Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ruthenium(II)-Catalyzed C–H Functionalizations of Benzoic Acids with Aryl, Alkenyl and Alkynyl Halides by Weak-*O*-Coordination

Ruhuai Mei,[¶] Cuiju Zhu,[¶] and Lutz Ackermann*

[¶] *Both authors contributed equally.*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität

Tammannstraße 2, 37077 Göttingen, Germany

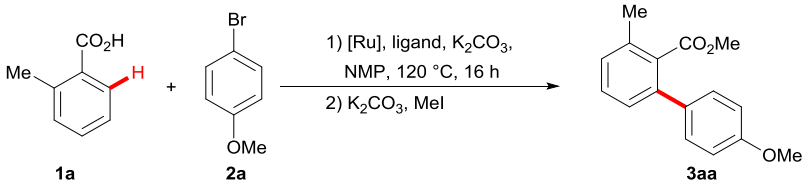
Fax: +49/ 551-39-6777

Lutz.Ackermann@chemie.uni-goettingen.de

General Remarks

Catalytic reactions were carried out in Schlenk tubes under a nitrogen atmosphere using pre-dried glassware. *N*-Methyl-2-pyrrolidon (NMP) was dried and distilled over CaH_2. The following starting materials were synthesized according to previously described procedures: [$Ru(O_2CMes)_2$(*p*-cymene)],[1] [$RuCl_2$(*p*-cymene)(PCy_3)],[2] [$RuCl_2$(*p*-cymene)(Ph*t*BuPOH)],[3] [$RuCl_2$(*p*-cymene)(*n*Bu_2POH)][3] and ruthenacycle **7**.[4] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC-analysis. Chromatography: Merck silica gel 60 (40-63 μm). NMR: Spectra were recorded on Varian Unity 300, Mercury 300 or Inova 500 in the solvent indicated; chemical shifts (δ) are given in ppm. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS- and ESI-MS-spectra were recorded with Finnigan MAT 95, 70 eV; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR, Bruker Daltonic. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

Table S-1 Optimization Study for Ruthenium (II)-Catalyzed C–H Arylation[a]



entry	[Ru]	ligand	**3aa**(%) [b]
1	$[RuCl_2(p\text{-cymene})]_2$	---	(11)
2	$[RuCl_2(p\text{-cymene})]_2$	IPrHCl	(<5)
3	$[RuCl_2(p\text{-cymene})]_2$	IMesHCl	(<5)
4	$[Ru(O_2CMes)_2(p\text{-cymene})]$	X-Phos	(7)
5	$[RuCl_2(p\text{-cymene})]_2$	DavePhos	(<5)
6	$[RuCl_2(p\text{-cymene})]_2$	JohnPhos	(8)
7	$[RuCl_2(p\text{-cymene})]_2$	tBu$_2$POH	16
8	$[RuCl_2(p\text{-cymene})]_2$	Cy$_2$POH	(<5)
9	$[RuCl_2(p\text{-cymene})(Ph$$t$$BuPOH)]$	---	(<5)
10	$[RuCl_2(p\text{-cymene})(nBu_2$POH)]	---	(6)
11	$[RuCl_2(p\text{-cymene})]_2$	P(nBu)(Adamantyl)$_2$	20
12	$[RuCl_2(p\text{-cymene})]_2$	PPh$_3$	(51)
13	$[RuCl_2(p\text{-cymene})]_2$	P^{t}Bu$_3$	(22)
14	$[RuCl_2(p\text{-cymene})]_2$	PCy$_3$	81
15[c]	$[RuCl_2(p\text{-cymene})]_2$	PCy$_3$	n.d.
16	---	PCy$_3$	n.d.
17[d]	$[RuCl_2(p\text{-cymene})]_2$	PCy$_3$	(5)
18	**$[Ru(O_2CMes)_2(p\text{-cymene})]$ (4)**	**PCy$_3$**	**87**
19	$[RuCl_2(p\text{-cymene})(PCy_3)]$	---	75
20[e]	$[Ru(O_2CMes)_2(p\text{-cymene})]$ (**4**)	PCy$_3$	54
21[f]	$[Ru(O_2CMes)_2(p\text{-cymene})]$ (**4**)	PCy$_3$	n.d.
22[g]	$[Ru(O_2CMes)_2(p\text{-cymene})]$ (**4**)	PCy$_3$	(32)

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), [Ru] (10 mol %), ligand (10 mol %), K_2CO_3 (2.0 equiv), and NMP (2.0 mL), 120 ºC, 16 h; then K_2CO_3 (3.0 equiv) and MeI (5.0 equiv) in MeCN (3.0 mL). [b] Yields of isolated product; in parentheses: GC conversion with 1,3,5-trimethoxybezene as the internal standard. [c] Without K_2CO_3. [d] Using 4-chloroanisole instead of 4-bromoanisole. [e] DMA (2.0 mL) as solvent. [f] PhMe (2.0 mL) as solvent. [g] DMPU (2.0 mL) as solvent.

General Procedures for the Ruthenium (II)-Catalyzed C–H Arylation and Alkynylation

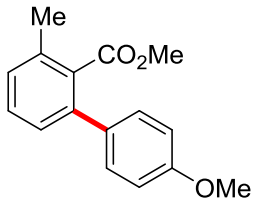
General Procedure for the C–H Arylations of Benzoic Acids (GP1)

A suspension of [Ru(O_2CMes)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (138 mg, 1.00 mmol), benzoic acid **1** (0.50 mmol), and aryl halide **2** (0.75 mmol, 1.50 equiv) in NMP (2.0 mL) was stirred under N_2 for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield the ester **3**.

General Procedure for the C–H Alkynylation of Benzoic Acids (GP2)

A suspension of [Ru(O_2CMes)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (138 mg, 1.00 mmol), benzoic acid **1** (0.50 mmol), and (bromoethynyl)triisopropylsilane (**10a**) (195 mg, 0.75 mmol) in NMP (2.0 mL) was stirred under N_2 for 16 h at 120 ºC. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield ester **11.**

Characterization Data of Products 3, 9 and 11

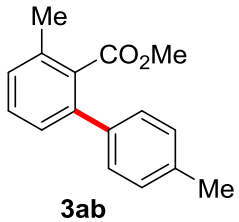


3aa

Methyl 4'-methoxy-3-methyl-[1,1'-biphenyl]-2-carboxylate (3aa)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3aa** (111 mg, 87%) as a white solid. M. p. = 69−70 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35–7.25 (m, 3H), 7.21–7.14 (m, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 3.61 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5 (C_q), 159.0 (C_q), 139.6 (C_q), 135.3 (C_q), 133.3 (C_q), 133.2 (C_q), 129.3 (CH), 129.3 (CH), 128.7 (CH), 127.2 (CH), 113.7 (CH), 55.2 (CH_3), 51.8 (CH_3), 19.7 (CH_3). IR (ATR): 2946, 2837, 1724, 1510, 1245, 1028, 791 cm^{-1}. MS (EI) *m/z* (relative intensity) 256 (100) [M^+], 225 (90), 209 (30), 197 (15), 182 (30), 153 (40). HR-MS (EI) *m/z* calcd for $C_{16}H_{16}O_3$ [M^+] 256.1099, found 256.1109.

The analytical data are in accordance with those previously reported in the literature.[5]



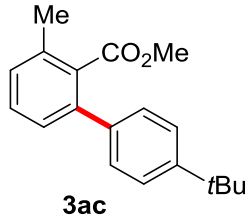
3ab

Methyl 3,4'-dimethyl-[1,1'-biphenyl]-2-carboxylate (3ab)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2b** (128 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ab** (104 mg, 87%) as a pale yellow oil. ^{1}H NMR (400

MHz, $CDCl_3$) δ = 7.36 (dd, J = 7.6, 7.6 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.24–7.19 (m, 4H), 3.64 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5 (C_q), 140.2 (C_q), 138.1 (C_q), 137.1 (C_q), 135.4 (C_q), 133.3 (C_q), 129.5 (CH), 129.1 (CH), 129.0 (CH), 128.2 (CH), 127.3 (CH), 51.9 (CH_3), 21.3 (CH_3), 19.8 (CH_3). IR (ATR): 3025, 1724, 1459, 1435, 1264, 1120, 1066, 823, 784, 529 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 240 (70) [M^+], 209 (100), 224 (100), 165 (68), 152 (12). HR-MS (EI): *m*/*z* calcd for $C_{16}H_{16}O_2$ [M^+] 240.1150, found 240.1139.

The analytical data are in accordance with those previously reported in the literature.[5,6]

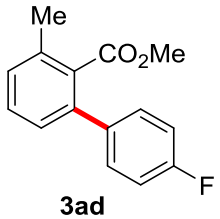


3ac

Methyl 4'-(*tert*-butyl)-3-methyl-[1,1'-biphenyl]-2-carboxylate (3ac)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2c** (160 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ac** (121 mg, 86%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, J = 8.4 Hz, 2H), 7.33 (dd, J = 8.0, 8.0 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.27–7.16 (m, 2H), 3.61 (s, 3H), 2.42 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6 (C_q), 150.3 (C_q), 140.2 (C_q), 138.0 (C_q), 135.4 (C_q), 133.3 (C_q), 129.5 (CH), 129.0 (CH), 128.0 (CH), 127.4 (CH), 125.3 (CH), 51.9 (CH_3), 34.7 (C_q), 31.5 (CH_3), 19.8 (CH_3). IR (ATR): 2960, 1726, 1461, 1267, 1085, 959, 839, 789, 750, 586 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 282 (33) [M^+], 267 (100), 207 (14), 193 (15), 165 (12); HR-MS (EI): *m*/*z* calcd for $C_{19}H_{22}O_2$ [M^+] 282.1620, found 282.1621.

The analytical data are in accordance with those previously reported in the literature.[5]

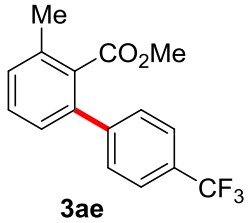


3ad

Methyl 4'-fluoro-3-methyl-[1,1'-biphenyl]-2-carboxylate (3ad)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2d** (131 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ad** (96 mg, 79%) as a pale yellow solid. M. p. = 68−69 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40–7.30 (m, 3H), 7.24–7.17 (m, 2H), 7.08 (dd, J = 8.8, 8.8 Hz, 2H), 3.61 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.3 (C_q), 162.3 (d, $^{1}J_{C\text{-}F}$ = 243.6 Hz, C_q), 139.2 (C_q), 137.0 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz, C_q), 135.6 (C_q), 133.4 (C_q), 130.0 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz, CH), 129.3 (d, $^{2}J_{C\text{-}F}$ = 19.6 Hz, CH), 127.3 (CH), 115.4 (CH), 115.2 (CH), 52.0 (CH_3), 19.8 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −115.19 (tt, J = 8.5, 5.3 Hz). IR (ATR): 2949, 1735, 1600, 1508, 1434, 1262, 843, 741 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 245 (4) [M+H$^+$] 267 (100) [M+Na$^+$]. HR-MS (ESI): *m*/*z* calcd for $C_{15}H_{14}FO_2$ [M+H$^+$] 245.0972, found 245.0971.

The analytical data are in accordance with those previously reported in the literature.[5]

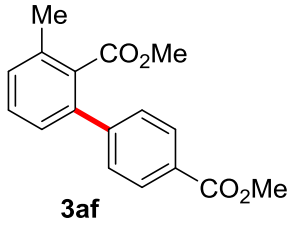


3ae

Methyl 3-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate (3ae)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2e** (169 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ae** (118 mg, 80%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dd, J = 8.0, 8.0 Hz, 2H), 7.48 (dd, J = 8.0, 8.0 Hz, 2H), 7.39 (dd, J = 7.7, 7.7 Hz, 1H), 7.27–7.24 (m, 1H), 7.20–7.17 (m, 1H), 3.60 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.0 (C_q), 144.7 (d, $^{5}J_{C\text{-}F}$ = 1.4 Hz, C_q), 138.9 (C_q), 136.0 (C_q), 133.2 (C_q), 130.1 (CH), 129.5 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz, C_q), 129.8 (CH), 128.8 (CH), 127.2 (CH), 125.4

(q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH), 124.2 (q, $^{1}J_{C\text{-}F}$ = 269.5 Hz, C_q), 52.1 (CH_3), 19.9 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −62.48 (s). IR (ATR): 2953, 1727, 1619, 1438, 1324, 1264, 1120, 847, 790, 584 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 294 (45) [M^+], 263 (100), 215 (20), 165 (48), 43 (22). HR-MS (EI): *m*/*z* calcd for $C_{16}H_{13}F_3O_2$ [M^+] 294.0868, found 294.0879.

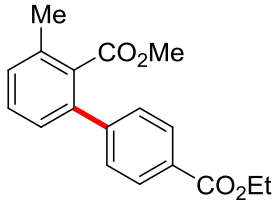


3af

Dimethyl 3-methyl-[1,1'-biphenyl]-2,4'-dicarboxylate (3af)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2f** (161 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 15:1) yielded **3af** (109 mg, 77%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.26–7.19 (m, 2H), 3.93 (s, 3H), 3.57 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.8 (C_q), 166.8 (C_q), 145.7 (C_q), 139.2 (C_q), 135.9 (C_q), 133.0 (C_q), 129.8 (CH), 129.6 (CH), 129.6 (CH), 129.1 (C_q), 128.3 (CH), 127.1 (CH), 52.2 (CH_3), 52.0 (CH_3), 19.9 (CH_3). IR (ATR): 2949, 1712, 1610, 1434, 1264, 1114, 1066, 862, 704 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 284 (96) [$M]^+$, 253 (100), 209 (60), 165 (85), 152 (18). HR-MS (EI): *m*/*z* calcd for $C_{17}H_{16}O_4$ [M^+] 284.1049, found 284.1040.

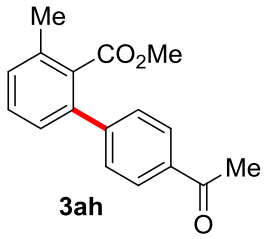
The analytical data are in accordance with those previously reported in the literature.[5]



3ag

4'-Ethyl 2-methyl 3-methyl-[1,1'-biphenyl]-2,4'-dicarboxylate (3ag)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2g** (172 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ag** (134 mg, 90%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.36–7.31 (m, 1H), 7.26–7.12 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.55 (s, 3H), 2.38 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.8 (C_q), 166.3 (C_q), 145.4 (C_q), 139.1 (C_q), 135.7 (C_q), 132.9 (C_q), 129.7 (CH), 129.4 (CH), 129.4 (C_q), 129.3 (CH), 128.1 (CH), 126.9 (CH), 60.9 (CH_2), 51.8 (CH_3), 19.6 (CH_3), 14.2 (CH_3). IR (ATR): 2981, 2950, 1712, 1610, 1460, 1366, 1100, 766 cm^{-1}. MS (EI) *m/z* (relative intensity) 298 (100) [M^+], 267 (30), 253 (80), 239 (20), 225 (20), 195 (80), 165 (60). HR-MS (EI) *m/z* calcd for $C_{18}H_{18}O_4$ [M^+] 298.1205, found 298.1210.



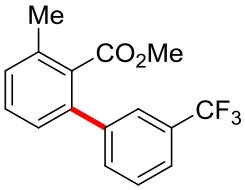
3ah

Methyl 4'-acetyl-3-methyl-[1,1'-biphenyl]-2-carboxylate (3ah)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2h** (149 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 15:1) yielded **3ah** (114 mg, 85%) as a yellow solid. M. p. = 132−133 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.25–7.17 (m, 2H), 3.58 (s, 3H), 2.60 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.7 (C_q), 170.0 (C_q), 145.8 (C_q), 139.1 (C_q), 136.0 (C_q), 135.9 (C_q), 133.0 (C_q), 129.9 (CH), 129.6 (CH), 128.5 (CH), 128.4 (CH), 127.1 (CH), 52.0 (CH_3), 26.7 (CH_3), 19.8 (CH_3). IR (ATR): 2949, 1718, 1680, 1605, 1434, 1268, 1061, 845,

795, 601 cm^{-1}. MS (EI) *m/z* (relative intensity): 268 (45) $[M]^+$, 253 (100), 195 (35), 165 (37), 43 (28). HR-MS (ESI): *m/z* calcd for $C_{17}H_{17}O_3$ $[M+H^+]$ 269.1172, found 269.1172.

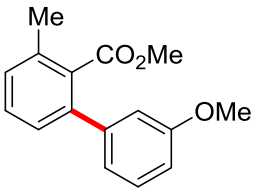
The analytical data are in accordance with those previously reported in the literature.[5]



3ai

Methyl 3-methyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate (3ai)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2i** (169 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ai** (115 mg, 78%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66–7.44 (m, 4H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.28–7.18 (m, 2H), 3.60 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.8 (C_q), 141.6 (C_q), 138.6 (C_q), 135.8 (C_q), 133.2 (C_q), 131.6 (q, $^4J_{C\text{-}F}$ = 1.3 Hz, CH), 130.7 (q, $^2J_{C\text{-}F}$ = 32.2 Hz, C_q), 129.8 (CH), 129.6 (CH), 128.8 (CH), 127.1 (CH), 125.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 124.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 124.0 (q, $^1J_{C\text{-}F}$ = 272.3 Hz, C_q), 124.0, 51.8 (CH_3), 19.7 (CH_3). ^{19}F NMR (283 MHz, $CDCl_3$) δ = -62.6 (s). IR (ATR): 2949, 1729, 1483, 1334, 1118, 1065, 703 cm^{-1}. MS (EI) *m/z* (relative intensity) 294 (40) $[M^+]$, 263 (100), 243 (5), 235 (10), 215 (20), 193 (5), 165 (40). HR-MS (EI) *m/z* calcd for $C_{16}H_{13}F_3O_2$ $[M^+]$ 294.0868, found 294.0866.

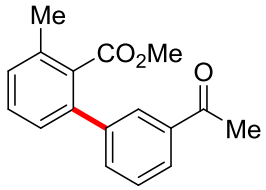


3aj

Methyl 3'-methoxy-3-methyl-[1,1'-biphenyl]-2-carboxylate (3aj)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2j** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica

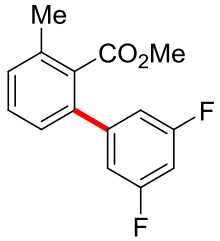
gel (*n*-hexane/EtOAc 20:1) yielded **3aj** (92.2 mg, 72%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40–7.27 (m, 2H), 7.26–7.19 (m, 2H), 7.03–6.80 (m, 3H), 3.83 (s, 3H), 3.63 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.2 (C_q), 159.5 (C_q), 142.3 (C_q), 140.0 (C_q), 135.4 (C_q), 133.2 (C_q), 129.4 (CH), 129.3 (CH), 129.2 (CH), 127.2 (CH), 120.8 (CH), 113.7 (CH), 113.4 (CH), 55.4 (CH_3), 52.0 (CH_3), 19.9 (CH_3). IR (ATR): 2999, 2835, 1724, 1489, 1318, 1228, 1066, 1040, 776, 698 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 256 (67) [M^+], 225 (78), 224 (100), 182 (27), 153 (28). HR-MS (EI): *m*/*z* calcd for $C_{16}H_{16}O_3$ [M^+] 256.1099, found 256.1090.



3ak

Methyl 3'-acetyl-3-methyl-[1,1'-biphenyl]-2-carboxylate (3ak)

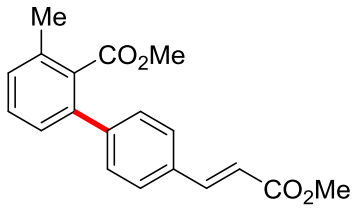
The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2k** (149 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 15:1) yielded **3ak** (103 mg, 77%) as a pale yellow solid. M. p. = 63−64 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00–7.88 (m, 2H), 7.57–7.54 (m, 1H), 7.47 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.25–7.20 (m, 2H), 3.59 (s, 3H), 2.60 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.9 (C_q), 170.1 (C_q), 141.3 (C_q), 139.1 (C_q), 137.2 (C_q), 135.7 (C_q), 133.3 (C_q), 132.8 (CH), 129.7 (CH), 129.6 (CH), 128.7 (CH), 128.3 (CH), 127.3 (CH), 127.2 (CH), 51.9 (CH_3), 26.7 (CH_3), 19.8 (CH_3). IR (ATR): 2950, 1725, 1600, 1357, 1238, 1066, 956, 808, 732 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 268 (45) [M^+], 253 (85), 236 (100), 221 (70), 195 (65). HR-MS (EI): *m*/*z* calcd for $C_{17}H_{16}O_3$ [M^+] 268.1099, found 268.1096.



3al

Methyl 3',5'-difluoro-3-methyl-[1,1'-biphenyl]-2-carboxylate (3al)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2l** (145 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3al** (110 mg, 84%) as a colorless solid. M. p. = 63−64 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37 (dd, J = 7.6, 7.6 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 6.96–6.85 (m, 2H), 6.83–6.75 (m, 1H), 3.67 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.6 (C_q), 162.7 (dd, $^{1,3}J_{C\text{-}F}$ = 248.7, 13.0 Hz, C_q), 144.1 (t, $^{3,3}J_{C\text{-}F}$ = 25.3 Hz, C_q), 137.8 (t, $^{4,4}J_{C\text{-}F}$ = 2.4 Hz, C_q), 135.8 (C_q), 132.9 (C_q), 130.1 (CH), 129.6 (CH), 126.8 (CH), 111.3 (dd, $^{2,4}J_{C\text{-}F}$ = 17.3, 8.1 Hz, CH), 102.8 (t, $^{2,2}J_{C\text{-}F}$ = 25.3 Hz, CH), 52.0 (CH_3), 19.7 (CH_3). ^{19}F NMR (283 MHz, $CDCl_3$) δ = -(109.8–109.9) (m). IR (ATR): 2951, 1726, 1622, 1454, 1337, 1117, 793 cm^{-1}. MS (EI) *m/z* (relative intensity) 262 (60) [M^+], 231 (100), 253 (80), 201 (60), 188 (30), 183 (50), 151 (50). HR-MS (ESI) *m/z* calcd for $C_{15}H_{13}F_2O_2$ [M+H^+] 263.0878, found 263.0875.

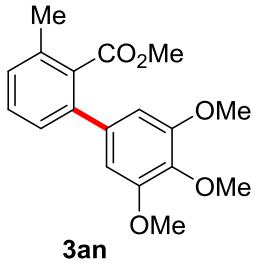


3am

Methyl (*E*)-4'-(3-methoxy-3-oxoprop-1-en-1-yl)-3-methyl-[1,1'-biphenyl]-2-carboxylate (3am)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2m** (181 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3am** (126 mg, 81%) as a colorless solid. M. p. = 91−92 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.71 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H),

7.41–7.31 (m, 3H), 7.28–7.18 (m, 2H), 6.47 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H), 3.60 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.9 (C_q), 167.2 (C_q), 144.2 (CH), 142.9 (C_q), 139.1 (C_q), 135.6 (C_q), 133.3 (C_q), 132.9 (C_q), 129.5 (CH), 129.4 (CH), 128.7 (CH), 128.0 (CH), 126.9 (CH), 117.8 (CH), 51.8 (CH_3), 51.6 (CH_3), 19.6 (CH_3). IR (ATR): 2944, 1729, 1708, 1604, 1436, 1270, 1170, 790 cm^{-1}. MS (EI) *m/z* (relative intensity) 310 (80) [M^+], 278 (50), 247 (100), 219 (50), 189 (40), 165 (30). HR-MS (ESI) *m/z* calcd for $C_{19}H_{18}O_4$ [M+H$^+$] 310.1205, found 310.1214.

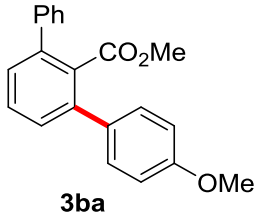


3an

Methyl 3',4',5'-trimethoxy-3-methyl-[1,1'-biphenyl]-2-carboxylate (3an)

The general procedure **GP1** was followed using benzoic acid **1a** (68 mg, 0.50 mmol) and aryl bromide **2n** (185 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3an** (133 mg, 84%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35–7.30 (m, 1H), 7.25–7.16 (m, 2H), 6.57 (s, 2H), 3.86 (s, 3H), 3.84 (s, 6H), 3.62 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.4 (C_q), 153.0 (C_q), 139.9 (C_q), 137.3 (C_q), 136.4 (C_q), 135.3 (C_q), 133.1 (C_q), 129.3 (CH), 129.1 (CH), 126.9 (CH), 105.4 (CH), 60.9 (CH_3), 56.0 (CH_3), 52.0 (CH_3), 19.6 (CH_3). IR (ATR): 2942, 2836, 1723, 1577, 1462, 1405, 1120 cm^{-1}. MS (EI) *m/z* (relative intensity) 316 (100) [M^+], 301 (80), 285 (10), 273 (15), 241 (10), 209 (10), 199 (10). HR-MS (EI) *m/z* calcd for $C_{18}H_{20}O_5$ [M+H$^+$] 316.1311, found 316.1301.

The analytical data are in accordance with those previously reported in the literature.[5]

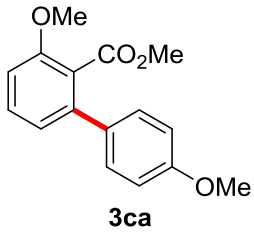


3ba

Methyl 4-methoxy-[1,1':3',1''-terphenyl]-2'-carboxylate (3ba)

The general procedure **GP1** was followed using benzoic acid **1b** (99 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ba** (140 mg, 88%) as a colorless solid. M. p. = 90−91 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 (dd, J = 7.5, 7.5 Hz, 1H), 7.47–7.42 (m, 4H), 7.42–7.35 (m, 5H), 6.99 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1 (C_q), 159.2 (C_q), 140.6 (C_q), 140.3 (C_q), 140.0 (C_q), 132.9 (C_q), 132.9 (C_q), 129.6 (CH), 129.4 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.6 (CH), 113.9 (CH), 55.3 (CH_3), 51.8 (CH_3). IR (ATR): 2947, 2834, 1727, 1584, 1453, 1249, 1116, 1029, 763 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 318 (97) [M^+], 287 (100), 255 (12), 215 (35), 189 (13). HR-MS (EI): *m*/*z* calcd for $C_{21}H_{18}O_3$ [M^+] 318.1256, found 318.1256.

The analytical data are in accordance with those previously reported in the literature.[5]



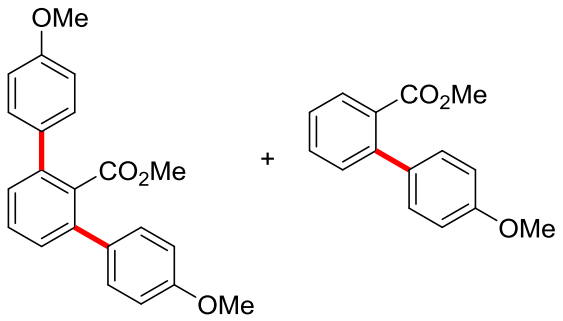
3ca

Methyl 3,4'-dimethoxy-[1,1'-biphenyl]-2-carboxylate (3ca)

The general procedure **GP1** was followed using benzoic acid **1c** (76 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ca** (79 mg, 58%) as a colorless solid. M. p. = 92−93 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43–7.29 (m, 3H), 6.99–6.88 (m, 4H), 3.87 (s, 3H), 3.83 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.7 (C_q), 159.2 (C_q), 156.4 (C_q), 140.8 (C_q), 132.4 (C_q), 130.4 (CH), 129.3 (CH), 123.0 (C_q), 121.9 (CH), 113.8 (CH), 109.5 (CH), 56.0 (CH_3), 55.2 (CH_3), 52.1 (CH_3). IR (ATR): 2959, 2860, 1726, 1464, 1238, 1102, 1018,

791 cm^{-1}. MS (EI) *m/z* (relative intensity) 272 (90) [M^+], 241 (100), 226 (40), 211 (15), 198 (20), 183 (15), 168 (10). HR-MS (EI) *m/z* calcd for $C_{16}H_{16}O_4$ [M^+] 272.1049, found 272.1045.

The analytical data are in accordance with those previously reported in the literature.[5]



3da **3da'**

The general procedure **GP1** was followed using benzoic acid **1d** (61 mg, 0.50 mmol), 1-iodo-4-methoxybenzene **2a'** (351 mg, 1.50 mmol, 3.0 equiv) and K_2CO_3 (276 mg, 2.00 mmol, 4.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3da** (143 mg, 82%) and the diarylated product **3da'** (19 mg, 16%).

Methyl 4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-carboxylate (3da)

Colorless solid. M. p. = 112−113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.39–7.30 (m, 6H), 6.95 (d, *J* = 8.9 Hz, 4H), 3.85 (s, 6H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2 (C_q), 159.1 (C_q), 139.8 (C_q), 132.9 (C_q), 132.7 (C_q), 129.5 (CH), 129.2 (CH), 128.5 (CH), 113.7 (CH), 55.2 (CH_3), 51.8 (CH_3). IR (ATR): 2920, 2835, 1730, 1586, 1513, 1246, 1103, 1027 cm^{-1}. MS (EI) *m/z* (relative intensity) 348 (100) [M^+], 317 (90), 302 (10), 285 (10), 274 (20), 259 (10), 202 (20). HR-MS (EI) *m/z* calcd for $C_{22}H_{20}O_4$ [M^+] 348.1362, found 348.1368.

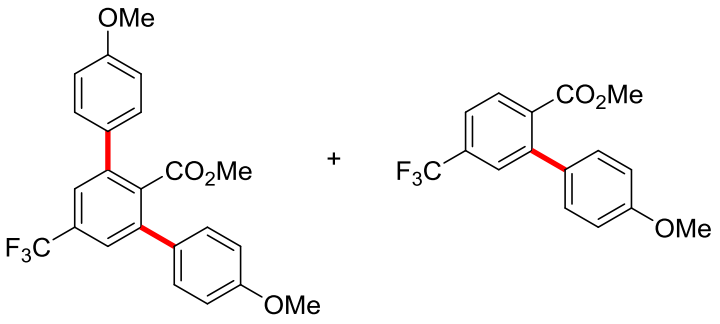
The analytical data are in accordance with those previously reported in the literature.[5]

Methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate (3da')

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.80–7.73 (m, 1H), 7.55–7.43 (m, 1H), 7.38–7.33 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.4 (C_q), 158.9 (C_q), 142.0 (C_q), 133.6 (C_q), 131.2 (CH), 130.8

(C_q), 130.7 (CH), 129.7 (CH), 129.4 (CH), 126.8 (CH), 113.5 (CH), 55.2 (CH_3), 51.9 (CH_3). IR (ATR): 2949, 2836, 1716, 1610, 1516, 1238, 761 cm^{-1}. MS (EI) *m/z* (relative intensity) 242 (95) [M^+], 211 (100), 196 (10), 183 (15), 168 (30), 139 (40). HR-MS (EI) *m/z* calcd for $C_{15}H_{14}O_3$ [M^+] 242.0943, found 242.0946.

The analytical data are in accordance with those previously reported in the literature.[5]



3ea **3ea'**

The general procedure **GP1** was followed using benzoic acid **1e** (95 mg, 0.50 mmol), 1-iodo-4-methoxybenzene **2a'** (351 mg, 1.50 mmol, 3.0 equiv) and K_2CO_3 (276 mg, 2.00 mmol, 4.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **3ea** (108 mg, 52%) and the diarylated product **3ea'** (39 mg, 25%).

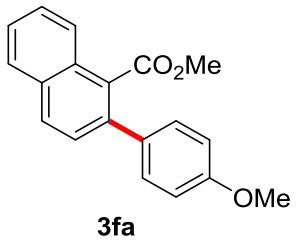
Methyl 4,4''-dimethoxy-5'-(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-carboxylate (3ea)

Colorless solid. M. p. = 133−134 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, J = 0.7 Hz, 2H), 7.33 (d, J = 8.9 Hz, 4H), 6.94 (d, J = 8.9 Hz, 4H), 3.83 (s, 6H), 3.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.1 (C_q), 159.6 (C_q), 140.8 (C_q), 135.9 (q, $^4J_{C\text{-}F}$ = 1.1 Hz, C_q), 131.3 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, C_q), 131.5 (C_q), 129.5 (CH), 125.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, CH), 123.7 (q, $^1J_{C\text{-}F}$ = 272.9 Hz, C_q), 114.0 (CH), 55.3 (CH_3), 52.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.79 (s). IR (ATR): 2943, 2841, 1735, 1609, 1517, 1363, 1120, 809 cm^{-1}. MS (ESI) *m/z* 439 [M+Na^+]. HR-MS (ESI) *m/z* calcd for $C_{23}H_{20}F_3O_4$ [M+H^+] 417.1308, found 417.1316.

Methyl 4'-methoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate (3ea')

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (dd, J = 8.6, 0.9 Hz, 1H), 7.64–7.57 (m, 2H), 7.24 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.4 (C_q), 159.5 (C_q), 142.5 (C_q), 134.2 (q, $^4J_{C\text{-}F}$ = 1.0 Hz, C_q), 132.8

(q, $^{2}J_{C\text{-}F}$ = 32.6 Hz, C_q), 132.0 (C_q), 130.1 (CH), 129.4 (CH), 127.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, CH), 123.6 (q, $^{4}J_{C\text{-}F}$ = 272.9 Hz, C_q), 123.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH), 113.8 (CH), 55.3 (CH_3), 52.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.00 (s). IR (ATR): 2953, 2840, 1724, 1610, 1518, 1244, 1125, 833 cm^{-1}. MS (ESI) *m/z* 333 [M+Na^{+}]. HR-MS (ESI) *m/z* calcd for $C_{16}H_{14}F_3O_3$ [M+H^{+}] 311.0890, found 311.0899.

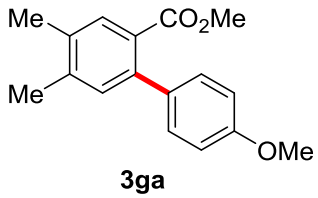


3fa

Methyl 2-(4-methoxyphenyl)-1-naphthoate (3fa)

The general procedure **GP1** was followed using benzoic acid **1f** (86 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3fa** (114 mg, 78%) as a colorless solid. M. p. = 121−122 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99–7.85 (m, 3H), 7.63–7.48 (m, 3H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.2 (C_q), 159.2 (C_q), 137.5 (C_q), 133.2 (C_q), 132.1 (C_q), 130.0 (C_q), 129.8 (CH), 129.7 (C_q), 129.6 (CH), 128.1 (CH), 127.5 (CH), 127.4 (CH), 126.1 (CH), 124.9 (CH), 113.9 (CH), 55.3 (CH_3), 52.2 (CH_3). IR (ATR): 2937, 1727, 1608, 1516, 1231, 1025, 815 cm^{-1}. MS (EI) *m/z* (relative intensity) 292 (98) [M^{+}], 261 (100), 246 (10), 218 (20), 189 (30), 163 (5), 146 (5). HR-MS (EI) *m/z* calcd for $C_{19}H_{16}O_3$ [M^{+}] 292.1099, found 292.1090.

The analytical data are in accordance with those previously reported in the literature.[5]

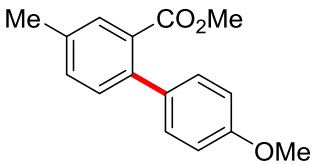


3ga

Methyl 4'-methoxy-4,5-dimethyl-[1,1'-biphenyl]-2-carboxylate (3ga)

The general procedure **GP1** was followed using benzoic acid **1g** (75 mg, 0.50 mmol) and 1-iodo-4-methoxybenzene (**2a'**) (175 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ga** (112 mg, 83%) as a colorless solid. M. p. = 82−83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.13 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.66 (s, 3H), 2.32 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2 (C_q), 158.7 (C_q), 140.3 (C_q), 139.8 (C_q), 135.2 (C_q), 133.8 (C_q), 132.1 (CH), 131.0 (CH), 129.4 (CH), 127.8 (C_q), 113.3 (CH), 55.2 (CH_3), 51.7 (CH_3), 19.7 (CH_3), 19.2 (CH_3). IR (ATR): 2951, 1724, 1607, 1488, 1443, 1241, 1026, 834 cm^{-1}. MS (EI) *m/z* (relative intensity) 270 (100) [M^+], 239 (90), 224 (15), 211 (15), 196 (30), 181 (15), 165 (15). HR-MS (EI) *m/z* calcd for $C_{17}H_{18}O_3$ [M^+] 270.1256, found 270.1247.

The analytical data are in accordance with those previously reported in the literature.[7]

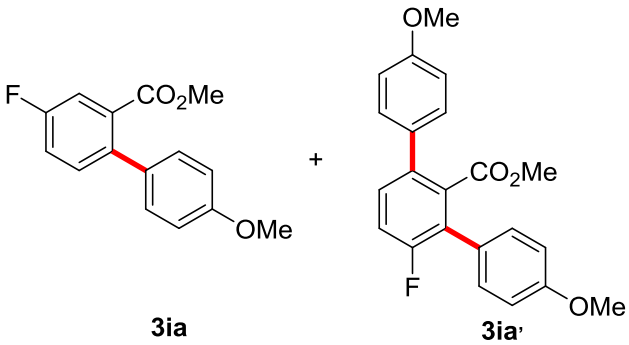


3ha

Methyl 4'-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxylate (3ha)

The general procedure **GP1** was followed using benzoic acid **1h** (68 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ha** (86 mg, 67%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50 (dd, *J* = 1.3, 0.6 Hz, 1H), 7.29–7.04 (m, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 3.56 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.4 (C_q), 158.8 (C_q), 139.1 (C_q), 136.5 (C_q), 133.5 (C_q), 131.8 (CH), 130.6 (C_q), 130.5 (CH), 130.1 (CH), 129.4 (CH), 113.4 (CH), 55.1 (CH_3), 51.8 (CH_3), 20.8 (CH_3). IR (ATR): 2948, 2836, 1715, 1609, 1488, 1289, 1238, 821 cm^{-1}. MS (EI) *m/z* (relative intensity) 256 (100) [M^+], 225 (80), 210 (10), 197 (15), 182 (20), 165 (15), 153 (20). HR-MS (EI) *m/z* calcd for $C_{16}H_{16}O_3$ [M^+] 256.1099, found 256.1091.

The analytical data are in accordance with those previously reported in the literature.[5]



3ia **3ia'**

The general procedure **GP1** was followed using benzoic acid **1i** (70 mg, 0.50 mmol) and 1-iodo-4-methoxybenzene (**2a'**) (175 mg, 0.75 mmol, 1.5 equiv) and K_2CO_3 (138 mg, 1.00 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ia** (73 mg, 56%) and the diarylated product **3ia'** (16 mg, 9%).

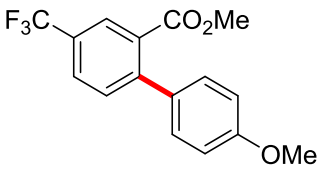
Methyl 4-fluoro-4'-methoxy-[1,1'-biphenyl]-2-carboxylate (3ia)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (dd, J = 9.0, 2.7 Hz, 1H), 7.32 (dd, J = 8.5, 5.5 Hz, 1H), 7.24–7.17 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.9 (d, $^4J_{C\text{-}F}$ = 2.4 Hz, C_q), 161.3 (d, $^1J_{C\text{-}F}$ = 247.3 Hz, C_q), 159.0 (C_q), 138.2 (d, $^4J_{C\text{-}F}$ = 3.4 Hz, C_q), 132.6 (C_q), 132.4 (d, $^3J_{C\text{-}F}$ = 7.6 Hz, CH), 132.2 (d, $^3J_{C\text{-}F}$ = 7.3 Hz, C_q), 129.4 (CH), 118.1 (d, $^2J_{C\text{-}F}$ = 21.1 Hz, CH), 116.5 (d, $^2J_{C\text{-}F}$ = 23.4 Hz, CH), 113.5 (CH), 55.2 (CH_3), 52.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -(115.28–115.37) (m). IR (ATR): 2951, 2837, 1718, 1608, 1484, 1235, 1175, 822 cm^{-1}. MS (EI) *m/z* (relative intensity) 261 (30) [M+H$^+$], 260 [M$^+$] (100), 245 (10), 229 (80), 214 (15), 186 (30). HR-MS (EI) *m/z* calcd for $C_{15}H_{13}FO_3$ [M$^+$] 260.0849, found 260.0857.

Methyl 4'-fluoro-4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-carboxylate (3ia')

Pale yellow solid. M. p. = 121−122 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34–7.27 (m, 5H), 7.23–7.20 (m, 1H), 6.96–6.92 (m, 4H), 3.84 (s, 3H), 3.84 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.7 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, C_q), 158.7 (d, $^1J_{C\text{-}F}$ = 246.1 Hz, C_q), 159.4 (C_q), 159.1 (C_q), 135.7 (d, $^3J_{C\text{-}F}$ = 4.1 Hz, C_q), 135.3 (d, $^3J_{C\text{-}F}$ = 2.7 Hz, C_q), 132.0 (C_q), 130.6 (d, $^4J_{C\text{-}F}$ = 1.4 Hz, CH), 130.2 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, CH), 129.5 (CH), 127.3 (d, $^2J_{C\text{-}F}$ = 18.1 Hz, C_q) 125.4 (C_q), 116.6 (d, $^2J_{C\text{-}F}$ = 23.2 Hz, CH), 113.8 (CH), 113.7 (CH), 55.2 (CH_3), 55.2 (CH_3),

51.9 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ = -117.71 (dd, *J* = 9.2, 5.0 Hz). IR (ATR): 2935, 2837, 1728, 1608, 1514, 1463, 1250, 822 cm^{-1}. MS (EI) *m/z* (relative intensity) 389 (100) [M+Na^+], 335 (10), 278 (5), 219 (10), 203 (5), 149 (5). HR-MS (ESI) *m/z* calcd for $C_{22}H_{20}FO_4$ [M+H^+] 367.1340, found 367.1344.

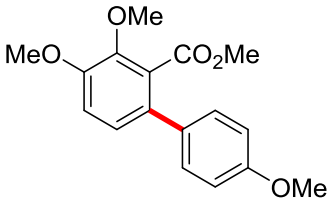


3ja

Methyl 4'-methoxy-4-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate (3ja)

The general procedure **GP1** was followed using benzoic acid **1j** (95 mg, 0.50 mmol) and 1-iodo-4-methoxybenzene (**2a'**) (175 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ja** (140 mg, 90%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) *δ* = 8.04 (dd, *J* = 1.4, 0.7 Hz, 1H), 7.73 (ddd, *J* = 8.1, 2.0, 0.8 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* = 168.0 (C_q), 159.5 (C_q), 145.5 (q, $^4J_{C-F}$ = 1.6 Hz, C_q), 132.1 (C_q), 131.3 (C_q), 131.3 (CH), 129.4 (CH), 129.1 (q, $^2J_{C-F}$ = 33.1 Hz, C_q), 127.7 (q, $^3J_{C-F}$ = 3.6 Hz, CH), 126.8 (q, $^3J_{C-F}$ = 3.8 Hz, CH), 123.7 (q, $^1J_{C-F}$ = 272.3 Hz, C_q), 113.8 (CH), 55.2 (CH_3), 52.3 (CH_3). ^{19}F NMR (283 MHz, $CDCl_3$) *δ* = - 62.62 (s). IR (ATR): 2952, 2839, 1726, 1609, 1522, 1334, 1240, 1081 cm^{-1}. MS (EI) *m/z* (relative intensity) 310 (100) [M^+], 279 (90), 264 (10), 251 (15), 236 (20), 207 (10), 188 (10). HR-MS (EI) *m/z* calcd for $C_{16}H_{13}F_3O_3$ [M^+] 310.0817, found 310.0821.

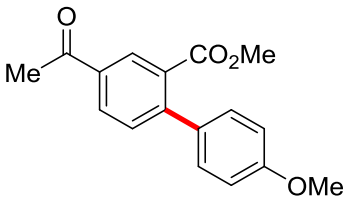
The analytical data are in accordance with those previously reported in the literature.[5]



3ka

Methyl 3,4,4'-trimethoxy-[1,1'-biphenyl]-2-carboxylate (3ka)

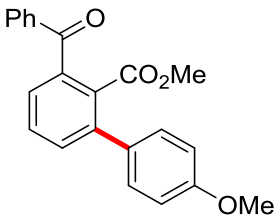
The general procedure **GP1** was followed using benzoic acid **1k** (91 mg, 0.50 mmol) and 1-iodo-4-methoxybenzene (**2a'**) (175 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ka** (141 mg, 93%) as a colorless solid. M. p. = 106−107 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.2 (C_q), 158.9 (C_q), 151.5 (C_q), 146.0 (C_q), 132.2 (C_q), 132.1 (C_q), 129.2 (CH), 128.7 (C_q), 125.2 (CH), 113.7 (CH), 113.5 (CH), 61.6 (CH_3), 56.0 (CH_3), 55.2 (CH_3), 52.1 (CH_3). IR (ATR): 2936, 2841, 1728, 1480, 1249, 1051, 804, 548 cm^{-1}. MS (EI) *m/z* (relative intensity) 302 (100) [M^+], 287 (20), 271 (30), 259 (20), 240 (20), 225 (15), 213 (20). HR-MS (EI) *m/z* calcd for $C_{17}H_{18}O_5$ [M^+] 302.1154, found 302.1146.



3la

Methyl 4-acetyl-4'-methoxy-[1,1'-biphenyl]-2-carboxylate (3la)

The general procedure **GP1** was followed using benzoic acid **1l** (82 mg, 0.50 mmol) and 1-iodo-4-methoxybenzene (**2a'**) (175 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3la** (115 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (dd, *J* = 1.9, 0.5 Hz, 1H), 8.05 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.44 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.68 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.8 (C_q), 168.6 (C_q), 159.5 (C_q), 146.3 (C_q), 135.3 (C_q), 132.3 (C_q), 131.1 (C_q), 131.0 (CH), 130.5 (CH), 129.9 (CH), 129.4 (CH), 113.7 (CH), 55.2 (CH_3), 52.2 (CH_3), 26.6 (CH_3). IR (ATR): 2950, 2837, 1719, 1682, 1602, 1518, 1226, 826 cm^{-1}. MS (EI) *m/z* (relative intensity) 284 (90) [M^+], 269 (100), 253 (20), 241 (10), 226 (20), 211 (15), 195 (10). HR-MS (EI) *m/z* calcd for $C_{17}H_{16}O_4$ [M^+] 284.1049, found 284.1043.

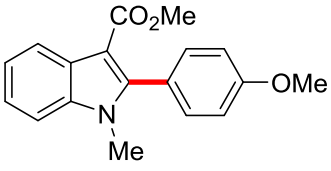


3ma

Methyl 3-benzoyl-4'-methoxy-[1,1'-biphenyl]-2-carboxylate (3ma)

The general procedure **GP1** was followed using benzoic acid **1m** (113 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ma** (92 mg, 53%) as a colorless solid. M. p. = 108−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91–7.79 (m, 2H), 7.63–7.50 (m, 3H), 7.53–7.42 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.4 (C_q), 168.9 (C_q), 159.3 (C_q), 141.2 (C_q), 138.5 (C_q), 136.8 (C_q), 133.1 (CH), 132.8 (CH), 132.7 (C_q), 132.1 (C_q), 130.1 (CH), 129.5 (CH), 129.2 (CH), 128.4 (CH), 127.8 (CH), 113.8 (CH), 55.2 (CH_3), 52.1 (CH_3). IR (ATR): 2950, 2841, 1936, 1730, 1606, 1516, 1247, 1050 cm^{-1}. MS (EI) *m/z* (relative intensity) 346 (100) [M^+], 315 (60), 297 (10), 269 (40), 237 (20), 181 (15), 215 (10). HR-MS (EI) *m/z* calcd for $C_{22}H_{18}O_4$ [M^+] 346.1205, found 346.1194.

The analytical data are in accordance with those previously reported in the literature.[5]



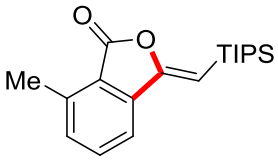
3na

Methyl 2-(4-methoxyphenyl)-1-methyl-1*H*-indole-3-carboxylate (3na)

The general procedure **GP1** was followed using benzoic acid **1n** (88 mg, 0.50 mmol) and aryl bromide **2a** (140 mg, 0.75 mmol, 1.5 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3na** (52 mg, 35%) as a brown solid. The yield could be

improved to 67% when using JohnPhos ligand (10 mol %) instead of PCy_3. M. p. = 153−154 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.32–8.19 (m, 1H), 7.45–7.26 (m, 5H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.8 (C_q), 160.2 (C_q), 147.1 (C_q), 136.8 (C_q), 131.8 (CH), 126.7 (C_q), 123.4 (C_q), 122.8 (CH), 122.1 (CH), 122.0 (CH), 113.7 (CH), 109.8 (CH), 104.9 (C_q), 55.4 (CH_3), 50.8 (CH_3), 30.9 (CH_3). IR (ATR): 3002, 2943, 1696, 1495, 1388, 1169, 1022, 834, 737 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 295 (90) [M^+], 264 (100), 249 (10), 237 (15), 192 (15). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{17}NO_3$ [M^+] 295.1208, found 295.1204.

The analytical data are in accordance with those previously reported in the literature.[8]

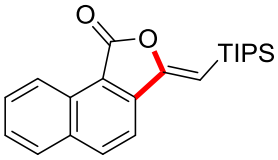


11aa

(*Z*)-7-Methyl-3-[(triisopropylsilyl)methylene]isobenzofuran-1(3*H*)-one (11aa)

The general procedure **GP2** was followed using benzoic acid **1a** (68 mg, 0.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **11aa** (97 mg, 61%) as a colorless solid. M. p. = 135−136 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61–7.49 (m, 2H), 7.36–7.27 (m, 1H), 5.53 (s, 1H), 2.69 (s, 3H), 1.41–1.29 (m, 3H), 1.11 (d, *J* = 7.2 Hz, 18H). ^{13}C NMR (75MHz, $CDCl_3$) δ = 167.6 (C_q), 156.5 (C_q), 139.7 (C_q), 139.1 (C_q), 133.9 (CH), 131.7 (CH), 122.6 (C_q), 118.2 (CH), 99.7 (CH), 18.8 (CH_3), 17.5 (CH_3) 11.7 (CH). IR (ATR): 2940, 2863, 1762, 1637, 1461, 1255, 974 cm^{-1}. MS (EI) *m/z* (relative intensity) 339 (30) [M+Na^+], 299 (10), 289 (15), 273 (85), 261 (20), 245 (15), 59 (100). HR-MS (ESI) *m/z* calcd for $C_{19}H_{29}O_2Si$ [M+H^+] 317.1931, found 317.1935.

The analytical data are in accordance with those previously reported in the literature.[9]



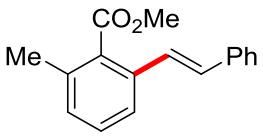
11fa

(*Z*)-3-[(Triisopropylsilyl)methylene]naphtho[1,2-c]furan-1(3*H*)-one (11fa)

The general procedure **GP2** was followed using benzoic acid **1f** (86 mg, 0.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **11fa** (88 mg, 50%) as a colorless solid. M. p. = 131−132 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.93–8.83 (m, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.77–7.66 (m, 2H), 7.60 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 5.71 (s, 1H), 1.38 (dq, *J* = 14.3, 7.4 Hz, 3H), 1.13 (d, *J* = 7.4 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.6 (C_q), 156.8 (C_q), 139.6 (C_q), 135.4 (CH), 133.9 (C_q), 129.2 (CH), 128.6 (C_q), 128.4 (CH), 127.6 (CH), 124.2 (CH), 119.2 (C_q), 117.2 (CH), 102.6 (CH), 18.8 (CH_3), 11.7 (CH). IR (ATR): 2940, 2862, 1755, 1633, 1458, 1111, 963, 751 cm^{-1}. MS (ESI) *m/z* 353 [M+H$^+$]. HR-MS (ESI) *m/z* calcd for $C_{22}H_{29}O_2Si$ [M+H$^+$] 353.1931, found 353.1938.

The analytical data are in accordance with those previously reported in the literature.[9]

Ruthenium (II)-Catalyzed C–H Alkeynylation



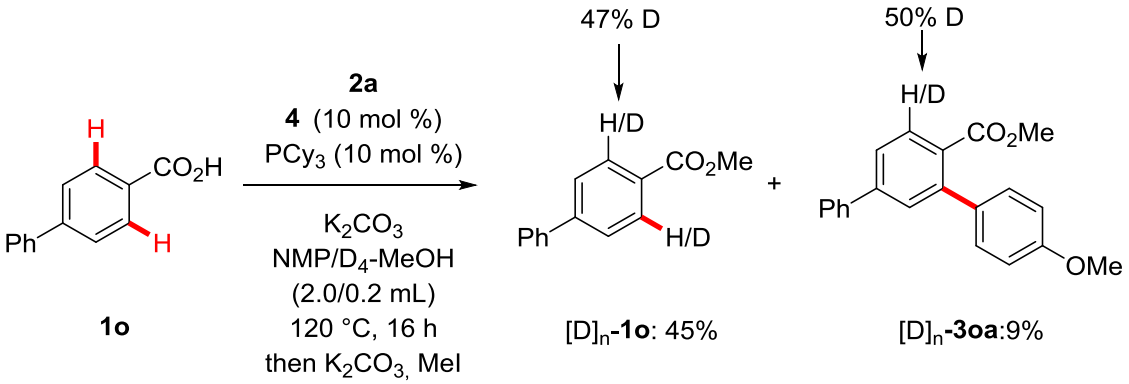
9aa

Methyl (*E*)-2-methyl-6-styrylbenzoate (9aa)

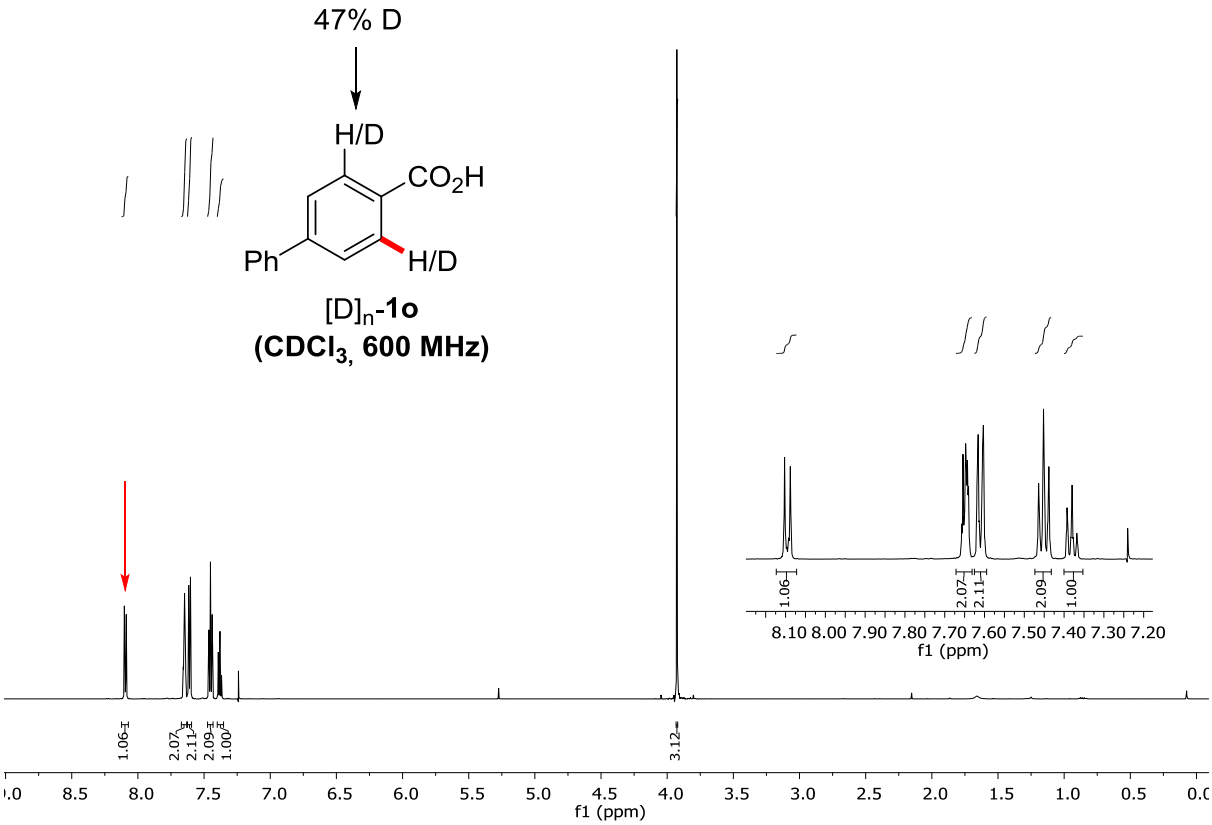
A suspension of [Ru(O_2CMes)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (276 mg, 2.00 mmol, 4.0 equiv), benzoic acid **1a** (68 mg, 0.50 mmol) and (*E*)-(2-bromovinyl)benzene (**8a**) (275 mg, 1.50 mmol, 3.0 equiv) in NMP (2.0 mL) was stirred under N_2 for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 30:1) to yield the methyl ester **9aa** (71 mg, 56%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.57–7.43 (m, 3H), 7.39–7.23 (m, 4H), 7.17–7.00 (m, 3H), 3.95 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.2 (C_q), 137.1 (C_q), 135.2 (C_q), 135.0 (C_q), 132.9 (C_q), 131.3 (CH), 129.5 (CH), 129.2 (CH), 128.6 (CH), 127.9 (CH), 126.7 (CH), 125.6 (CH), 123.0 (CH), 52.1 (CH_3), 19.7 (CH_3). IR (ATR): 3026, 2949, 2862, 1721, 1588, 1436, 1265, 1068 cm^{-1}. MS (EI) *m/z* (relative intensity) 252 (100) [M^+], 237 (10), 220 (50), 193 (30), 178 (50), 165 (20). HR-MS (EI) *m/z* calcd for $C_{17}H_{16}O_2$ [M^+] 252.1150, found 252.1148.

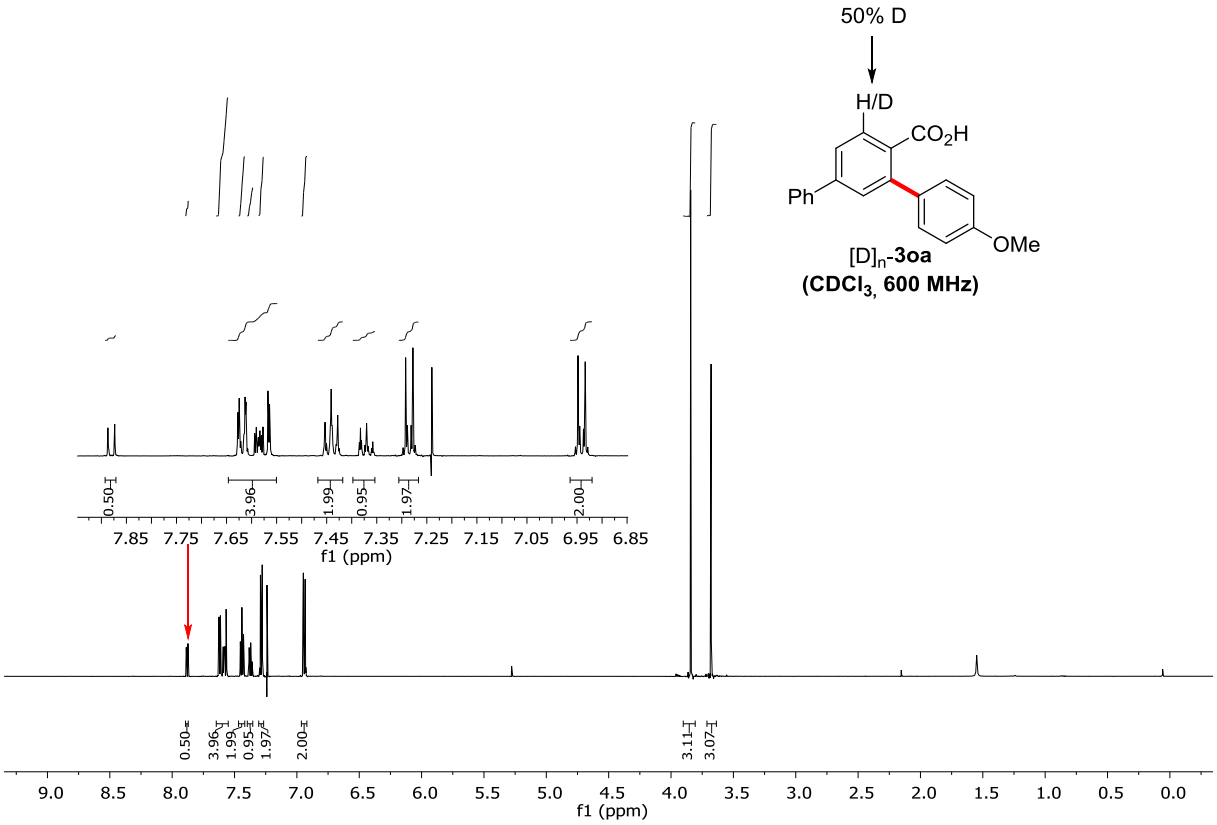
The analytical data are in accordance with those previously reported in the literature.[10]

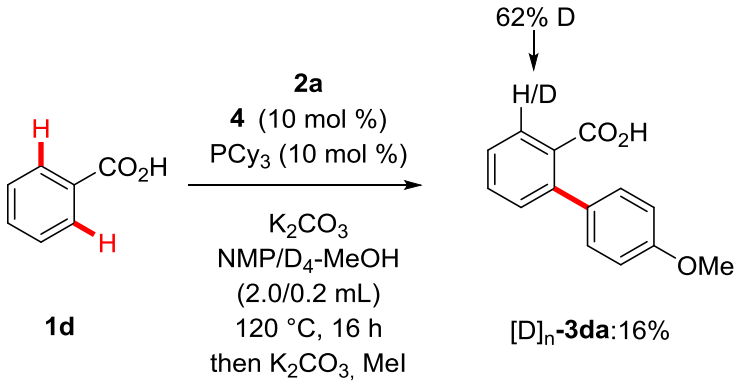
H-D Exchange Experiments



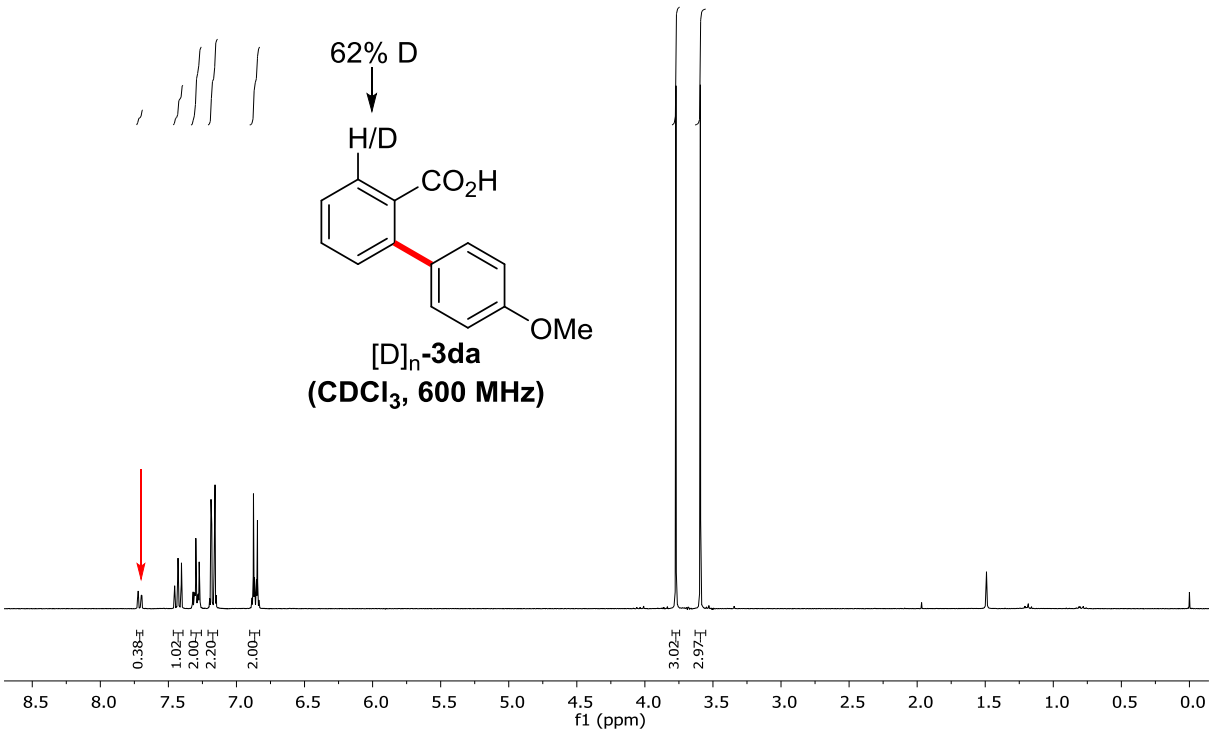
A suspension of 1-bromo-4-methoxybenzene (**2a**) (140 mg, 0.75 mmol), 4-phenylbenzoic acid (**1o**) (99 mg, 0.50 mmol), [Ru(O_2CMes)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (138 mg, 1.00 mmol) in a solvent mixture of NMP (2.0 mL) and CD_3OD (0.2 mL) was stirred at 120 ºC for 16 h in a seal tube under N_2 atmosphere. At ambient temperature, MeCN (3.0 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2.0 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) to yield [D]$_n$-**1o** (48 mg, 45%) and [D]$_n$-**3oa** (14 mg, 9%). The D-incorporation in [D]$_n$-**1o** and [D]$_n$-**3oa** was estimated by ^{1}H-NMR spectroscopy.


47% D
H/D
CO2H
Ph
H/D
[D]n-1o
(CDCl3, 600 MHz)
1.06
2.07
2.11
2.09
1.00
3.12
f1 (ppm)


50% D
H/D
CO2H
Ph
OMe
[D]n-3oa
(CDCl3, 600 MHz)
0.50
3.96
1.99
0.95
1.97
2.00
3.11
3.07
f1 (ppm)

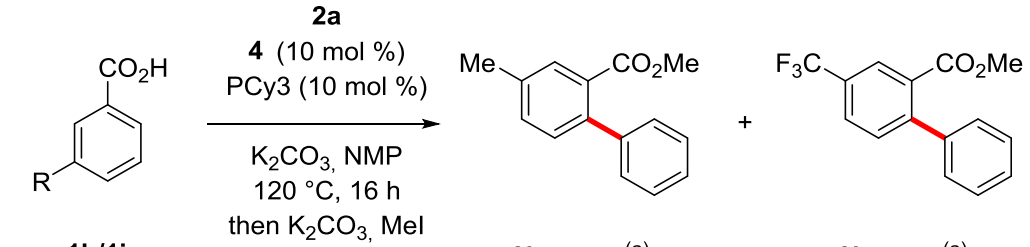


A suspension of 1-bromo-4-methoxybenzene (**2a**) (140 mg, 0.75 mmol), benzoic acid (**1d**) (61 mg, 0.50 mmol), [Ru(MesCO$_2$)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy$_3$ (14.0 mg, 10 mol %), K$_2$CO$_3$ (138 mg, 1.00 mmol) in a solvent mixture of NMP (2.0 mL) and CD$_3$OD (0.2 mL) was stirred at 120 ºC for 16 h in a seal tube under N$_2$ atmosphere. At ambient temperature, MeCN (3.0 mL), K$_2$CO$_3$ (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2.0 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H$_2$O (20 mL), and brine (20 mL) sequentially. The organic phase was dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield [D]$_n$-**3da** (18 mg, 16%). The D-incorporation in [D]$_n$-**3da** was estimated by ^{1}H-NMR spectroscopy.



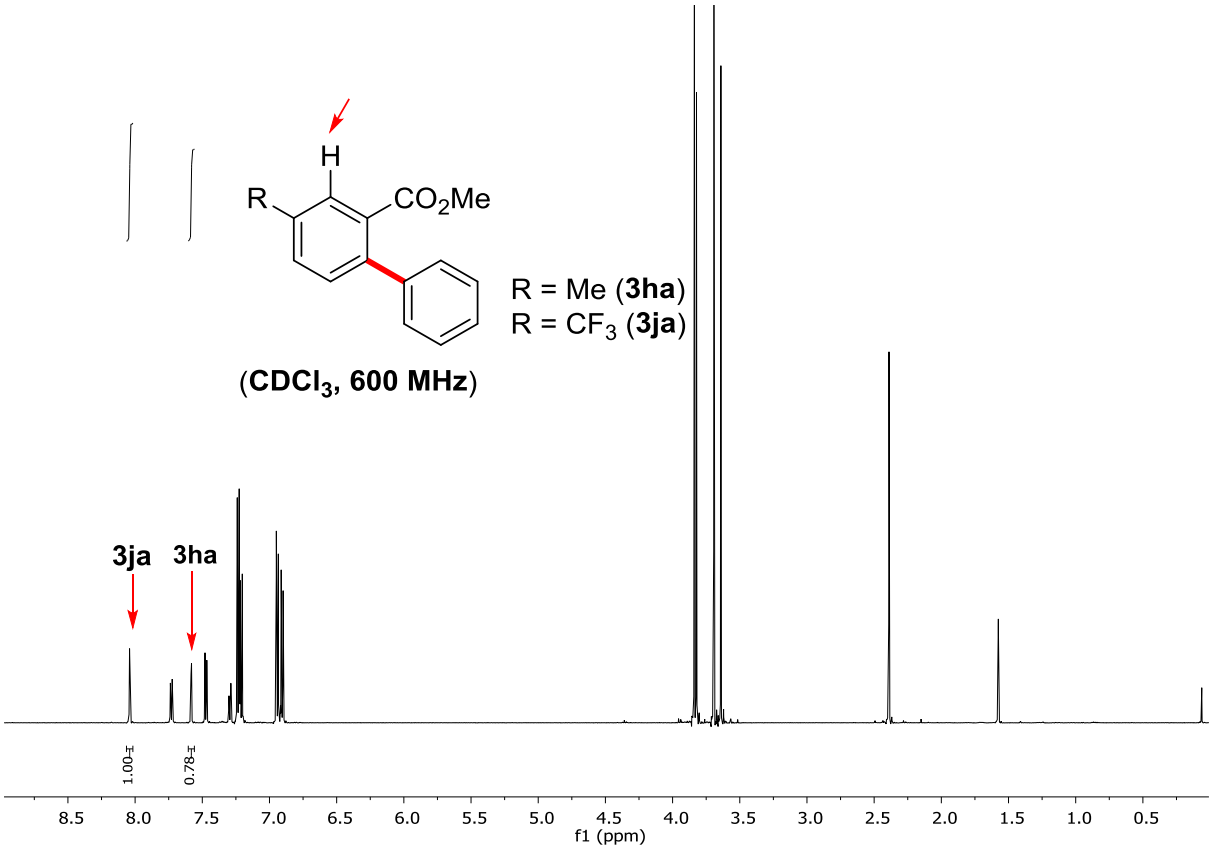
Competition Experiments

Intermolecular competition experiment between benzoic acid **1h** and **1j**

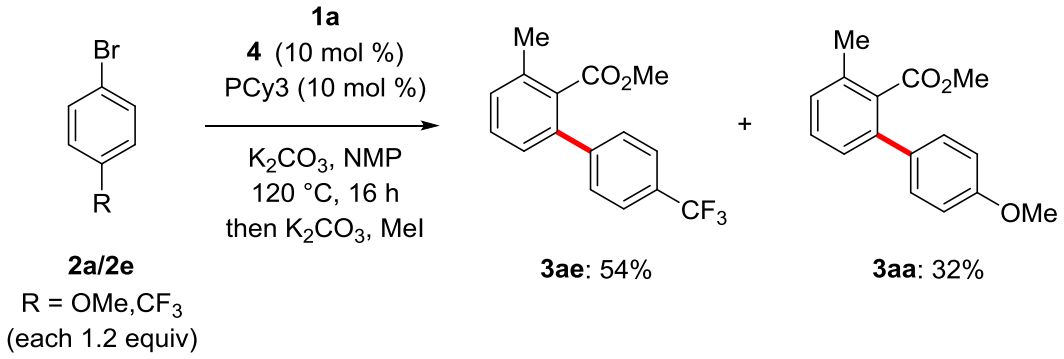


A suspension of 1-bromo-4-methoxybenzene (**2a**) (94 mg, 0.50 mmol), 3-methylbenzoic acid (**1h**) (82 mg, 0.60 mmol), 3-(trifluoromethyl)benzoic (**1j**) (114 mg, 0.60 mmol), [$Ru(O_2CMes)_2$(*p*-cymene)] (28.1 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (138 mg, 1.00 mmol) in NMP (2.0 mL) was stirred under N_2 for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2 h. At ambient temperature, the mixture was

diluted with MTBE (120 mL), then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) to yield the mixture of **3ha** and **3ja** (41 mg). The ratio was calculated based on ^{1}H-NMR analysis.



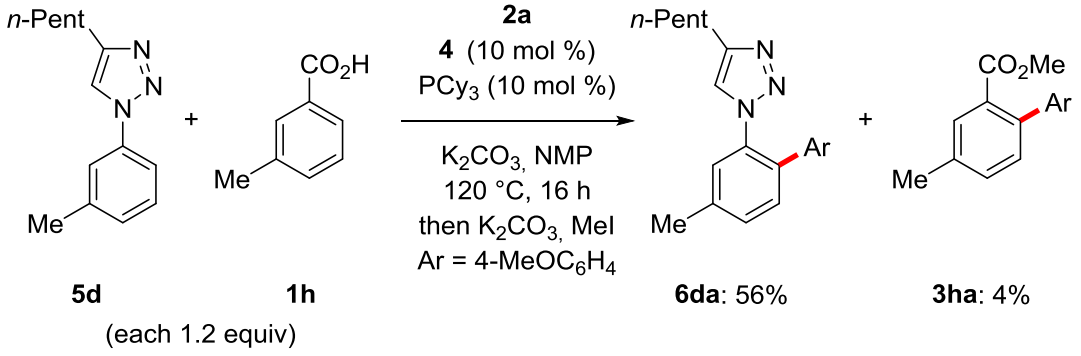
Intermolecular Competition Experiment between aryl bromides **2a** and **2e.**



A suspension of 2-methylbenzoic acid (**1a**) (68 mg, 0.50 mmol), 1-bromo-4-methoxybenzene (**2a**) (112 mg, 0.60 mmol), 1-bromo-4-(trifluoromethyl)benzene (**2e**) (135 mg, 0.60 mmol),

[Ru(MesCO$_2$)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy$_3$ (14.0 mg, 10 mol %), K$_2$CO$_3$ (138 mg, 1.00 mmol) in NMP (2.0 mL) was stirred under N$_2$ for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K$_2$CO$_3$ (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2.0 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H$_2$O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield **3ae** (79 mg, 54%) and **3aa** (41 mg, 32%).

Intermolecular Competition Experiment between Benzoic acid **1h** and triazole **5d**.



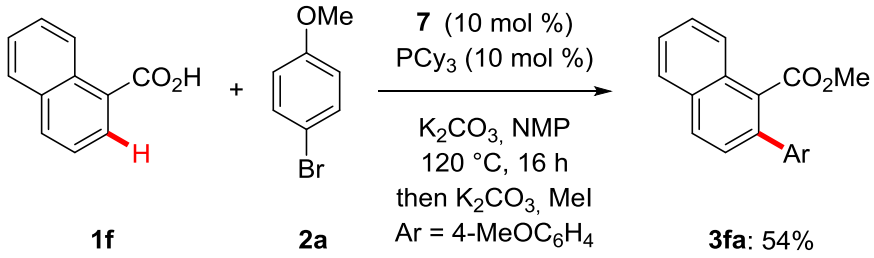
A suspension of 1-bromo-4-methoxybenzene (**2a**) (94 mg, 0.50 mmol), 3-methylbenzoic acid (**1h**) (82 mg, 0.60 mmol), 4-*n*-pentyl-1-(*m*-tolyl)-1*H*-1,2,3-triazole (**5d**) (138 mg, 0.60 mmol), [Ru(O$_2$CMes)$_2$(*p*-cymene)] (**4**) (28.1 mg, 10 mol %), PCy$_3$ (14.0 mg, 10 mol %), K$_2$CO$_3$ (138 mg, 1.00 mmol) in NMP (2.0 mL) was stirred under N$_2$ for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K$_2$CO$_3$ (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2.0 h. At ambient temperature, the mixture was diluted with MTBE (120 mL), then washed with H$_2$O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield **6da** (94 mg, 56%) and **3ha** (5.1 mg, 4%).

1-(4'-Methoxy-4-methyl-[1,1'-biphenyl]-2-yl)-4-pentyl-1*H*-1,2,3-triazole (6da)

Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ =7.41 (s, 1H), 7.36–7.28 (m, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.90 (s, 1H), 6.77 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H), 2.60 (t, J = 7.5 Hz, 2H), 2.42

(s, 3H), 1.53 (p, J = 7.5 Hz, 2H), 1.34–1.10 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.0 (C_q), 147.8 (C_q), 138.2 (C_q), 134.9 (C_q), 133.6 (C_q), 130.6 (CH), 130.3 (CH), 129.7 (C_q), 129.5 (CH), 127.0 (CH), 122.9 (CH), 113.9 (CH), 55.1 (CH_3), 31.0 (CH_2), 28.9 (CH_2), 25.2 (CH_2), 22.3 (CH_2), 20.8 (CH_3), 13.8 (CH_3). IR (ATR): 2927, 2837, 1609, 1638, 1493, 1464, 1245, 1018 cm^{-1}. MS (EI) *m/z* (relative intensity) 335 (10) [M^+], 306 (60), 292 (30), 278 (30), 264 (30), 250 (100), 237 (30). HR-MS (EI) *m/z* calcd for $C_{21}H_{25}N_3O$ [M^+] 335.1998, found 335.1991.

C–H Arylations with Ruthenacycle 7



A suspension of 1-naphthoic acid (**1f**) (0.50 mmol, 86 mg), 1-bromo-4-methoxybenzene (**2a**) (140 mg, 0.75 mmol), ruthenacycle **7** (24.2 mg, 10 mol %), PCy_3 (14.0 mg, 10 mol %), K_2CO_3 (138 mg, 1.00 mmol) in NMP (2.0 mL) was stirred under N_2 for 16 h at 120 ºC. At ambient temperature, MeCN (3.0 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (355 mg, 2.50 mmol) were added and the mixture was stirred at 50 ºC for another 2.0 h. At ambient temperature, the mixture was diluted with MTBE (120 mL) then washed with H_2O (20 mL) and brine (20 mL) sequentially. The organic phase was dried over Na_2SO_4, and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) to yield **3fa** (95 mg, 54%, based on 0.60 mmol) and starting material methyl 1-naphthoate (31 mg, 28%).

References

[1] L. Ackermann, R. Vicente, H. K. Potukuchi, V. Pirovano, *Org. Lett*. **2010**, *12*, 5032–5035.

[2] A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136.

[3] D. Zell, S. Warratz, D. Gelman, S. J. Garden, L. Ackermann, *Chem. Eur. J.* **2016**, *22*, 1248–1252.

[4] S. Warratz, C. Kornhaaß, A. Cajaraville, B. Niepötter, D. Stalke, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 5513–5517.

[5] L. Huang, D. Hackenberger, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2015**, *54*, 12607–12611.

[6] D.-H. Wang, T.-S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 17676–17677.

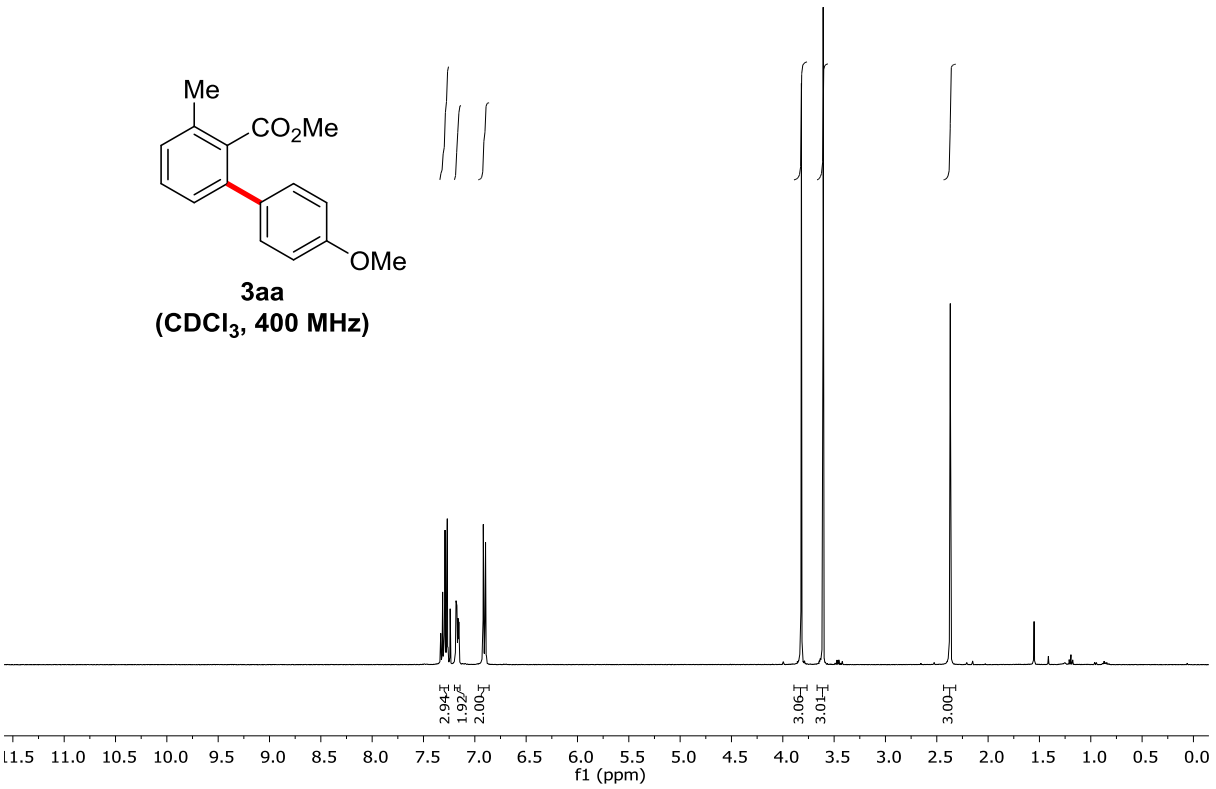
[7] F. Pünner, J. Schieven, G. Hilt, *Org. Lett*. **2013**, *15*, 4888–4891.

[8] M. Miyasaka, A. Fukushima, T. Satoh, K. Hirano, M. Miura, *Chem. Eur. J.* **2009**, *15*, 3674–3677.

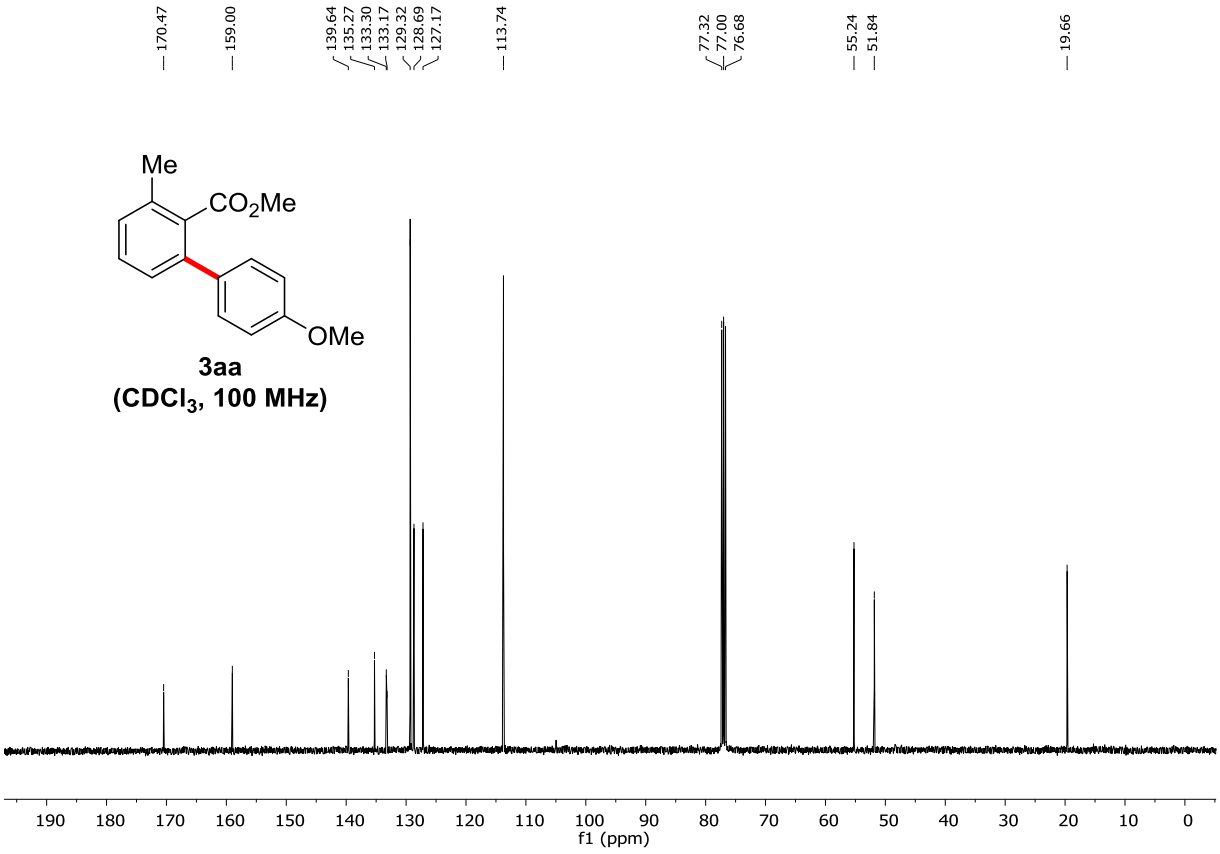
[9] Y. Liu, Y. Yang, Y. Shi, X. Wang, L. Zhang, Y. Cheng, J. You, *Organometallics* **2016**, *35*, 1350–1353.

[10] S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024–3033.

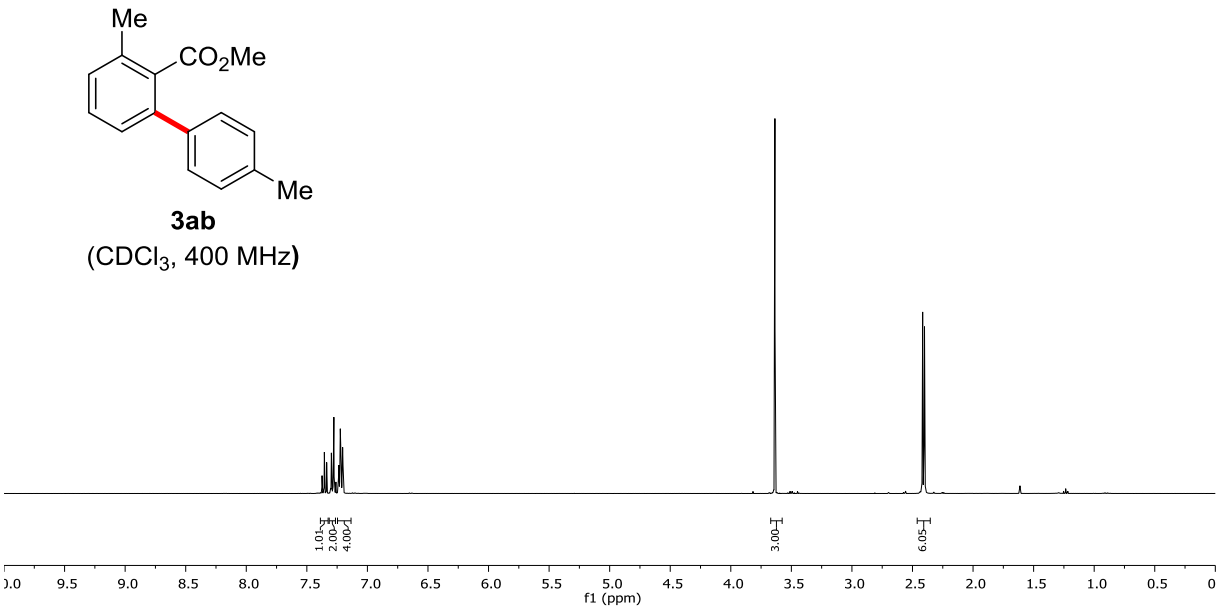
NMR Spectra

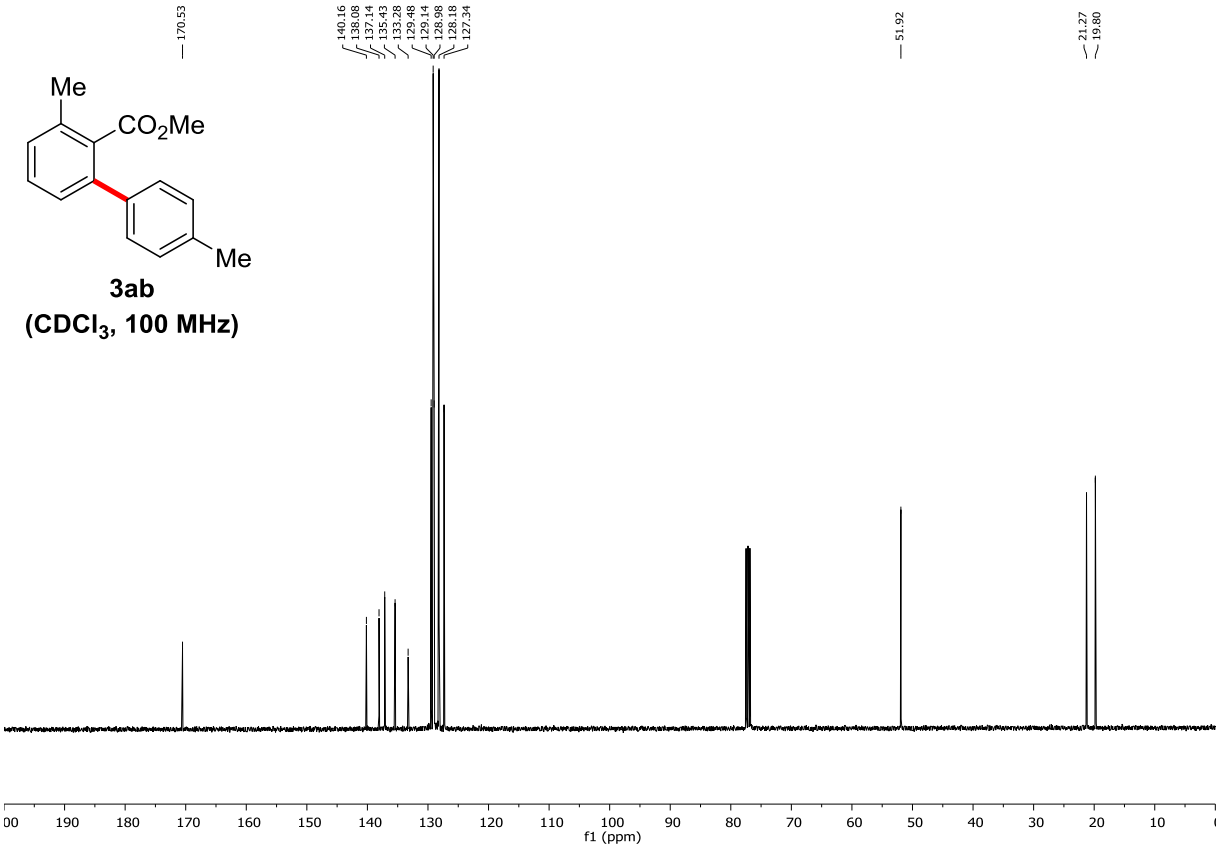


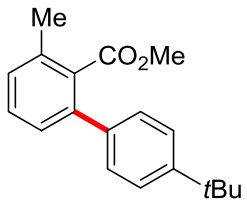
3aa
($CDCl_3$, 400 MHz)



3aa
($CDCl_3$, 100 MHz)

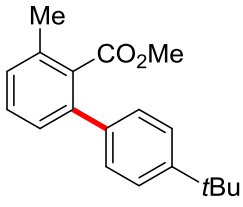

Me
CO2Me
Me
3ab
(CDCl3, 400 MHz)
1.01
2.00
4.00
3.00
6.05
f1 (ppm)


170.53
140.16
138.08
137.14
135.43
133.28
129.48
129.14
128.98
128.18
127.34
51.92
21.27
19.80
Me
CO2Me
Me
3ab
(CDCl3, 100 MHz)
f1 (ppm)



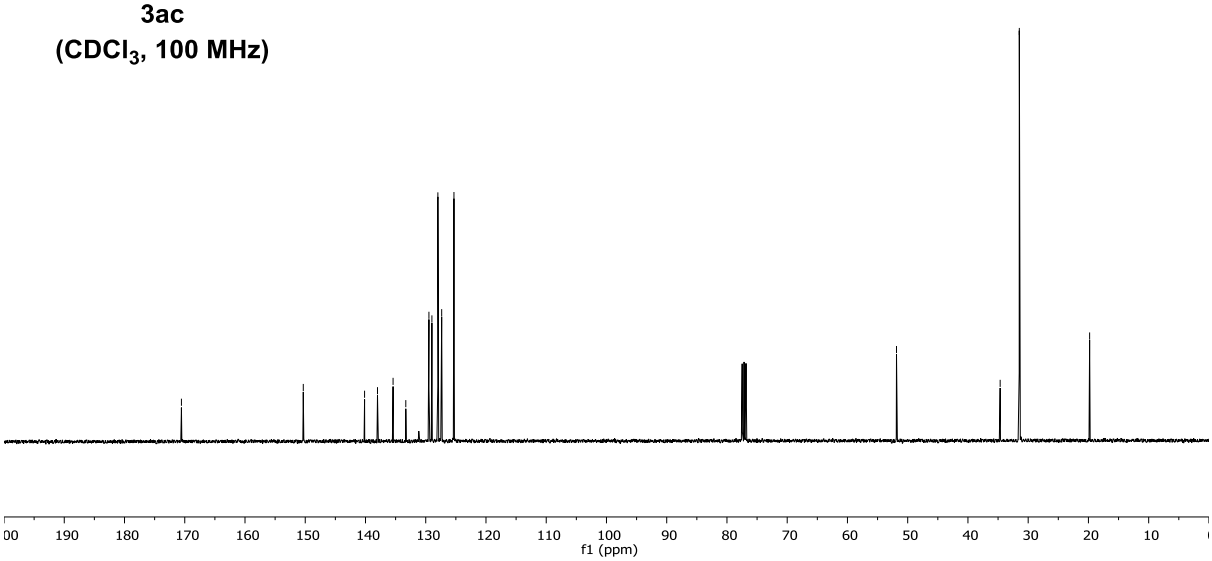
3ac

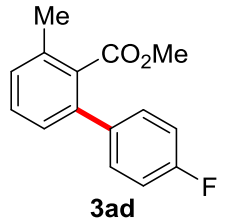
($CDCl_3$, 400MHz)



3ac

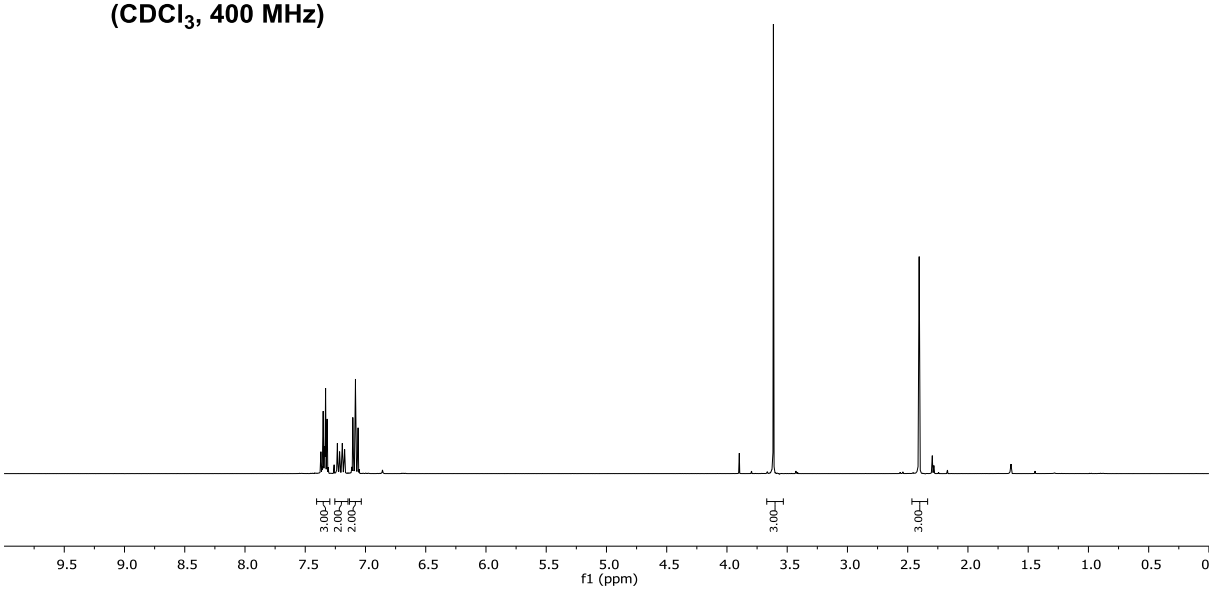
($CDCl_3$, 100 MHz)

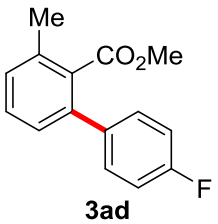




3ad

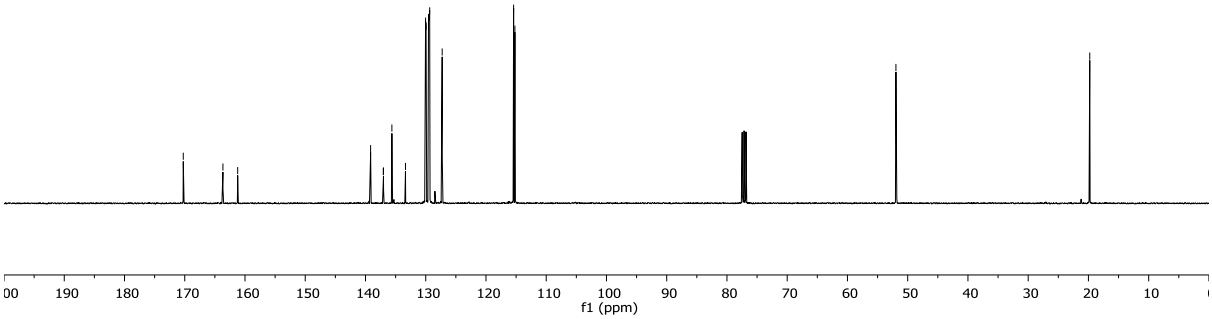
($CDCl_3$, 400 MHz)

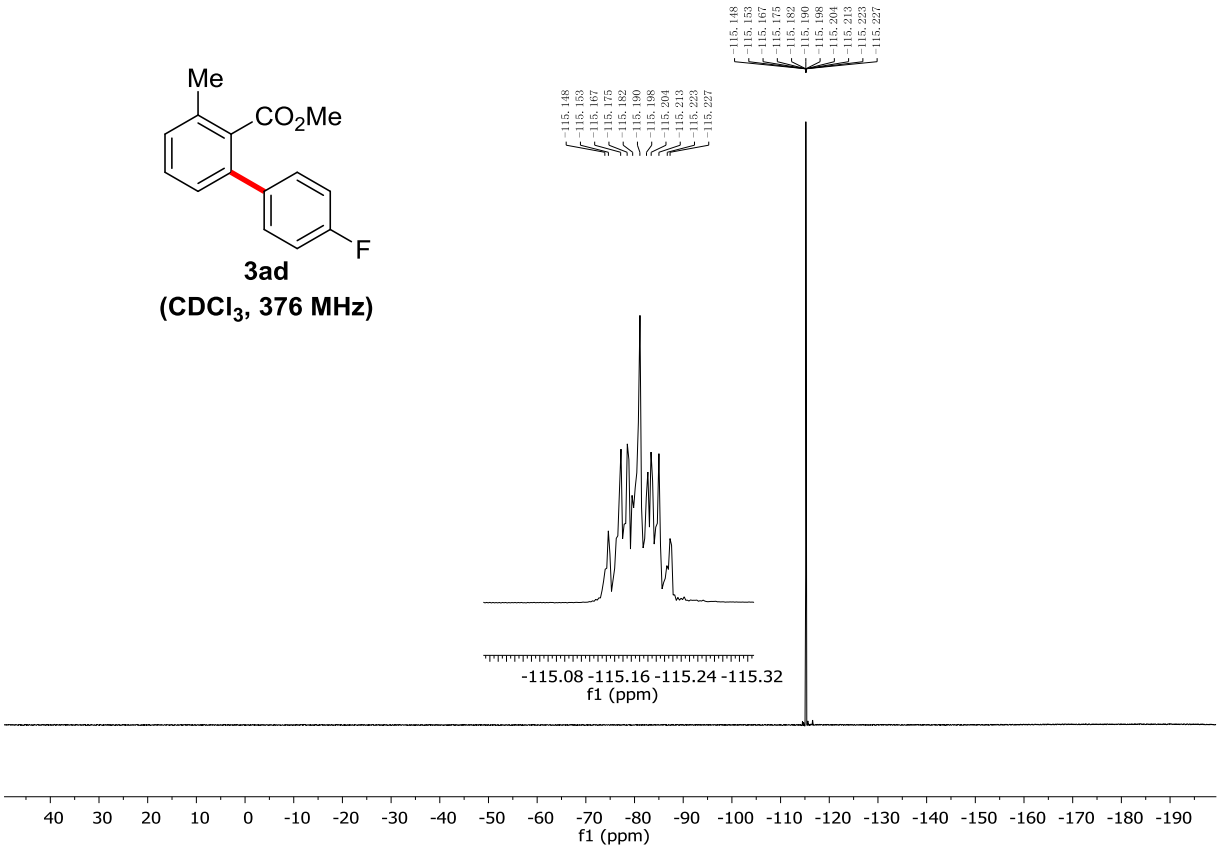




3ad

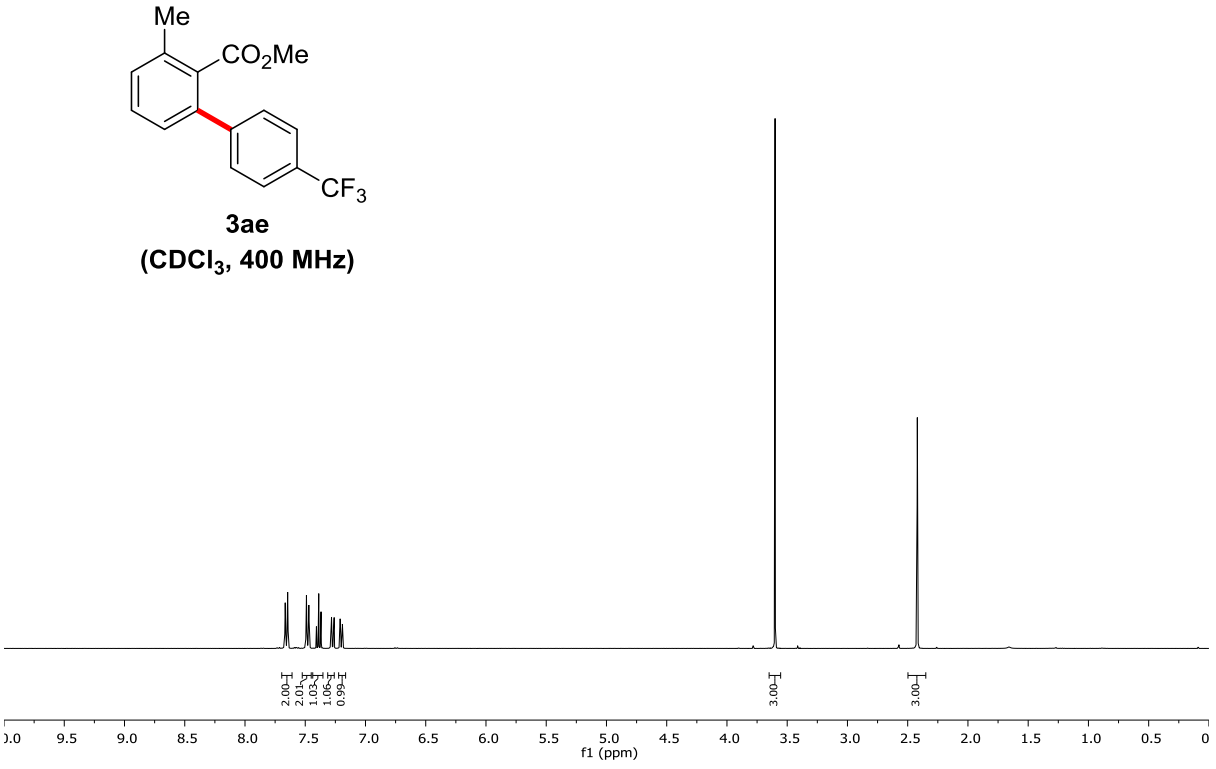
($CDCl_3$, 100 MHz)





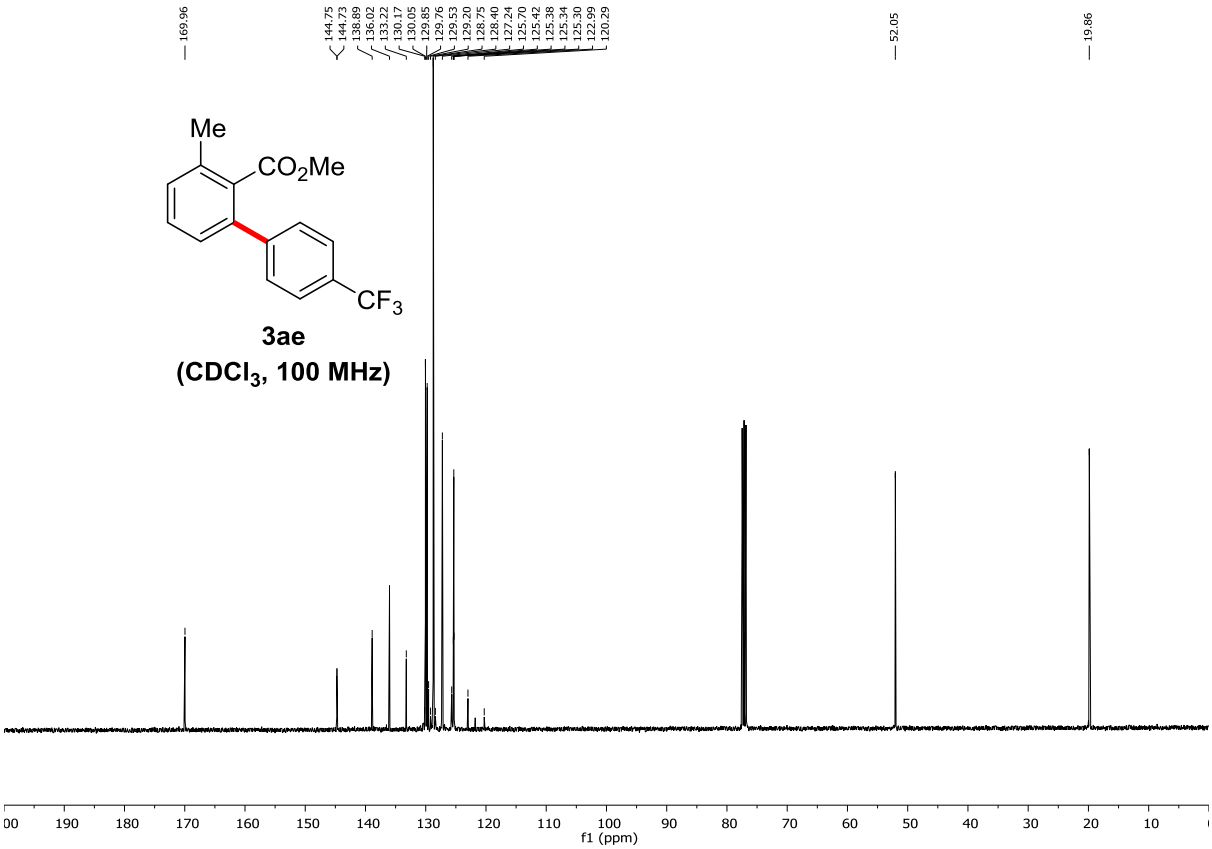
3ad

($CDCl_3$, 376 MHz)



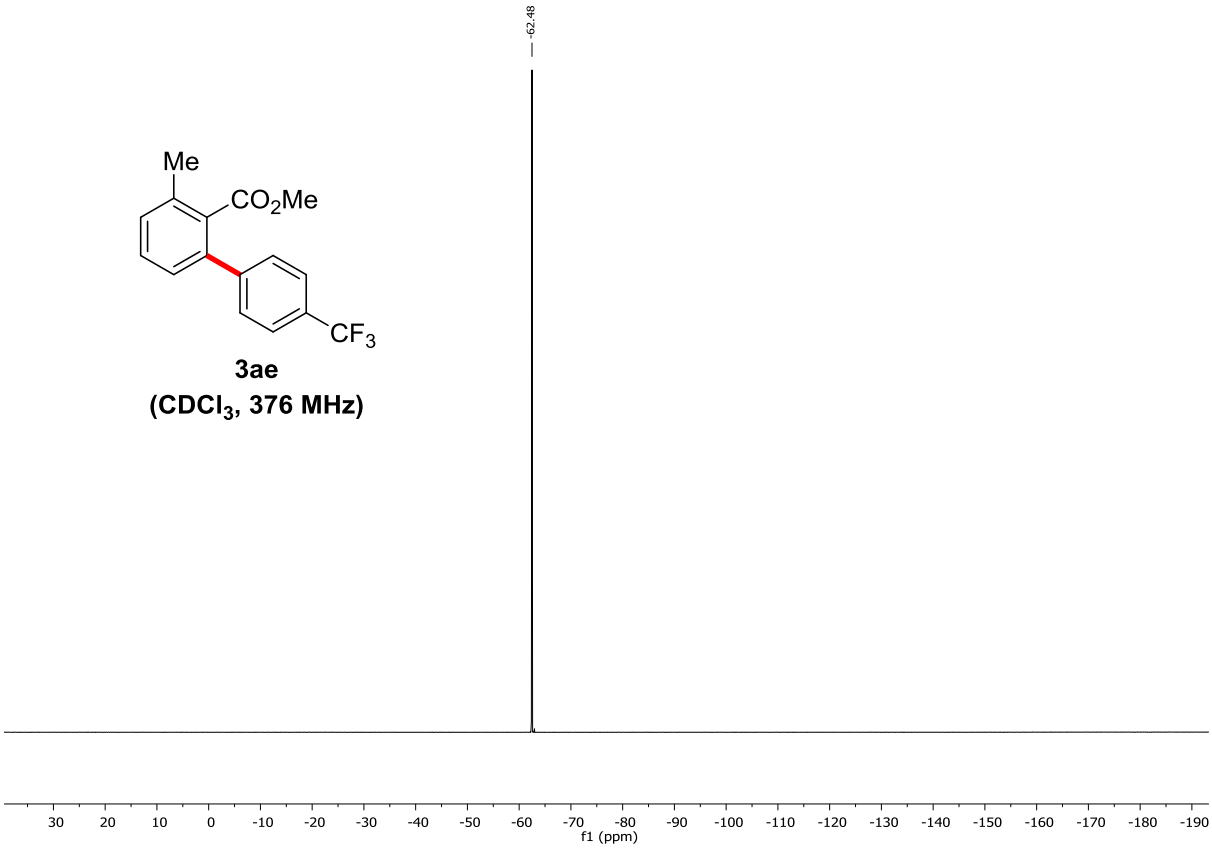
3ae

($CDCl_3$, 400 MHz)



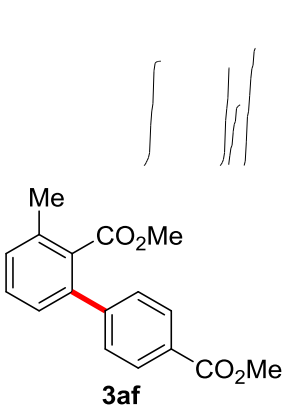
3ae

($CDCl_3$, 100 MHz)



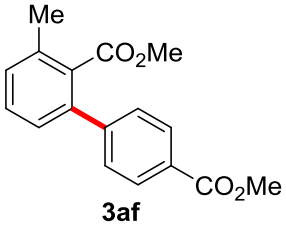
3ae

($CDCl_3$, 376 MHz)



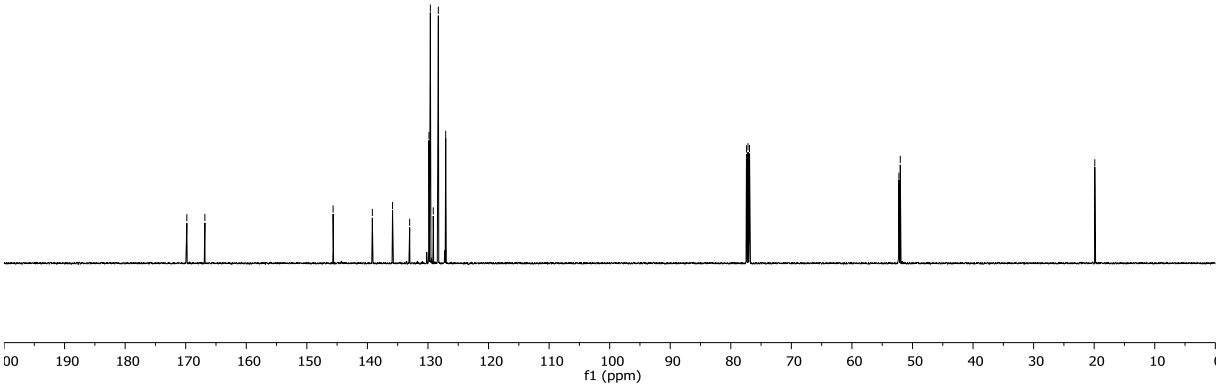
3af

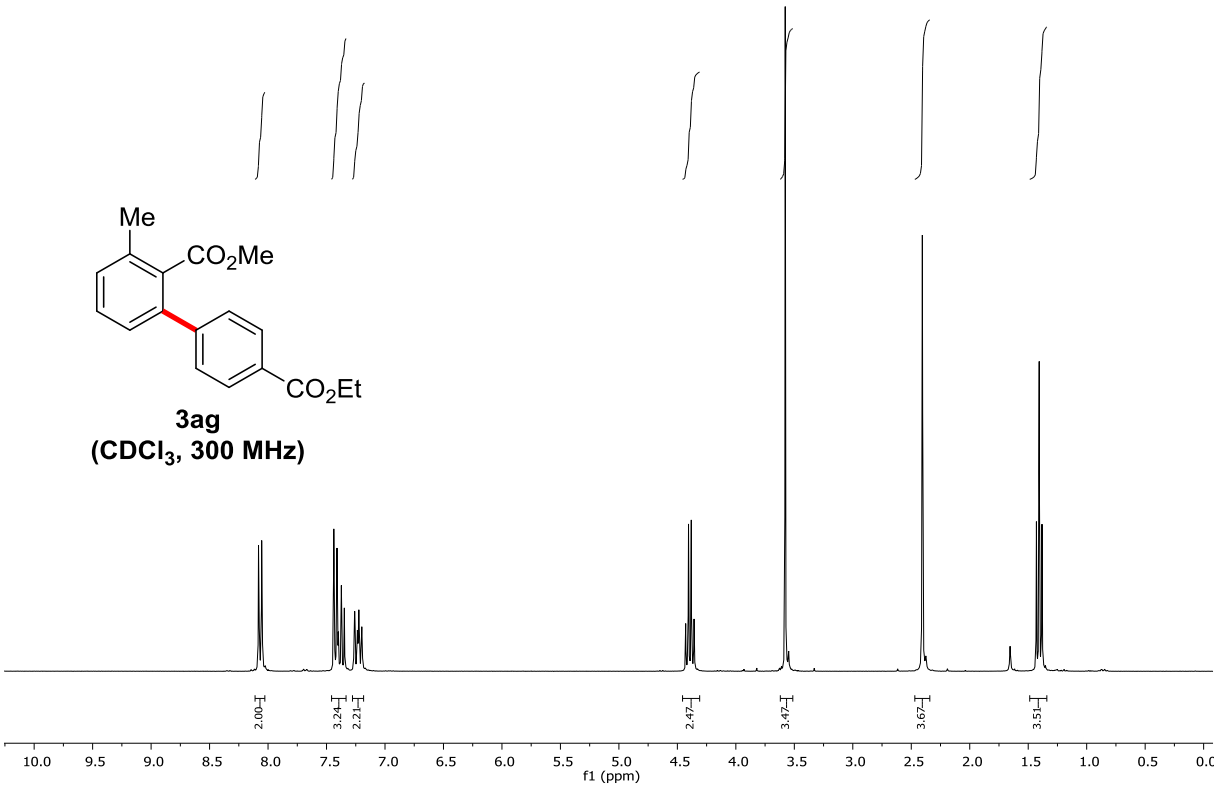
($CDCl_3$, 300 MHz)



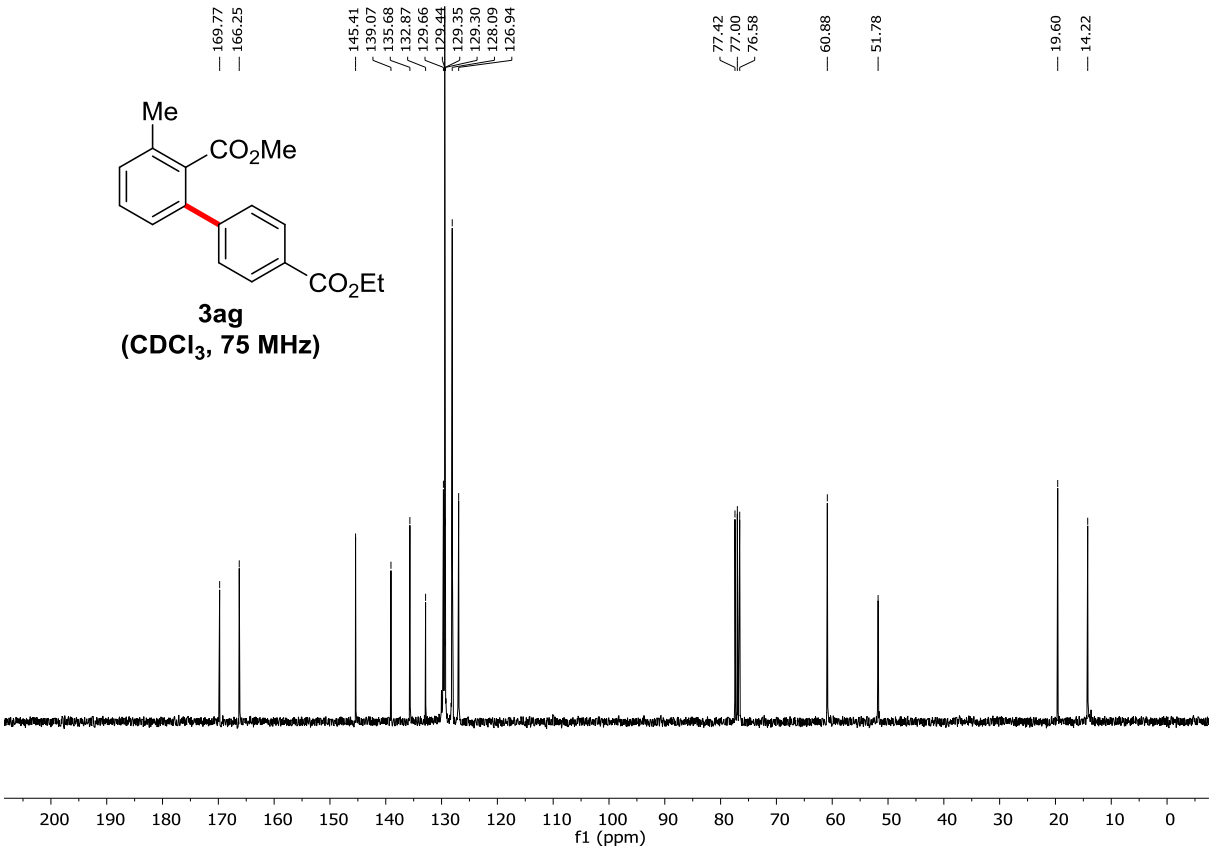
3af

($CDCl_3$, 75 MHz)

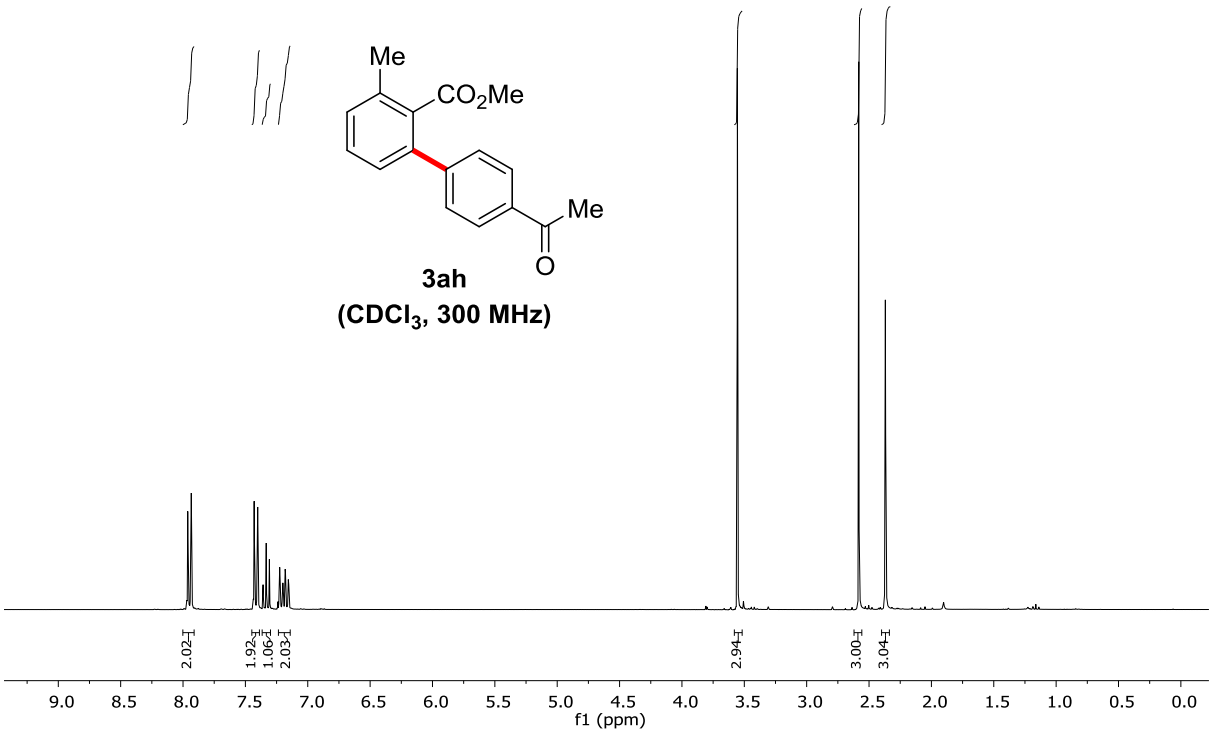


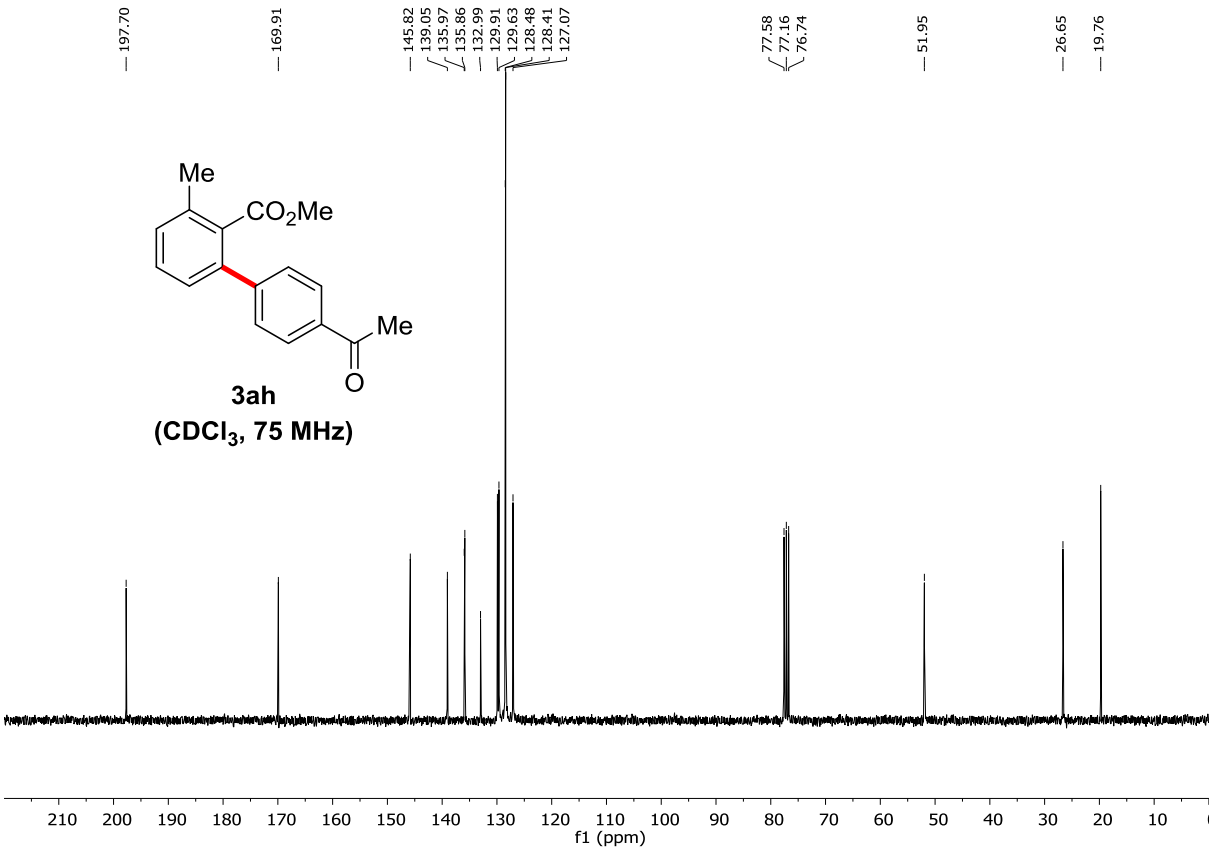


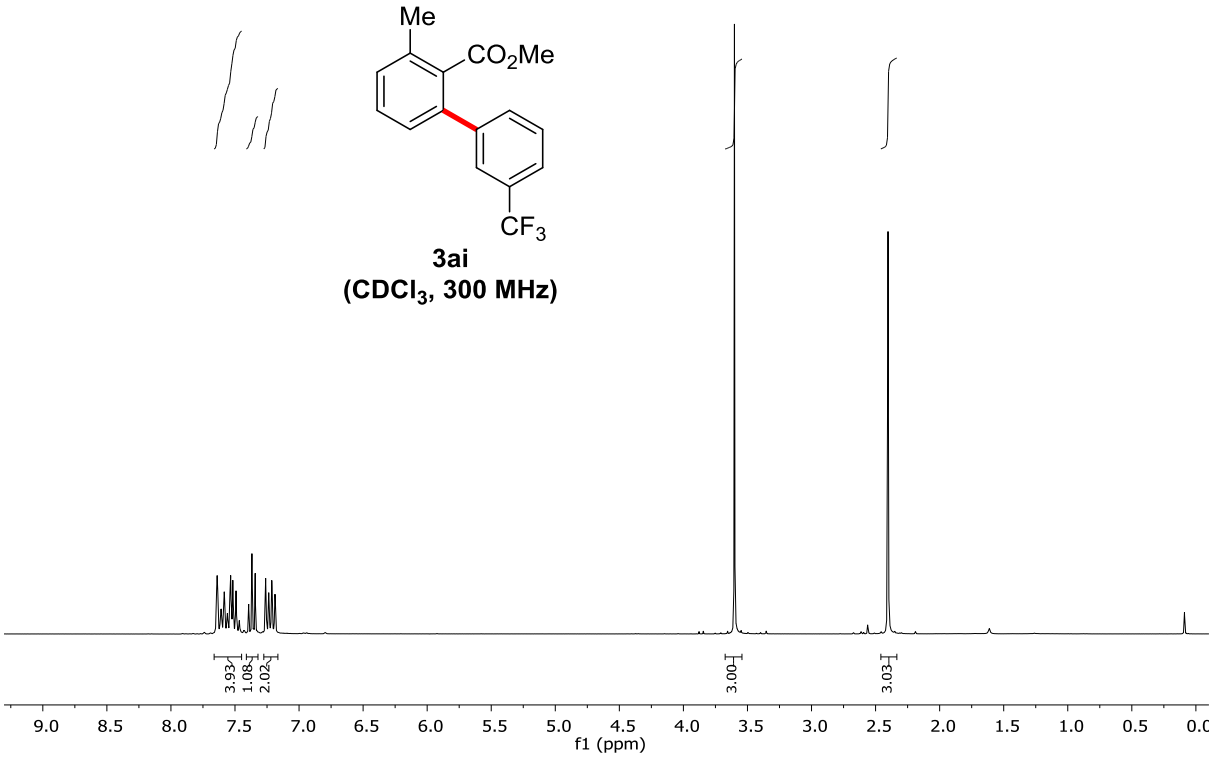
3ag
($CDCl_3$, 300 MHz)

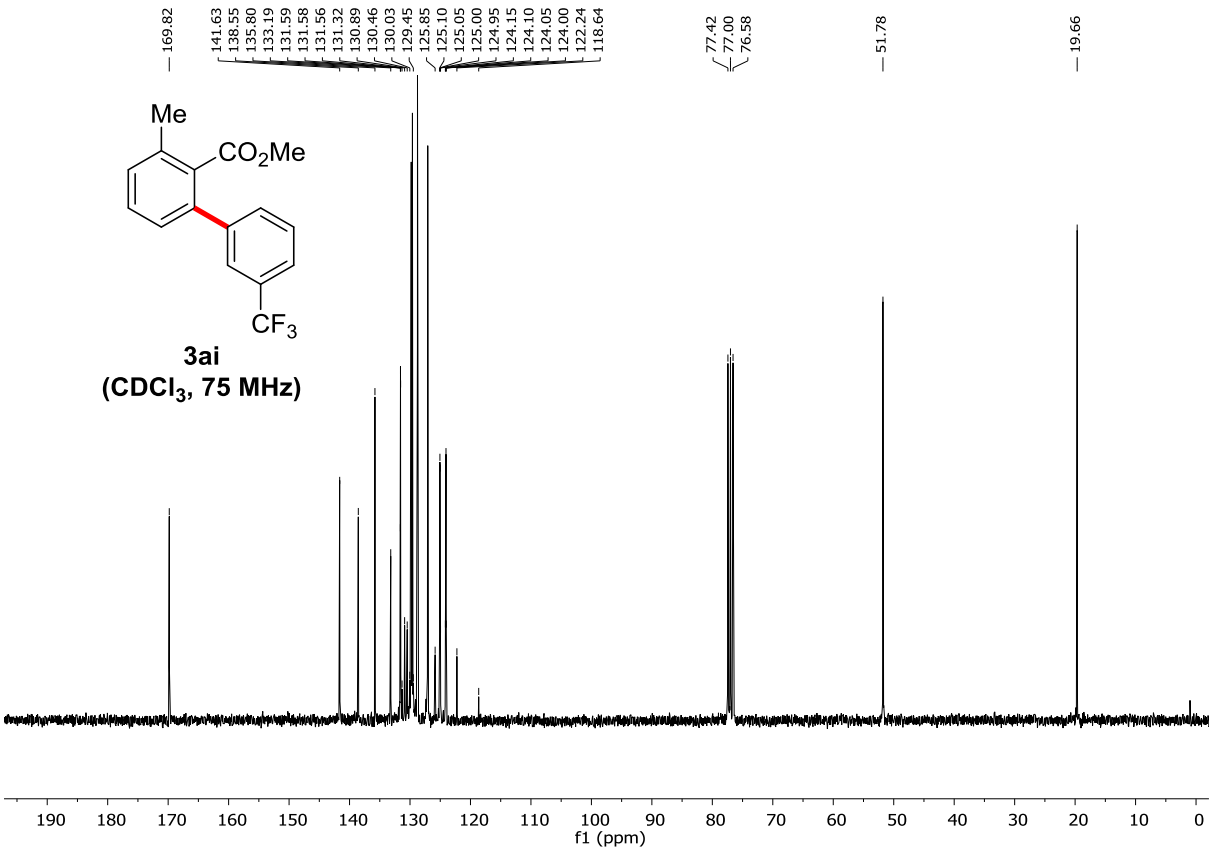


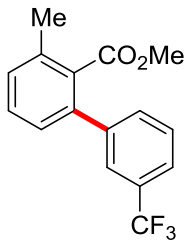
3ag
($CDCl_3$, 75 MHz)


Me
CO2Me
Me
O
3ah
(CDCl3, 300 MHz)
2.02
1.92
1.06
2.03
2.94
3.00
3.04
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)

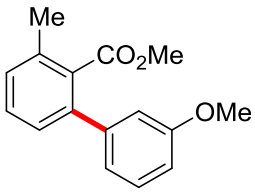

197.70
169.91
145.82
139.05
135.97
135.86
132.99
129.91
129.63
128.48
128.41
127.07
77.58
77.16
76.74
51.95
26.65
19.76
Me
CO2Me
Me
O
3ah
(CDCl3, 75 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
CO2Me
CF3
3ai
(CDCl3, 300 MHz)
3.93
1.08
2.02
3.00
3.03
f1 (ppm)

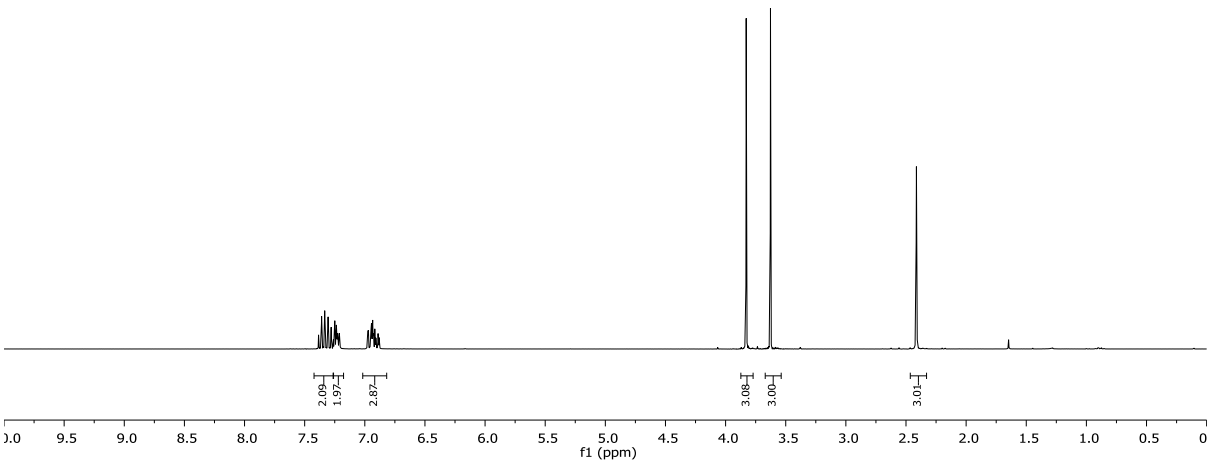

169.82
141.63
138.55
135.80
133.19
131.59
131.58
131.56
131.32
130.89
130.46
130.03
129.45
125.85
125.10
125.05
125.00
124.95
124.15
124.10
124.05
124.00
122.24
118.64
77.42
77.00
76.58
51.78
19.66
Me
CO2Me
CF3
3ai
(CDCl3, 75 MHz)
f1 (ppm)

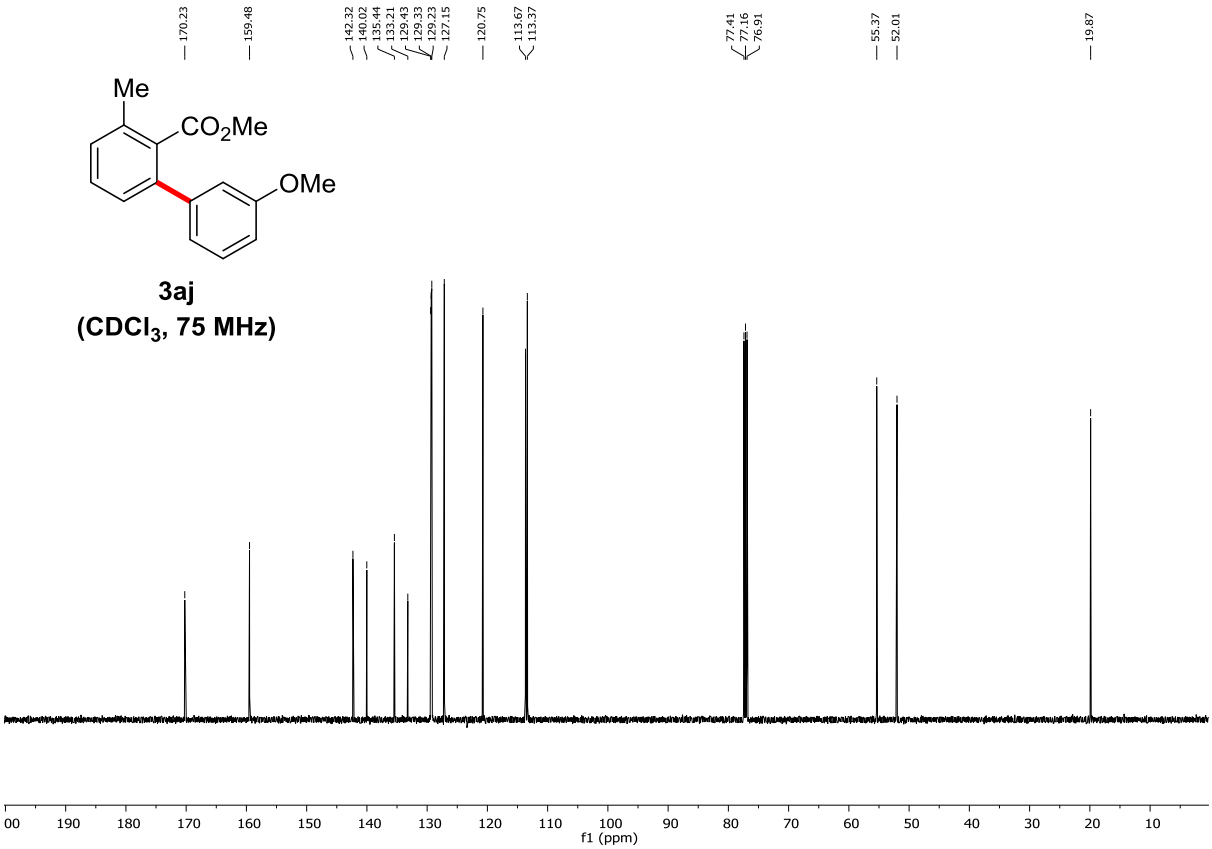


3ai
($CDCl_3$, 283 MHz)

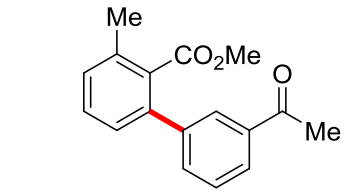


3aj
($CDCl_3$, 300 MHz)

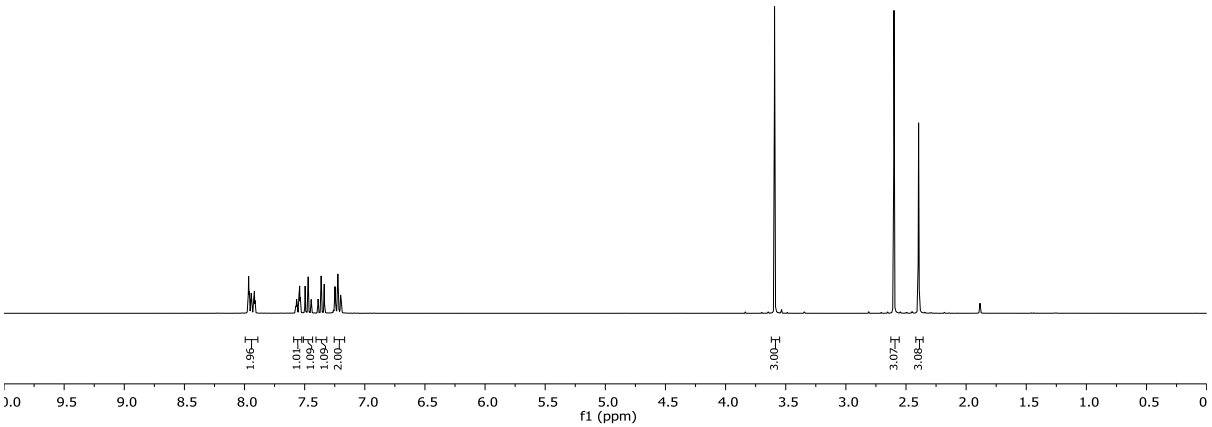


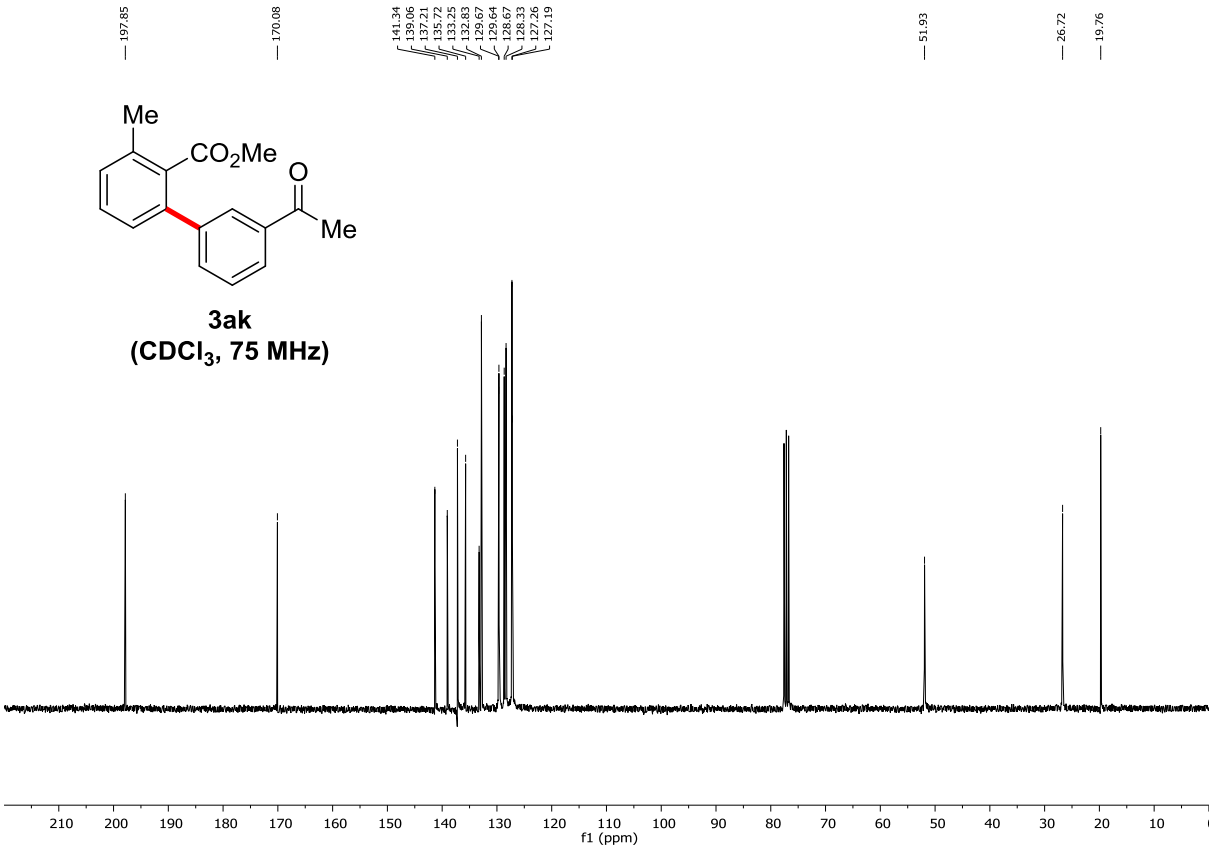


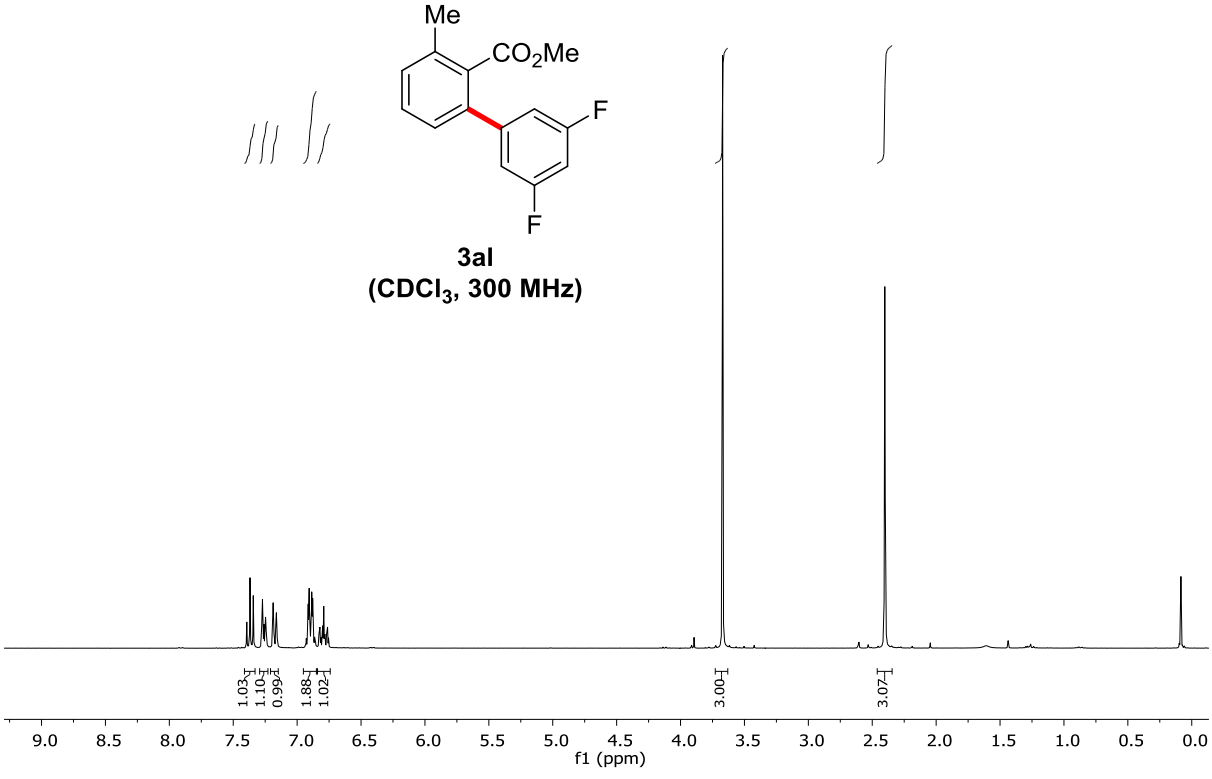
3aj
($CDCl_3$, 75 MHz)

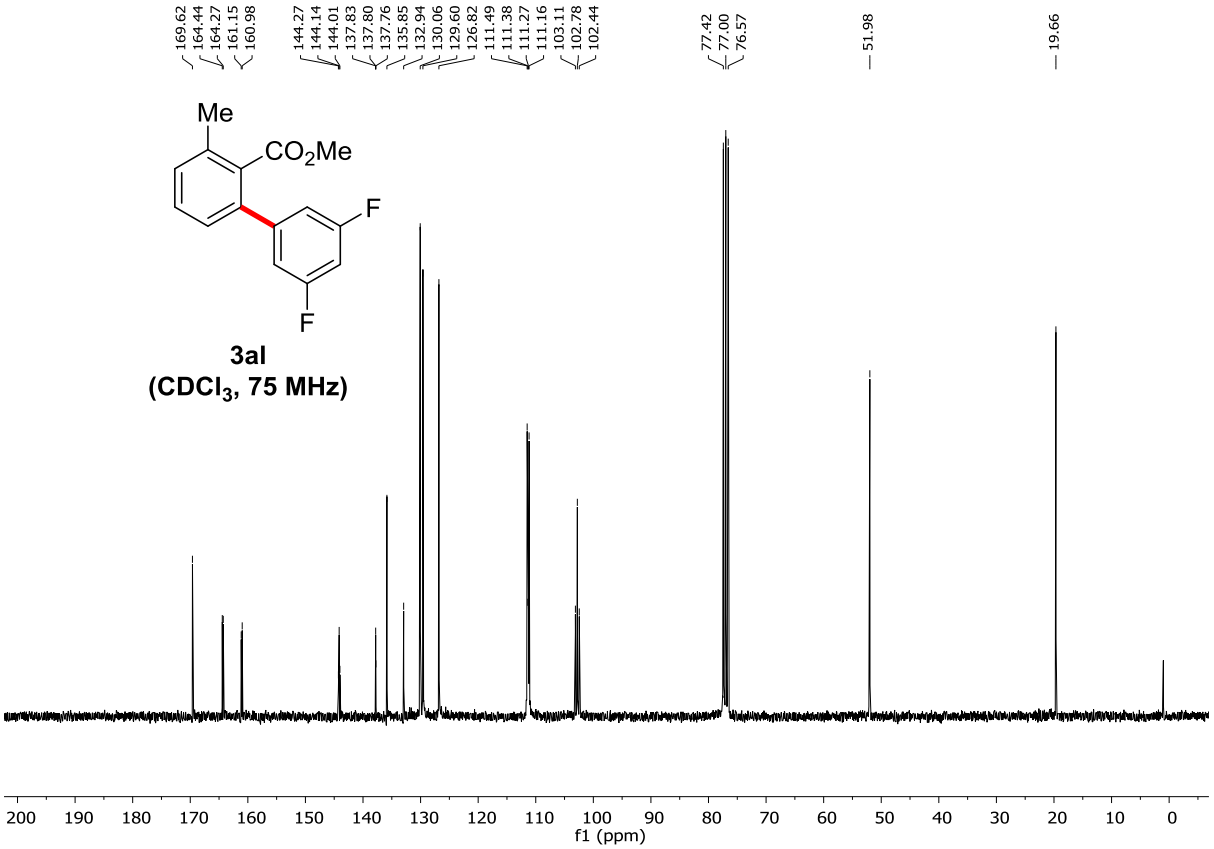


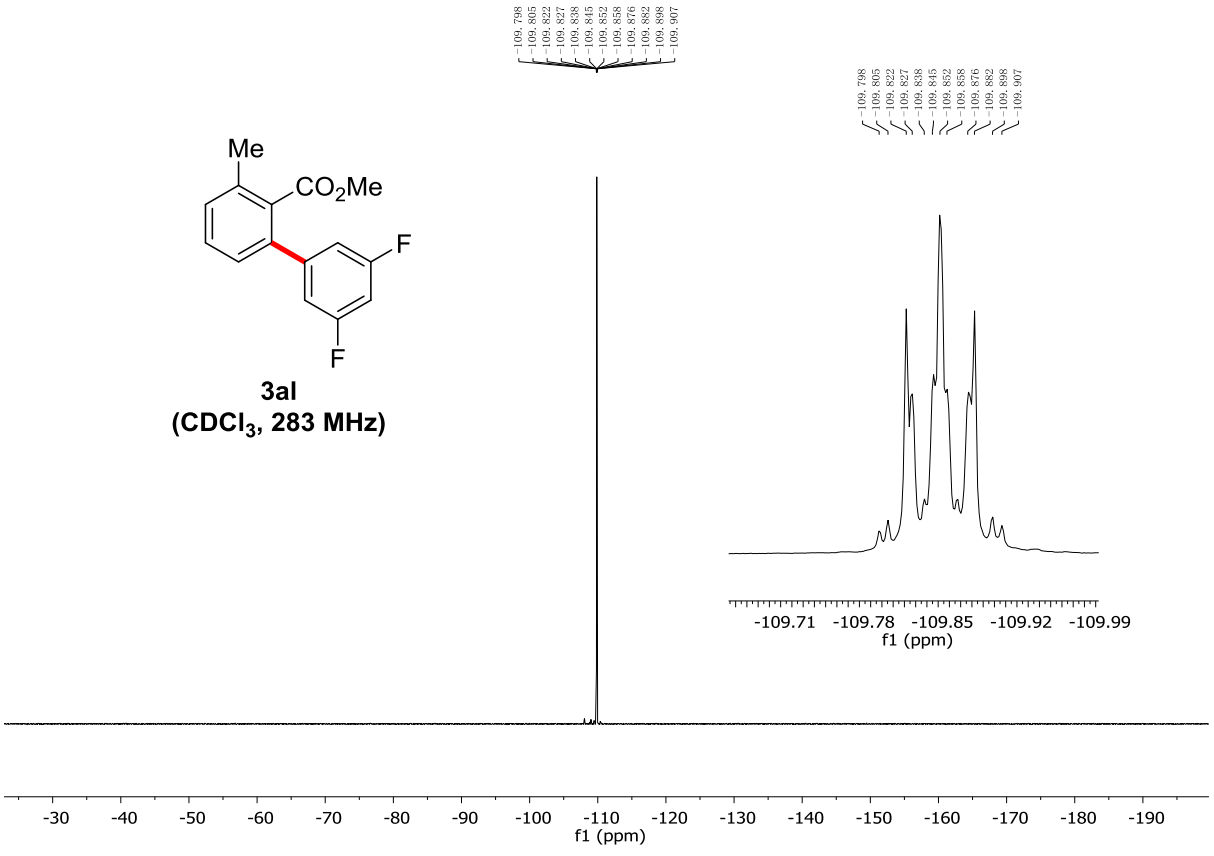
3ak
($CDCl_3$, 300 MHz)

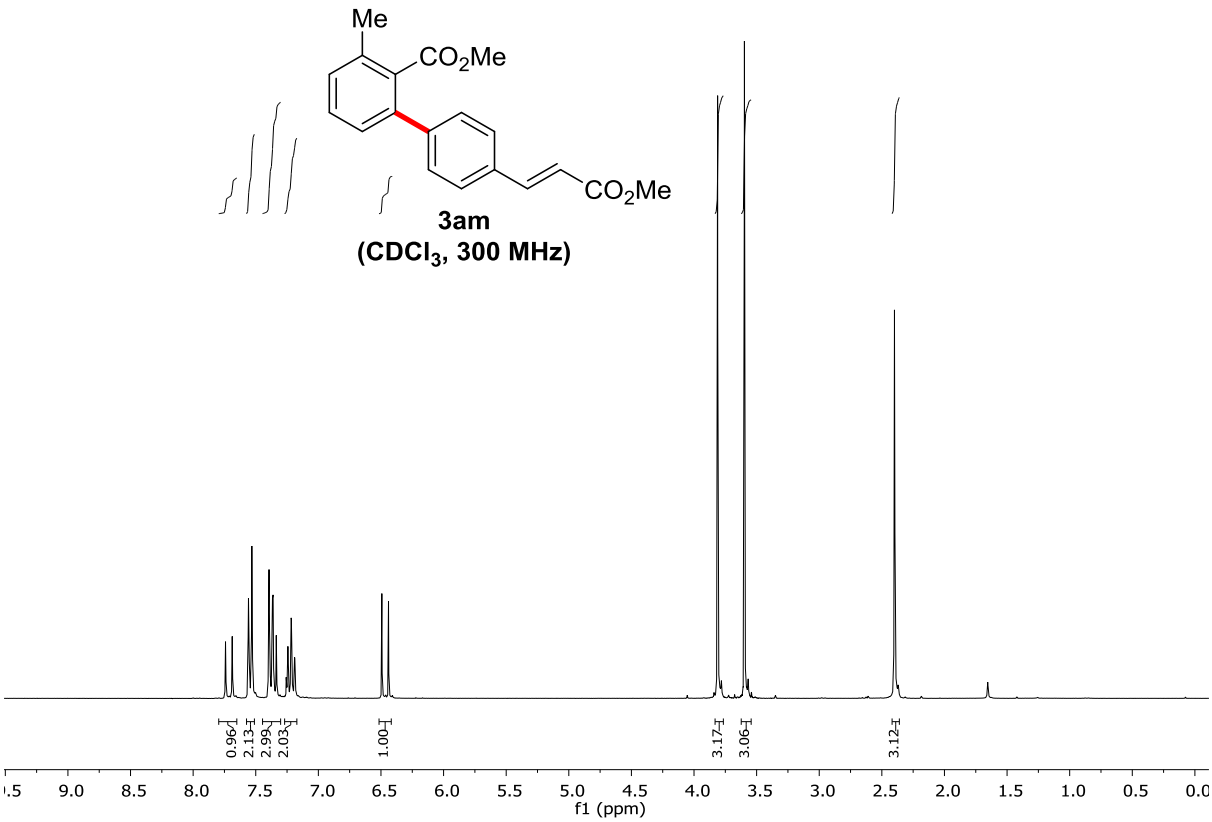


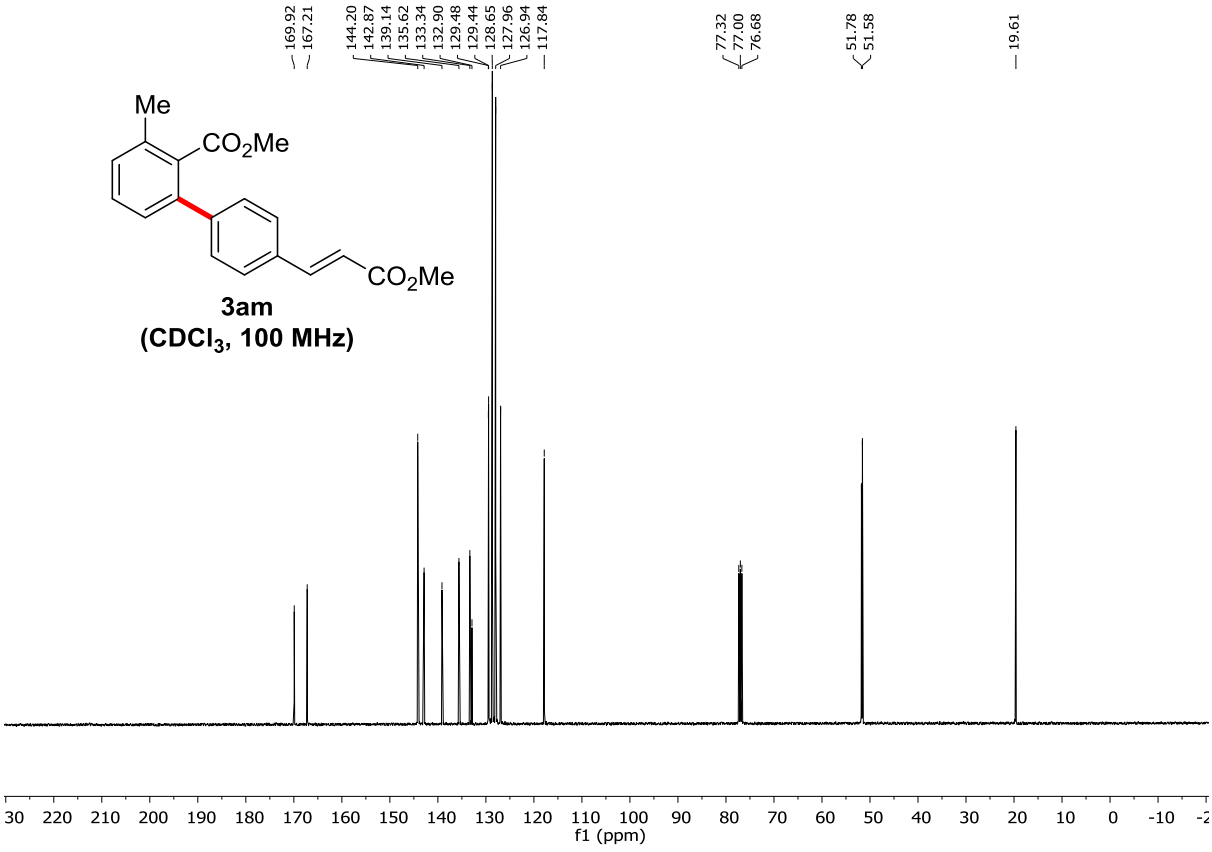

197.85
170.08
141.34
139.06
137.21
135.72
133.25
132.83
129.67
129.64
128.67
128.33
127.26
127.19
51.93
26.72
19.76
Me
CO2Me
O
Me
3ak
(CDCl3, 75 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

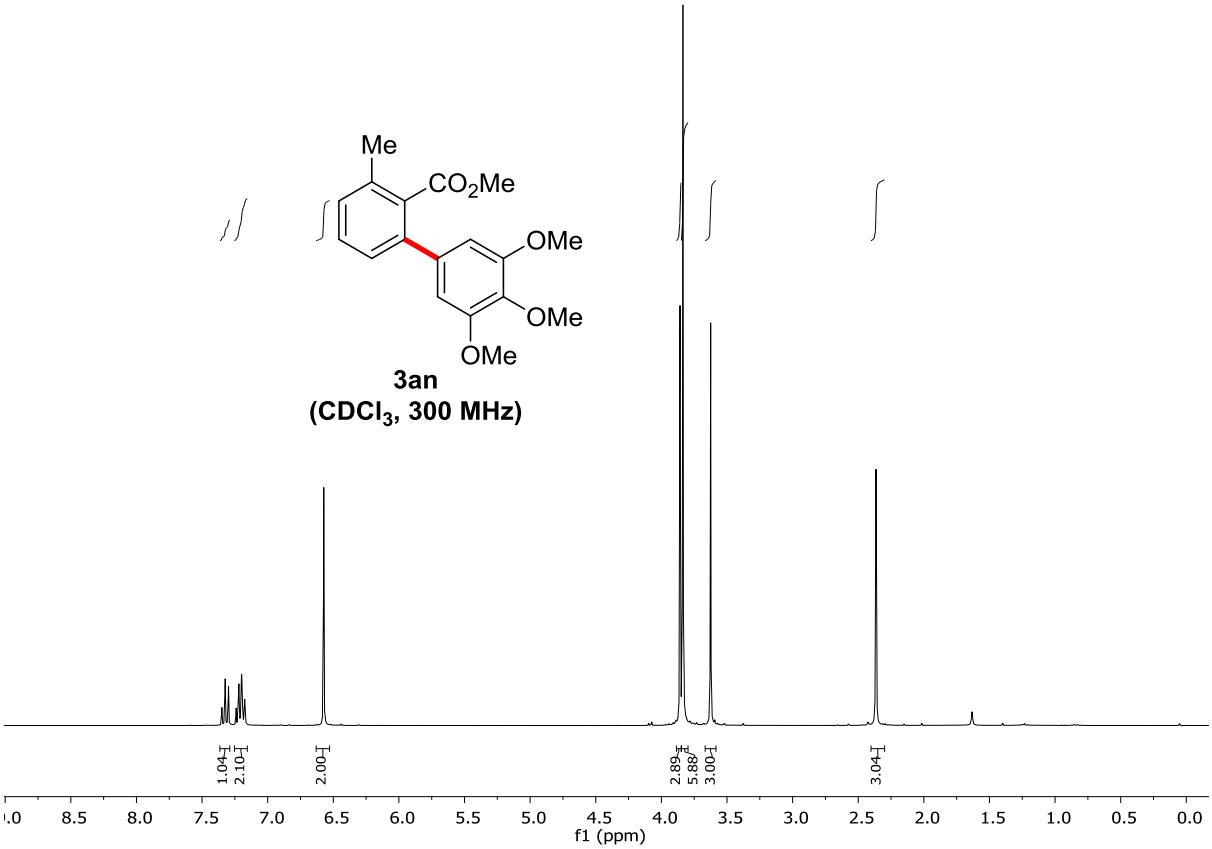

Me
CO2Me
F
F
3al
(CDCl3, 300 MHz)
1.03
1.10
0.99
1.88
1.02
3.00
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.62
164.44
164.27
161.15
160.98
144.27
144.14
144.01
137.83
137.80
137.76
135.85
132.94
130.06
129.60
126.82
111.49
111.38
111.27
111.16
103.11
102.78
102.44
77.42
77.00
76.57
51.98
19.66
Me
CO2Me
F
F
3al
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

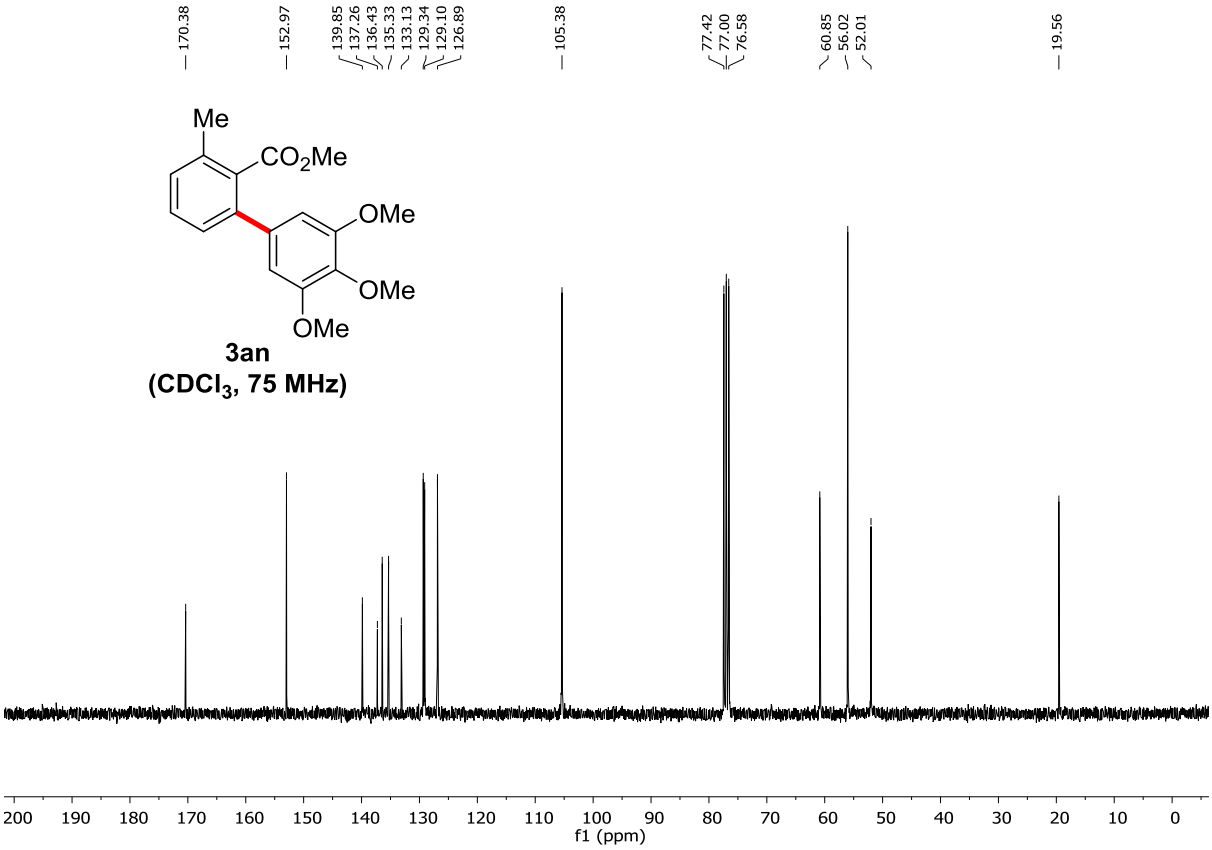

-109.798
-109.805
-109.822
-109.827
-109.838
-109.845
-109.852
-109.858
-109.876
-109.882
-109.898
-109.907
Me
CO2Me
F
F
3al
(CDCl3, 283 MHz)
-109.71 -109.78 -109.85 -109.92 -109.99
f1 (ppm)
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


Me
CO2Me
CO2Me
3am
(CDCl3, 300 MHz)
0.96
2.13
2.99
2.03
1.00
3.17
3.06
3.12
f1 (ppm)

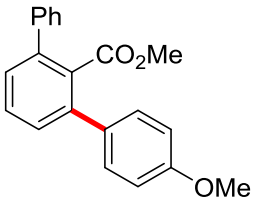

169.92
167.21
144.20
142.87
139.14
135.62
133.34
132.90
129.48
129.44
128.65
127.96
126.94
117.84
77.32
77.00
76.68
51.78
51.58
19.61
Me
CO2Me
CO2Me
3am
(CDCl3, 100 MHz)
f1 (ppm)



3an
($CDCl_3$, 300 MHz)

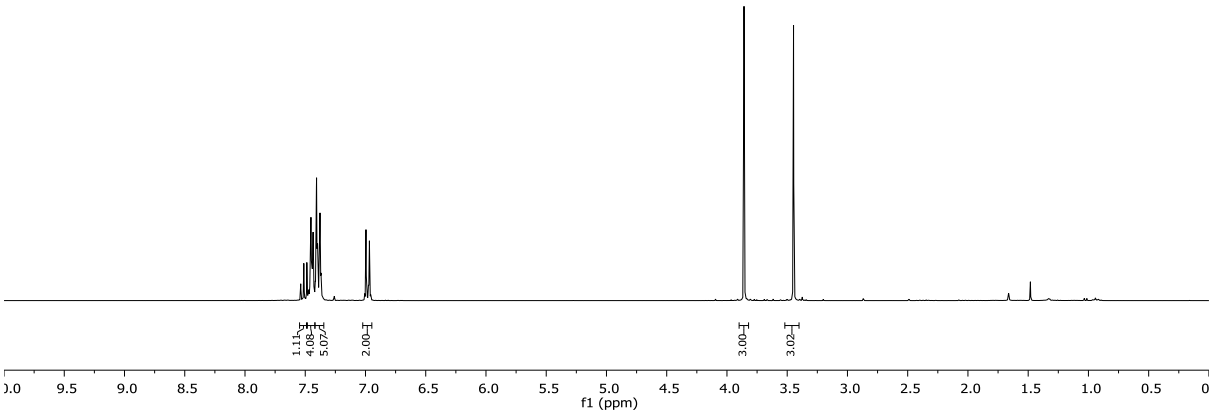


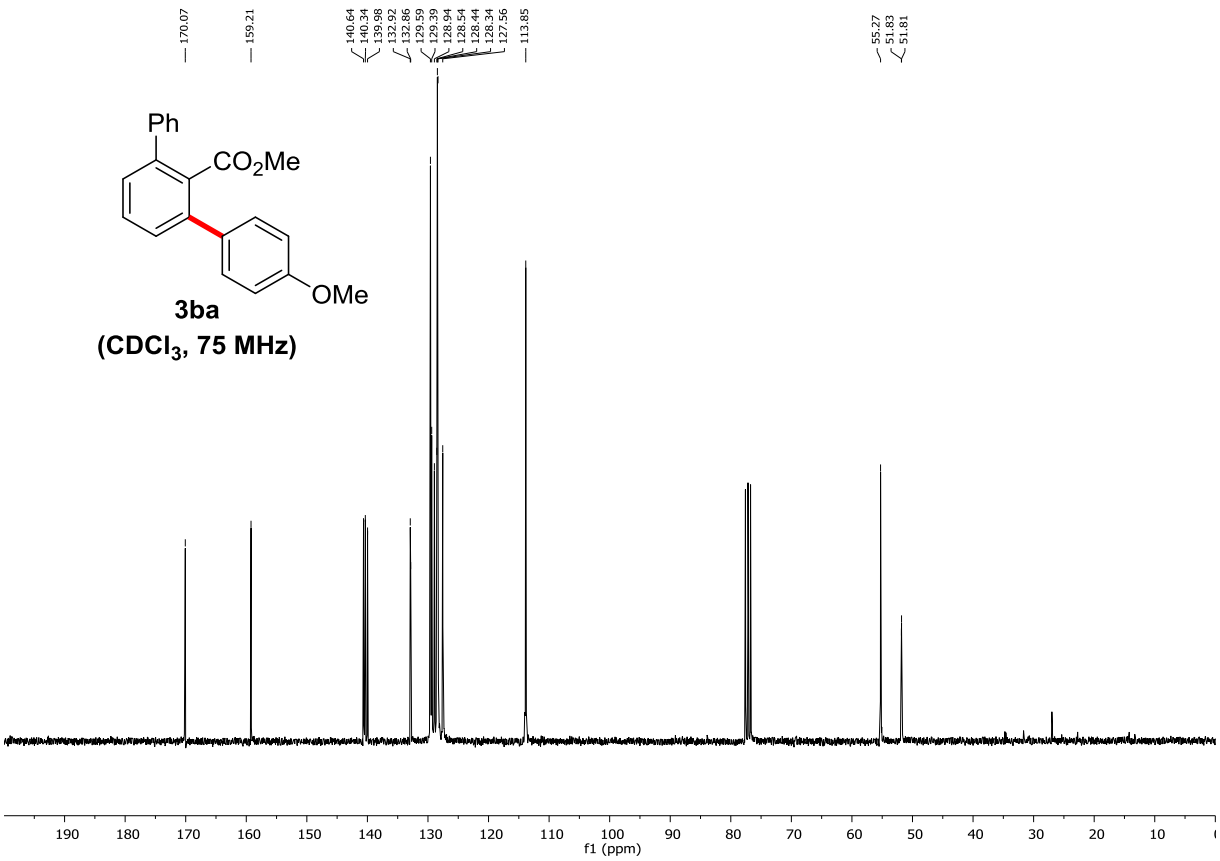
3an
($CDCl_3$, 75 MHz)



3ba

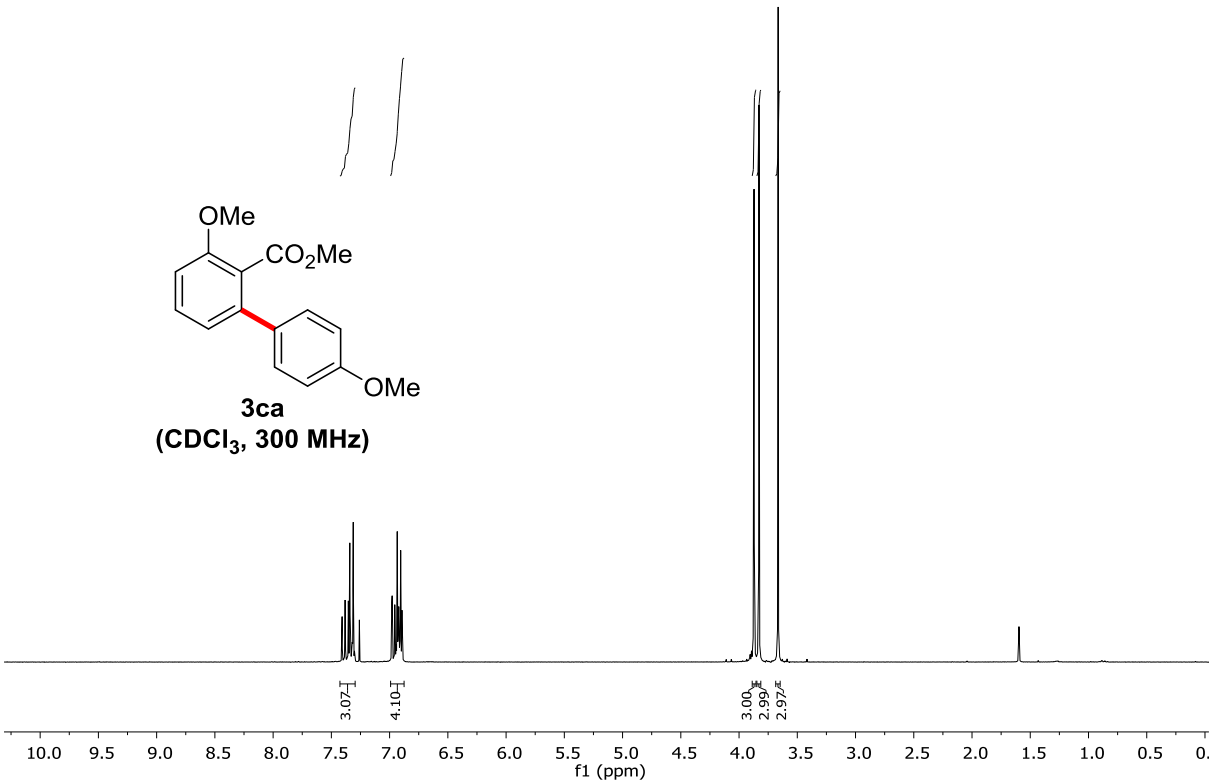
($CDCl_3$, 300 MHz)

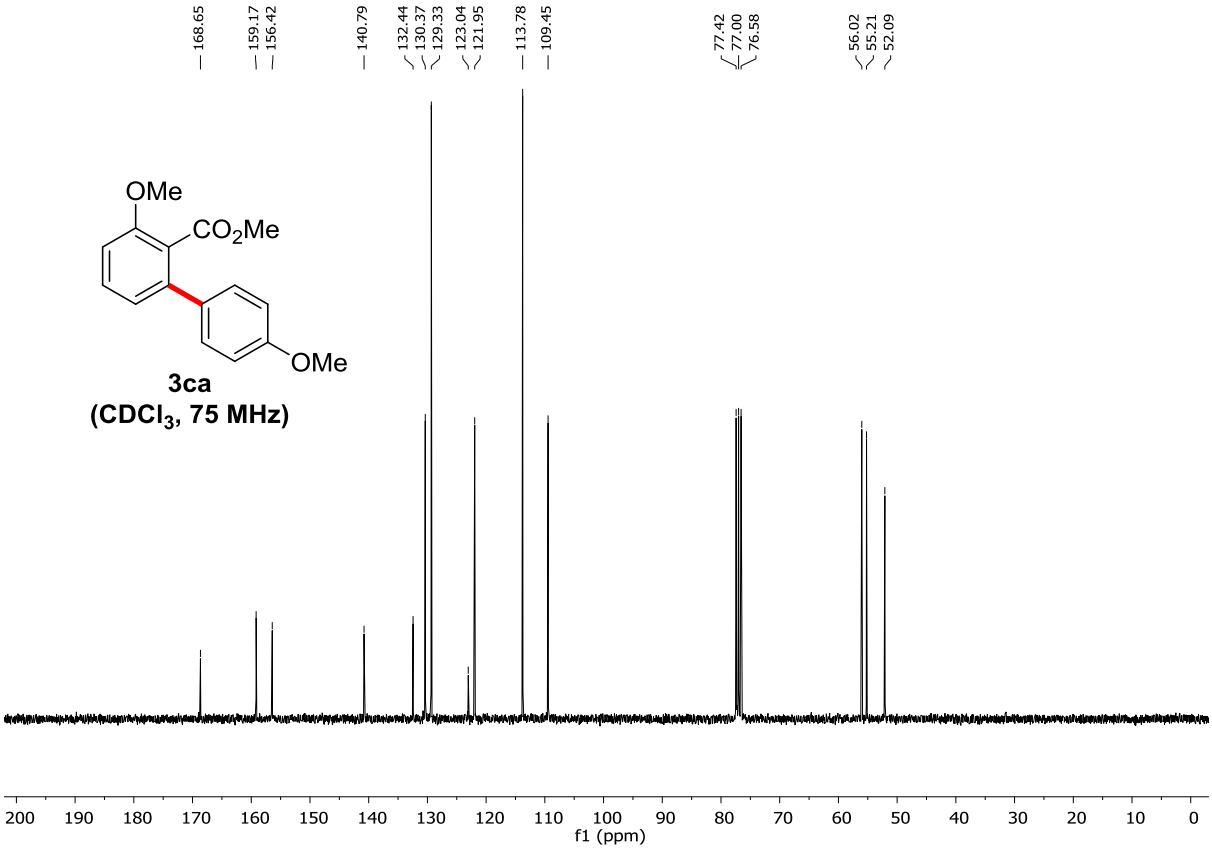


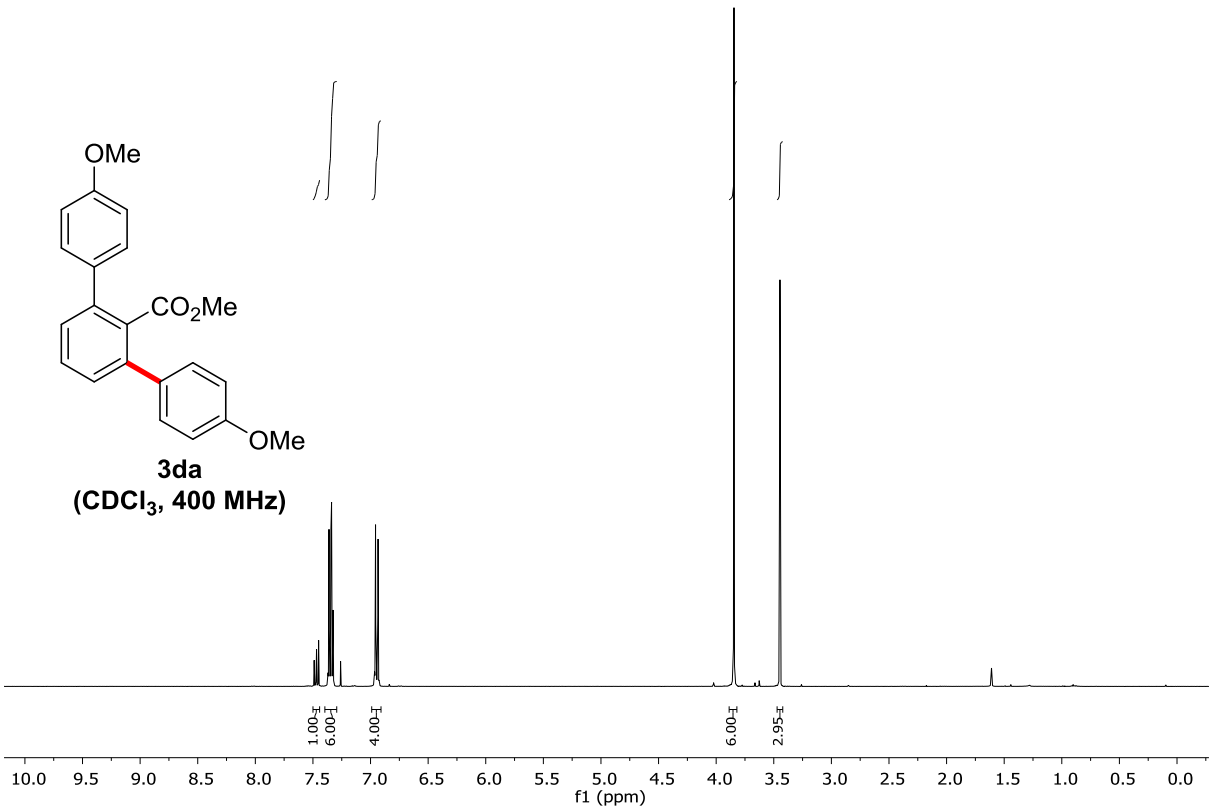


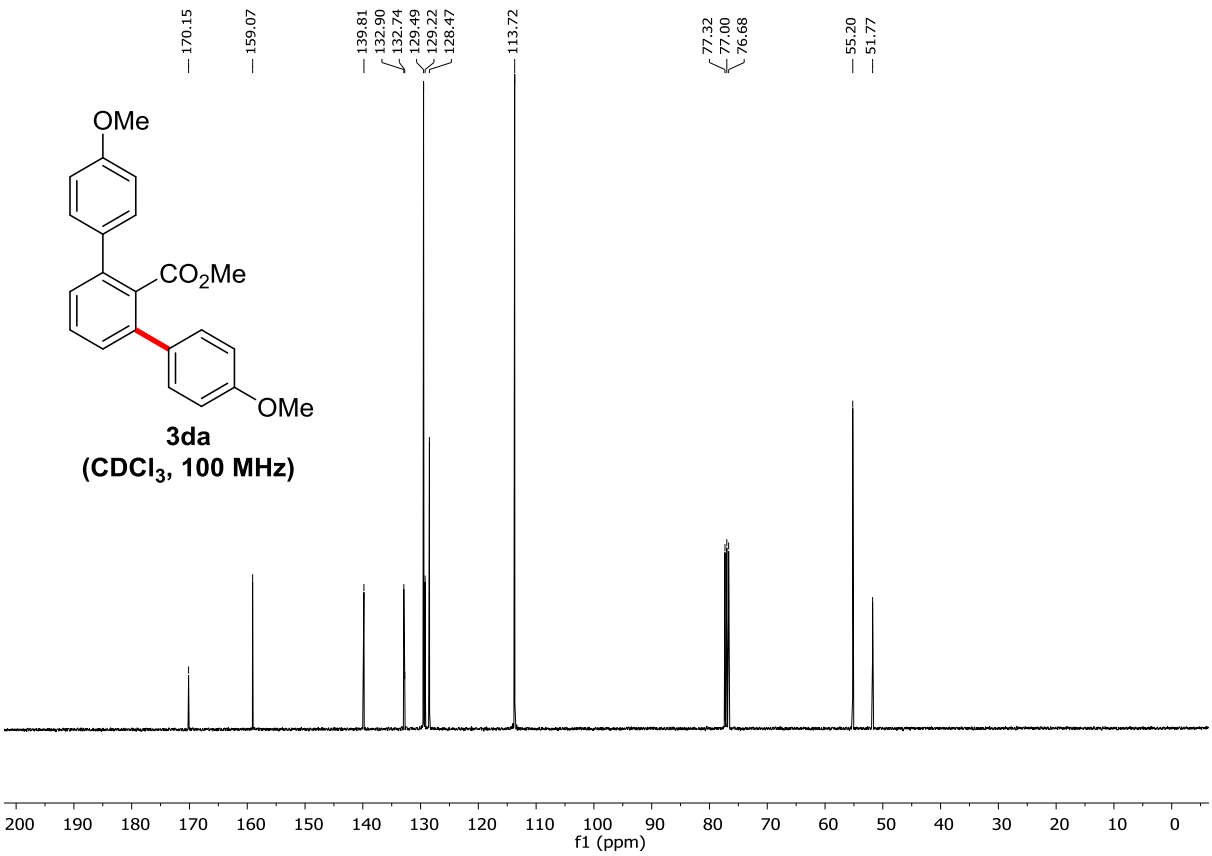
3ba

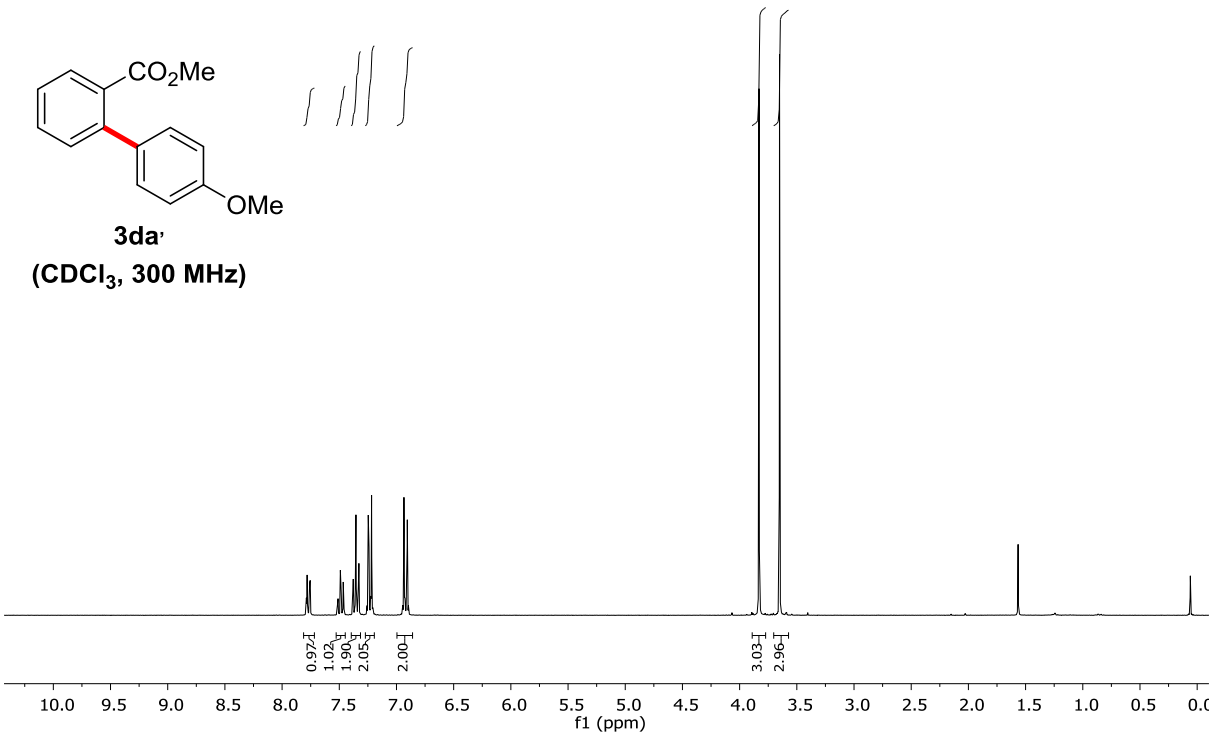
($CDCl_3$, 75 MHz)


OMe
CO2Me
OMe
3ca
(CDCl3, 300 MHz)
3.07
4.10
3.00
2.99
2.97
10.0 9.5 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.
f1 (ppm)


168.65
159.17
156.42
140.79
132.44
130.37
129.33
123.04
121.95
113.78
109.45
77.42
77.00
76.58
56.02
55.21
52.09
OMe
CO2Me
OMe
3ca
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

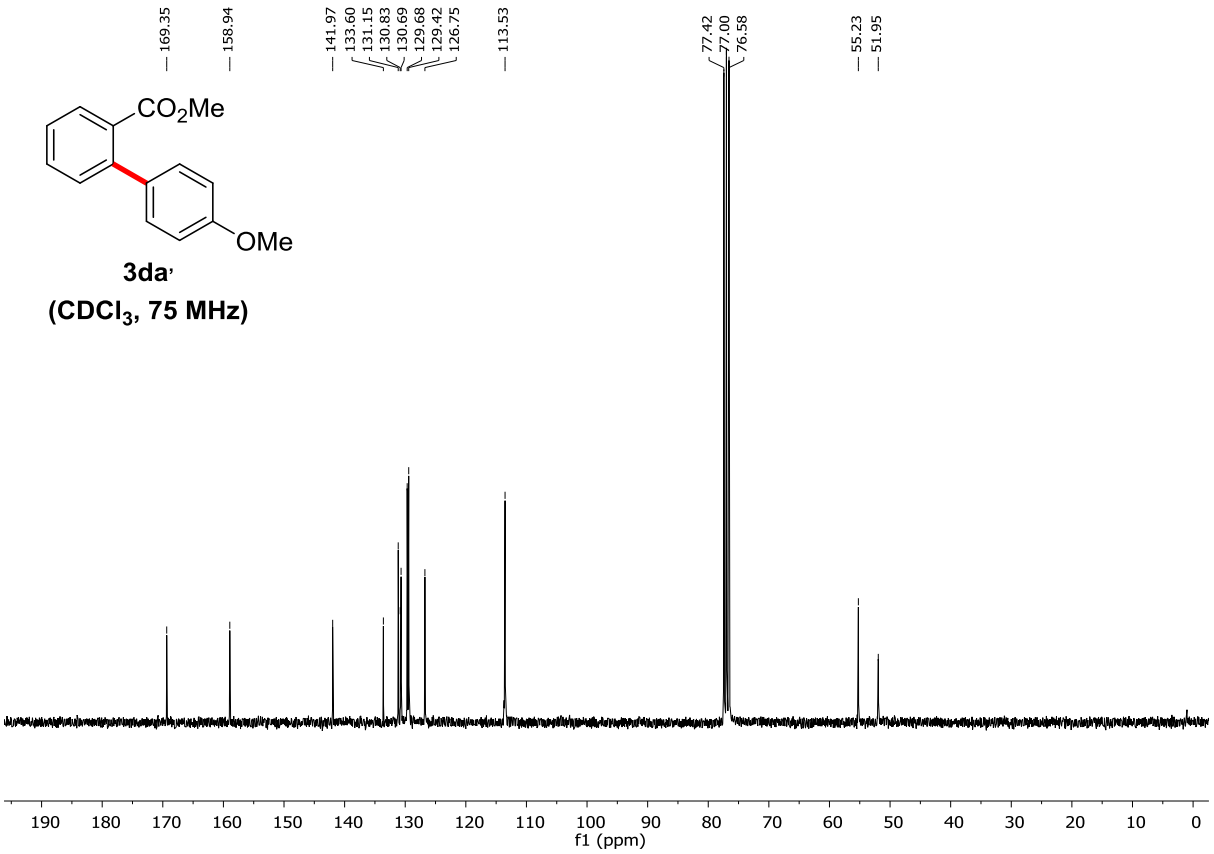

OMe
CO2Me
OMe
3da
(CDCl3, 400 MHz)
1.00
6.00
4.00
6.00
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.15
159.07
139.81
132.90
132.74
129.49
129.22
128.47
113.72
77.32
77.00
76.68
55.20
51.77
OMe
CO2Me
OMe
3da
(CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



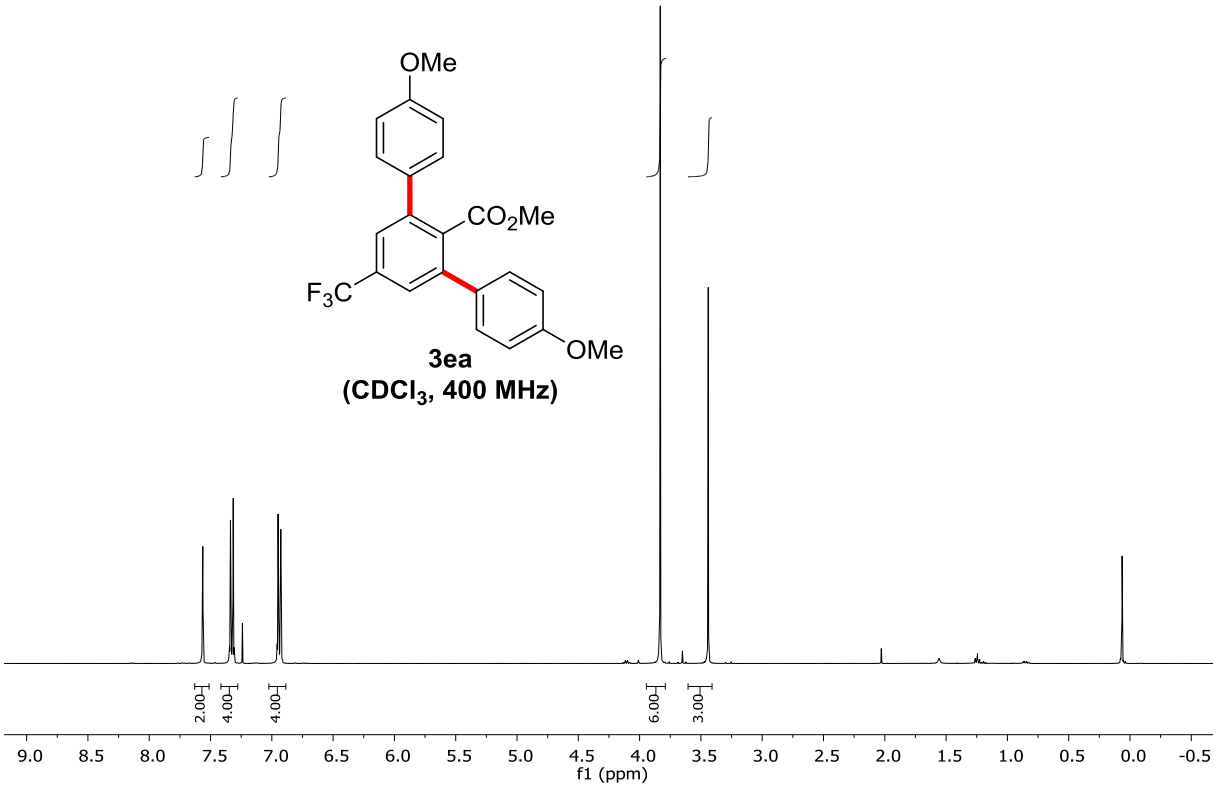
3da'

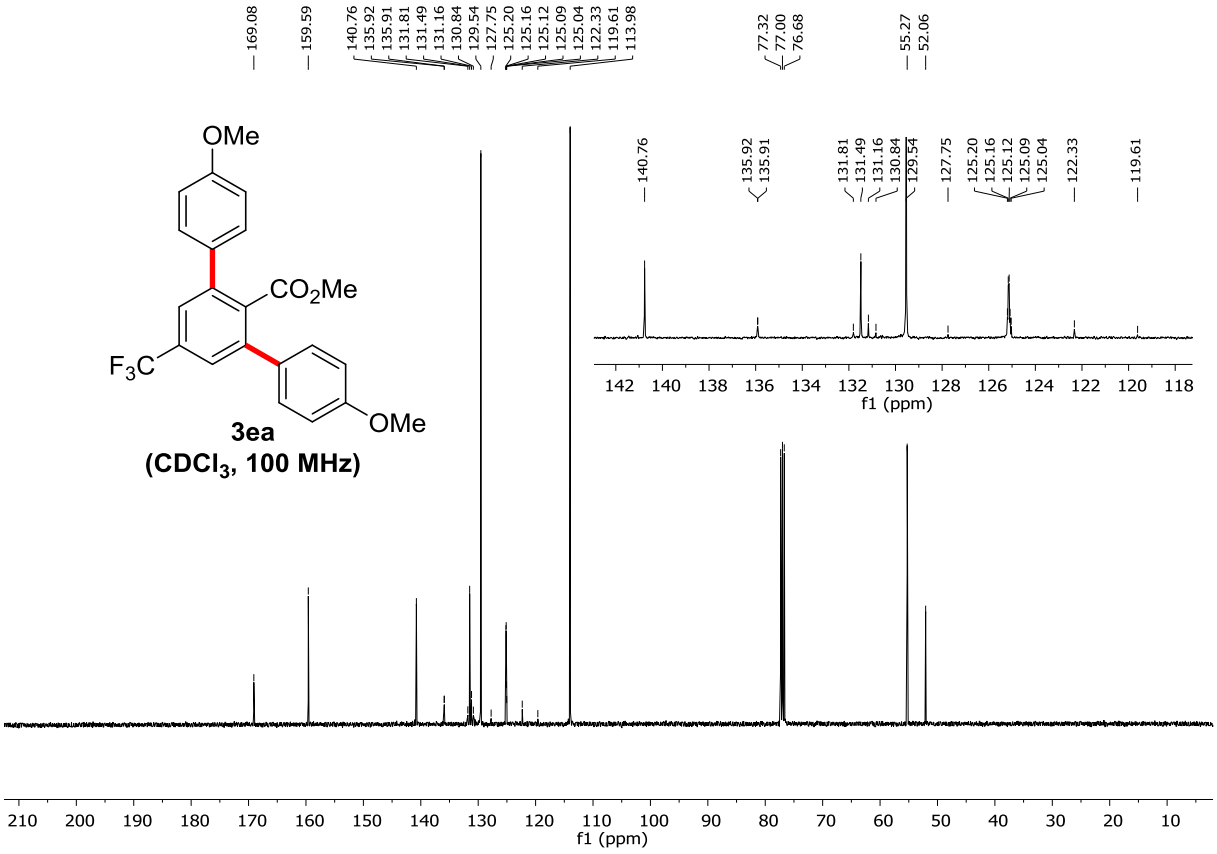
($CDCl_3$, 300 MHz)

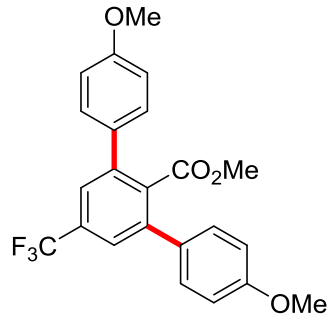


3da'

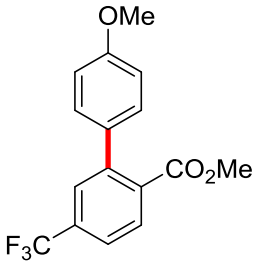
($CDCl_3$, 75 MHz)


OMe
CO2Me
F3C
OMe
3ea
(CDCl3, 400 MHz)
2.00
4.00
4.00
6.00
3.00
f1 (ppm)

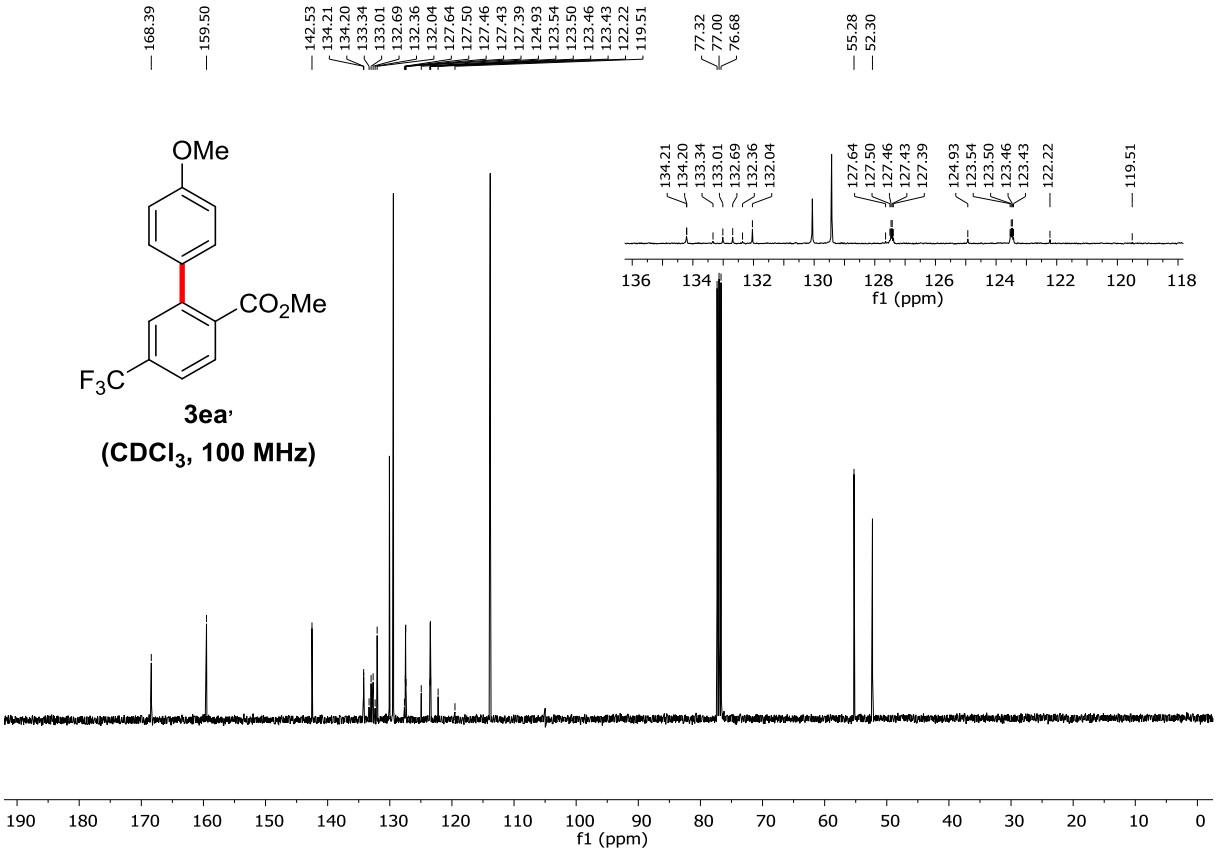

169.08
159.59
140.76
135.92
135.91
131.81
131.49
131.16
130.84
129.54
127.75
125.20
125.16
125.12
125.09
125.04
122.33
119.61
113.98
77.32
77.00
76.68
55.27
52.06
OMe
CO2Me
F3C
OMe
3ea
(CDCl3, 100 MHz)
f1 (ppm)

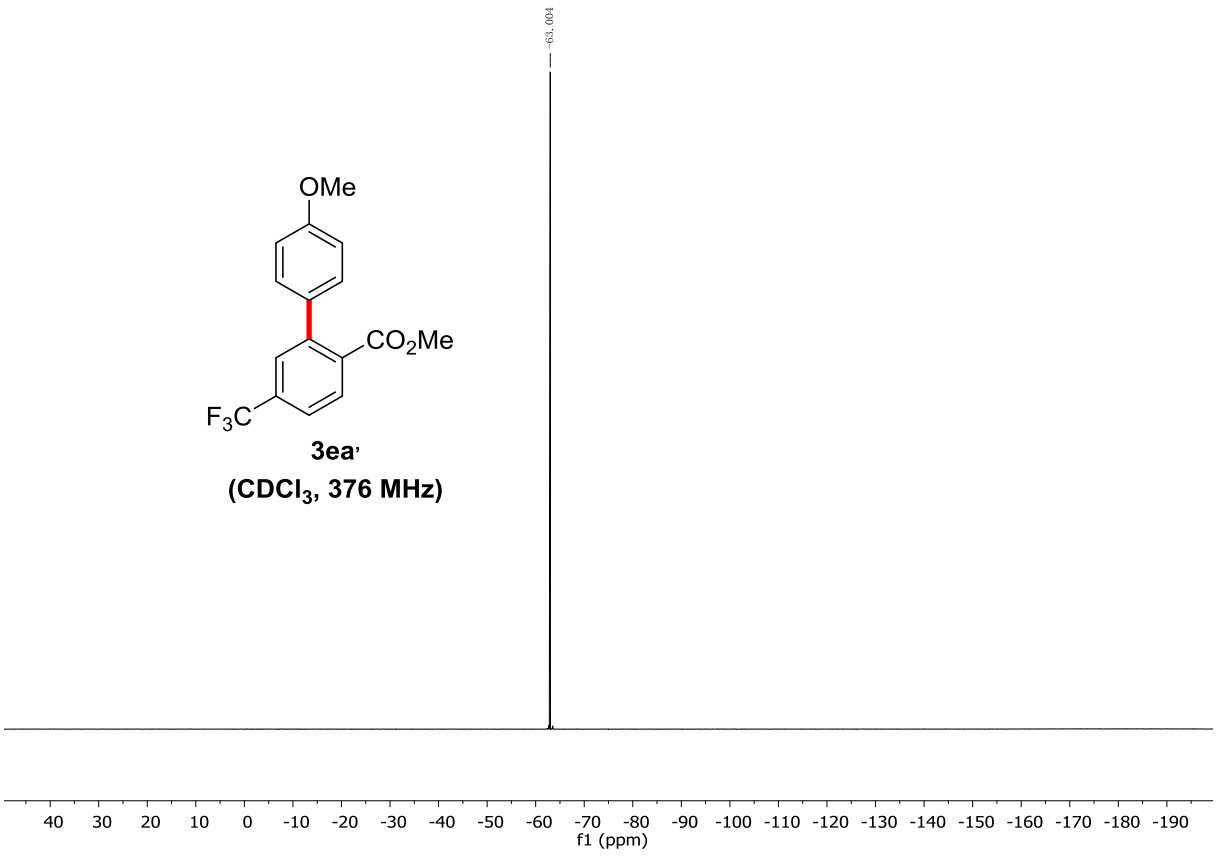


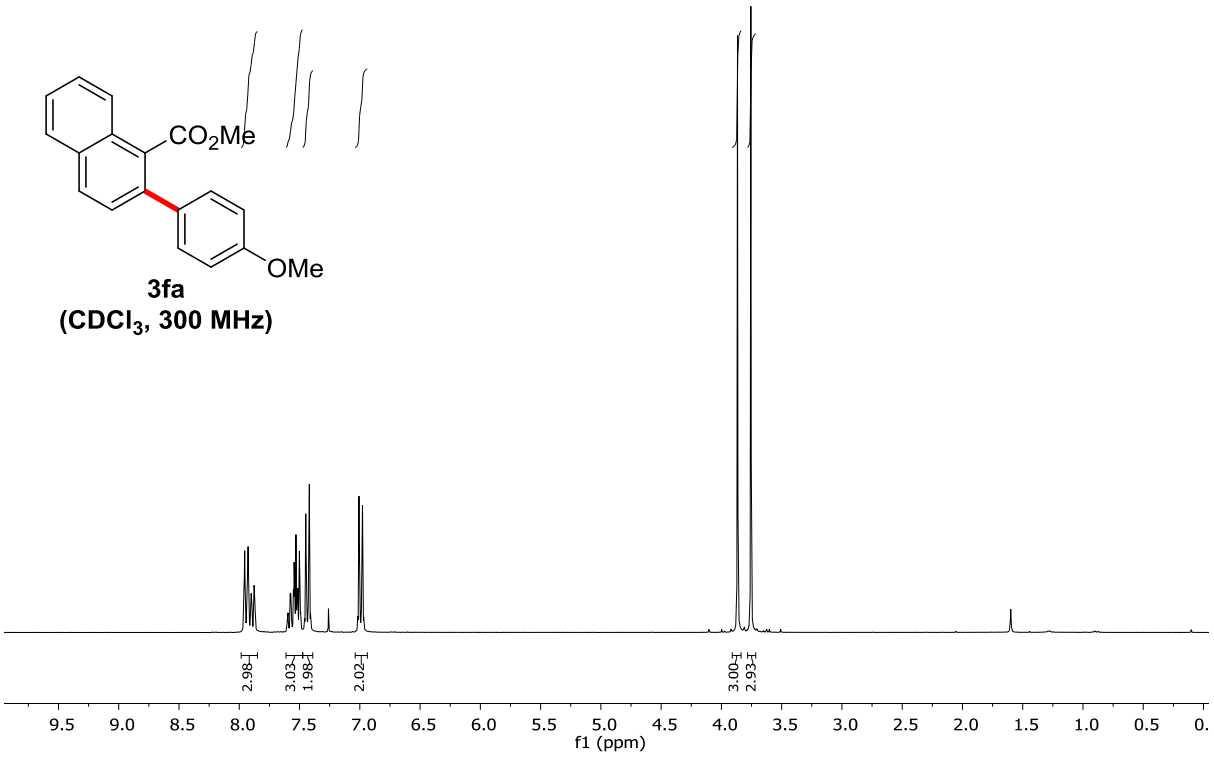
3ea
($CDCl_3$, 376 MHz)

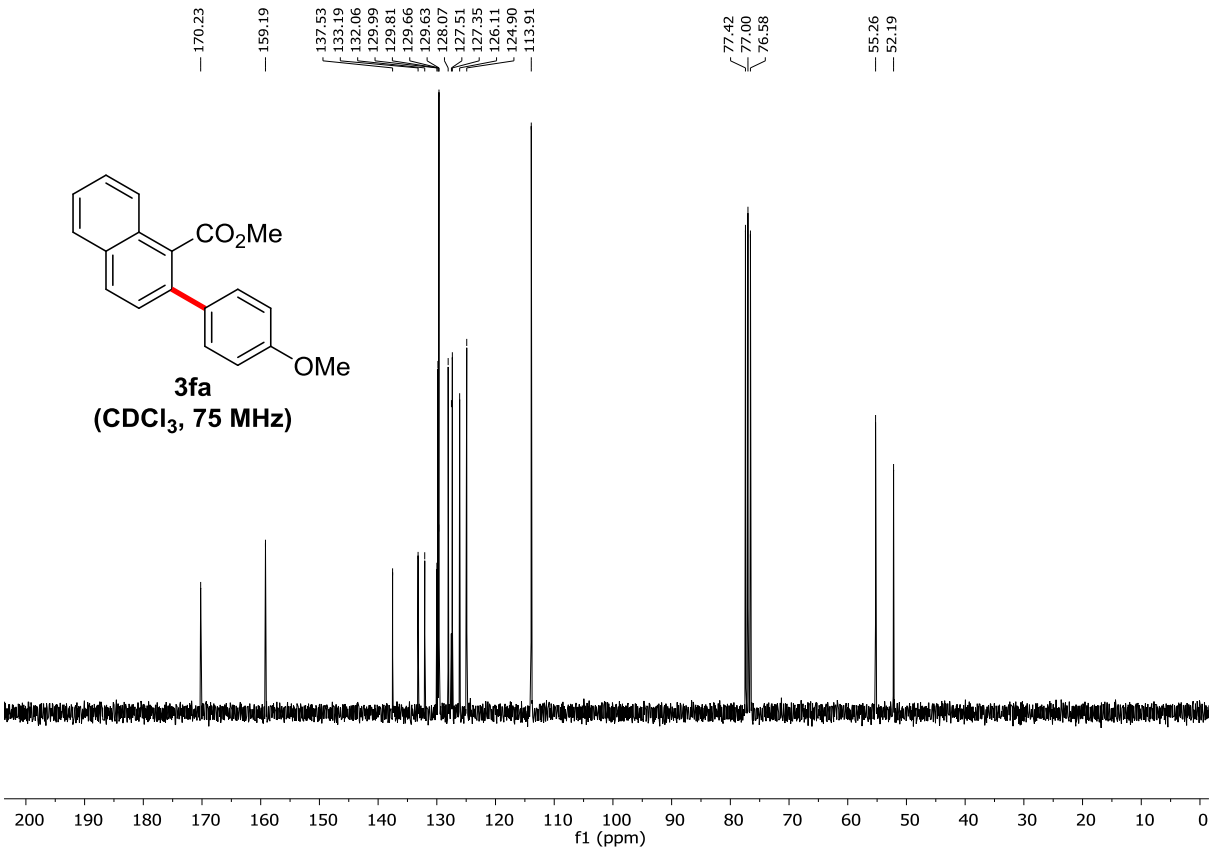


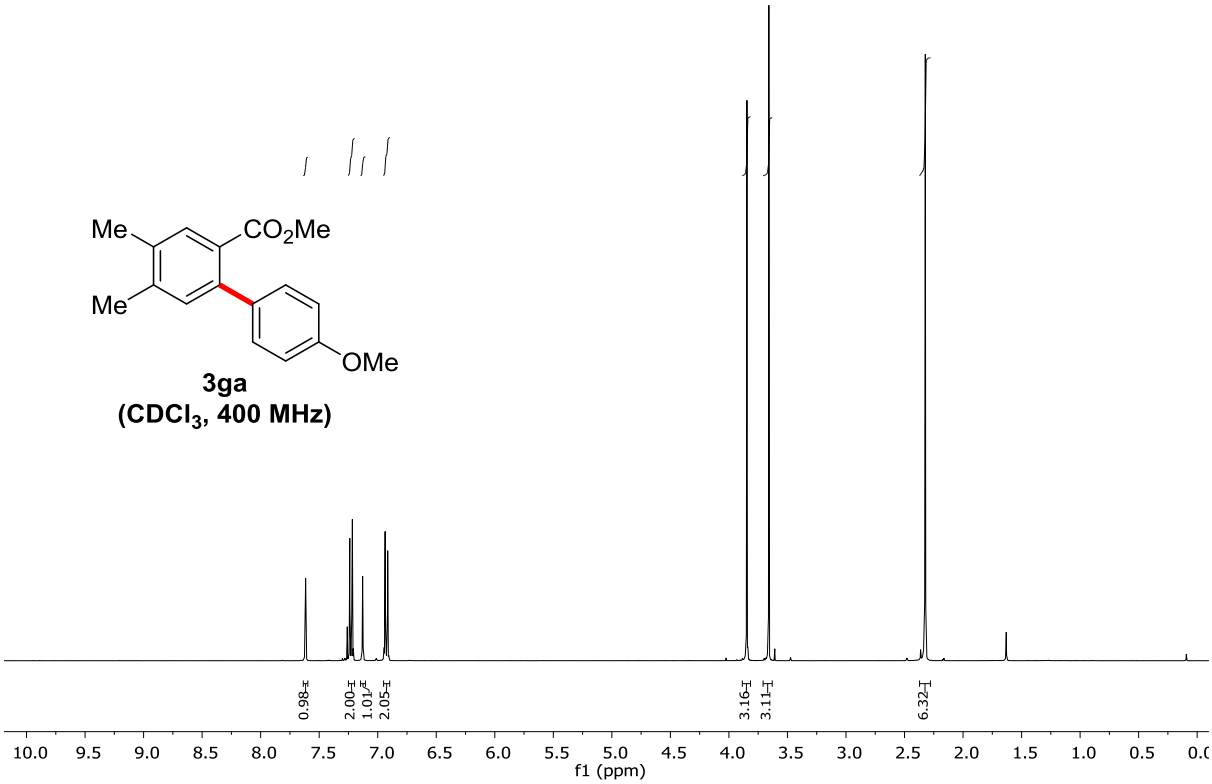
3ea'
($CDCl_3$, 400 MHz)

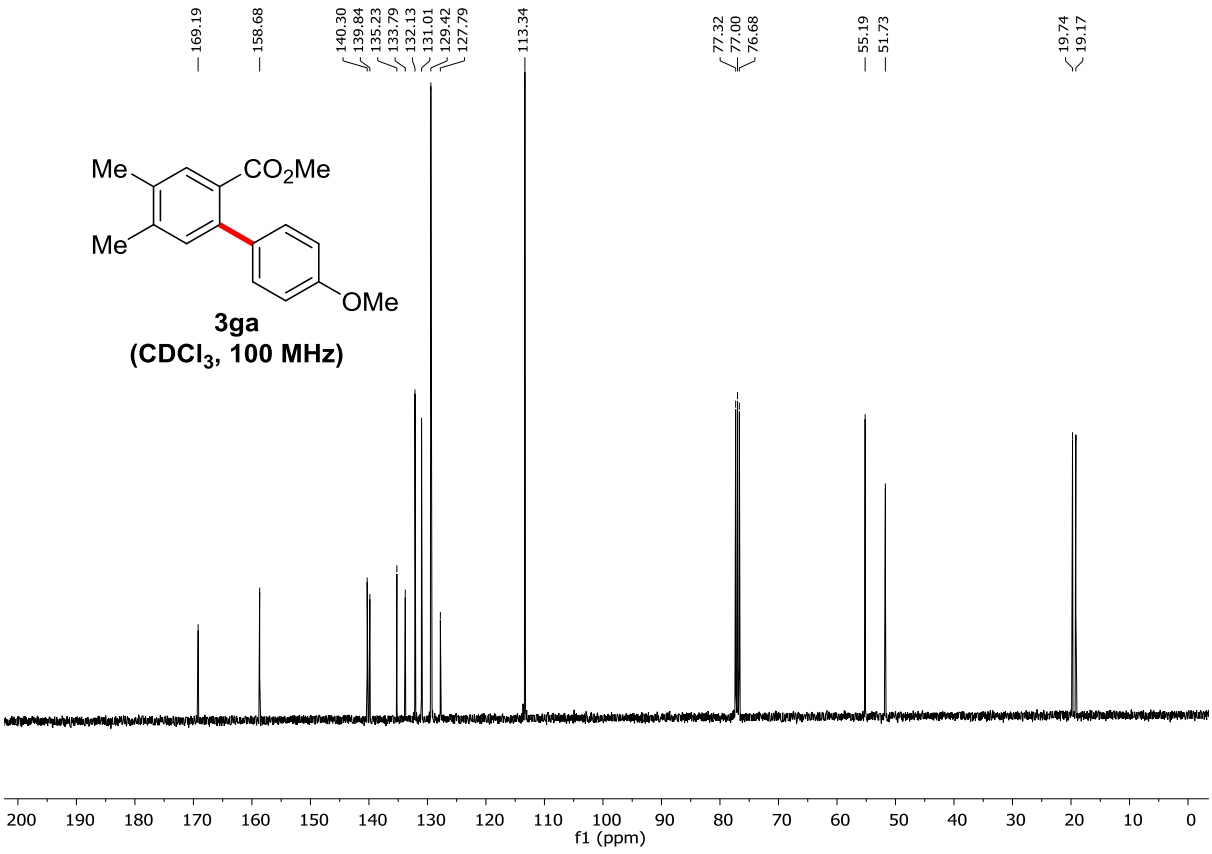

168.39
159.50
142.53
134.21
134.20
133.34
133.01
132.69
132.36
132.04
127.64
127.50
127.46
127.43
127.39
124.93
123.54
123.50
123.46
123.43
122.22
119.51
77.32
77.00
76.68
55.28
52.30
OMe
CO2Me
F3C
3ea'
(CDCl3, 100 MHz)
f1 (ppm)

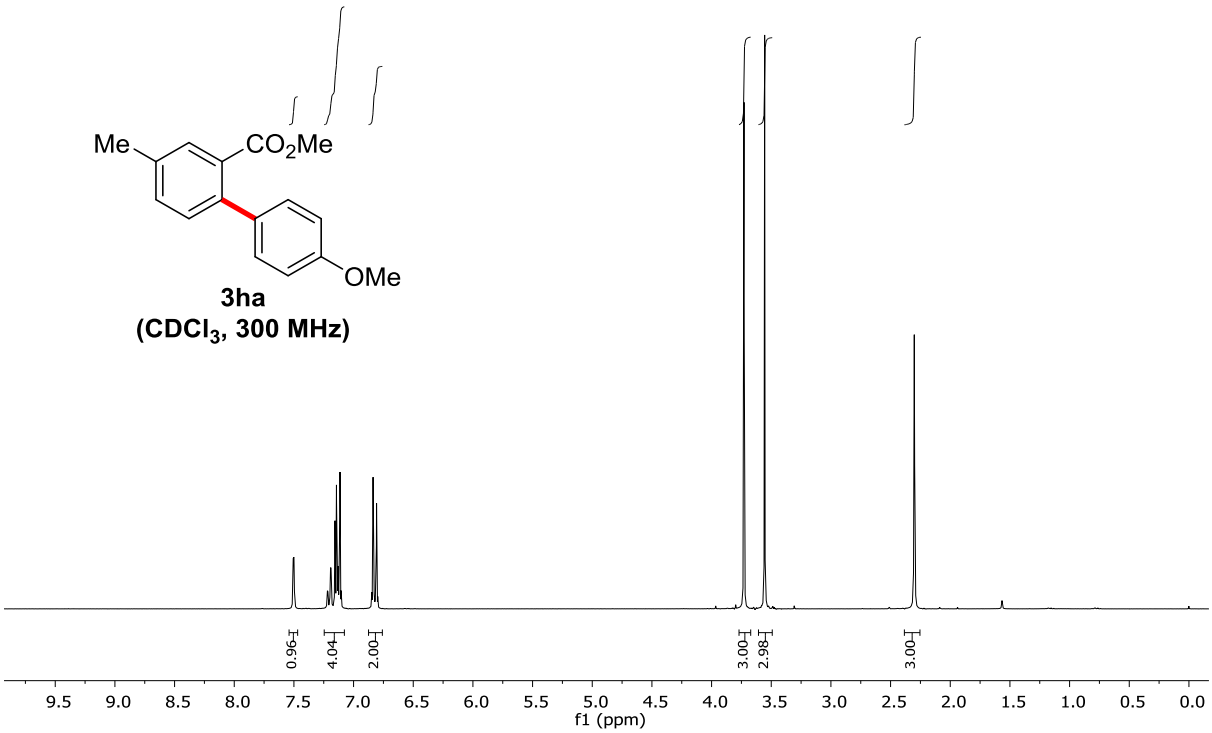

-63.004
OMe
CO2Me
F3C
3ea'
(CDCl3, 376 MHz)
f1 (ppm)

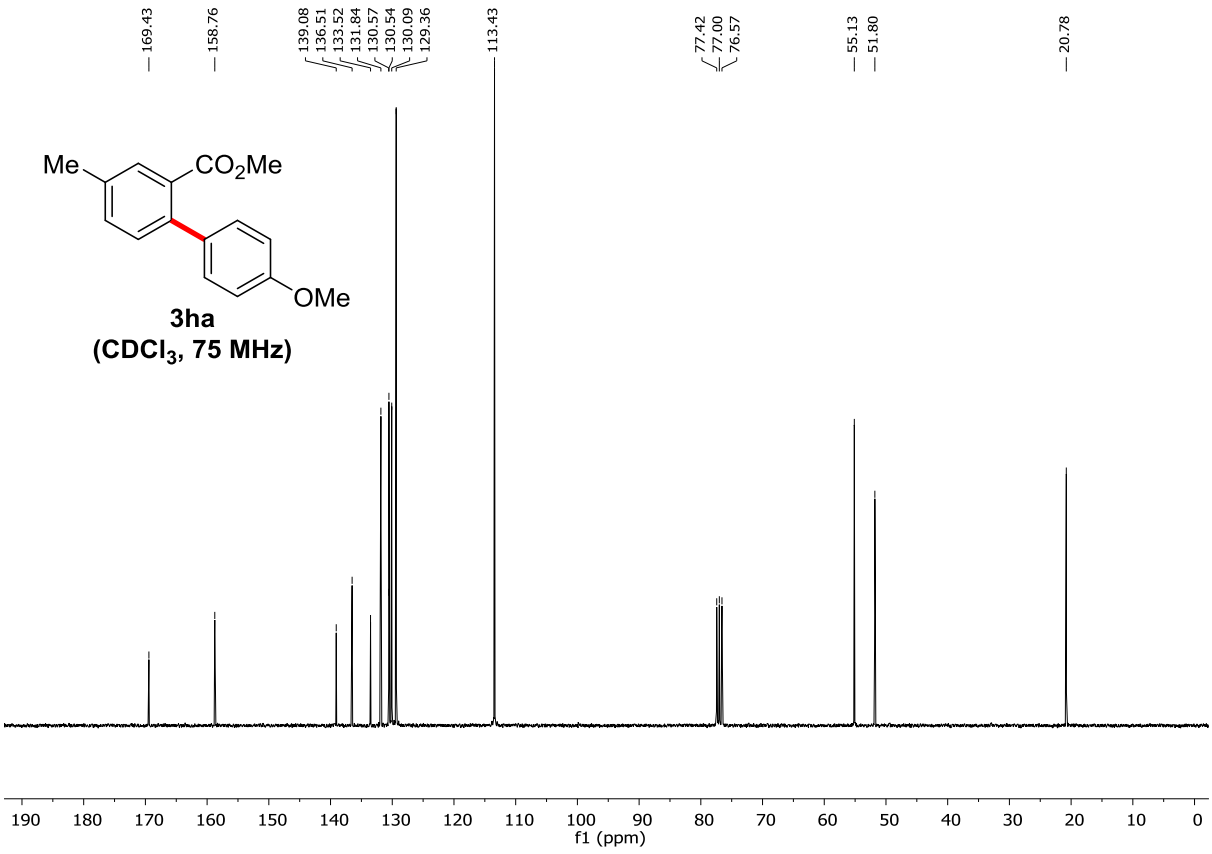

CO2Me
OMe
3fa
(CDCl3, 300 MHz)
2.98
3.03
1.98
2.02
3.00
2.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

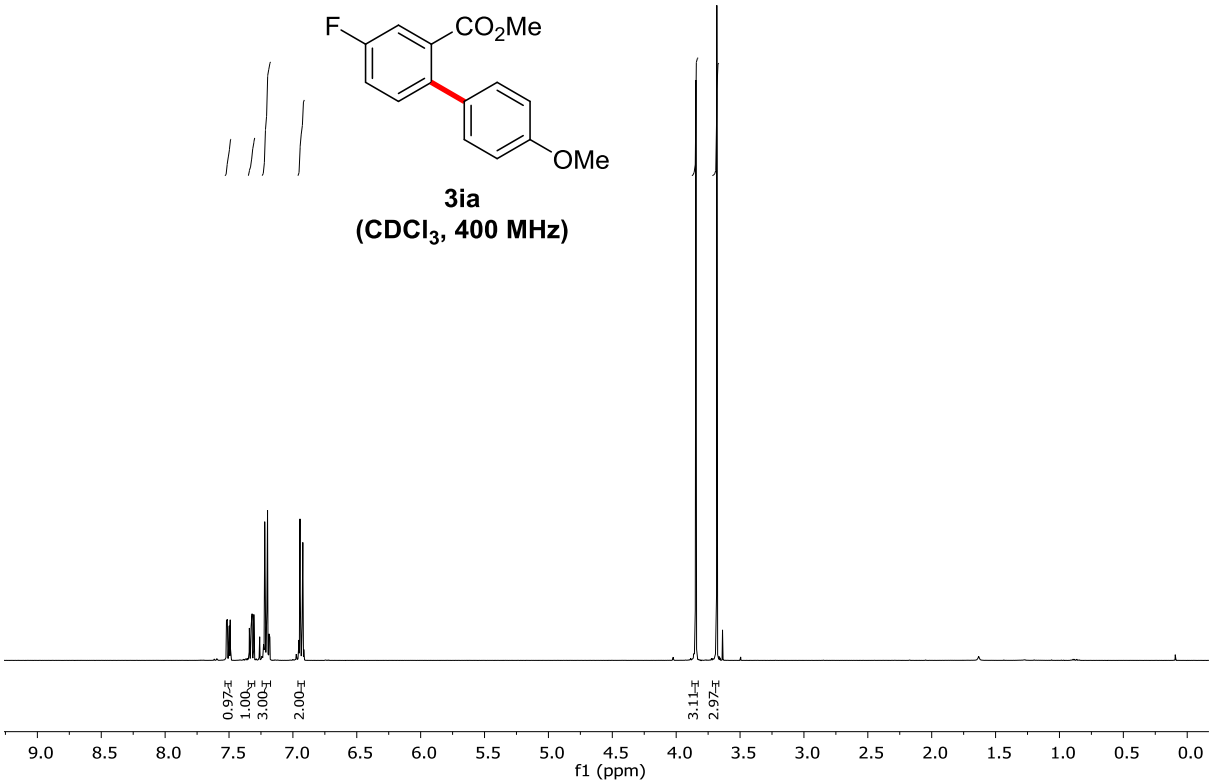

170.23
159.19
137.53
133.19
132.06
129.99
129.81
129.66
129.63
128.07
127.51
127.35
126.11
124.90
113.91
77.42
77.00
76.58
55.26
52.19
CO2Me
OMe
3fa
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CO2Me
Me
OMe
3ga
(CDCl3, 400 MHz)
0.98
2.00
1.01
2.05
3.16
3.11
6.32
10.0 9.5 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)

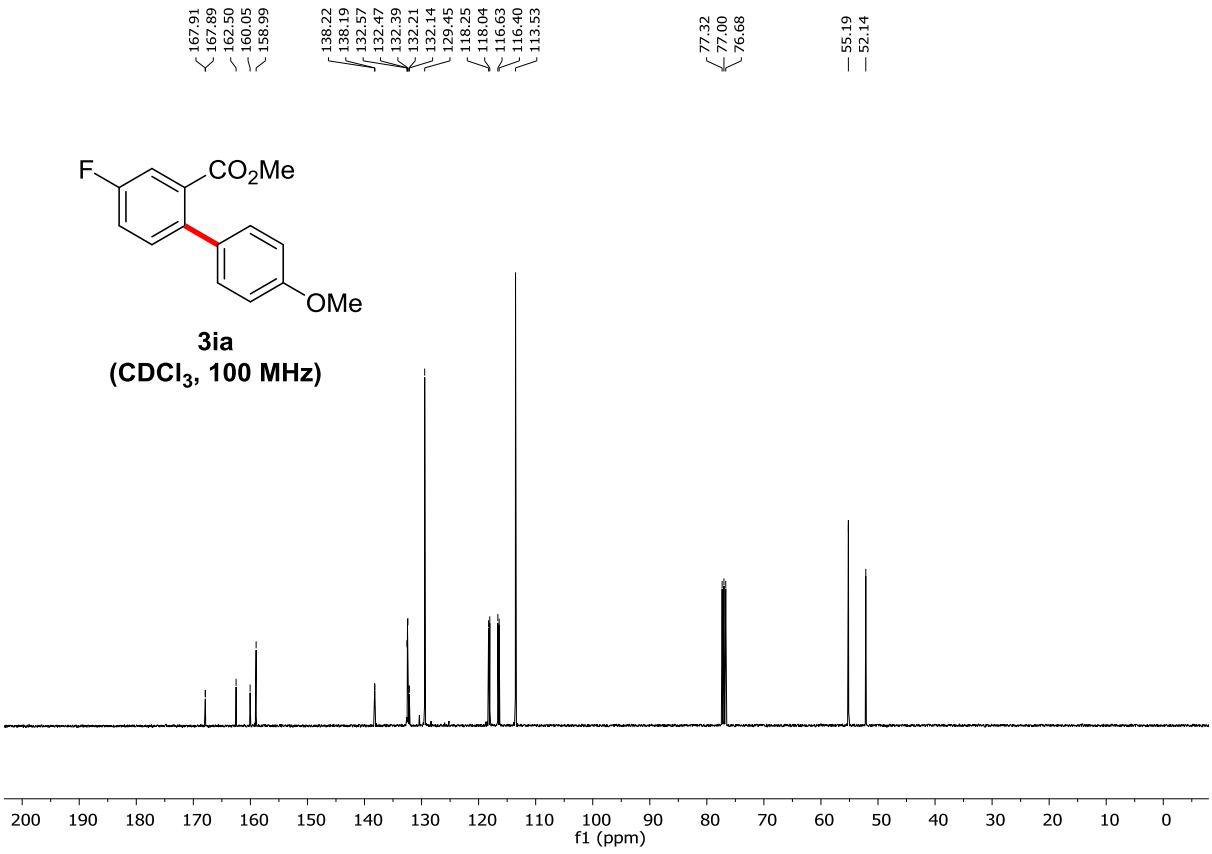

169.19
158.68
140.30
139.84
135.23
133.79
132.13
131.01
129.42
127.79
113.34
77.32
77.00
76.68
55.19
51.73
19.74
19.17
Me
CO2Me
Me
OMe
3ga
(CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CO2Me
OMe
3ha
(CDCl3, 300 MHz)
0.96
4.04
2.00
3.00
2.98
3.00
9.5 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)

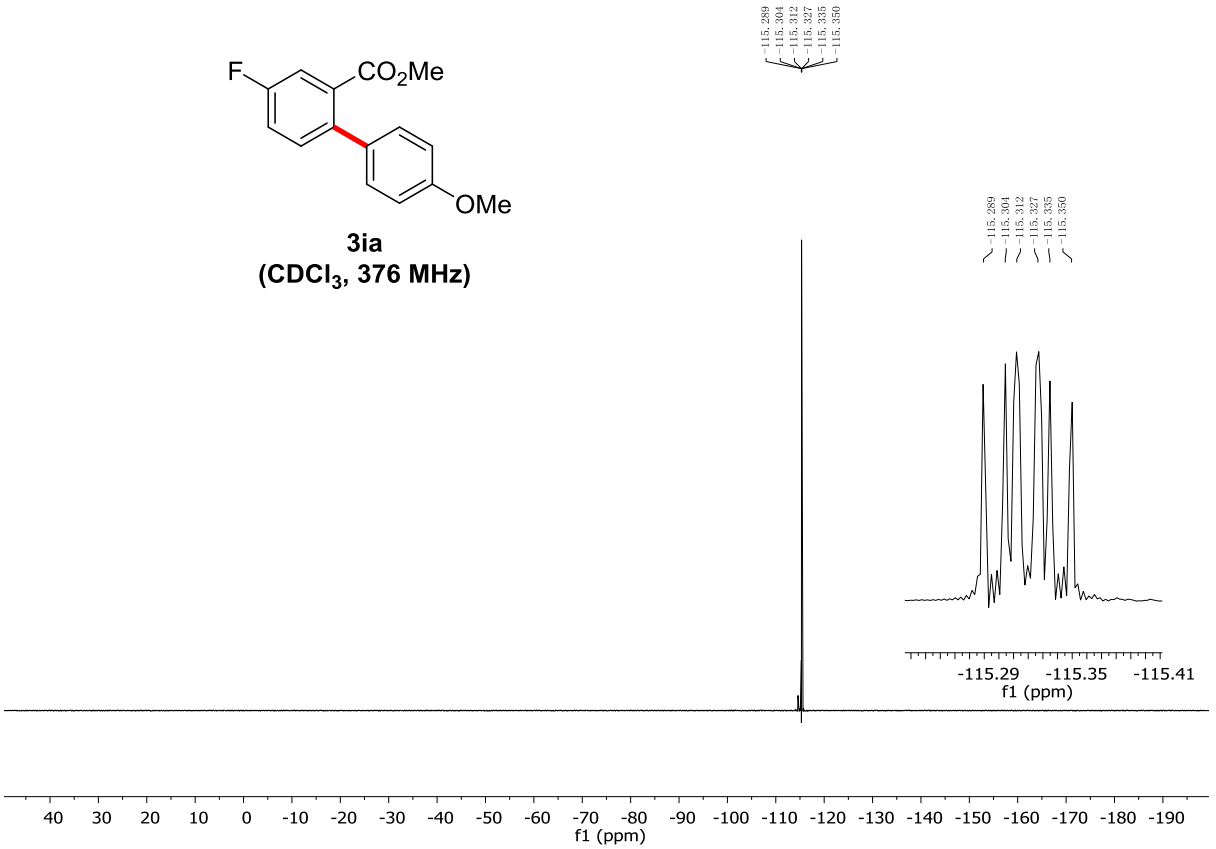

169.43
158.76
139.08
136.51
133.52
131.84
130.57
130.54
130.09
129.36
113.43
77.42
77.00
76.57
55.13
51.80
20.78
Me
CO2Me
OMe
3ha
(CDCl3, 75 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

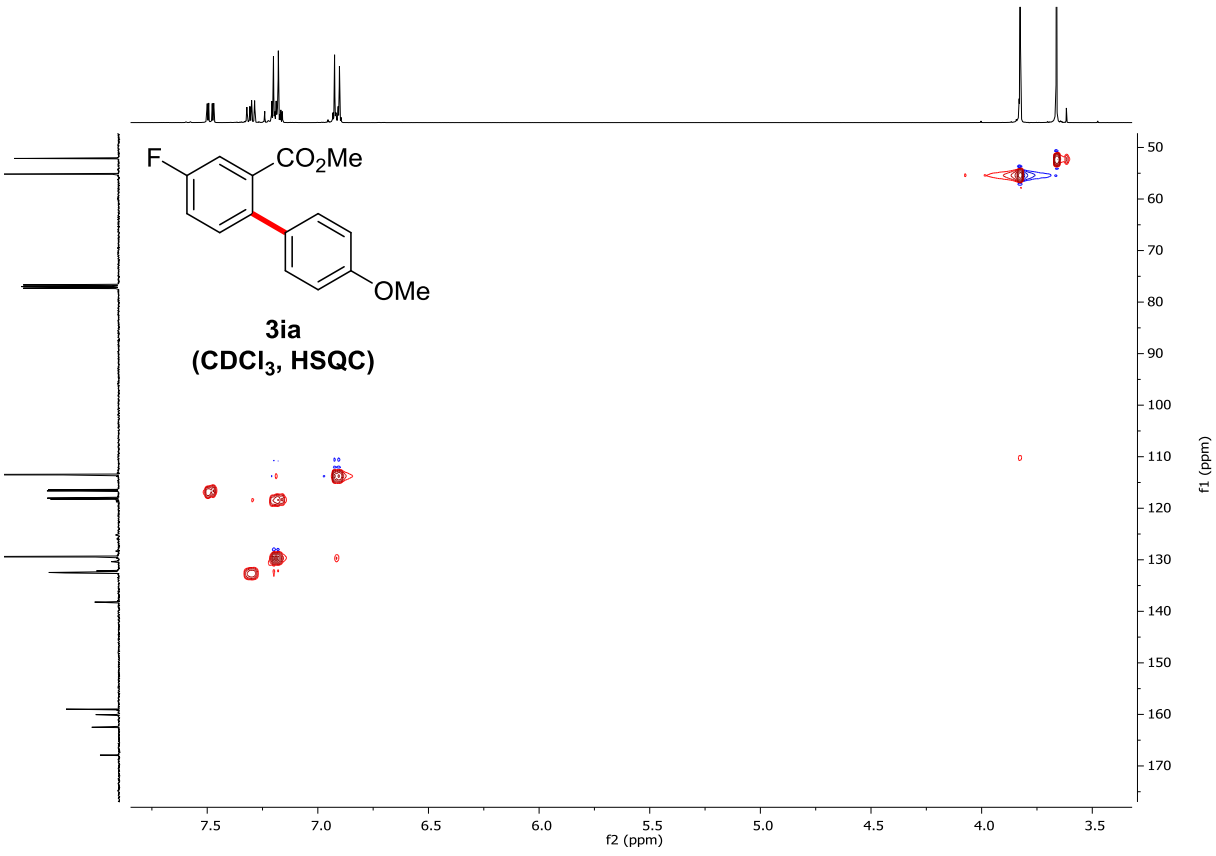


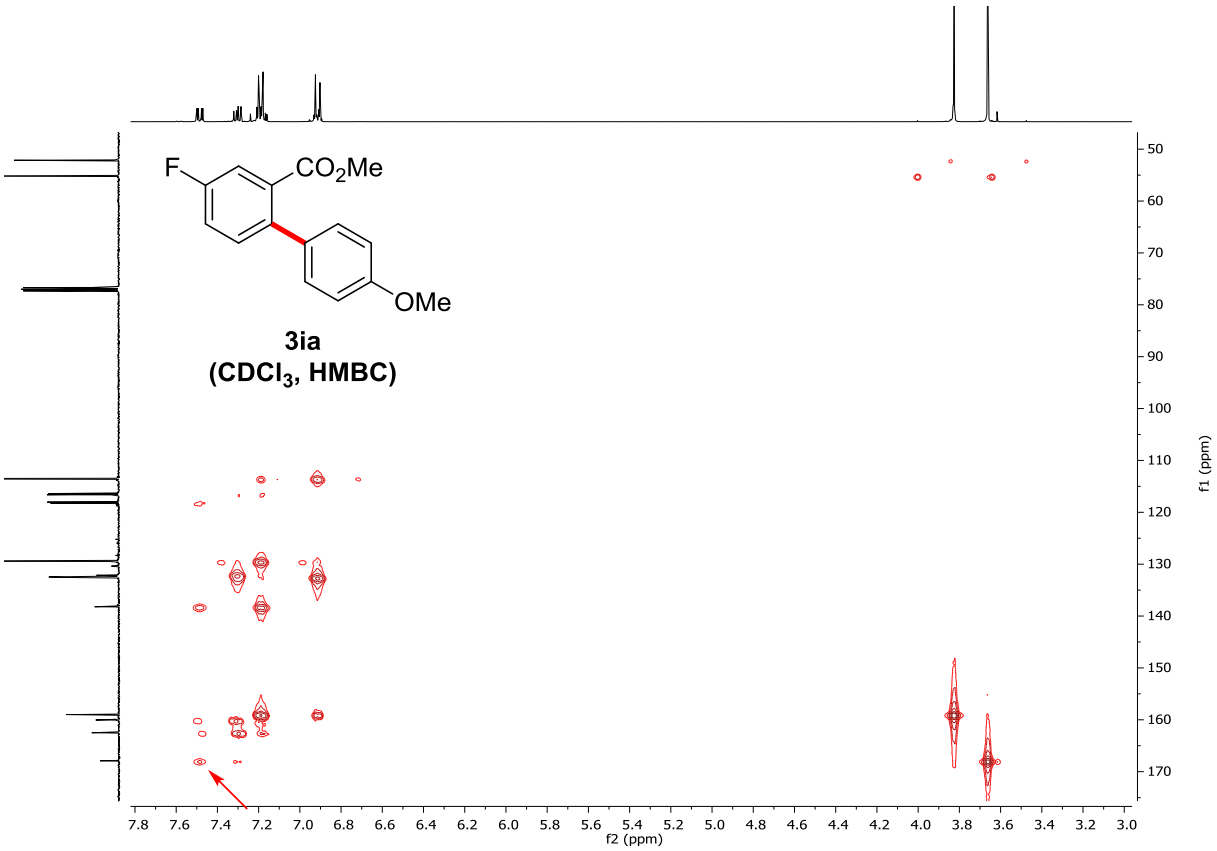
3ia
($CDCl_3$, 400 MHz)



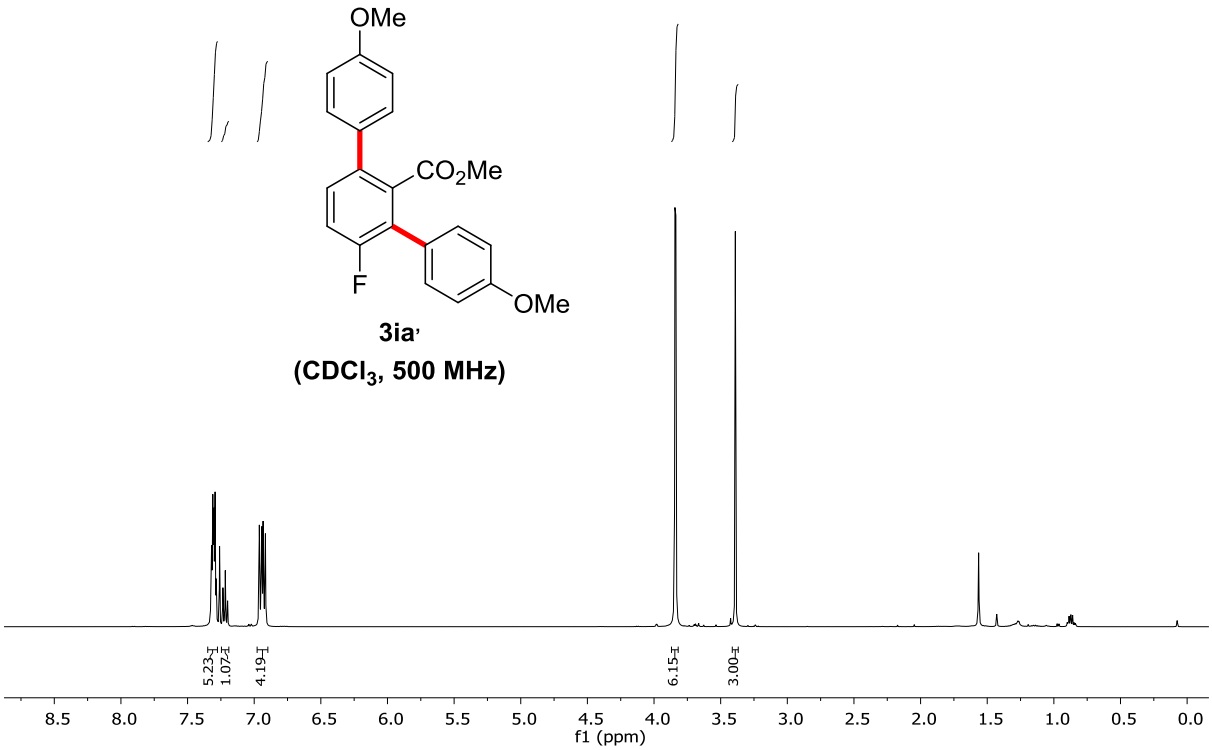
3ia
($CDCl_3$, 100 MHz)


F
CO2Me
OMe
3ia
(CDCl3, 376 MHz)
-115.289
-115.304
-115.312
-115.327
-115.335
-115.350
-115.29
-115.35
-115.41
f1 (ppm)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

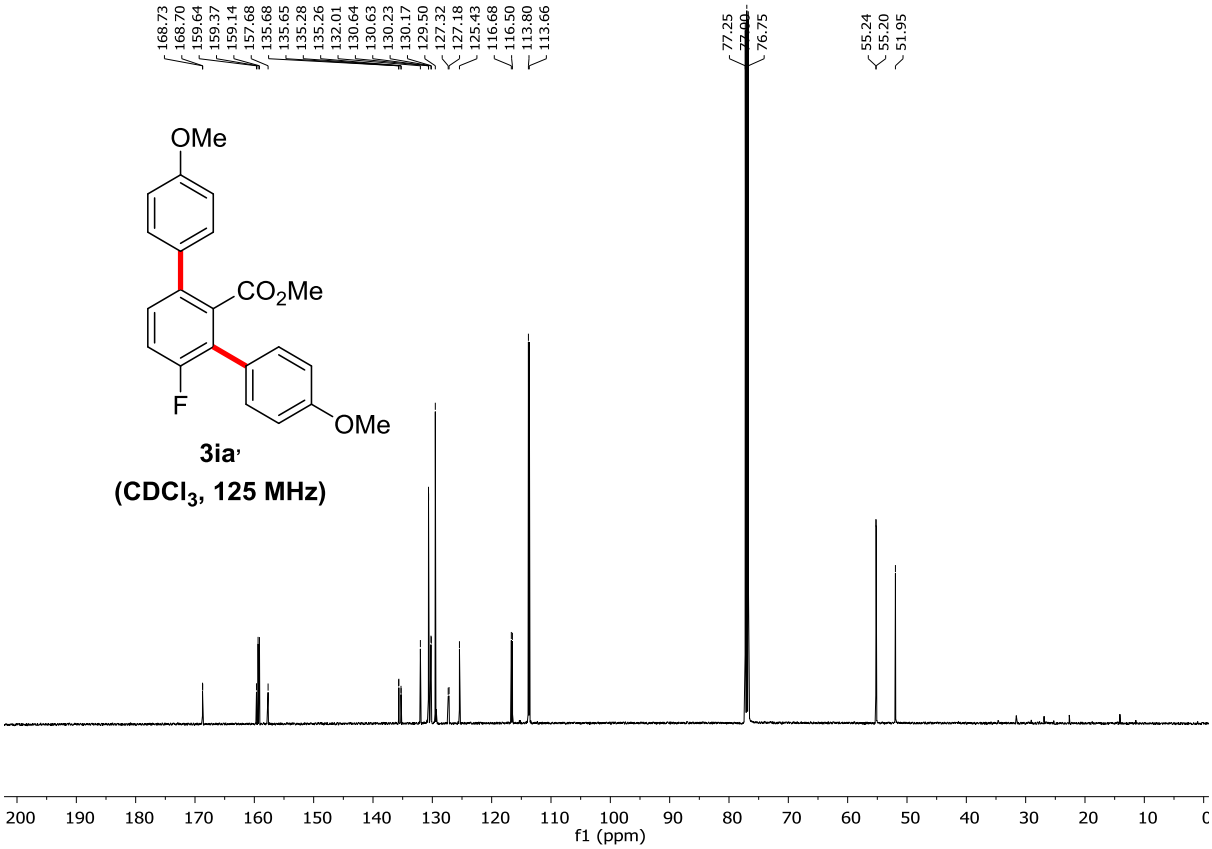

F
CO2Me
OMe
3ia
(CDCl3, HSQC)
50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
f2 (ppm)



3ia
($CDCl_3$, HMBC)

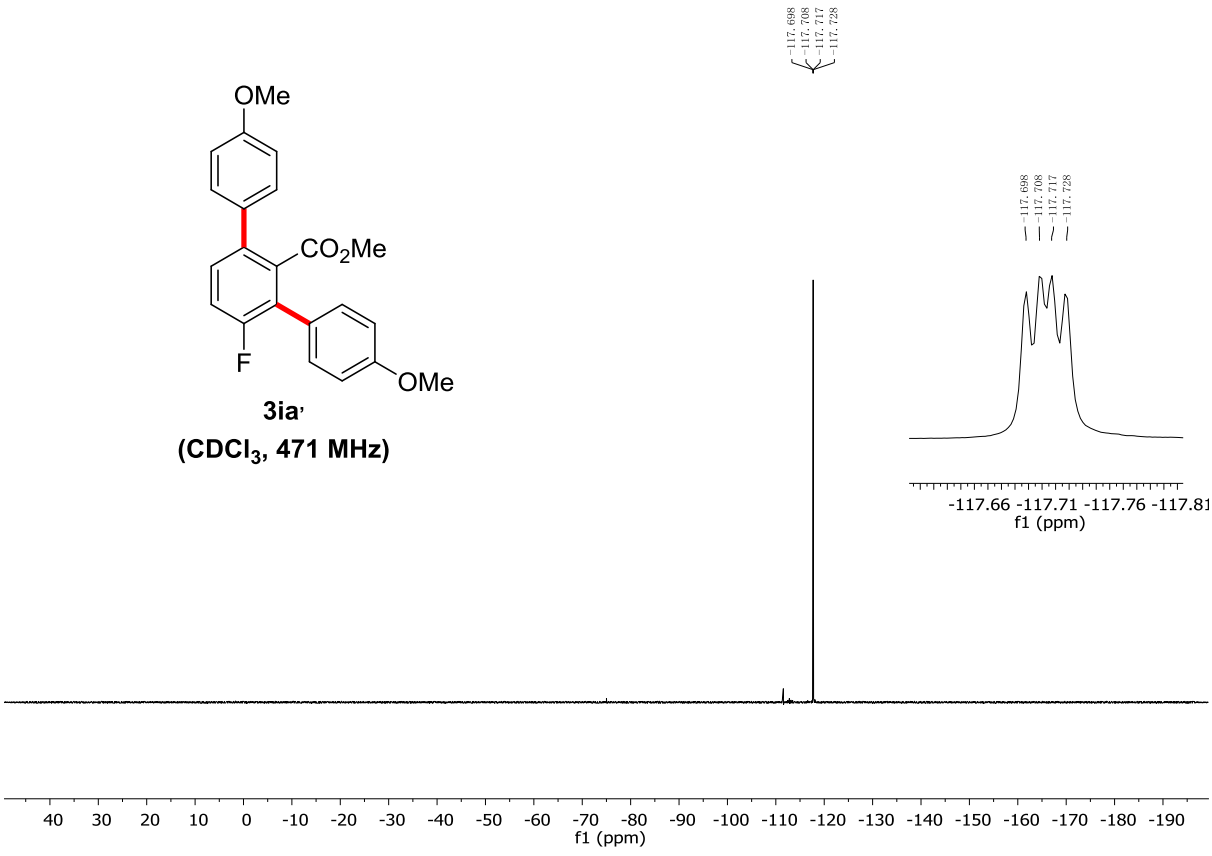


3ia'
($CDCl_3$, 500 MHz)



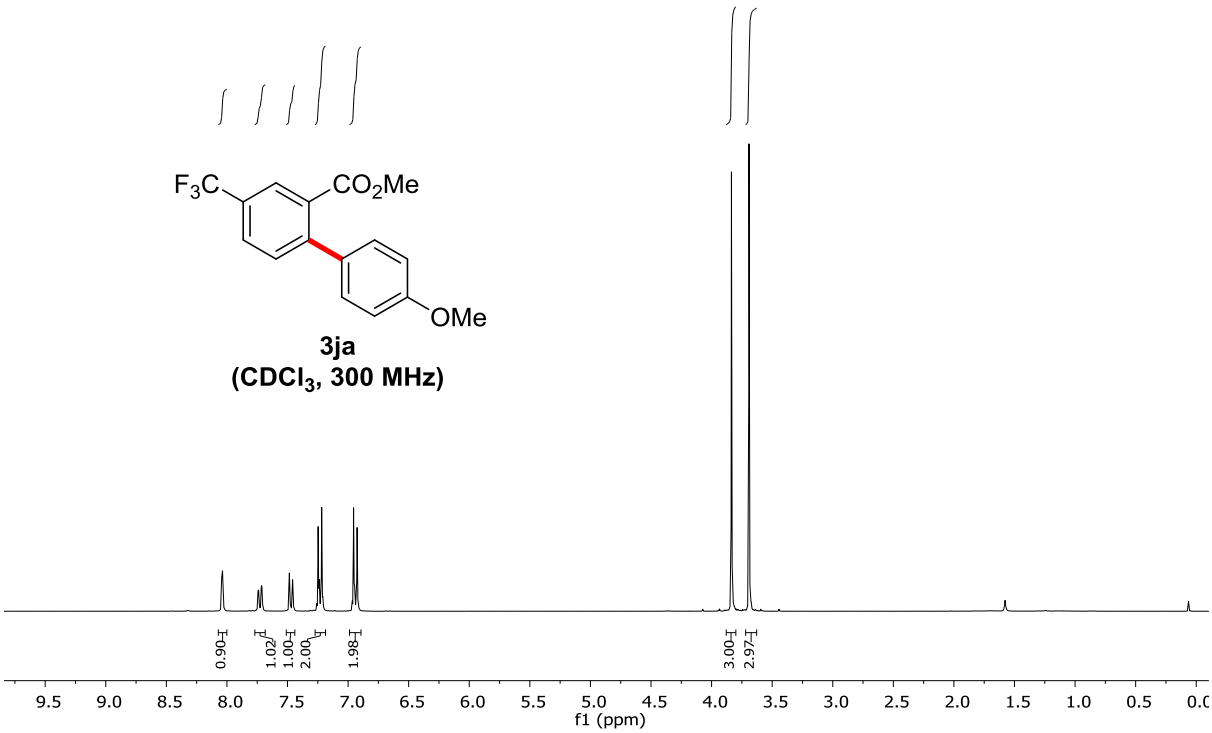
3ia'

($CDCl_3$, 125 MHz)

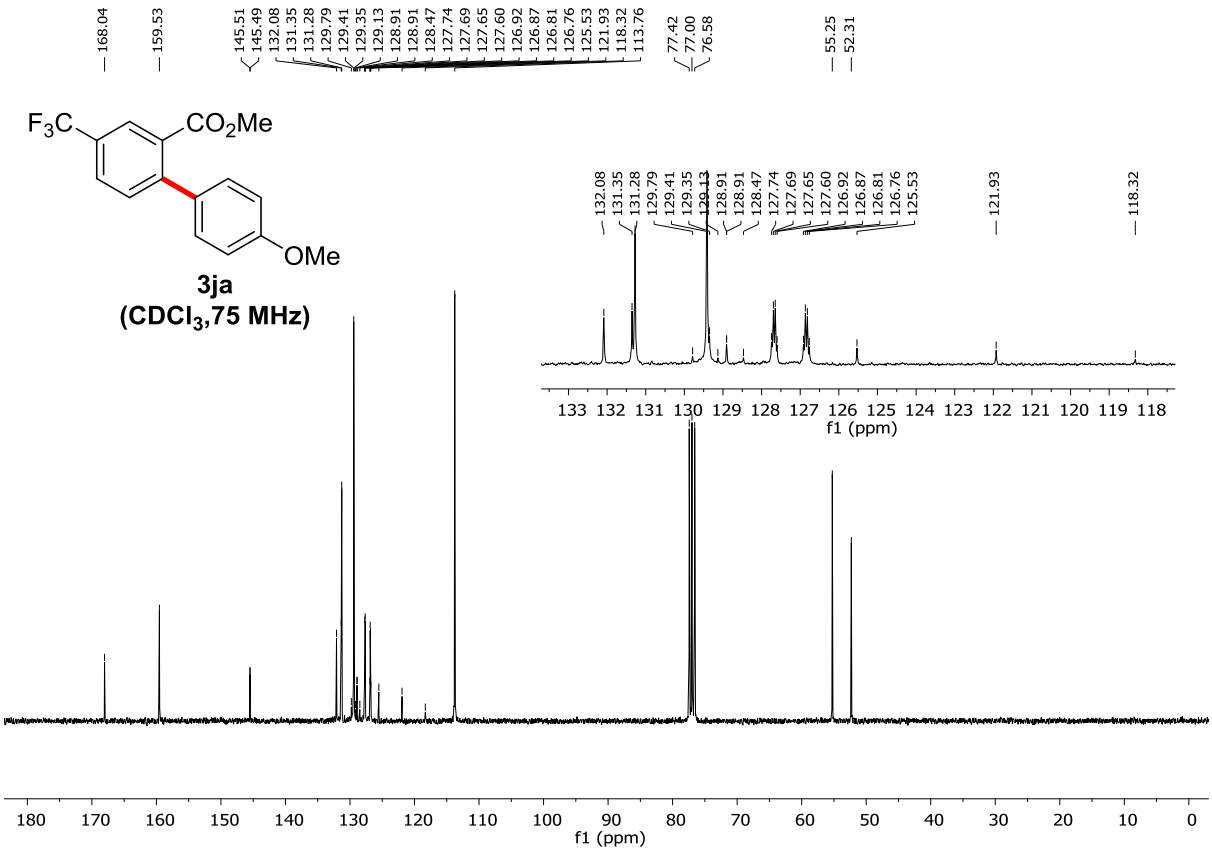


3ia'

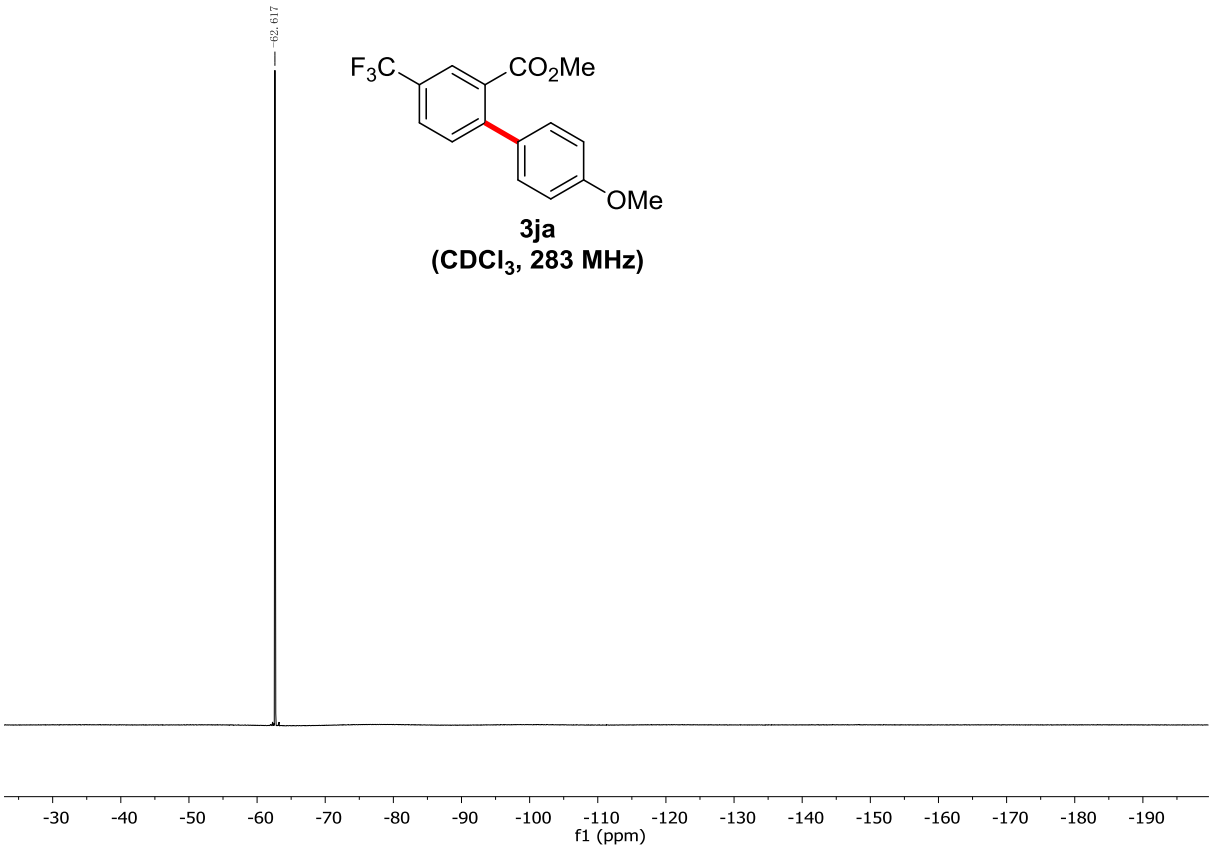
($CDCl_3$, 471 MHz)



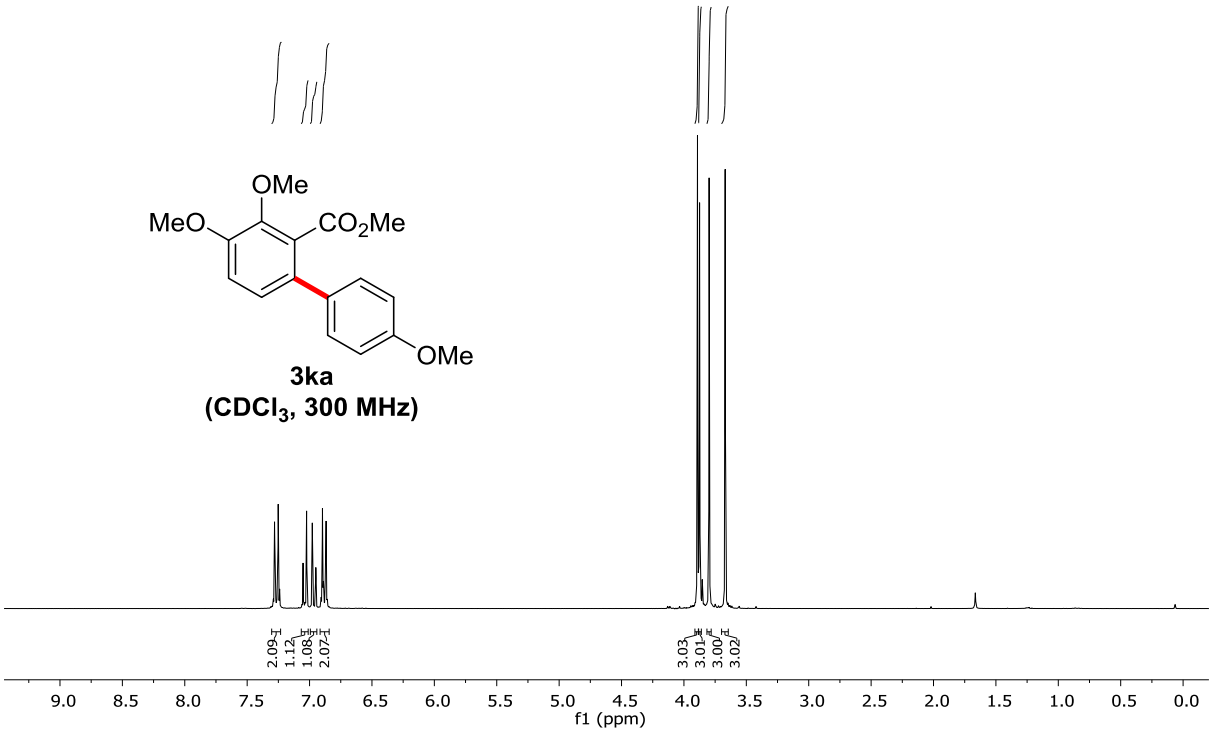
3ja
($CDCl_3$, 300 MHz)



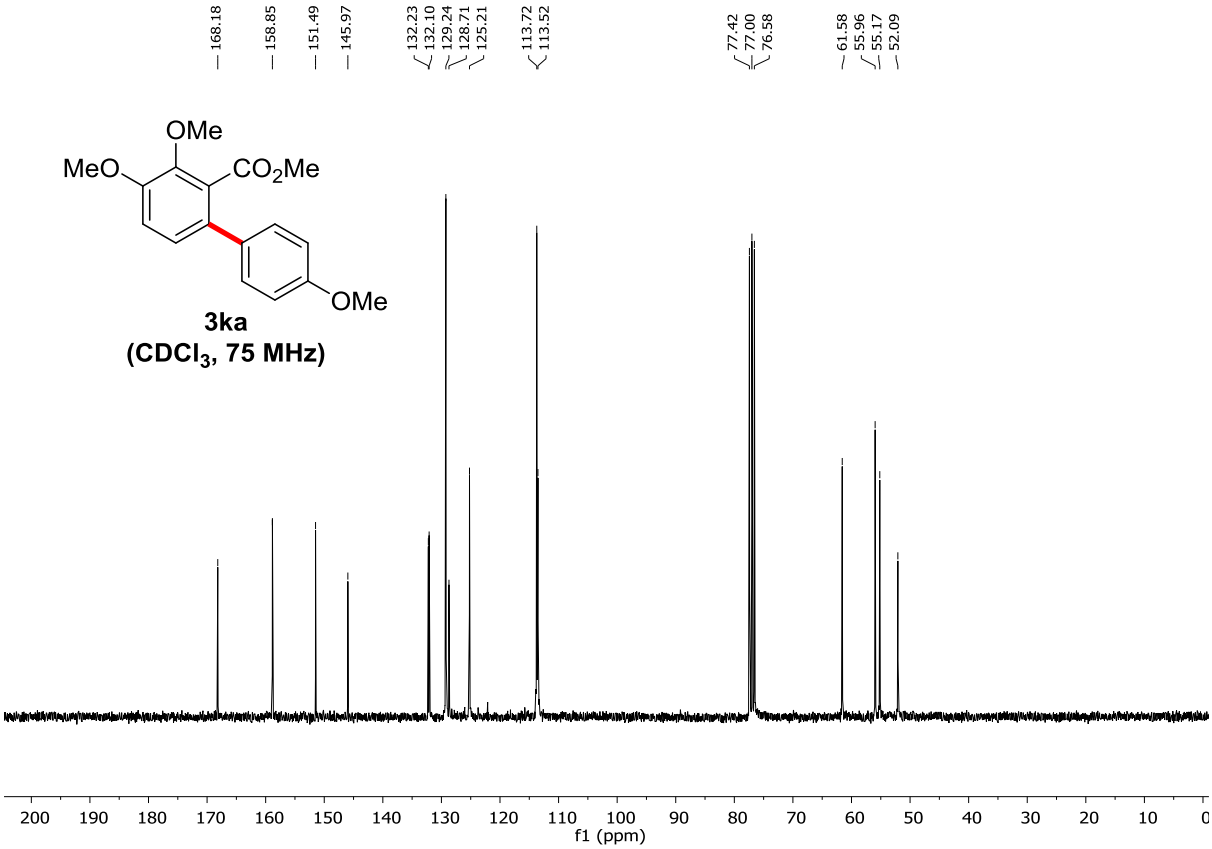
3ja
($CDCl_3$,75 MHz)

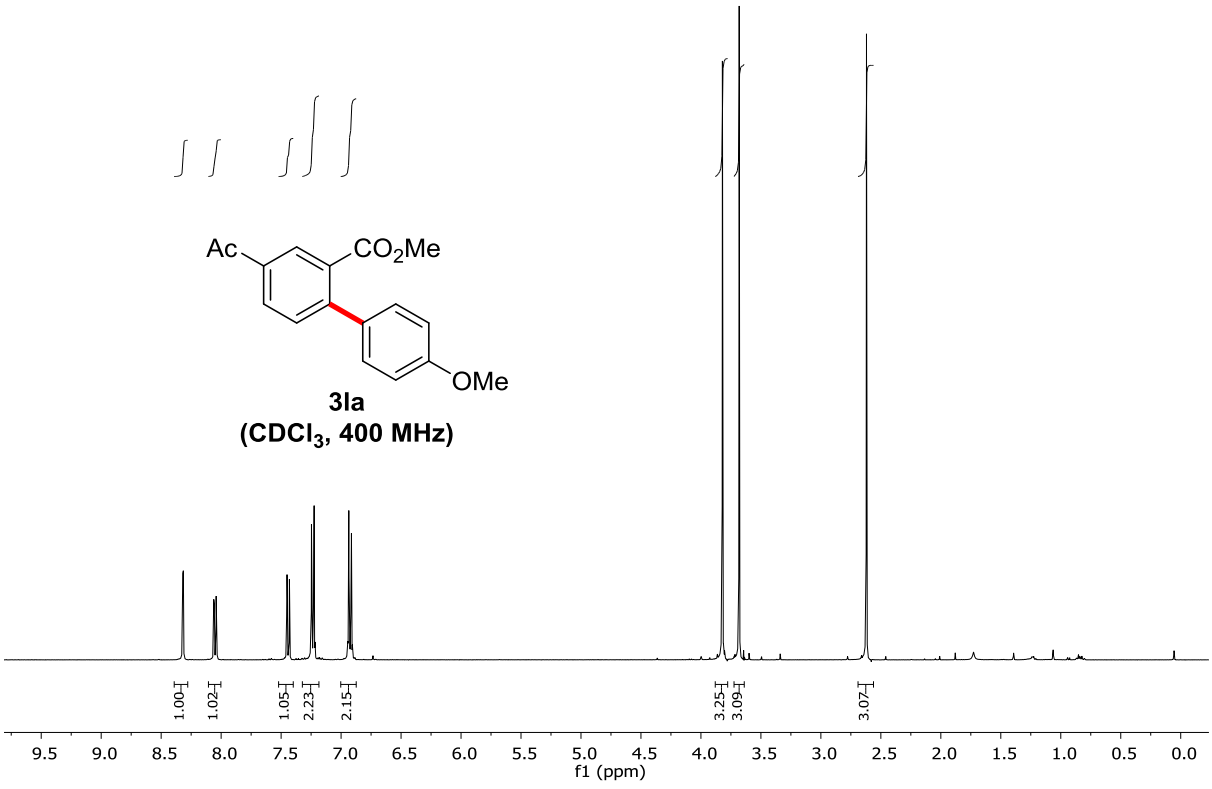


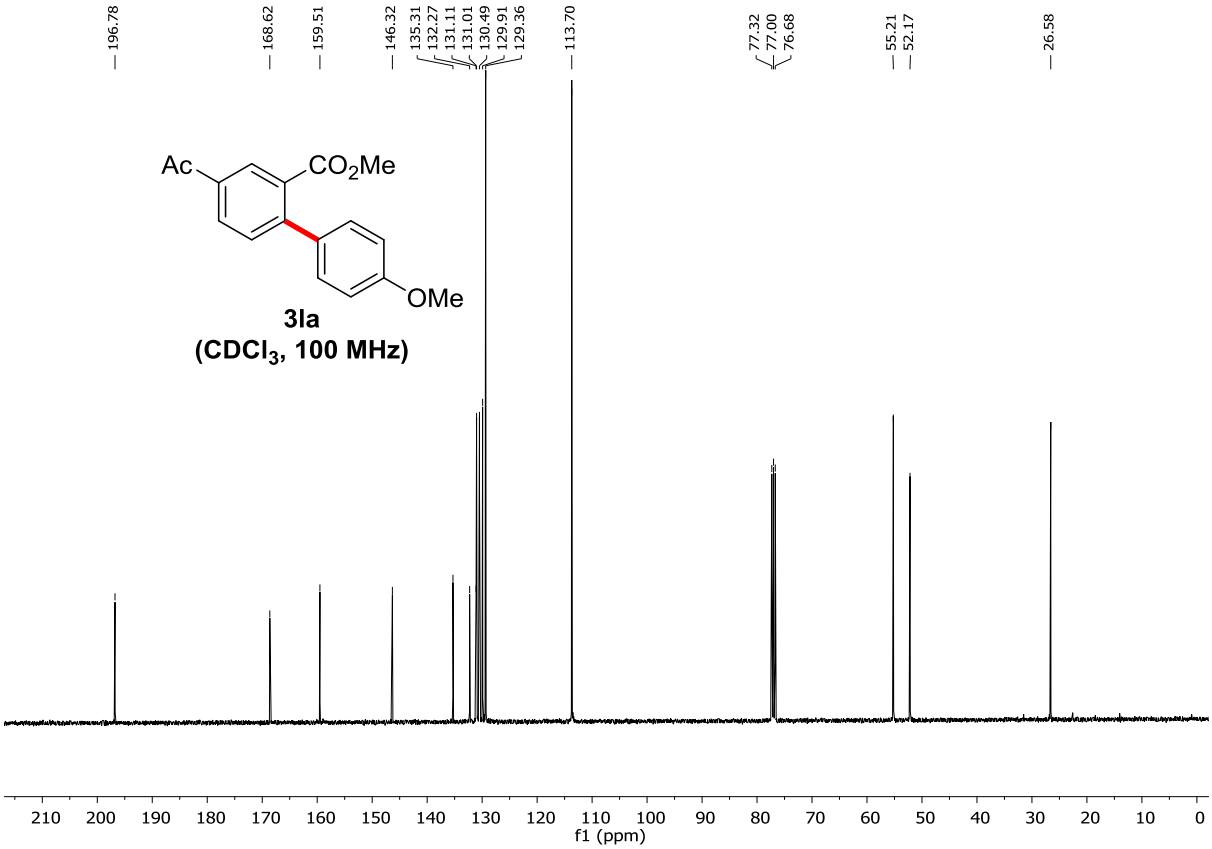
3ja
($CDCl_3$, 283 MHz)

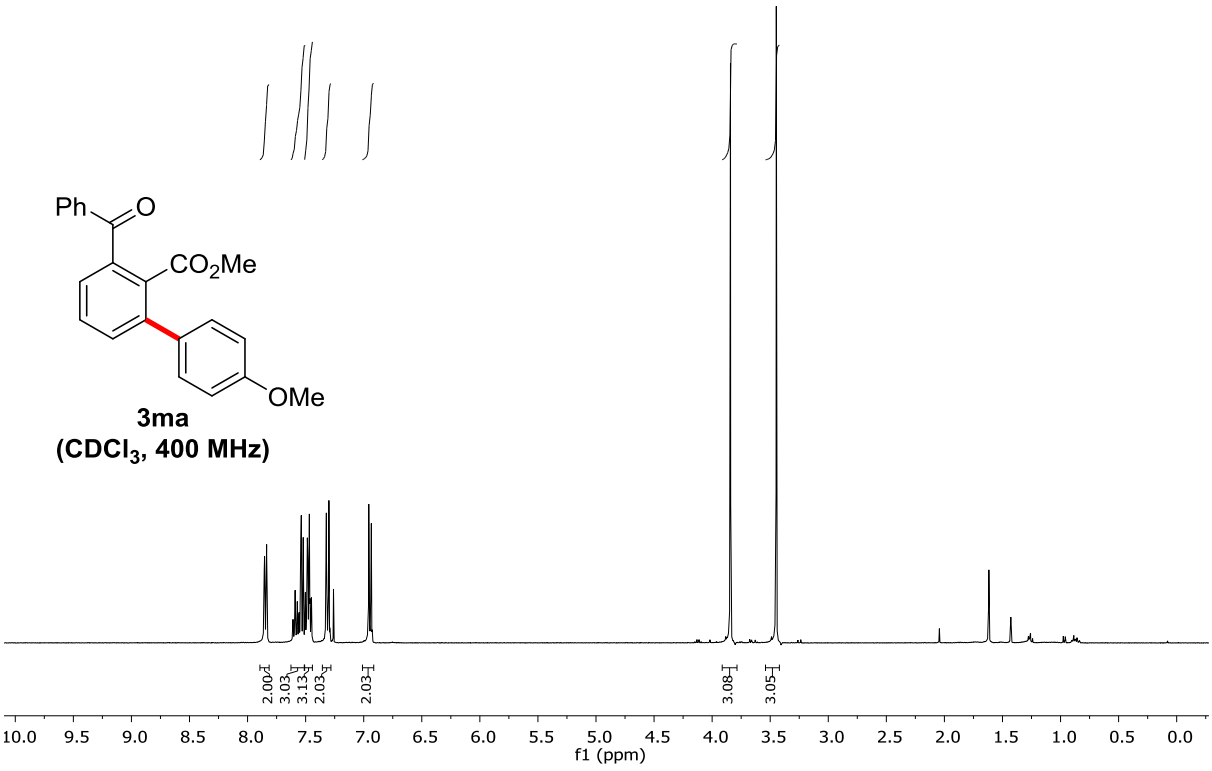


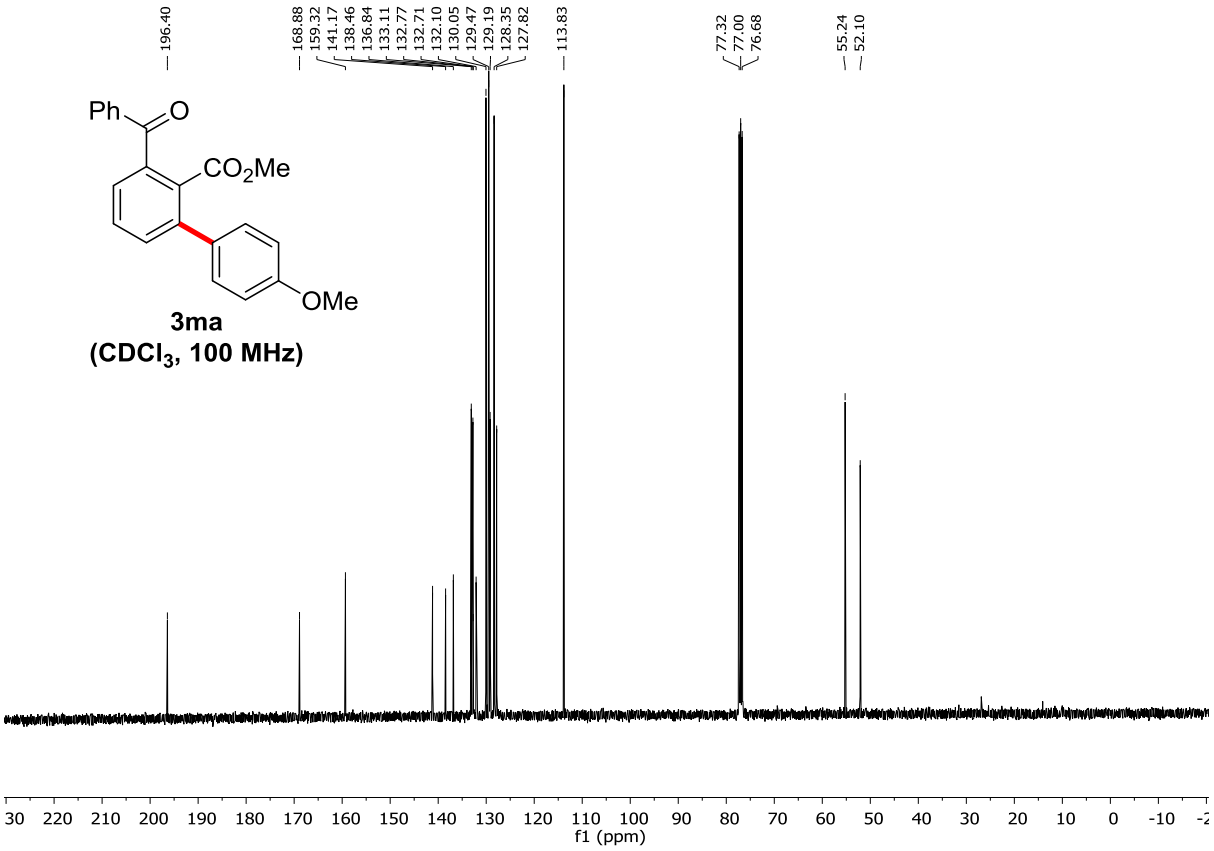
3ka
($CDCl_3$, 300 MHz)


168.18
158.85
151.49
145.97
132.23
132.10
129.24
128.71
125.21
113.72
113.52
77.42
77.00
76.58
61.58
55.96
55.17
52.09
OMe
MeO
CO2Me
OMe
3ka
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

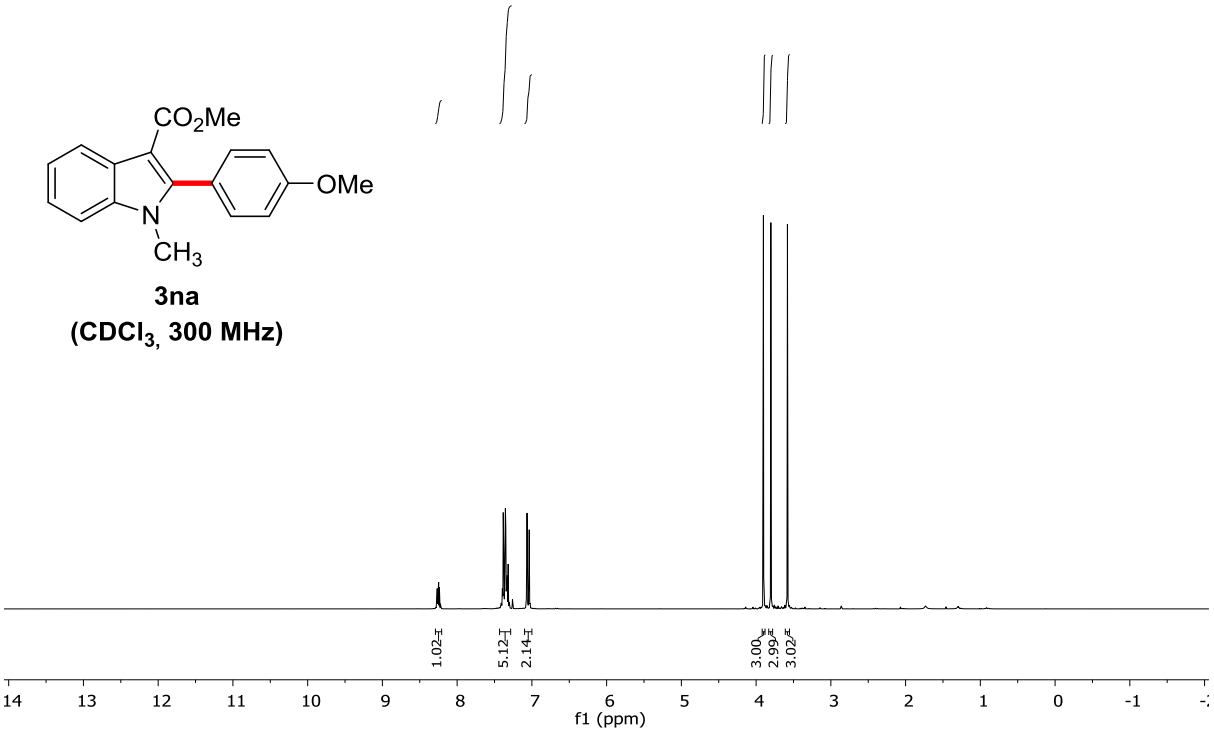

Ac
CO2Me
OMe
3la
(CDCl3, 400 MHz)
1.00
1.02
1.05
2.23
2.15
3.25
3.09
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.78
168.62
159.51
146.32
135.31
132.27
131.11
131.01
130.49
129.91
129.36
113.70
77.32
77.00
76.68
55.21
52.17
26.58
Ac
CO2Me
OMe
3la
(CDCl3, 100 MHz)
f1 (ppm)

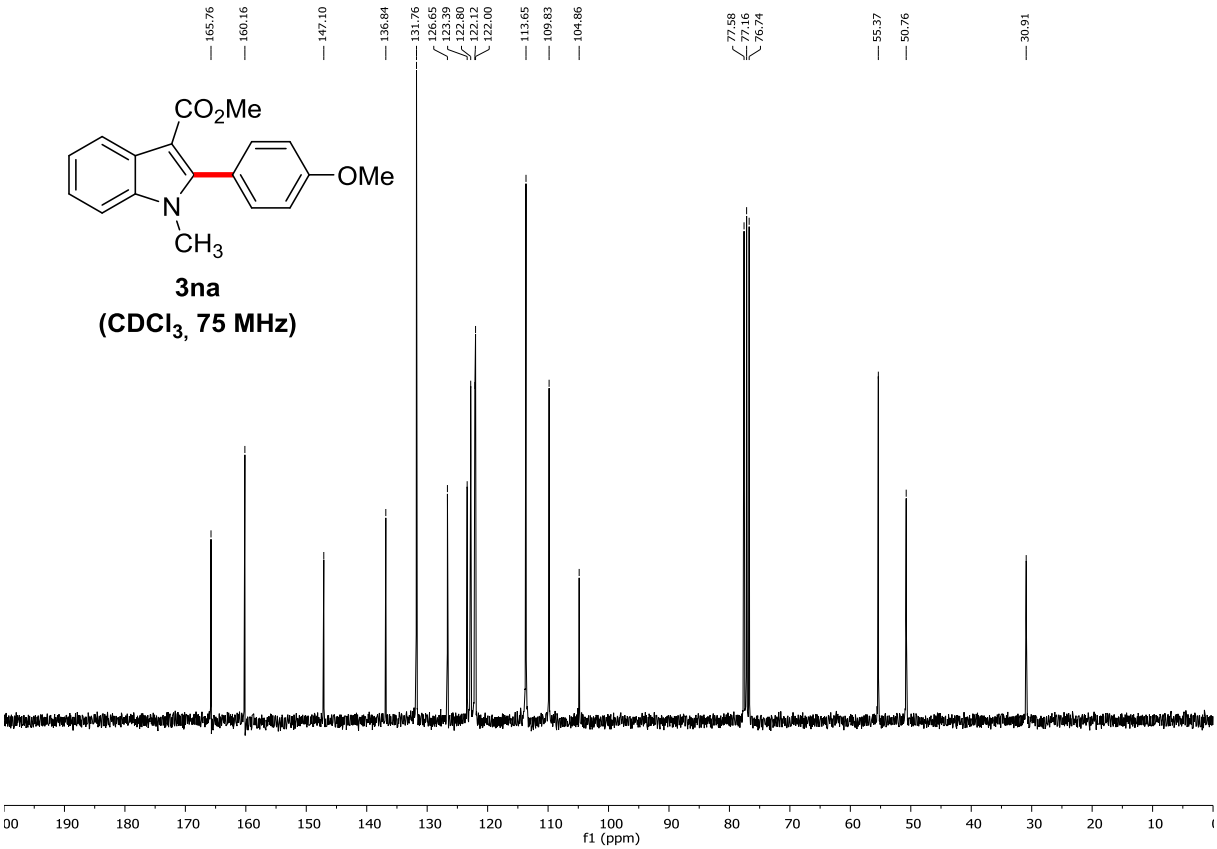

Ph
O
CO2Me
OMe
3ma
(CDCl3, 400 MHz)
2.00
3.03
3.13
2.03
2.03
3.08
3.05
f1 (ppm)



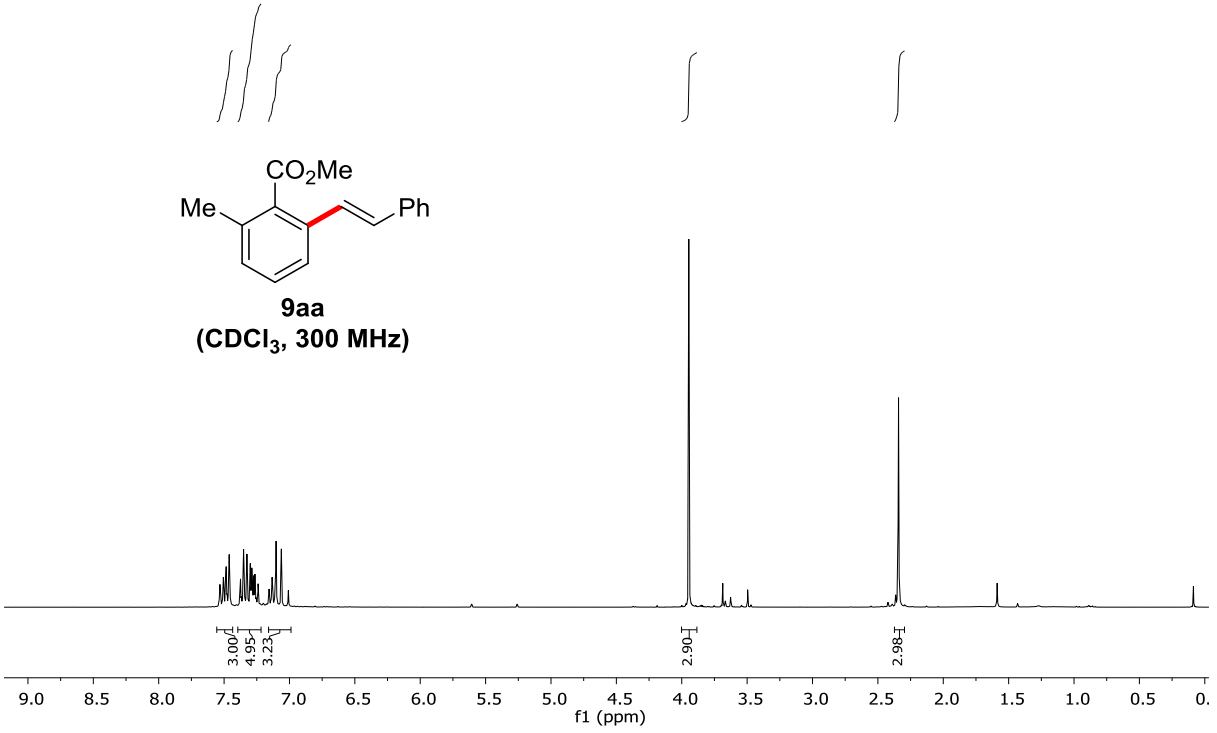
3ma
($CDCl_3$, 100 MHz)



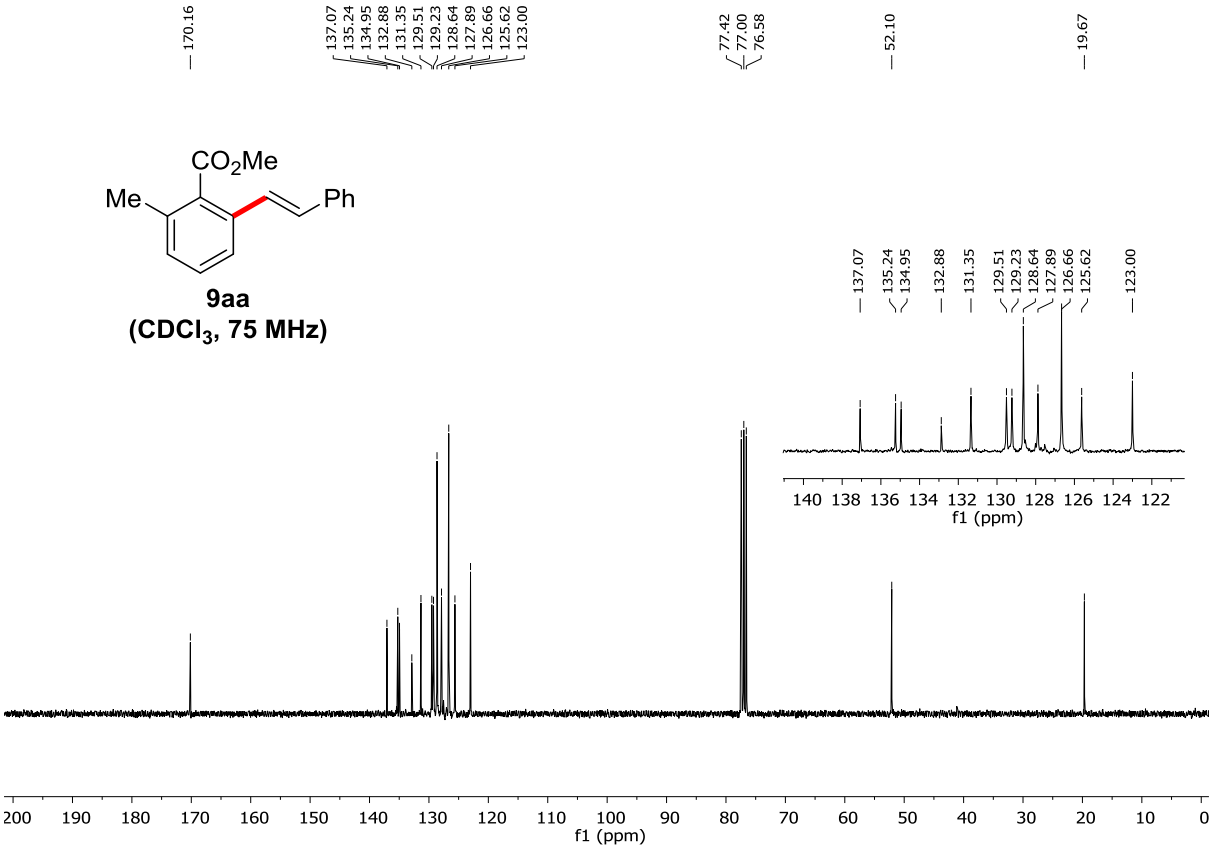
3na
($CDCl_3$, 300 MHz)

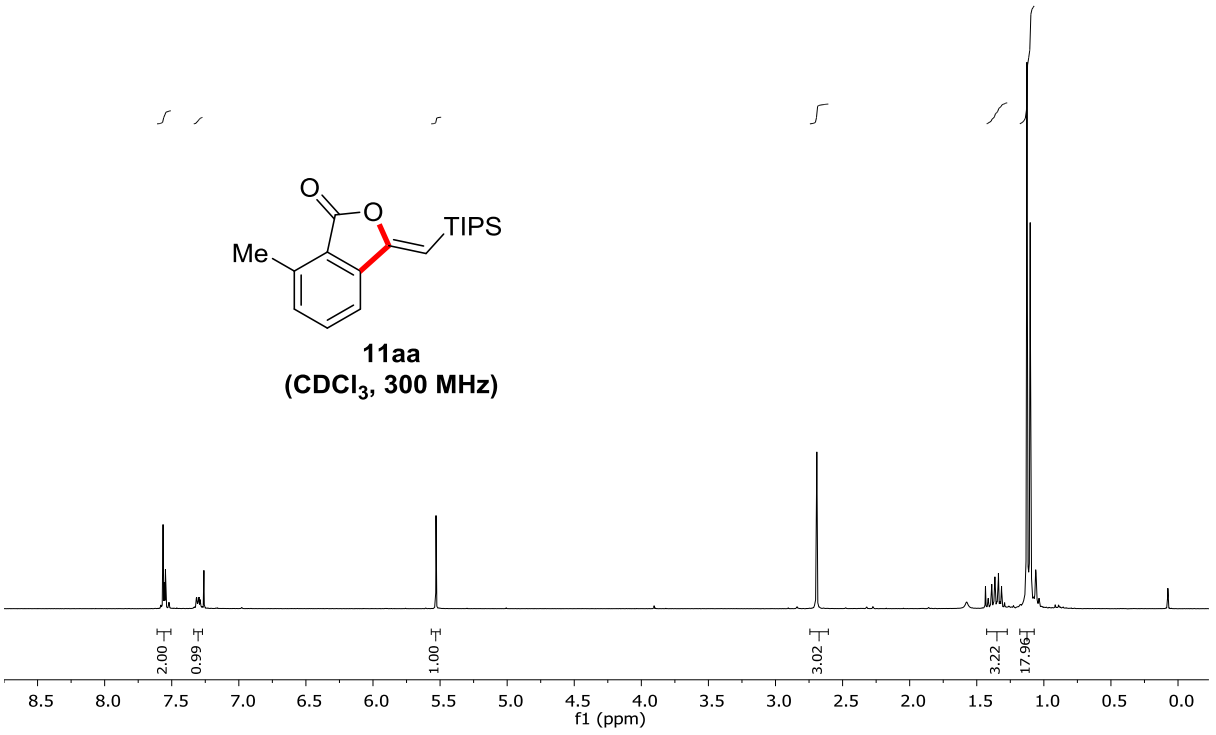


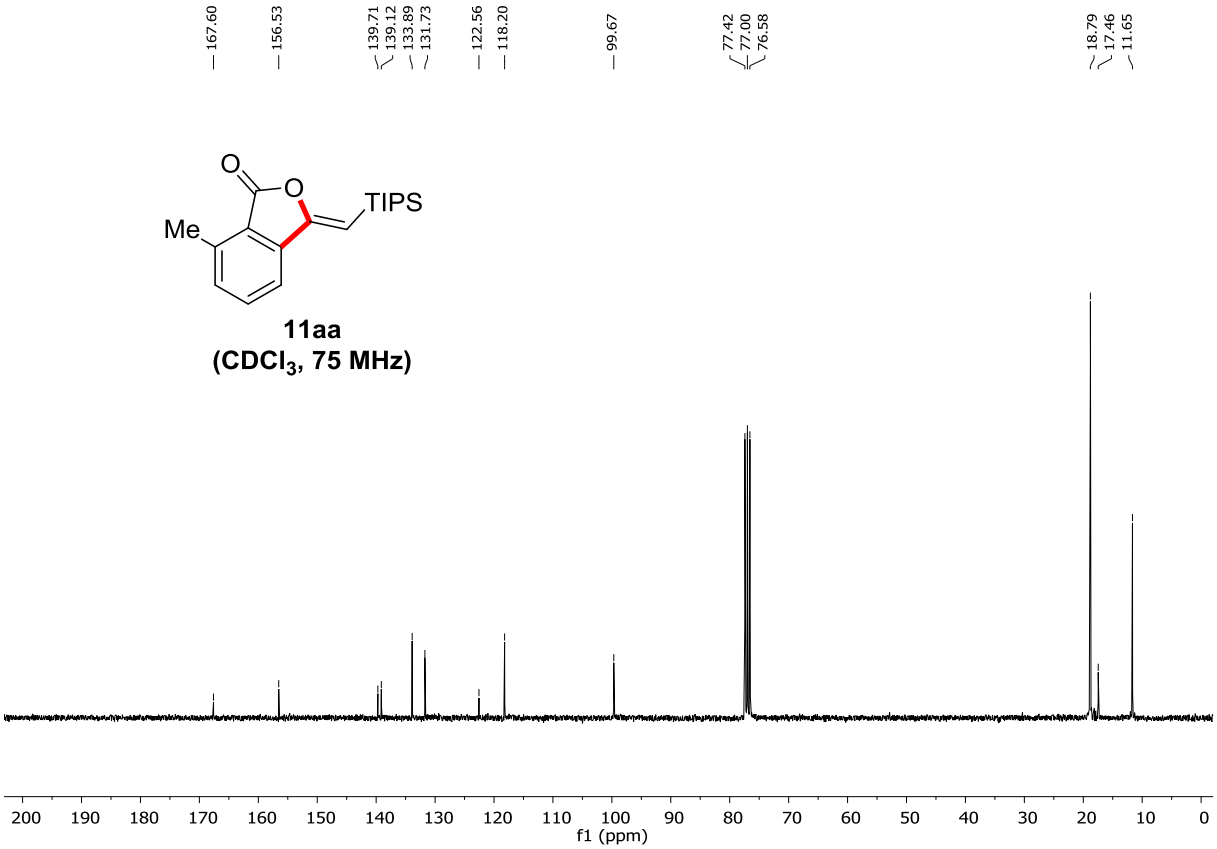
3na
($CDCl_3$, 75 MHz)

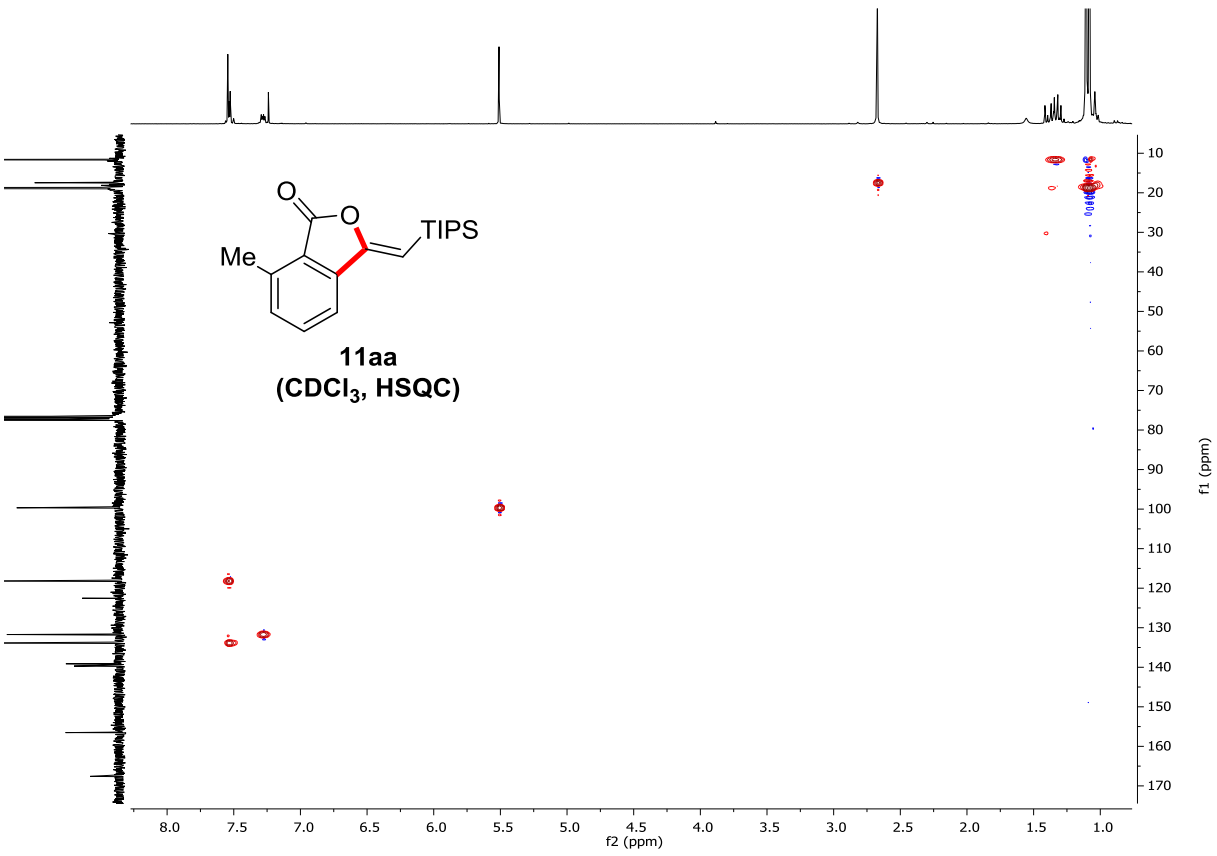


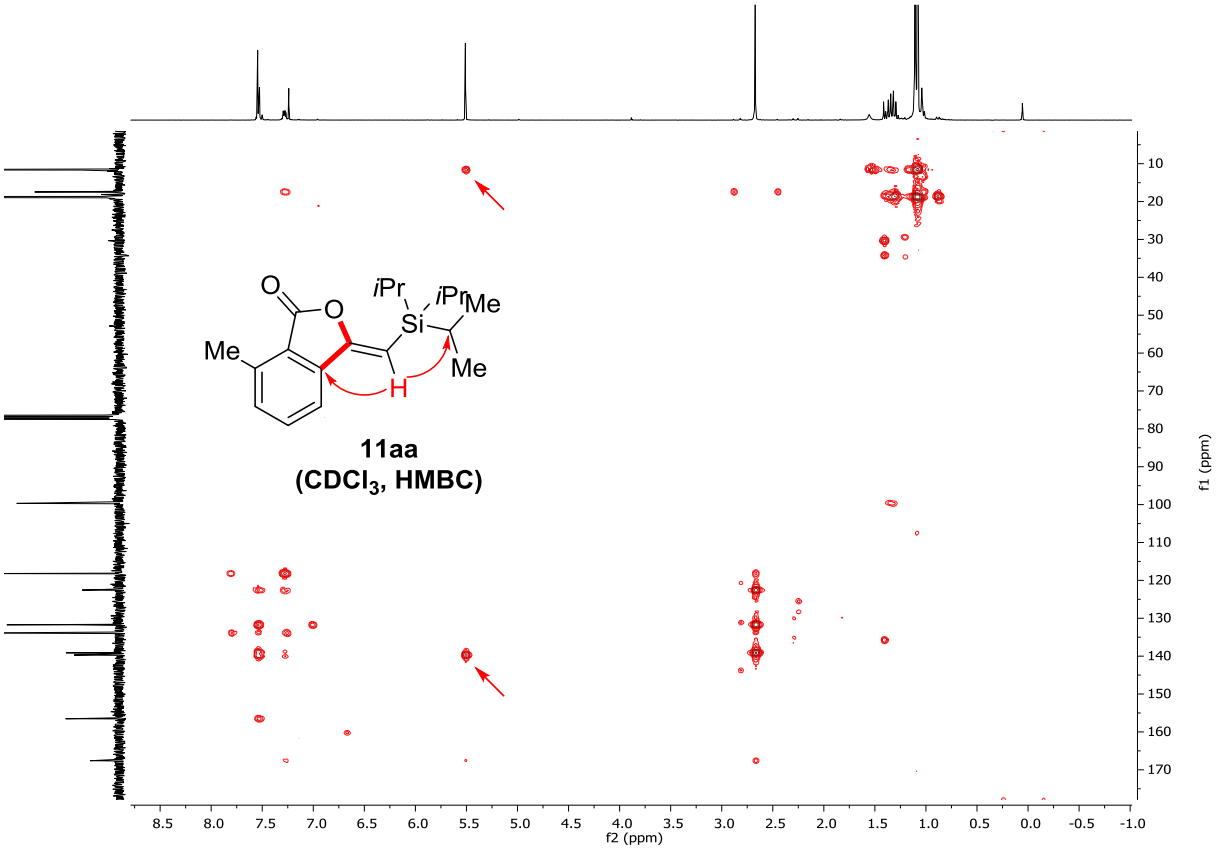
9aa
($CDCl_3$, 300 MHz)


170.16
137.07
135.24
134.95
132.88
131.35
129.51
129.23
128.64
127.89
126.66
125.62
123.00
77.42
77.00
76.58
52.10
19.67
CO2Me
Me
Ph
9aa
(CDCl3, 75 MHz)
f1 (ppm)

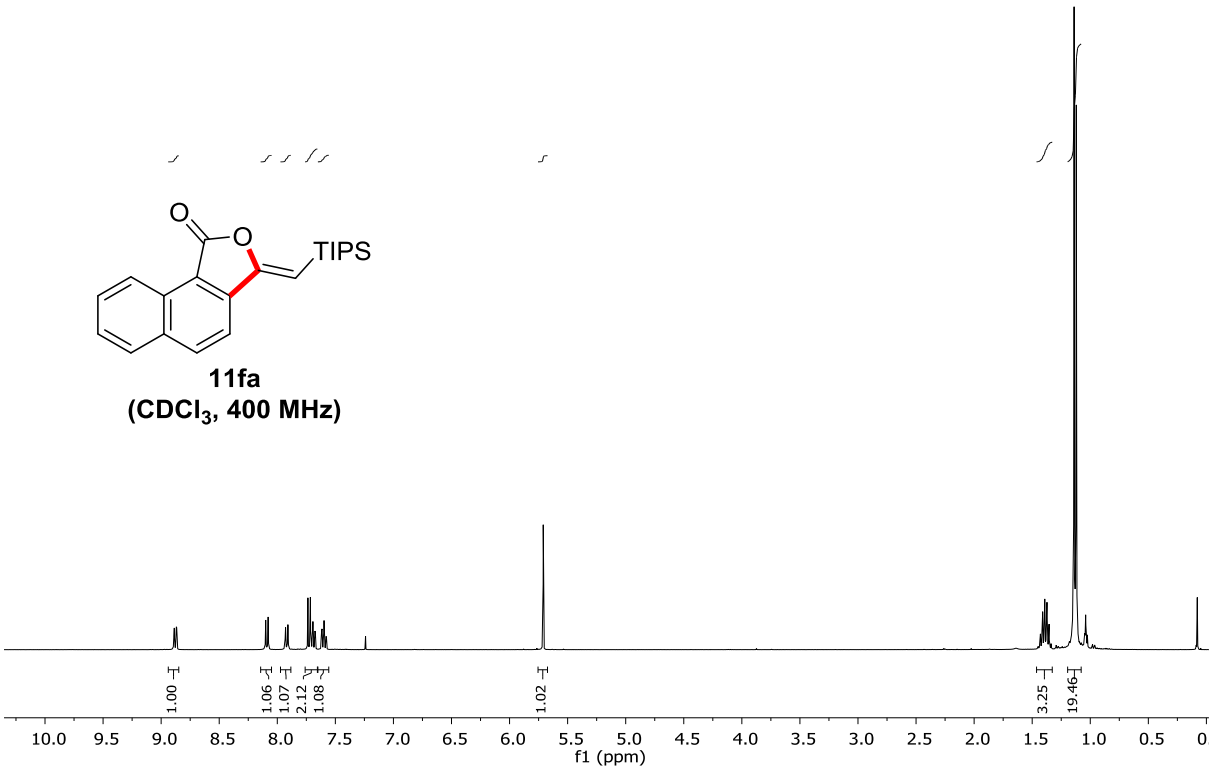

O
O
TIPS
Me
11aa
(CDCl3, 300 MHz)
2.00
0.99
1.00
3.02
3.22
17.96
f1 (ppm)


167.60
156.53
139.71
139.12
133.89
131.73
122.56
118.20
99.67
77.42
77.00
76.58
18.79
17.46
11.65
O
O
TIPS
Me
11aa
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

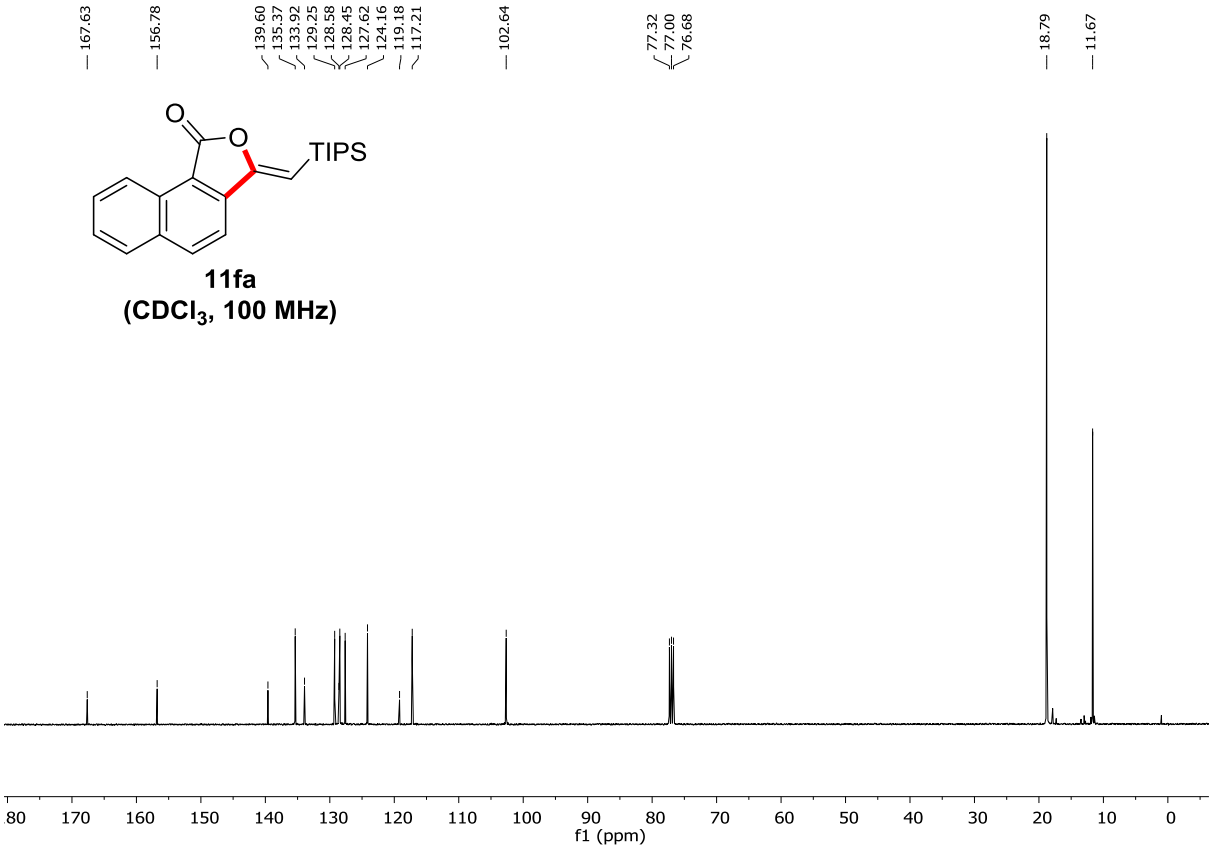

O
O
TIPS
Me
11aa
(CDCl3, HSQC)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)

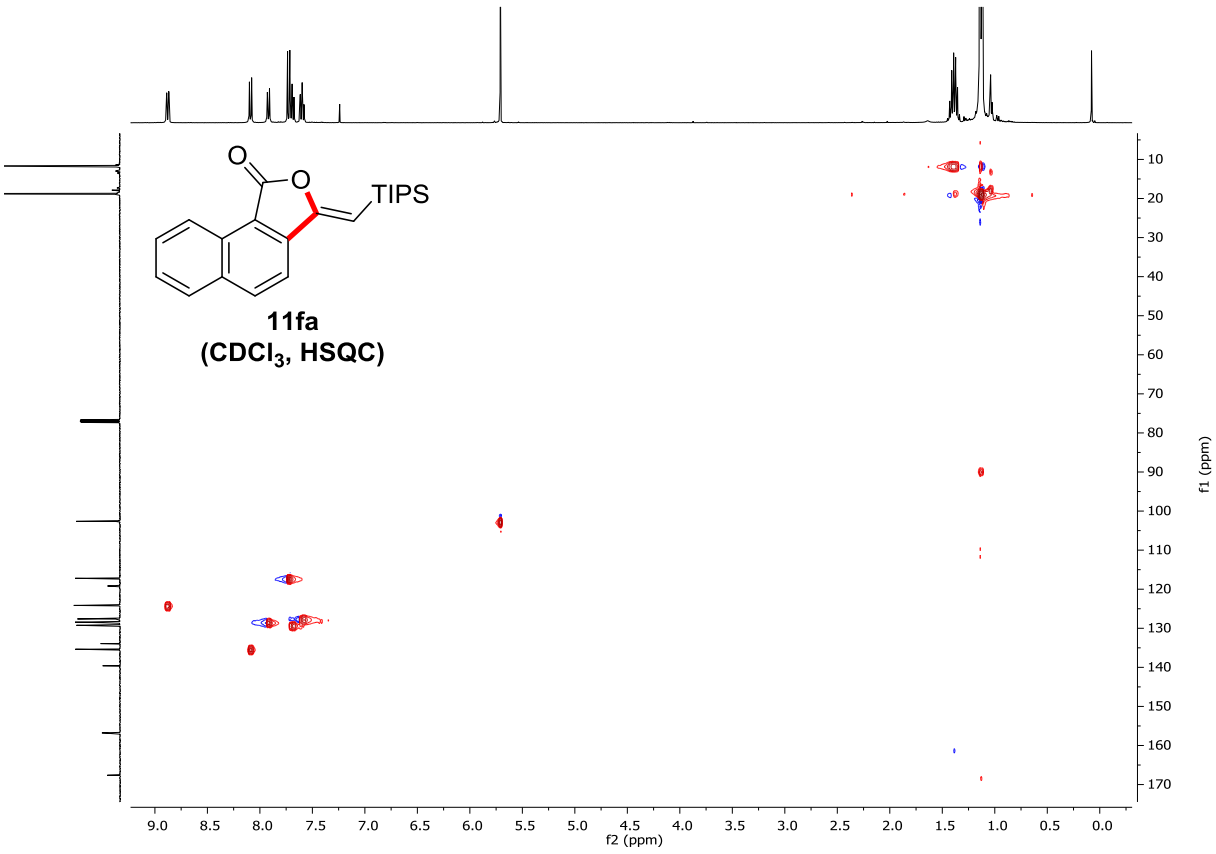


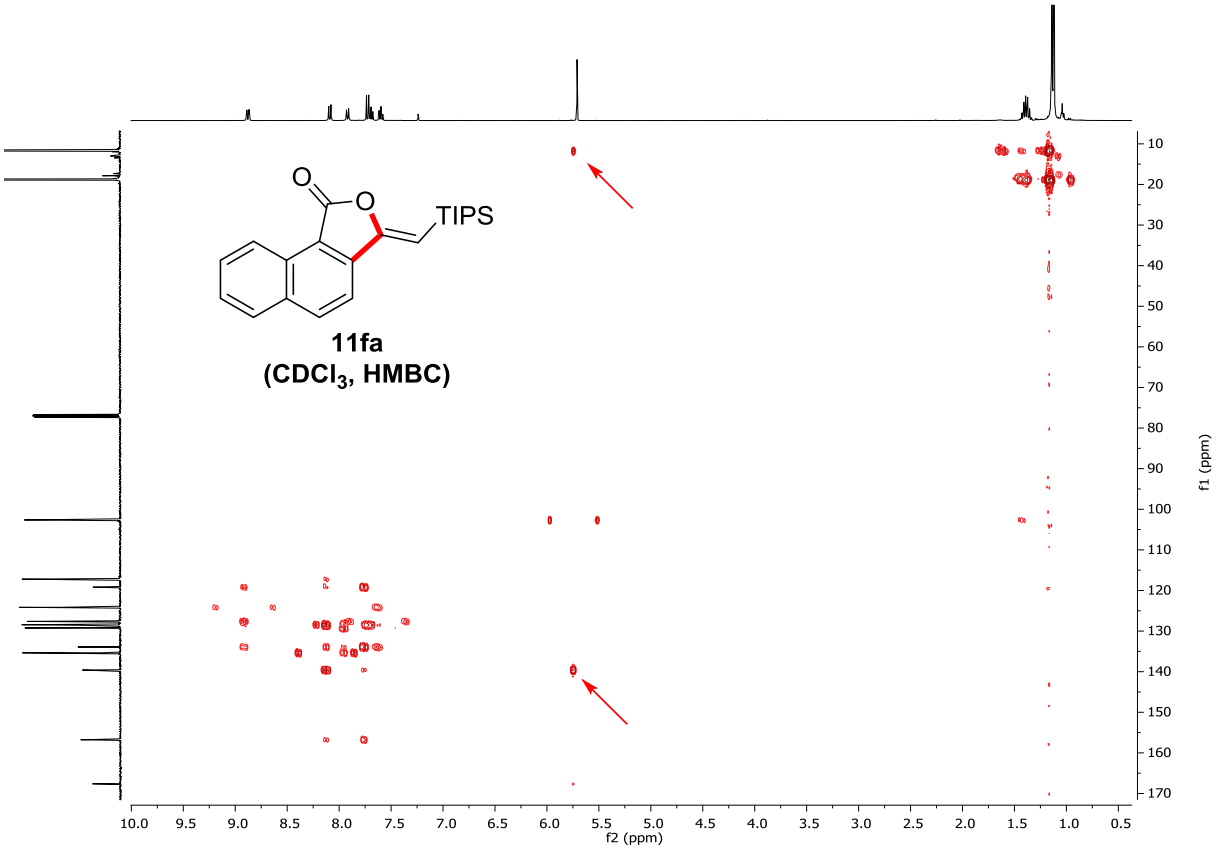
11aa
($CDCl_3$, HMBC)

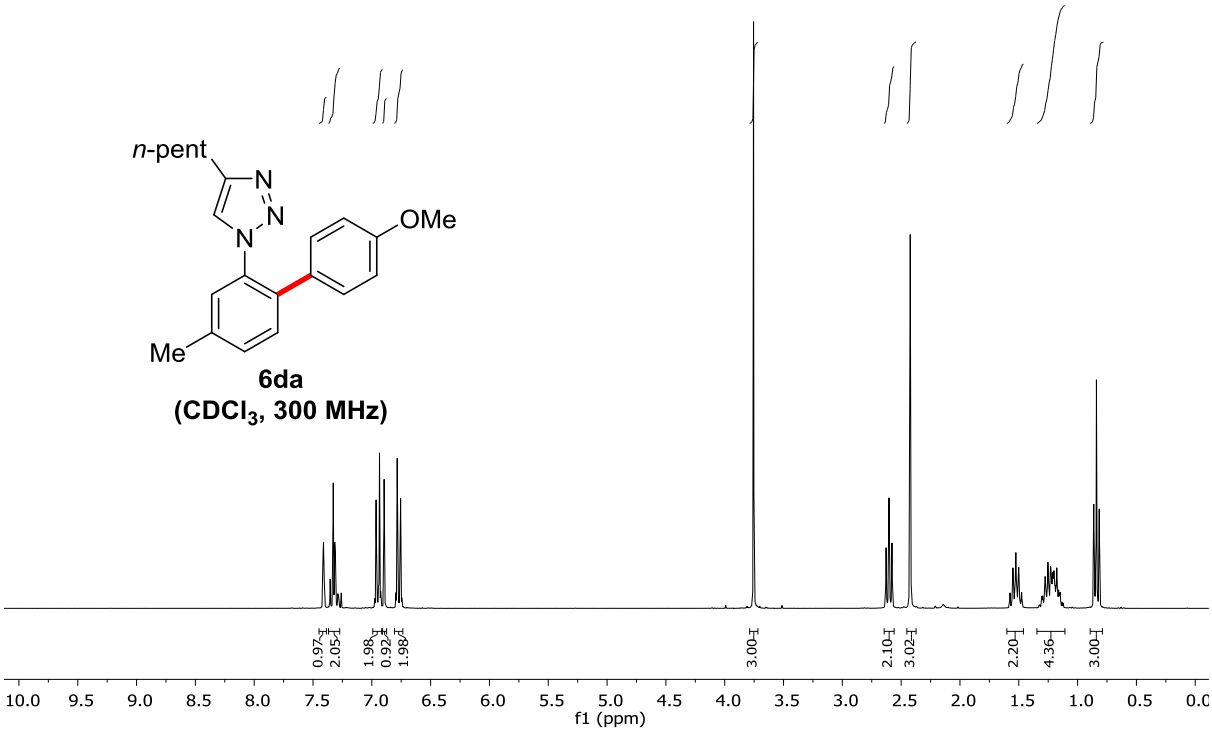


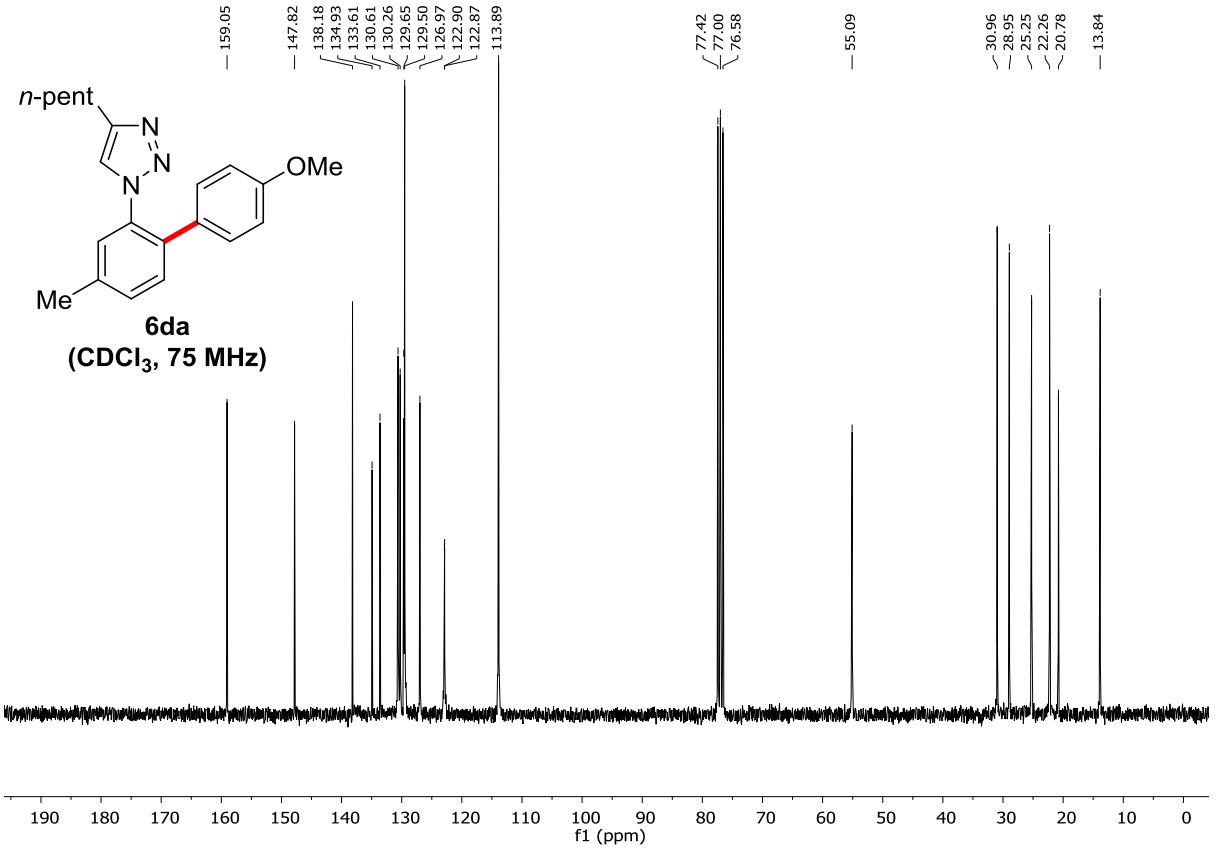
11fa
($CDCl_3$, 400 MHz)


167.63
156.78
139.60
135.37
133.92
129.25
128.58
128.45
127.62
124.16
119.18
117.21
102.64
77.32
77.00
76.68
18.79
11.67
O
O
TIPS
11fa
(CDCl3, 100 MHz)
f1 (ppm)


O
O
TIPS
11fa
(CDCl3, HSQC)
f2 (ppm)
f1 (ppm)


O
O
TIPS
11fa
(CDCl3, HMBC)
f2 (ppm)
f1 (ppm)


n-pent
N
N
N
OMe
Me
6da
(CDCl3, 300 MHz)
0.97
2.05
1.98
0.92
1.98
3.00
2.10
3.02
2.20
4.36
3.00
f1 (ppm)


159.05
147.82
138.18
134.93
133.61
130.61
130.26
129.65
129.50
126.97
122.90
122.87
113.89
77.42
77.00
76.58
55.09
30.96
28.95
25.25
22.26
20.78
13.84
n-pent
N
N
N
OMe
Me
6da
(CDCl3, 75 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)