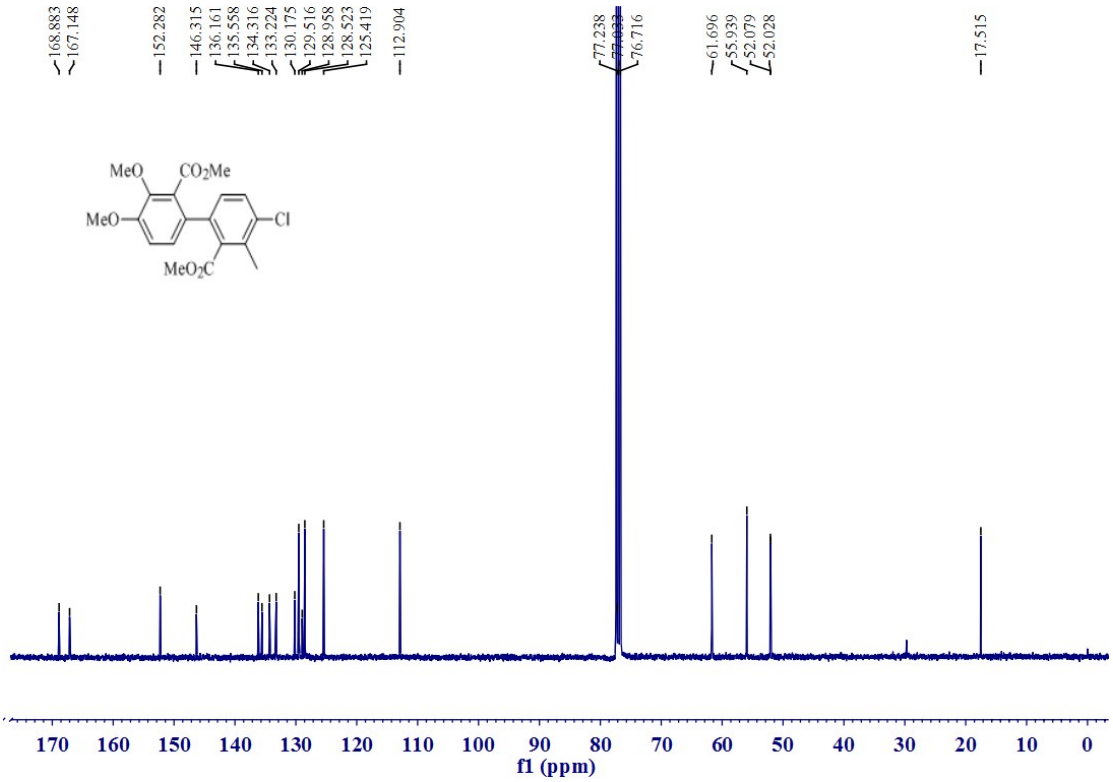


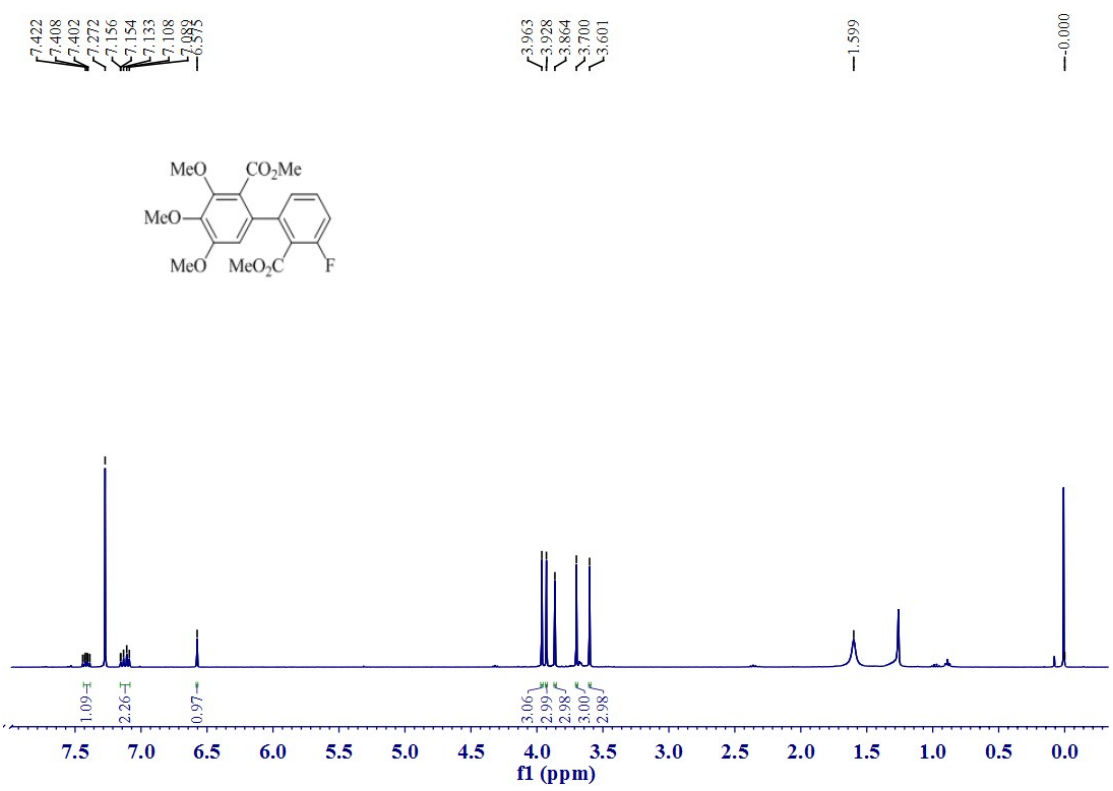

170.248
167.287
153.833
151.401
141.196
136.630
135.615
135.111
133.722
133.543
130.305
126.820
121.313
109.277
77.345
76.710
61.939
60.958
56.095
51.927
51.844
20.110
16.811
MeO
CO2Me
MeO
MeO
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

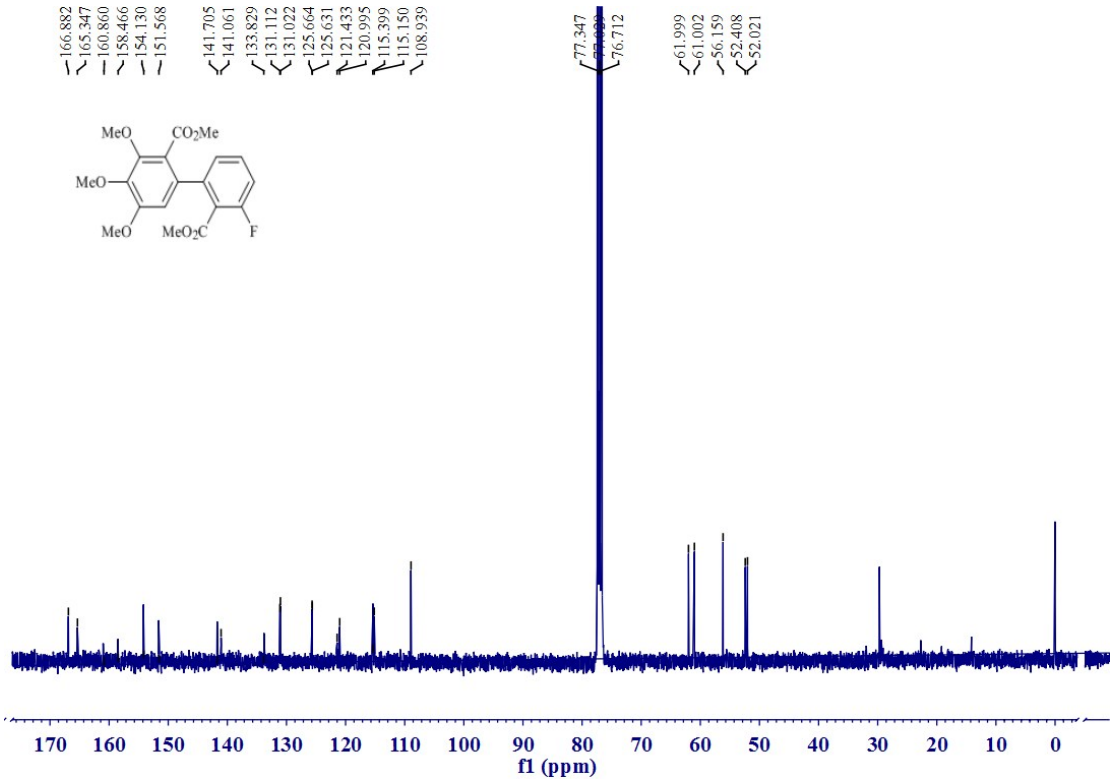

7.397
7.377
7.341
7.322
7.301
7.267
7.206
7.187
7.008
6.987
6.967
6.946
3.915
3.910
3.660
3.623
1.619
0.000
MeO
CO2Me
MeO
MeO2C
Cl
1.05
1.14
1.02
2.16
6.00
3.00
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.092
167.053
152.550
146.324
139.407
133.434
131.086
129.764
129.597
128.924
128.592
128.384
125.480
112.938
77.380
77.062
76.745
61.762
55.944
52.364
52.147
MeO
CO2Me
MeO
MeO2C
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.383
7.363
7.276
7.077
7.056
6.939
3.908
3.902
3.642
3.588
2.380
1.254
0.000
MeO
CO2Me
MeO
Cl
MeO2C
1.00
1.00
2.01
6.03
3.02
3.00
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.883
167.148
152.282
146.315
136.161
135.558
134.316
133.224
130.175
129.516
128.958
128.523
125.419
112.904
77.238
77.033
76.716
61.696
55.939
52.079
52.028
17.515
MeO
CO2Me
MeO
Cl
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.422
7.408
7.402
7.272
7.156
7.154
7.133
7.108
7.082
6.575
3.963
3.928
3.864
3.700
3.601
1.599
0.000
MeO
CO2Me
MeO
MeO
MeO2C
F
1.09
2.26
0.97
3.06
2.99
2.98
3.00
2.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.882
165.347
160.860
158.466
154.130
151.568
141.705
141.061
133.829
131.112
131.022
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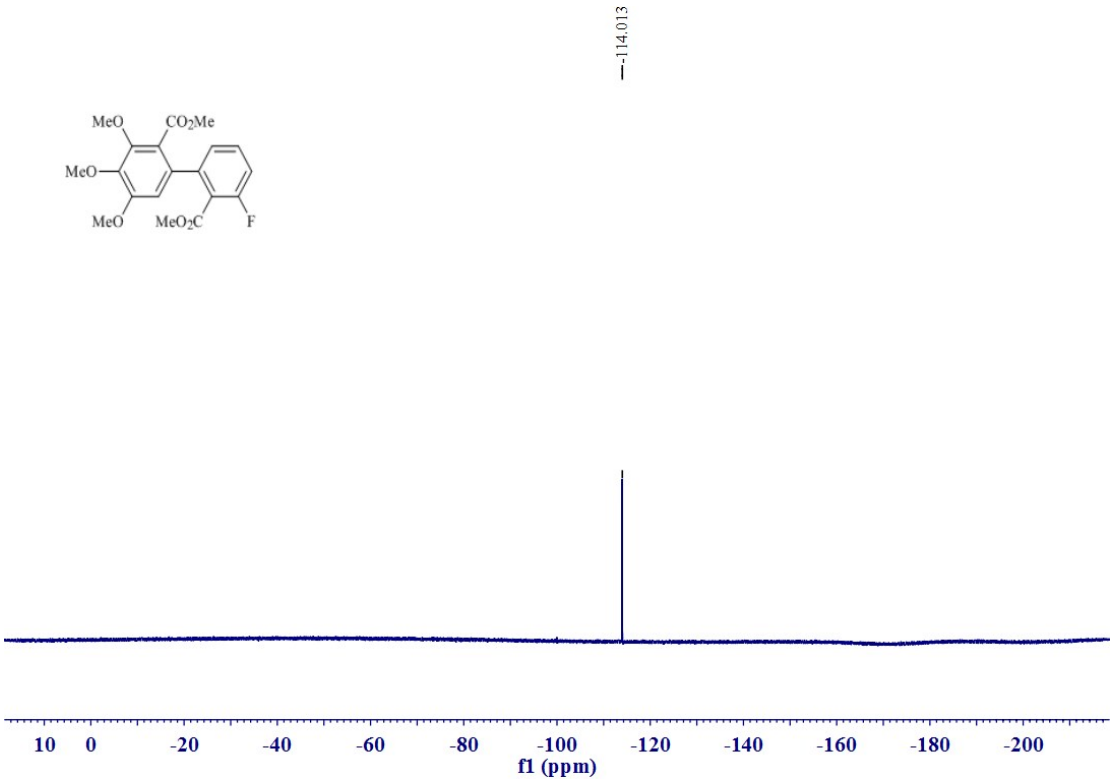
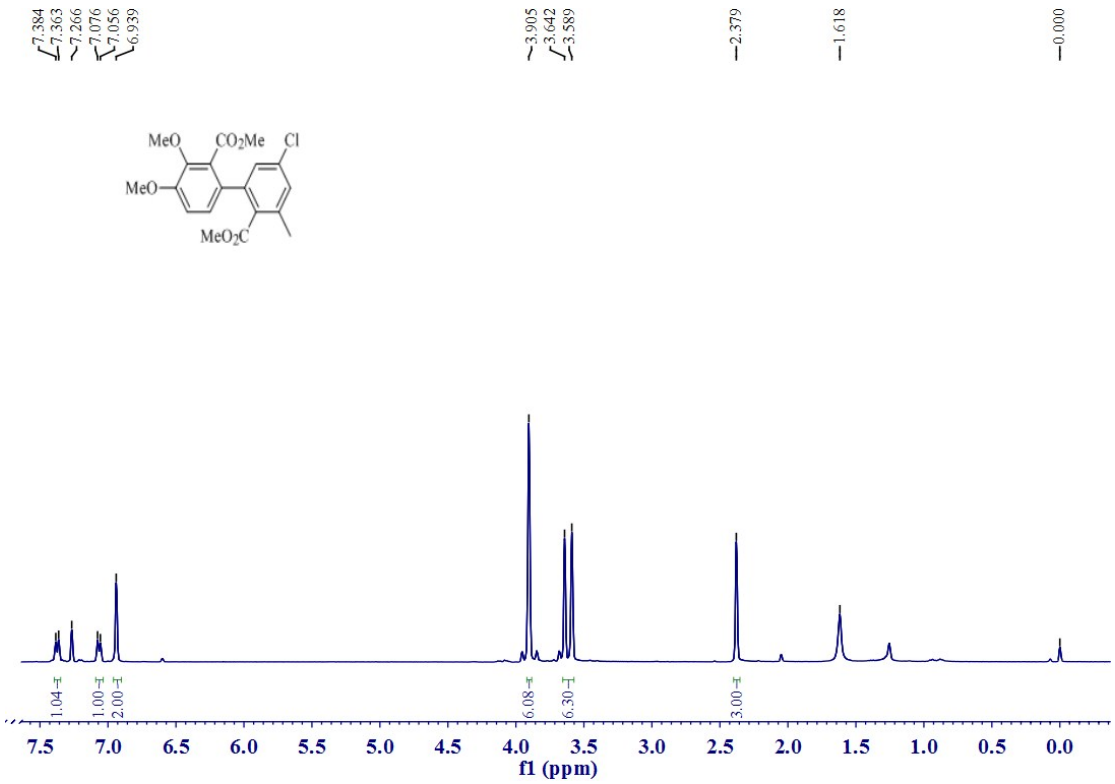
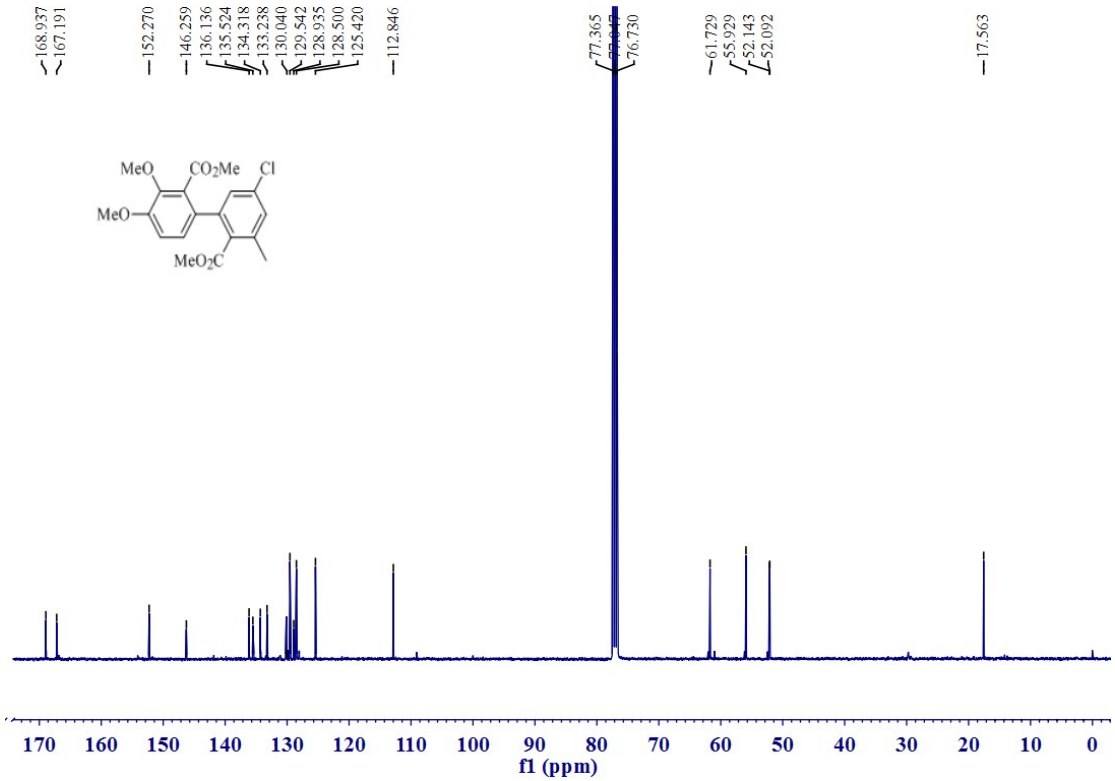
125.631
121.433
120.995
115.399
115.150
108.939
77.347
76.712
61.999
61.002
56.159
52.408
52.021
MeO
CO2Me
MeO
MeO
MeO2C
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.013
MeO
CO2Me
MeO
MeO
MeO2C
F
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.384
7.363
7.266
7.076
7.056
6.939
3.905
3.642
3.589
2.379
1.618
0.000
MeO
CO2Me
Cl
MeO
MeO2C
1.04
1.00
2.00
6.08
6.30
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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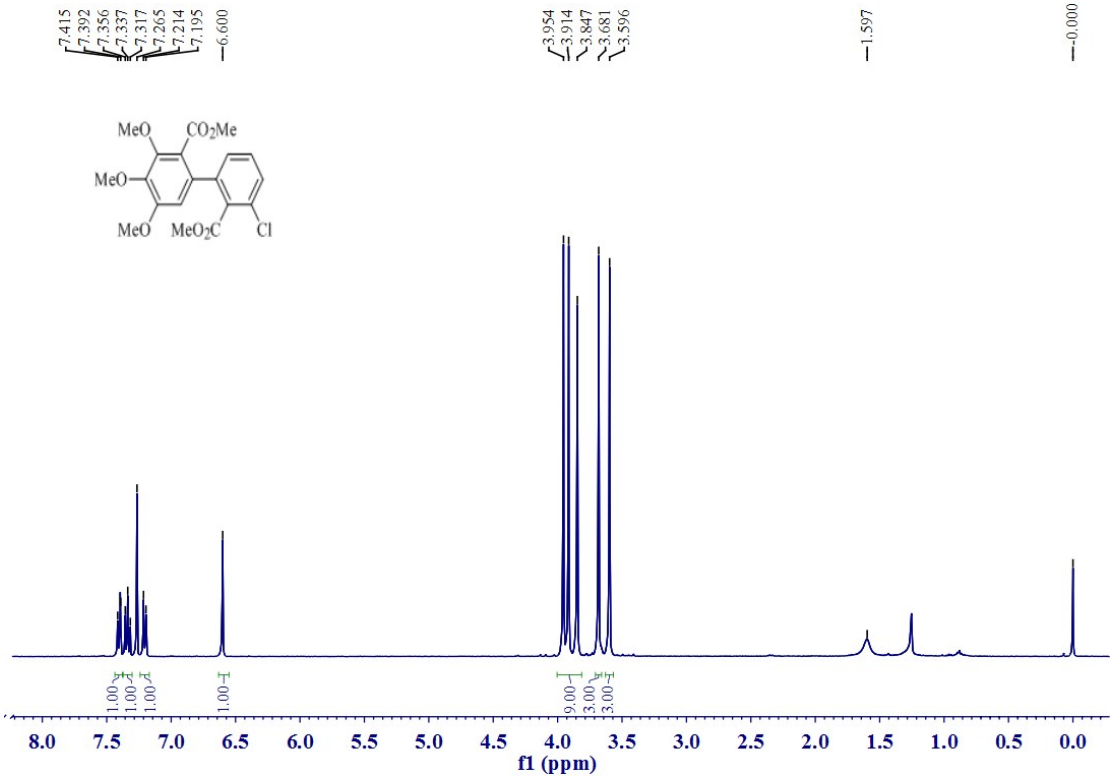
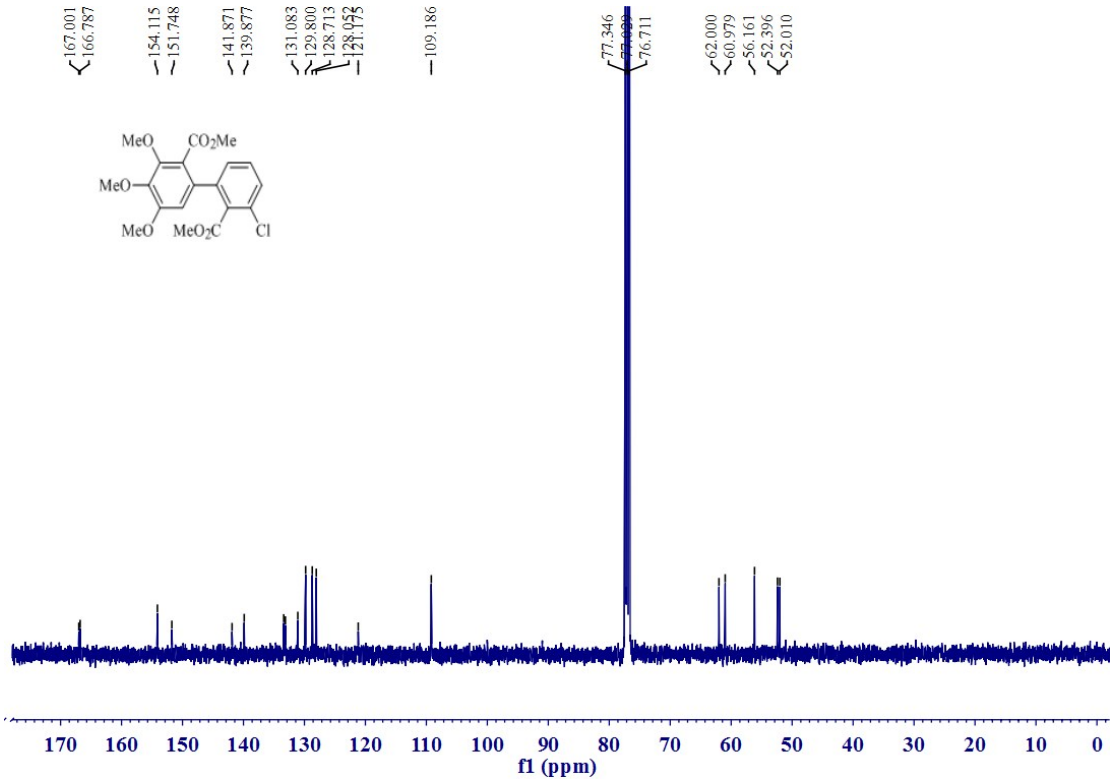
167.191
152.270
146.259
136.136
135.524
134.318
133.238
130.040
129.542
128.935
128.500
125.420
112.846
77.365
76.730
61.729
55.929
52.143
52.092
17.563
MeO
CO2Me
Cl
MeO
MeO2C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.415
7.392
7.356
7.337
7.317
7.265
7.214
7.195
6.600
3.954
3.914
3.847
3.681
3.596
1.597
0.000
MeO
CO2Me
MeO
MeO
MeO2C
Cl
1.00
1.00
1.00
1.00
9.00
3.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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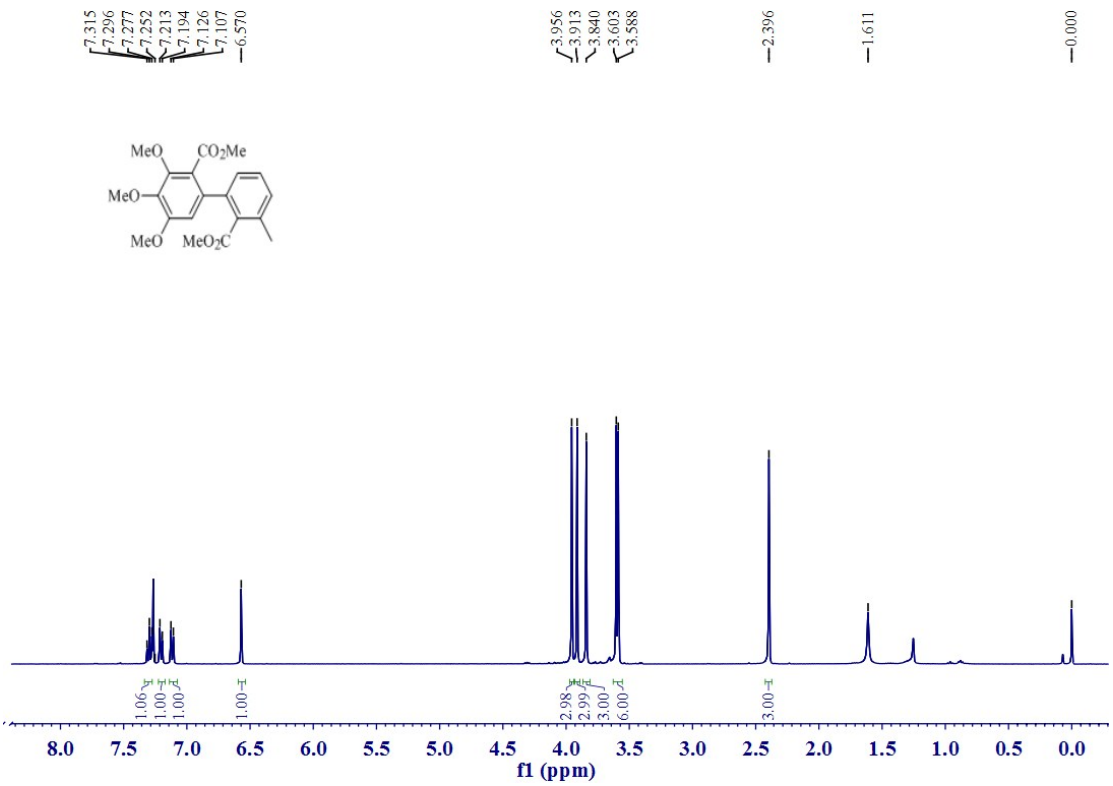
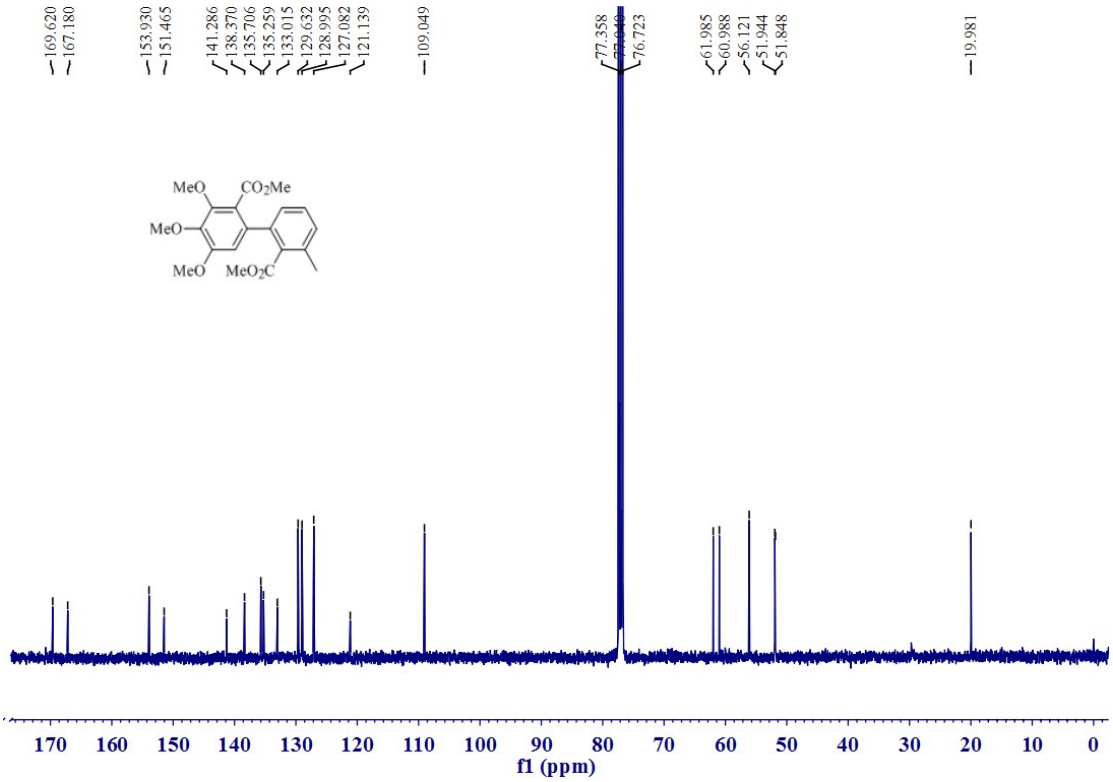
166.787
154.115
151.748
141.871
139.877
131.083
129.800
128.713
128.052
121.175
109.186
77.346
77.030
76.711
62.000
60.979
56.161
52.396
52.010
MeO
CO2Me
MeO
MeO
MeO2C
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.315
7.296
7.277
7.252
7.213
7.194
7.126
7.107
6.570
3.956
3.913
3.840
3.603
3.588
2.396
1.611
0.000
MeO
CO2Me
MeO
MeO
MeO2C
1.06
1.00
1.00
1.00
2.98
2.99
3.00
6.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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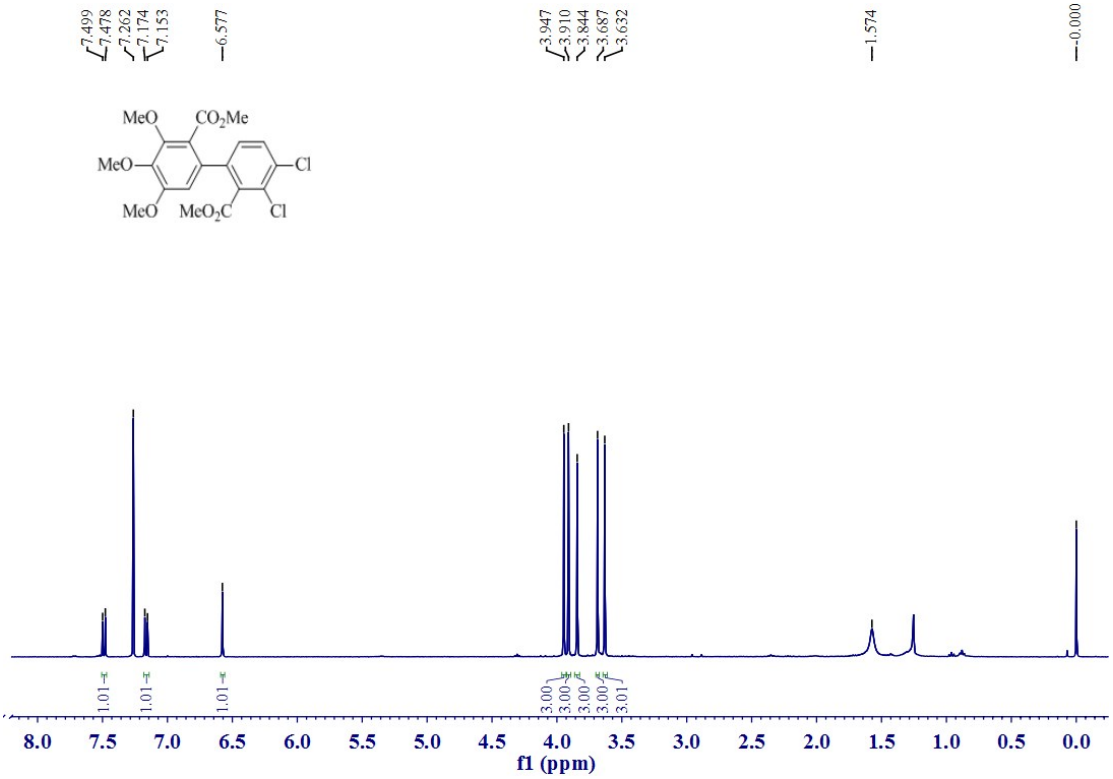
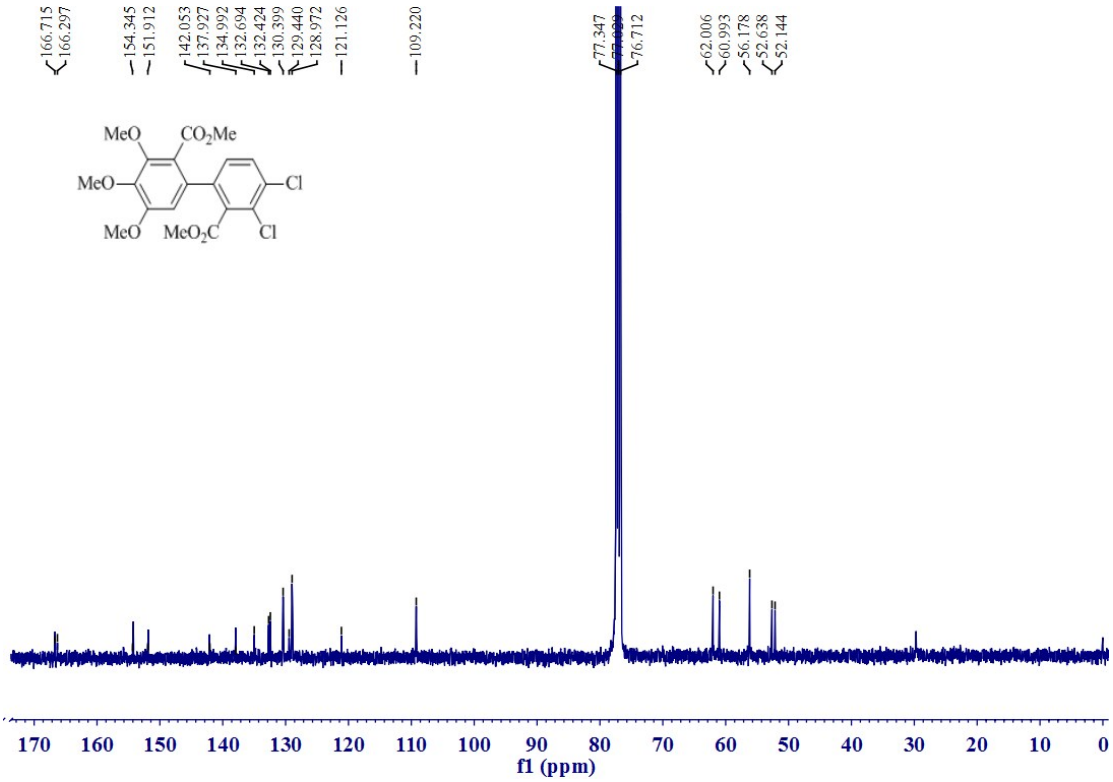
167.180
153.930
151.465
141.286
138.370
135.706
135.259
133.015
129.632
128.995
127.082
121.139
109.049
77.358
76.723
61.985
60.988
56.121
51.944
51.848
19.981
MeO
CO2Me
MeO
MeO
MeO2C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.499
7.478
7.262
7.174
7.153
6.577
3.947
3.910
3.844
3.687
3.632
1.574
0.000
MeO
CO2Me
MeO
Cl
MeO
MeO2C
Cl
1.01
1.01
1.01
3.00
3.00
3.00
3.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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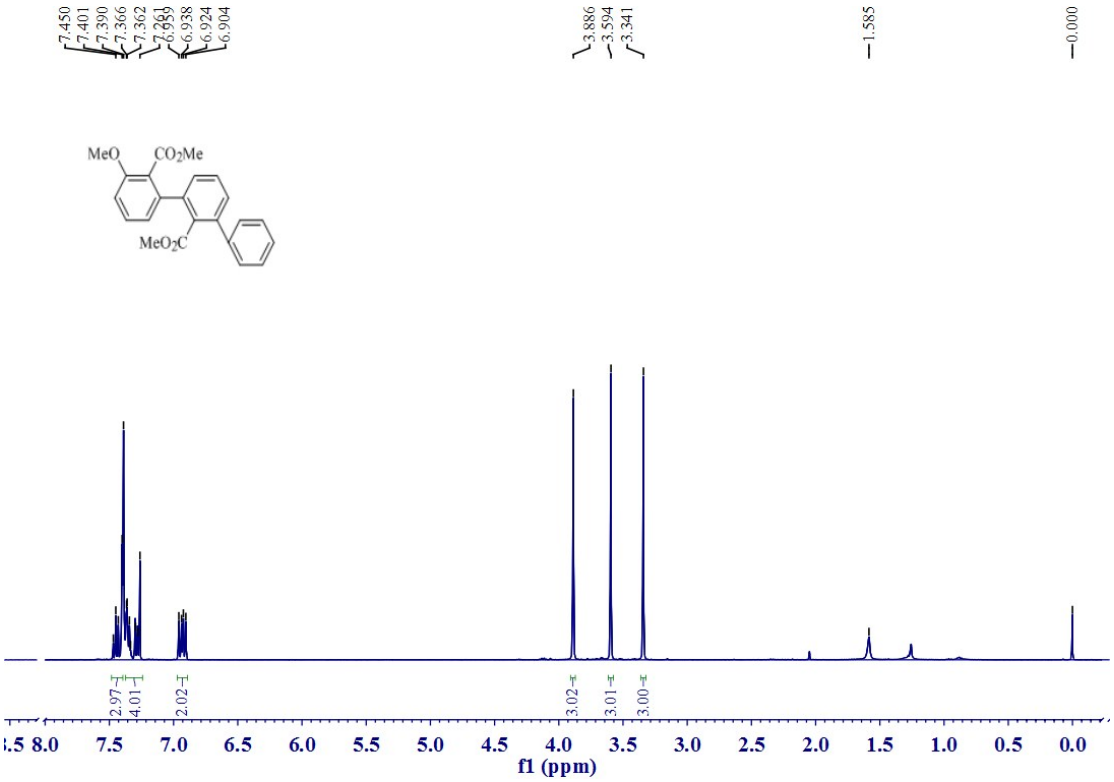
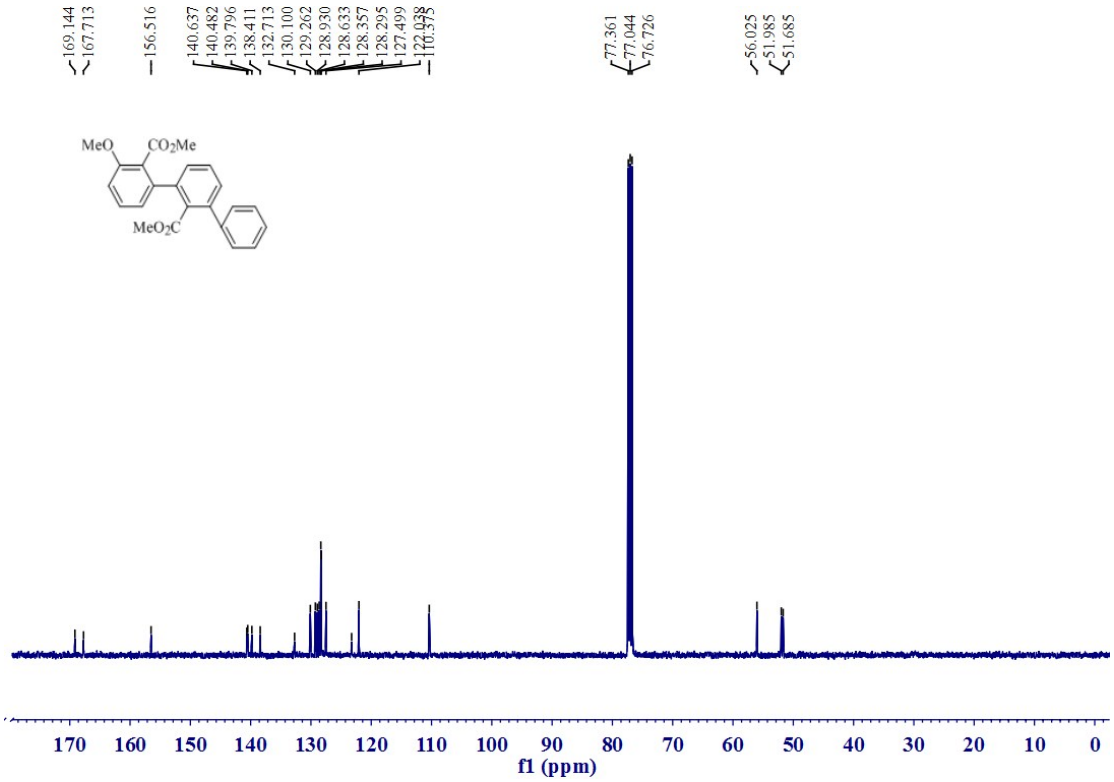
134.992
132.694
132.424
130.399
129.440
128.972
121.126
109.220
77.347
77.032
76.712
62.006
60.993
56.178
52.638
52.144
MeO
CO2Me
MeO
Cl
MeO
MeO2C
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.450
7.401
7.390
7.366
7.362
6.938
6.924
6.904
3.886
3.594
3.341
1.585
0.000
MeO
CO2Me
MeO2C
2.97
4.01
2.02
3.02
3.01
3.00
f1 (ppm)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139.796
138.411
132.713
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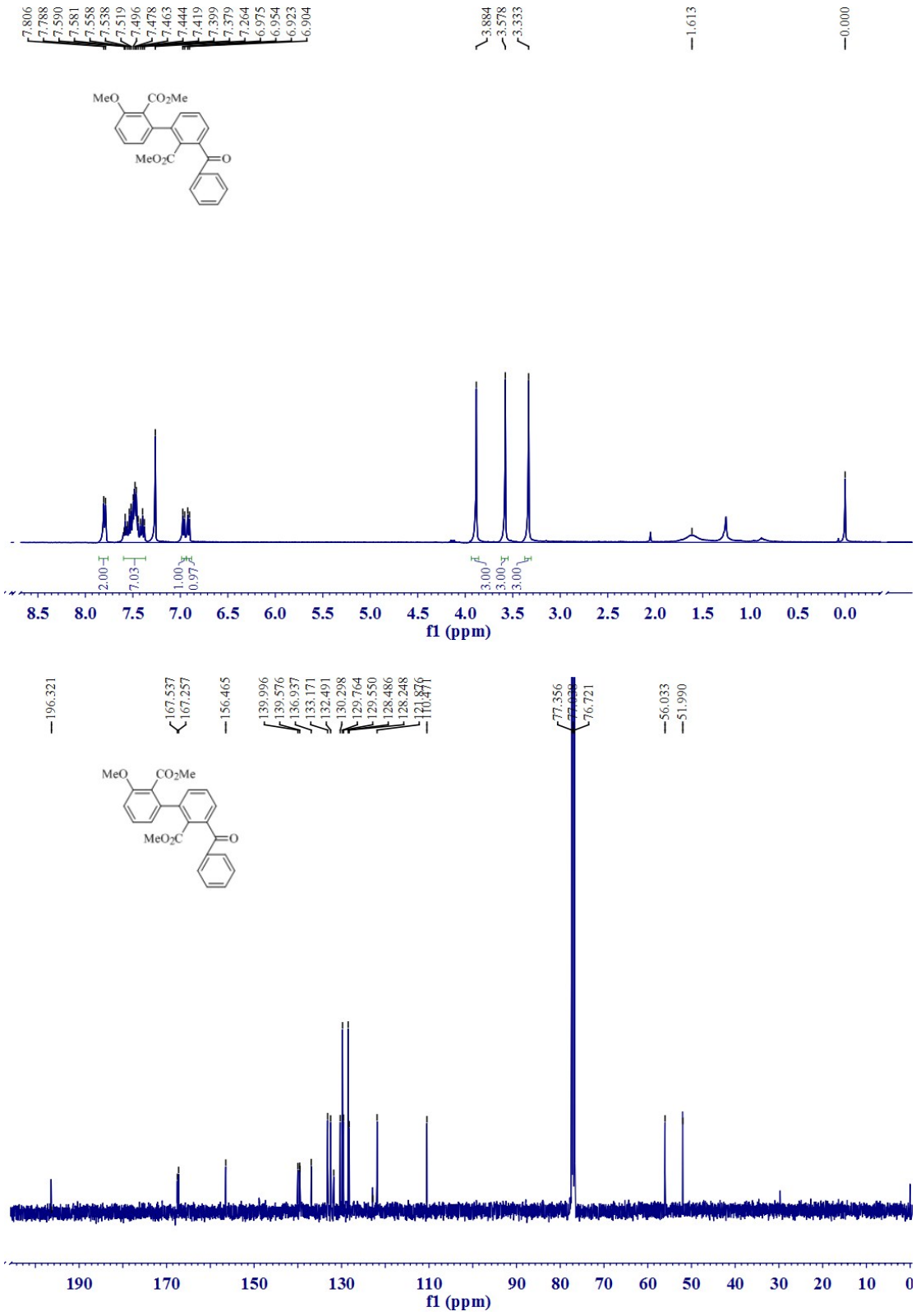
128.930
128.633
128.357
128.295
127.499
77.361
77.044
76.726
56.025
51.985
51.685
MeO
CO2Me
MeO2C
f1 (ppm)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7.519
7.496
7.478
7.463
7.444
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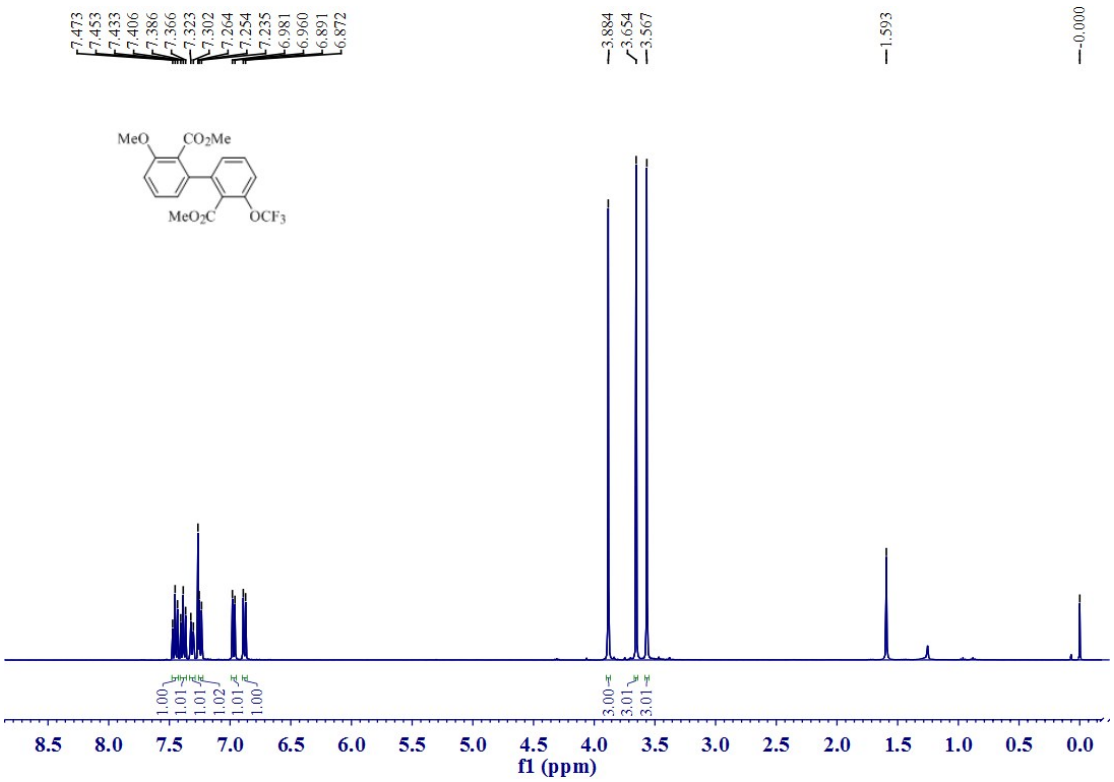
7.399
7.379
7.264
6.975
6.954
6.923
6.904
3.884
3.578
3.333
1.613
0.000
MeO
CO2Me
MeO2C
O
2.00
7.03
1.00
0.97
3.00
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
196.321
167.537
167.257
156.465
139.996
139.576
136.937
133.171
132.491
130.298
129.764
129.550
128.486
128.248
120.876
120.471
77.356
77.039
76.721
56.033
51.990
MeO
CO2Me
MeO2C
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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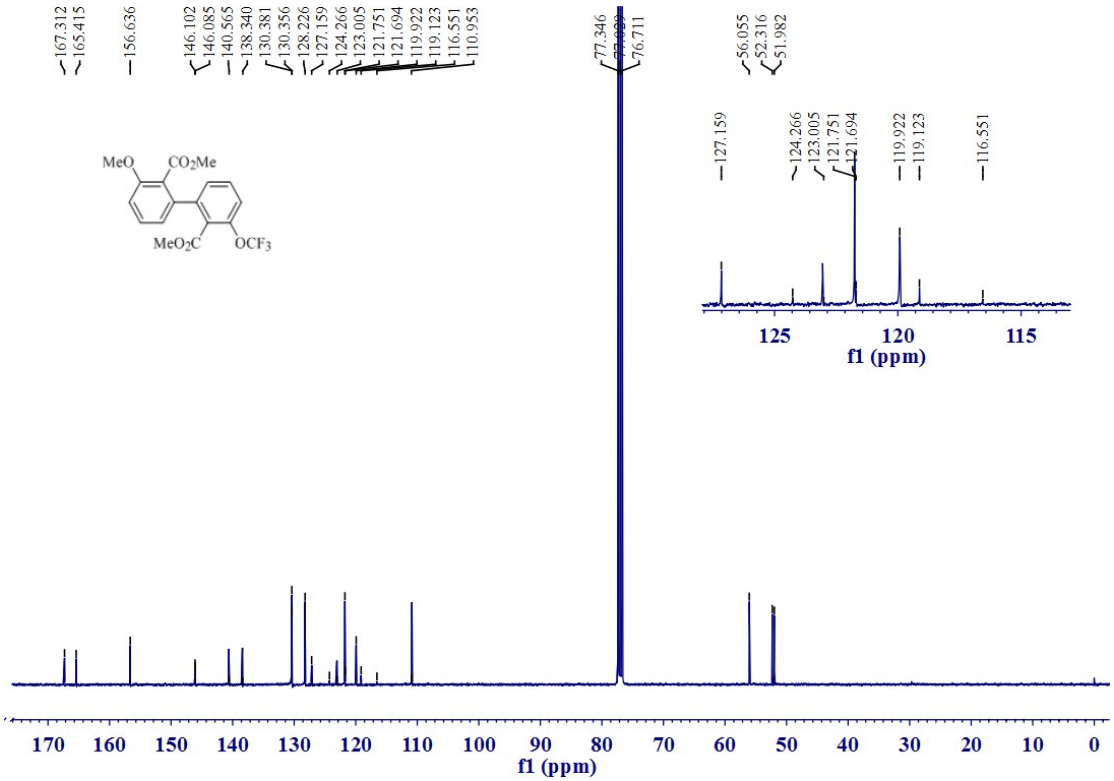
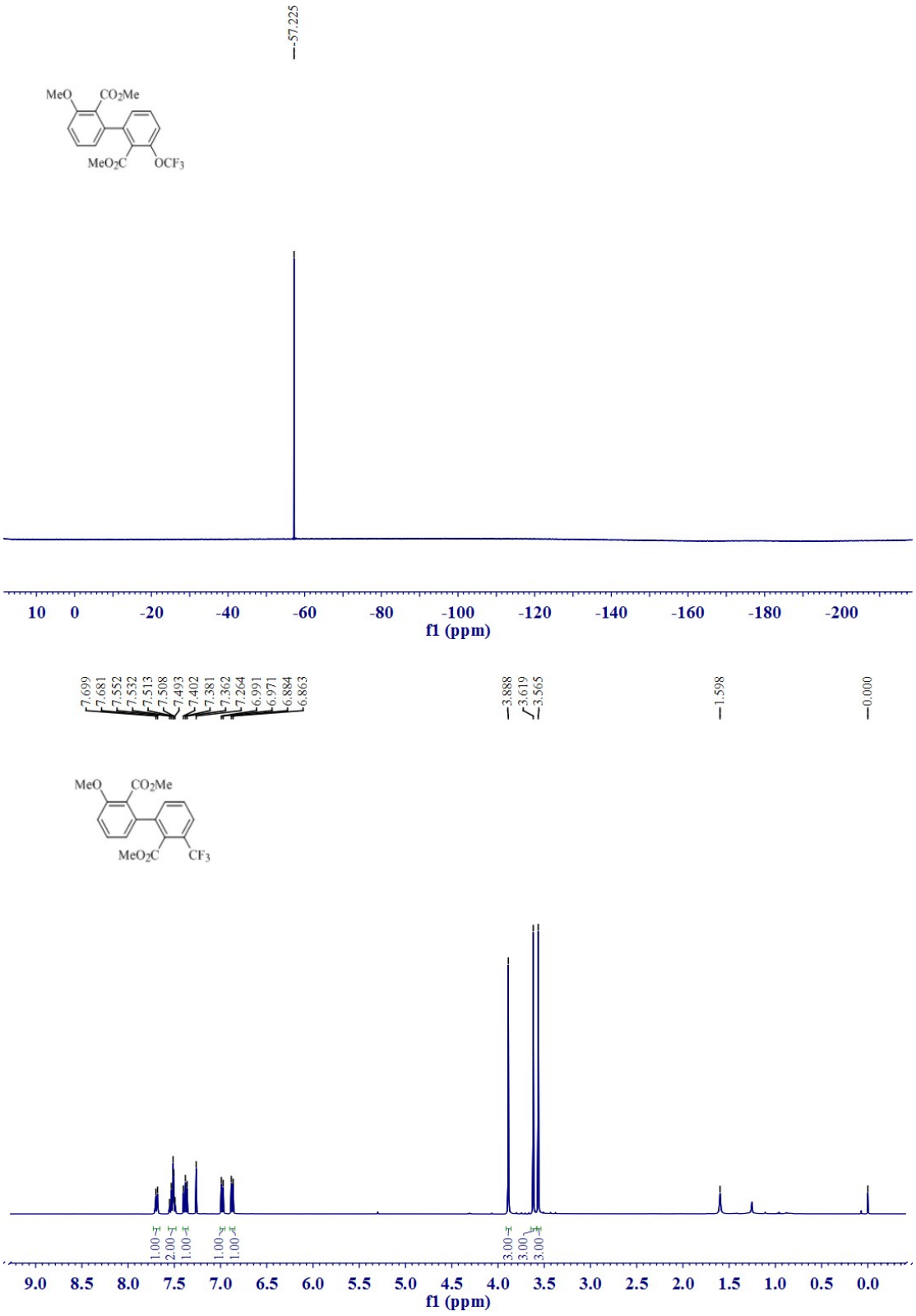
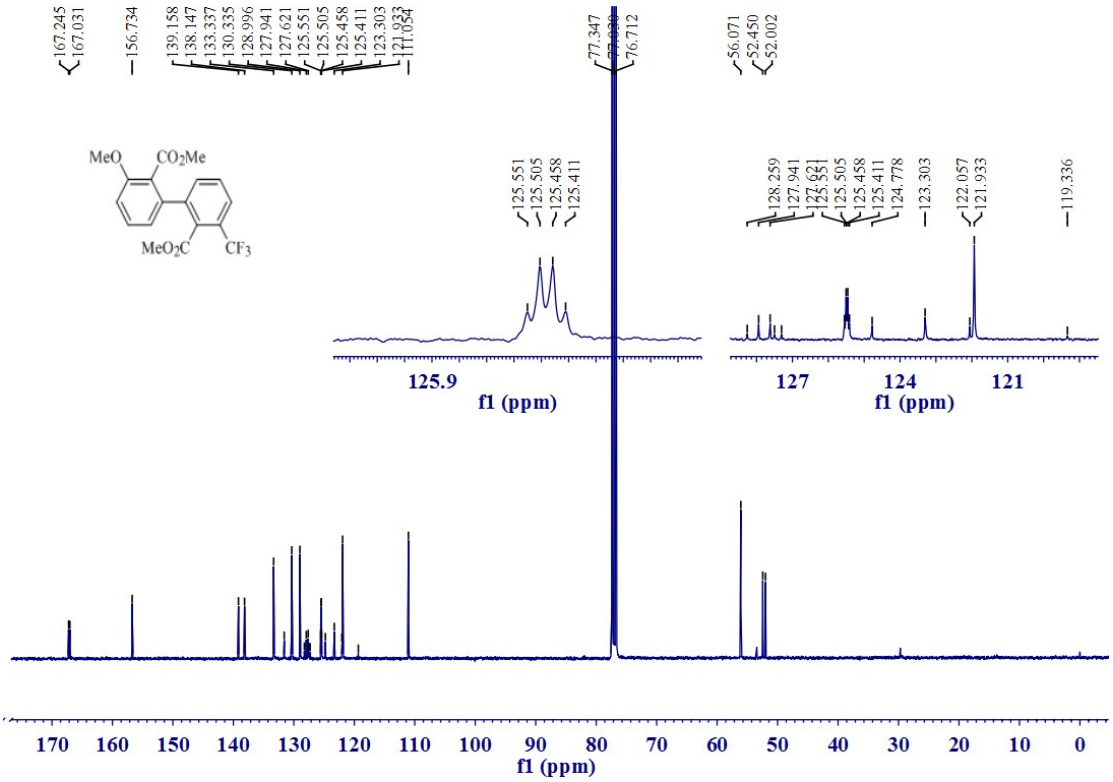
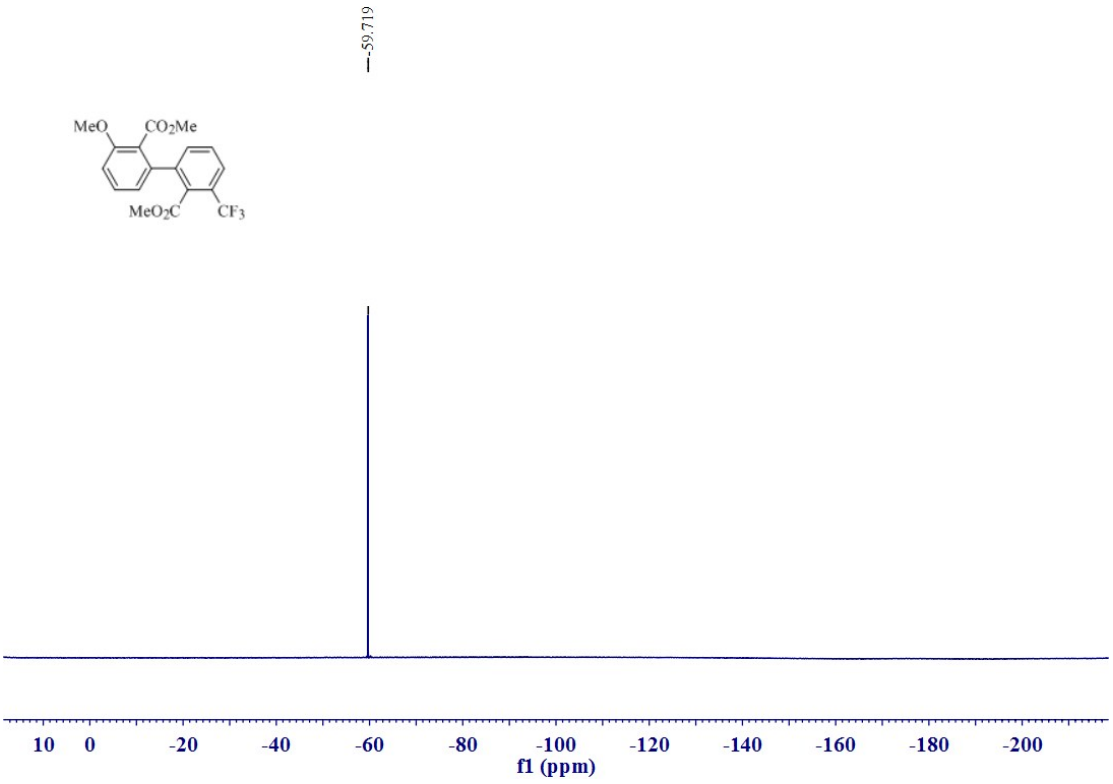
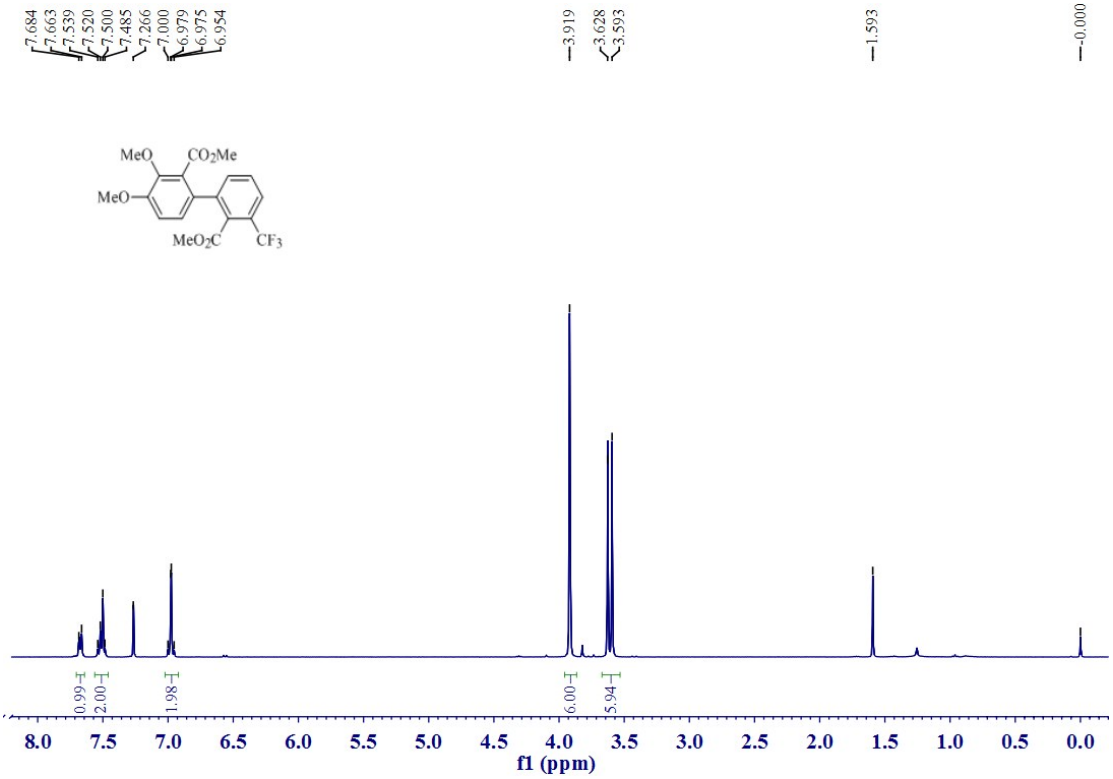
7.453
7.433
7.406
7.386
7.366
7.323
7.302
7.264
7.254
7.235
6.981
6.960
6.891
6.872
3.884
3.654
3.567
1.593
-0.000
MeO
CO2Me
MeO2C
OCF3
1.00
1.01
1.01
1.02
1.01
1.00
3.00
3.01
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

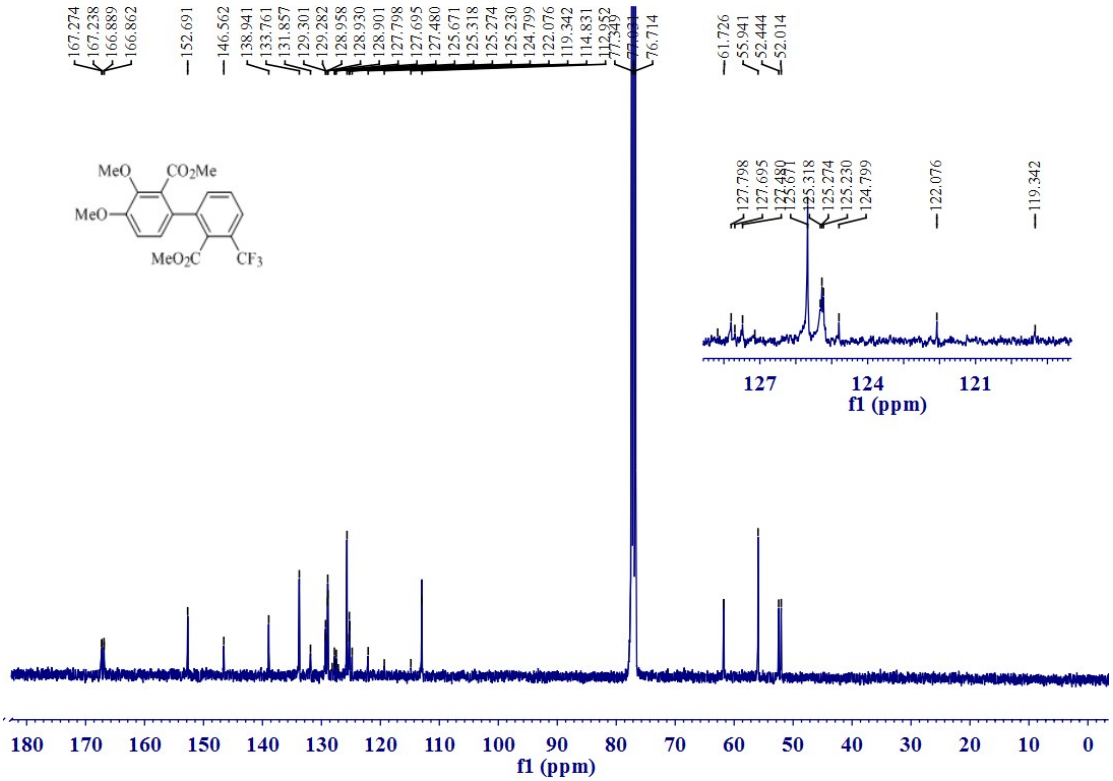

167.312
165.415
156.636
146.102
146.085
140.565
138.340
130.381
130.356
128.226
127.159
124.266
123.005
121.751
121.694
119.922
119.123
116.551
110.953
77.346
77.029
76.711
56.055
52.316
51.982
MeO
CO2Me
MeO2C
OCF3
127.159
124.266
123.005
121.751
121.694
119.922
119.123
116.551
125 120 115
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

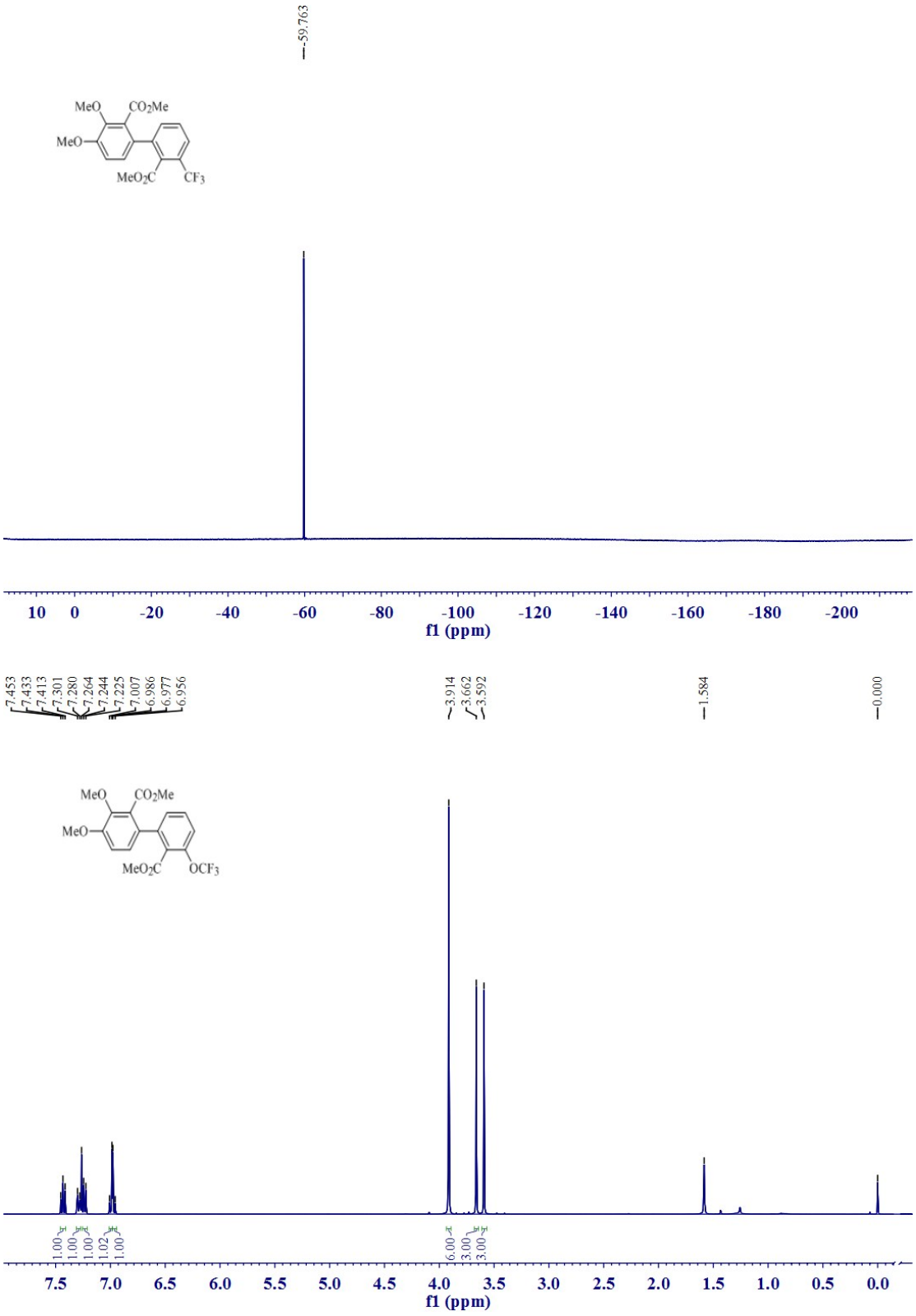

-57.225
MeO
CO2Me
MeO2C
OCF3
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)
7.699
7.681
7.552
7.532
7.513
7.508
7.493
7.402
7.381
7.362
7.264
6.991
6.971
6.884
6.863
3.888
3.619
3.565
1.598
0.000
MeO
CO2Me
MeO2C
CF3
1.00
2.00
1.00
1.00
1.00
3.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

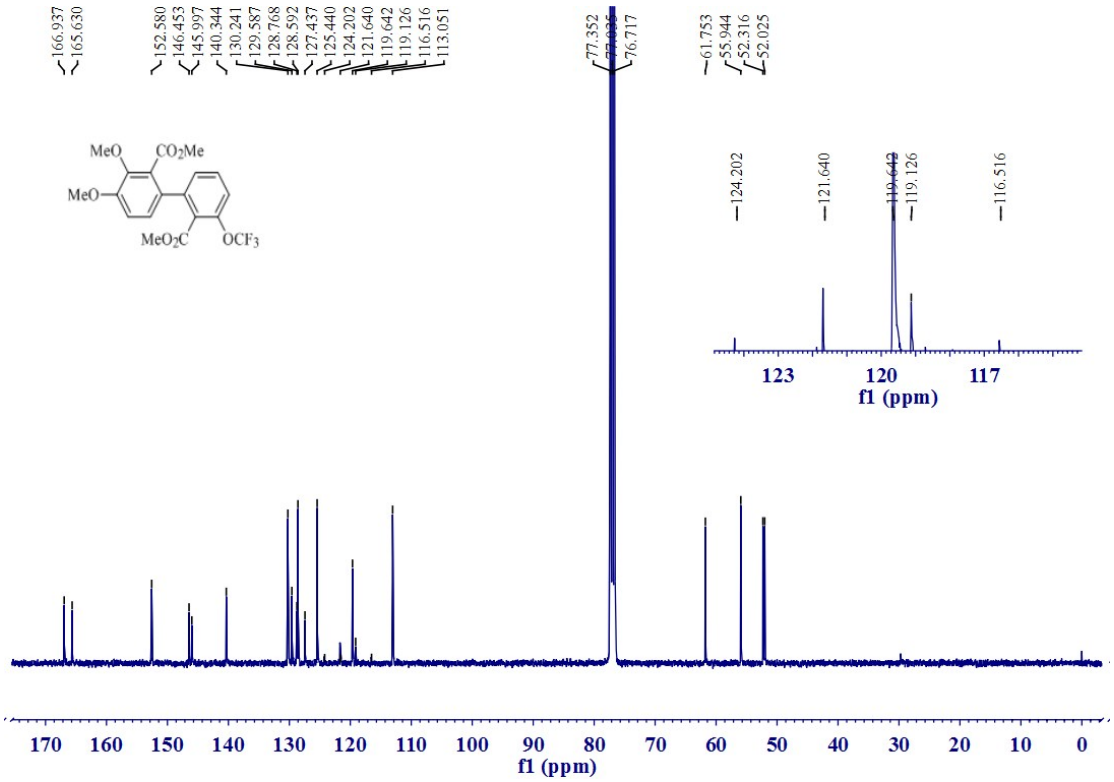

167.245
167.031
156.734
139.158
138.147
133.337
130.335
128.996
127.941
127.621
125.551
125.505
125.458
125.411
123.303
121.933
111.054
77.347
77.030
76.712
56.071
52.450
52.002
MeO
CO2Me
MeO2C
CF3
125.551
125.505
125.458
125.411
128.259
127.941
127.621
125.551
125.505
125.458
125.411
124.778
123.303
122.057
121.933
119.336
125.9
f1 (ppm)
127
124
121
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

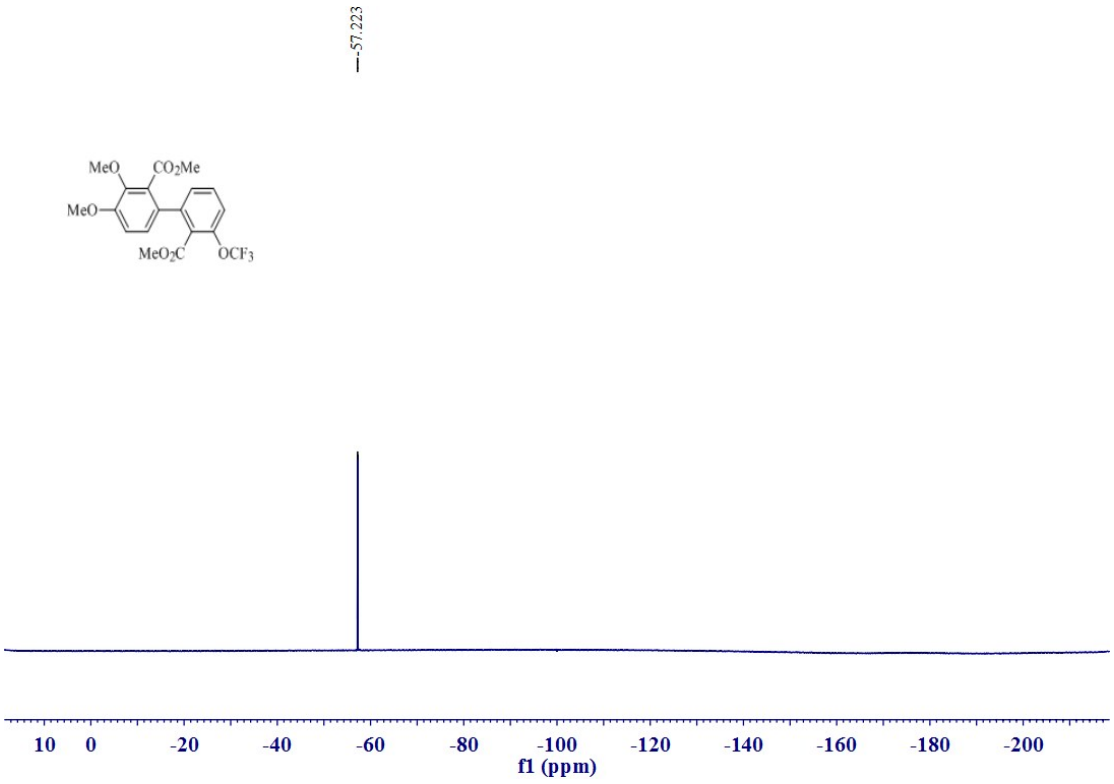

-59.719
MeO
CO2Me
MeO2C
CF3
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

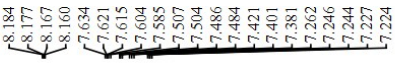

7.684
7.663
7.539
7.520
7.500
7.485
7.266
7.000
6.979
6.975
6.954
3.919
3.628
3.593
1.593
0.000
MeO
CO2Me
MeO
MeO2C
CF3
0.99
2.00
1.98
6.00
5.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

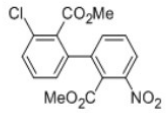

167.274
167.238
166.889
166.862
152.691
146.562
138.941
133.761
131.857
129.301
129.282
128.958
128.930
128.901
127.798
127.695
127.480
125.671
125.318
125.274
125.230
124.799
122.076
119.342
114.831
112.952
77.341
77.027
76.714
61.726
55.941
52.444
52.014
MeO
CO2Me
MeO
MeO2C
CF3
127.798
127.695
127.480
125.671
125.318
125.274
125.230
124.799
122.076
119.342
127
124
121
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

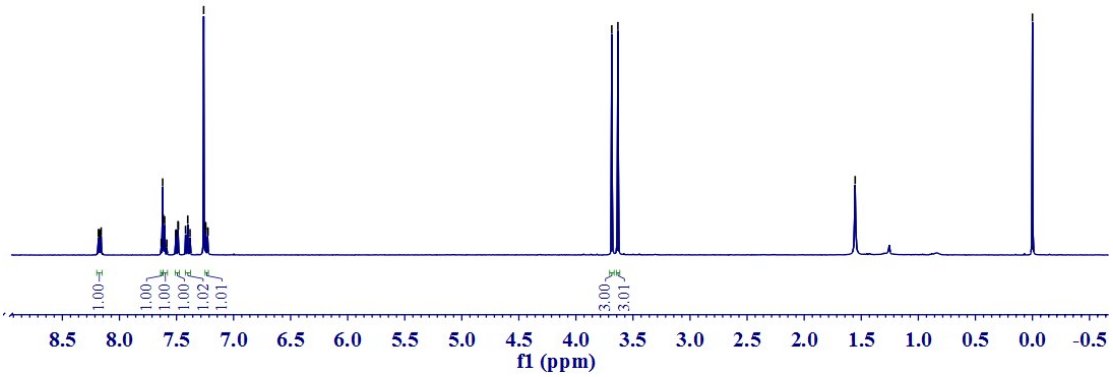

-59.763
MeO
CO2Me
MeO
MeO2C
CF3
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)
7.453
7.433
7.413
7.301
7.280
7.264
7.244
7.225
7.007
6.986
6.977
6.956
3.914
3.662
3.592
1.584
0.000
MeO
CO2Me
MeO
MeO2C
OCF3
1.00
1.00
1.00
1.02
1.00
6.00
3.00
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

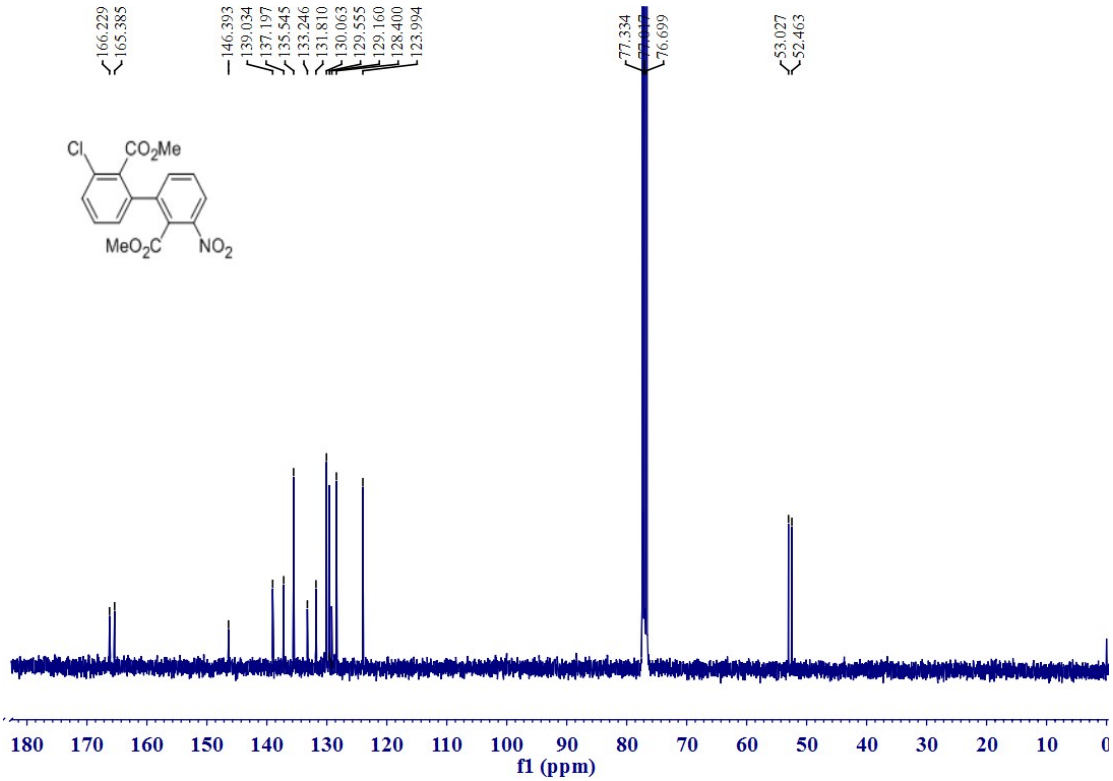

166.937
165.630
152.580
146.453
145.997
140.344
130.241
129.587
128.768
128.592
127.437
125.440
124.202
121.640
119.642
119.126
116.516
113.051
77.352
77.036
76.717
61.753
55.944
52.316
52.025
MeO
CO2Me
MeO
MeO2C
OCF3
124.202
121.640
119.642
119.126
116.516
123
120
117
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-57.223
MeO
CO2Me
MeO
MeO2C
OCF3
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


8.184
8.177
8.167
8.160
7.634
7.621
7.615
7.604
7.585
7.507
7.504
7.486
7.484
7.421
7.401
7.381
7.262
7.246
7.244
7.227
7.224
3.686
3.632
1.554
0.000


Cl
CO2Me
MeO2C
NO2


1.00
1.00
1.00
1.00
1.02
1.01
3.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.229
165.385
146.393
139.034
137.197
135.545
133.246
131.810
130.063
129.555
129.160
128.400
123.994
77.334
76.699
53.027
52.463
Cl
CO2Me
MeO2C
NO2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)