Heterogeneous Palladium-Catalysed Catellani Reaction in Biomass-Derived γ-Valerolactone

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SUPPORTING INFORMATION

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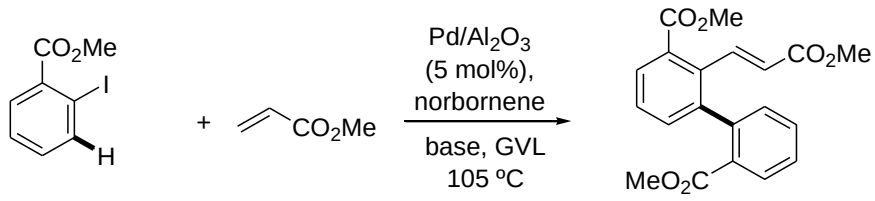
General Information

Unless otherwise stated, all chemicals were purchased and used without any further purification. Pd/Al_2O_3, 10 wt. % loading, was purchased from Sigma-Aldrich. GC analyses were performed by using a Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and helium as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.
All ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and at 100.6 MHz, respectively, using a Bruker DRX-ADVANCE 400 MHz spectrometer. The deuterated solvent used was $CDCl_3$, and the spectra were calibrated using its residual peak. Chemical shifts are reported in ppm and coupling constants in Hertz. Elemental analyses were realized by using a FISONS instrument EA 1108 CHN.
Compounds **3a** and **5** are known while **3b**-**3o**, **3'h**, **4j**, **4k** are new compounds.

Typical Procedure for the Catellani Reaction

To a 4 mL vial containing the palladium catalyst (0.00825 mmol, 5 mol %), the base (0.34 mmol), and 2-norbornene (12 mg, 0.127 mmol) was added a GVL solution (3.75 mL) of the aryl iodide (0.33 mmol) and the terminal olefin (0.195 mmol). The resulting mixture was stirred at 105°C.
The solids were then separated from the solution by vacuum filtration and rinsed with cyclopentyl methyl ether. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The products were isolated by flash column chromatography using a 4:1 mixture of petroleum ether and ethyl acetate as the eluent.

Screening of Bases



1a **2a** **3a**

Entry	Base	Time	Yield (%)[a]
1	K_2CO_3	24h	100
2	KOAc	2d	59
3	DABCO	2d	0
4	TEA[b]	2d	12
5	PS-TEA[c]	2d	11

[a]Determined by GC analysis. [b]Triethylamine. [c]Diethylaminomethyl-polystyrene.

Hg-Poisoning Tests

For each catalyst two reactions, with **1a** and **2a** as substrates and under the optimized reaction conditions, were run in parallel. After one hour, 100 equivalents (relative to the catalyst) of Hg(0) were added and the reactions were kept under stirring at the reaction temperature. Product formation was monitored through GC analysis.

Catalyst		**Product yield (%)**[a]			
		1h	3h	20h	4 days
Pd/Al_2O_3	control	5	44	100	-
	test	4	10	4	11
PdEnCat™ 30	control	32	57	99	-
	test	29	51	46	57[b]

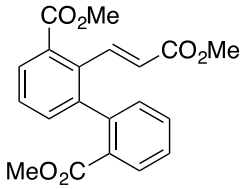
[a]Determined by CG analysis. [b]The reaction is not clean, and the formation of several byproducts was observed.

Procedure for Catalyst Recovery and Recycling

After stirring at 105 ^{o}C for 24h, the reaction mixture was centrifuged and the solvent was decanted. The catalyst was washed, first with water (0.2 mL) and GVL (3.0 mL), then with GVL (3.8 mL). New substrates (**1a** and **2a**), reagents and solvent were added and left for 24 h at 105 ^{o}C for the next run. In four consecutive reaction runs Pd/Al_2O_3 consistently led to full conversion to the expected product in 24 hours.

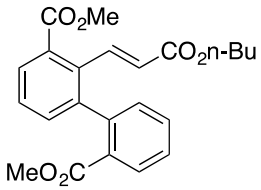
Spectral Data

Dimethyl (*E*)-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3a).[1]



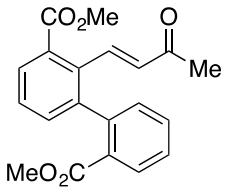
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (s, 3H), 3.65 (s, 3H), 3.89 (s, 3H), 5.52 (d, J = 16.2 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.42 (m, 2H), 7.52 (dd, J =7.5 Hz, 1H), 7.85-7.92 (m, 2H), 7.95 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 51.5, 52.00, 52.3, 123.6, 127.7, 127.8, 129.3, 130.2, 130.3, 130.4, 131.4, 131.8, 133.0, 134.8, 141.4, 142.1, 143.4, 166.4, 167.2, 167.8. GC-EIMS (m/z, %): 176 (17), 263 (73), 264 (15), 295 (100), 296 (21), 254 (5). Anal. calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.71; H, 5.08.

Dimethyl (*E*)-2'-(3-butoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3b).



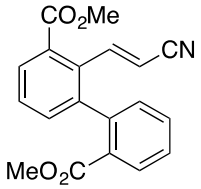
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, J = 7.3 Hz, 3H), 1.27-1.35 (m, 2H), 1.52-1.59 (m, 2H), 3.64 (s, 3H), 3.88 (s, 3H), 4.05 (t, J = 6.5 Hz, 2H), 5.50 (d, J = 16.3 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.40-7.44 (m, 2H), 7.52 (dd, J = 7.5 Hz, 1H), 7.81 (d, J = 16.3 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 13.7, 19.0, 30.5, 52.0, 52.3, 64.1, 124.0, 127.7, 127.7, 129.2, 130.1, 130.3, 130.3, 131.4, 131.8, 132.9, 134.7, 141.4, 142.1, 143.0, 166.0, 167.2, 168.0. GC-EIMS (m/z, %): 176 (16), 177 (17), 205 (15), 263 (44), 295 (100), 296 (20), 396 (3). Anal. calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.91; H, 5.97.

Dimethyl (*E*)-2'-(3-oxobut-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3c).



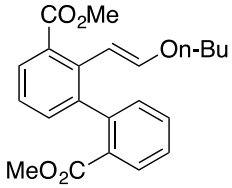
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.13 (s, 3H), 3.64 (s, 3H), 3.88 (s, 3H), 5.67 (d, J = 16.7 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.37-7.46 (m, 3H), 7.52 (dd, J = 7.5 Hz, 1H), 7.73 (d, J = 16.7 Hz, 1H), 7.92-7.95 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 26.5, 52.0, 52.3, 127.8, 127.9, 129.5, 129.7, 130.2, 130.3, 131.4, 131.9, 133.2, 135.2, 141.3, 141.9, 142.5, 167.2, 167.6, 198.1. GC-EIMS (m/z, %): 176 (11), 279 (22), 295 (100), 296 (21), 338 (1). Anal. calcd for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36. Found: C, 71.17; H, 5.43.

Dimethyl (*E*)-2'-(2-cyanovinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3d).



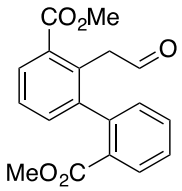
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.69 (s, 3H), 3.92 (s, 3H), 5.04 (d, J = 16.8 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.43-7.49 (m, 2H), 7.56 (dd, J = 7.4 Hz, 1H), 7.75 (d, J = 16.8 Hz, 1H), 7.97-8.01 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 52.1, 52.5, 102.2, 117.4, 128.1, 128.4, 129.5, 129.6, 129.9, 130.6, 131.2, 132.1, 133.4, 134.0, 141.0, 141.9, 149.9, 167.0, 167.1. GC-EIMS (m/z, %): 59 (34), 88 (48), 175 (28), 176 (32), 177 (25), 190 (25), 201 (43), 202 (73), 203 (75), 205 (27), 218 (32), 230 (100), 236 (41), 262 (51), 274 (50), 321 (51). Anal. calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.93; H, 4.65; N, 4.39.

Dimethyl (*E*)-2'-(2-butoxyvinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3e).



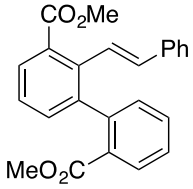
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J = 7.4 Hz, 3H), 1.22-1.29 (m, 2H), 1.42-1.49 (m, 2H), 3.45-3.58 (m, 2H), 3.54 (s, 3H), 3.84 (s, 3H), 5.08 (d, J = 7.0 Hz, 1H), 5.87 (d, J = 6.9 Hz, 1H), 7.26-7.30 (m, 3H), 7.41 (dd, J = 7.5 Hz, 1H), 7.52 (dd, J = 7.2 Hz, 1H), 7.71-7.73 (m, 1H), 7.90 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 13.8, 18.8, 31.5, 51.7, 51.8, 72.6, 102.0, 125.6, 127.2, 128.6, 129.7, 130.8, 131.2, 131.3, 131.4, 131.8, 133.1, 142.1, 142.2, 146.3, 168.1, 169.3. GC-EIMS (m/z, %): 164 (26), 165 (79), 193 (43), 220 (36), 221 (100), 252 (86), 368 (64). Anal. calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.89; H, 6.67.

Dimethyl 2'-(2-oxoethyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3f).



Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.62 (s, 3H), 3.68 (d, J = 17.9 Hz, 1H), 3.88 (s, 3H), 3.97 (d, J = 17.7 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.38 (dd, J = 7.7 Hz, 1H), 7.47 (dd, J = 7.5 Hz, 1H), 7.54 (dd, J = 7.3 Hz, 1H), 8.01 d, J = 7.6 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 9.62 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 46.1, 52.0, 52.2, 126.5, 128.0, 129.4, 129.8, 130.2, 130.4, 131.1, 131.9, 132.9, 133.0, 141.4, 144.3, 167.0, 167.7, 199.4. GC-EIMS (m/z, %): 163 (21), 164 (30), 165 (100), 166 (27), 193 (34), 221 (57), 224 (30), 252 (86), 253 (22). Anal. calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.15; H, 5.03.

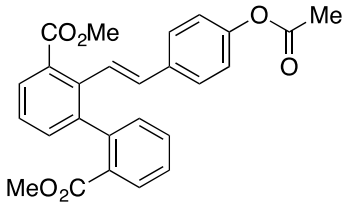
Dimethyl (*E*)-2'-styryl-[1,1'-biphenyl]-2,3'-dicarboxylate (3g).



Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.59 (s, 3H), 3.85 (s, 3H), 6.19 (d, J = 16.5 Hz, 1H), 7.11-7.28 (m, 7H), 7.34-7.40 (m, 3H), 7.51 (dd, J = 7.6 Hz, 1H), 7.81 (dd, J = 2.5 Hz, 6.5 Hz, 1H), 7.90 (d, J = 7.4 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 51.9, 52.2, 126.2, 126.3, 126.4, 127.3, 127.4, 128.4, 129.0, 130.0, 130.5, 130.6, 131.5, 131.6, 132.5, 134.7, 136.9, 137.3, 141.7, 142.1, 167.5, 169.1. GC-EIMS (m/z, %): 252 (42), 253 (30), 281 (100), 282 (23), 372 (50). Anal. calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.59; H, 5.33.

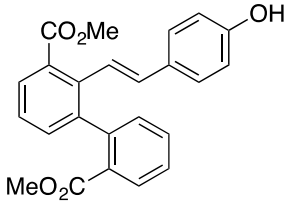
3h and **3'h** were obtained in 79% yield (Table 2, entry 8) as a 1.6:1 mixture of the acetyl product and the phenol deriving from ester hydrolysis. Isolated pure compounds **3h** and **3'h** were obtained after further chromatographic purification in 48% and 14% yields, respectively.

Dimethyl (*E*)-2'-(4-acetoxystyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3h).



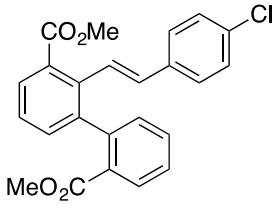
Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.27 (s, 3H), 3.60 (s, 3H), 3.85 (s, 3H), 6.15 (d, J = 16.5 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 7.09-7.16 (m, 3H), 7.25-7.27 (m, 1H), 7.33-7.41 (m, 3H), 7.51 (dd, J = 8.6 Hz, 1H), 7.83 (dd, J = 2.3 Hz, 6.7 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.1, 51.9, 52.2, 121.5, 126.4, 126.6, 127.3, 127.4, 129.0, 130.1, 130.4, 130.5, 131.5, 131.6, 132.6, 133.6, 135.2, 136.8, 141.8, 142.1, 149.9, 167.5, 169.0, 169.5. GC-EIMS (m/z, %): 107 (14), 239 (52), 268 (21), 269 (20), 297 (99), 298 (24), 388 (100), 389 (29), 430 (38). Anal. calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15. Found: C, 72.63; H, 5.11.

Dimethyl (*E*)-2'-(4-hydroxystyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3'h).



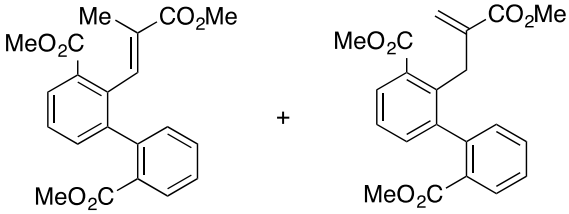
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.58 (s, 3H), 3.85 (s, 3H), 5.66 (brs, 1H), 6.12 (d, J = 16.4 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H), 6.95 (m, J = 16.5 Hz, 1H), 7.00 (d, J = 8.3 Hz, 2H), 7.27 (m, 1H), 7.33-7.35 (m, 2H), 7.38 (dd, J = 7.5 Hz, 1H), 7.51 (dd, J = 7.5 Hz, 1H), 7.77-7.79 (m, 1H), 7.89 (d, J = 7.5 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 52.0, 52.3, 115.3, 123.8, 126.2, 127.3, 127.7, 129.0, 130.0, 130.2, 130.4, 130.7, 131.6, 131.6, 132.5, 134.4, 137.1, 141.7, 142.2, 155.4, 167.8, 169.5. GC-EIMS (m/z, %): 107 (13), 239 (33), 269 (22), 297 (100), 298 (22), 388 (83), 389 (22). Anal. calcd for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19. Found: C, 74.32; H, 5.12.

Dimethyl (*E*)-2'-(4-chlorostyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3i).



Yellow/orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.59 (s, 3H), 3.85 (s, 3H), 6.09 (d, J = 16.5 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 16.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 7.35-7.40 (m, 3H), 7.51 (dd, J = 8.4 Hz, 1H), 7.84 (dd, J = 3.1 Hz, 6.0 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 51.9, 52.2, 126.6, 126.9, 127.3, 127.4, 128.5, 129.1, 130.0, 130.2, 130.6, 131.5, 131.6, 132.7, 133.0, 133.3, 135.8, 136.8, 141.7, 142.0, 167.5, 168.8. GC-EIMS (m/z, %): 250 (22), 251 (20), 252 (56), 253 (23), 281 (26), 315 (100), 316 (23), 317 (35), 406 (62), 408 (23). Anal. calcd for $C_{24}H_{19}ClO_4$: C, 70.85; H, 4.71. Found: C, 70.69; H, 4.66.

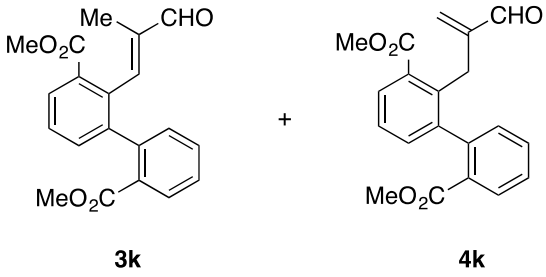
Dimethyl (*E*)-2'-(3-methoxy-2-methyl-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3j) + dimethyl 2'-(2-(methoxycarbonyl)allyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (4j).



3j **4j**

The two isomers were obtained as an inseparable mixture. Yellow/orange oil. Representative ^{1}H NMR resonances of products **3j** (400 MHz, $CDCl_3$) δ*:* 1.25 (s, 3H), 3.67 (s, 6H), 3.84 (s, 3H), 7.21 (d, J = 7.6 Hz, 1H), 7.62 (s, 1H). Representative ^{1}H NMR resonances of products **4j** (400 MHz, $CDCl_3$) δ*:* 3.58 (d, J = 17.2 Hz, 1H), 3.59 (s, 3H), 3.65 (s, 3H), 3.82 (s, 3H), 3.97 (d, J = 17.2 Hz, 1H), 4.96 (d, J = 1.1 Hz, 1H), 6.05 (d, J = 1.1 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.92 (dd, J = 1.3 Hz, 7.7 Hz, 1H), 7.98 (dd, J = 0.98 Hz, 7.7 Hz, 1H). ^{13}C NMR of both isomers (100.6 MHz, $CDCl_3$) δ: 13.7, 32.4, 51.8, 51.8, 51.9, 52.0, 52.2, 124.8, 125.8, 127.3, 127.6, 127.7, 129.3, 129.7, 130.0, 130.2, 130.4, 130.8, 130.9, 131.2, 131.5, 131.6, 132.9, 133.1, 136.8, 138.4, 140.0, 141.3, 141.6, 141.8, 143.7, 167.1, 167.2, 167.2, 167.9, 168.0. GC-EIMS of **3j** (m/z, %): 165 (10), 189 (30), 205 (12), 277 (22), 309 (100), 310 (21), 368 (2). GC-EIMS of **4j** (m/z, %): 165 (24), 178 (19), 189 (78), 190 (33), 191 (24), 205 (28), 217 (24), 218 (28), 233 (20), 245 (39), 249 (24), 269 (23), 272 (78), 273 (30), 276 (22), 277 (58), 304 (46), 305 (41), 309 (100), 310 (20), 336 (29), 368 (5).

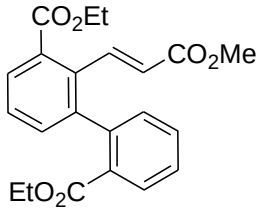
Dimethyl (*E*)-2'-(2-methyl-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3k) + dimethyl 2'-(2-formylallyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (4k).



3k **4k**

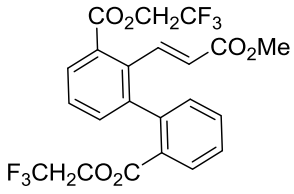
The two isomers were obtained as an inseparable mixture. Yellow/orange oil. Representative ^{1}H NMR resonances of products **3k** (400 MHz, $CDCl_3$) *δ:* 1.31 (s, 3H), 3.66 (s, 3H), 3.84 (s, 3H), 7.20 (dd, *J* = 1.2 Hz, 7.7 Hz, 1H), 7.90 (dd, *J* = 1.3 Hz, 7.8 Hz, 1H), 8.01 (dd, *J* = 1.3 Hz, 7.7 Hz, 1H), 9.36 (s, 1H). Representative ^{1}H NMR resonances of products **4k** (400 MHz, $CDCl_3$) *δ:* 3.54 (d, *J* = 17.4 Hz, 1H), 3.61 (s, 3H), 3.80 (d, *J* = 17.2 Hz, 1H), 3.81 (s, 3H), 5.73 (s, 1H), 5.87 (s, 1H), 7.13 (dd, *J* = 1.3 Hz, 7.9 Hz, 1H), 7.94 (dd, *J* = 1.5 Hz, 7.7 Hz, 1H), 7.98 (dd, *J* = 1.6 Hz, 7.7 Hz, 1H) 9.40 (s, 1H). ^{13}C NMR of both isomers (100.6 MHz, $CDCl_3$) *δ*: 10.3, 29.2, 51.9, 52.0, 52.1, 52.3, 125.9, 127.8, 128.0, 129.5, 129.6, 129.8, 130.1, 130.3, 130.5, 130.6, 130.8, 131.0, 131.6, 131.8, 133.0, 133.2, 134.1, 136.6, 139.5, 141.0, 141.5, 141.6, 143.8, 149.3, 149.6, 166.9, 167.1, 167.3, 167.9, 193.5, 194.7. GC-EIMS of **3k** (m/z, %): 165 (11), 289 (22), 219 (19), 279 (15), 309 (100), 310 (24). GC-EIMS of **4k** (m/z, %): 165 (43), 189 (80), 190 (42), 191 (66), 218 (62), 219 (80), 245 (35), 246 (40), 247 (50), 269 (31), 274 (20), 277 (39), 278 (24), 279 (20), 306 (27), 309 (100), 310 (31), 338 (2).

Diethyl (*E*)-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3l).



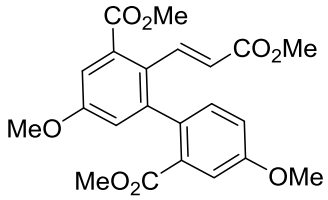
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.00 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 3.63 (s, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 5.54 (d, *J* = 16.2 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45-7.35 (m, 2H), 7.50 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.5 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) *δ*: 13.8, 14.2, 51.6, 61.0, 61.5, 123.6, 127.8, 127.9, 129.2, 130.5, 130.8, 130.9, 131.3, 131.8, 133.0, 134.7, 141.3, 142.3, 143.6, 166.5, 167.1, 167.6. IR (ATR): 2983, 1710, 1246, 1168, 1135, 1092, 1056, 1013, 763, 716 cm^{-1}. GC-EIMS (m/z, %): 249 (54), 277 (75), 295 (83), 323 (100), 382 (14). HR-EIMS (m/z): 382.1416 calcd for $C_{22}H_{22}O_6^+$, found: 382.1421.

Bis(2,2,2-trifluoroethyl) (*E*)-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3m).



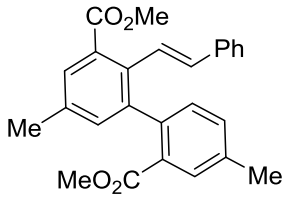
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 3.65 (s, 3H), 4.35-4.54 (m, 2H), 4.59-4.74 (m, 2H), 5.49 (d, *J* = 16.3 Hz, 1H), 7.23 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1H), 7.40 (ddd, *J* = 7.7, 1.5, 0.4 Hz, 1H), 7.44-7.53 (m, 2H), 7.60 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.83 (dd, *J* = 16.3, 0.4 Hz, 1H), 7.97-8.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 51.7, 61.0 (q, *J* = 36.8 Hz), 61.1 (q, *J* = 36.8 Hz), 122.8 (q, *J* = 277.3 Hz), 122.9 (q, *J* = 277.3 Hz), 124.5, 128.2, 128.3, 128.3, 128.4, 130.3, 131.2, 131.8, 133.1, 134.0, 135.8, 141.8, 141.9, 142.7, 165.1, 165.4, 166.2. ^{19}F NMR (282 MHz, $CDCl_3$) *δ*: -73.73 (t, *J* = 8.5 Hz), -73.51 (t, *J* = 8.4 Hz). IR (ATR): 1728, 1440, 1411, 1286, 1242, 1167, 1137, 1098, 1069, 971, 765 cm^{-1}. GC-EIMS (m/z, %): 176 (29), 205 (18), 220 (16), 331 (100), 363 (24), 431 (59), 490 (4). HR-ESIMS (m/z): 491.0924 calcd for $C_{22}H_{16}F_6O_6$+H^+, found: 491.0924.

Dimethyl (*E*)-4,5'-dimethoxy-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3n).



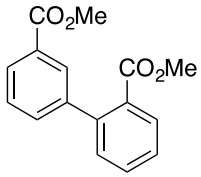
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.64 (s, 3H), 3.65 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 3.88 (s, 3H), 5.46 (d, J = 16.2 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 7.02-7.12 (m, 2H), 7.34 (d, J = 2.8 Hz, 1H), 7.45 (dd, J = 2.5, 0.6 Hz, 1H), 7.77 (d, J = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 51.6, 52.2, 52.6, 55.6, 55,7, 114.1, 115.1, 118.2, 119.4, 122.6, 127.4, 131.4, 132.2, 132.5, 133.7, 143.1, 143.8, 158.8, 159.0, 166.9, 167.2, 168.2. IR (ATR): 2952, 1717, 1599, 1436, 1283, 1216, 1169, 1061, 908, 726 cm^{-1}. GC-EIMS (m/z, %): 44 (22), 191 (10), 207 (100), 253 (12), 281 (17), 323 (43), 355 (13), 414 (5). HR-EIMS (m/z): 414.1315 calcd for $C_{22}H_{22}O_8^+$, found: 414.1321.

Dimethyl (*E*)-4,5'-dimethyl-2'-styryl-[1,1'-biphenyl]-2,3'-dicarboxylate (3o).



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.40 (s, 3H), 3.58 (s, 3H), 3.83 (s, 3H), 6.19 (d, J = 16.5 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 7.13-7.20 (m, 5H), 7.21-7.26 (m, 2H), 7.31 (dd, J = 7.8, 1.9 Hz, 1H), 7.59 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 21.1, 21.1, 52.0, 52.3, 126.4, 126.5, 127.4, 128.5, 129.5, 130.6, 130.7, 130.7, 131.6, 132.4, 133.5, 134.2, 134.2, 136.3, 137.2, 137.8, 139.5, 141.9, 167.9, 169.7. IR (ATR): 2950, 1722, 1435, 1324, 1294, 1252, 1203, 1094, 1066, 747 cm^{-1}. GC-EIMS (m/z, %): 207 (11), 265 (18), 282 (15), 309 (100), 400 (51).). HR-EIMS (m/z): 400.1675 calcd for $C_{26}H_{24}O_4^+$, found: 400.1667.

Dimethyl [1,1'-biphenyl]-2,3'-dicarboxylate (5).[2]

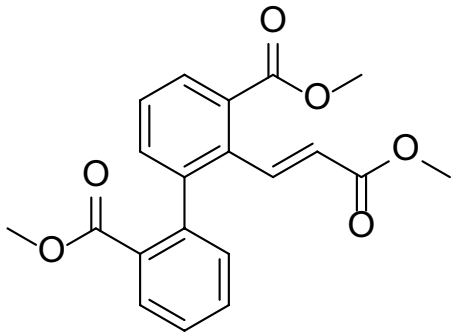


Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (s, 3H), 3.92 (s, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.43-7.51 (m, 3H), 7.55 (dd, J = 7.5 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 8.01 (s, 1H), 8.03-8.05 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 52.0, 52.2, 127.6, 128.0, 128.4, 129.4, 129.9, 130.1, 130.4, 130.8, 131.5, 132.9, 141.6 (2C), 166.9, 168.5. GC-EIMS (m/z, %): 151 (45), 152 (45), 181 (28), 207 (100), 239 (79), 270 (90). Anal. calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.21; H, 5.10.

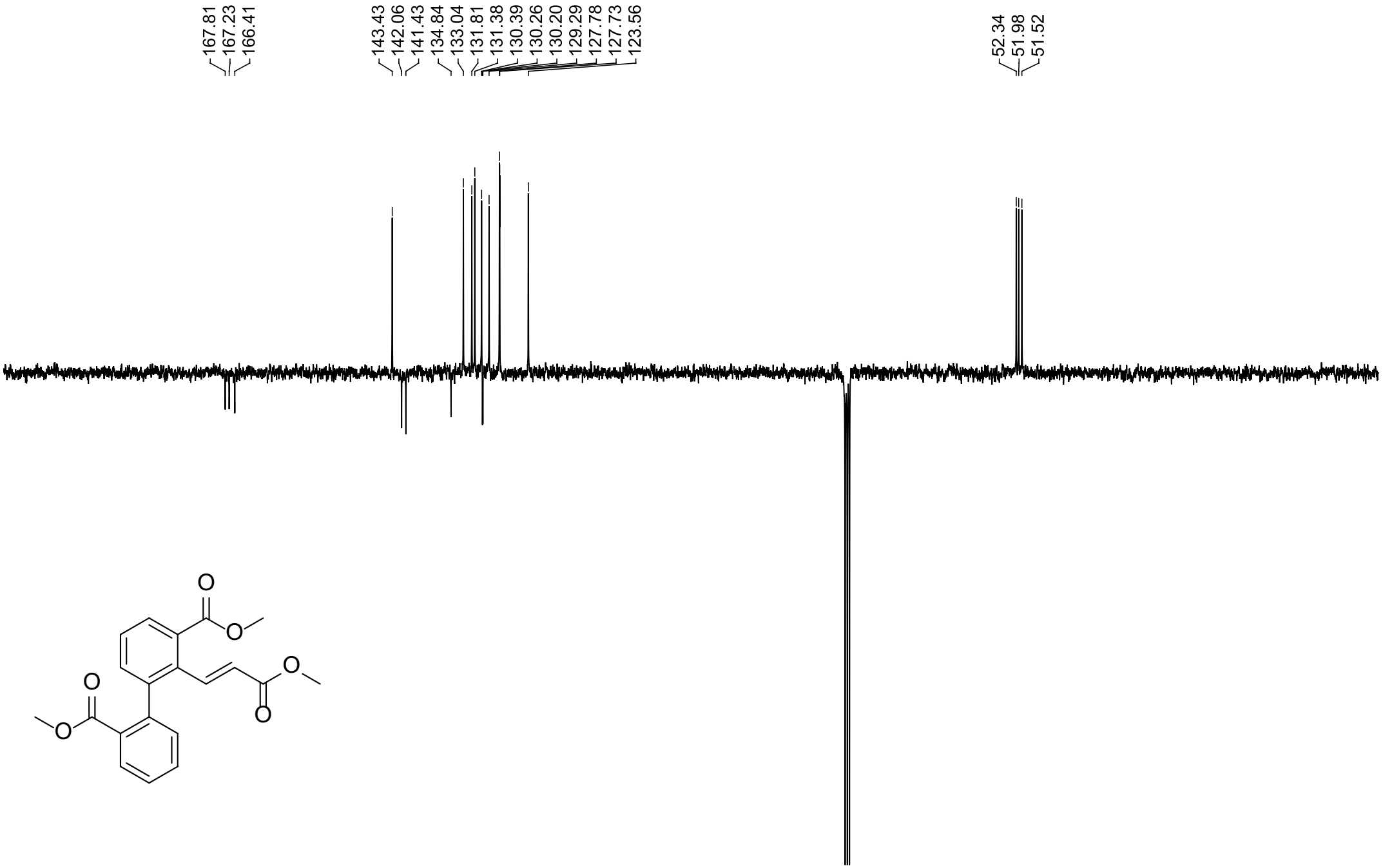
References

1. Motti, E.; Ippomei, G.; Deledda, S.; Catellani, M. *Synthesis* **2003**, 2671-2678.
2. Deledda, S.; Motti, E.; Catellani, M. *Can. J. Chem.* **2005**, *83*, 741-747.

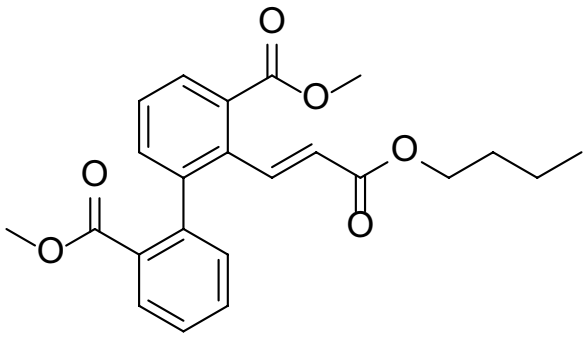
Dimethyl (E)-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3a)



Dimethyl (E)-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3a)

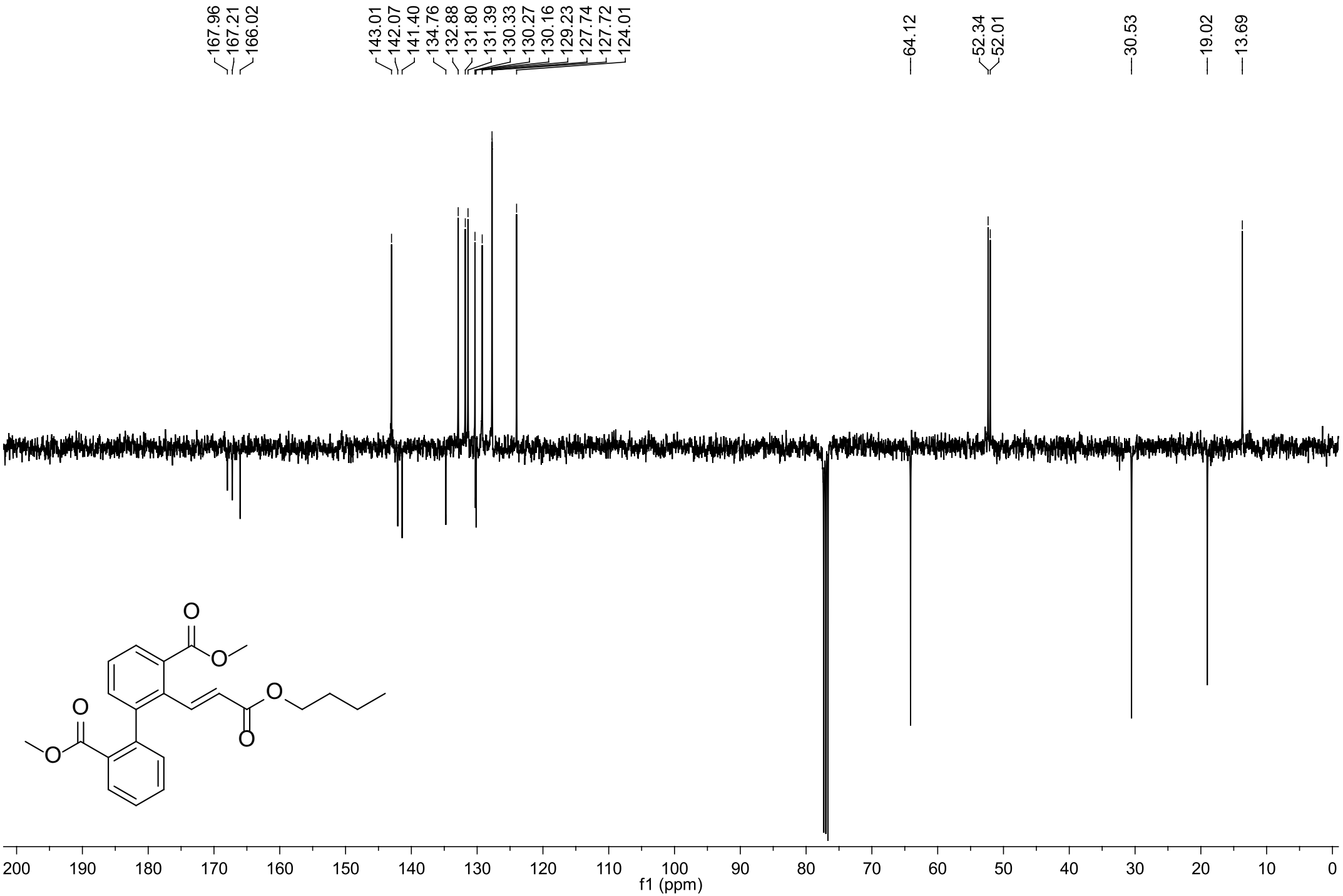


(E)-Dimethyl 2'-(3-butoxy-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate (3b)



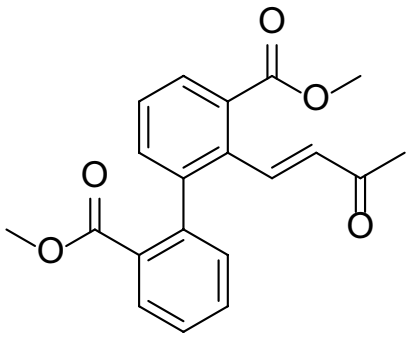
ESI - 11

(E)-Dimethyl 2'-(3-butoxy-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate



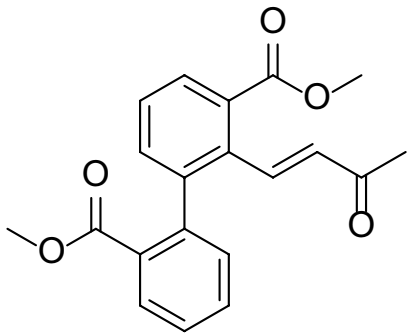
ESI - 12

Dimethyl 2’-(3-oxobut-1-en1-yl)-[1,1’-biphenyl]-2,3’-dicarboxylate (3c)



ESI - 13

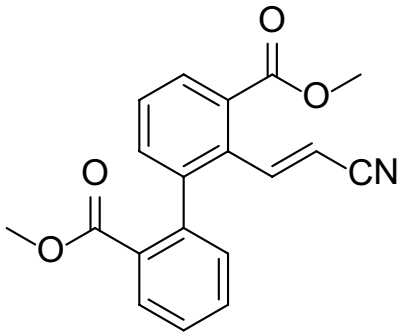
Dimethyl 2'-(3-oxobut-1-en1-yl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3c)



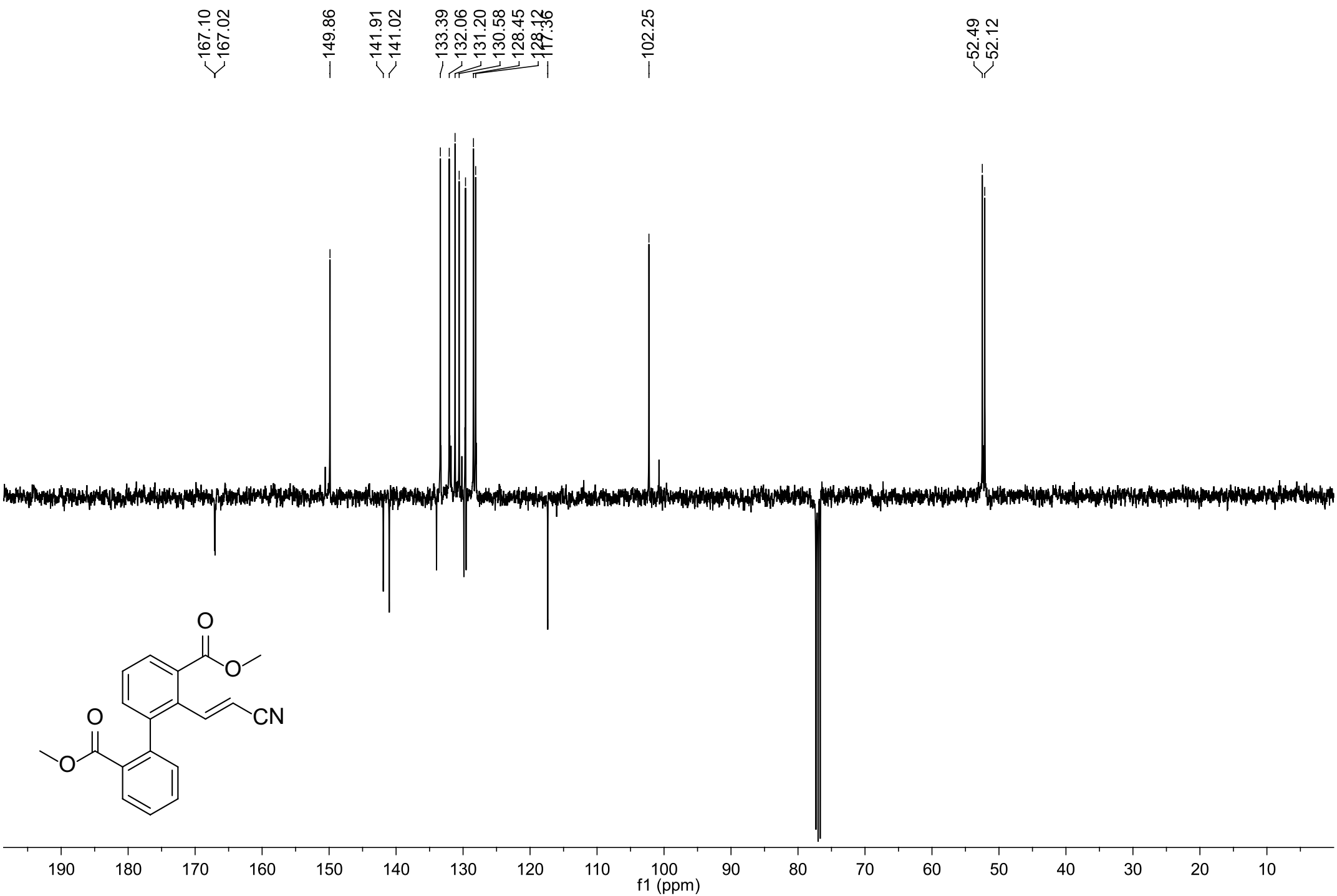
198.15
167.62
167.21
142.55
141.91
141.34
135.21
133.17
131.86
131.38
130.29
130.17
129.73
129.47
127.91
127.82
52.33
52.02
26.50

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

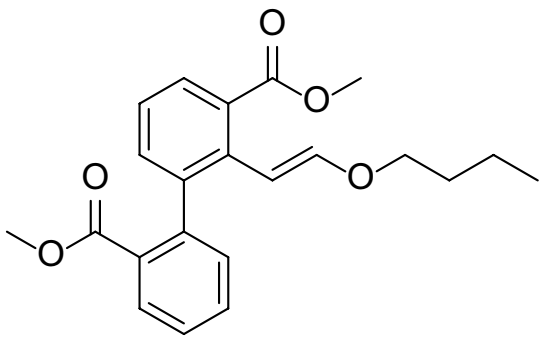
Dimethyl (E)-2'-(2-cyanovinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3d)



Dimethyl (E)-2'-(2-cyanovinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3d)

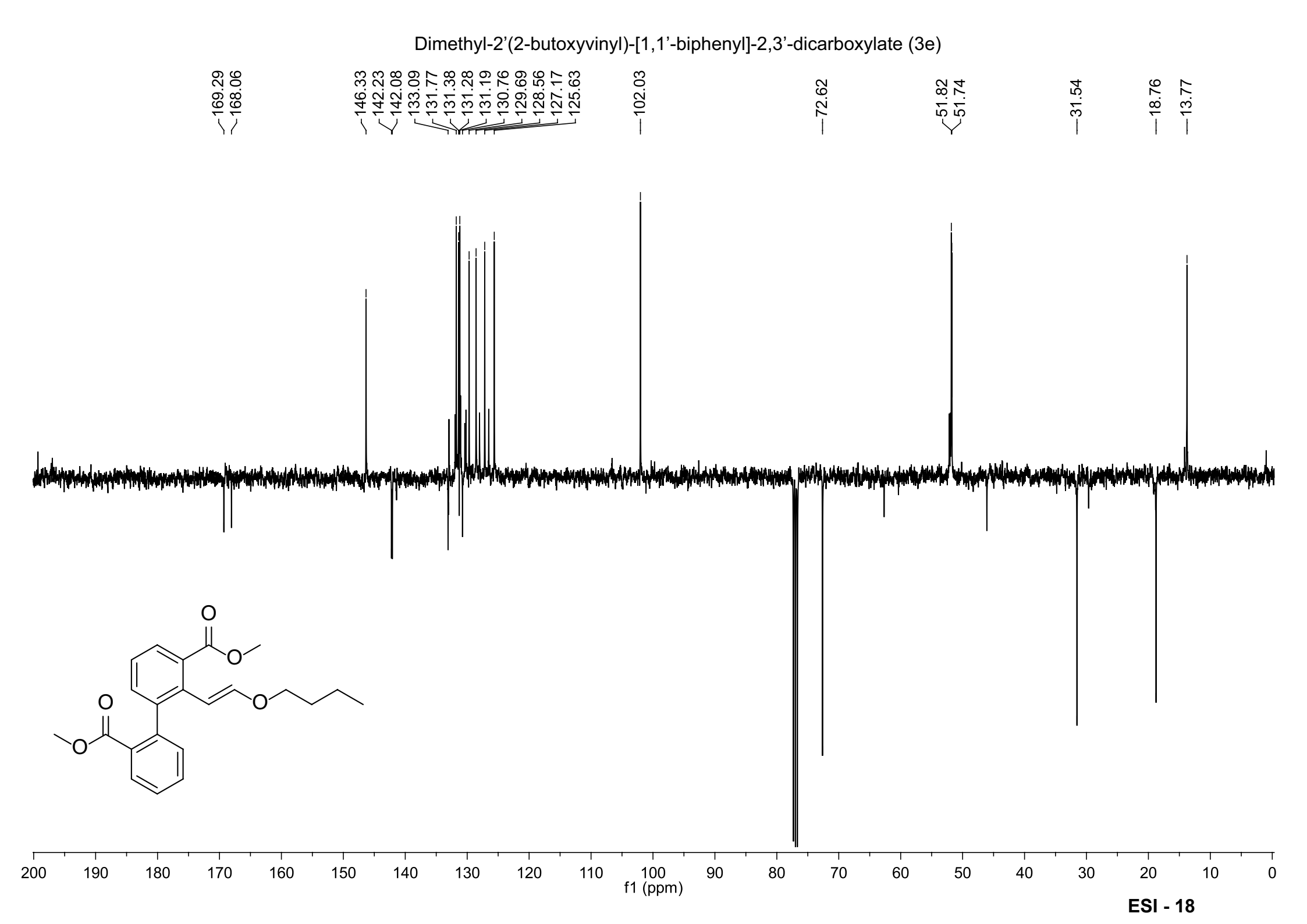


Dimethyl-2'(2-butoxyvinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3e)



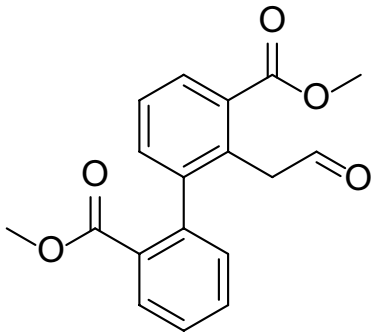
ESI - 17

Dimethyl-2'(2-butoxyvinyl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3e)

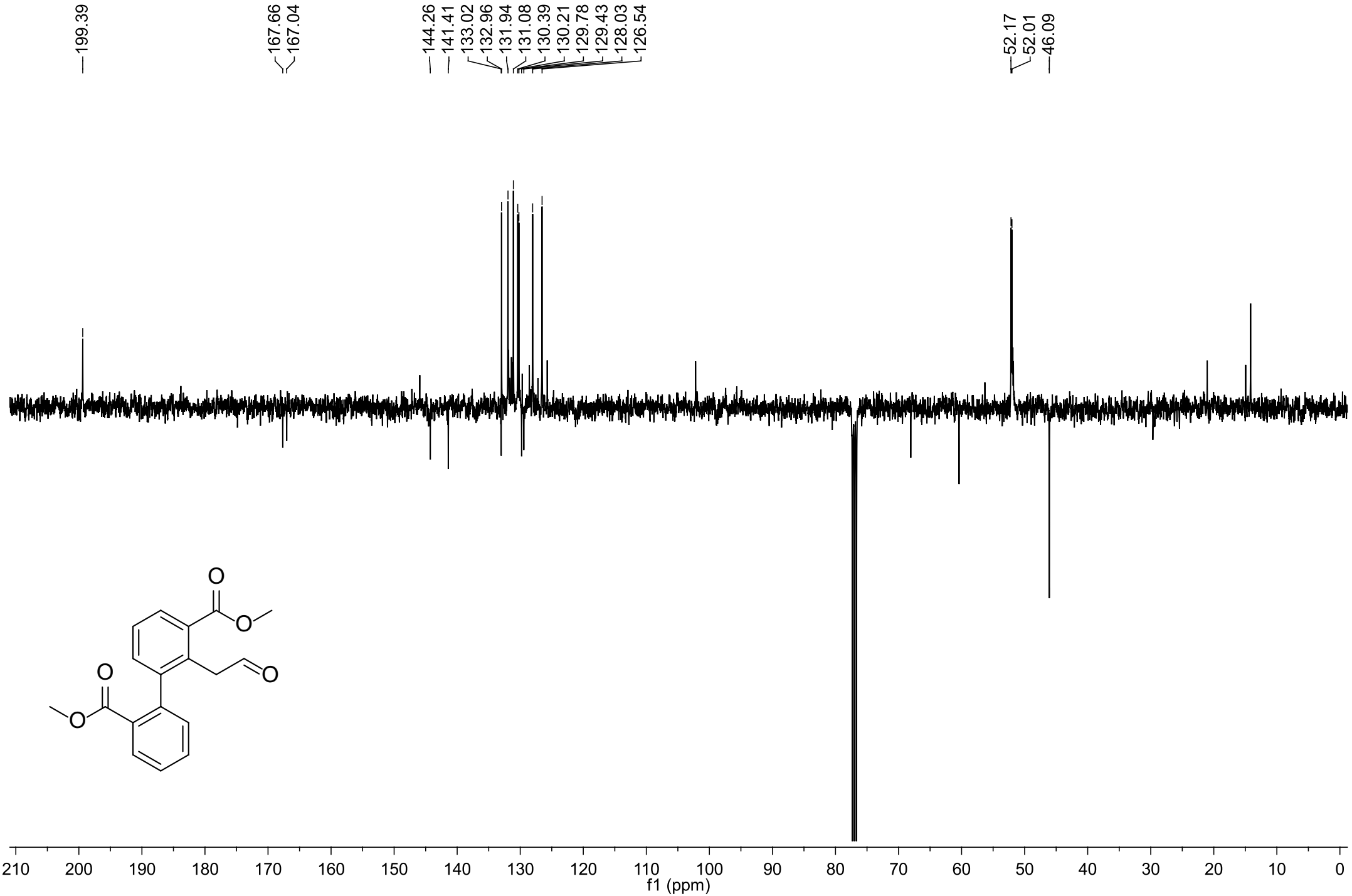


ESI - 18

Dimethyl 2'-(2-oxoethyl)biphenyl-2,3'-dicarboxylate (3f)

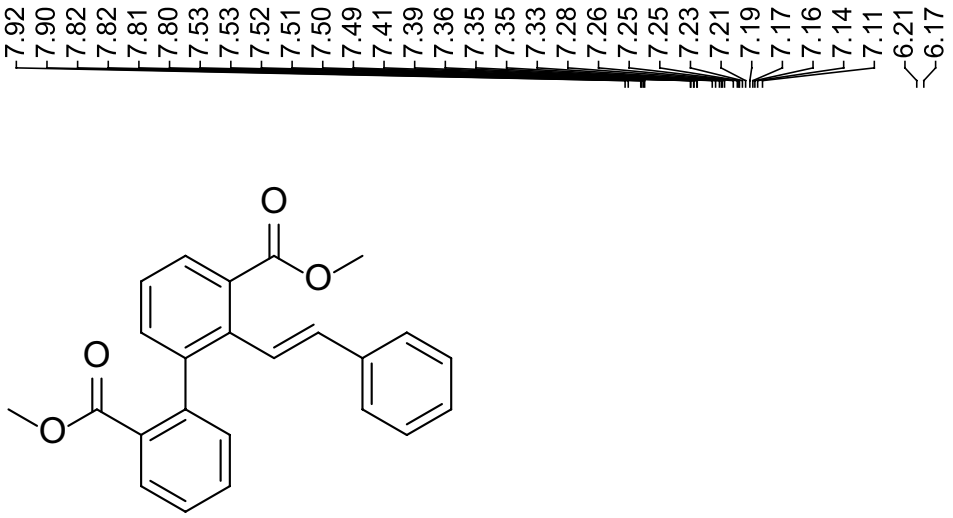


Dimethyl 2'-(2-oxoethyl)biphenyl-2,3'-dicarboxylate (3f)

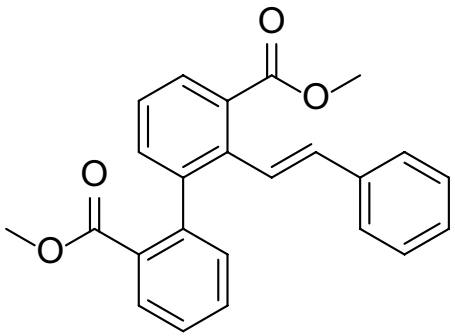


ESI - 20

Dimethyl (E)-2'-styryl-[1,1'-biphenyl]-2,3'-dicarboxylate (3g)



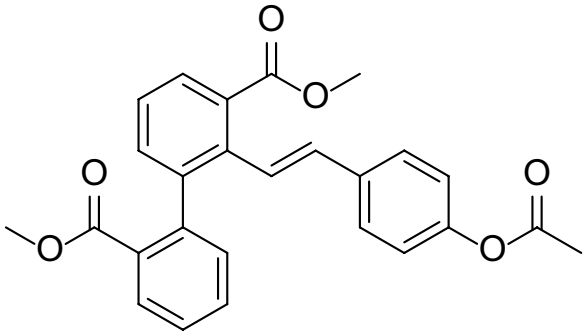
Dimethyl (E)-2'-styryl-[1,1'-biphenyl]-2,3'-dicarboxylate (3g)



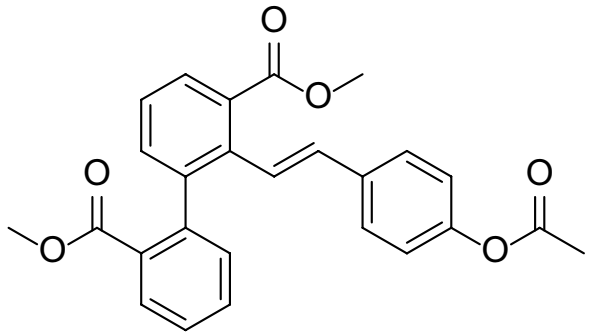
169.11
167.54
142.11
141.74
137.33
136.90
134.67
132.50
131.58
131.54
130.61
130.48
130.04
128.96
128.36
127.45
127.30
126.38
126.28
126.23
52.18
51.88

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Dimethyl (E)-2'-(4-acetoxystyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3h)

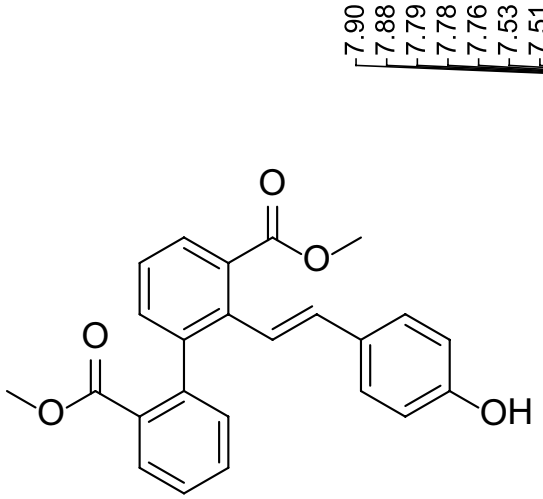


Dimethyl (E)-2'-(4-acetoxystyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3h)



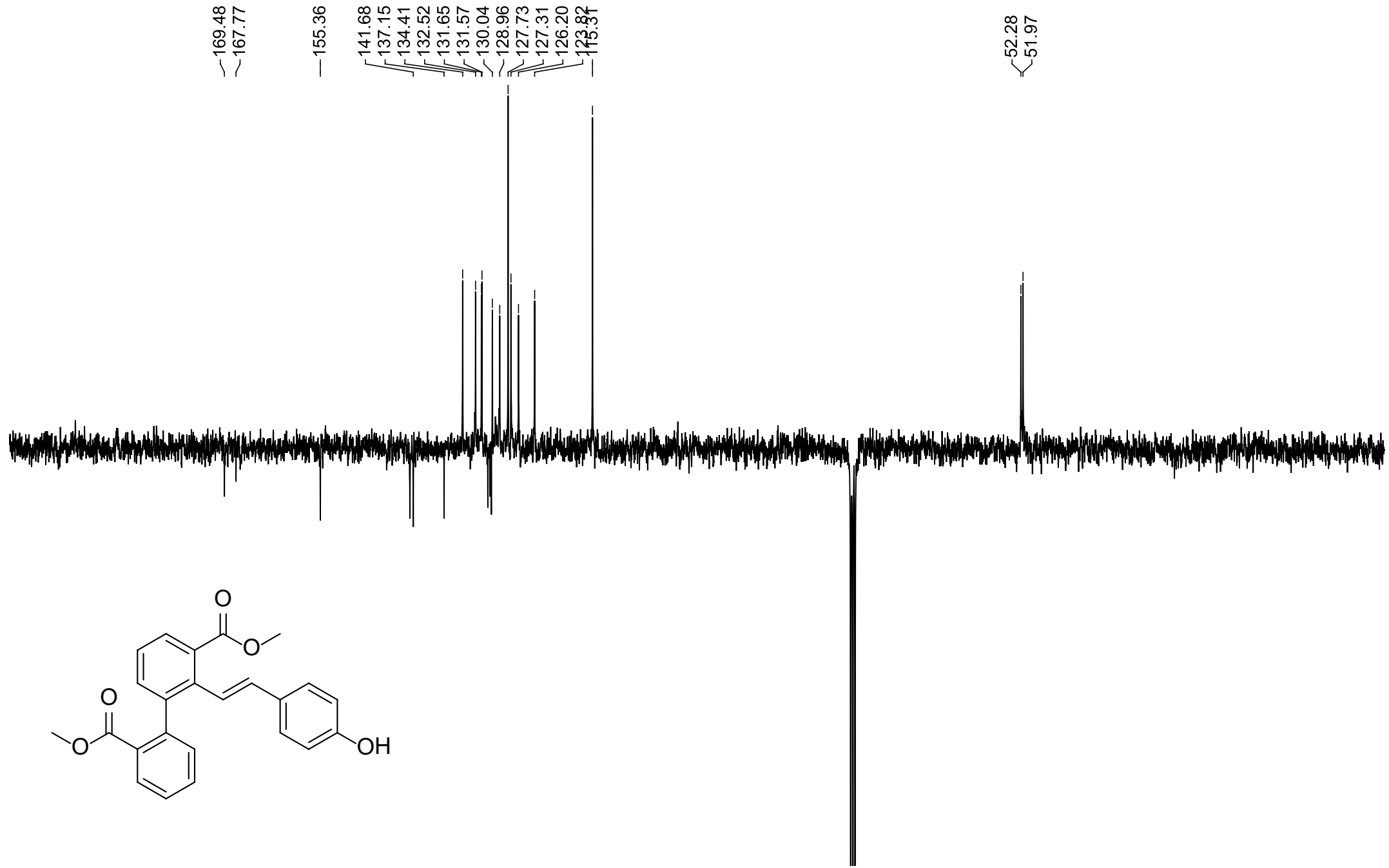
ESI - 24

(E)-Dimethyl 2'-(4-hydroxystyryl)biphenyl-2,3'-dicarboxylate (3`h)

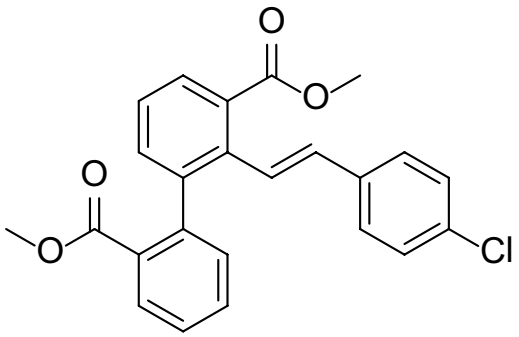


ESI - 25

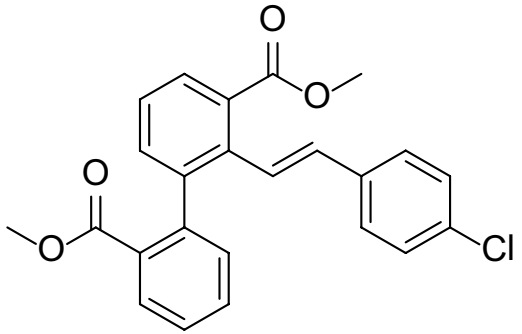
(E)-Dimethyl 2'-(4-hydroxystyryl)biphenyl-2,3'-dicarboxylate (3`h)



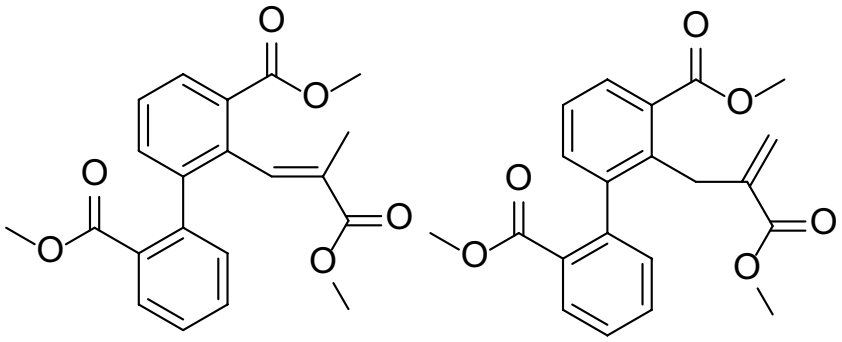
Dimethyl (E)-2'-(4-chlorostyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3i)



Dimethyl (E)-2'-(4-chlorostyryl)-[1,1'-biphenyl]-2,3'-dicarboxylate (3i)

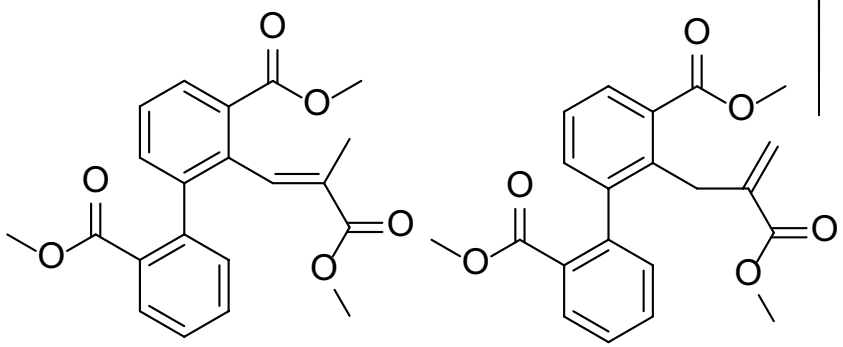


(E)-Dimethyl 2'-(3-methoxy-2-methyl-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate (3j)
Dimethyl 2'-(2-(methoxycarbonyl)allyl)biphenyl-2,3'-dicarboxylate (4j)



(E)-Dimethyl 2'-(3-methoxy-2-methyl-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate (3j)
Dimethyl 2'-(2-(methoxycarbonyl)allyl)biphenyl-2,3'-dicarboxylate (4j)

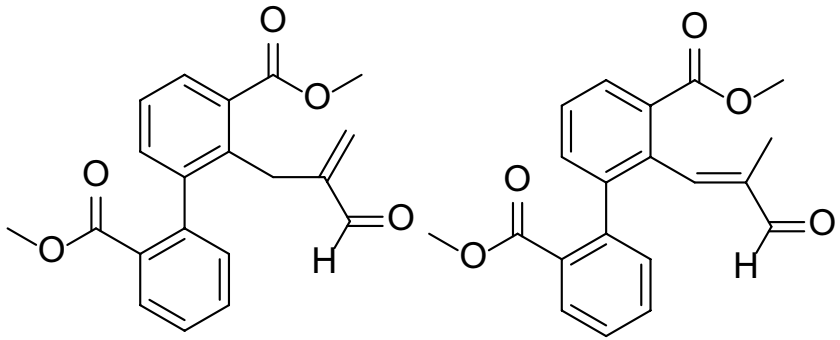
168.05
167.89
167.22
167.16
167.08
143.73
141.77
141.63
141.27
139.97
138.39
136.85
133.14
132.89
131.62
131.52
131.17
130.85
130.79
130.38
130.17
129.97
129.74
129.30
127.70
127.65
127.36
125.80
124.76
52.22
52.04
51.90
51.83
51.77
32.43
13.75



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

ESI - 30

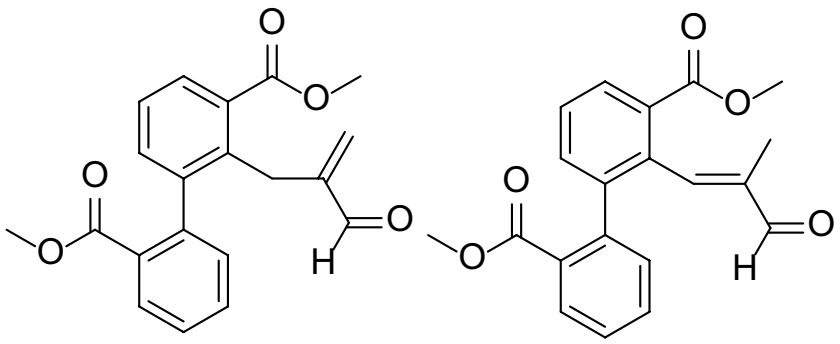
(E)-Dimethyl 2'-(2-methyl-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate (3k)
Dimethyl 2'-(2-formylallyl)biphenyl-2,3'-dicarboxylate (4k)



f1 (ppm)

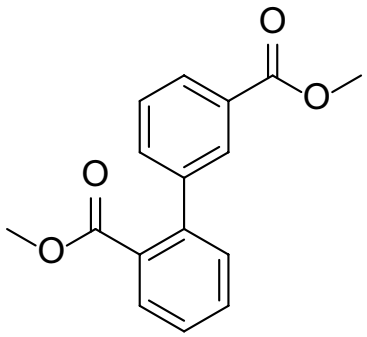
(E)-Dimethyl 2'-(2-methyl-3-oxoprop-1-enyl)biphenyl-2,3'-dicarboxylate (3k)
Dimethyl 2'-(2-formylallyl)biphenyl-2,3'-dicarboxylate (4k)

194.74
193.48
167.94
167.28
167.07
166.95
149.58
149.31
143.83
141.55
141.50
140.97
139.55
136.58
134.07
133.16
132.96
131.80
131.60
131.02
130.84
130.64
130.52
130.32
130.08
129.83
129.60
129.46
127.96
127.81
125.89
52.30
52.06
52.00
51.86
29.21
10.32



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Dimethyl biphenyl-2,3'-dicarboxylate (5)



Dimethyl biphenyl-2,3'-dicarboxylat e (5)