Electronic Supplementary Information (ESI)

Transition-metal-free oxidative trifluoromethylation of unsymmetrical biaryls with trifluoromethanesulfinate

Yu-Dong Yang, Kanji Iwamoto, Etsuko Tokunaga and Norio Shibata*

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan.

Fax: +81 52 735 7543; Tel: +81 52 735 7543; E-mail: nozshiba@nitech.ac.jp

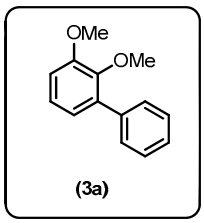
Experimental

General experimental details

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 μm. The ^1H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra for solution in $CDCl_3$, were recorded on a Varian Mercury 300. ^{13}C NMR (150.9 MHz) spectra were recorded on a BRUKER 600 UltraShield^{TR}. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CFCl_3$. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2010EV (ESI-MS and APCI-MS). Infrared spectra were recorded on a JASCO FT/IR-200 or a JASCO FT/IR-4100 spectrometer. 1-iodo-2,3-dimethoxybenzene was synthesized according to literature[1] and 2,3-dimethoxy phenyl boronic acid was synthesized according to previous report[2]. The ^1H NMR spectrums of compounds **3a**, **3d-f** were in accordance with that reported[2]. The ^1H NMR, ^{13}C NMR, ^{19}F NMR spectrums of compounds **2a**,[3] **2c**,[4] **2e**,[3] **2f**[4] were in accordance with literatures.

Synthesis of diaryl compounds

2,3-Dimethoxy-1,1'-biphenyl[2]



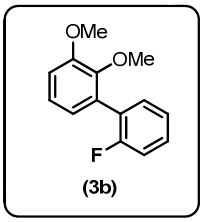
(3a)

To a 30 mL schlenk tube, 1-iodo-2,3-dimethoxybenzene (264.0 mg, 1.0 mmol), phenyl boronic acid (183.0 mg, 1.5 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added

and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Ether 95/5) to afford the desired product.

Yield: 89%; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.53 (m, 2H), 7.44-7.33 (m, 3H), 7.11 (t, *J* = 8.1 Hz, 1H), 6.97-6.91 (m, 2H), 3.92 (s, 3H), 3.59 (s, 2H); EI-MS: m/z (%) 214 (M^+, 100), 199 (49), 184 (37).

2'-Fluoro-2,3-dimethoxy-1,1'-biphenyl

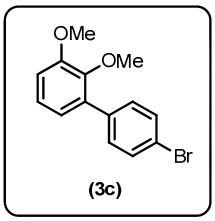


(3b)

To a 30 mL schlenk tube, 2,3-dimethoxy phenyl boronic acid (273.0 mg, 1.5 mmol), 1-bromo-2-fluorobenzene (315.0 mg, 1.8 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) and K_3PO_4 (955.2 mg, 4.5 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Ether 95/5) to afford the desired product.

Yield: 87%; slightly yellow oil. IR (neat) 2939, 2835, 1584, 1499, 1424, 1265, 1023, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.29 (m, 2H), 7.17-7.08 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 3.65 (s, *J* = 3.0 Hz, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 159.9 (d, *J* = 247.5 Hz), 153.0, 147.1, 131.9 (d, *J* = 3.0 Hz), 130.2, 129.2 (d, *J* = 3.0 Hz), 126.1 (d, *J* = 15.0 Hz), 123.9 (d, *J* = 4.5 Hz), 123.8, 123.2 (d, *J* = 1.5 Hz), 115.5 (d, *J* = 22.6 Hz), 112.5, 60.8, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.9 (m, 1F); EI-MS: m/z (%) 232 (M^+, 100), 217 (61), 202 (23), 146 (35); HRMS (EI) Calcd. for $C_{14}H_{13}FO_2$ $[M]^+$, 232.0900, found 232.0901.

4'-Bromo-2,3-dimethoxy-1,1'-biphenyl

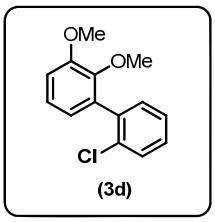


(3c)

To a 30 mL schlenk tube, 1-iodo-2,3-dimethoxybenzene (316.8 mg, 1.2 mmol), 4-bromophenyl boronic acid (200.8 mg, 1.0 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Acetone 97/3) to afford the desired product.

Yield: 66%; white solid. m.p.: 54-56 °C; IR (KBr) 2962, 2936, 1578, 1492, 1264, 1116, 995 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 8.1 Hz, 1H), 6.96-6.89 (m, 2H), 3.91 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.3, 146.5, 137.2, 134.8, 131.4, 131.1, 124.4, 122.4, 121.5, 111.9, 60.7, 56.1; EI-MS: m/z (%) 294 ($M+2^+$, 43), 292 (M^+, 43), 198 (100); HRMS (EI) Calcd. for $C_{14}H_{13}BrO_2$ $[M]^+$, 292.0099, found 292.0092.

2'-Chloro-2,3-dimethoxy-1,1'-biphenyl[2]



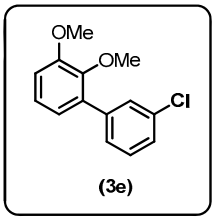
(3d)

To a 30 mL schlenk tube, 2,3-dimethoxy phenyl boronic acid (182.0 mg, 1.0 mmol), 1-iodo-2-chlorobenzene (286.1 mg, 1.2 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/EtOAc 95/5) to afford the desired product.

Yield: 96%; slightly yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.32-7.25 (m, 3H),

7.11 (t, J = 7.8 Hz, 1H), 6.97 (dd, J = 8.4, 1.2 Hz, 1H), 6.82 (d, J = 8.4, 1.2 Hz, 1H), 3.91 (s, 3H), 3.61 (s, 3H); EI-MS: m/z (%) 250 ($M+2^+$, 33), 248 (M^+, 95), 198 (100).

3'-Chloro-2,3-dimethoxy-1,1'-biphenyl[2]

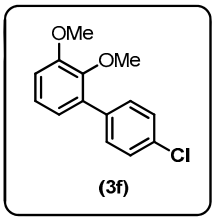


(3e)

To a 30 mL schlenk tube, 2,3-dimethoxy phenyl boronic acid (182.0 mg, 1.0 mmol), 1-iodo-3-chlorobenzene (286.1 mg, 1.2 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Et_2O 95/5) to afford the desired product.

Yield: 96%; slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.46-7.43 (m, 1H), 7.36-7.31 (m, 2H), 7.11 (t, J = 8.1 Hz, 1H), 6.96-6.90 (m, 1H), 3.91 (s, 3H), 3.60 (s, 3H); EI-MS: m/z (%) 250 ($M+2^+$, 33), 248 (M^+, 97), 198 (100).

4'-Chloro-2,3-dimethoxy-1,1'-biphenyl[2]

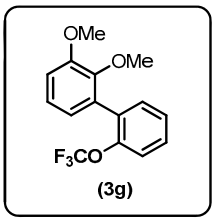


(3f)

To a 30 mL schlenk tube, 1-iodo-2,3-dimethoxybenzene (264.0 mg, 1.0 mmol), 4-chlorophenyl boronic acid (235.0 mg, 1.5 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Acetone 97/3) to afford the desired product.

Yield: 90%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.12 (t, J = 8.1 Hz, 1H), 6.96-6.91 (m, 2H), 3.92 (s, 3H), 3.60 (s, 3H); EI-MS: m/z (%) 250 ($M+2^+$, 30), 248 (M^+, 89), 233 (25), 198 (100).

2,3-Dimethoxy-2'-(trifluoromethoxy)-1,1'-biphenyl

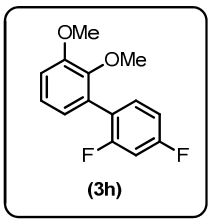


(3g)

To a 30 mL schlenk tube, 1-iodo-2,3-dimethoxybenzene (264.0 mg, 1.0 mmol), (2-(trifluoromethoxy)phenyl)boronic acid (308.9 mg, 1.0 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and K_3PO_4 (637.0 mg, 3.0 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Et_2O 95/5) to afford the desired product.

Yield: 75%; white solid. m.p.: 71-73 °C; IR (KBr) 3011, 2993, 2939, 1583, 1499, 1468, 1255, 1131, 922 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.31 (m, 4H), 7.09 (t, J = 8.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 152.9, 146.9, 146.8, 132.4, 131.9, 131.1, 128.9, 126.5, 123.6, 123.2, 120.6 (q, J = 256.5 Hz), 120.7, 112.5, 60.7, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.4 (s, 3F); EI-MS: m/z (%) 298 (M^+, 100), 283.2 (29), 197 (38); HRMS (EI) Calcd. for $C_{15}H_{13}F_3O_3$ $[M]^+$, 298.0817, found 298.0823.

2',4'-Difluoro-2,3-dimethoxy-1,1'-biphenyl



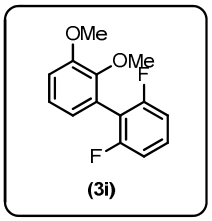
(3h)

To a 30 mL schlenk tube, 2,3-dimethoxy phenyl boronic acid (273.0 mg, 1.5 mmol), 1-iodo-2,4-difluorobenzene (430.0 mg, 1.8 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) and K_3PO_4 (955.2 mg, 4.5 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at

80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Et_2O 95/5) to afford the desired product.

Yield: 90%; white solid. m.p.: 54-56 °C; IR (KBr) 3073, 2988, 2933, 1616, 1507, 1419, 1317, 1121, 856 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.98-6.85 (m, 4H), 3.90 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 162.5 (dd, *J* = 249.0, 12.0 Hz), 160.0 (dd, *J* = 249.0, 12.0 Hz), 153.0, 147.1, 132.6 (q, *J* = 4.5 Hz), 129.4, 123.9, 123.1, 122.1 (dd, *J* = 16.6, 4.5 Hz), 112.6, 111.0 (dd, *J* = 21.1, 4.5 Hz), 104.0 (apparent t, *J* = 25.6 Hz), 60.8, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.5 (q, *J* = 7.9 Hz, 1F), 112.0 (quint, *J* = 7.9 Hz, 1F); EI-MS: m/z (%) 250 (M^+, 100), 235 (67), 164 (37); HRMS (EI) Calcd. for $C_{14}H_{12}F_2O_2$ $[M]^+$, 250.0805, found 250.0781.

2',6'-Difluoro-2,3-dimethoxy-1,1'-biphenyl



(3i)

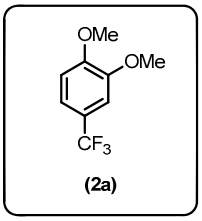
To a 30 mL schlenk tube, 2,3-dimethoxy phenyl boronic acid (273.0 mg, 1.5 mmol), 1-bromo-2,6-difluorobenzene (347.4 mg, 1.8 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) and K_3PO_4 (955.2 mg, 4.5 mmol) was added. Excluding the air under vacuum and recharged with N_2 for 3 times. Then EtOH (5 mL) was added and changed the septum to a glass cap. The mixture was stirred at 80 °C overnight. After the reaction was completed, the solvent was removed under reduced pressure, then water was added and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. Then filtered and removed the solvent under reduced pressure. The resulting mixture was purified by flash column chromatography (Hexane/Et_2O 95/5) to afford the desired product.

Yield: 67%; slightly yellow oil. IR (neat) 3065, 2941, 2836, 1626, 1460, 1234, 1120, 999, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.25 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.01-6.94 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 160.6 (dd, *J* = 249.0, 7.5 Hz), 153.0, 147.6, 129.3 (t, *J* = 10.6 Hz), 123.8, 123.6, 123.5, 115.3 (t, *J* = 6.0 Hz), 113.2, 111.3 (dd, *J* = 21.1, 6.0 Hz), 60.9, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.5 (t, *J* = 6.0 Hz, 1F); EI-MS: m/z (%) 250 (M^+, 100), 235 (31), 207 (22); HRMS (EI) Calcd. for $C_{14}H_{12}F_2O_2$ $[M]^+$, 250.0805, found 250.0784.

General procedure for metal-free oxidative trifluoromethylation of arenes at room temperature

To a mixture of arenes (0.2 mmol) and $NaSO_2CF_3$ (0.4 mmol) in HFIP (0.5 mL), PIFA (0.4 mmol) was added. After stirring vigorously at room temperature over 5 minutes, water was added to quench the reaction. And the resulting mixture was extracted with CH_2Cl_2, the combined organic phase was dried over anhydrous Na_2SO_4. Then filtered, the filtrate was evaporated under vacuum and purified by flash column chromatography (Hexane/Ether or Hexane/EtOAc) to afford the desired product. Further purification could be attempted on preparative thin-layer plate with Hexane/CH_2Cl_2 or Hexane/Toluene. (Note: For **2e**, PIDA (2.0 eq.) and $NaSO_2CF_3$ (10.0 eq.) were added instead; For **4b**, **4d**, **4e**, **4h** and **4i**, PIFA (2.3 eq.) and $NaSO_2CF_3$ (2.3 eq.) were added)

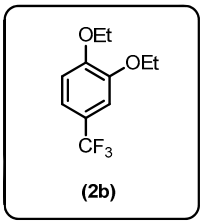
1,2-Dimethoxy-4-(trifluoromethyl)benzene[3]



(2a)

Yield: 56%; Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.1 Hz, 1H), 7.07 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.92 (s, 6H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 151.7, 149.1, 124.5 (q, J = 271.6 Hz), 123.0 (q, J = 33.2 Hz), 118.4 (q, J = 4.5 Hz), 110.7, 108.0 (q, J = 3.0 Hz), 56.1 (overlapped), 56.1 (overlapped); ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.0 (s, 3F); EI-MS: m/z (%) 206 (M^+, 100), 191 (27), 163 (25), 143 (59);

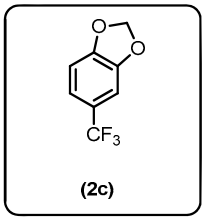
1,2-Diethoxy-4-(trifluoromethyl)benzene



(2b)

Yield: 48%; Slightly yellow solid. IR (KBr) 3092, 2992, 2940, 1608, 1432, 1323, 1224, 1106, 861 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, J = 8.7 Hz, 1H), 7.08 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.16-4.08 (m, 4H), 1.47 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 152.4, 151.0, 123.6 (q, J = 273.1 Hz), 120.1 (q, J = 31.7 Hz), 119.0, 115.1, 113.5 (q, J = 6.0 Hz), 65.5, 64.4, 14.9, 14.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.0 (s, 3F); EI-MS: m/z (%) 362 234 (M^+, 22), 206 (6), 178 (100); HRMS (EI) Calcd. for $C_{11}H_{13}F_3O_2$ $[M]^+$, 234.0868, found 234.0875.

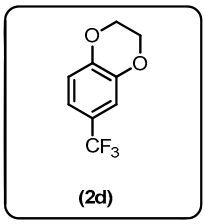
5-(Trifluoromethyl)benzo[d][1,3]dioxole[4]



(2c)

Yield: 32%; Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, J = 9.0 Hz, 1H), 7.04 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.04 (s, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 150.4, 148.1, 124.2 (q, J = 271.6 Hz), 124.4 (q, J = 33.2 Hz), 120.0 (q, J = 4.5 Hz), 108.4, 106.0, 102.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.0 (s, 3F).

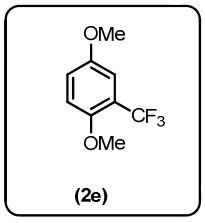
6-(Trifluoromethyl)-2,3-dihydrobenzo[b][1,4]dioxine



(2d)

Yield: 43%; Colorless oil. IR (neat) 2989, 2884, 1591, 1463, 1328, 1123, 900 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.10 (d, J = 8.7 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 4.29 (t, J = 5.1 Hz, 4H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 146.4, 143.6, 124.2 (q, J = 270.1 Hz), 123.8 (q, J = 33.2 Hz), 118.7 (q, J = 4.5 Hz), 117.7, 115.0 (q, J = 4.5 Hz), 64.6, 64.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.3 (s, 3F); MS (EI): m/z (%) 204.2 (M^+, 100); HRMS (EI) Calcd. for $C_9H_7F_3O_2$ $[M]^+$, 204.0398, found 204.0424.

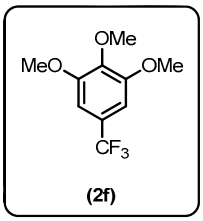
1,4-Dimethoxy-2-(trifluoromethyl)benzene[3]



(2e)

Yield: 31%; Slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.02 (d, J = 9.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.3, 151.9, 123.8 (q, J = 272.5 Hz), 119.8 (q, J = 31.2 Hz), 118.5, 114.0, 113.2 (q, J = 5.4 Hz), 57.0, 56.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9 (s, 3F); MS (EI): m/z (%) 206 (M^+, 69), 191 (100);

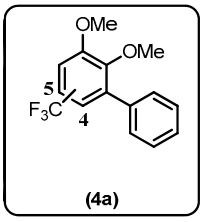
1,2,3-Trimethoxy-5-(trifluoromethyl)benzene[4]



(2f)

Yield: 34%; slightly yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 2H) 3.91 (s, 3H), 3.90 (s, 6H); ^{13}C NMR (150.9MHz, $CDCl_3$) δ 153.5, 140.7, 124.2 (q, J = 271.6 Hz), 125.8 (q, J = 33.2 Hz), 102.6 (q, J = 4.5 Hz), 61.0, 56.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6 (s, 3F); MS (EI): m/z (%) 236 (M^+, 100), 221(51), 193 (26);

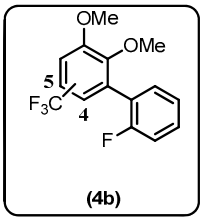
Trifluoromethyl-2,3-dimethoxy-1,1'-biphenyl



(4a)

Yield: 34%, **C5:C4** = 9:4; Data for **4a-C5**: slightly yellow oil. IR (neat) 2940, 2832, 1593, 1499, 1366, 1258, 904 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.46-7.35 (m, 3H), 7.24 (s, 1H), 7.13 (s, 1H), 3.95 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.4, 149.3, 137.2, 136.4, 129.3, 128.5, 127.9, 124.2 (q, J = 271.6 Hz), 126.2 (q, J = 33.2 Hz), 120.0 (q, J = 4.5 Hz), 108.3 (q, J = 4.5 Hz), 60.9, 56.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5 (s, 3F); EI-MS: m/z (%) 282 (M^+, 100), 267 (24), 247 (18), 198 (44); HRMS (EI) Calcd. for $C_{15}H_{13}F_3O_2$ $[M]^+$, 282.0868, found 282.0852. Data for **4a-C4**: slightly yellow solid. m.p.: 52-54 °C; IR (KBr) 3009, 2971, 2941, 1600, 1577, 1456, 1321, 1280, 1115, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz), 7.41-7.38 (m, 3H), 7.28 (d, J = 5.4 Hz), 6.98 (d, J = 8.4 Hz), 3.95 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (150.9MHz, $CDCl_3$) δ 155.6, 147.6, 136.3, 134.7, 129.8, 127.7, 127.6, 124.1 (q, J = 273.1 Hz), 122.2 (q, J = 30.0 Hz), 122.2 (q, J = 6.0 Hz), 110.6, 60.9, 56.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.1 (s, 3F); EI-MS: m/z (%) 282 (M^+, 100), 267 (28), 247 (38), 198 (54); HRMS (EI) Calcd. for $C_{15}H_{13}F_3O_2$ $[M]^+$, 282.0868, found 282.0872.

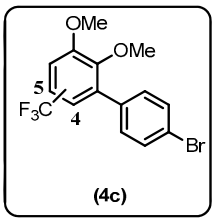
Trifluoromethyl-2'-fluoro-2,3-dimethoxy-1,1'-biphenyl



(4b)

Yield: 35%, **C5:C4** = 7:3; Data for **4b-C5**: yellow oil. IR (neat) 2944, 2840, 1594, 1498, 1367, 1138, 907 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.31 (m, 2H), 7.23-7.12 (m, 4H), 3.95 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 160.0 (d, *J* = 247.5 Hz), 153.1, 149.8, 131.7 (d, *J* = 3.0 Hz), 130.5, 129.9 (d, *J* = 9.1 Hz), 124.1 (q, *J* = 273.1 Hz), 125.9 (q, *J* = 33.2 Hz), 125.0 (d, *J* = 18.1 Hz), 124.1 (d, *J* = 3.0 Hz), 120.4 (q, *J* = 3.0 Hz), 115.8 (d, *J* = 22.6 Hz), 109.3 (q, *J* = 3.0 Hz), 61.0, 56.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5 (s, 3F), -114.8 (t, *J* = 14.7 Hz, 1F); EI-MS: m/z (%) 300 (M^+, 100), 285 (28), 216 (57); HRMS (EI) Calcd. for $C_{15}H_{12}F_4O_2$ $[M]^+$, 300.0773, found 300.0761. Data for **4b-C4**: yellow oil. IR (neat) 2942, 2845, 1601, 1457, 1321, 1119, 815 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.7 Hz, 1H), 7.4 (q, *J* = 7.8 Hz,1H), 7.26-7.10 (m, 3H), 7.01 (d, *J* = 8.7 Hz,1H), 3.95 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (150.9MHz, $CDCl_3$) δ 160.1 (d, *J* = 245.9 Hz), 155.5, 147.9, 131.9, 130.0 (d, *J* = 7.5 Hz), 129.44, 123.9 (q, *J* = 271.6 Hz), 123.4 (d, *J* = 4.5 Hz), 122.6 (q, *J* = 30.2 Hz), 122.5, 122.4 (t, *J* = 4.5 Hz), 115.2 (d, *J* = 21.1 Hz), 111.4, 60.8, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.8 (s, 3F), -113.9 (s, 1F); EI-MS: m/z (%) 300 (M^+, 100), 285 (28), 216 (53); HRMS (EI) Calcd. for $C_{15}H_{12}F_4O_2$ $[M]^+$, 300.0773, found 300.0770.

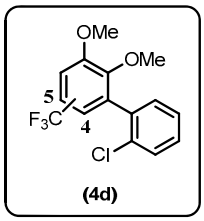
Trilfuoromethyl-4'-bromo-2,3-dimethoxy-1,1'-biphenyl



(4c)

Yield: 34%, **C5:C4** = 2:1; Data for **4c-C5**: Slightly yellow solid. m.p.: 56-58 °C; IR (KBr) 2945, 2842, 1594, 1495, 1368, 1136, 824 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 32.4, 8.4 Hz, 4H), 7.19 (s, 1H), 7.13 (s, 1H), 3.96 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.8, 149.4, 136.3, 135.4, 131.9, 131.2, 126.7 (q, *J* = 33.2 Hz), 124.4 (q, *J* = 273.1 Hz), 122.5, 119.8 (q, *J* = 3.0 Hz), 109.0 (q, *J* = 3.0 Hz), 61.1, 56.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6 (s, 3F); EI-MS: m/z (%) 362 ($M+2^+$, 52), 360 (M^+, 60), 266 (100); HRMS (EI) Calcd. for $C_{15}H_{12}BrF_3O_2$ $[M]^+$, 359.9973, found 359.9945. Data for **4c-C4**: Slightly yellow solid. m.p.: 796-98 °C; IR (KBr) 2932, 2853, 1602, 1453, 1278, 1115, 811 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.47 (q, *J* = 8.7 Hz,1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.7 Hz,1H), 3.94 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (150.9MHz, $CDCl_3$) δ 155.6, 147.4, 134.9, 133.7, 131.5, 130.9, 124.0 (q, *J* = 273.1 Hz), 122.3 (q, *J* = 6.0 Hz), 122.1 (q, *J* = 28.7 Hz), 122.0, 110.9, 60.9, 56.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.0 (s, 3F); EI-MS: m/z (%) 362 ($M+2^+$, 55), 360 (M^+, 58), 266 (100); HRMS (EI) Calcd. for $C_{15}H_{12}BrF_3O_2$ $[M]^+$, 359.9973, found 360.0000.

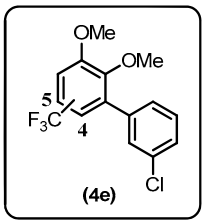
Trifluoromethyl-2'-chloro-2,3-dimethoxy-1,1'-biphenyl



(4d)

Yield: 49%, **C5:C4** = 11:4; Data for **4d-C5**: colorless oil. IR (neat) 2941, 1598, 1464, 1365, 1233, 1141, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.47 (m, 1H), 7.34-7.30 (m, 2H), 7.17 (s, 1H), 7.12 (s, 1H), 3.95 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.0, 149.5, 136.4, 134.0, 133.5, 131.5, 129.7, 129.4, 126.7, 125.7 (q, J = 31.7 Hz), 124.2 (q, J = 271.6 Hz), 120.3 (q, J = 4.5 Hz), 109.1 (q, J = 3.0 Hz), 61.0, 56.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.4 (s, 3F); EI-MS: m/z (%) 318 ($M+2^+$, 38), 316 (M^+, 100), 266 (79); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0468. Data for **4d-C4**: slightly yellow solid. m.p.: 88-90 °C; IR (KBr) 2948, 2848, 1604, 1482, 1421, 1272, 1158, 1119, 835, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 4.2 Hz, 2H), 7.37-7.22 (m, 3H), 7.01 (d, J = 4.3 Hz, 1H), 3.95 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 155.5, 147.4, 134.3, 134.0, 132.9, 131.5, 129.4, 129.1, 126.0, 123.9 (q, J = 273.1 Hz), 122.3 (q, J = 6.0 Hz), 121.7 (q, J = 30.2 Hz), 111.3, 60.8, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.9 (s, 3F); EI-MS: m/z (%) 318 ($M+2^+$, 30), 316 (M^+, 84), 281 (16), 266 (100); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0477.

Trifluoromethyl-3'-chloro-2,3-dimethoxy-1,1'-biphenyl

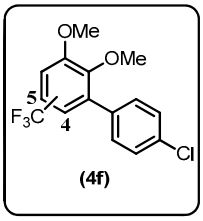


(4e)

Yield: 38%, **C5:C4** = 7:3; Data for **4e-C5**: yellow oil. IR (neat) 2941, 2843, 1592, 1464, 1364, 1233, 911 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42-7.35 (m, 3H), 7.20 (s, 1H), 7.14 (s, 1H), 3.96 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.5, 149.2, 138.9, 134.9, 134.3, 129.7, 129.4, 128.0, 127.6, 126.4 (q, J = 33.2 Hz), 124.1 (q, J = 271.6 Hz), 119.6 (q, J = 4.5 Hz), 108.8 (q, J = 4.5 Hz), 61.0, 56.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6 (s, 3F); EI-MS: m/z (%) 318 ($M+2^+$, 37), 316 (M^+, 100), 281 (16), 266 (64); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0467. Data for **4e-C4**: yellow oil. IR (neat) 2939, 2843, 1595, 1455, 1320, 1128, 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 1H), 7.39-7.30 (m, 2H), 7.27 (s, 1H), 7.15 (d, J = 6.9 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 3.95 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 155.6, 147.5, 136.5, 134.6, 133.5, 129.9, 128.9, 128.1, 128.0, 123.9 (q, J = 273.1 Hz), 122.3 (q, J = 6.0 Hz), 121.8 (q, J = 30.2 Hz), 111.0, 61.0, 56.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.0 (s, 3F); EI-MS: m/z

(%) 318 ($M+2^+$, 27),316 (M^+, 100), 281 (31), 266 (58); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0504.

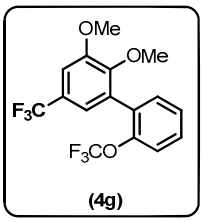
Trifluoromethyl-4'-chloro-2,3-dimethoxy-1,1'-biphenyl



(4f)

Yield: 39%, **C5:C4** = 5:2; Data for **4f-C5**: slightly yellow solid. m.p.: 54-56 °C; IR (KBr) 2945, 2843, 1594, 1498, 1455, 1367, 1094, 997; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, J = 20.1, 6.6 Hz, 4H), 7.20 (s, 1H), 7.13 (s, 1H), 3.95 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.5, 149.2, 135.5, 135.1, 134.0, 130.7, 128.7, 126.4 (q, J = 33.2 Hz), 124.1 (q, J = 271.6 Hz), 119.6 (q, J = 3.0 Hz), 108.6 (q, J = 3.0 Hz), 60.9, 56.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6 (s, 3F); EI-MS: m/z (%) 318 ($M+2^+$, 31), 316 (M^+, 100), 301 (23), 266 (63); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0496. Data for **4f-C4**: m.p.: 81-83 °C; slightly yellow solid. IR (KBr) 2969, 2839, 1603, 1454, 1321, 1262, 1115, 1013, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 155.6, 147.5, 134.9, 133.8, 133.2, 131.2, 127.9, 124.0 (q, J = 273.1 Hz), 122.3 (q, J = 6.0 Hz), 122.1 (d, J = 30.0 Hz), 110.9, 60.9, 56.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.0 (s, 3F); EI-MS: m/z (%) 318 ($M+2^+$, 34), 316 (M^+, 100), 281 (21), 266 (62); HRMS (EI) Calcd. for $C_{15}H_{12}ClF_3O_2$ $[M]^+$, 316.0478, found 316.0495.

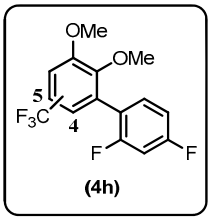
Trifluoromethyl-2,3-dimethoxy-2'-(trifluoromethoxy)-1,1'-biphenyl



(4g)

Yield: 43%, Data for **4g-C5**: yellow oil. IR (neat) 2945, 2842, 1594, 1423, 1259, 1141, 907 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.34 (m, 4H), 7.17 (s, 1H), 7.15 (s, 1H), 3.95 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 153.0, 149.6, 146.8, 132.1, 131.3, 130.7, 129.5, 126.7, 125.7 (q, J = 33.2 Hz), 124.1 (q, J = 271.6 Hz), 120.8, 120.5 (q, J = 256.5 Hz), 120.4 (q, J = 3.0 Hz), 109.3 (q, J = 3.0 Hz), 60.8, 56.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.6 (s, 3F), -62.5 (s, 3F); EI-MS: m/z (%) 366 (M^+, 100), 282 (30), 265 (39); HRMS (EI) Calcd. for $C_{16}H_{12}F_6O_3$ $[M]^+$, 366.0691, found 366.0668.

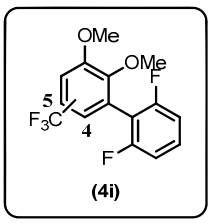
Trifluoromethyl-2',4'-difluoro-2,3-dimethoxy-1,1'-biphenyl



(4h)

Yield: 45%, **C5:C4** = 5:2; Data for **4h-C5**: yellow oil. IR (neat) 2945, 2846, 1599, 1465, 1368, 1139, 968 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 14.7, 4.1 Hz, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 6.93 (dd, *J* = 18.9, 10.2 Hz, 2H), 3.95 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 162.9 (dd, *J* = 250.5, 12.1 Hz), 160.0 (dd, *J* = 250.5, 12.1 Hz),153.1, 149.8, 132.4 (q, *J* = 4.5 Hz), 129.6, 126.0 (q, *J* = 33.2 Hz), 124.1 (q, *J* = 271.6 Hz), 121.0 (dd, *J* = 12.0, 4.5 Hz), 120.3 (d, *J* = 4.5 Hz), 111.4 (dd, *J* = 21.1, 3.0 Hz), 109.4 (q, *J* = 3.0 Hz), 104.2 (t, *J* = 27.2 Hz), 60.9, 56.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ 62.5 (s, 3F), -110.3 (q, *J* = 9.0 Hz, 1F), -110.8 (quint, *J* = 7.9 Hz, 1F); EI-MS: m/z (%) 318 (M^+, 100), 303 (35), 234 (55); HRMS (EI) Calcd. for $C_{15}H_{11}F_5O_2$ $[M]^+$, 318.0679, found 318.0696. Data for **4h-C4**: yellow oil. IR (neat) 2942, 2846, 1600, 1492, 1321, 1015, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 1H), 7.18 (dd, *J* = 15, 8.1 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.91 (dd, *J* =16.5, 7.8 Hz, 2H), 3.95 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 163.0 (dd, *J* = 249.0, 12.1 Hz), 160.2 (dd, *J* = 249.0, 12.1 Hz), 155.5, 148.0, 132.5 (q, *J* = 4.5 Hz), 128.5, 123.8 (q, *J* = 273.1 Hz), 122.7 (q, *J* = 31.7 Hz), 122.4 (q, *J* = 4.5 Hz), 118.4 (dd, *J* = 18.1, 4.5 Hz), 111.5, 110.8 (q, *J* = 3.0 Hz), 103.7 (t, *J* = 25.6 Hz), 60.9, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ 58.8 (s, 3F), -109.5 (d, *J* = 6.8 Hz, 1F), -110.9 (quint, *J* = 7.9 Hz, 1F); EI-MS: m/z (%) 318 (M^+, 100), 303 (31), 234 (53); HRMS (EI) Calcd. for $C_{15}H_{11}F_5O_2$ $[M]^+$, 318.0679, found 318.0686.

Trifluoromethyl-2',6'-difluoro-2,3-dimethoxy-1,1'-biphenyl

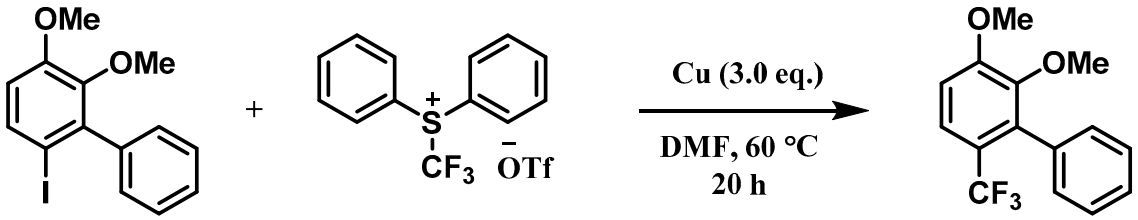


(4i)

Yield: 45%, **C5:C4** = 5:2; Data for **4i-C5**: slightly yellow solid. m.p.: 58-60 °C; IR (KBr) 2977, 2942, 1587, 1500, 1363, 1230, 1138, 872 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (quint, *J* = 7.2 Hz, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 6.98 (t, *J* = 11.3 Hz, 2H), 3.95 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 161.2 (d, *J* = 6.0 Hz), 159.6 (d, *J* = 6.0 Hz), 153.1, 150.3, 129.9 (t, *J* = 10.6 Hz), 125.9 (q, *J* = 33.2 Hz), 124.1 (q, *J* = 271.6 Hz), 123.9, 120.8 (q, *J* = 3.0 Hz), 114.2 (t, *J* = 21.1 Hz), 111.5 (dd, *J* = 21.1, 4.5 Hz), 109.9 (q, *J* = 3.0 Hz), 61.0, 56.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.4

(s, 3F), -112.4 (m, 2F); EI-MS: m/z (%) 318 (M^+, 100), 303 (29), 138 (31); HRMS (EI) Calcd. for $C_{15}H_{11}F_5O_2$ $[M]^+$, 318.0679, found 318.0675. Data for **4i-C4**: slightly yellow solid. m.p.: 89-91 °C; IR (KBr) 2946, 2846, 1630, 1466, 1281, 1119, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz), 7.37 (quint, *J* = 6.6 Hz), 7.05 (d, *J* = 8.7 Hz), 6.98 (t, *J* = 6.9 Hz), 3.96 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 161.4 (d, *J* = 6.0 Hz), 159.8 (d, *J* = 6.0 Hz), 155.6, 148.1, 130.3 (t, *J* = 10.6 Hz), 123.7 (q, *J* = 271.6 Hz), 122.9 (q, *J* = 31.7 Hz), 122.8 (d, *J* = 1.5 Hz), 122.5 (d, *J* = 6.0 Hz), 112.0, 111.8 (t, *J* = 22.6 Hz), 111.1 (dd, *J* = 21.1, 4.5 Hz), 60.9, 56.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.0 (s, 3F), -111.4 (s, 2F); EI-MS: m/z (%) 318 (M^+, 100), 303 (33); HRMS (EI) Calcd. for $C_{15}H_{11}F_5O_2$ $[M]^+$, 318.0679, found 318.0672.

Synthesis of authentic sample compound 4a-C4



1.0 eq. **2.0 eq.** **yield 40%**

The authentic sample was synthesized according to a literature procedure.[5] In a 10 mL test tube, 6-iodo-2,3-dimethoxy-1,1'-biphenyl[2] (68.0 mg, 0.2 mmol) and $[Ph_2SCF_3]^+[OTf]^-$ (161.7 mg, 0.4 mmol) were dissolved in DMF (1 mL), then Cu (38.1 mg, 0.6 mmol) was added. The mixture was stirred at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with diethyl ether, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified through column chromatography on silica gel (Hexane/EtOAc 95/5) to afford slightly yellow solid (22.7 mg, 40%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz), 7.41-7.37 (m, 3H), 7.28 (d, *J* = 5.4 Hz), 6.97 (d, *J* = 9.0 Hz), 3.94 (s, 3H), 3.52 (s, 3H).

References

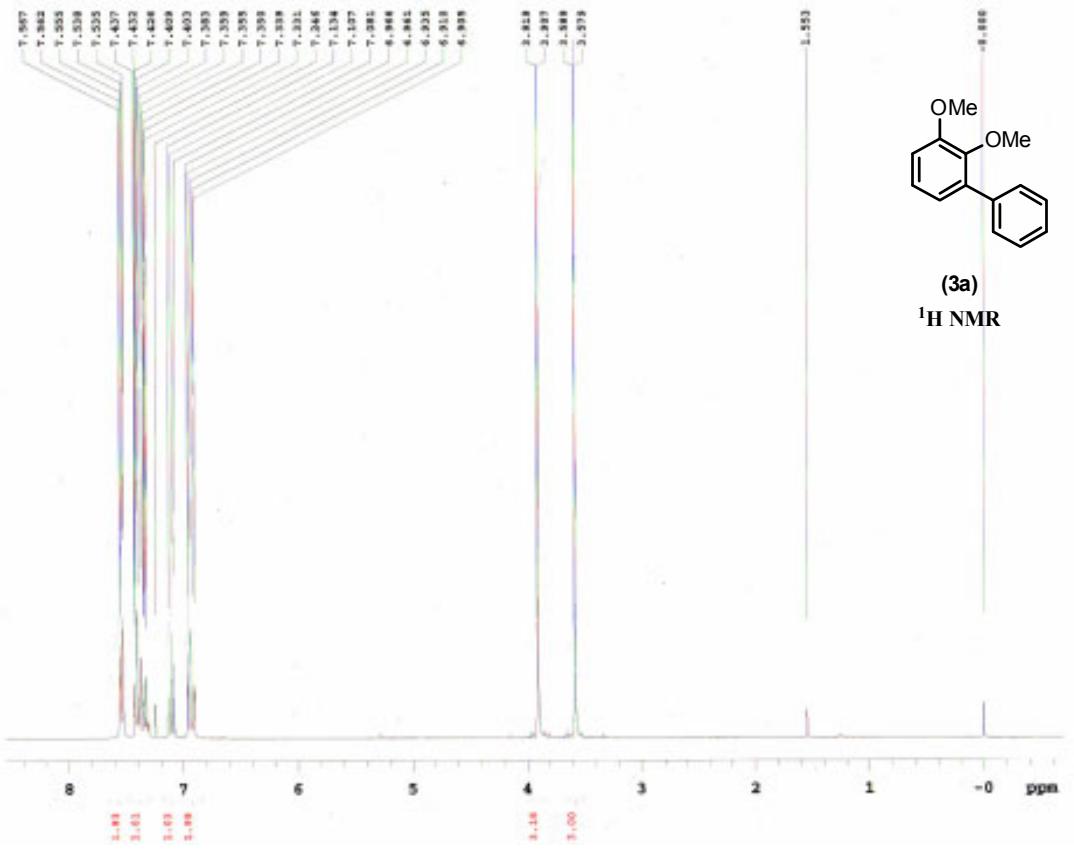
[1] U. Kiehne, A. Lützen, *Eur. J. Org. Chem.*, 2007, 5703;

[2] S. Nerdinger, C. Kendall, X. Cai, R. Marchart, P. Riebel, M. R. Johnson, C.-F. Yin, N. Hénaff, L. D. Eltis, V. Snieckus, *J. Org. Chem.*, 2007, **72**, 5960;

[3] Y. Ye, S. H. Lee, M. S. Sanford, *Org. Lett.*, 2011, **13**, 5464;

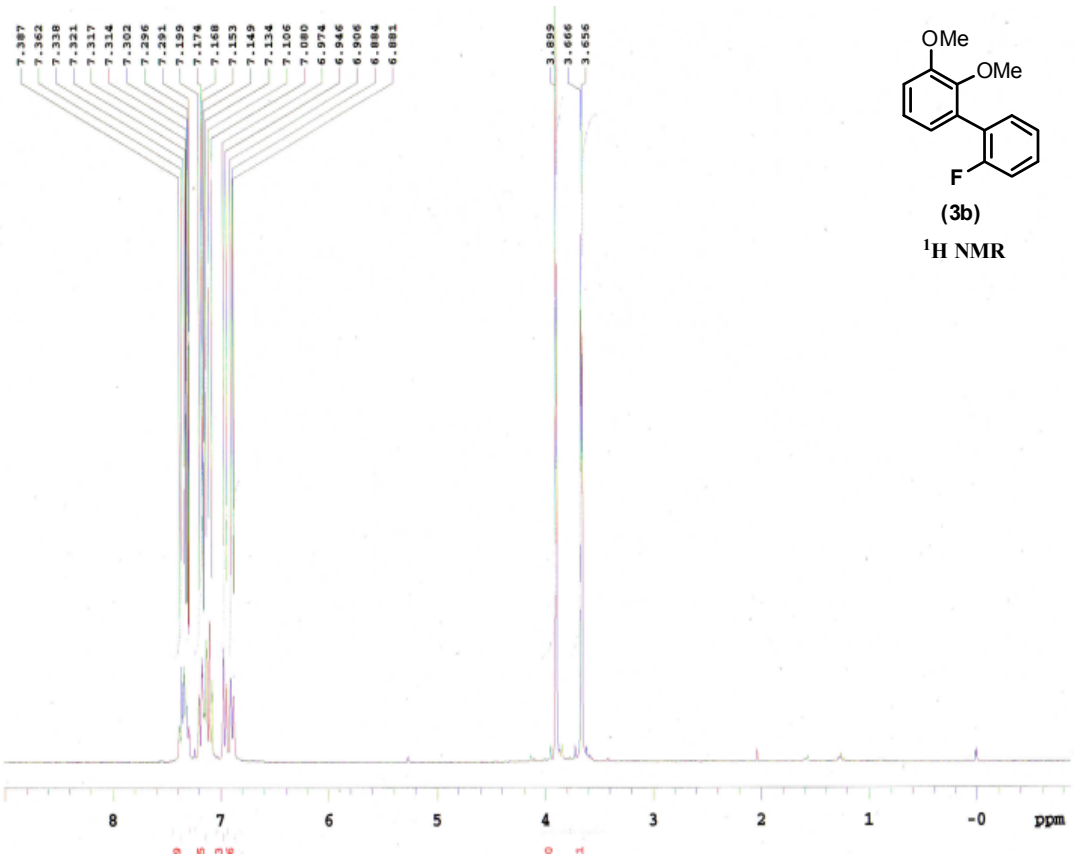
[4] B. A. Khan, A. E. Buda, L. J. Gooßen, *Chem. Eur. J.*, 2012, **18**, 1577.

[5] C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhao, Y.-C. Gu, J.-C. Xiao, *Angew. Chem. Int. Ed.*, 2011, **50**, 1896-1900.



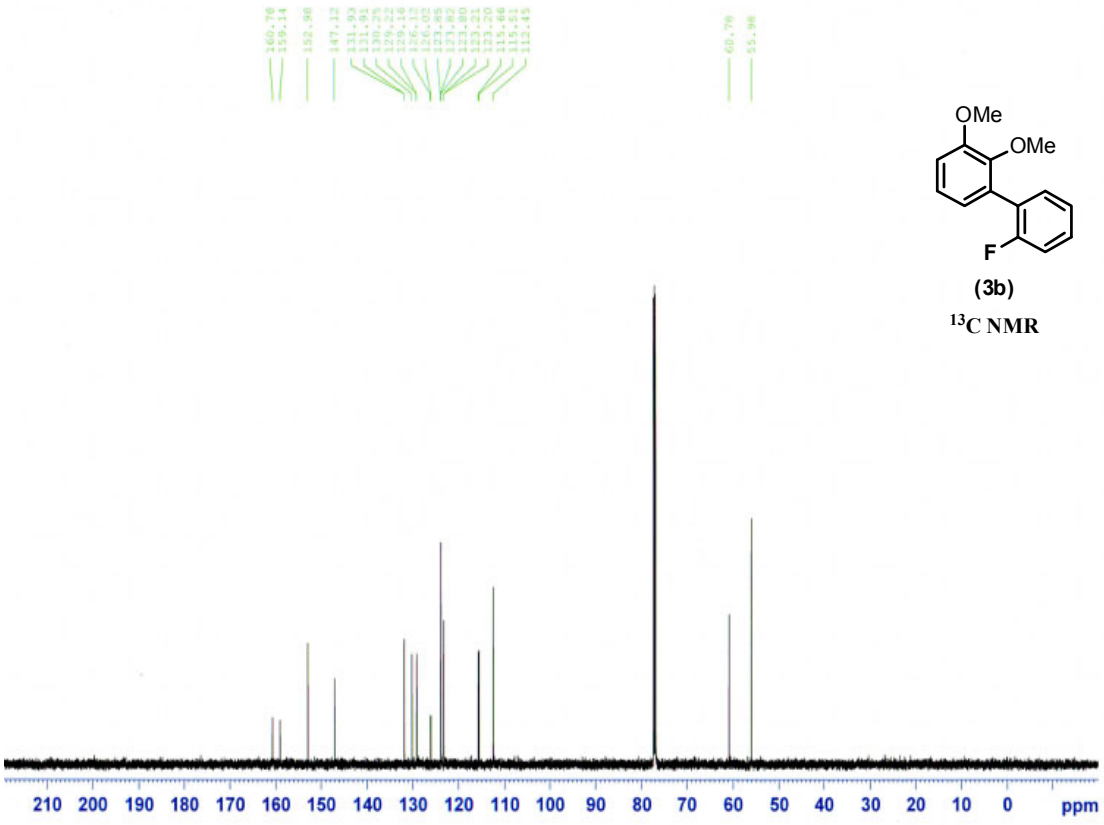
(3a)

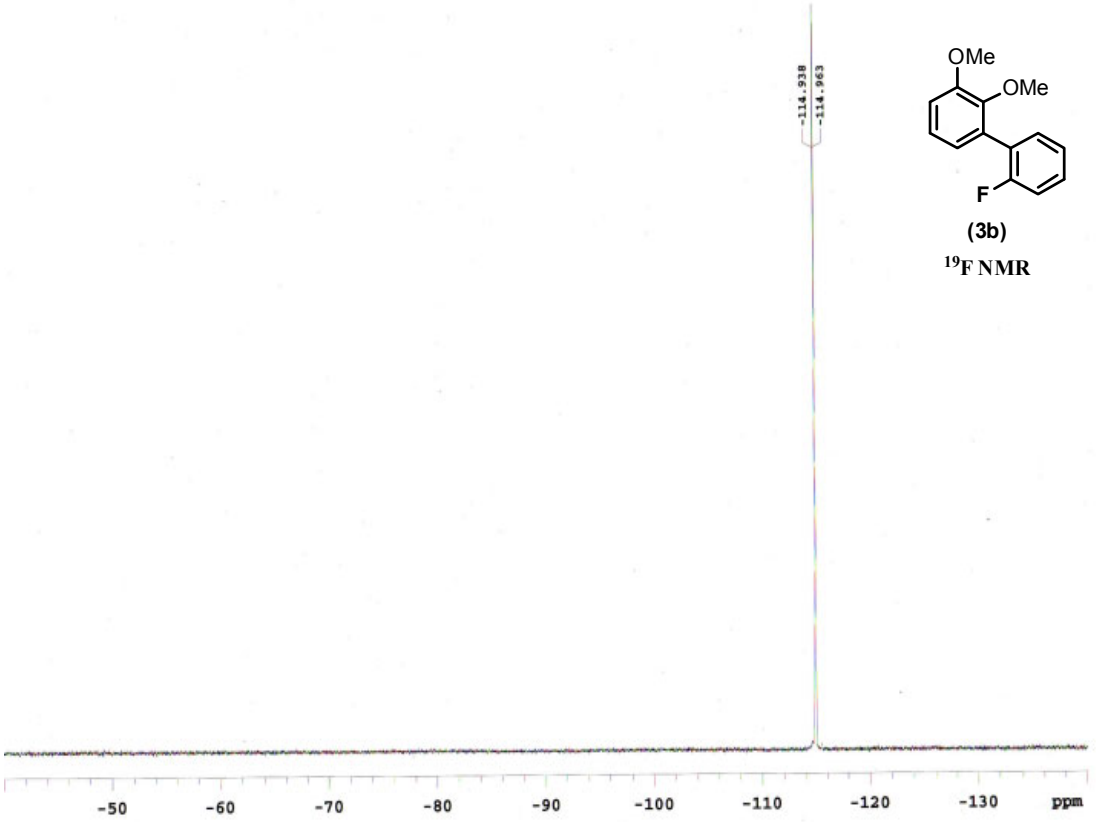
^{1}H NMR

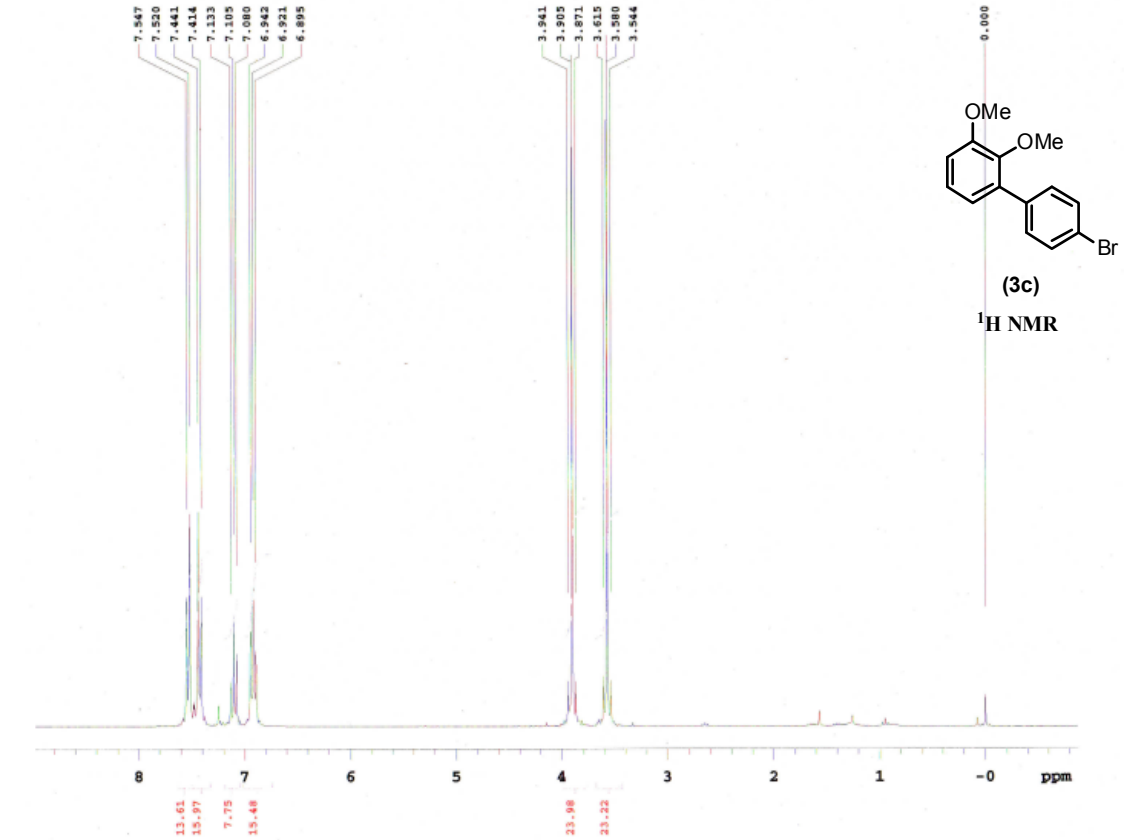


(3b)

^{1}H NMR

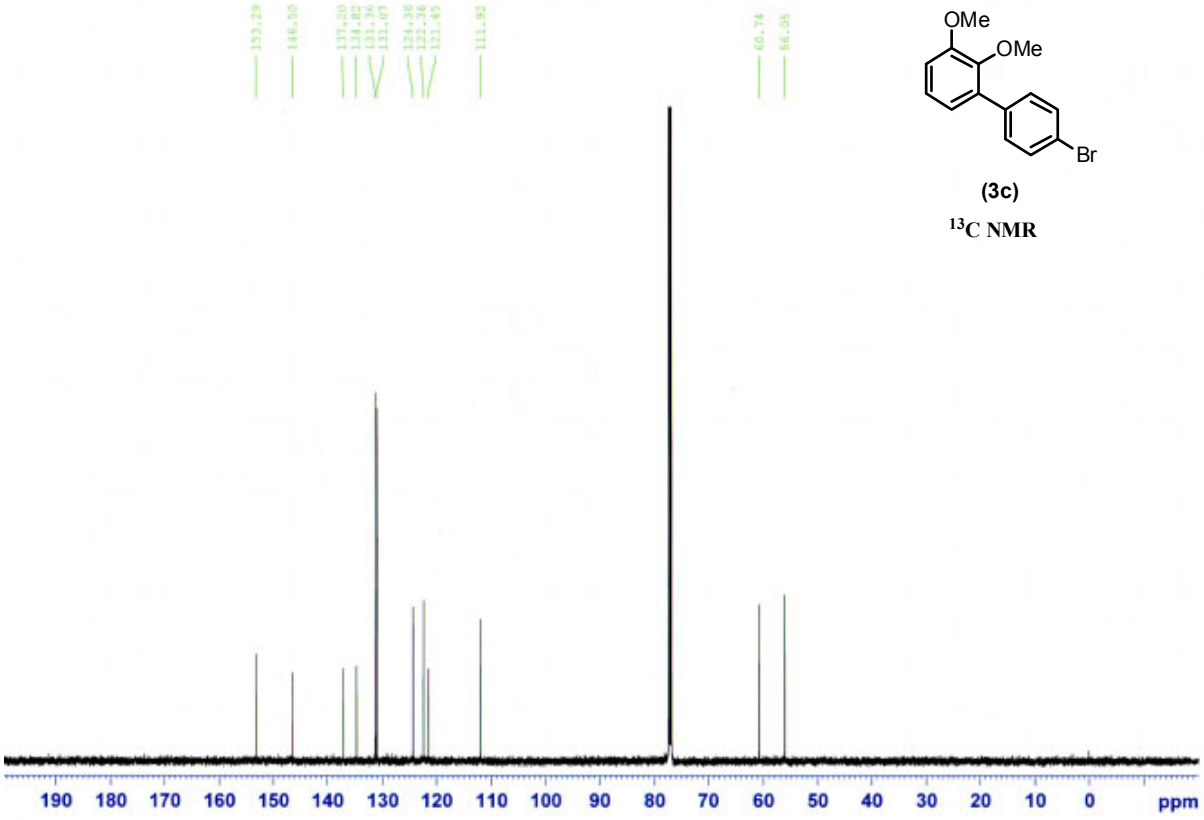

OMe
OMe
F
(3b)
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
OMe
F
(3b)
19F NMR
-50 -60 -70 -80 -90 -100 -110 -120 -130 ppm



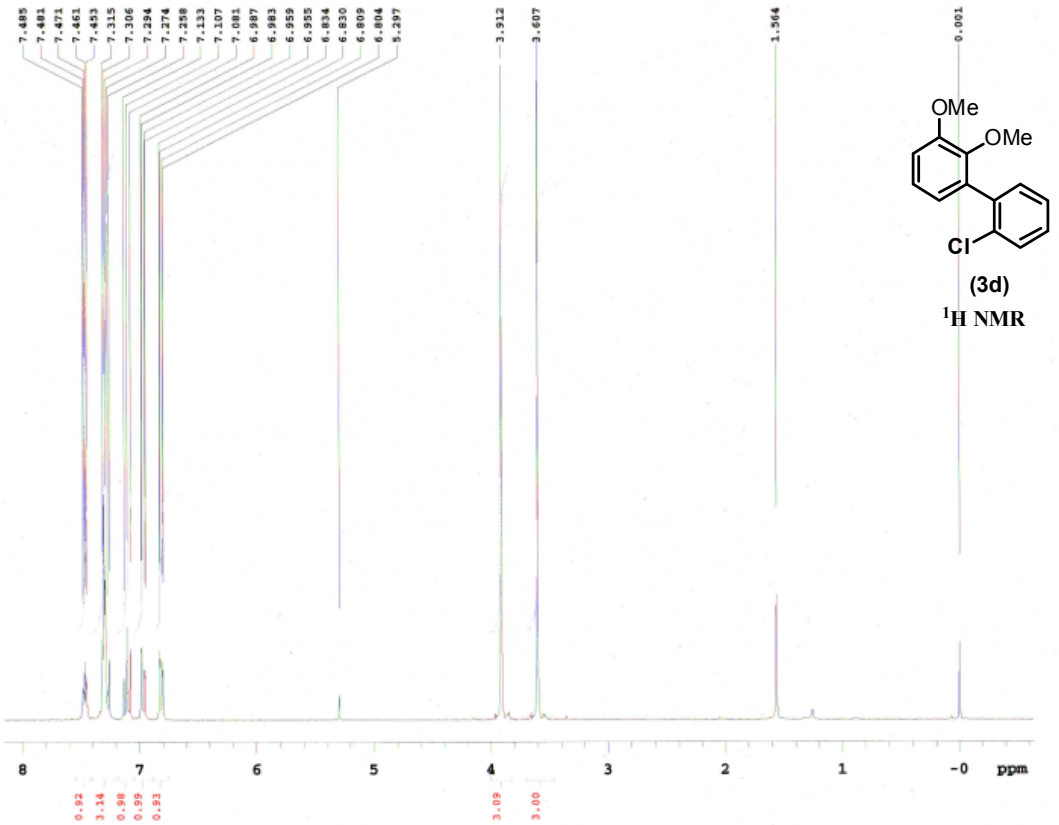
(3c)

^{1}H NMR



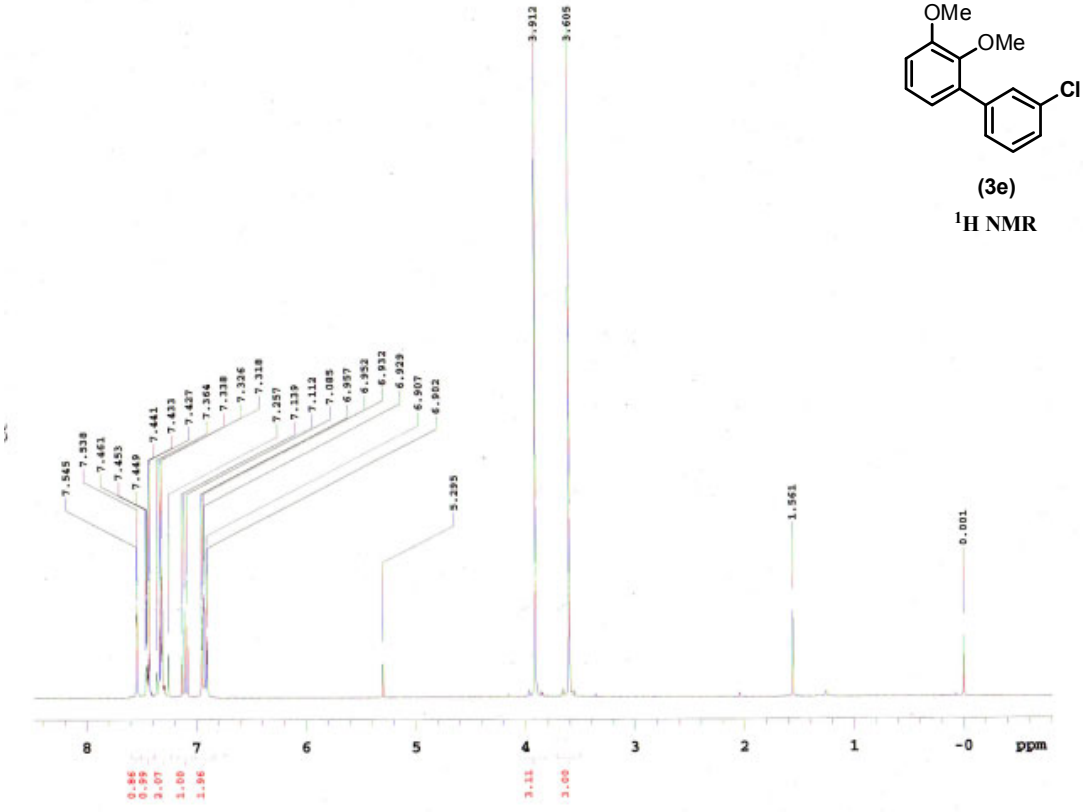
(3c)

^{13}C NMR



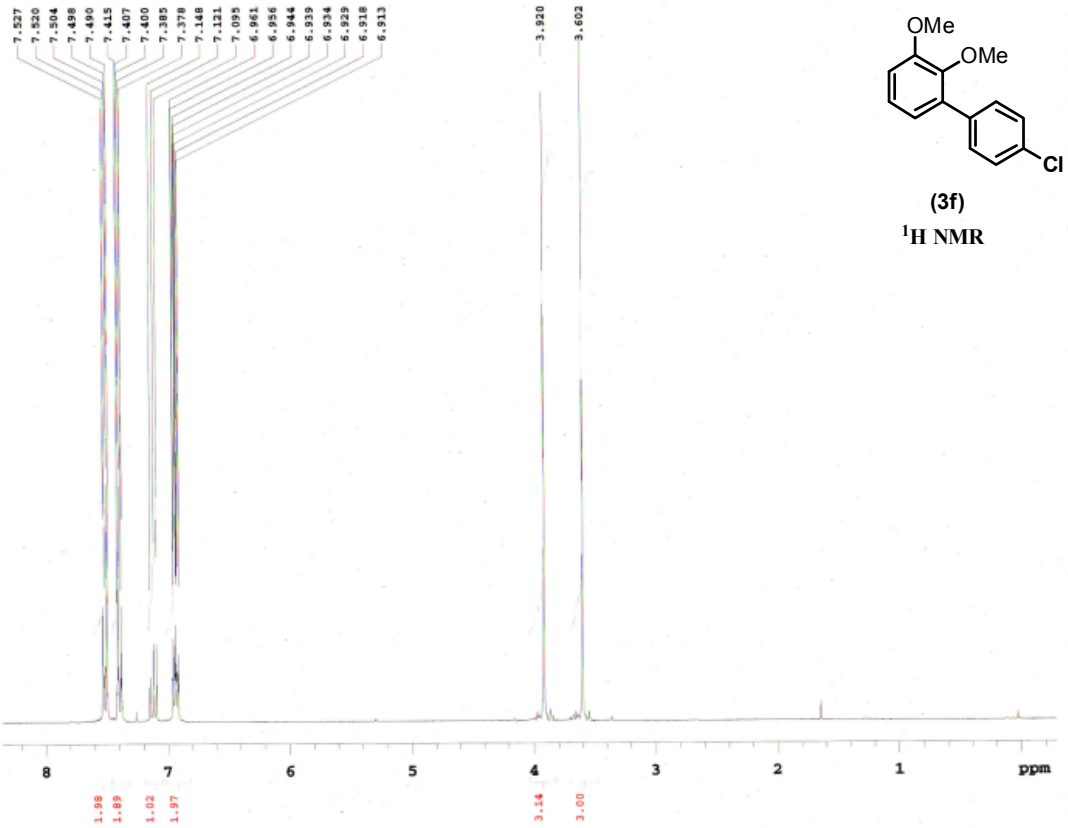
(3d)

^{1}H NMR



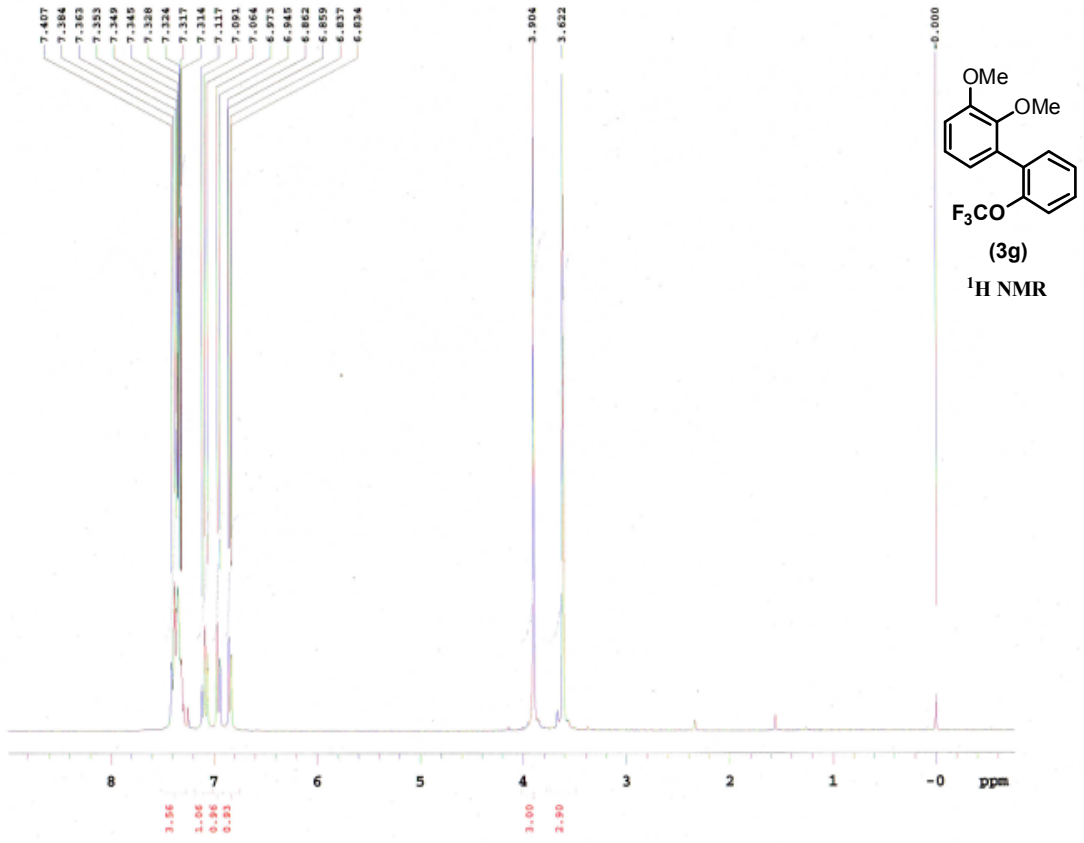
(3e)

^{1}H NMR



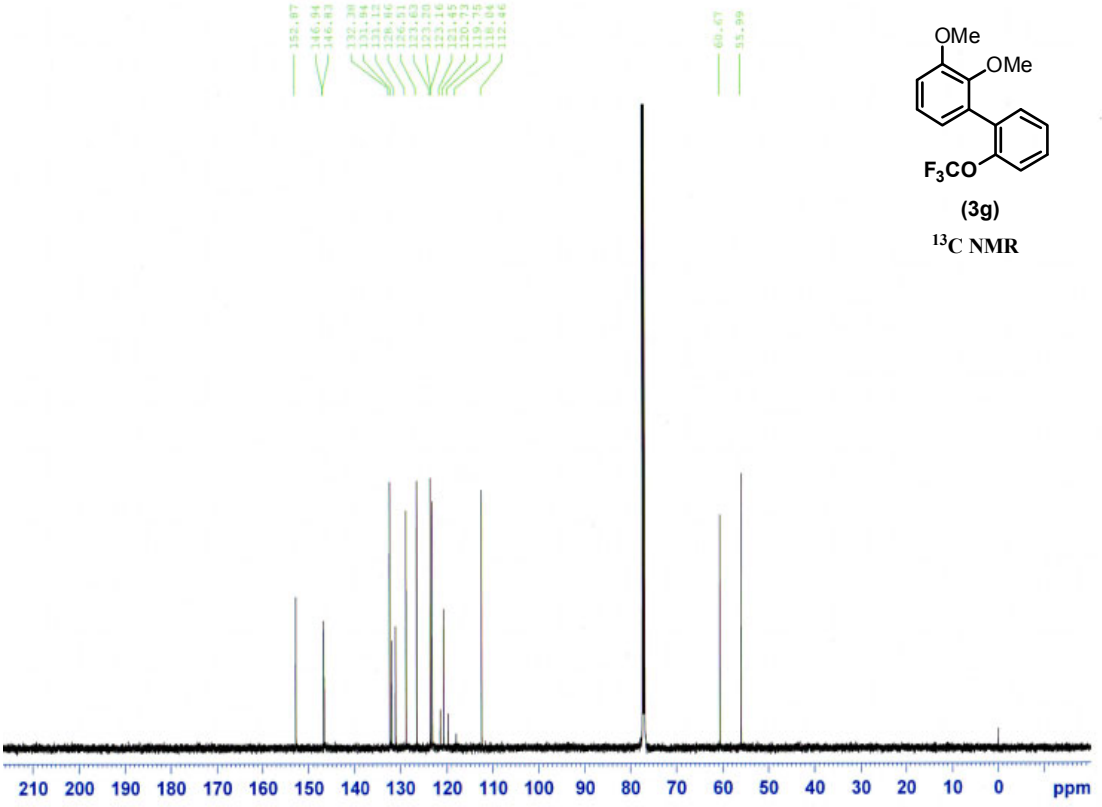
(3f)

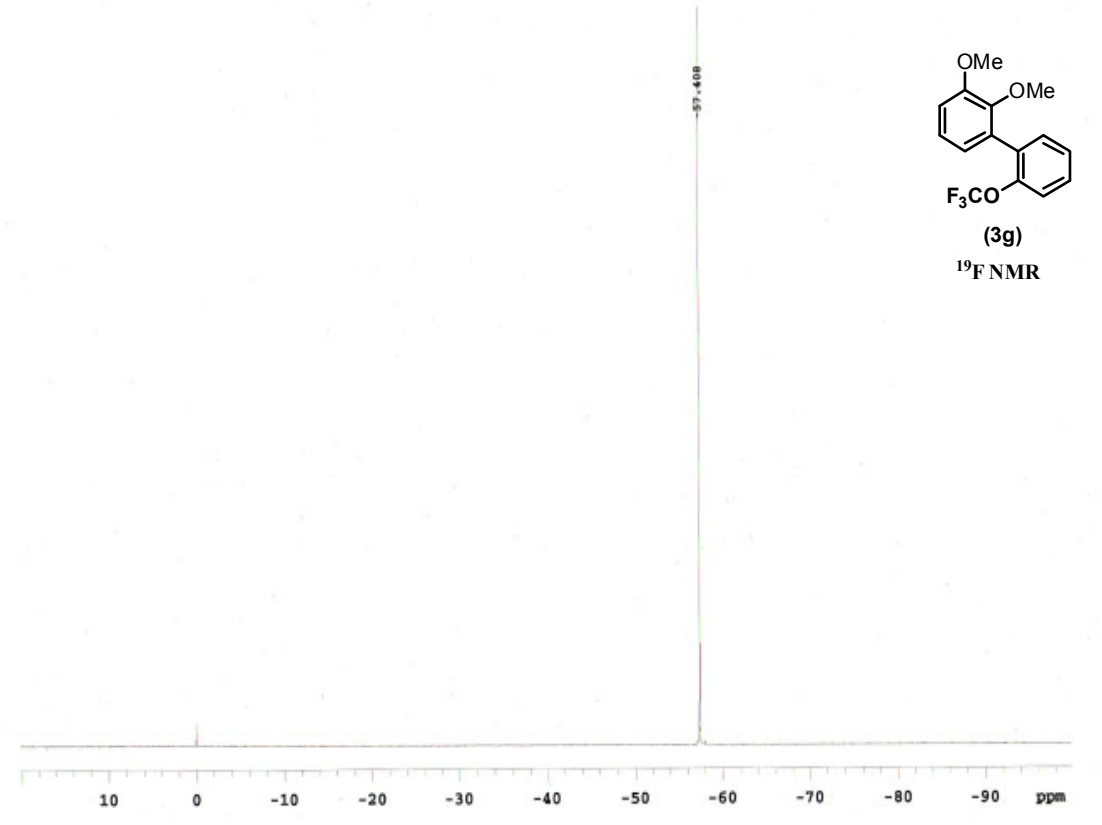
^{1}H NMR

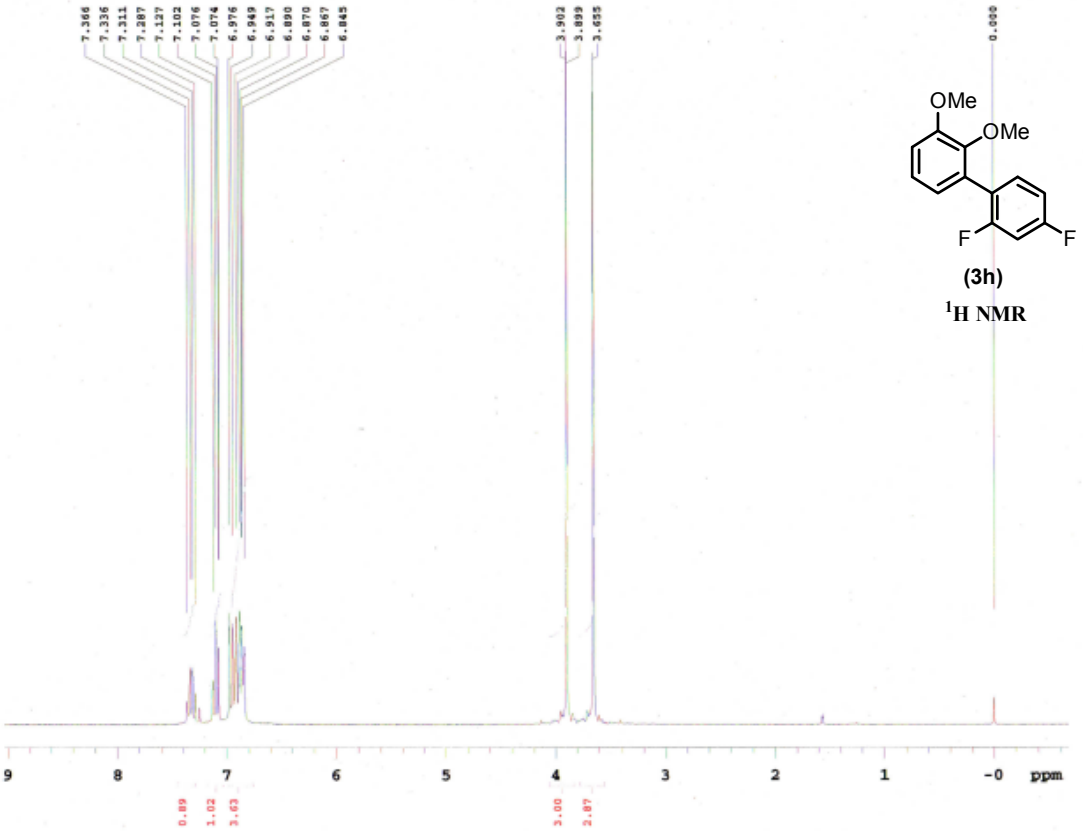


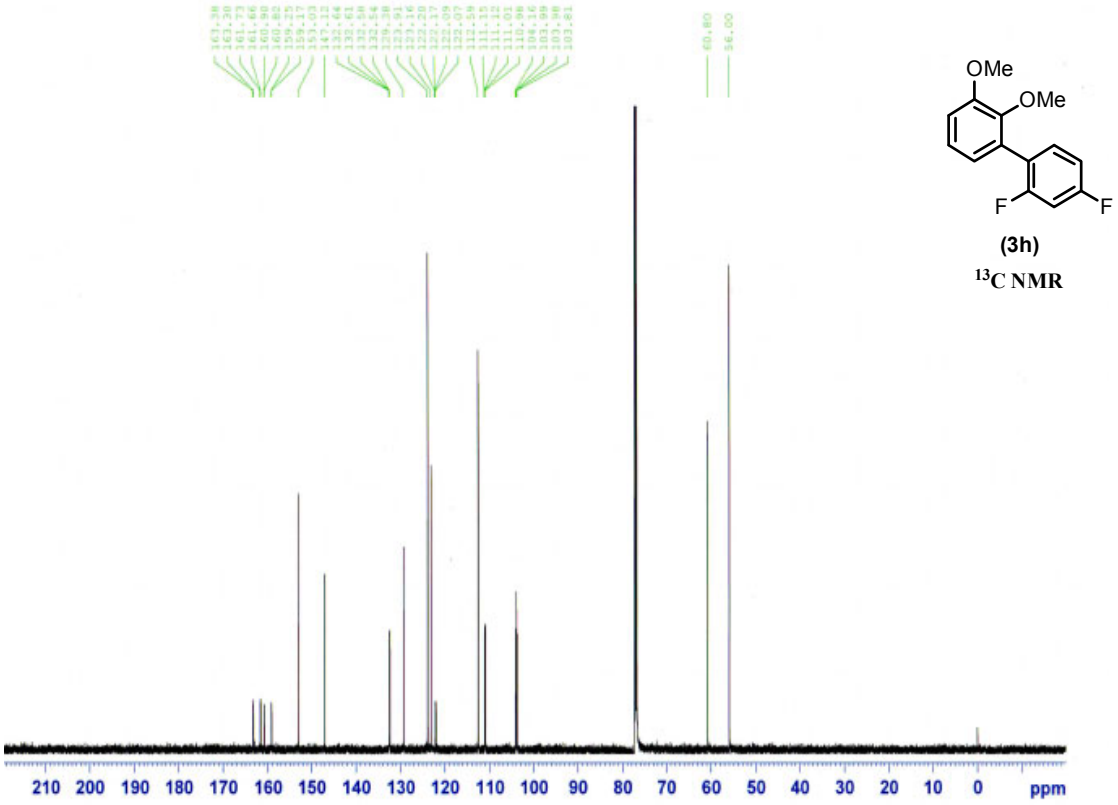
(3g)

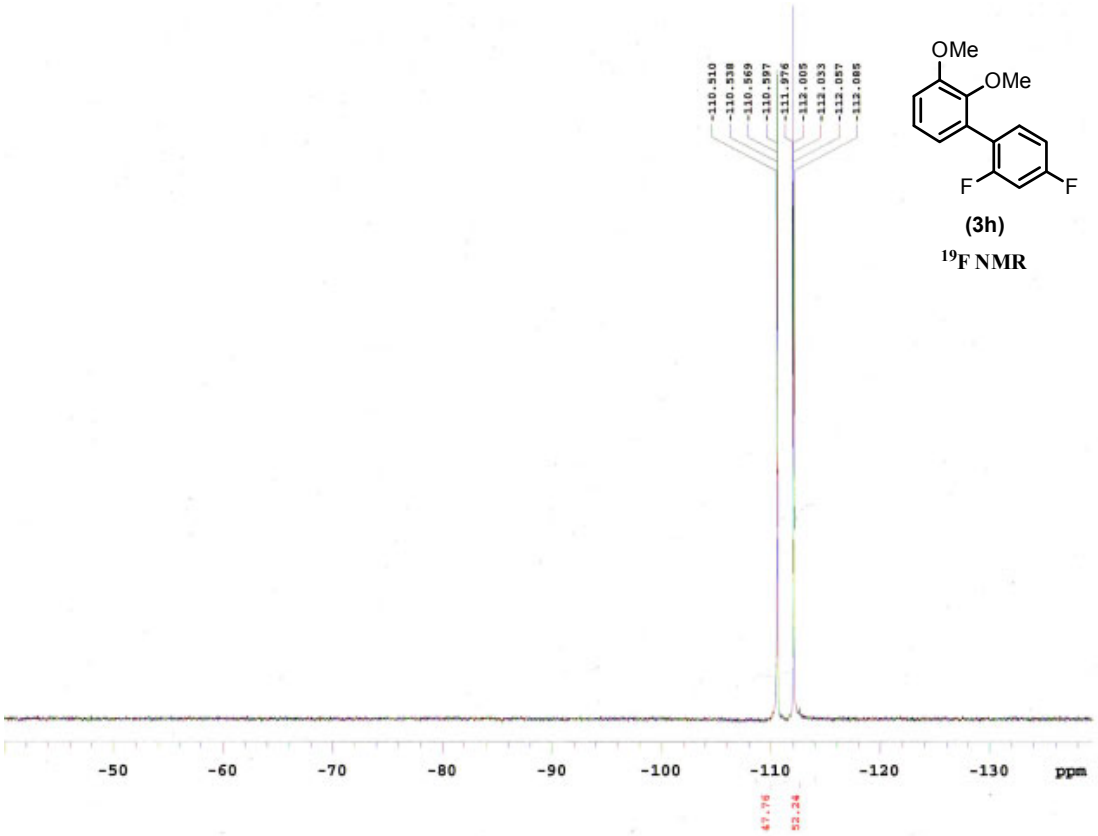
^{1}H NMR


OMe
OMe
F3CO
(3g)
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
OMe
F3CO
(3g)
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

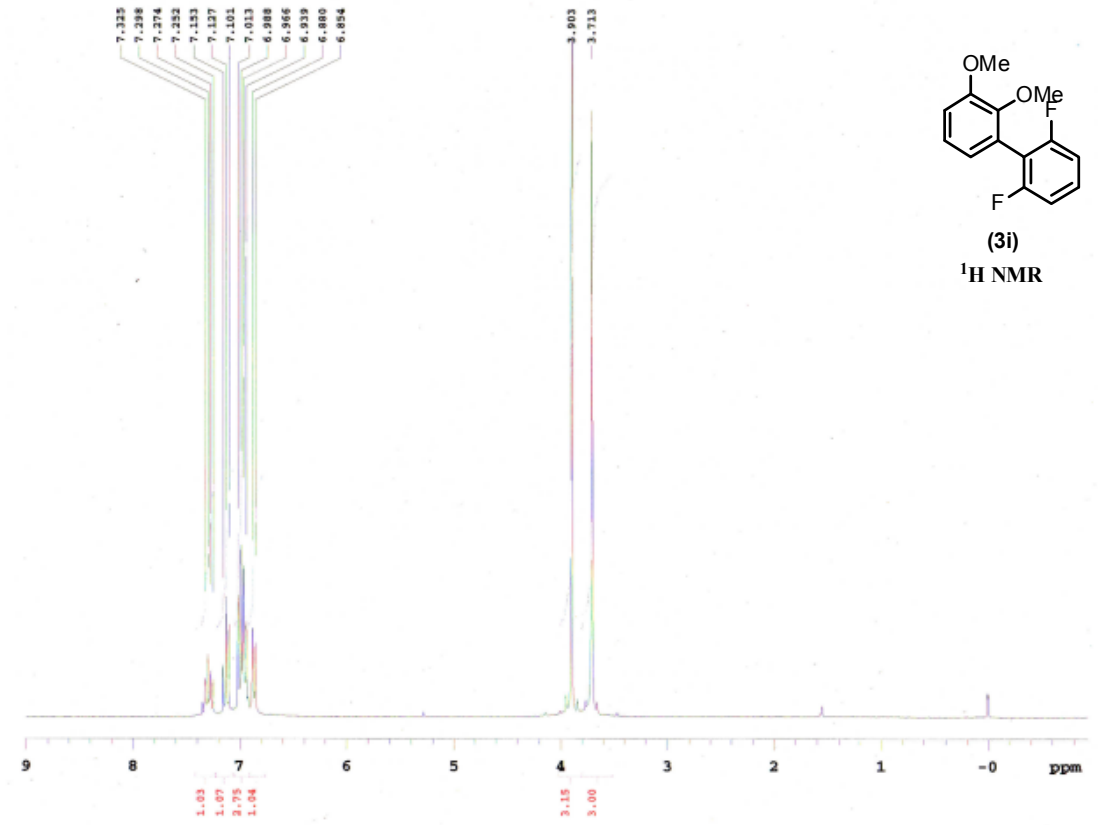

OMe
OMe
F
F
(3h)
1H NMR
ppm


OMe
OMe
F
F
(3h)
13C NMR
ppm



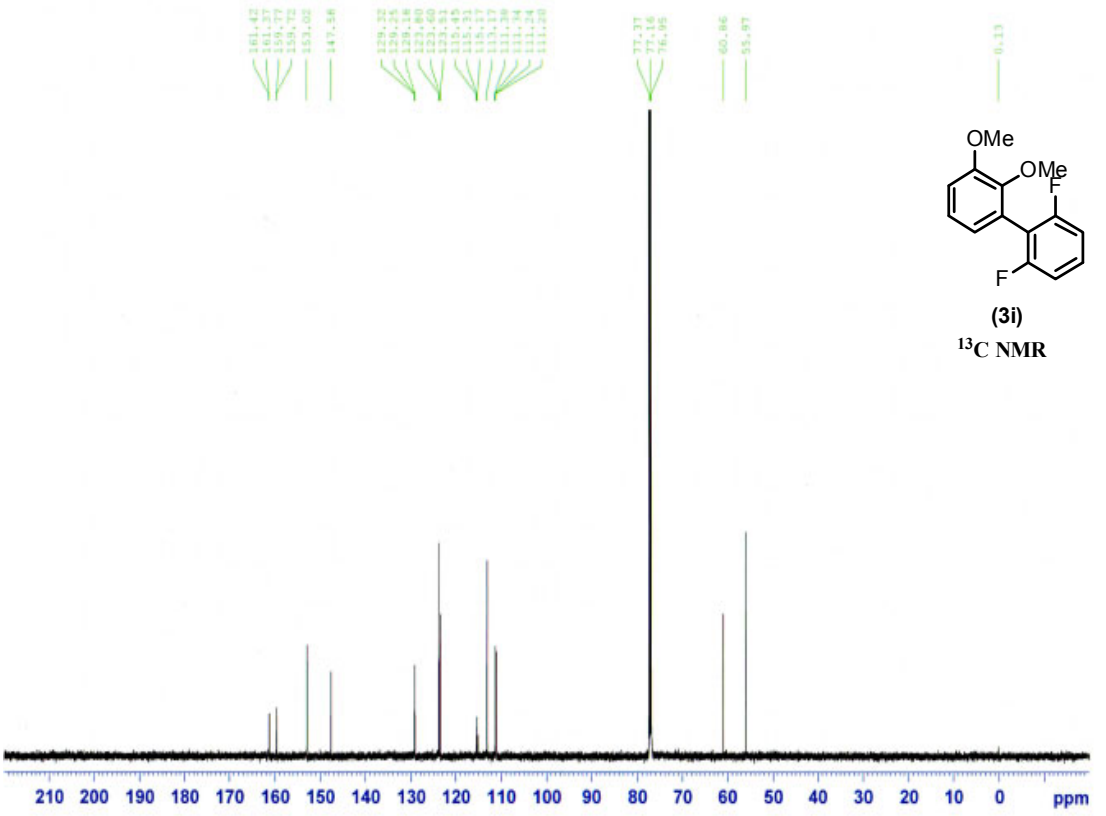
(3h)

^{19}F NMR



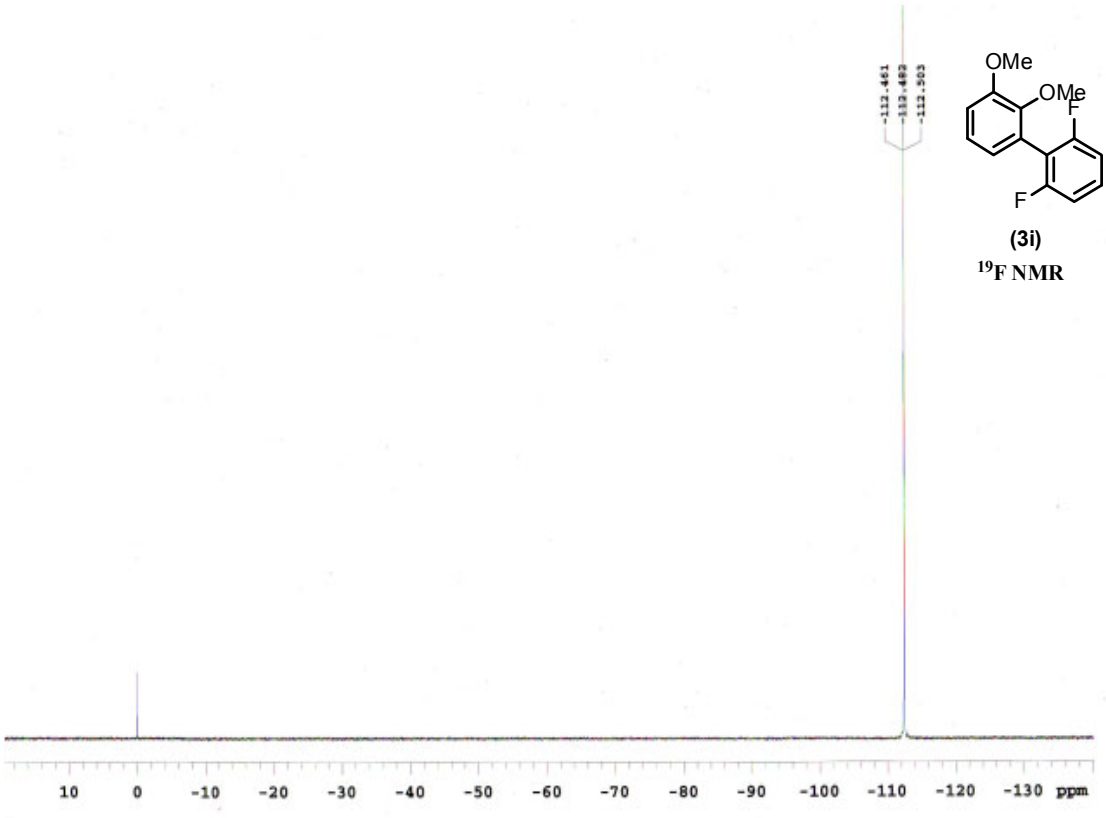
(3i)

^{1}H NMR



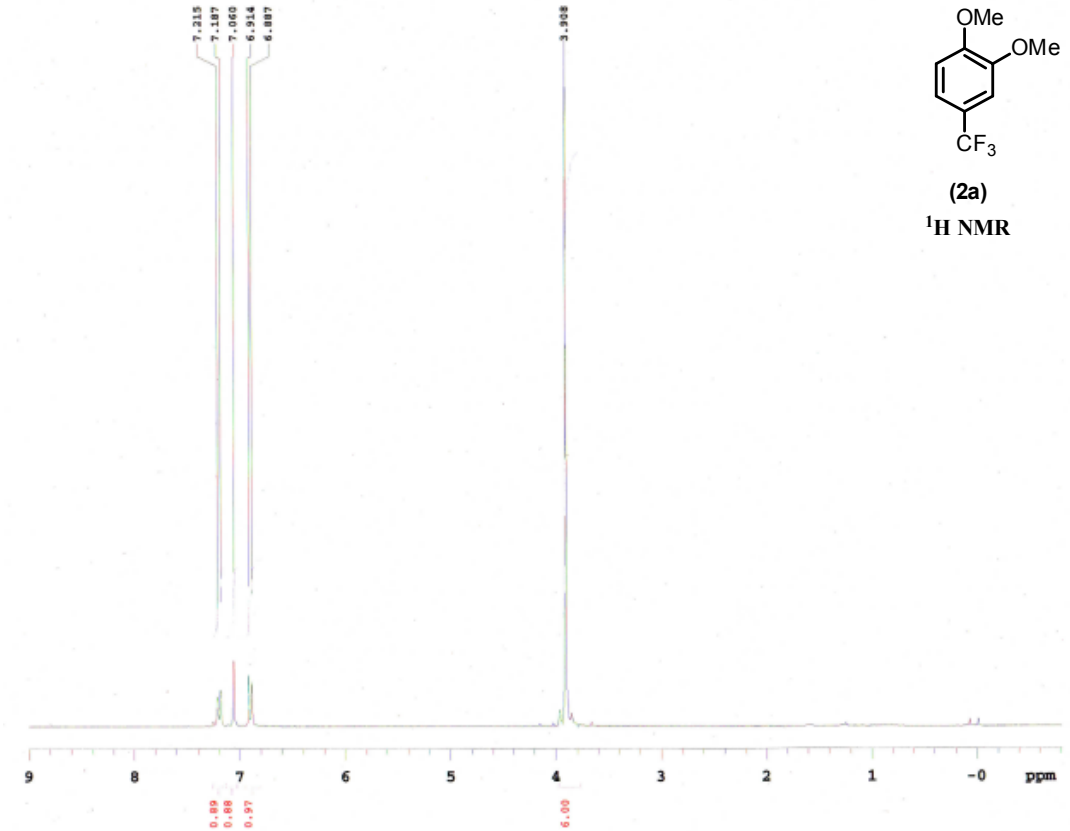
(3i)

^{13}C NMR



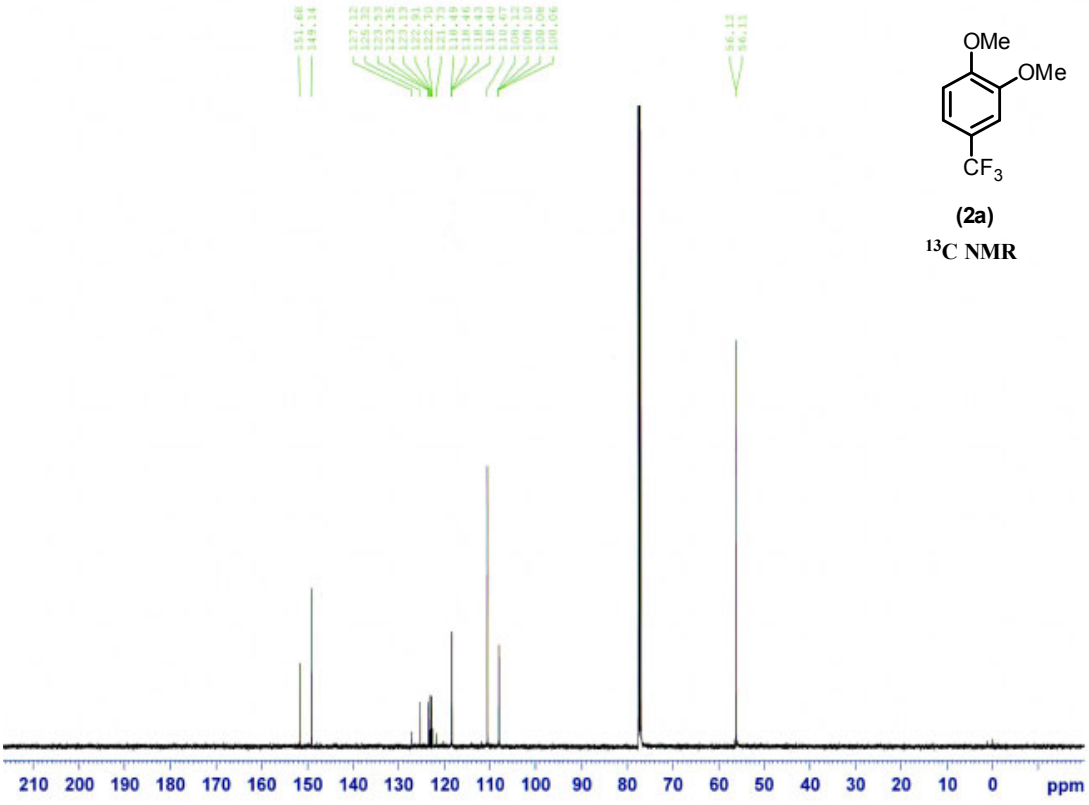
(3i)

^{19}F NMR



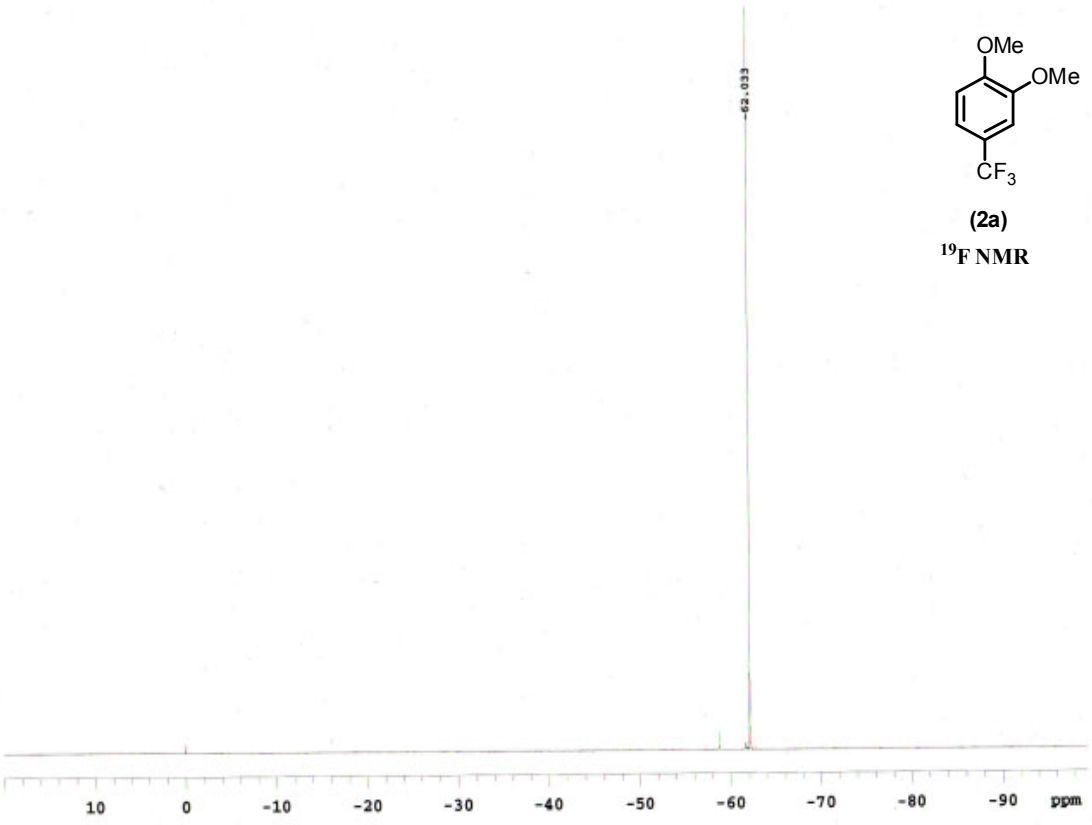
(2a)

^{1}H NMR



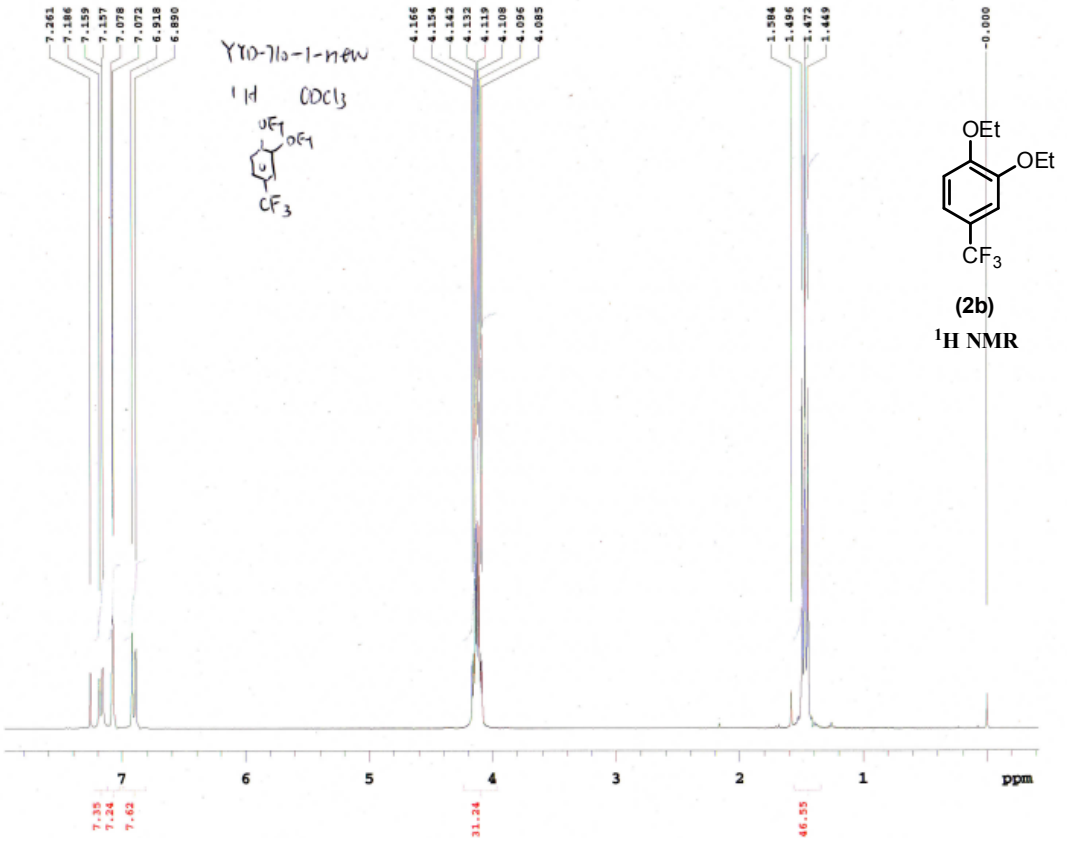
(2a)

^{13}C NMR



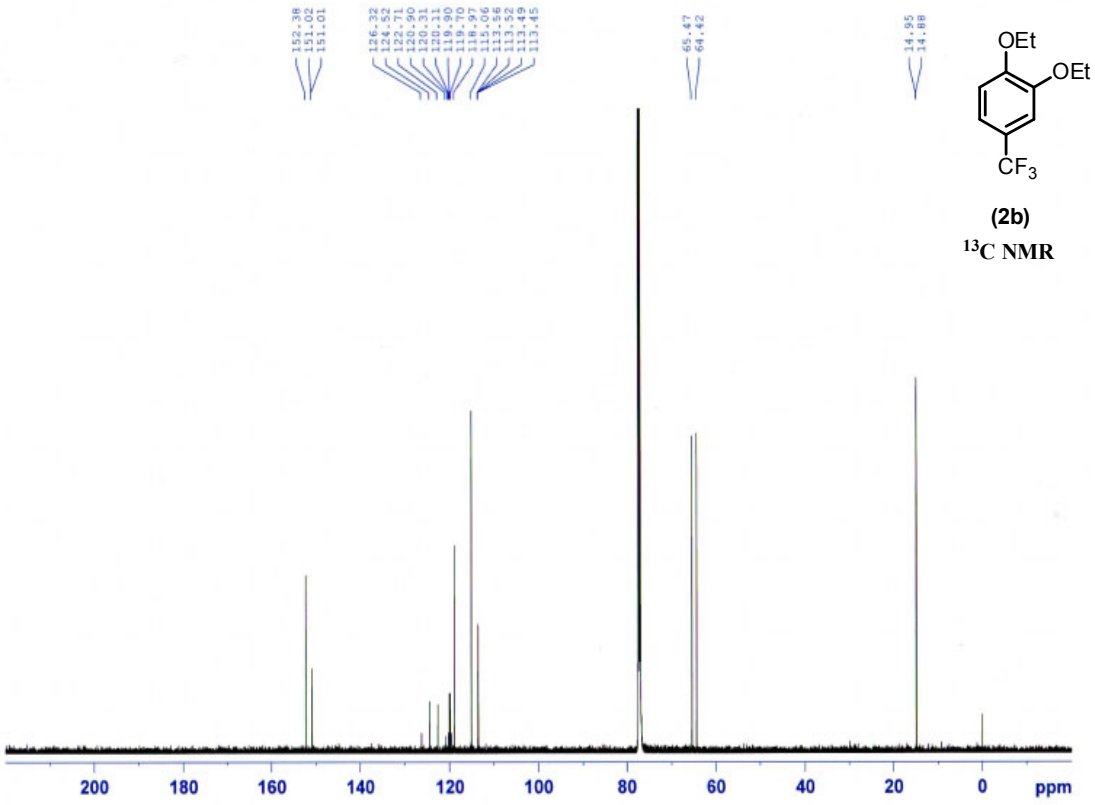
(2a)

^{19}F NMR



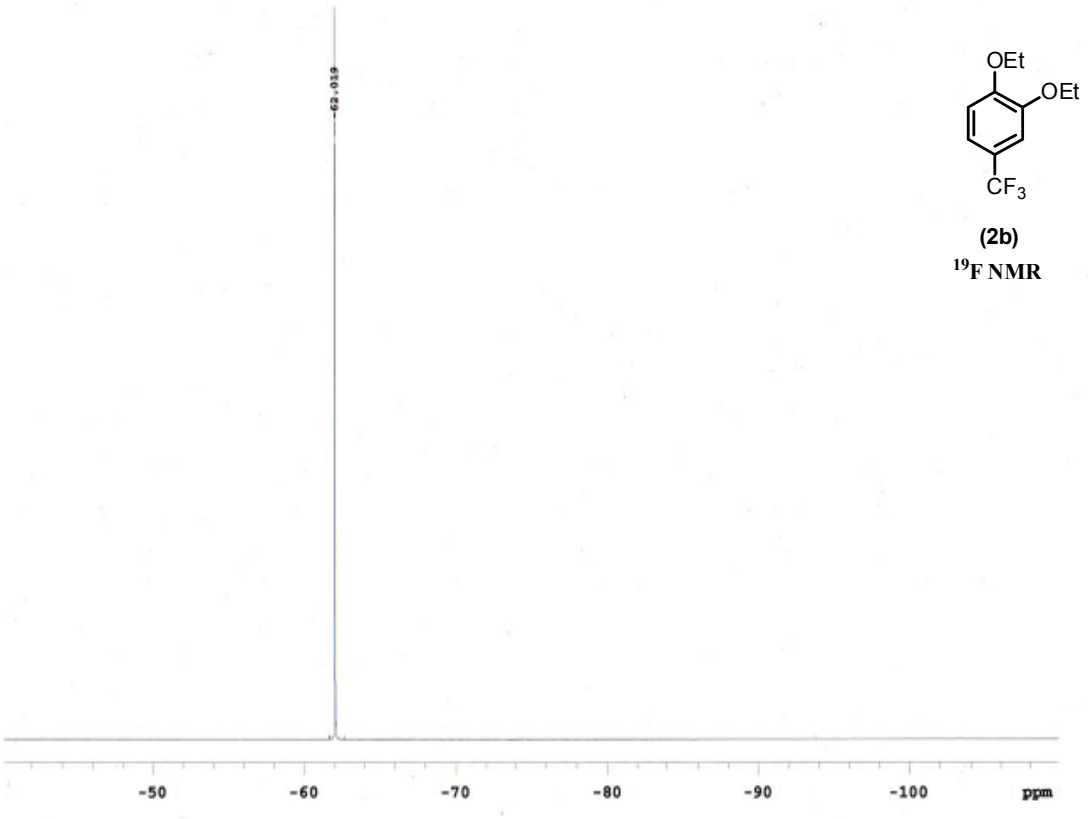
(2b)

^{1}H NMR



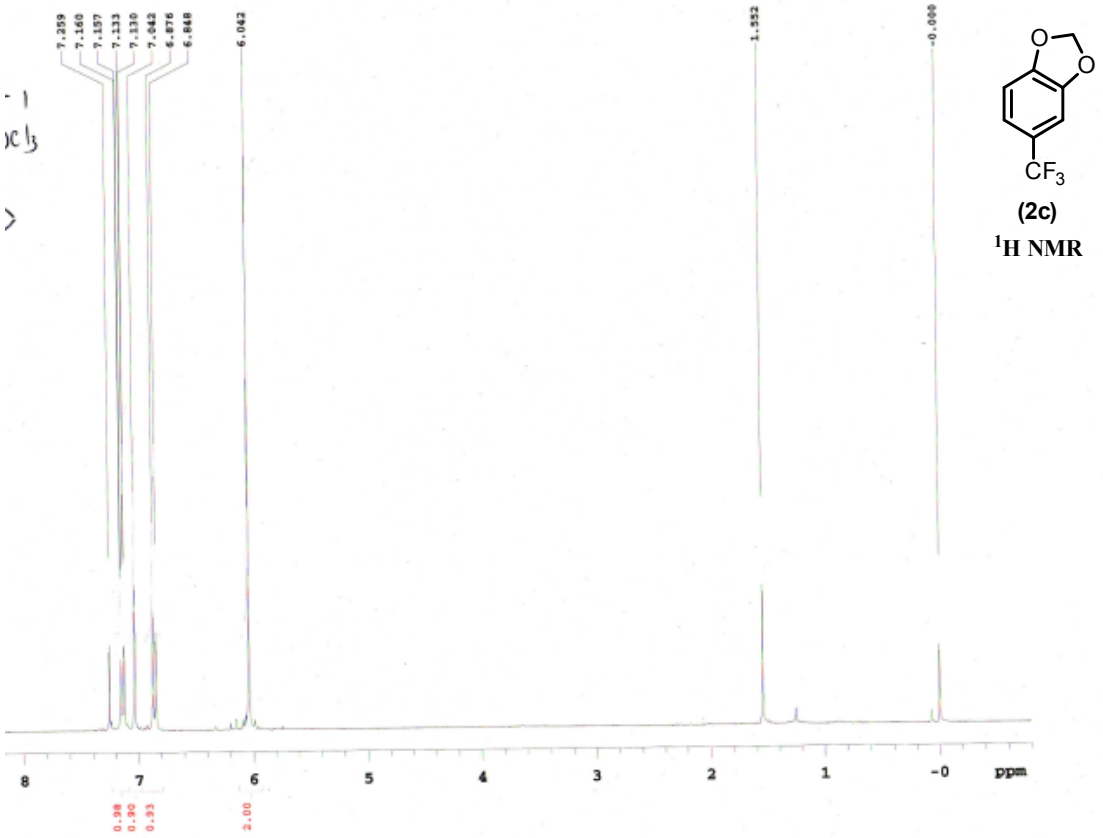
(2b)

^{13}C NMR



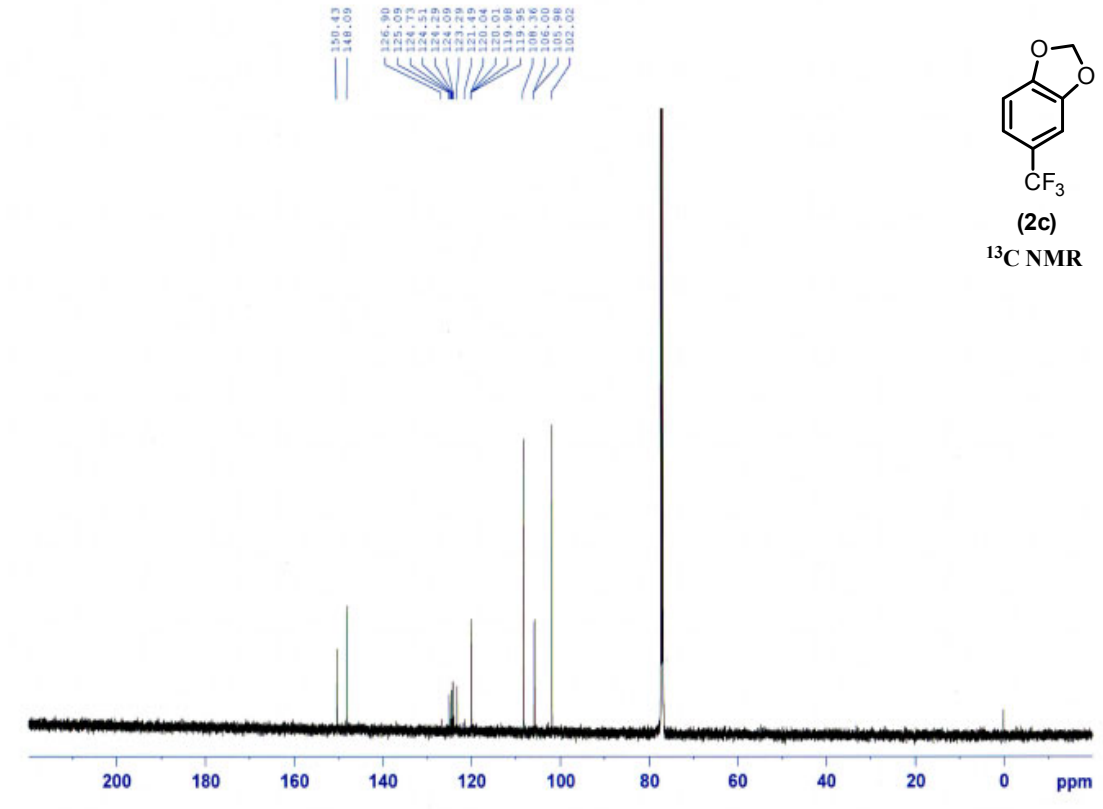
(2b)

^{19}F NMR



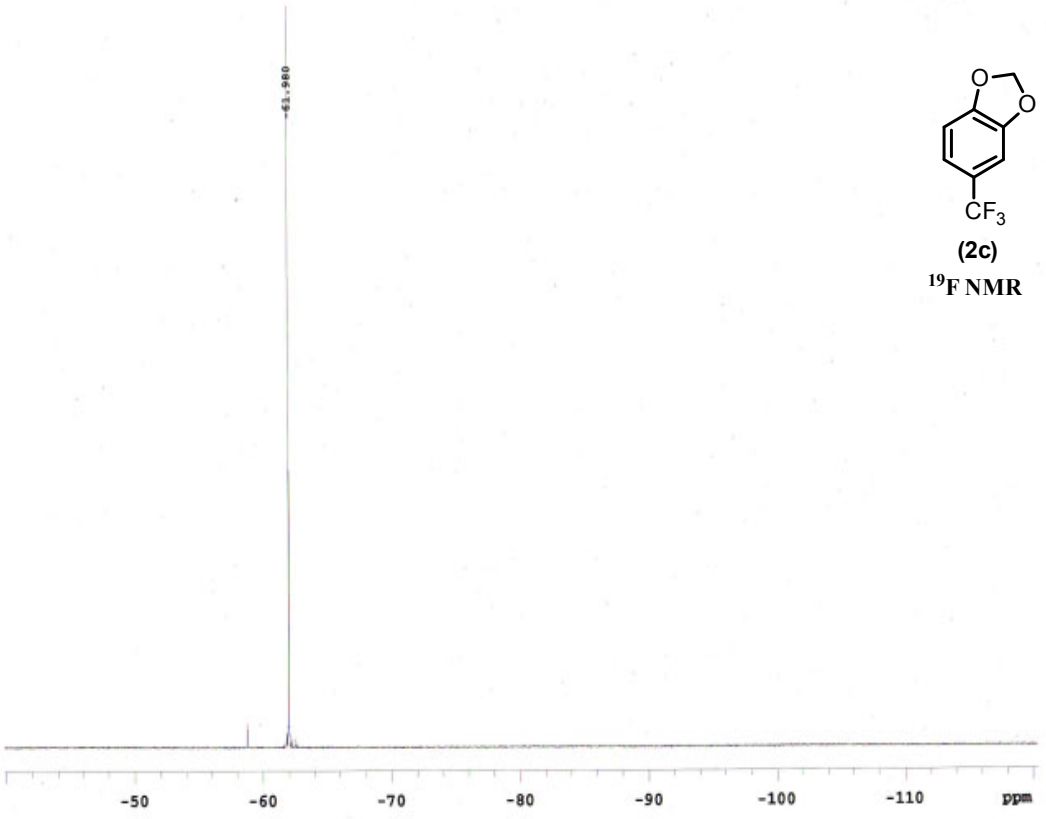
(2c)

^{1}H NMR



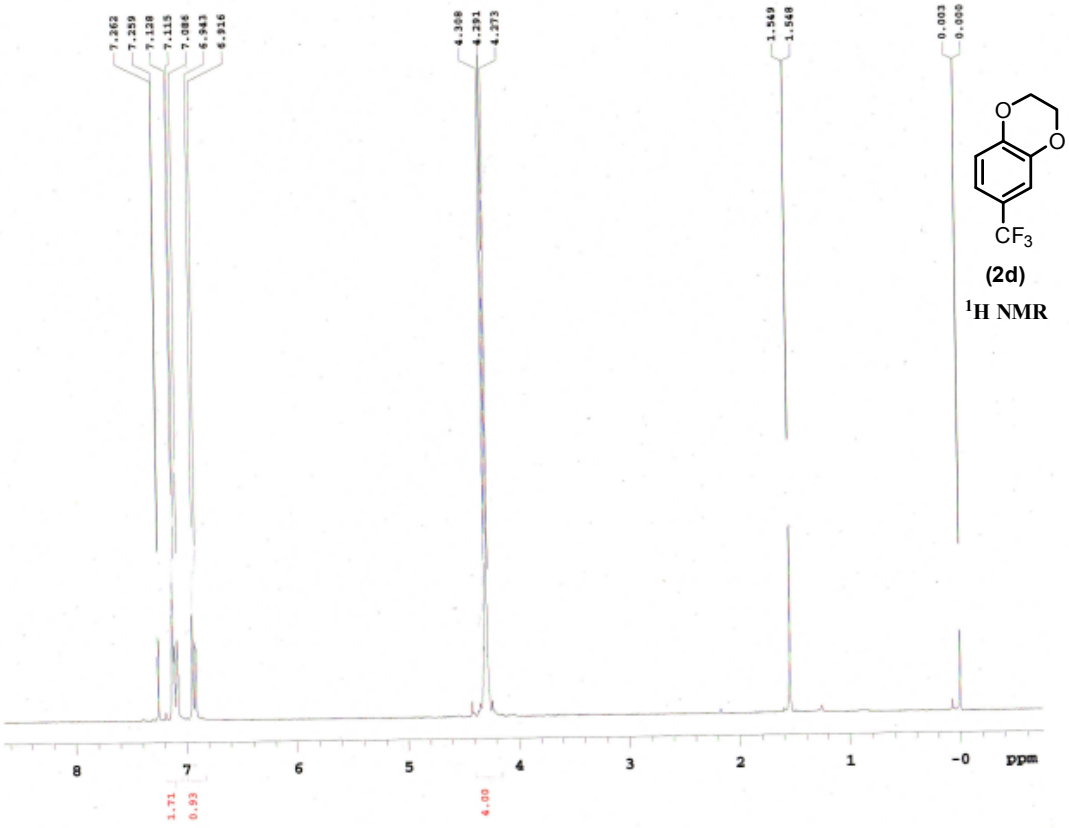
(2c)

^{13}C NMR



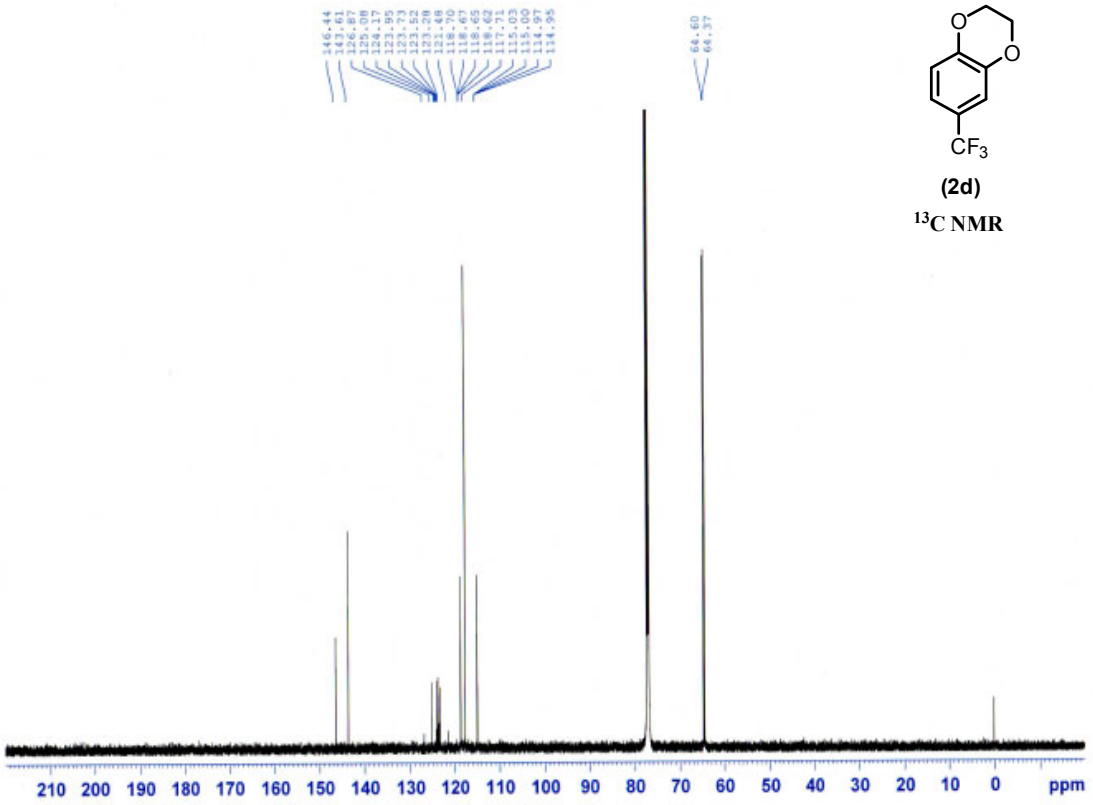
(2c)

^{19}F NMR



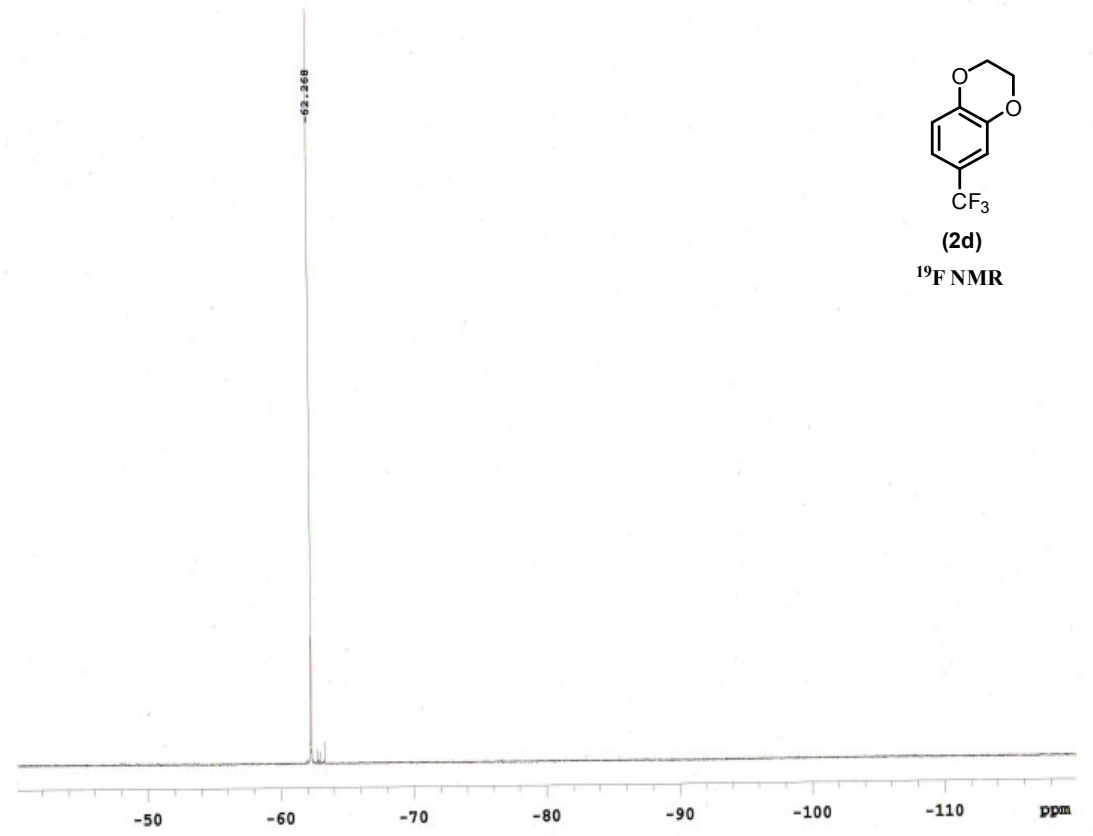
(2d)

^{1}H NMR



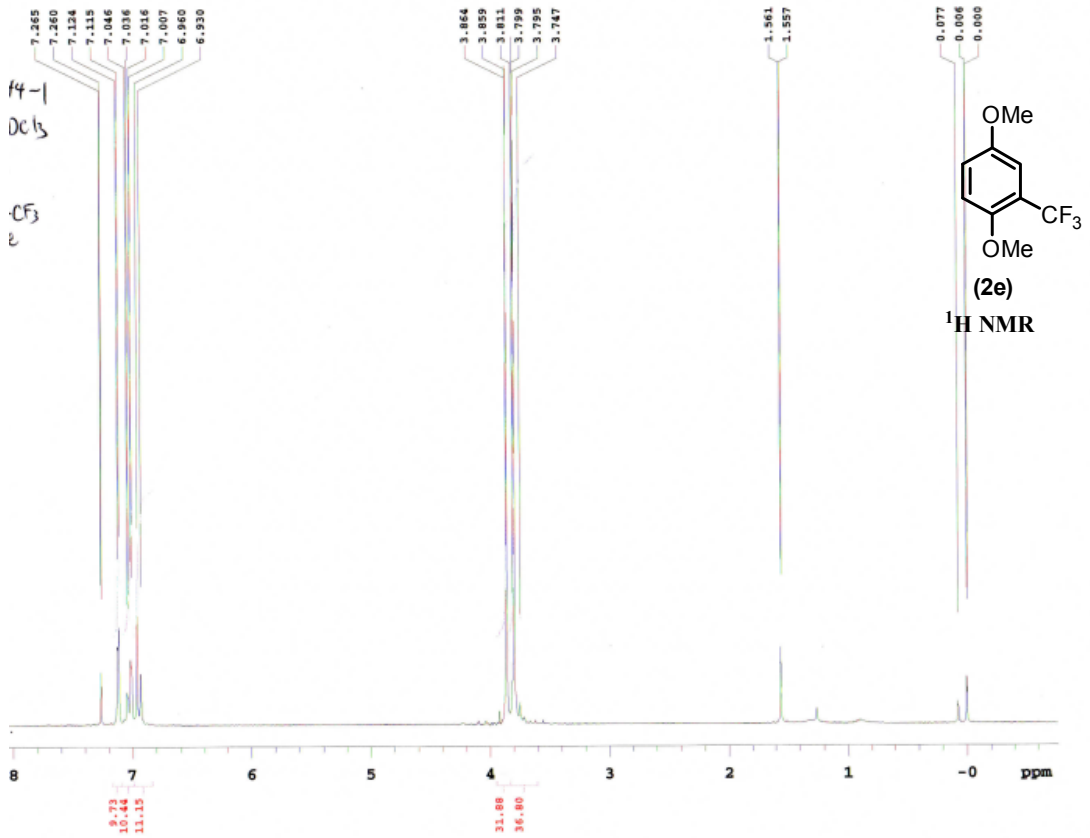
(2d)

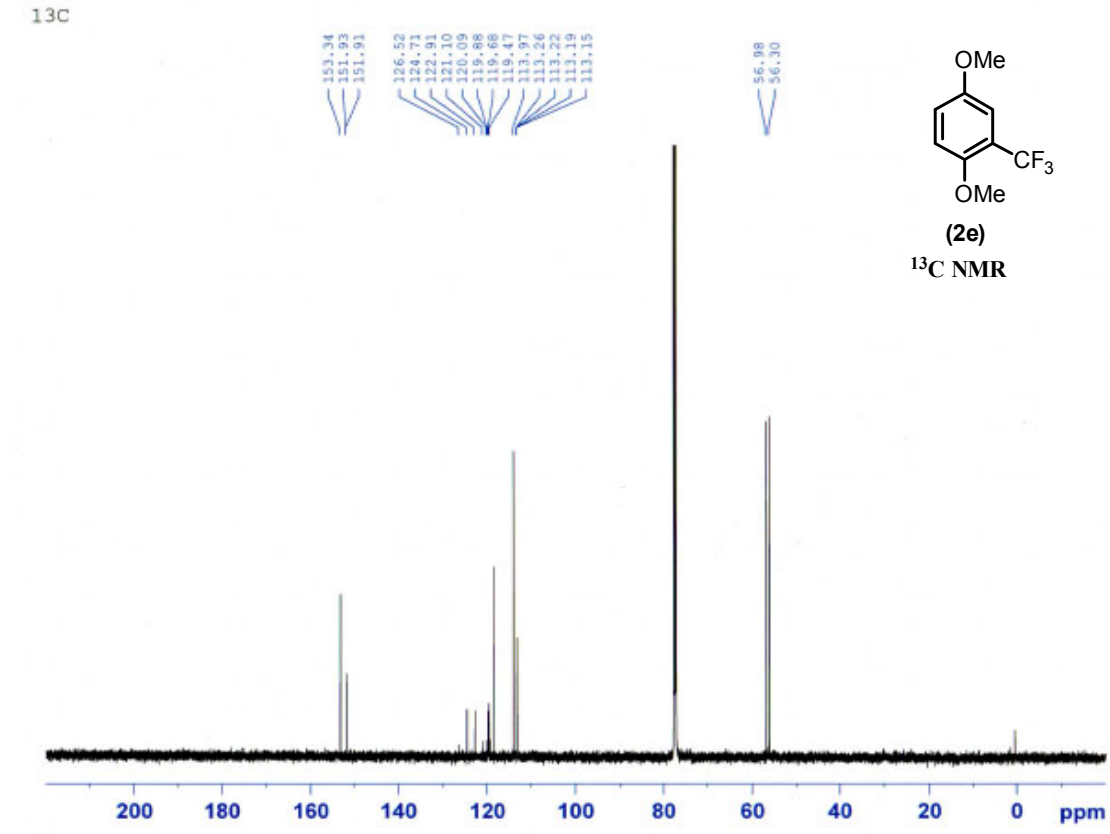
^{13}C NMR

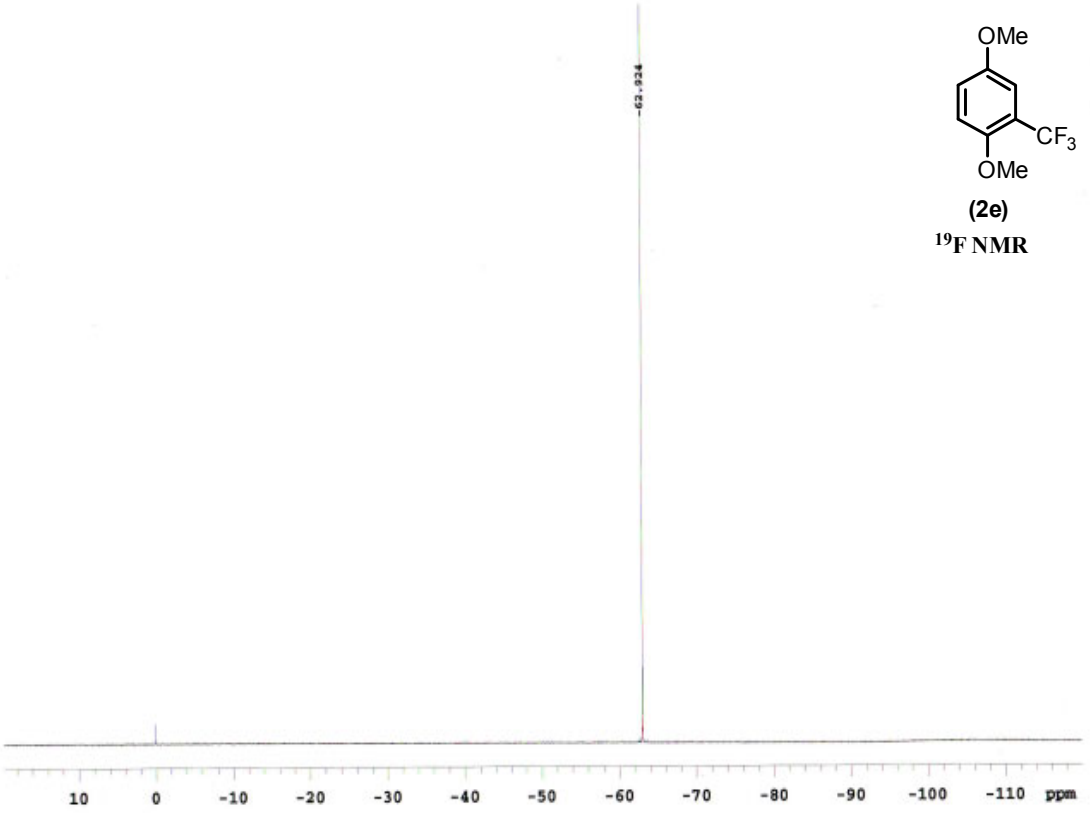


(2d)

^{19}F NMR

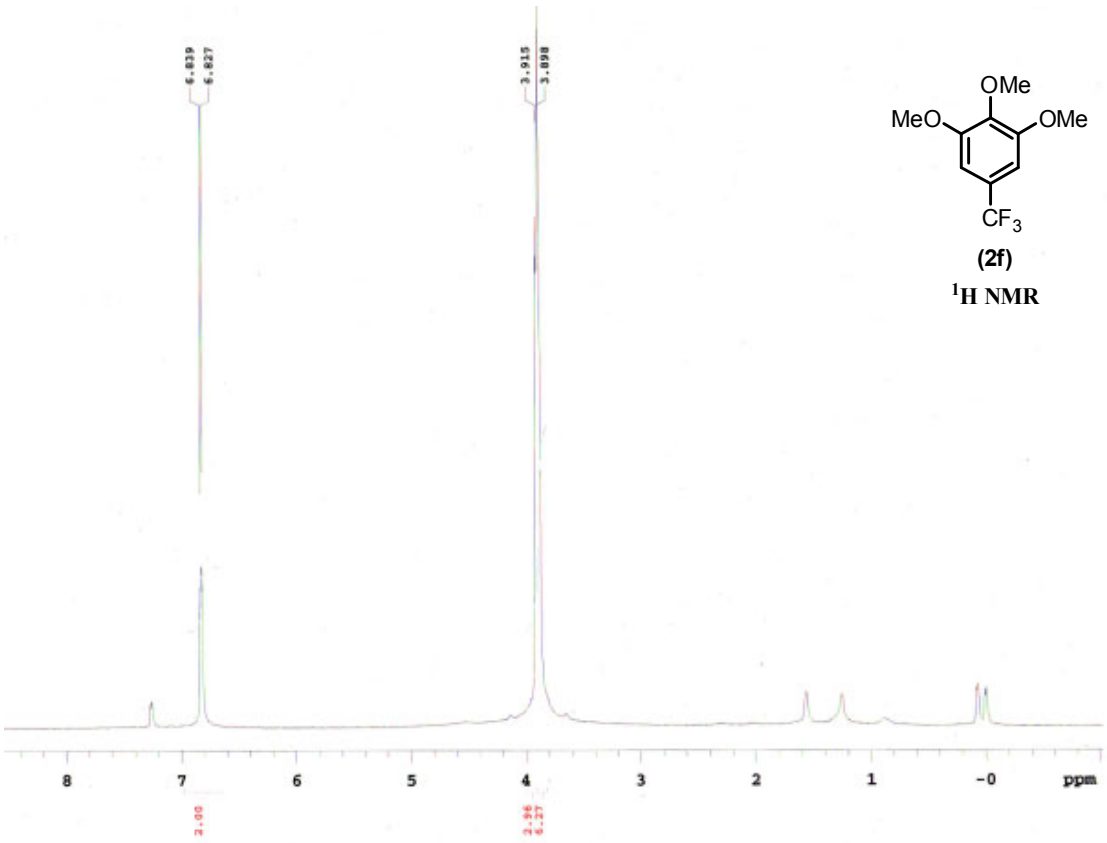

7.265
7.260
7.124
7.115
7.046
7.036
7.016
7.007
6.960
6.930
3.864
3.859
3.831
3.799
3.795
3.747
1.561
1.557
0.077
0.006
0.000
f4-1
DCl3
CF3
2
OMe
CF3
OMe
(2e)
1H NMR
8
7
6
5
4
3
2
1
-0
ppm
9.73
10.44
11.15
31.88
36.80


13C
153.34
151.93
151.91
126.52
124.71
122.91
121.10
120.09
119.88
119.68
119.47
113.97
113.26
113.22
113.19
113.15
56.98
56.30
OMe
CF3
OMe
(2e)
13C NMR
200
180
160
140
120
100
80
60
40
20
0
ppm



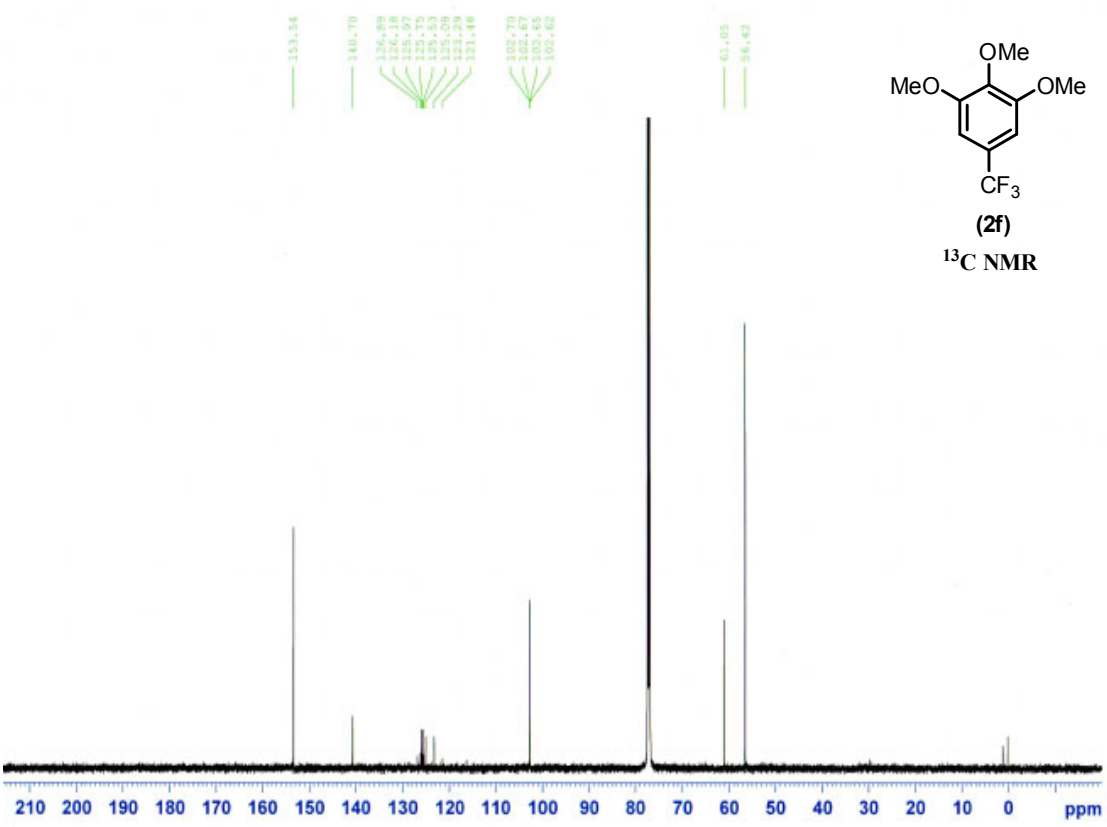
(2e)

^{19}F NMR



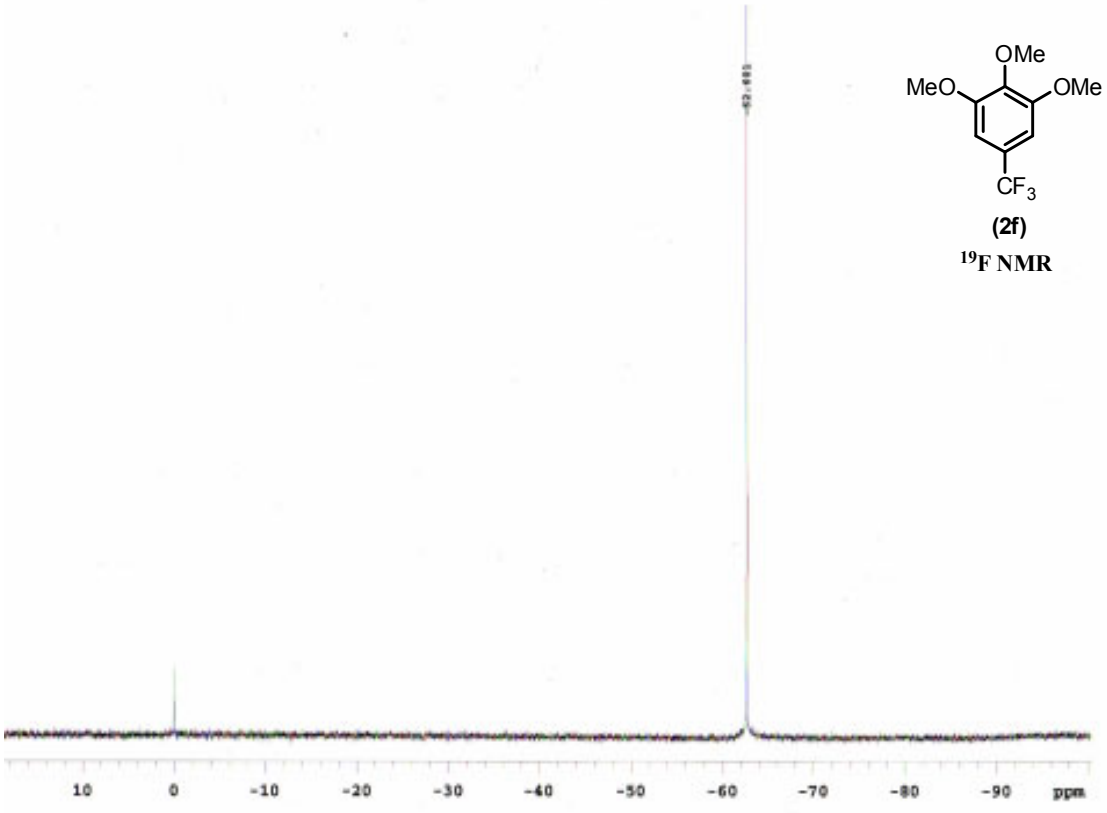
(2f)

^{1}H NMR



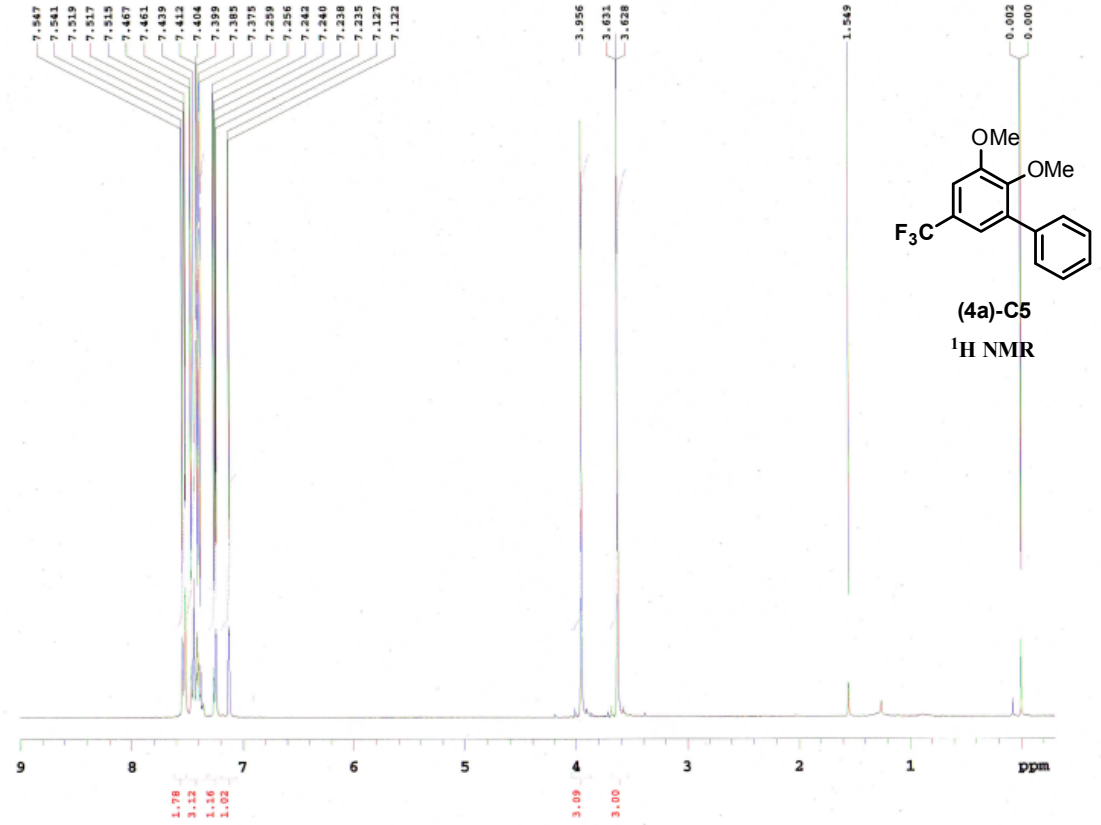
(2f)

^{13}C NMR



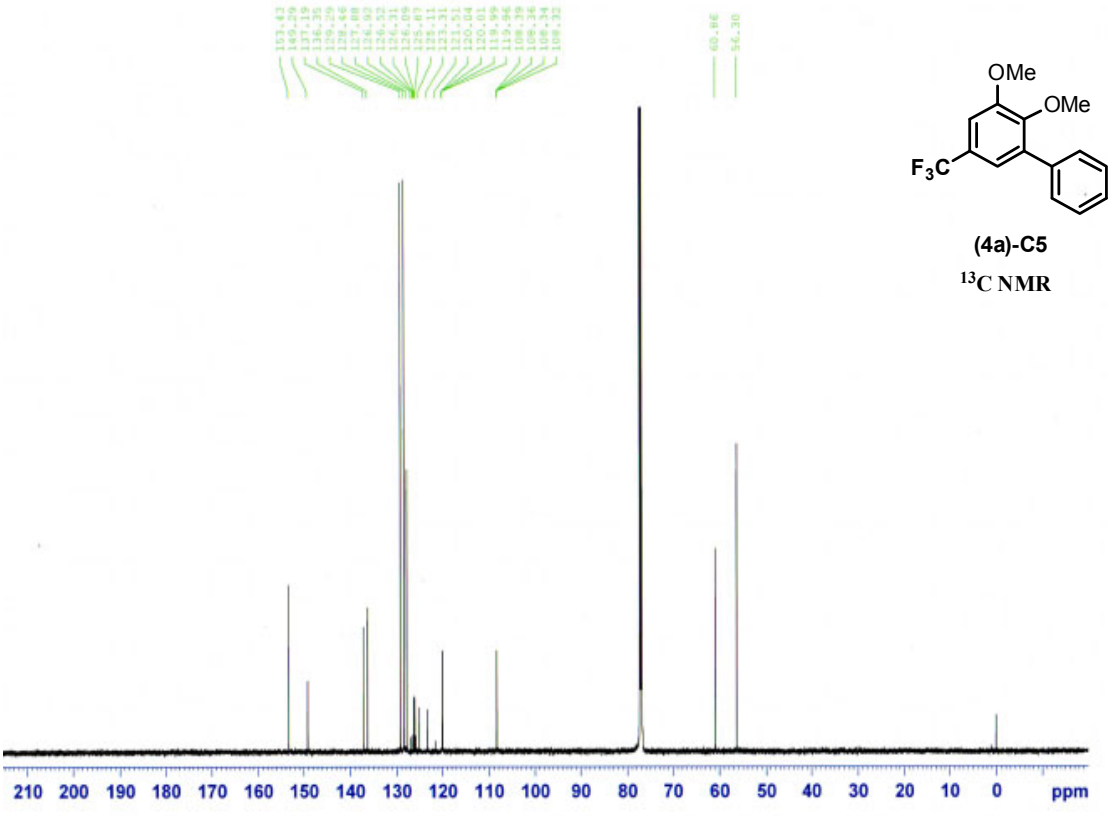
(2f)

^{19}F NMR



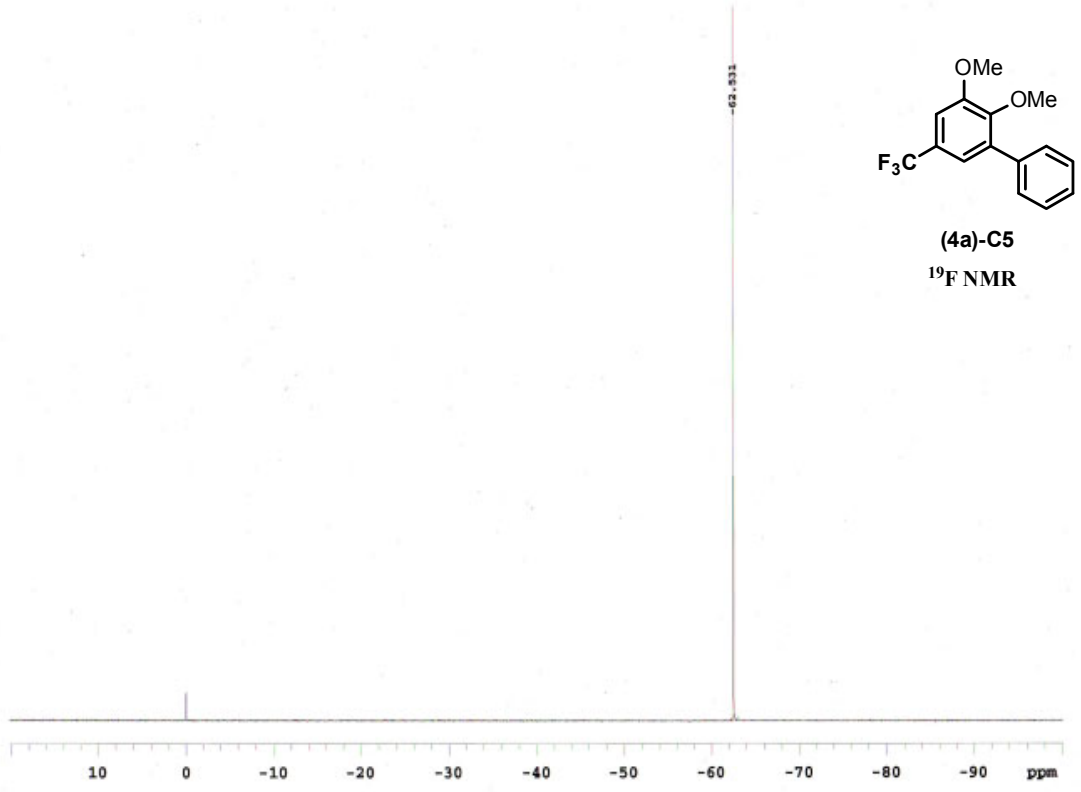
(4a)-C5

^{1}H NMR



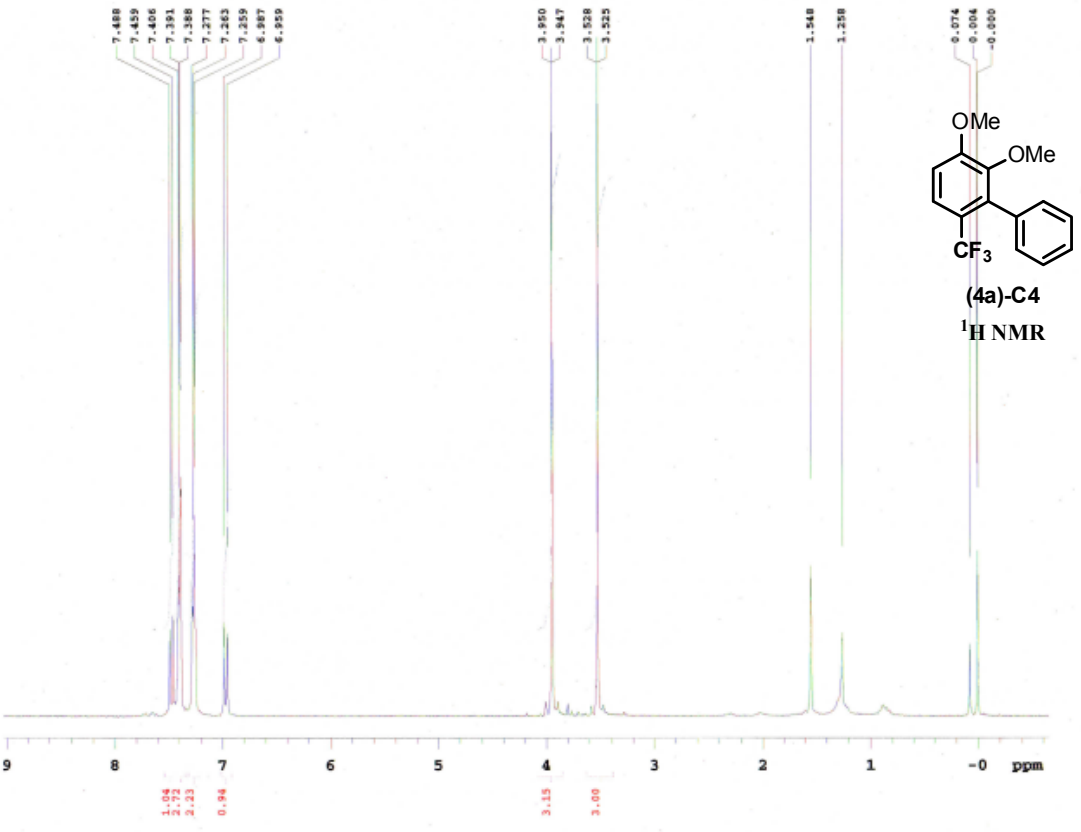
(4a)-C5

^{13}C NMR



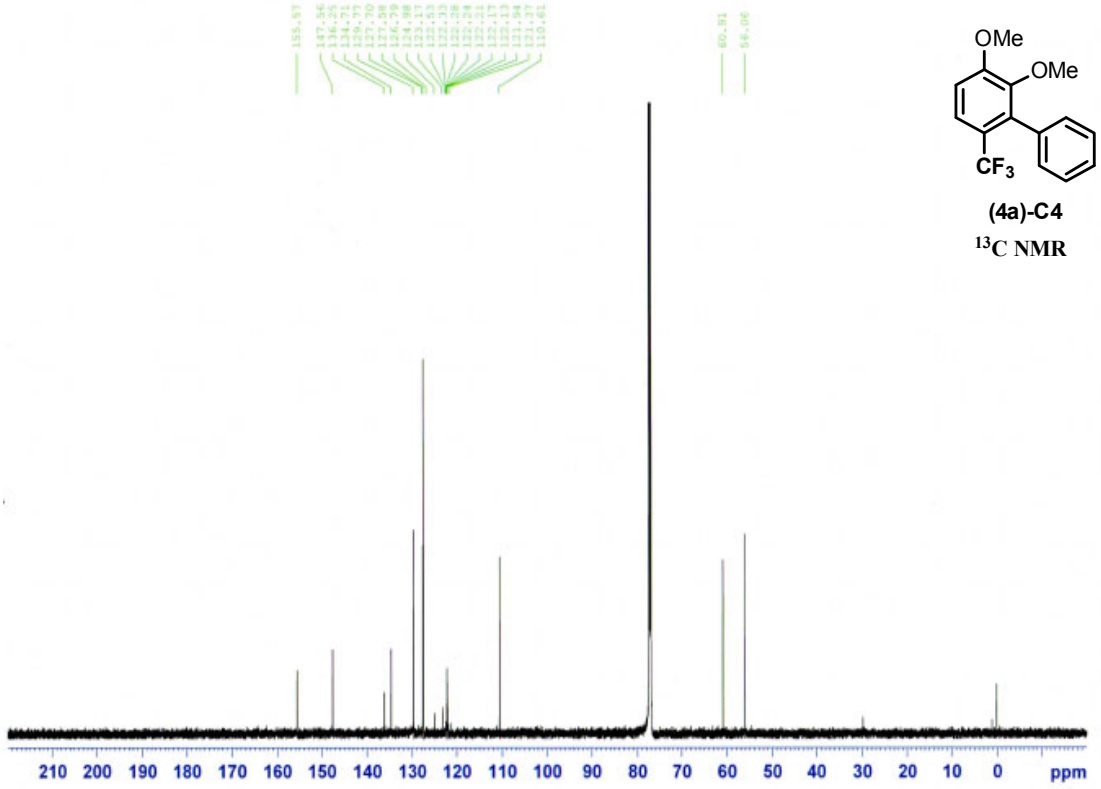
(4a)-C5

^{19}F NMR



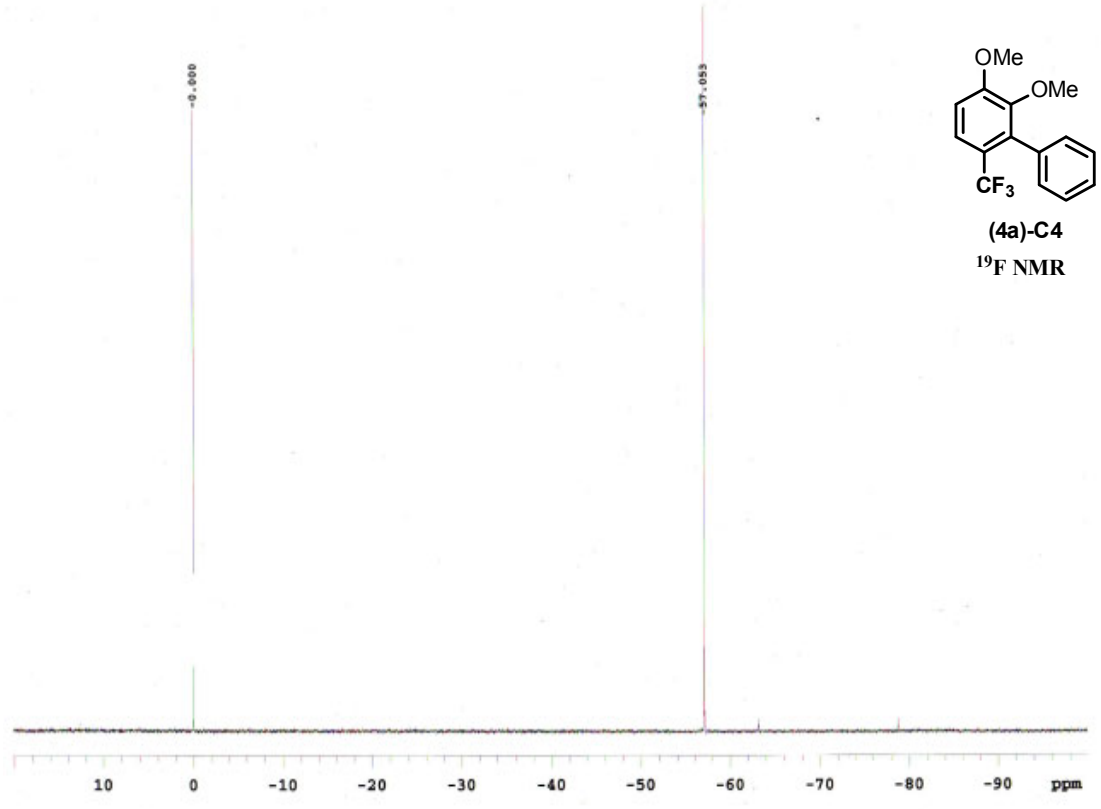
(4a)-C4

^{1}H NMR



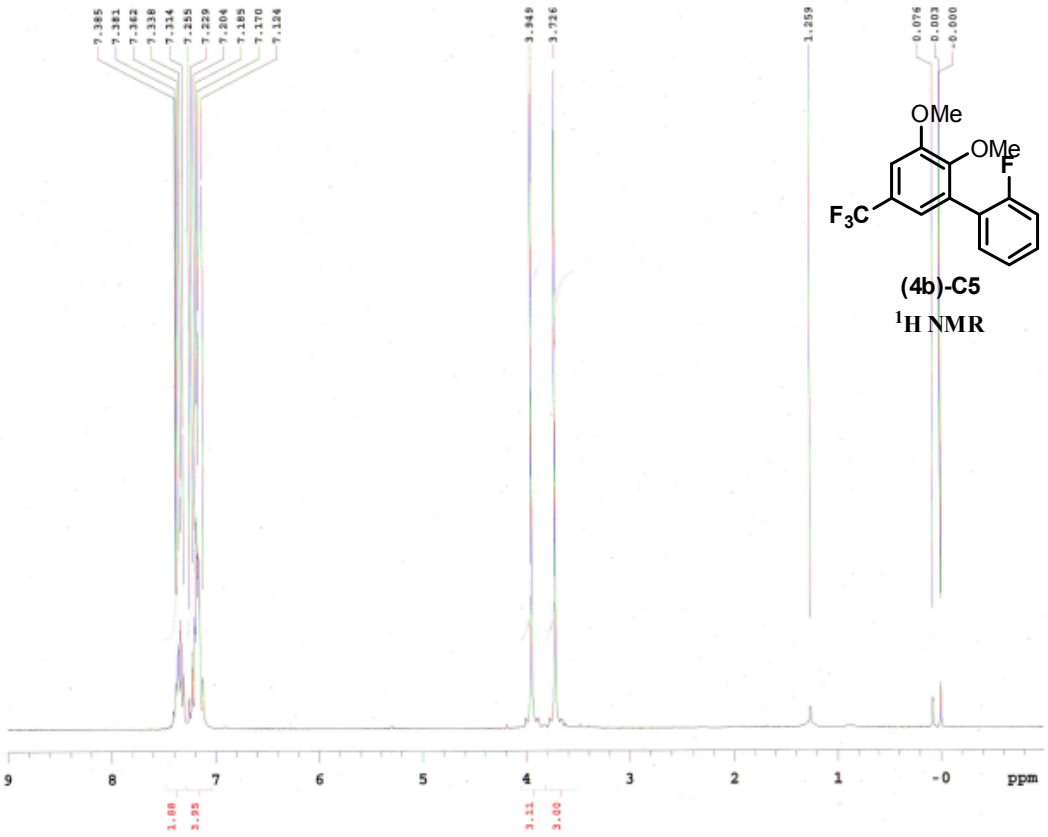
(4a)-C4

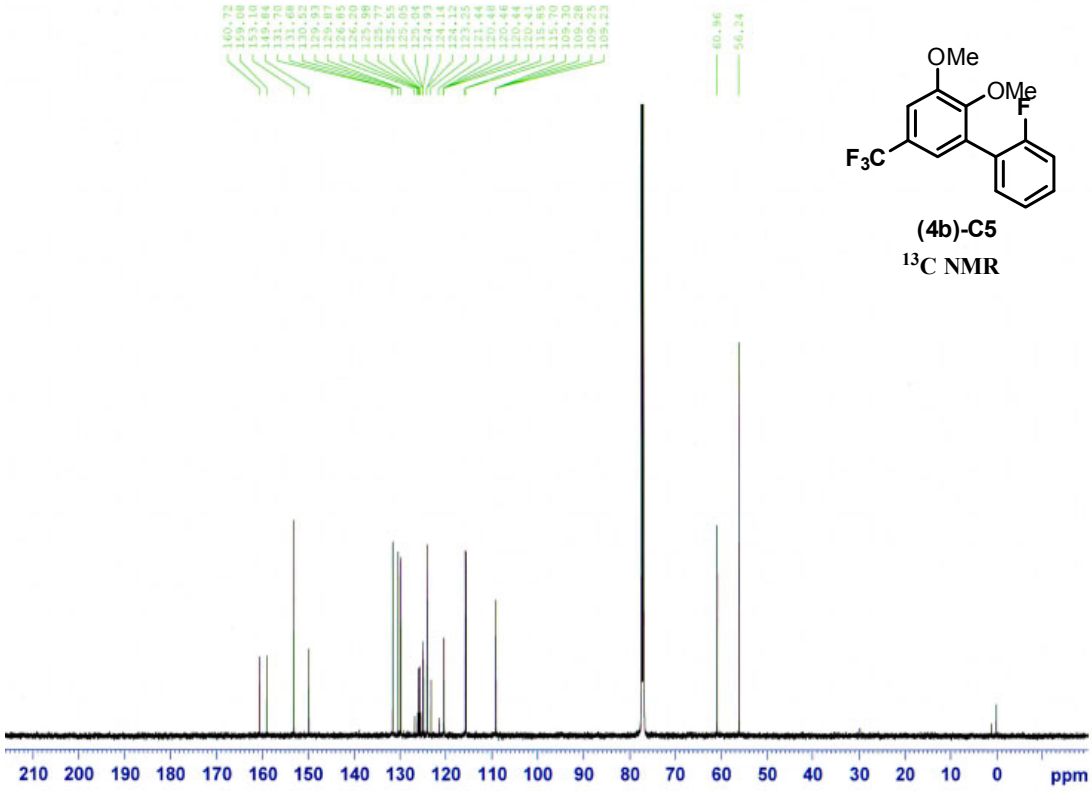
^{13}C NMR

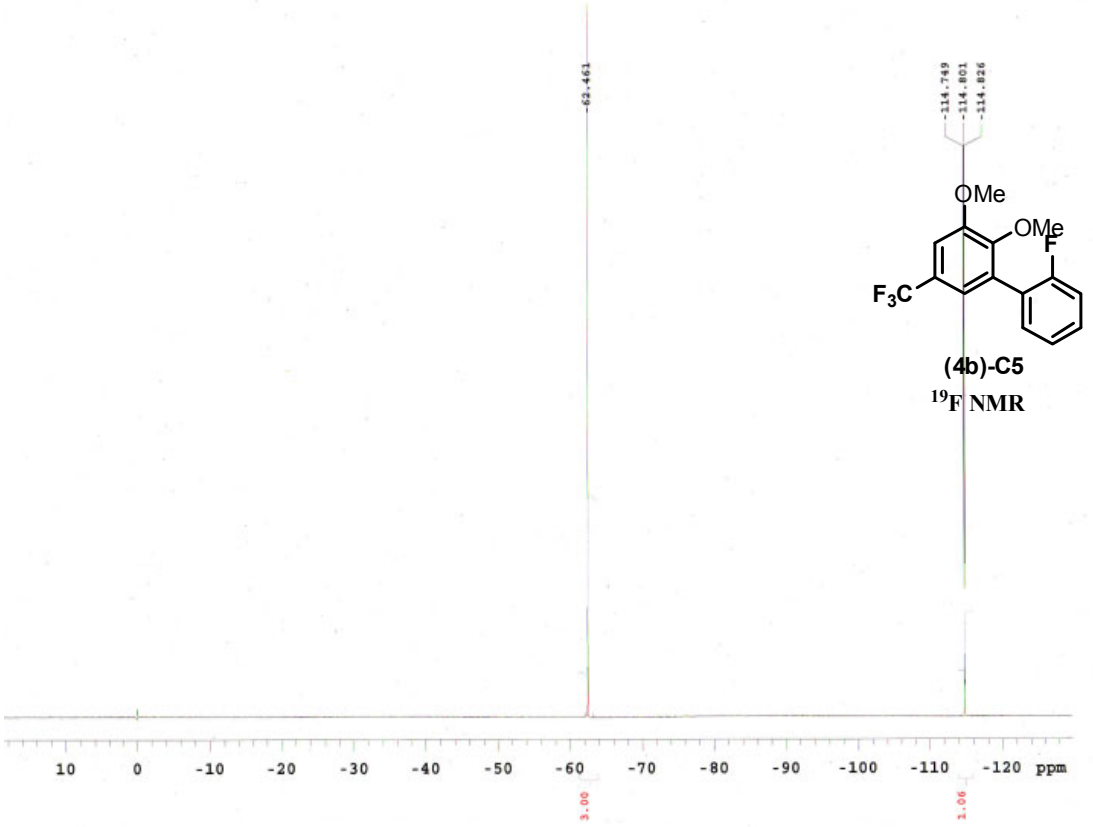


(4a)-C4

^{19}F NMR

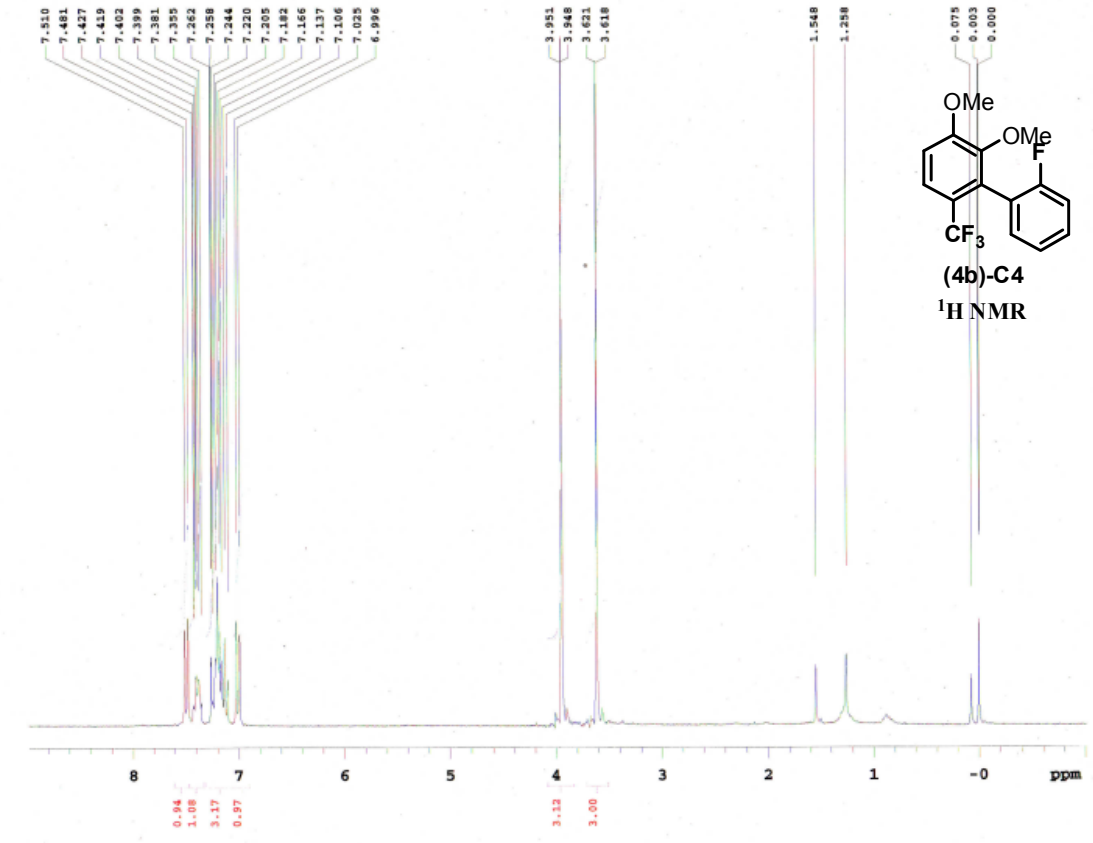

OMe
OMe
F
F3C
(4b)-C5
1H NMR
ppm


OMe
OMe
F
F3C
(4b)-C5
13C NMR
ppm



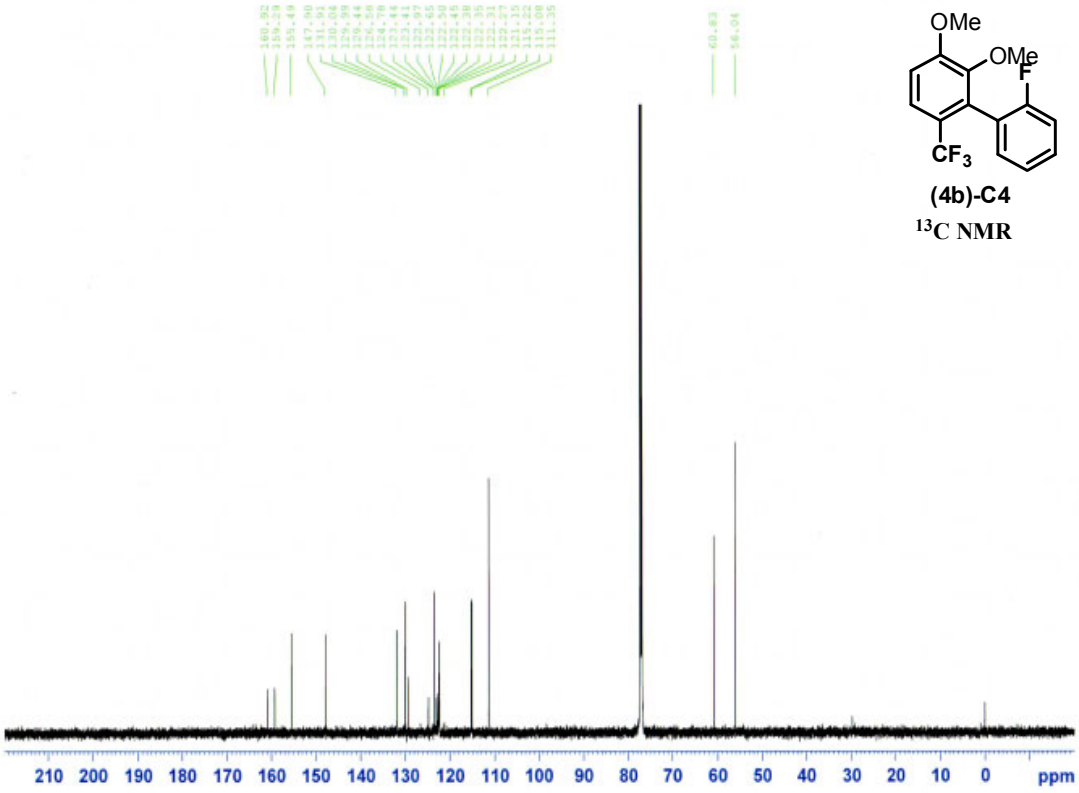
(4b)-C5

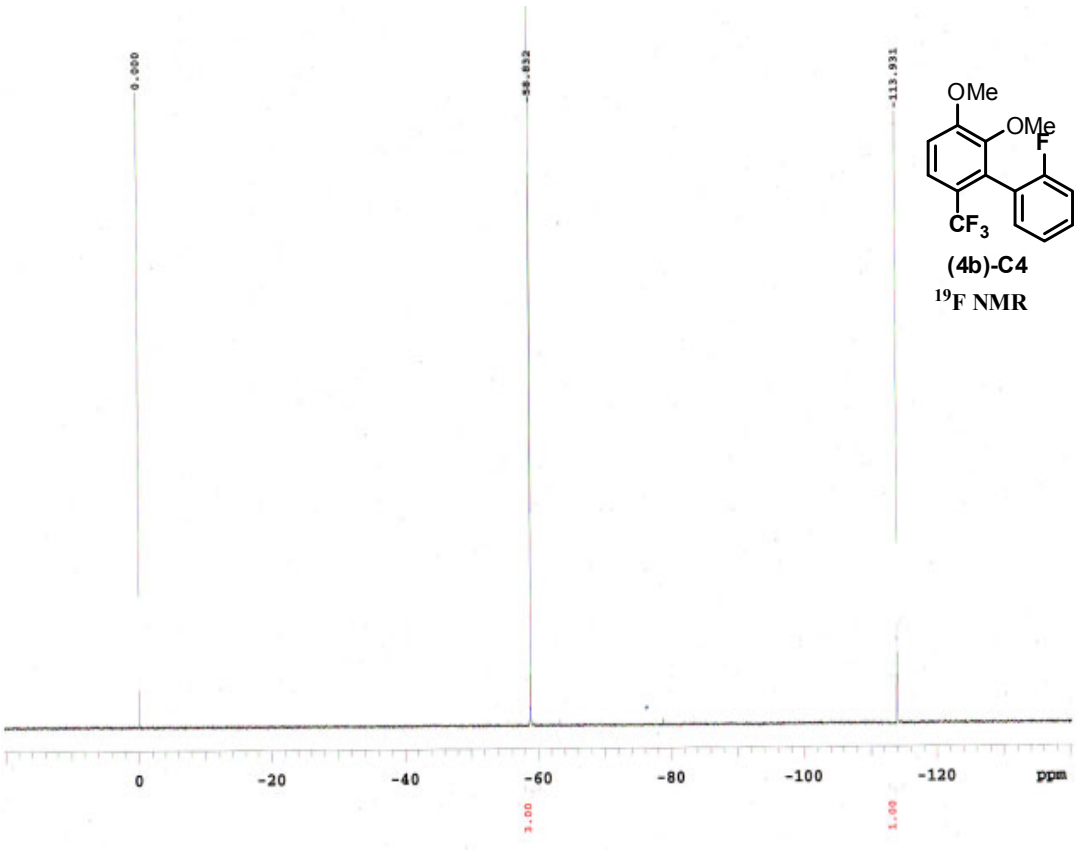
^{19}F NMR

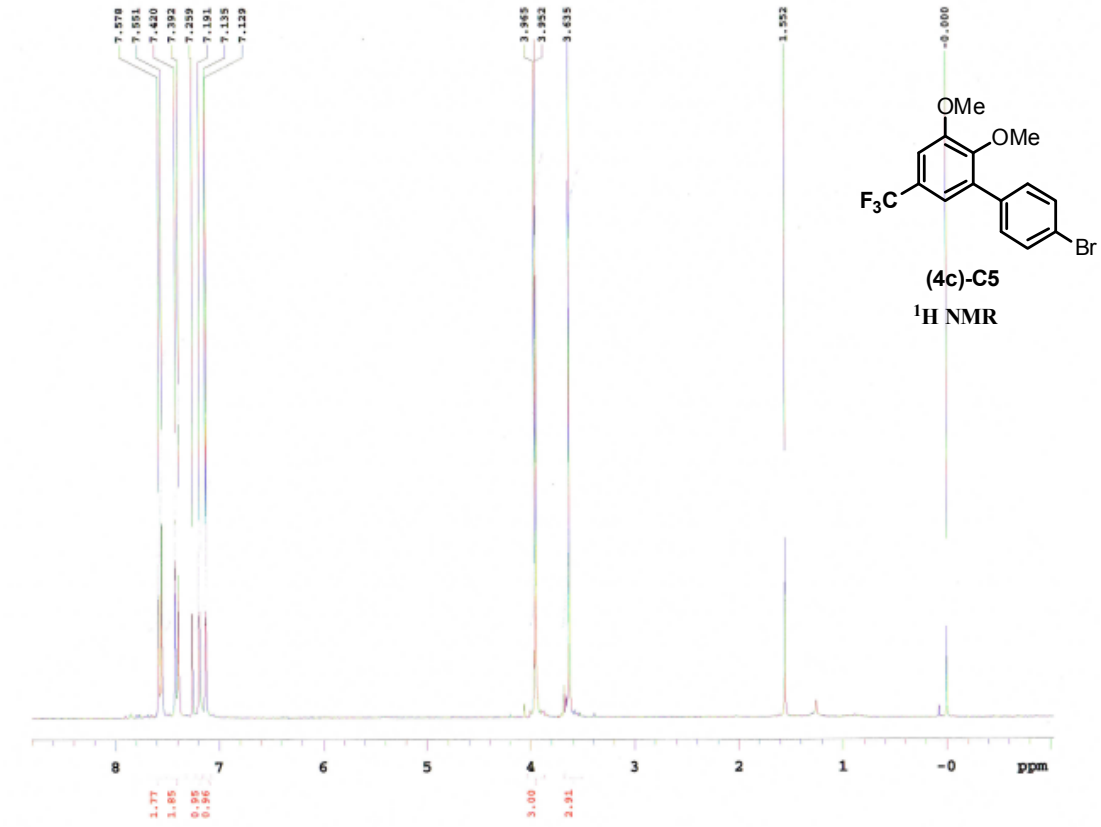


(4b)-C4

^{1}H NMR

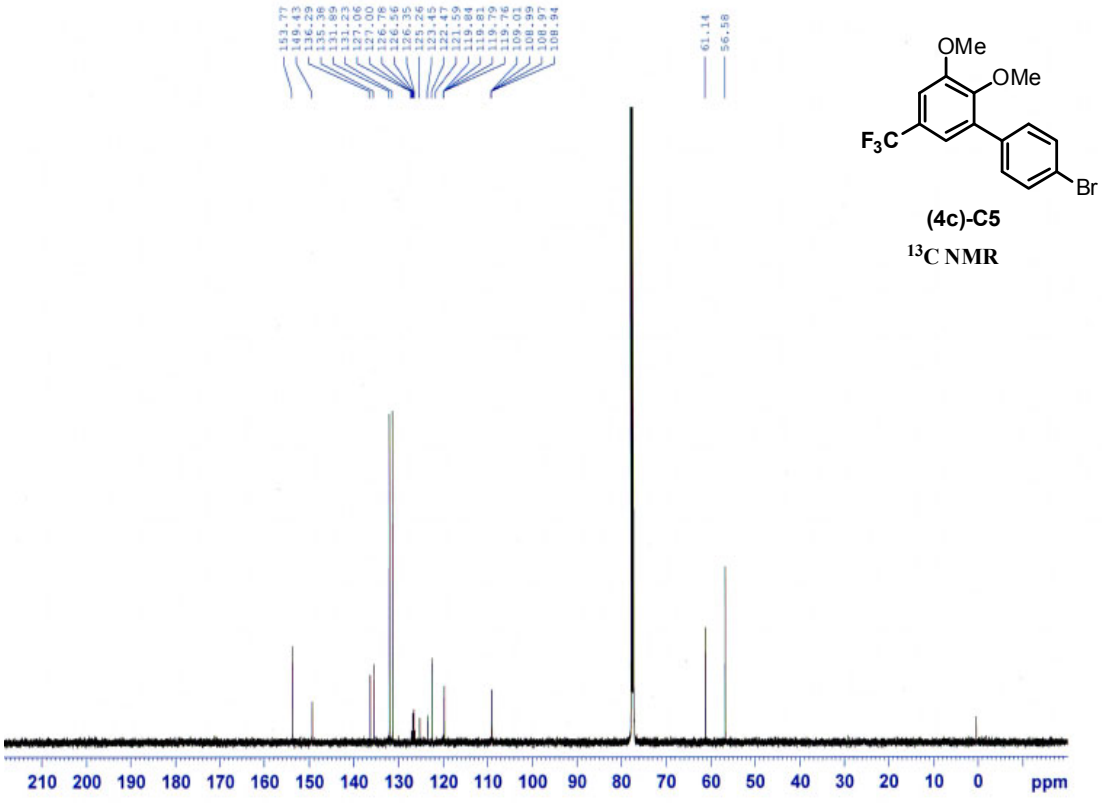

OMe
OMe
F
CF3
(4b)-C4
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
OMe
F
CF3
(4b)-C4
19F NMR
0 -20 -40 -60 -80 -100 -120 ppm



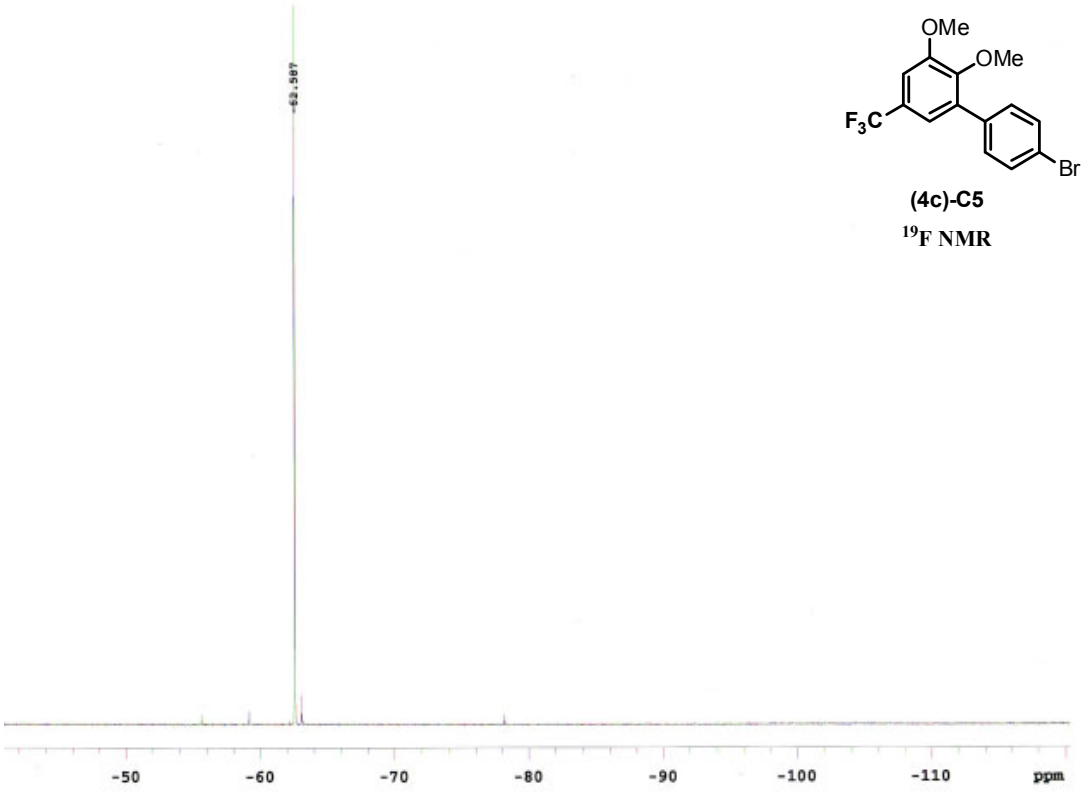
(4c)-C5

^{1}H NMR



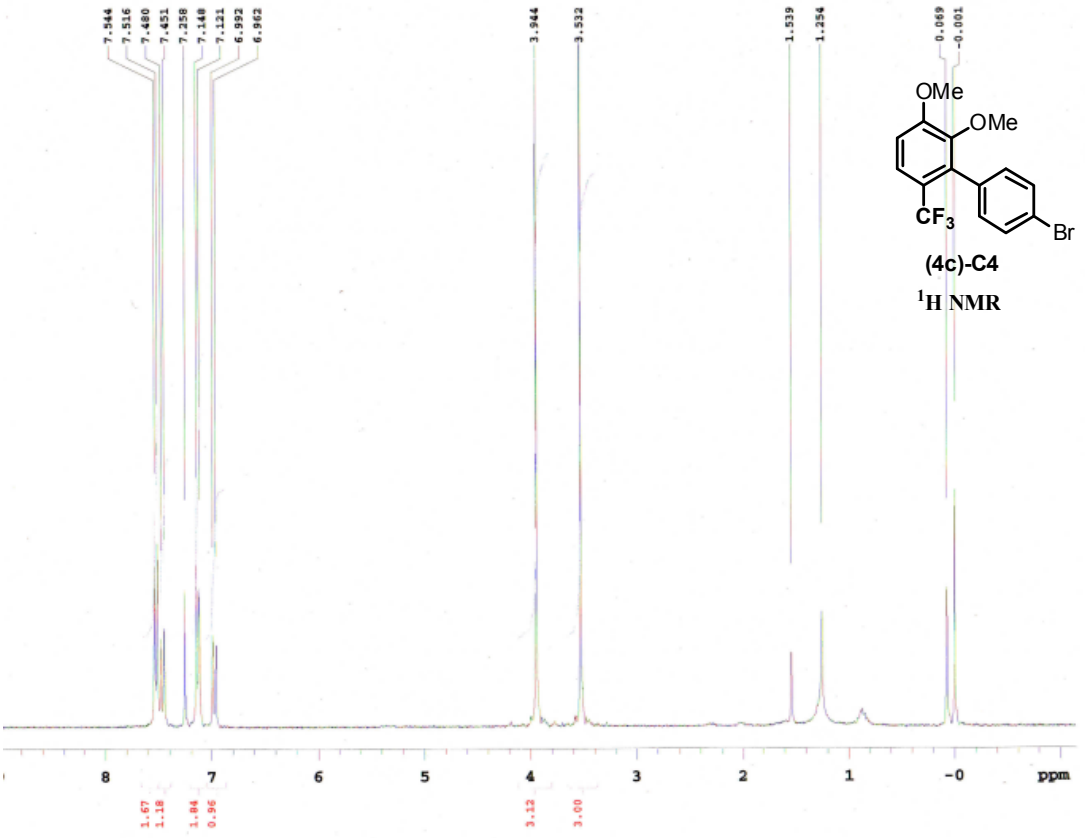
(4c)-C5

^{13}C NMR



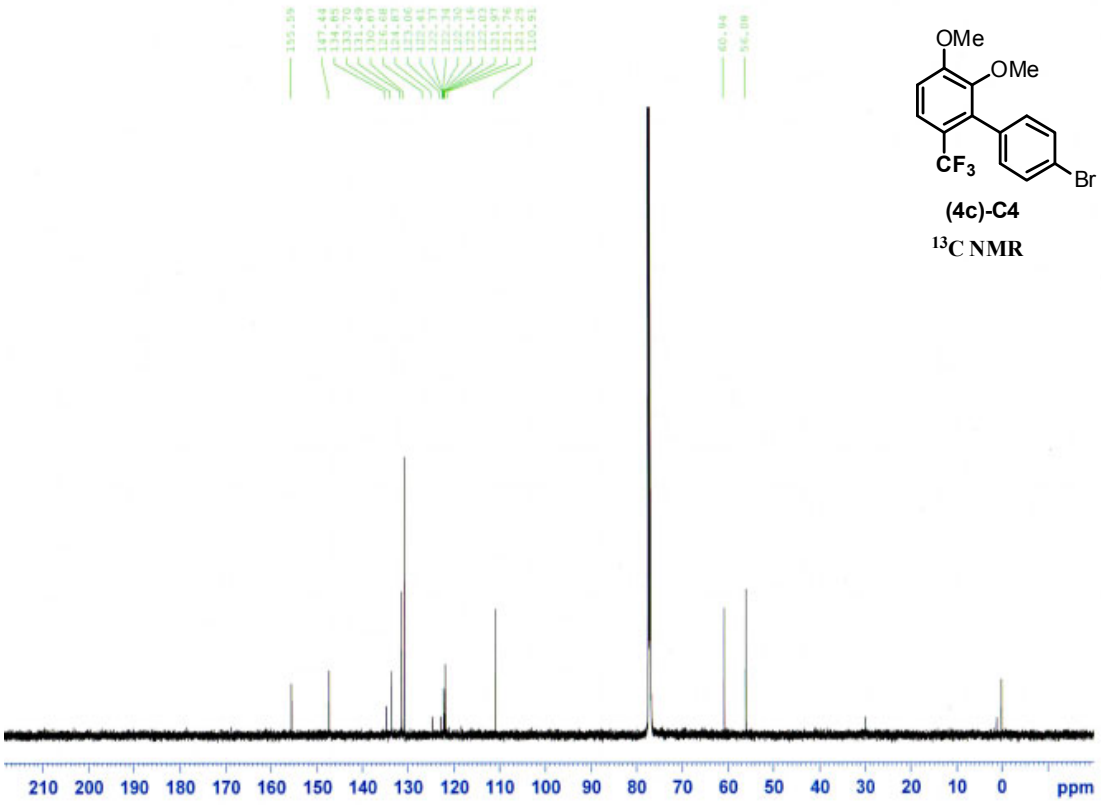
(4c)-C5

^{19}F NMR



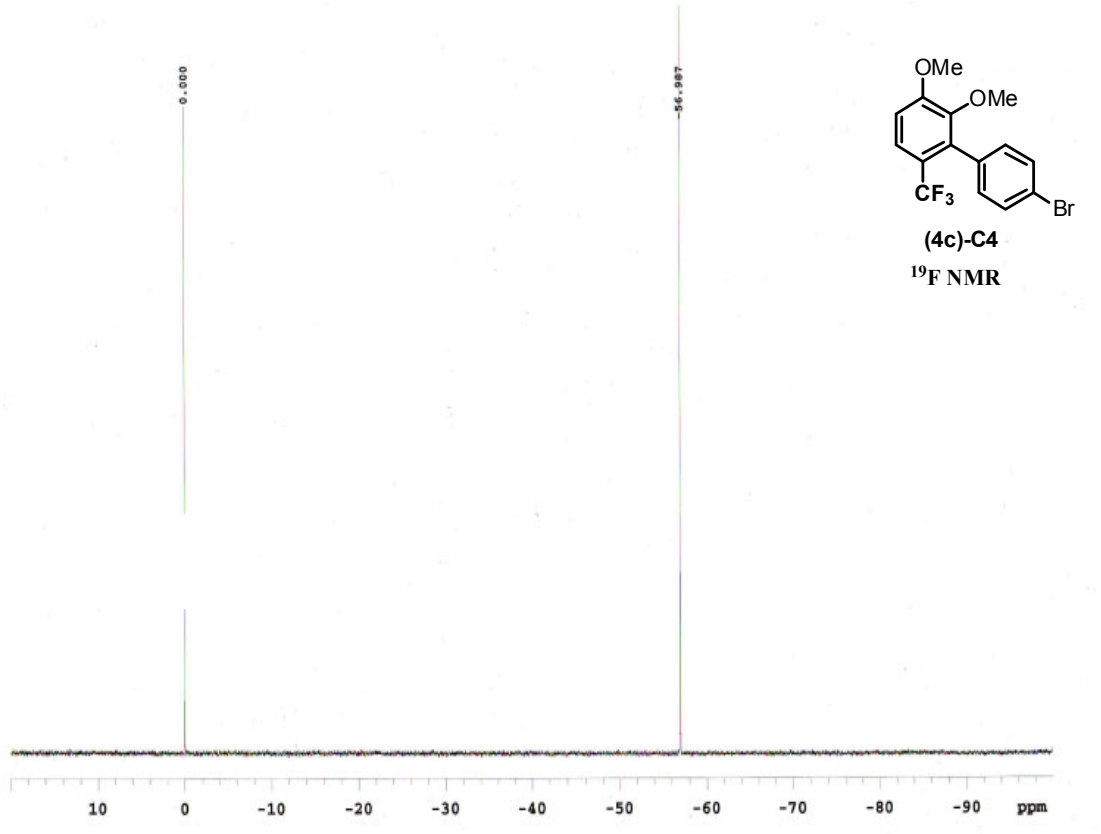
(4c)-C4

^{1}H NMR



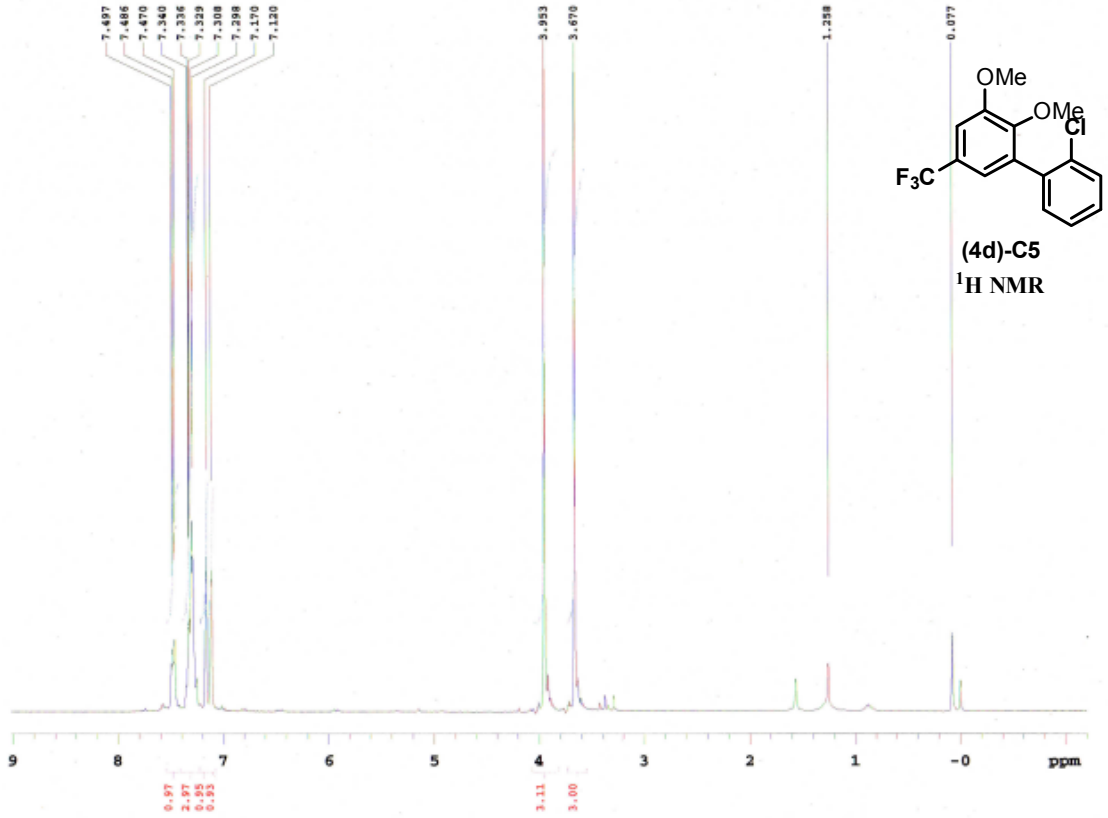
(4c)-C4

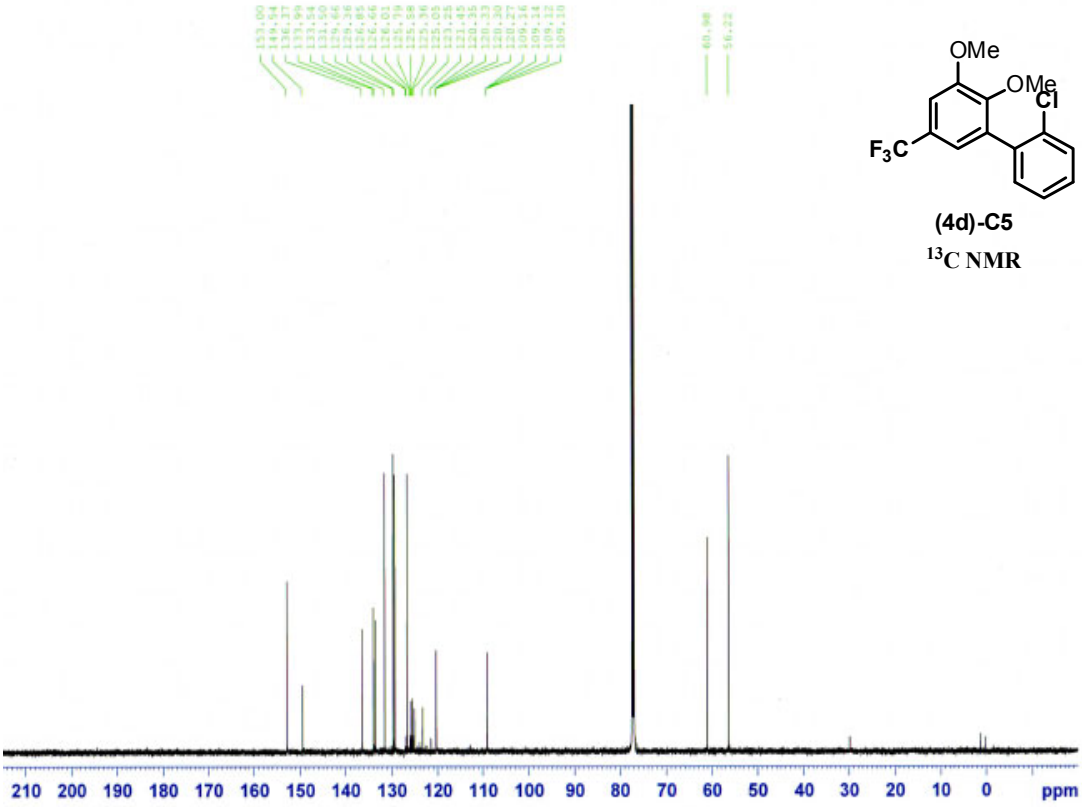
^{13}C NMR

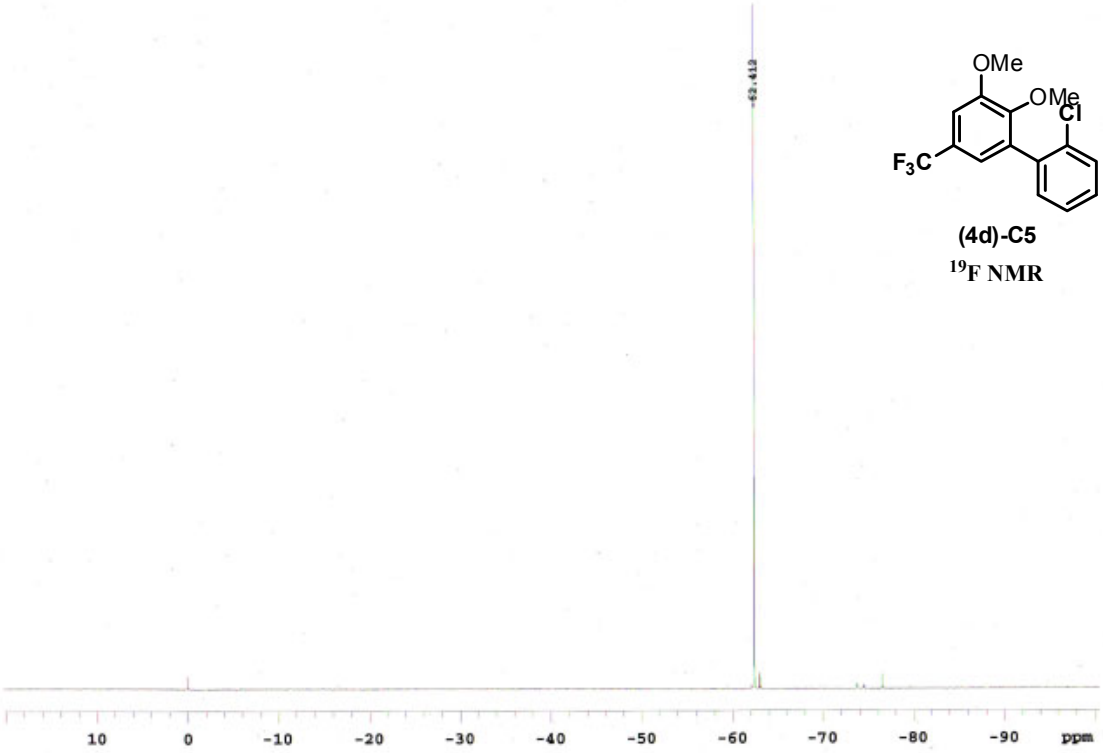


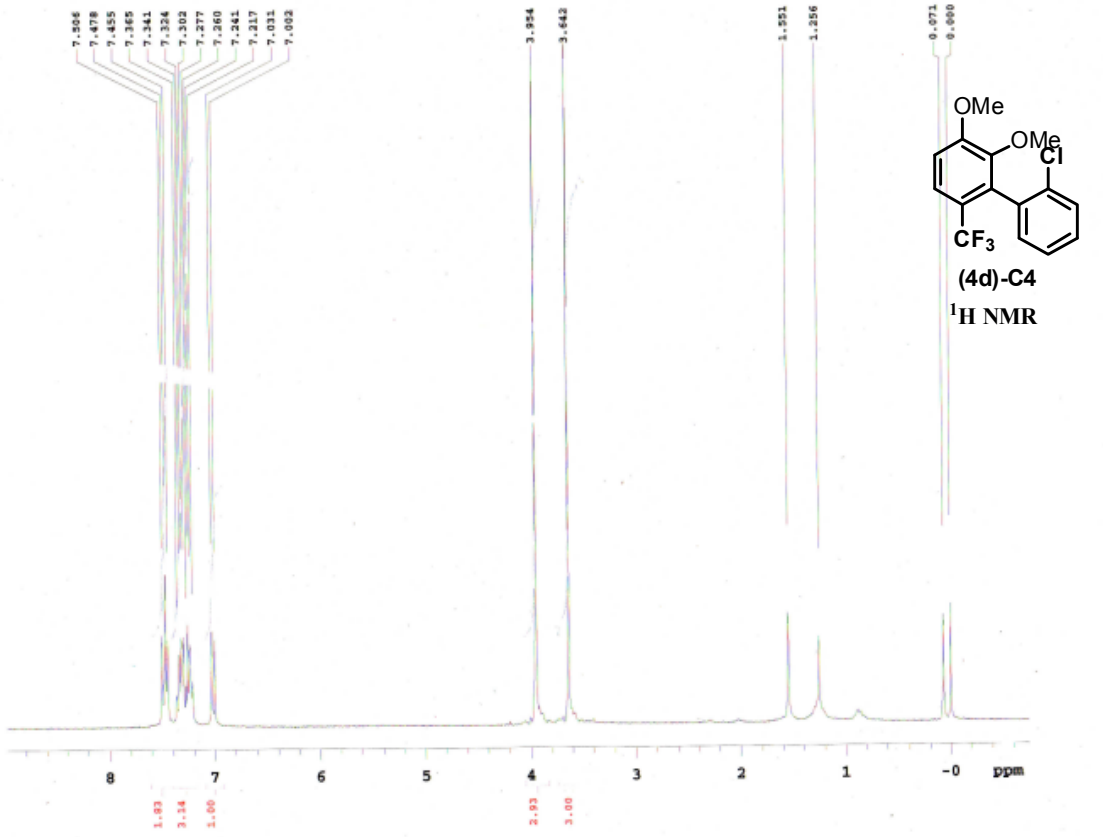
(4c)-C4

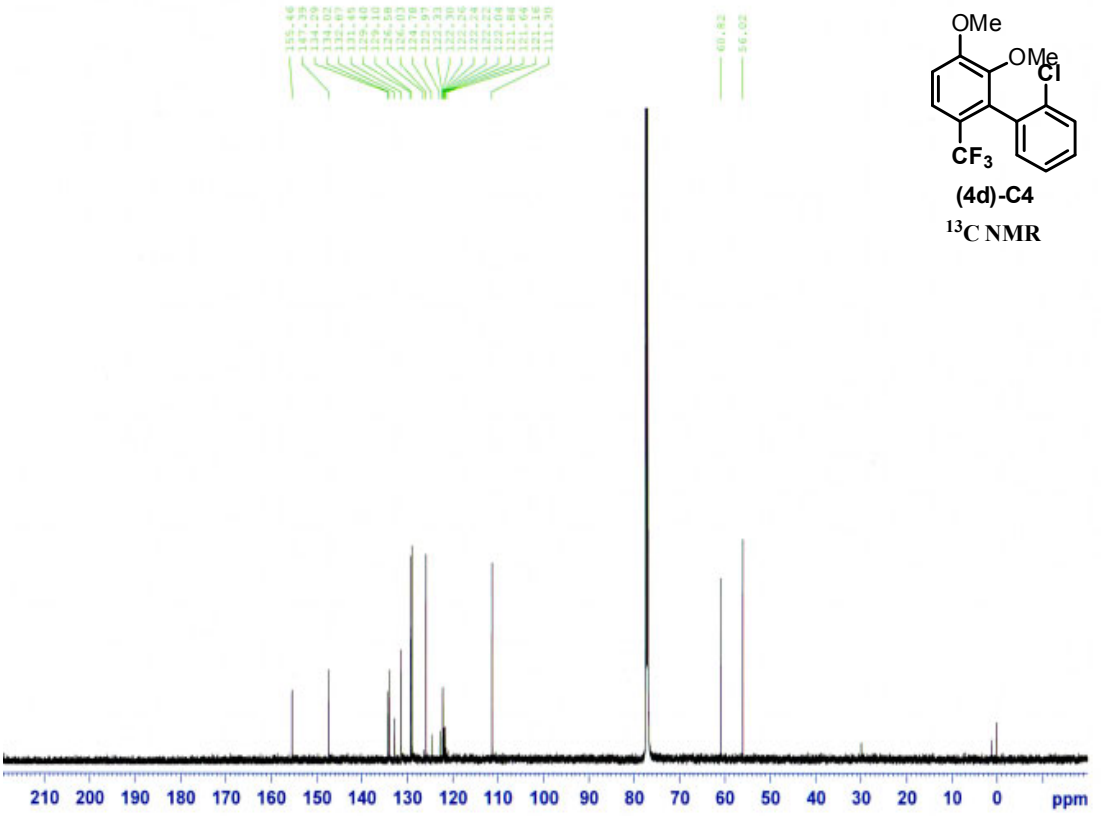
^{19}F NMR

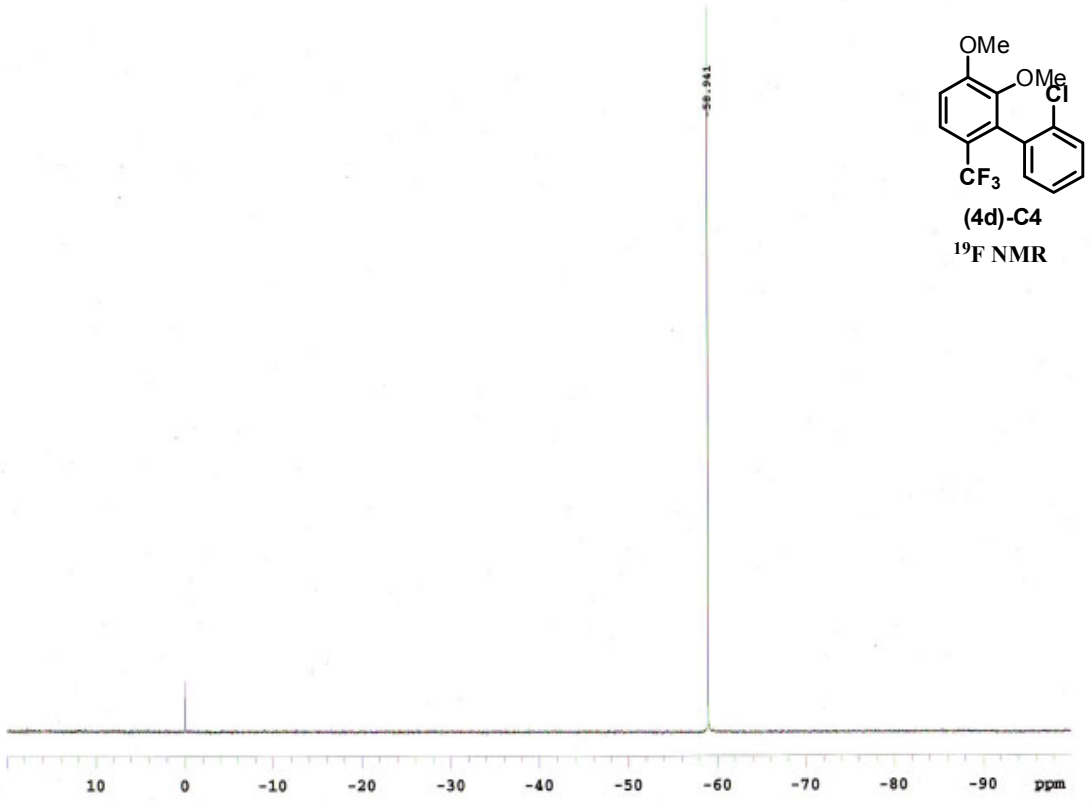

OMe
OMe
Cl
F3C
(4d)-C5
1H NMR
ppm

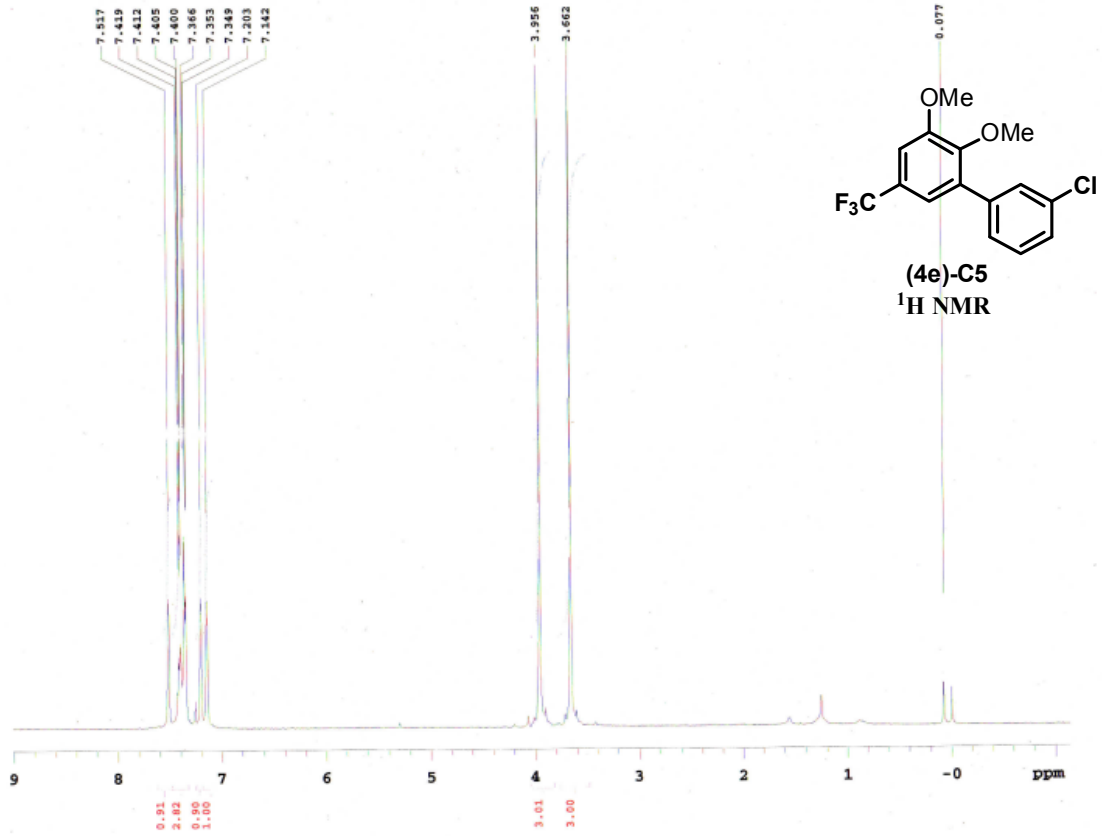

OMe
OMe
Cl
F3C
(4d)-C5
13C NMR
ppm


OMe
OMe
Cl
F3C
(4d)-C5
19F NMR
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
ppm

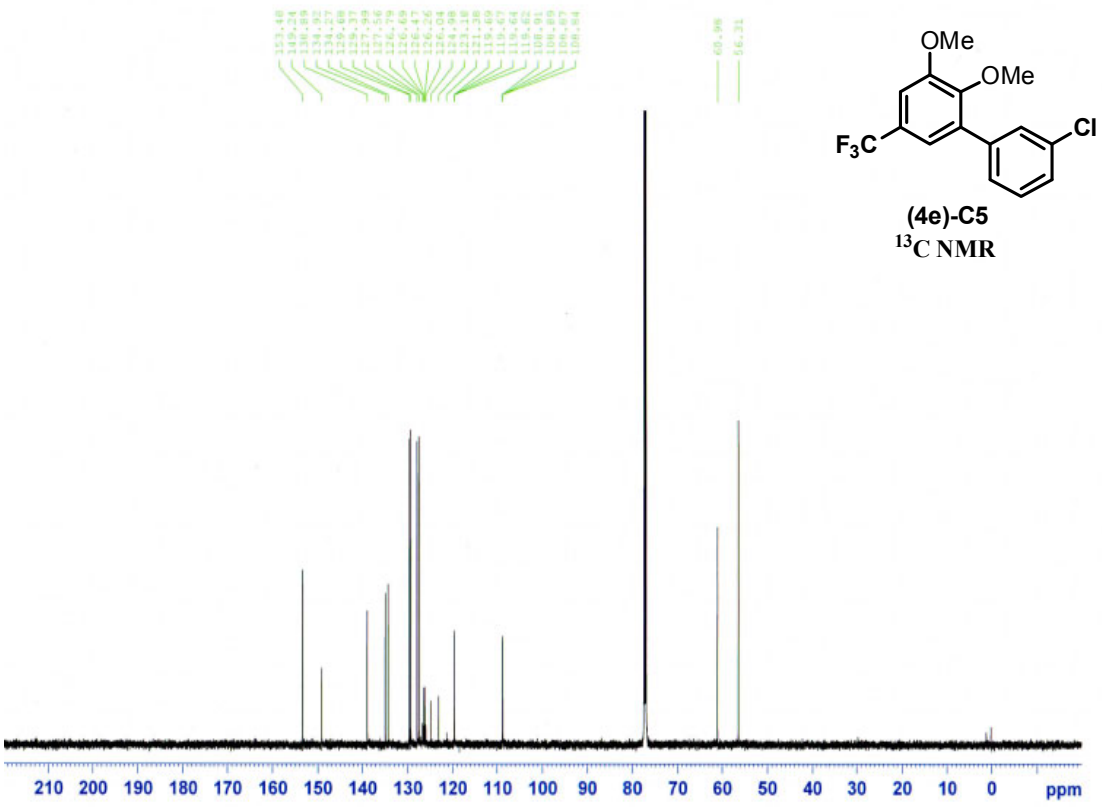

OMe
OMe
Cl
CF3
(4d)-C4
1H NMR
8
7
6
5
4
3
2
1
-0
ppm


OMe
OMe
Cl
CF3
(4d)-C4
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

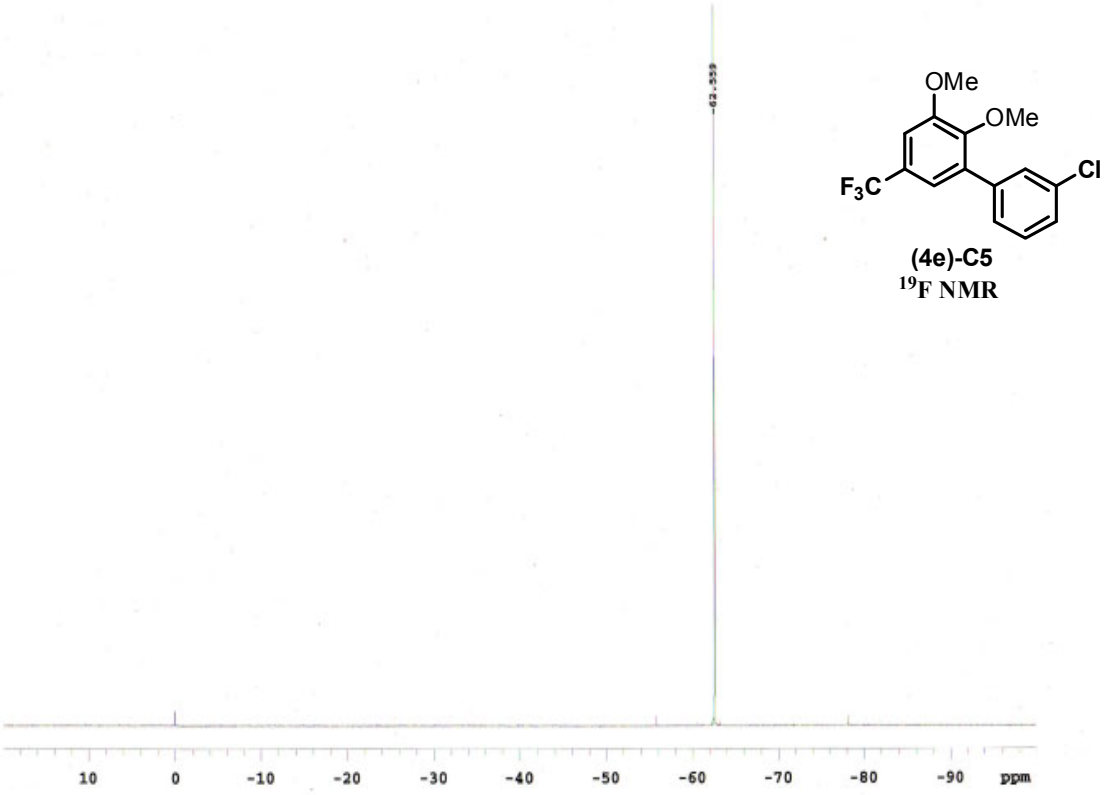

OMe
OMe
Cl
CF3
(4d)-C4
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm



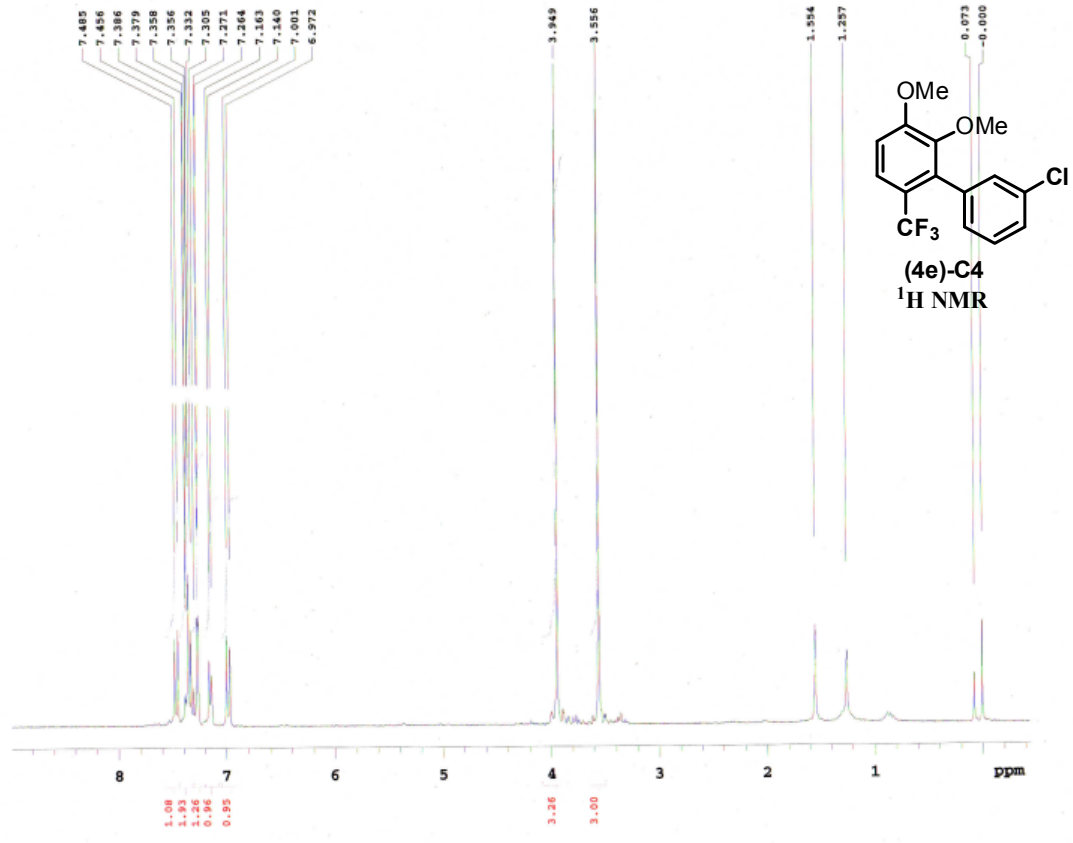
(4e)-C5
^{1}H NMR



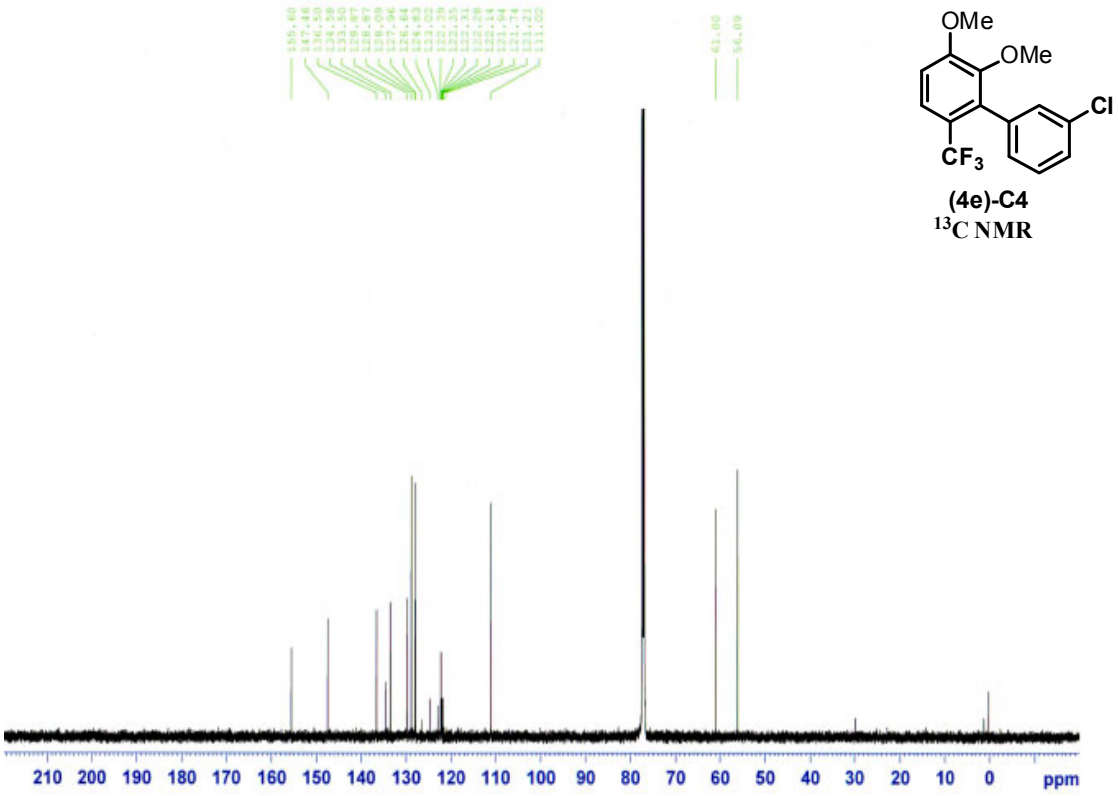
(4e)-C5
^{13}C NMR



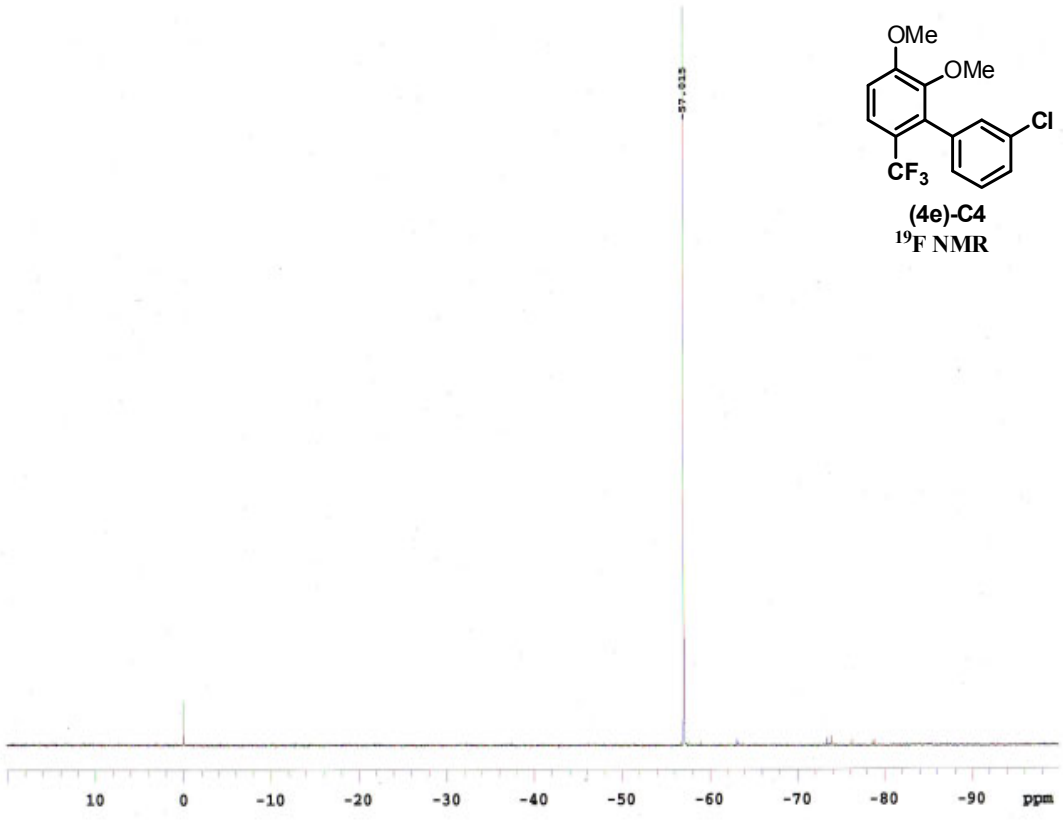
(4e)-C5
^{19}F NMR



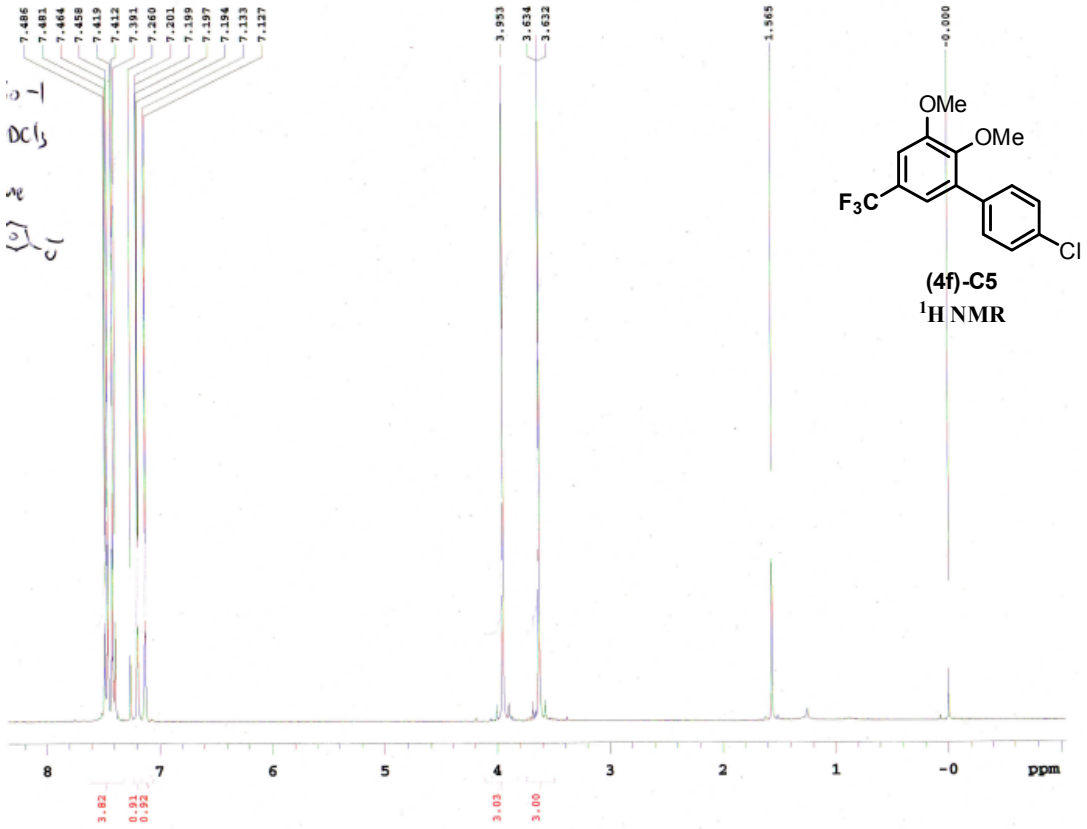
(4e)-C4
^{1}H NMR



(4e)-C4
^{13}C NMR



(4e)-C4
^{19}F NMR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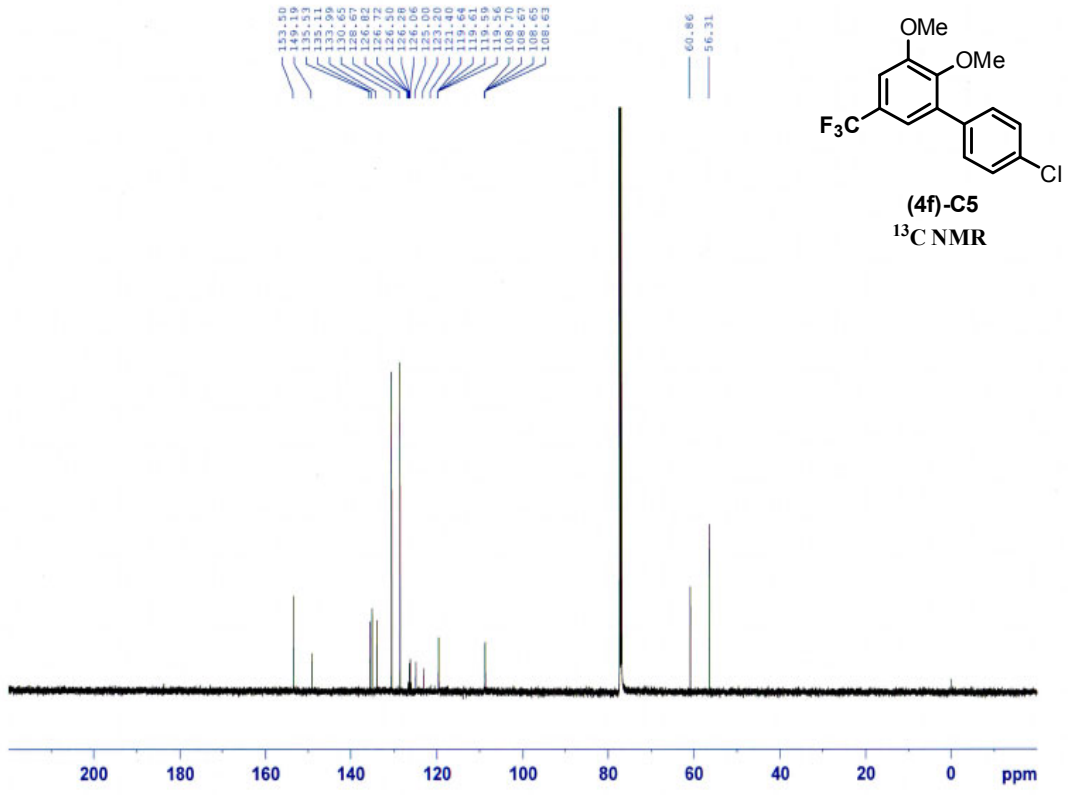
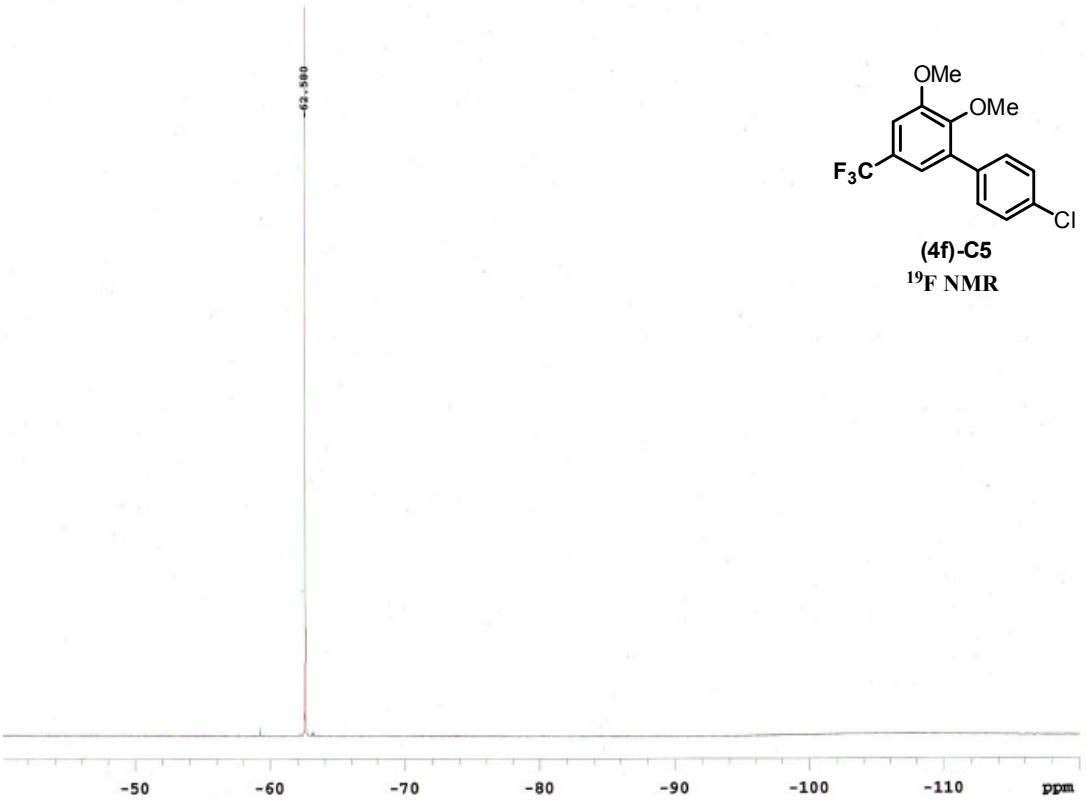
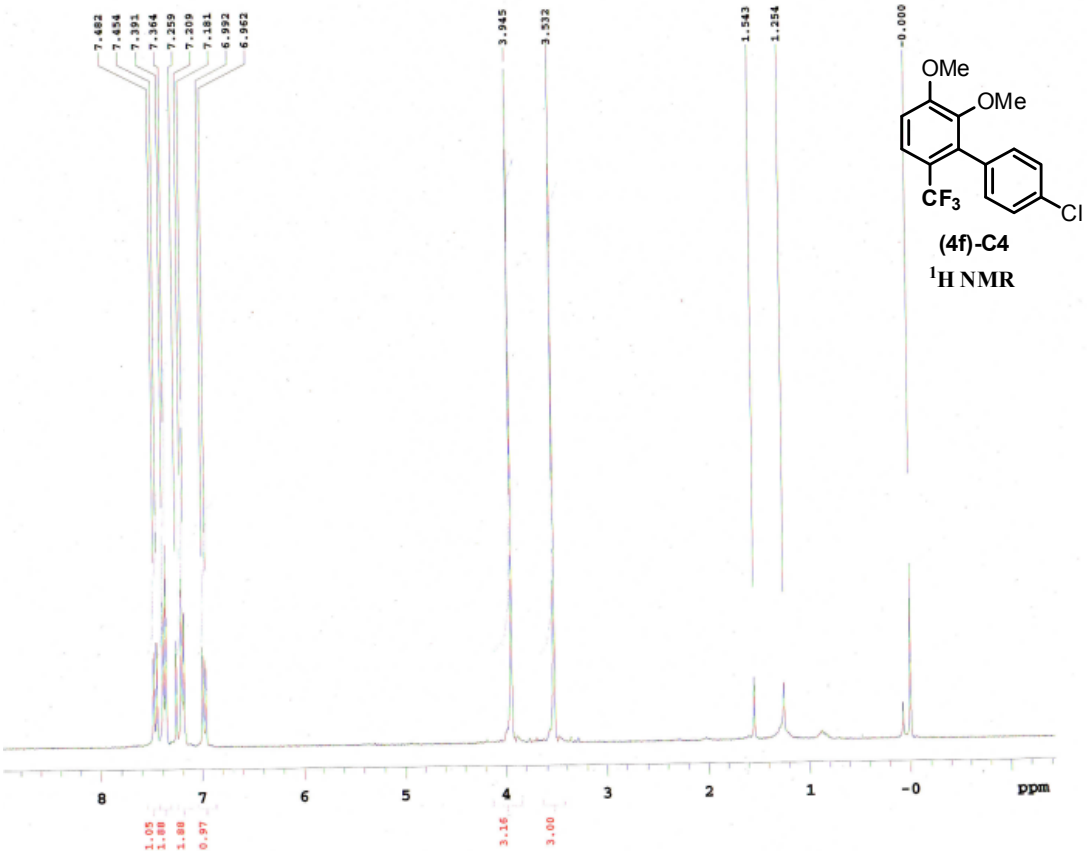
7.481
7.464
7.458
7.419
7.412
7.391
7.260
7.201
7.199
7.197
7.194
7.133
7.127
3.953
3.634
3.632
1.565
0.000
OMe
OMe
F3C
Cl
(4f)-C5
1H NMR
8
7
6
5
4
3
2
1
-0
ppm
3.82
0.91
0.92
3.03
3.00

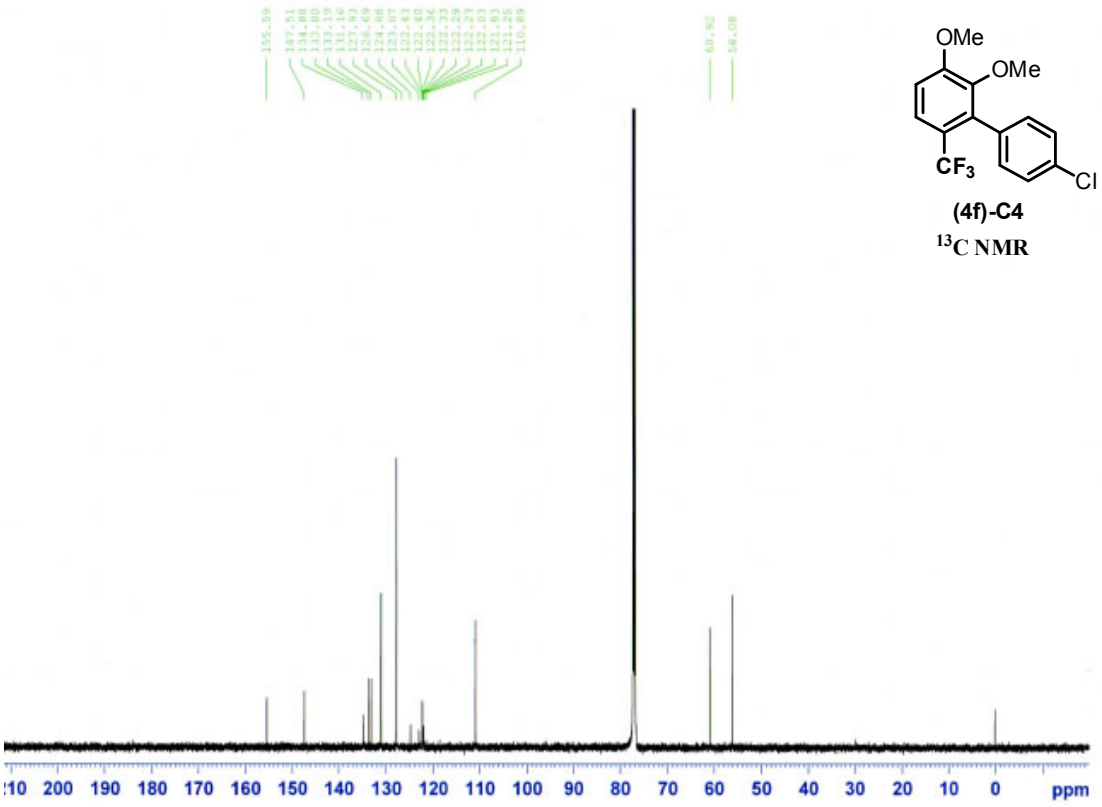

153.50
149.19
135.53
133.11
133.99
130.65
128.67
126.82
126.72
126.50
126.38
126.06
125.00
123.20
121.40
119.64
119.41
119.09
119.56
108.70
108.67
108.65
108.63
60.86
56.31
OMe
OMe
F3C
Cl
(4f)-C5
13C NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

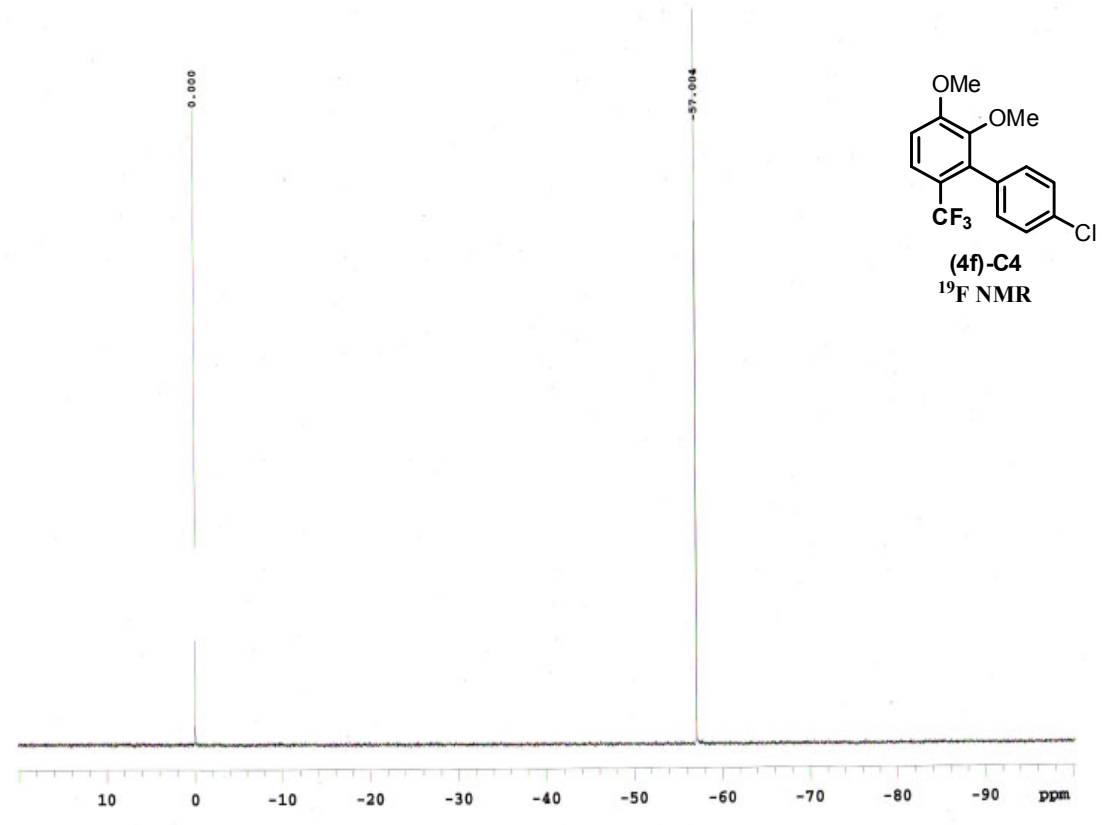


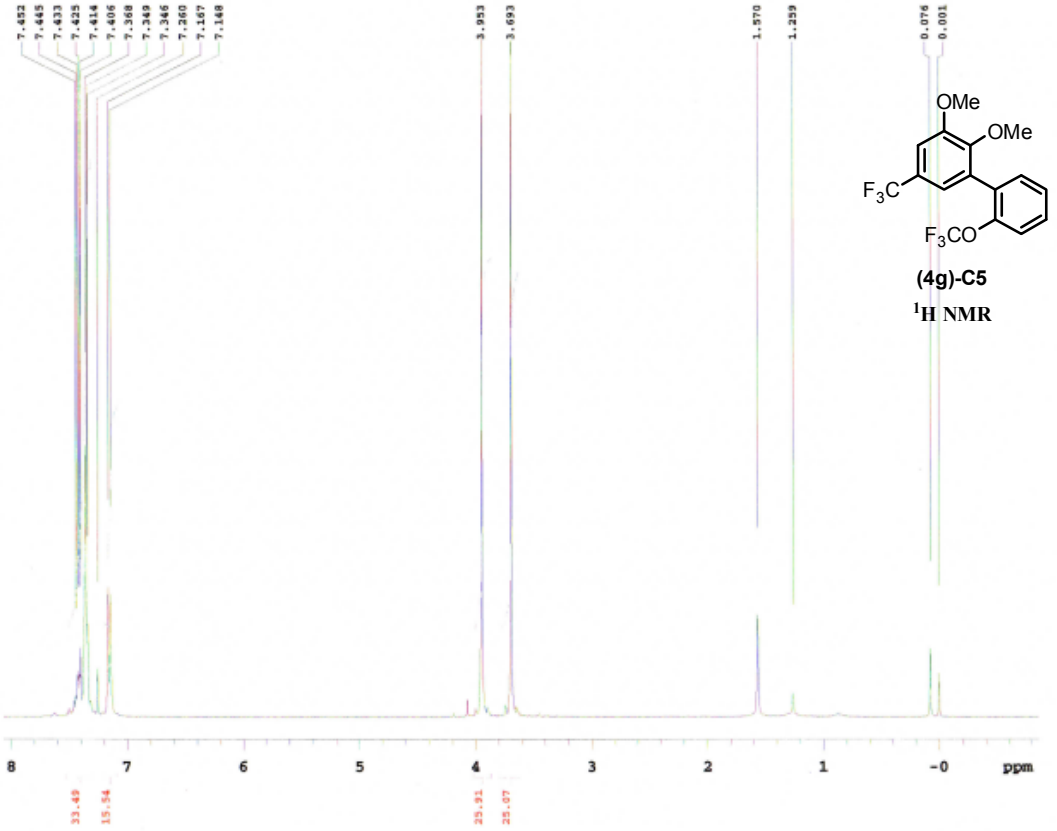
(4f)-C5
^{19}F NMR



(4f)-C4
^{1}H NMR

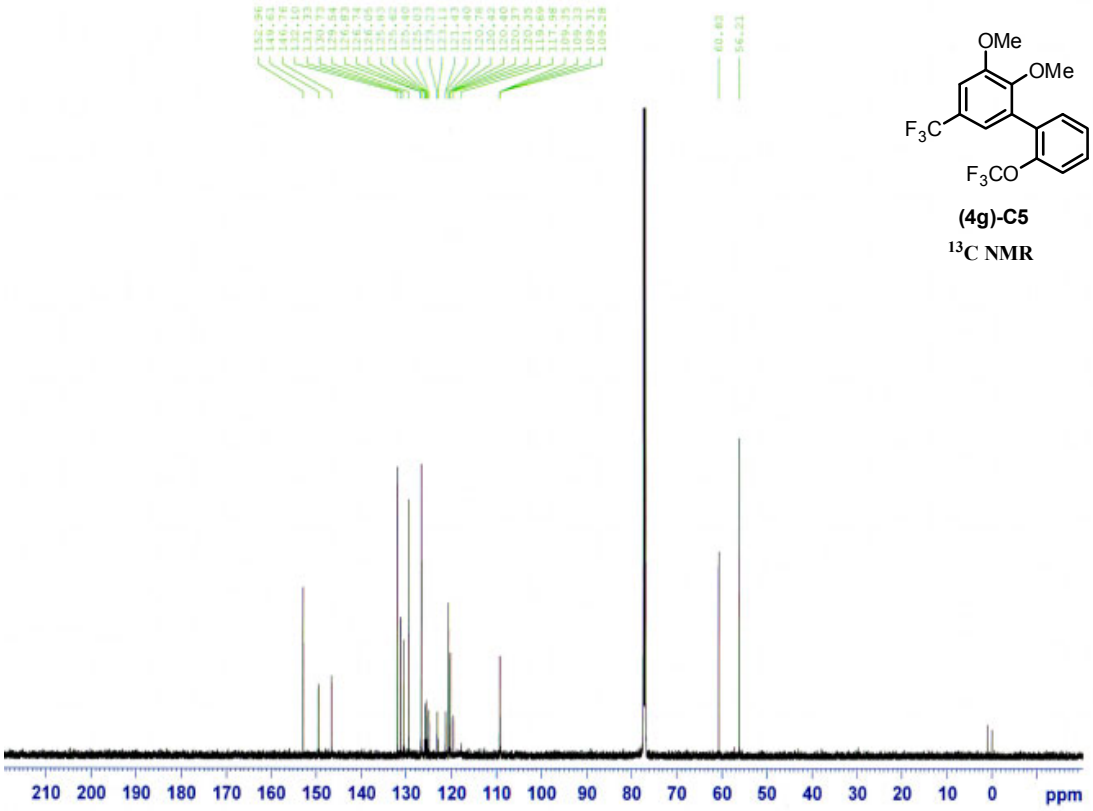

OMe
OMe
CF3
Cl
(4f)-C4
13C NMR
ppm


OMe
OMe
CF3
Cl
(4f)-C4
19F NMR
ppm



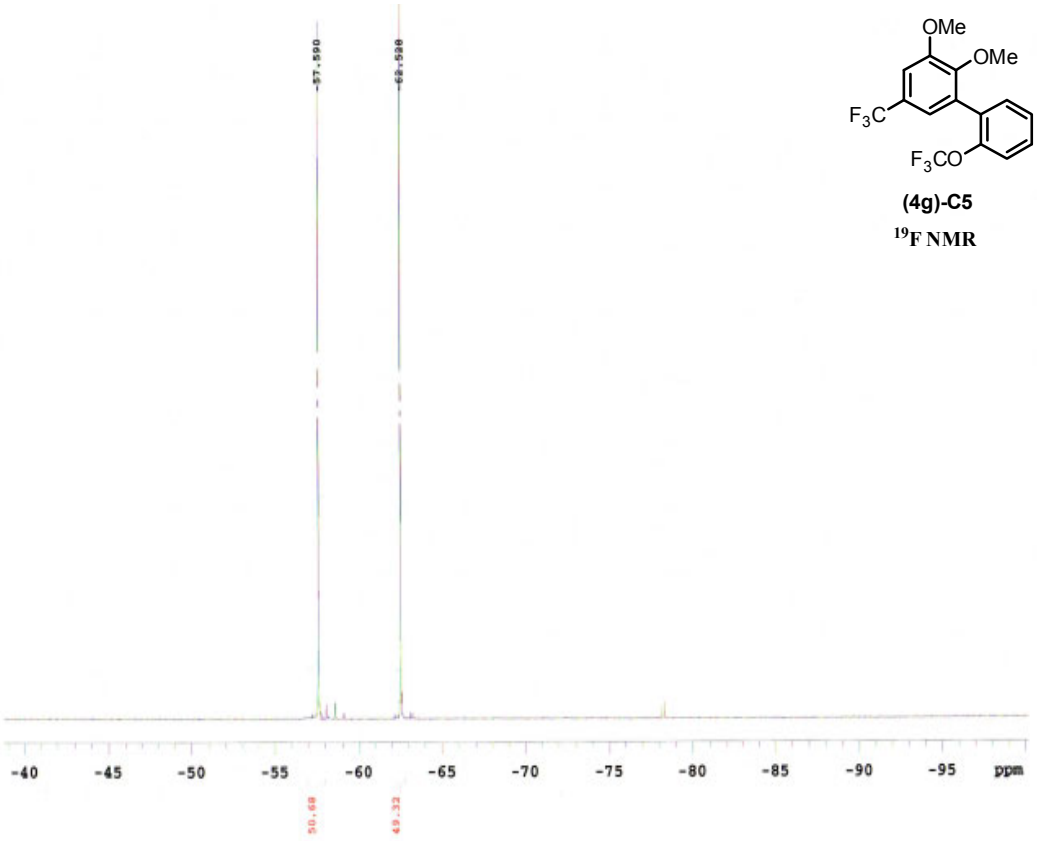
(4g)-C5

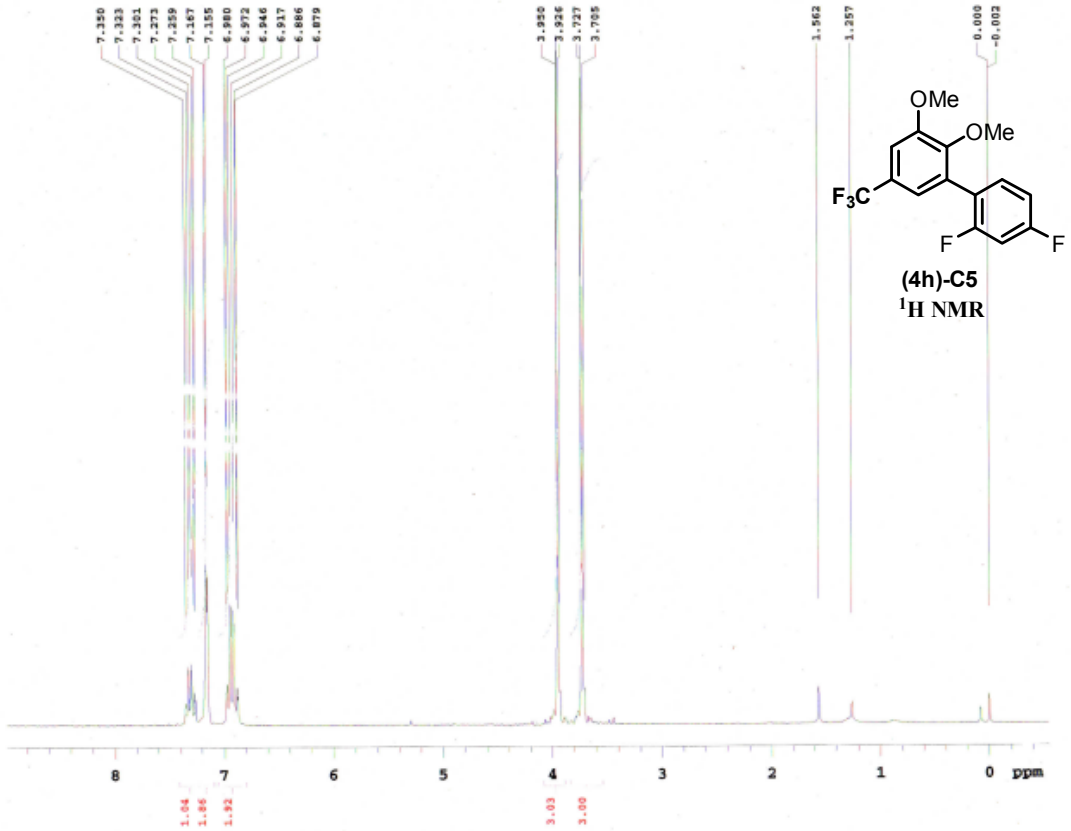
^{1}H NMR

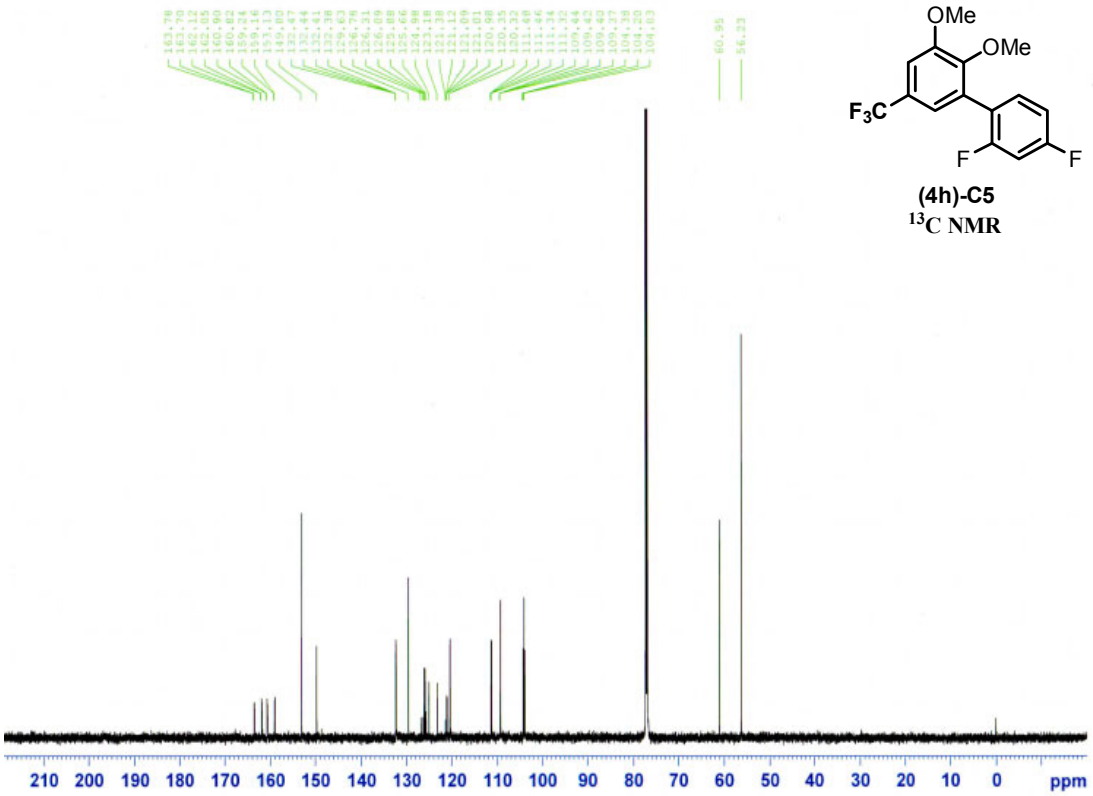


(4g)-C5

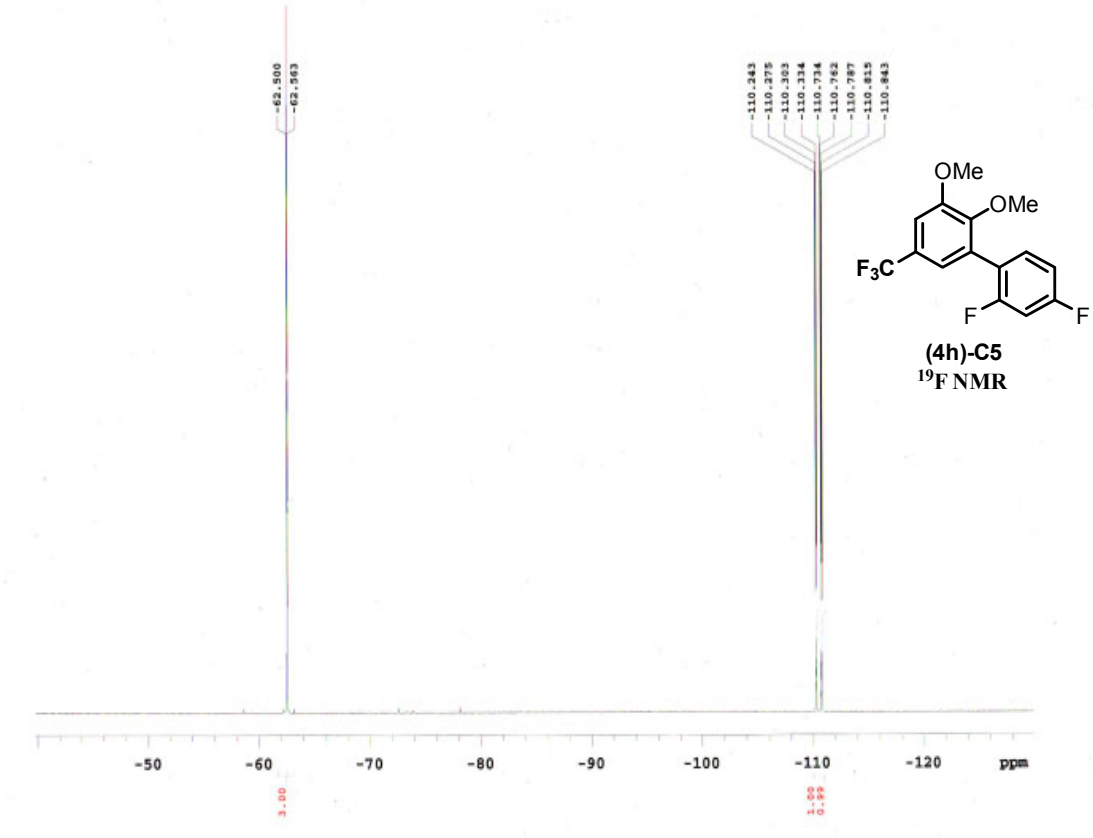
^{13}C NMR


OMe
OMe
F3C
F3CO
(4g)-C5
19F NMR
-57.590
-62.530
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm
50.68
49.32

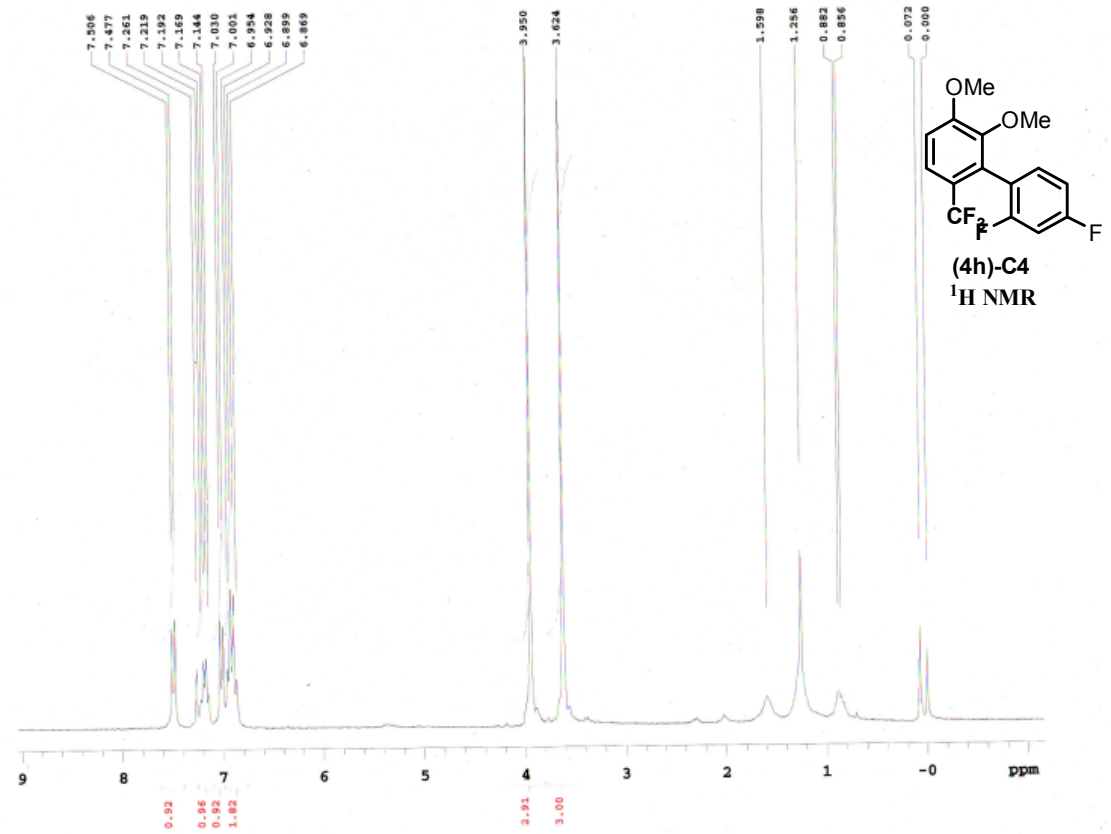

OMe
OMe
F3C
F
F
(4h)-C5
1H NMR
7.350
7.333
7.301
7.273
7.259
7.167
7.155
6.980
6.972
6.946
6.917
6.886
6.879
3.956
3.926
3.727
3.705
1.562
1.257
0.000
-0.002
8
7
6
5
4
3
2
1
0
ppm
1.04
1.86
1.92
3.03
3.00



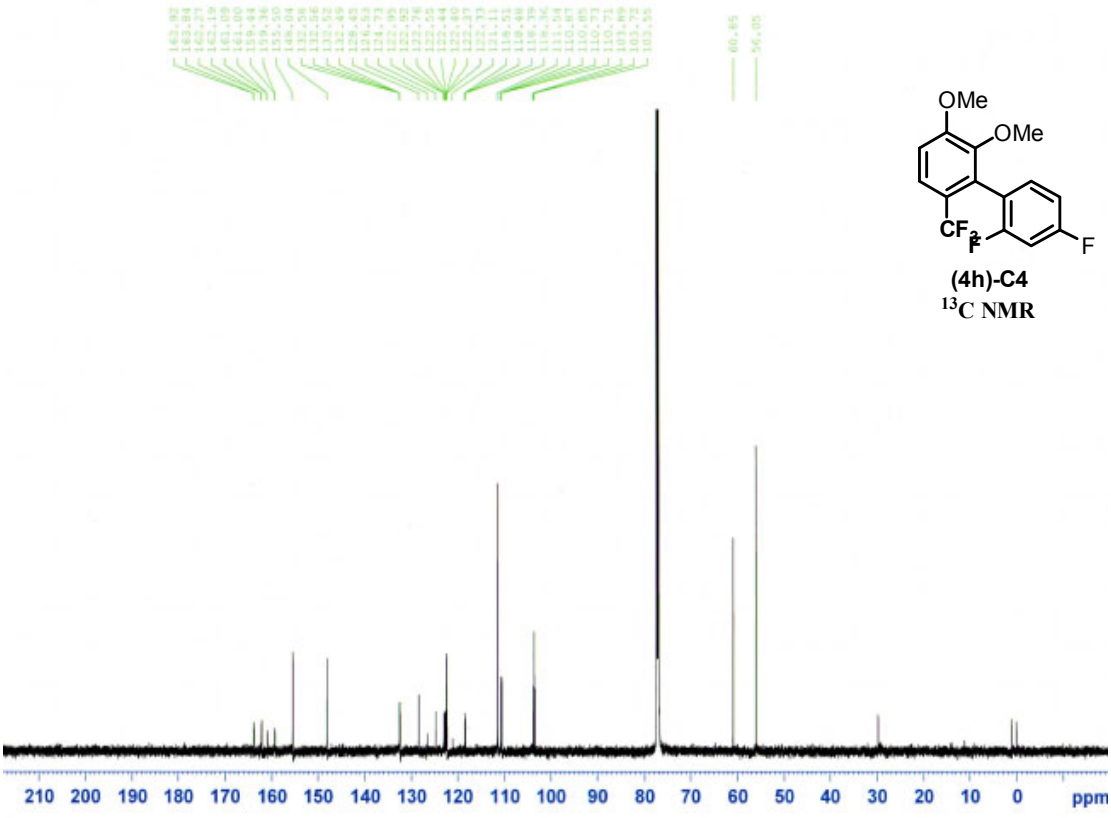
(4h)-C5
^{13}C NMR



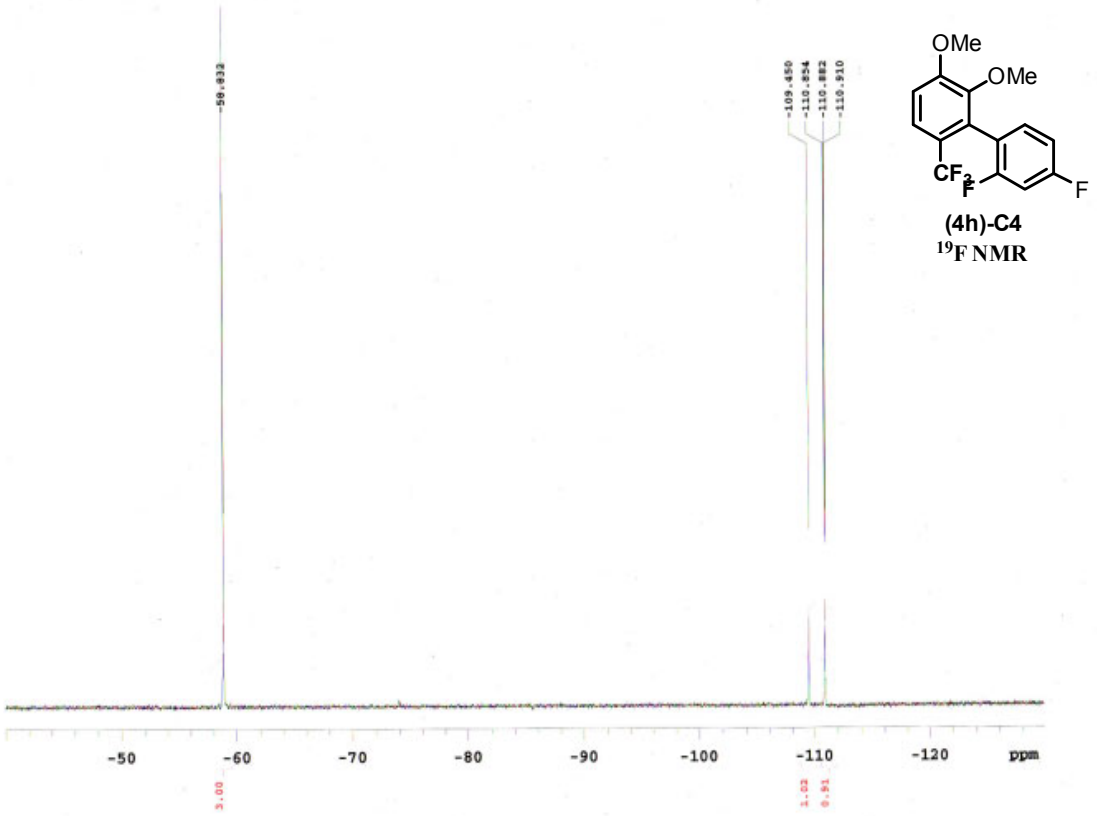
(4h)-C5
^{19}F NMR

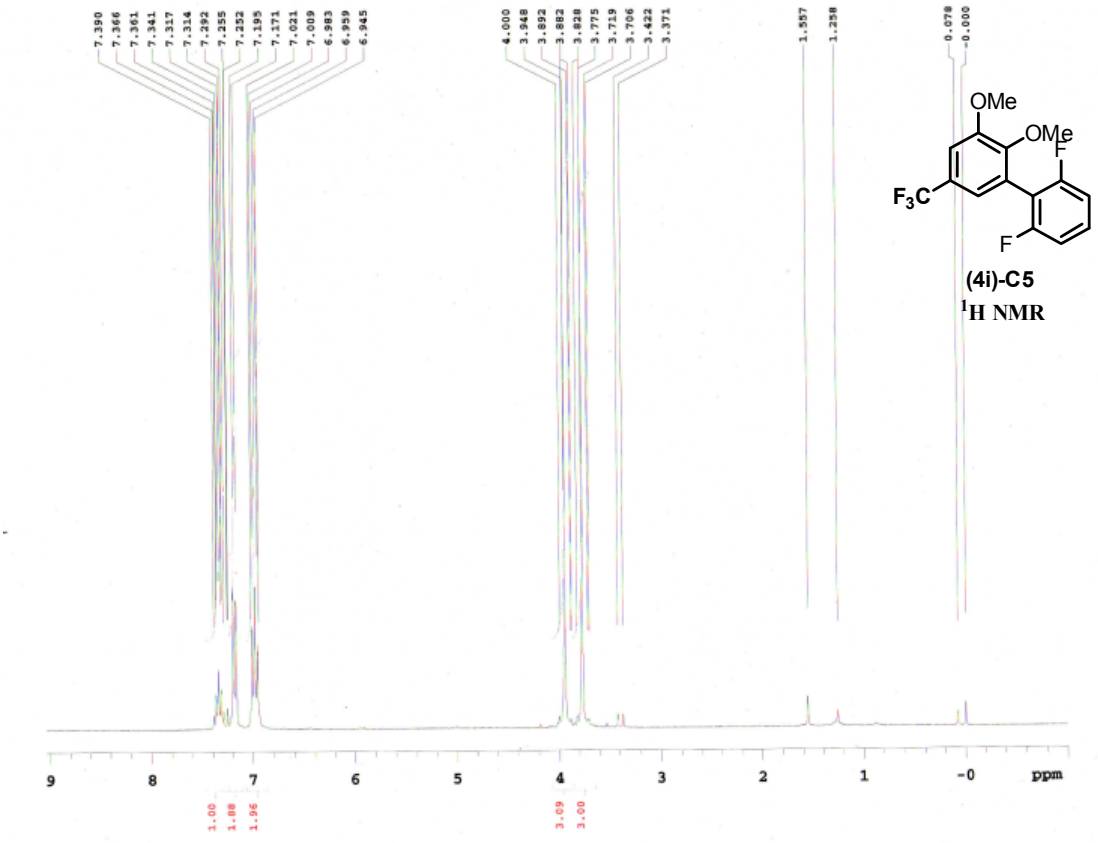


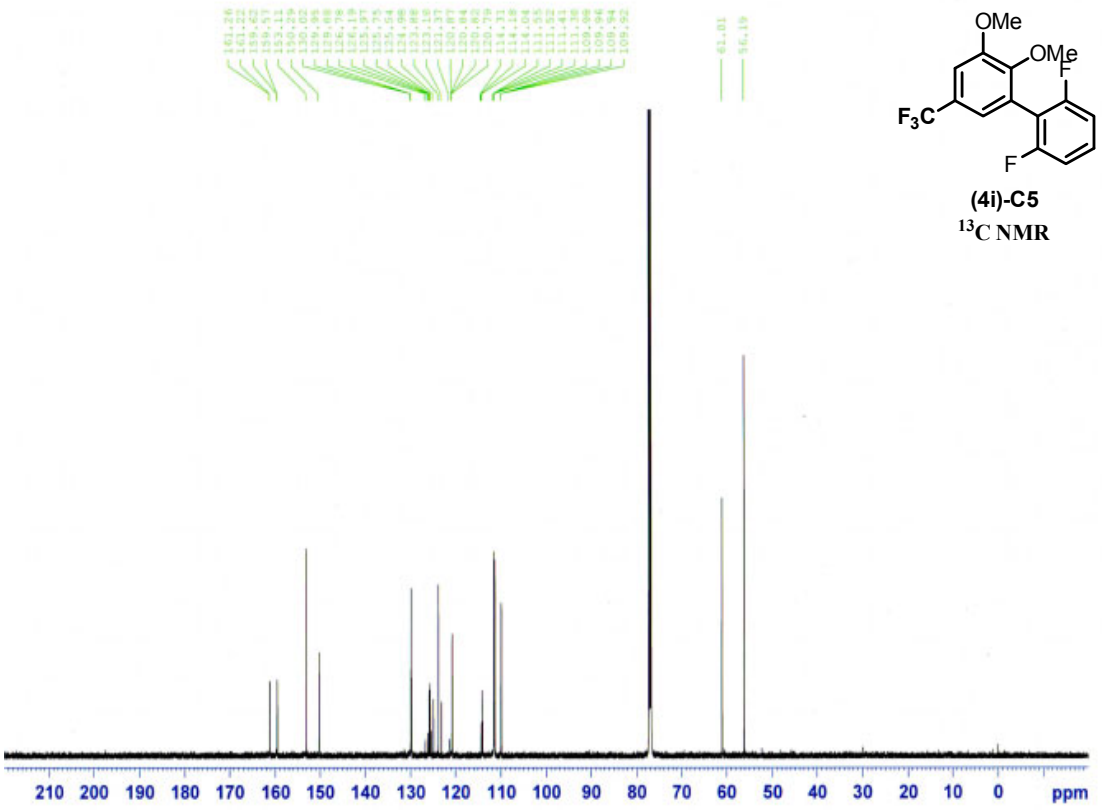
(4h)-C4
^{1}H NMR

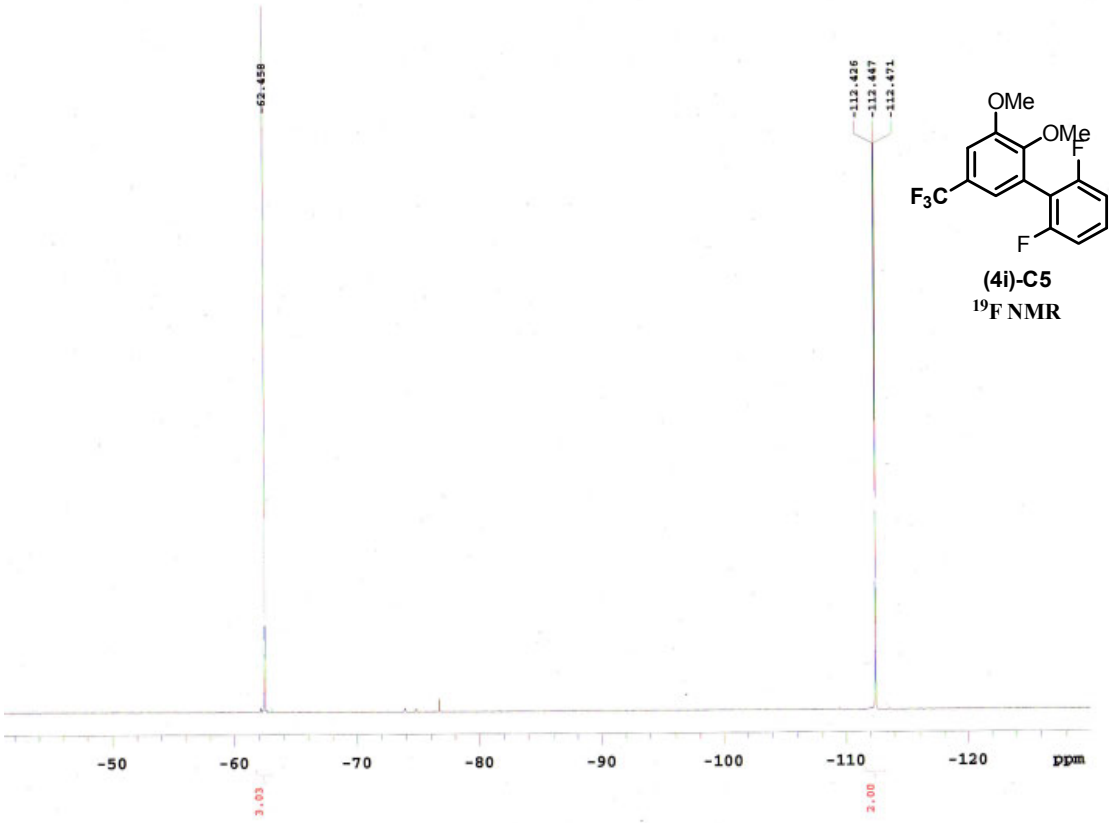


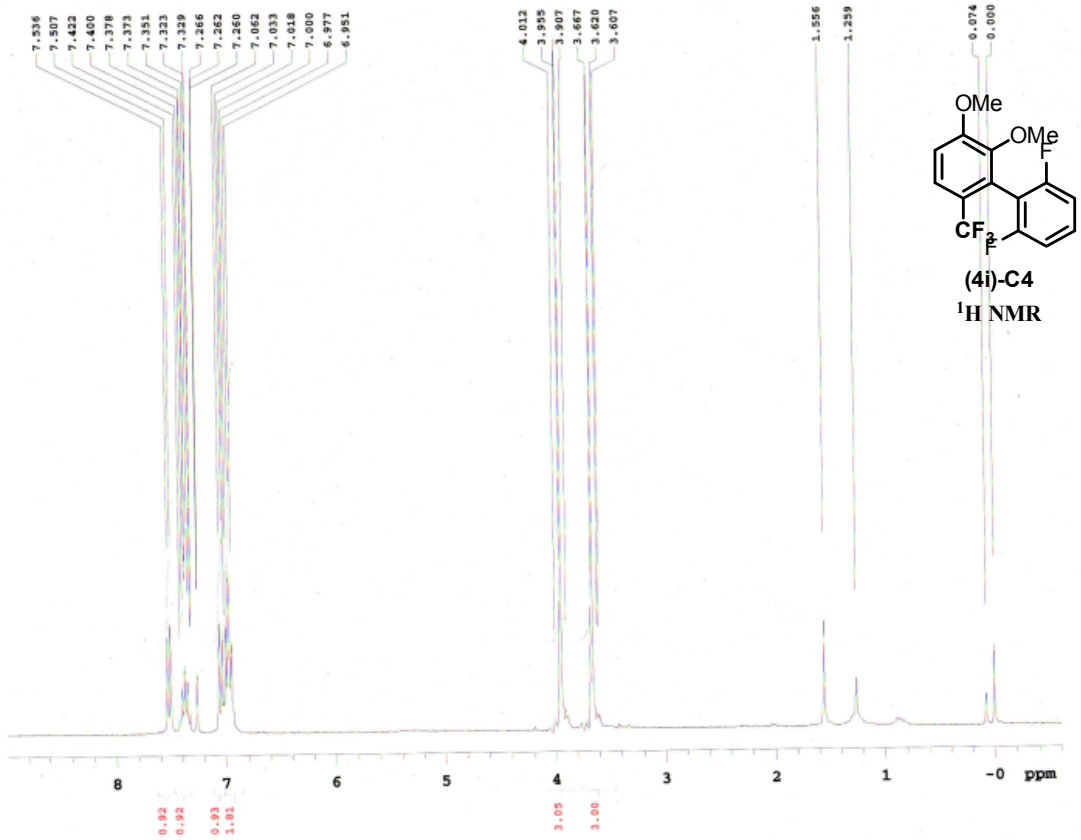
(4h)-C4
^{13}C NMR

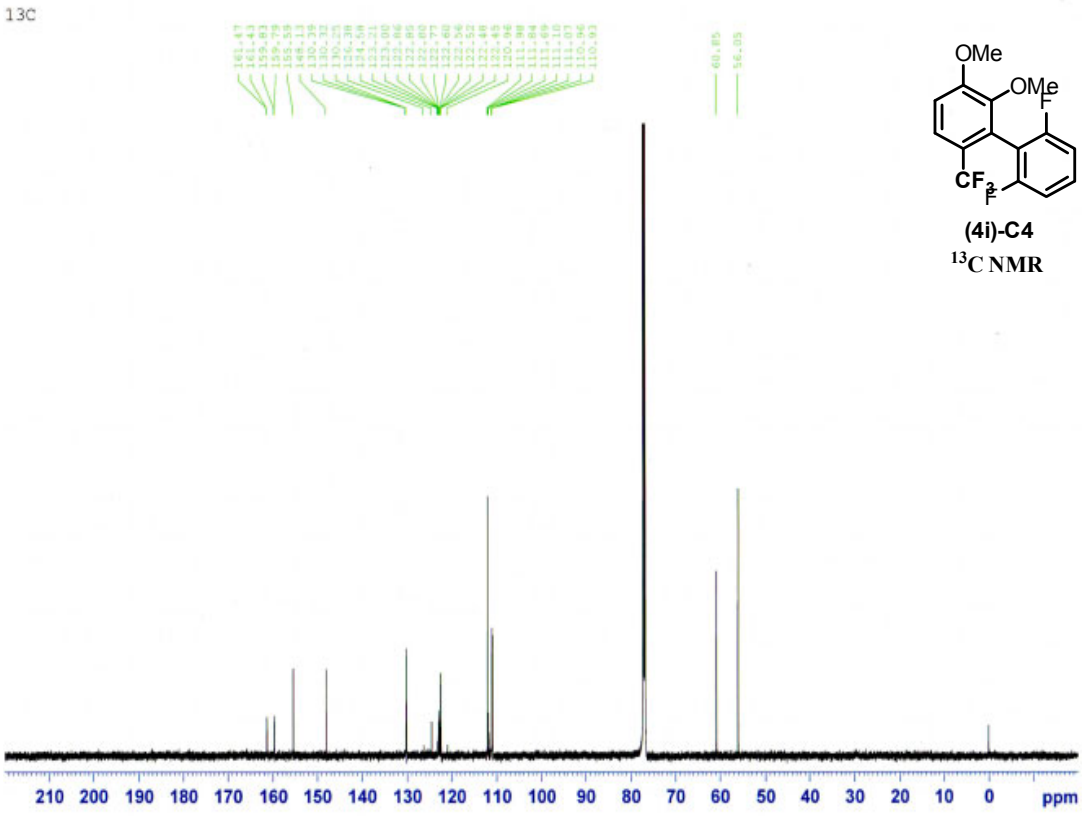

OMe
OMe
CF2
F
F
(4h)-C4
19F NMR
-50
-60
-70
-80
-90
-100
-110
-120
ppm

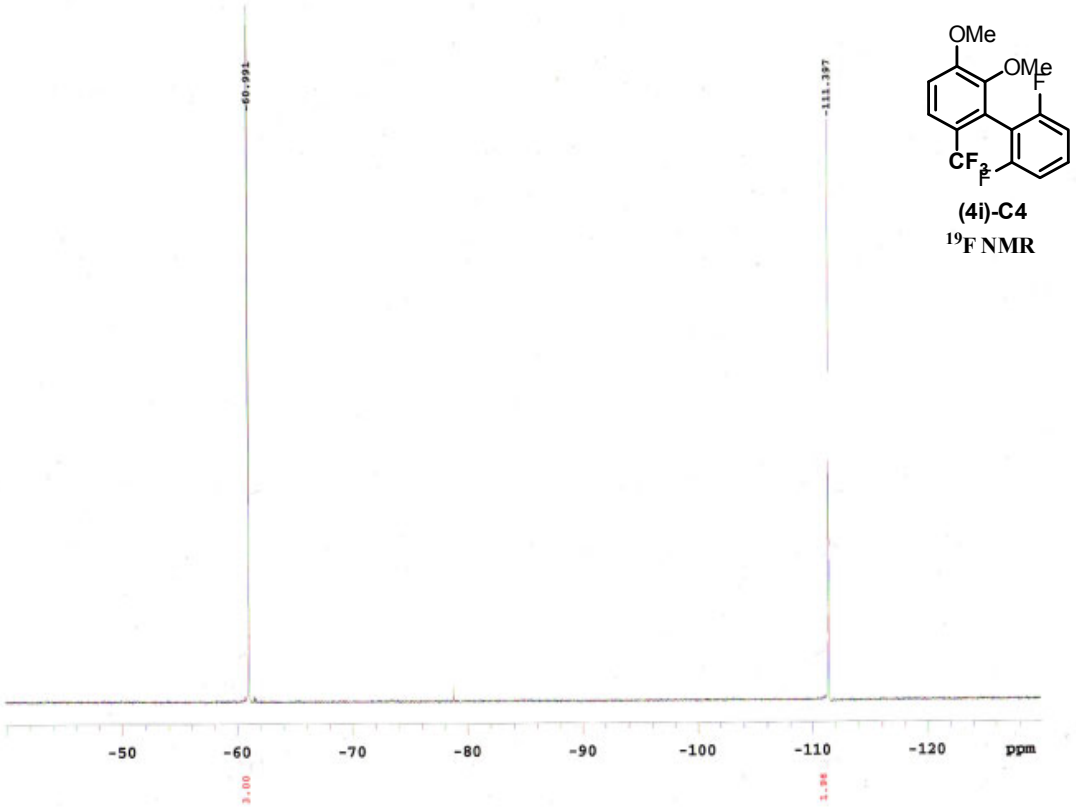

OMe
OMe
F
F3C
F
(4i)-C5
1H NMR
9
8
7
6
5
4
3
2
1
-0
ppm


OMe
OMe
F
F3C
F
(4i)-C5
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
OMe
F
F3C
F
(4i)-C5
19F NMR
-50 -60 -70 -80 -90 -100 -110 -120 ppm


OMe
OMe
F
CF3
F
(4i)-C4
1H NMR
ppm


13C
OMe
OMe
F
CF3
F
(4i)-C4
13C NMR
ppm


-60.991
-111.397
OMe
OMe
F
CF3
F
-50
-60
-70
-80
-90
-100
-110
-120
ppm
3.00
1.96

(4i)-C4
^{19}F NMR