Palladium Catalyzed Selective Distal C-H Olefination of Biaryl Systems

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Supporting Information

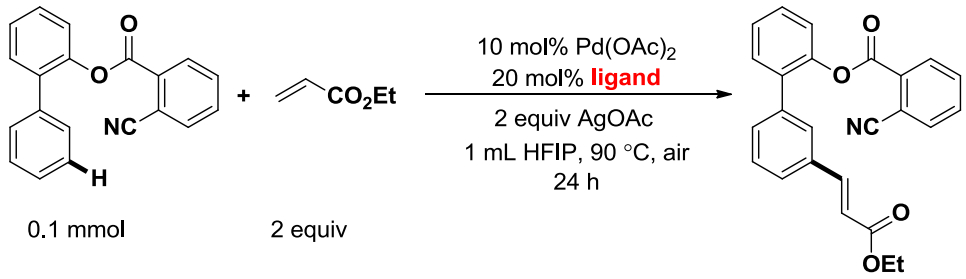
General Consideration:

Reagent Information. Unless otherwise stated, all reactions were carried out in screw cap reaction tubes. All the solvents were bought from commercial sources and were used without further purification. Palladium acetate and other palladium salts were purchased from Alfa Aesar and Aldrich. Silica gel (100–200 mesh) obtained from SRL Co. was used for column chromatography. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254)}$.

Analytical Information. All compounds are characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and HR-MS. Copies of the ^{1}H NMR, ^{13}C NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 500 MHz/400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. High-resolution mass spectra (HR-MS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

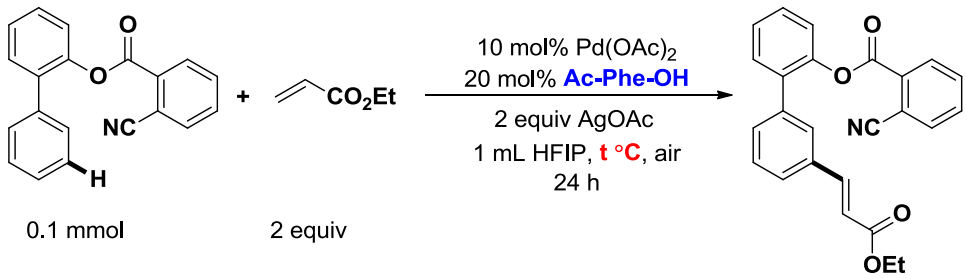
Optimization details for *Distal*-C-H olefination:

S1. Optimization of **ligands**:



Entry	Ligand	Yield (*meta*: others)
1	N-Formylglycine	21(2:1)
2	Ac-Gly-OH	63(4.8:1)
3	**Ac-Phe-OH**	**67 (5.8:1)**
4	Boc-Val-OH	57 (2.7:1)
5	Ac-Val-OH	55 (4.6:1)
6	Boc-Ala-OH	52 (3.8:1)
7	Ac-Ala-OH	56 (4.2:1)
8	Boc-Ile-OH	56 (4.4:1)
9	Boc-Leu-OH	58 (4.5:1)
10	Ac-Leu-OH	58 (4.8:1)
11	Boc-Lys-OH	-
12	Boc-Pro-OH	42 (5.2: 1)
13	Boc-Gly-OH	62 (4.3:1)

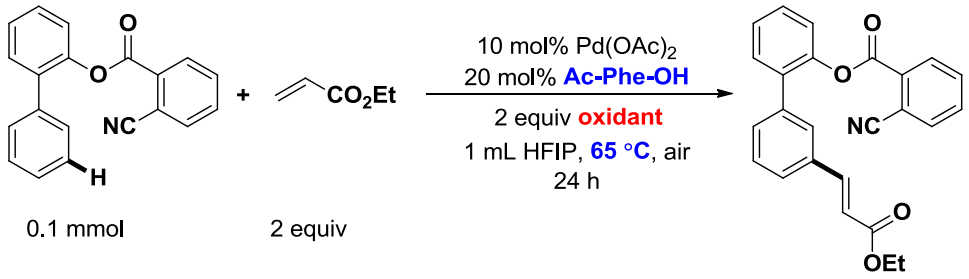
S2. Optimization of **temperature:**



Entry	Temperature (°C)	Yield (*meta*: others)
1	100	58 (2.3:1)
2	90	62 (2.9:1)
3	80	69 (3.3:1)
4	70	68 (4.4:1)
5	**65**	**70 (5.8:1)**
6	60	62 (6:1)

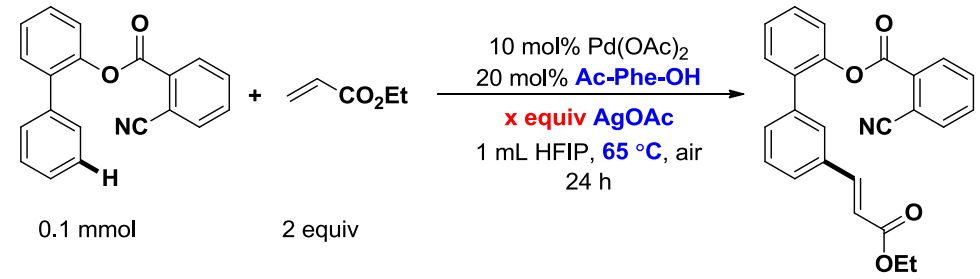
7	55	68 (6:1)

S3. Optimization of **oxidants**:



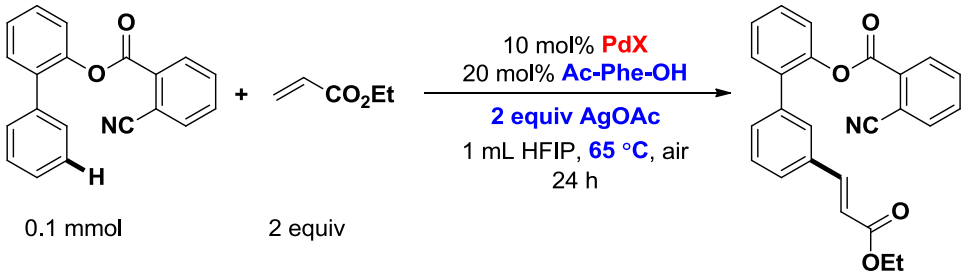
Entry	Oxidant	Yield (*meta*: others)
1	**AgOAc**	**70 (5.8:1)**
2	Ag_2CO_3	65 (5.3:1)
3	$AgNO_3$	58 (1:1.4)
4	Ag_2O	--
5	$AgNO_2$	54 (1:1.2)
6	Ag_2SO_4	11
7	AgOAc + Ag_2SO_4 (1 equiv.)	62 (5.1:1)
8	AgOAc + Ag_2SO_4 (0.5 equiv.)	63 (5.:1)

S4. Optimization of **oxidant amount**:



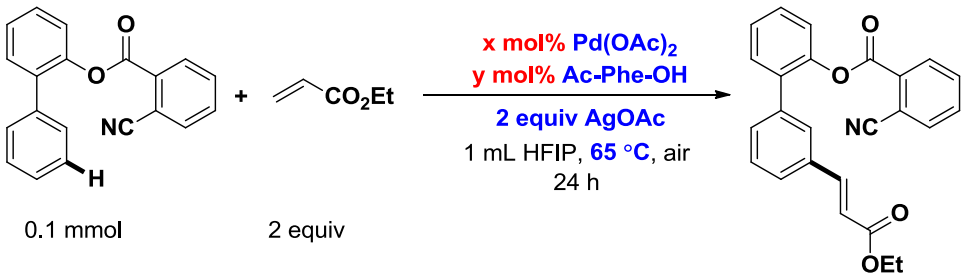
Entry	AgOAc amount (equiv.)	Yield (*meta*: others)
1	1.0	52 (6.5:1)
2	1.5	67 (5.8:1)
3	**2.0**	**70 (5.8:1)**
4	3.0	73 (4.2:1)

S5. Optimization of **Pd source**:



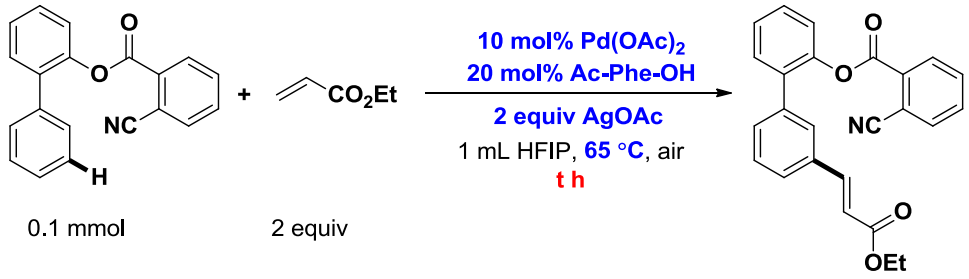
Entry	Pd salt	Yield (*meta*: others)
1	$PdCl_2$	67 (4.8:1)
2	**$Pd(OAc)_2$**	**70 (5.8:1)**
3	$Pd(OPiv)_2$	68 (5:1)
4	$Pd(TFA)_2$	69 (5.2:1)
5	$Pd_2(dba)_3$	60 (2:1)
6	$Pd(acac)_2$	-
7	$Pd(dppf)Cl_2$	66 (5.5:1)
8	$Pd(MeCN)_2Cl_2$	72 (2.5:1)

S6. Optimization of **Pd/ligand loading**:



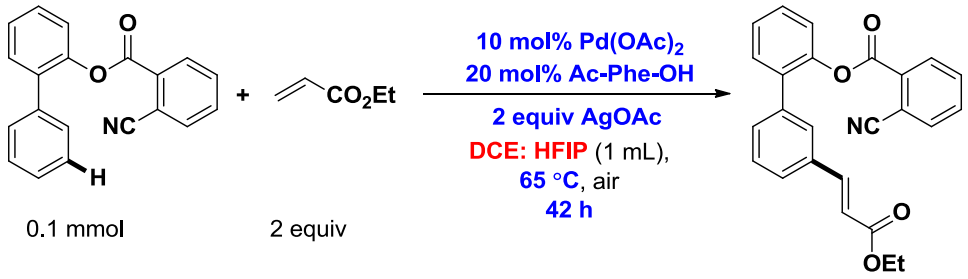
Entry	Pd loading (mol%)	Ligand loading (mol%)	Yield (*meta*: others)
1	5	10	46 (9:1)
2	7.5	15	62 (5.8:1)
3	**10**	**20**	**70 (5.8:1)**
4	12.5	25	76 (4.8:1)
5	15	30	82 (3.5:1)
6	10	15	67 (5.2:1)
7	10	25	69 (5.5:1)
8	10	30	68 (5.3:1)

S7. Optimization of **time**:



Entry	Time (h)	Yield (*meta*: others)
1	16	45 (4.2:1)
2	24	70 (5.8:1)
3	36	63 (6.7:1)
4	**42**	**73 (8:1)**

1.1 Optimization of ***ratio*** of **solvents**:



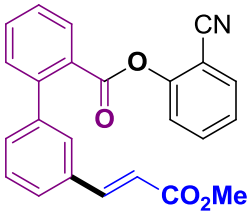
Entry	Solvent (1 mL)	Yield (*meta*: others)
1	DCE:HFIP (10:1)	61 (12:1)
2	DCE:HFIP (9:1)	68 (7:1)
3	DCE:HFIP (8:1)	59 (9:1)
4	**DCE:HFIP (7:1)**	**70 (14:1)**
5	DCE:HFIP (6:1)	62 (13:1)
6	DCE:HFIP (5:1)	67 (10:1)
7	DCE:HFIP(4:1)	61 (6.6:1)
8	DCE:HFIP (2:1)	61 (6:1)
11	DCE:HFIP (1:1)	60 (5.1:1)

General procedure for palladium catalyzed distal C–H olefination of biaryl systems

To an oven-dried screw cap reaction tube charged with a magnetic stir-bar was added the starting biphenyl ester (0.3 mmol, 1 equiv), $Pd(OAc)_2$ (10 mol%), Ac-Phe-OH (20 mol%), AgOAc (0.6 mmol, 2 equiv) and 2 mL solvent (DCE: HFIP = 7:1). Coupling partner olefins (0.6 mmol; 2 equiv) was added with a micro litter pipette and solvent was introduced with a disposable laboratory syringe.

Note that, commercially purchased solvents were used without further purification or drying. The tube was placed in a preheated oil bath at 65 ºC and the reaction mixture was stirred under aerobic condition (at 900 rpm) for 42 h. The reaction mixture was then cooled to room temperature and filtered through a celite pad with ethyl acetate. The filtrate was concentrated and purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

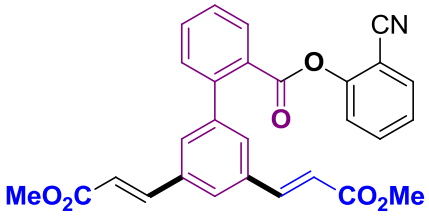
Characterization Data of Synthesized Compounds:



3a

(*E*)-2-cyanophenyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3a).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and methyl acrylate (0.6 mmol, 54 µL).
Eluent: ethyl acetate/ petroleum ether (5:95 v/v);
Appearance: Creamy white solid.
Isolated yield: 65% (75 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 1H), 7.72 (t, *J* = 12.8 Hz, 1H), 7.65 (ddd, *J* = 6.9, 5.0, 4.5 Hz, 2H), 7.59 – 7.49 (m, 5H), 7.47 – 7.40 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.53, 165.12, 152.48, 144.71, 143.34, 141.83, 134.51, 134.24, 133.45, 132.97, 131.35, 131.17, 130.84, 128.91, 128.34, 128.27, 128.15, 127.37, 126.50, 123.07, 118.45, 115.40, 107.40, 51.91.
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{24}H_{17}NNaO_4$ *m/z* 406.1050 and found *m/z* 406.1040.



3a'

(2*E*,2'*E*)-dimethyl-3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (Scheme 3, 3a').

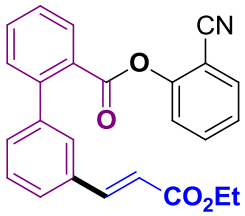
Di-olefinated product was isolated from the same reaction.

Isolated yield: 15% (21 mg)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 16.0 Hz, 2H), 7.66 – 7.62 (m, 2H), 7.60 – 7.54 (m, 5H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.49 (dd, *J* = 16.0, 7.1 Hz, 2H), 3.79 (d, *J* = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.29, 164.71, 152.46, 143.86, 142.90, 142.65, 135.18, 134.30, 133.49, 133.25, 131.47, 131.43, 129.82, 128.55, 127.99, 126.88, 126.59, 123.06, 119.44, 115.37, 107.39, 52.01.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{28}H_{21}NNaO_6$ *m/z* 490.1261 and found *m/z* 490.1264.



3b

(*E*)-2-cyanophenyl-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3b).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and ethyl acrylate (0.6 mmol, 65 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

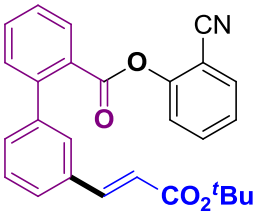
Appearance: Sticky liquid

Isolated yield: 67% (80 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.66 (ddd, *J* = 7.7, 5.7, 1.6 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.46 – 7.42 (m, 3H), 7.30 (td, *J* = 7.7, 1.0 Hz, 1H), 7.08 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.50 – 6.43 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 165.19, 152.53, 144.46, 143.39, 141.87, 134.65, 134.26, 133.50, 132.97, 131.38, 131.20, 130.80, 128.93, 128.43, 128.31, 128.18, 127.35, 126.52, 123.11, 118.99, 115.42, 107.46, 60.74, 14.51.

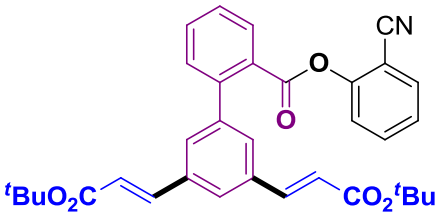
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{19}NNaO_4$ *m/z* 420.1206 and found *m/z* 420.1206.



3c

(*E*)-2-cyanophenyl-3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3c).

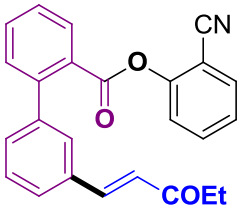
Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and *tert*-butyl acrylate (0.6 mmol, 88 µL).
Eluent: ethyl acetate/ petroleum ether (5:95 v/v);
Appearance: Sticky whitish liquid.
Isolated yield: 63% (80 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.63 (dd, *J* = 11.2, 8.7 Hz, 2H), 7.58 – 7.53 (m, 3H), 7.53 – 7.49 (m, 1H), 7.44 (dd, *J* = 8.0, 4.1 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 1.52 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.43, 165.25, 152.53, 143.37, 141.80, 134.87, 134.26, 133.48, 132.92, 131.36, 131.15, 130.54, 128.88, 128.50, 128.19, 128.14, 127.29, 126.50, 123.12, 120.94, 115.43, 107.47, 80.75, 28.40.
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{27}H_{23}NNaO_4$ *m/z* 448.1519 and found *m/z* 448.1521.



3c'

(2*E*,2'*E*)-di-tert-butyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (Scheme 3, 3c').

Di-olefinated product was isolated from the same reaction.
Isolated yield: 17% (28 mg)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (t, *J* = 8.1 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.62 (s, 2H), 7.59 – 7.53 (m, 5H), 7.44 – 7.38 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 8.7 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 2H), 1.52 (s, 18H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.15, 164.86, 152.47, 142.89, 142.59, 142.49, 135.43, 134.30, 133.48, 133.11, 131.36, 129.53, 128.46, 128.21, 126.55, 126.51, 123.08, 121.79, 115.37, 107.40, 80.91, 28.37.



3d

(*E*)-2-cyanophenyl 3'-(3-oxopent-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3d).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and ethyl vinyl ketone (0.6 mmol, 59 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

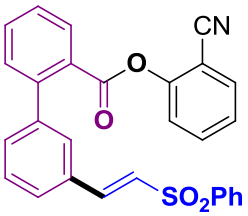
Appearance: Sticky reddish liquid.

Isolated yield: 64% (73 mg). The isolated compound is contaminated with *ca*. 7% inseparable aliphatic impurities which could not be purified further by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.66 (ddd, *J* = 13.6, 7.5, 1.3 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.53 (m, 3H), 7.47 – 7.42 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 2.69 (q, *J* = 7.3 Hz, 2H), 1.15 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.14, 165.11, 152.49, 143.42, 142.05, 141.83, 134.73, 134.25, 133.47, 132.99, 131.38, 131.19, 130.78, 128.96, 128.50, 128.29, 128.13, 127.52, 126.58, 126.54, 123.10, 115.44, 107.44, 34.27, 8.37.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{19}NNaO_3$ *m/z* 404.1257 and found *m/z* 404.1256.



3e

(*E*)-2-cyanophenyl 3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3e).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and phenyl vinyl sulfone (0.6 mmol, 101 mg).

Eluent: ethyl acetate/ petroleum ether (7:93 v/v);

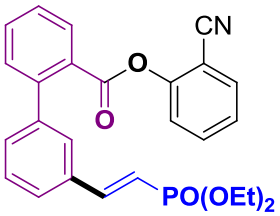
Appearance: White solid.

Isolated yield: 65% (91 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.74 – 7.68 (m, 1H), 7.68 – 7.63 (m, 1H), 7.61 (dt, *J* = 11.2, 2.7 Hz, 2H), 7.57 – 7.50 (m, 5H), 7.49 – 7.43 (m, 3H), 7.39 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 15.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.86, 152.41, 143.17, 142.26, 142.05, 140.75, 134.28, 133.53, 133.42, 133.10, 132.45, 131.65, 131.38, 131.27, 129.46, 129.08, 128.47, 128.27, 128.09, 127.99, 127.93, 127.84, 126.56, 123.07, 115.39, 107.34.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{28}H_{19}NNaO_4S$ *m/z* 488.0927 and found *m/z* 488.0926.



3f

(*E*)-2-cyanophenyl-3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3f).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and diethyl vinylphosphonate (0.6 mmol, 92 µL).

Eluent: ethyl acetate/ petroleum ether (7:93 v/v);

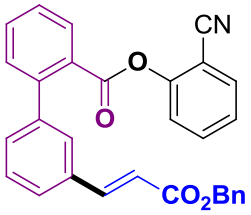
Appearance: Sticky reddish brown liquid.

Isolated yield: 71% (98 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.55 (dd, *J* = 14.5, 8.1 Hz, 4H), 7.50 – 7.46 (m, 1H), 7.42 (t, *J* = 5.3 Hz, 3H), 7.32 – 7.27 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.34 – 6.24 (m, 1H), 4.15 – 4.07 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.06, 152.44, 148.54, 148.49, 143.34, 141.76, 135.04, 134.86, 134.20, 133.38, 132.93, 131.31, 131.12, 130.72, 128.84, 128.26, 128.10, 127.69, 127.15, 126.48, 123.06, 115.39, 115.34, 113.87, 107.37, 62.06, 62.01, 16.55, 16.49.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{26}H_{24}NNaO_5P$ *m/z* 484.1284 and found *m/z* 484.1284.



3g

(*E*)-2-cyanophenyl-3'-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3g).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and benzyl acrylate (0.6 mmol, 92 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

Appearance: Sticky liquid

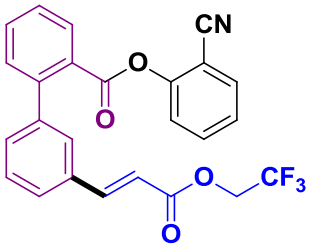
Isolated yield: 71% (98 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 16.3, 7.7 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.42 (ddd, *J* = 9.4, 5.4, 2.3 Hz, 6H), 7.38 – 7.33 (m,

2H), 7.29 (dd, *J* = 13.5, 5.9 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.88, 165.14, 152.50, 145.04, 143.33, 141.85, 136.22, 134.51, 134.25, 133.47, 132.97, 131.36, 131.19, 130.91, 128.94, 128.77, 128.41, 128.38, 128.17, 127.38, 126.50, 123.09, 118.57, 115.41, 107.42, 66.54.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{30}H_{21}NNaO_4$ *m/z* 482.1363 and found *m/z* 482.1364.



3h

(*E*)-2-cyanophenyl 3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3h).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and 2,2,2-trifluoroethyl acrylate (0.6 mmol, 76 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

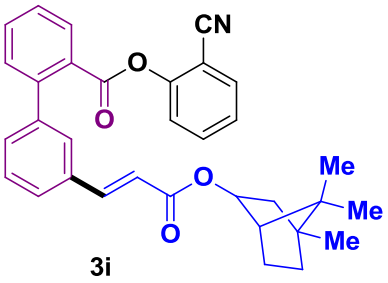
Appearance: Yellow solid.

Isolated yield: 65% (88 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.66 (ddd, *J* = 15.8, 7.8, 1.3 Hz, 2H), 7.61 (s, 1H), 7.59 – 7.53 (m, 3H), 7.51 – 7.45 (m, 2H), 7.45 – 7.42 (m, 1H), 7.30 (td, *J* = 7.7, 0.8 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.52 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.59 (q, *J* = 8.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.24, 165.01, 152.49, 147.00, 143.26, 141.96, 134.22, 133.99, 133.47, 133.02, 131.41, 131.38, 131.23, 129.00, 128.60, 128.26, 128.22, 127.57, 126.53, 124.37, 123.07, 122.16, 116.57, 115.38, 107.42, 60.96, 60.67, 60.38, 60.09.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{16}F_3NNaO_4$ *m/z* 474.0924 and found *m/z* 474.0920.



3i

2-cyanophenyl-3'-((*E*)-3-oxo-3-(((1*R*,4*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3i).

Distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and isobornyl acrylate (0.6 mmol, 126 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

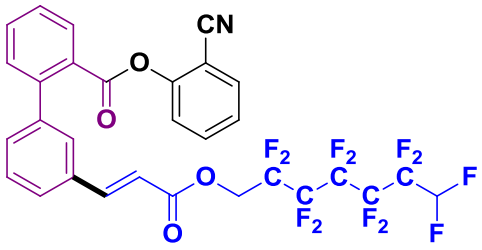
Appearance: Sticky yellow liquid.

Isolated yield: 84% (127 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 16.4, 7.5 Hz, 3H), 7.59 – 7.52 (m, 4H), 7.44 (d, *J* = 5.2 Hz, 3H), 7.28 (dd, *J* = 13.1, 5.4 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.46 (d, *J* = 16.1 Hz, 1H), 4.81 (dd, *J* = 7.1, 3.9 Hz, 1H), 1.84 (t, *J* = 10.3 Hz, 2H), 1.74 (d, *J* = 22.1 Hz, 2H), 1.58 (td, *J* = 12.2, 3.4 Hz, 1H), 1.23 – 1.17 (m, 1H), 1.14 – 1.08 (m, 1H), 1.06 (d, *J* = 5.3 Hz, 3H), 0.89 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.52, 165.07, 152.44, 143.99, 143.32, 141.75, 134.62, 134.17, 133.37, 132.88, 131.30, 131.08, 130.63, 128.83, 128.34, 128.15, 128.06, 127.33, 126.45, 123.02, 119.50, 115.31, 107.38, 81.24, 49.01, 47.09, 45.19, 38.97, 33.87, 27.19, 20.26, 20.15, 11.62.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{33}H_{31}NNaO_4$ *m/z* 528.2145 and found *m/z* 528.2144.



3j

(*E*)-2-cyanophenyl 3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3j).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl acrylate (0.6 mmol, 146 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

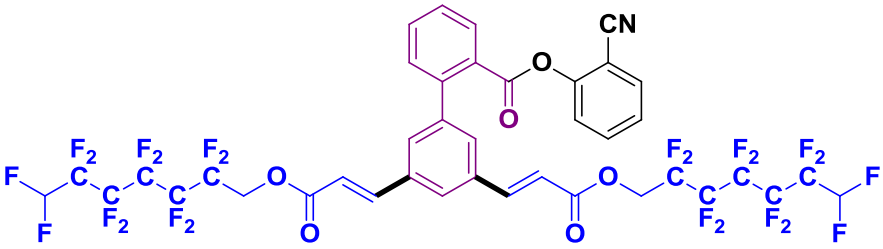
Appearance: Yellow semi-solid.

Isolated yield: 68% (139 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 16.0 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 3H), 7.46 (dd, *J* = 17.2, 7.4 Hz, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.06 (tt, *J* = 51.9, 4.8 Hz, 1H), 4.72 (t, *J* = 13.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.31, 165.04, 152.52, 147.14, 143.32, 142.02, 134.25, 133.99, 133.50, 133.07, 131.48, 131.43, 131.29, 129.03, 128.59, 128.26, 127.67, 126.56, 123.10, 116.51, 115.42, 107.46, 59.79.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{30}H_{17}F_{12}NNaO_4$ *m/z* 706.0858 and found *m/z* 706.0784.



3j'

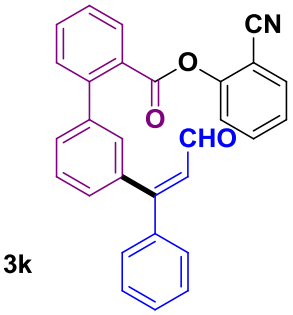
(2*E*,2'*E*)-bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)-3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (Scheme 3, 3j').

Di-olefinated product was isolated from the same reaction.

Isolated yield: 11% (35 mg)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dt, *J* = 8.0, 4.0 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 2H), 7.73 – 7.67 (m, 2H), 7.67 – 7.62 (m, 3H), 7.62 – 7.59 (m, 1H), 7.59 – 7.55 (m, 1H), 7.44 – 7.41 (m, 1H), 7.34 – 7.30 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.59 – 6.52 (m, 2H), 6.06 (ddt, *J* = 57.0, 51.9, 5.1 Hz, 2H), 4.72 (t, *J* = 13.5 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.02, 164.57, 152.51, 146.05, 142.97, 142.80, 134.78, 134.32, 133.54, 133.42, 131.64, 131.53, 130.65, 128.74, 127.81, 127.32, 126.69, 123.11, 117.72, 115.41, 107.49, 59.91.



3k

(*Z*)-2-cyanophenyl-3'-(3-oxo-1-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3k).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and cinnamaldehyde (0.6 mmol, 75 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

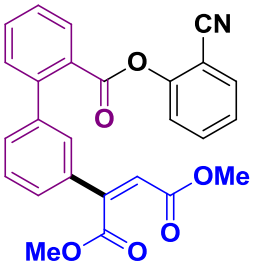
Appearance: Sticky yellow liquid.

Isolated yield: 53% (68 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.9 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.65 – 7.62 (m, 1H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.52 – 7.49 (m, 1H), 7.48 – 7.43 (m, 2H), 7.40 (dd, *J* = 4.9, 3.0 Hz, 3H), 7.37 – 7.28 (m, 5H), 7.15 (dd, *J* = 8.3, 0.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.61, 164.89, 162.14, 152.51, 143.45, 141.56, 139.89, 136.67, 134.24, 133.54, 133.04, 131.47, 131.28, 131.11, 130.96, 129.75, 128.86, 128.63, 128.56, 128.19, 128.06, 127.83, 126.54, 123.12, 115.35, 107.37.

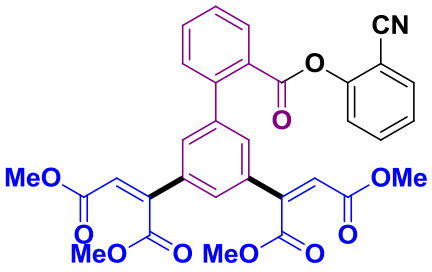
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{29}H_{19}NNaO_3$ *m/z* 452.1257 and found *m/z* 452.1254.



3l

Dimethyl 2-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3-yl)maleate (Scheme 3, 3l).

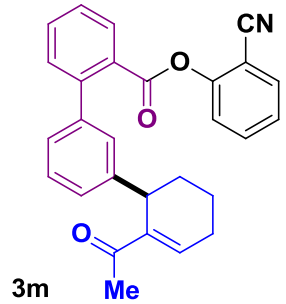
Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and dimethyl maleate (0.6 mmol, 75 µL).
Eluent: ethyl acetate/ petroleum ether (15:85 v/v);
Appearance: Sticky creamy liquid.
Isolated yield: 63% (83 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 11.0, 4.5 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.48 – 7.42 (m, 3H), 7.29 (dd, *J* = 14.7, 6.8 Hz, 3H), 7.07 (d, *J* = 8.3 Hz, 1H), 7.05 – 7.02 (m, 1H), 3.77 – 3.72 (m, 3H), 3.50 (d, *J* = 1.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.76, 165.69, 165.45, 152.52, 143.76, 143.15, 140.63, 134.18, 133.95, 133.27, 132.60, 131.35, 130.76, 129.29, 129.23, 129.13, 128.96, 128.28, 127.91, 127.85, 126.40, 123.45, 115.46, 107.50, 53.07, 51.99.
HR-MS (ESI-QTOF): $[M+K]^+$ calculated for $C_{26}H_{19}KNO_6$ *m/z* 480.0844 and found *m/z* 480.0837.



3l'

(*Z*)-tetramethyl-2,2'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)dimaleate (Scheme 3, 3l').

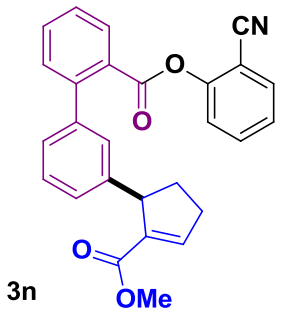
Di-olefinated product was isolated from the same reaction.
Isolated yield: 20% (35 mg)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.54 (dt, *J* = 16.7, 7.7 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 14.6, 4.5 Hz, 3H), 7.13 (d, *J* = 1.4 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 1.2 Hz, 2H), 3.73 (d, *J* = 1.2 Hz, 6H), 3.50 (d, *J* = 1.1 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 165.67, 165.45, 152.47, 142.78, 142.33, 140.23, 134.18, 133.66, 133.11, 132.48, 131.36, 130.59, 129.96, 129.56, 129.32, 128.89, 128.07, 126.39, 123.85, 115.49, 107.54, 53.06, 52.04.



3m

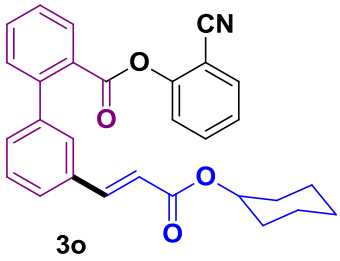
2-cyanophenyl-6''-acetyl-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate (Scheme 3, 3m).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and 1-acetyl-1-cyclohexene (0.6 mmol, 77 µL).
Eluent: ethyl acetate/ petroleum ether (5:95 v/v);
Appearance: Sticky liquid
Isolated yield: 56% (71 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 9.8, 5.9 Hz, 1H), 7.28 (dd, *J* = 12.7, 5.1 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.10 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.08 (s, 1H), 2.34 (dt, *J* = 11.2, 5.5 Hz, 1H), 2.30 – 2.25 (m, 1H), 2.17 (s, 3H), 1.85 (ddd, *J* = 15.3, 10.3, 5.9 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.49 – 1.41 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.76, 165.87, 152.48, 145.17, 143.70, 142.51, 140.90, 140.87, 134.42, 133.22, 132.34, 131.21, 130.41, 129.28, 128.30, 128.17, 127.61, 127.34, 126.50, 126.37, 123.35, 115.49, 107.33, 38.43, 31.35, 26.28, 26.03, 16.90.
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{28}H_{23}NaNO_3$ *m/z* 444.1570 and found *m/z* 444.1570.



3n

2-cyanophenyl-3'-(2-(methoxycarbonyl)cyclopent-2-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3n).
Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and methyl 1-cyclopentene-1-carboxylate (0.6 mmol, 73 µL).
Eluent: ethyl acetate/ petroleum ether (5:95 v/v);
Appearance: Sticky light yellowish liquid.
Isolated yield: 45% (57 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.62 (ddd, *J* = 14.2, 7.7, 1.4 Hz, 2H), 7.57 (td, *J* = 8.3, 1.6 Hz, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 1.3 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.01 – 6.97 (m, 2H), 4.20 (dd, *J* = 7.4, 1.6 Hz, 1H), 3.51 (s, 3H), 2.70 – 2.61 (m, 1H), 2.55 – 2.48 (m, 2H), 1.92 (ddd, *J* = 12.1, 7.2, 3.0 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.68, 165.25, 152.51, 145.34, 143.74, 141.08, 139.14, 134.21, 133.27, 132.41, 131.21, 130.53, 129.05, 128.46, 127.59, 127.55, 126.74, 126.34, 126.31, 123.26, 115.41, 107.41, 51.38, 50.16, 34.26, 32.35.
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{27}H_{21}NNaO_4$ *m/z* 446.1363 and found *m/z* 446.1361.



3o

(*E*)-2-cyanophenyl-3'-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 3, 3o).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (0.3 mmol, 90 mg) and cyclohexyl acrylate (0.6 mmol, 94 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

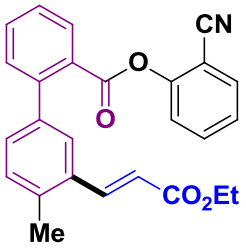
Appearance: Sticky liquid

Isolated yield: 64% (86 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.68 – 7.63 (m, 2H), 7.57 (t, *J* = 2.1 Hz, 1H), 7.54 (dddd, *J* = 9.7, 5.1, 3.5, 1.8 Hz, 3H), 7.43 (dd, *J* = 5.3, 3.1 Hz, 3H), 7.30 (td, *J* = 7.7, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.92 – 4.85 (m, 1H), 1.95 – 1.87 (m, 2H), 1.76 (dd, *J* = 9.1, 3.9 Hz, 2H), 1.60 – 1.53 (m, 1H), 1.49 (ddd, *J* = 12.1, 9.9, 3.2 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.26 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.56, 165.21, 152.52, 144.10, 143.37, 141.82, 134.73, 134.25, 133.48, 132.94, 131.35, 131.16, 130.69, 128.90, 128.45, 128.28, 128.15, 127.32, 126.51, 123.11, 119.60, 115.41, 107.44, 72.95, 31.90, 25.61, 23.96.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{29}H_{25}NNaO_4$ *m/z* 474.1676 and found *m/z* 474.1675.



4a

(*E*)-2-cyanophenyl-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-methyl-[1,1'-biphenyl]-2-carboxylate (Scheme 4, 4a).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl 4'-methyl-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 93 mg) and ethyl acrylate (0.6 mmol, 65 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

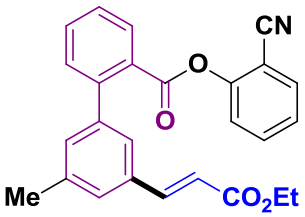
Appearance: Light yellowish solid.

Isolated yield: 64% (79 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 15.9 Hz, 1H), 7.65 (dd, *J* = 10.0, 3.8 Hz, 2H), 7.59 (dd, *J* = 8.0, 4.1 Hz, 2H), 7.54 (dd, *J* = 10.3, 2.9 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.26 (s, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.16, 165.24, 152.53, 143.44, 142.12, 139.15, 137.10, 134.21, 133.44, 132.88, 131.38, 131.07, 130.84, 130.46, 128.32, 127.91, 126.58, 126.46, 123.16, 119.89, 115.38, 107.40, 60.66, 19.74, 14.47.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{26}H_{21}NNaO_4$ *m/z* 434.1363 and found *m/z* 434.1365.



4b

(*E*)-2-cyanophenyl-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate (Scheme 4, 4b).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl 3'-methyl-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 93 mg) and ethyl acrylate (0.6 mmol, 65 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

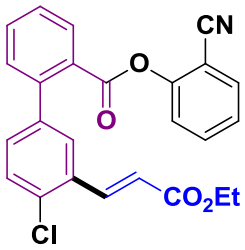
Appearance: Bright yellow sticky liquid.

Isolated yield: 71% (87 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.64 (ddd, *J* = 5.3, 3.5, 1.4 Hz, 2H), 7.55 (dt, *J* = 15.0, 4.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 17.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.28 – 4.22 (m, 2H), 2.40 (d, *J* = 11.3 Hz, 3H), 1.32 (td, *J* = 7.0, 0.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.19, 165.28, 152.55, 144.63, 143.44, 141.76, 138.66, 134.55, 134.23, 133.46, 132.85, 131.54, 131.29, 131.05, 128.48, 128.07, 128.02, 126.48, 125.59, 123.03, 118.71, 115.39, 107.44, 60.66, 21.47, 14.48.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{26}H_{21}NNaO_4$ *m/z* 434.1363 and found *m/z* 434.1363.



4c

(*E*)-2-cyanophenyl-4'-chloro-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 4, 4c).

Distal C-H olefination was carried out following general procedure with 2-cyanophenyl 4'-chloro-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 100 mg) and ethyl acrylate (0.6 mmol, 65 µL).

Eluent: ethyl acetate/ petroleum ether (3:97 v/v);

Appearance: White solid.

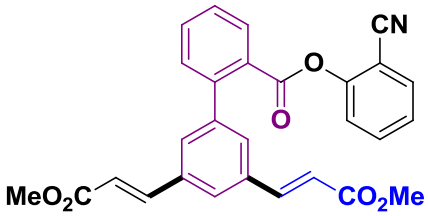
Isolated yield: 59% (76 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.10 (d, *J* = 16.1 Hz, 1H), 7.70 – 7.64 (m, 3H), 7.59 (dddd, *J* = 11.3, 8.9, 7.7, 1.5 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.40 (dd,

J = 7.6, 0.9 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.17 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.64, 164.80, 152.48, 142.64, 140.29, 140.22, 134.45, 134.33, 133.54, 133.20, 132.70, 131.56, 131.43, 130.04, 128.47, 128.02, 127.81, 126.63, 123.16, 121.55, 115.39, 107.42, 60.87, 14.47.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{18}ClNNaO_4$ *m/z* 454.0817 and found *m/z* 454.0812.



4d

(2*E*,2'*E*)-dimethyl-3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (Scheme 4, 4d).

Sequential distal homo *di*-C-H olefination was carried out following general procedure with (*E*)-2-cyanophenyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 115 mg) and methyl acrylate (0.6 mmol, 54 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

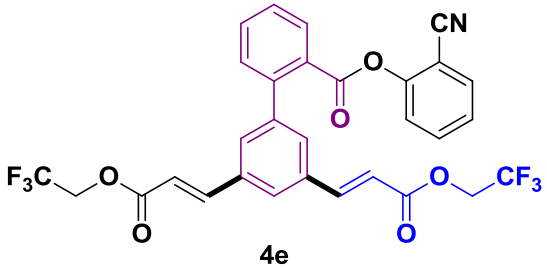
Appearance: Creamy solid.

Isolated yield: 71% (99 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.69 – 7.62 (m, 3H), 7.61 – 7.53 (m, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.53 – 6.45 (m, 2H), 3.80 (t, *J* = 2.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.29, 164.72, 152.49, 143.86, 142.92, 142.68, 135.22, 134.31, 133.50, 133.25, 131.49, 131.44, 129.83, 128.56, 128.04, 126.90, 126.60, 123.08, 119.48, 115.38, 107.43, 52.02.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{28}H_{21}NNaO_6$ *m/z* 490.1261 and found *m/z* 490.1265.



4e

(2*E*,2'*E*)-bis(2,2,2-trifluoroethyl) 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (Scheme 4, 4e).

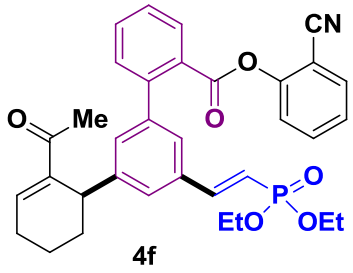
Sequential distal homo *di*-C-H olefination was carried out following general procedure with (*E*)-2-cyanophenyl 3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 135 mg) and 2,2,2-trifluoroethyl acrylate (0.6 mmol, 76 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

Appearance: Yellowish semi-solid.

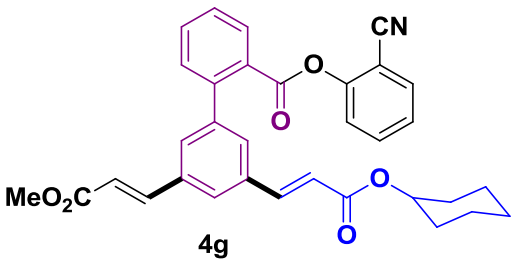
Isolated yield: 67% (121 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 16.0 Hz, 2H), 7.70 (d, *J* = 6.7 Hz, 2H), 7.66 – 7.61 (m, 3H), 7.58 (dd, *J* = 13.1, 4.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 2H), 4.59 (q, *J* = 8.4 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.99, 164.57, 152.51, 145.96, 142.95, 142.77, 134.81, 134.32, 133.56, 133.39, 131.62, 131.50, 130.63, 128.73, 127.86, 127.23, 126.68, 124.34, 123.11, 122.14, 117.81, 115.40, 107.48, 61.14, 60.84, 60.55, 60.26.
HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{30}H_{19}F_6NaNO_6$ *m/z* 626.1008 and found *m/z* 626.1008.



4f

(*R*,*E*)-2-cyanophenyl-6''-acetyl-5'-(2-(diethoxyphosphoryl)vinyl)-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate (Scheme 4, 4f).
Sequential distal hetero *di*-C-H olefination was carried out following general procedure with (*R*)-2-cyanophenyl 6"-acetyl-1",2",3",4"-tetrahydro-[1,1':3',1"-terphenyl]-2-carboxylate (0.1 mmol, 42 mg) and diethyl vinylphosphonate (0.2 mmol, 92 µL).
Eluent: ethyl acetate/ petroleum ether (15:85 v/v);
Appearance: Light yellowish sticky liquid.
Isolated yield: 60% (35 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.63 (dt, *J* = 11.6, 3.0 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.54 – 7.46 (m, 2H), 7.42 (d, *J* = 17.2 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.14 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.24 (t, *J* = 17.6 Hz, 1H), 4.15 – 4.04 (m, 5H), 2.38 (d, *J* = 19.9 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.19 (s, 3H), 1.89 – 1.79 (m, 1H), 1.77 – 1.70 (m, 1H), 1.49 – 1.40 (m, 2H), 1.33 (td, *J* = 7.0, 1.0 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.48, 165.29, 152.45, 149.00, 148.94, 145.99, 143.21, 141.61, 140.53, 134.93, 134.74, 134.41, 133.24, 132.68, 131.30, 130.81, 130.32, 128.76, 128.01, 127.00, 126.44, 125.33, 123.30, 115.42, 115.04, 113.52, 107.24, 62.07, 62.05, 38.20, 31.17, 26.25, 25.88, 16.78, 16.59, 16.53.
HR-MS (ESI-QTOF): $[M+H]^+$ calculated for $C_{34}H_{35}NO_6P$ *m/z* 584.2197 and found *m/z* 584.2196.



4g

2-cyanophenyl-3'-((*E*)-3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-5'-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (Scheme 4, 4g).

Sequential distal hetero *di*-C-H olefination was carried out following general procedure with (*E*)-2-cyanophenyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (0.3 mmol, 115 mg) and cyclohexyl acrylate (0.6 mmol, 94 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

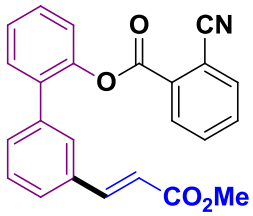
Appearance: Yellow sticky liquid.

Isolated yield: 70% (112 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.69 – 7.62 (m, 4H), 7.55 (t, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.49 (dd, *J* = 16.0, 2.2 Hz, 2H), 4.91 – 4.84 (m, 1H), 3.78 (s, 3H), 1.92 – 1.86 (m, 2H), 1.75 (dd, *J* = 8.9, 3.8 Hz, 2H), 1.57 – 1.44 (m, 3H), 1.42 – 1.28 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.18, 166.14, 164.66, 152.38, 143.82, 143.11, 142.80, 142.51, 135.31, 135.08, 134.22, 133.39, 133.12, 131.34, 129.77, 129.65, 128.43, 128.00, 126.67, 126.51, 122.99, 120.50, 119.33, 115.28, 107.32, 72.97, 51.89, 31.78, 25.51, 23.83.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{33}H_{29}NNaO_6$ *m/z* 558.1887 and found *m/z* 558.1885.



5a

(*E*)-3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5a).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and methyl acrylate (0.6 mmol, 54 µL).

Eluent: ethyl acetate/ petroleum ether (3:97 v/v);

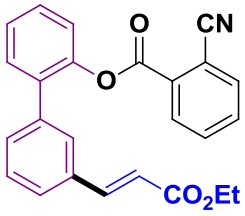
Appearance: Sticky whitish liquid.

Isolated yield: 62% (71 mg); *m*:*other* = 14:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 7.6, 3.5 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.68 – 7.60 (m, 5H), 7.49 (dd, *J* = 5.2, 3.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 3H), 6.42 – 6.36 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.44, 162.52, 147.54, 144.54, 138.10, 135.19, 134.59, 134.28, 133.43, 132.74, 131.55, 131.44, 131.08, 131.06, 129.30, 129.13, 128.61, 127.55, 127.17, 123.04, 118.36, 117.25, 113.41, 51.89.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{24}H_{17}NNaO_4$ *m/z* 406.1050 and found *m/z* 406.1047.



5b

(*E*)-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5b).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and ethyl acrylate (0.6 mmol, 65 µL).

Eluent: ethyl acetate/ petroleum ether (3:97 v/v);

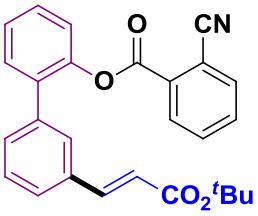
Appearance: Sticky liquid.

Isolated yield: 65% (77 mg); *m*:*other* = 13:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 1H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.62 (d, *J* = 4.1 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.40 – 7.33 (m, 3H), 6.41 – 6.35 (m, 1H), 4.28 – 4.21 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 162.56, 147.60, 144.30, 138.15, 135.24, 134.74, 134.35, 133.44, 132.76, 131.61, 131.11, 131.05, 129.33, 129.15, 128.65, 127.54, 127.20, 123.09, 118.90, 117.28, 113.51, 60.73, 14.52.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{19}NNaO_4$ *m/z* 420.1206 and found *m/z* 420.1204.



5c

(*E*)-3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl-2-cyanobenzoate (Scheme 5, 5c).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and *tert*-butyl acrylate (0.6 mmol, 88 µL).

Eluent: ethyl acetate/ petroleum ether (3:97 v/v);

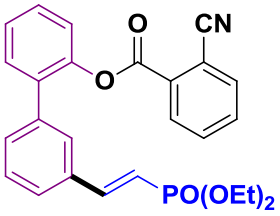
Appearance: Sticky liquid.

Isolated yield: 60% (76 mg); *m*:*other* = 16:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 1H), 7.82 – 7.78 (m, 1H), 7.69 – 7.63 (m, 2H), 7.62 (t, *J* = 4.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.49 – 7.44 (m, 3H), 7.42 – 7.37 (m, 2H), 7.34 (ddd, *J* = 7.7, 5.5, 4.4 Hz, 2H), 6.34 – 6.28 (m, 1H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.32, 162.53, 147.57, 143.22, 138.03, 135.19, 134.91, 134.37, 133.39, 132.73, 131.57, 131.51, 131.07, 130.75, 129.25, 129.05, 128.49, 127.43, 127.15, 123.03, 120.79, 117.25, 113.47, 80.73, 28.36.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{27}H_{23}NNaO_4$ *m/z* 448.1519 and found *m/z* 448.1519.



5d

(*E*)-3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5d).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and diethyl vinylphosphonate (0.6 mmol, 92 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

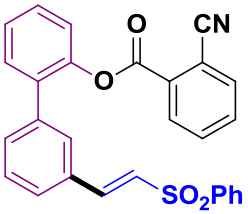
Appearance: Sticky yellowish liquid.

Isolated yield: 57% (79 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 1H), 7.80 – 7.76 (m, 1H), 7.67 – 7.63 (m, 2H), 7.63 – 7.61 (m, 1H), 7.49 – 7.47 (m, 1H), 7.45 (ddd, *J* = 6.6, 4.0, 1.6 Hz, 3H), 7.38 (dd, *J* = 11.9, 4.2 Hz, 2H), 7.33 (dd, *J* = 12.6, 4.6 Hz, 2H), 6.27 – 6.17 (m, 1H), 4.14 – 4.03 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.48, 148.38, 148.33, 147.51, 138.05, 135.15, 134.96, 134.29, 133.41, 132.76, 131.57, 131.41, 131.04, 130.98, 129.27, 129.07, 128.07, 127.38, 127.14, 123.02, 117.24, 115.32, 113.80, 113.37, 62.08, 62.04, 16.55, 16.50.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{26}H_{24}NNaO_5P$ *m/z* 484.1284 and found *m/z* 484.1283.



5e

(*E*)-3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5e).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and phenyl vinyl sulfone (0.6 mmol, 101 mg).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

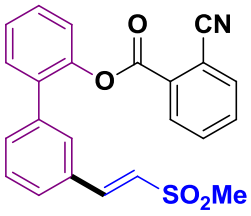
Appearance: Sticky white solid.

Isolated yield: 61% (85 mg); *m*:*other* = 14:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.76 (dd, *J* = 10.8, 3.9 Hz, 1H), 7.67 – 7.59 (m, 5H), 7.57 – 7.50 (m, 4H), 7.44 (dd, *J* = 14.3, 6.7 Hz, 2H), 7.38 (d, *J* = 4.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 15.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.49, 147.50, 142.04, 140.77, 138.36, 135.28, 133.96, 133.62, 133.58, 132.83, 132.60, 131.99, 131.61, 131.30, 131.01, 129.55, 129.52, 129.42, 128.77, 128.45, 127.94, 127.89, 127.27, 123.11, 117.37, 113.31.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{28}H_{19}NNaO_4S$ *m/z* 488.0927 and found *m/z* 488.0924.



5f

(*E*)-3'-(2-(methylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5f).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and methyl vinyl sulfone (0.6 mmol, 52 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

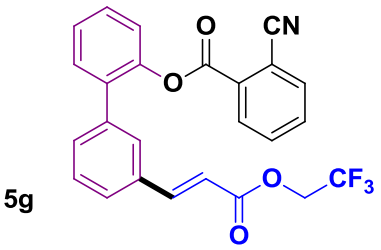
Appearance: Sticky reddish brown liquid.

Isolated yield: 47% (57 mg); *m*:*other* = 12:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.83 – 7.79 (m, 1H), 7.71 – 7.65 (m, 3H), 7.59 – 7.53 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.42 (m, 1H), 7.42 – 7.39 (m, 2H), 7.34 (dd, *J* = 6.1, 1.9 Hz, 1H), 6.92 (d, *J* = 15.5 Hz, 1H), 3.00 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.54, 147.53, 143.47, 138.42, 135.31, 134.01, 133.64, 132.90, 132.35, 132.09, 131.66, 131.29, 131.03, 129.56, 129.45, 128.76, 128.46, 127.30, 126.91, 123.10, 117.39, 113.28, 43.37.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{23}H_{17}NNaO_4S$ *m/z* 426.0770 and found *m/z* 426.0770.



5g

(*E*)-3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-yl-2-cyanobenzoate (Scheme 5, 5g).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and 2,2,2-trifluoroethyl acrylate (0.6 mmol, 76 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

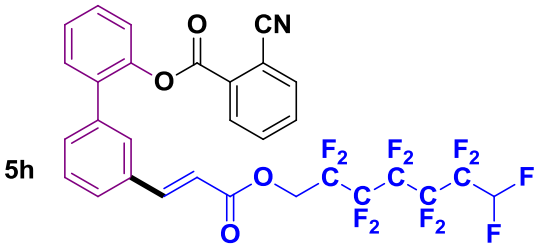
Appearance: Sticky yellowish liquid.

Isolated yield: 67% (91 mg); *m*:*other* = 12:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 7.9, 3.3 Hz, 1H), 7.81 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.69 (s, 1H), 7.66 (ddd, *J* = 8.1, 4.7, 1.5 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.41 – 7.37 (m, 2H), 7.36 – 7.34 (m, 1H), 6.44 – 6.38 (m, 1H), 4.58 (q, *J* = 8.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.17, 162.52, 147.57, 146.88, 138.27, 135.25, 134.10, 133.50, 132.74, 131.70, 131.58, 131.44, 131.05, 129.44, 129.30, 128.80, 127.88, 127.24, 123.09, 116.47, 113.45, 60.96, 60.67, 60.38, 60.09.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{25}H_{16}F_3NNaO_4$ *m/z* 474.0924 and found *m/z* 474.0920.



(*E*)-3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (Scheme 5, 5h).

Distal C-H olefination was carried out following general procedure with [1,1'-biphenyl]-2-yl 2-cyanobenzoate (0.3 mmol, 90 mg) and 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl acrylate (0.6 mmol, 146 µL).

Eluent: ethyl acetate/ petroleum ether (10:90 v/v);

Appearance: Sticky yellowish liquid.

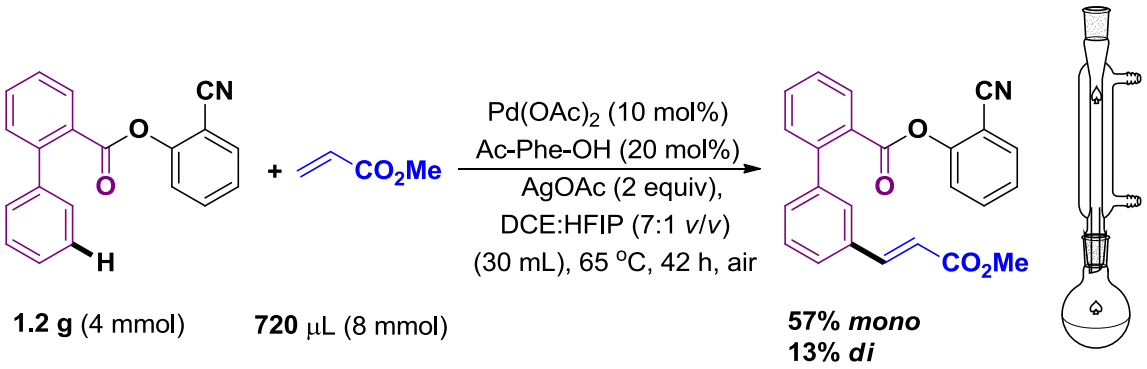
Isolated yield: 57% (117 mg); *m*:*other* = 11:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 1H), 7.81 – 7.79 (m, 1H), 7.75 – 7.71 (m, 1H), 7.69 (s, 1H), 7.67 – 7.63 (m, 2H), 7.54 (dd, *J* = 6.1, 1.3 Hz, 1H), 7.47 (ddd, *J* = 14.1, 6.1, 4.7 Hz, 3H), 7.40 (dd, *J* = 14.2, 6.7 Hz, 2H), 7.36 – 7.33 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.19 – 5.96 (m, 1H), 4.71 (t, *J* = 13.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.20, 162.52, 147.58, 146.98, 138.30, 135.24, 134.13, 134.09, 133.48, 132.73, 131.74, 131.59, 131.46, 131.07, 129.45, 129.30, 128.85, 127.91, 127.25, 123.09, 117.27, 116.41, 113.46, 59.97, 59.76, 59.55.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{30}H_{17}F_{12}NNaO_4$ *m/z* 706.0858 and found *m/z* 706.0784.

Procedure for gram-scale distal C-H olefination:



Gram-scale distal C–H olefination was carried out following general procedure with 2-cyanophenyl [1,1'-biphenyl]-2-carboxylate (4 mmol, 1.2 g) and methyl acrylate (8 mmol, 720 µL).

Eluent: ethyl acetate/ petroleum ether (5:95 v/v);

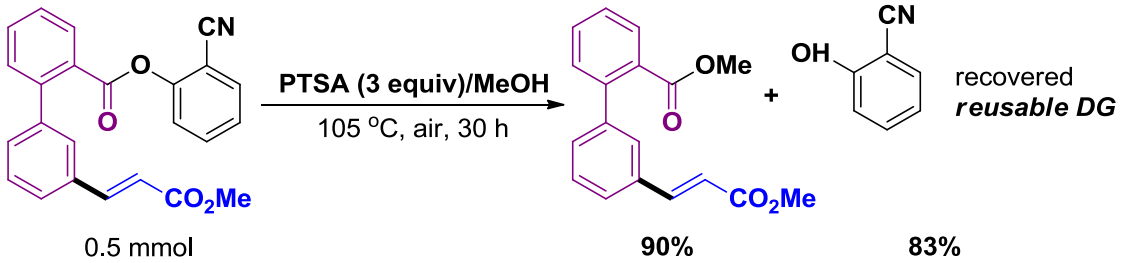
Isolated yield: *mono*-olefinated product: 57% (873 mg); *di*-olefinated product: 13% (242 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 1H), 7.72 (t, *J* = 12.8 Hz, 1H), 7.65 (ddd, *J* = 6.9, 5.0, 4.5 Hz, 2H), 7.59 – 7.49 (m, 5H), 7.47 – 7.40 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.53, 165.12, 152.48, 144.71, 143.34, 141.83, 134.51, 134.24, 133.45, 132.97, 131.35, 131.17, 130.84, 128.91, 128.34, 128.27, 128.15, 127.37, 126.50, 123.07, 118.45, 115.40, 107.40, 51.91.

HR-MS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{24}H_{17}NNaO_4$ *m/z* 406.1050 and found *m/z* 406.1040.

Procedure for removal of directing group:



0.5 mmol **90%** **83%**

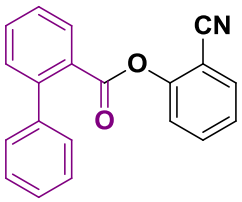
Removal of the directing group was performed with PTSA/MeOH under reflux condition. (*E*)-2-cyanophenyl-3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (0.5 mmol, 191 mg) and PTSA (1.5 mmol,) was treated with 3 mL MeOH for 30 h at 105 °C. Trans-esterified product was obtained in 90% isolated yield and the directing group could be recovered in 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.73 (d, *J* = 16.0 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.47 (t, *J* = 1.7 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.42 (dd, *J* = 7.7, 4.5 Hz, 1H), 7.36 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.34 – 7.31 (m, 1H), 6.48 – 6.44 (m, 1H), 3.81 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.87, 167.58, 144.90, 142.34, 142.00, 134.46, 131.67, 130.88, 130.85, 130.57, 130.24, 128.75, 128.18, 127.78, 127.11, 118.34, 52.20, 51.91.

Procedure for synthesis of starting ester:

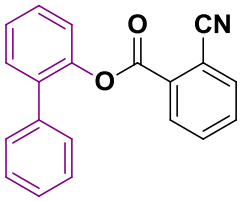
To a oven dried flask was added the carboxylic acid (10 mmol), DCC (1.1 equiv), DMAP (30 mol%) and DCM solvent. The reaction was kept at 0 °C for 30 min and then the alcohol (20 mmol, 2 equiv) was added. The reaction was brought to rt and left for overnight stirring. Work-up with brine and isolation through alumina column gave the desired ester product in 70% yields.



2-cyanophenyl [1,1'-biphenyl]-2-carboxylate.

^{1}H **NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.58 – 7.50 (m, 2H), 7.48 – 7.42 (m, 5H), 7.38 (ddd, *J* = 9.3, 5.6, 3.1 Hz, 1H), 7.29 (td, *J* = 7.7, 1.0 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.62, 152.56, 143.89, 141.06, 134.18, 133.41, 132.66, 131.30, 130.84, 128.79, 128.76, 128.39, 127.73, 126.42, 123.11, 115.42, 107.48.



[1,1'-biphenyl]-2-yl 2-cyanobenzoate.

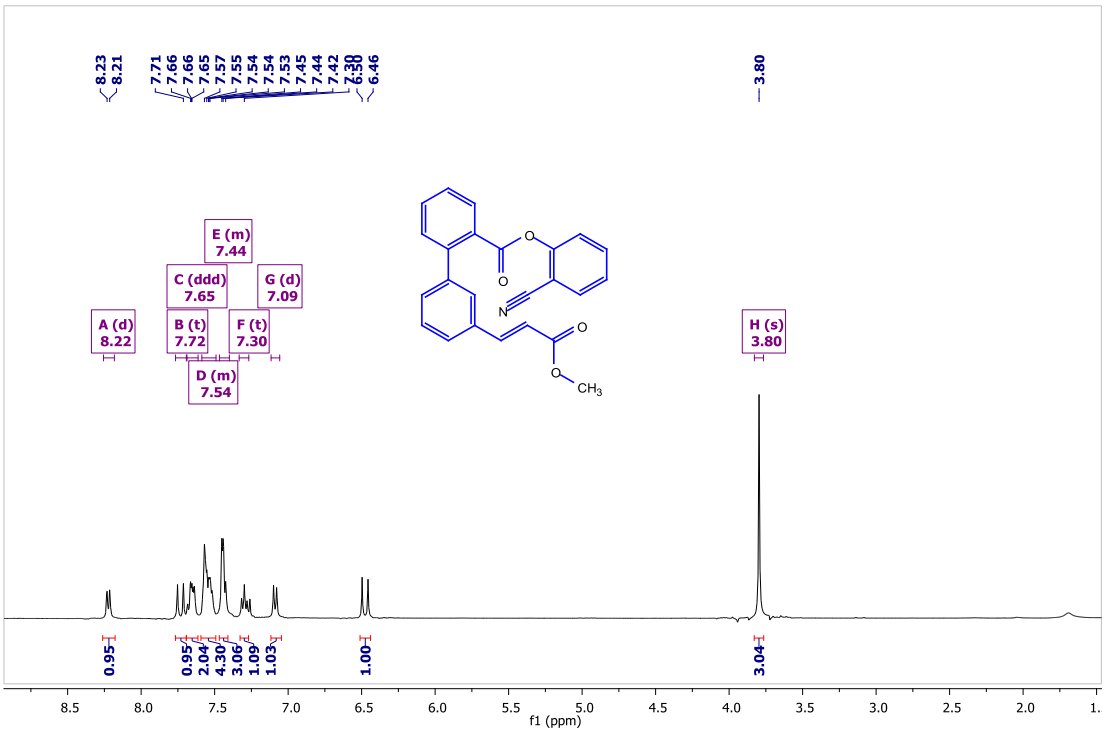
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 1H), 7.81 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.49 – 7.45 (m, 3H), 7.45 – 7.42 (m, 1H), 7.39 (dd, *J* = 6.3, 5.3 Hz, 1H), 7.35 (dd, *J* = 8.2, 7.2 Hz, 3H), 7.29 (dd, *J* = 10.1, 3.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.62, 147.58, 137.43, 135.18, 135.14, 133.29, 132.67, 131.71, 131.60, 131.25, 129.14, 128.87, 128.48, 127.73, 127.04, 122.93, 117.31, 113.48.

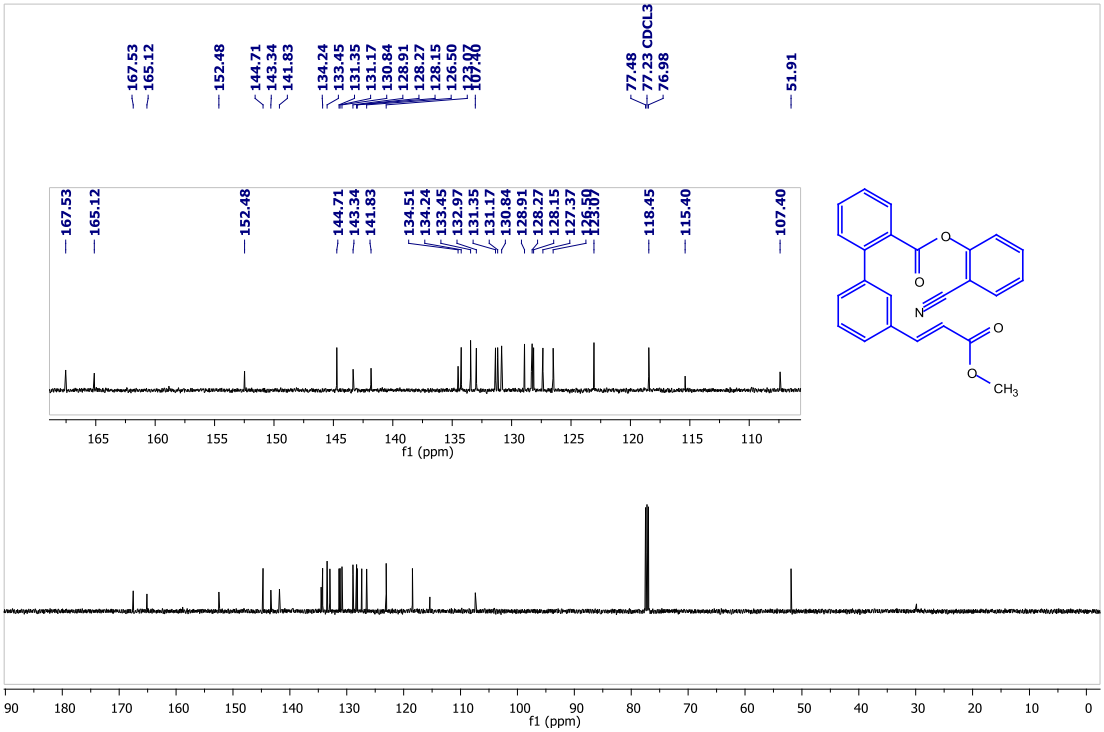
NMR Spectra

(**Scheme 3, 3a**)

(E)-2-cyanophenyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

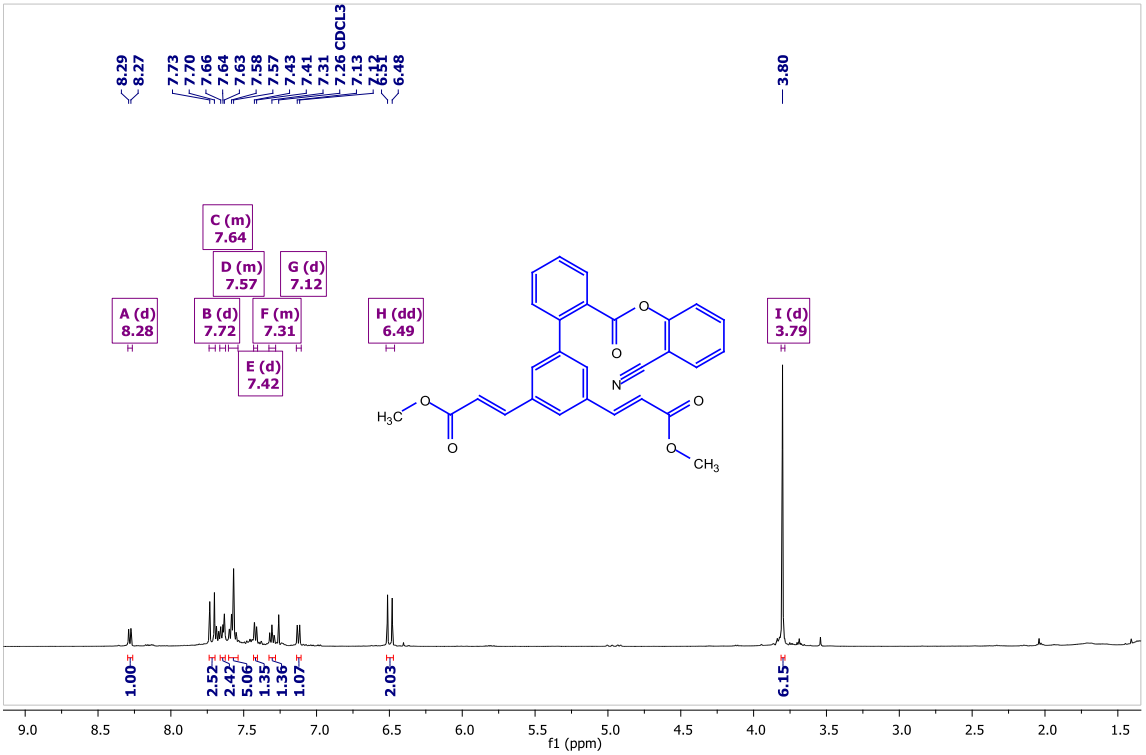


(E)-2-cyanophenyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

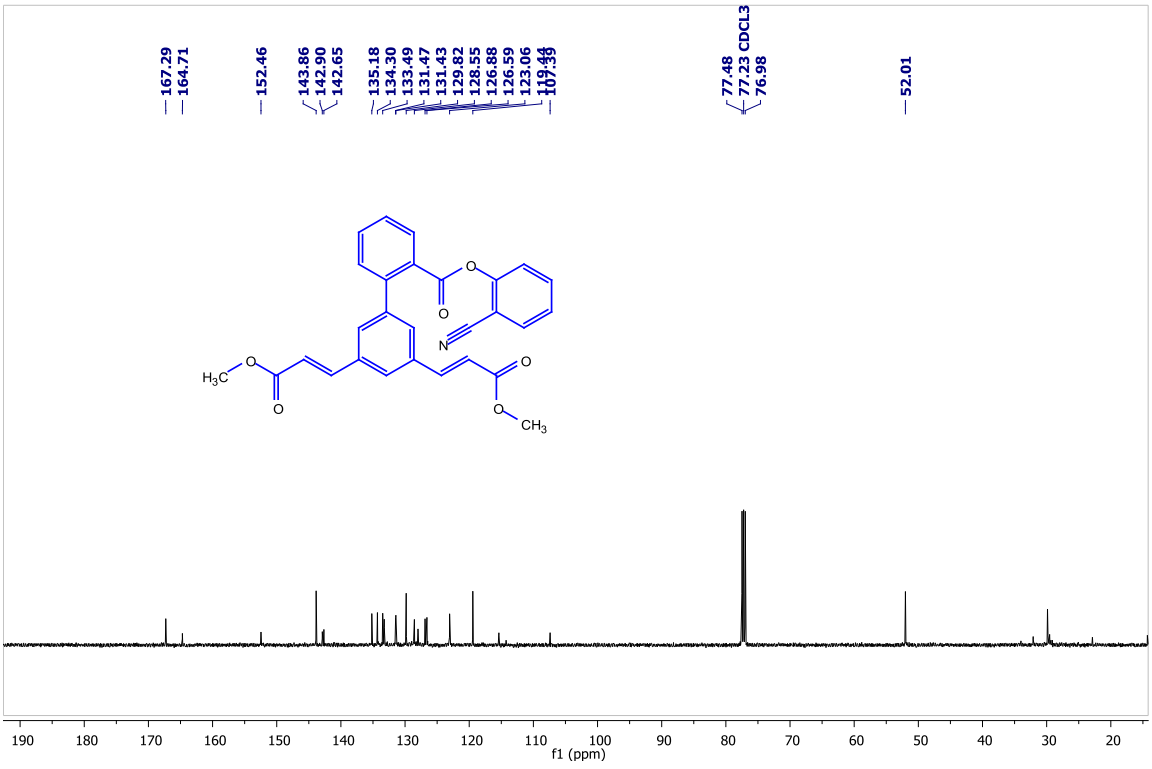


(**Scheme 3, 3a'**)

(2E,2'E)-dimethyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

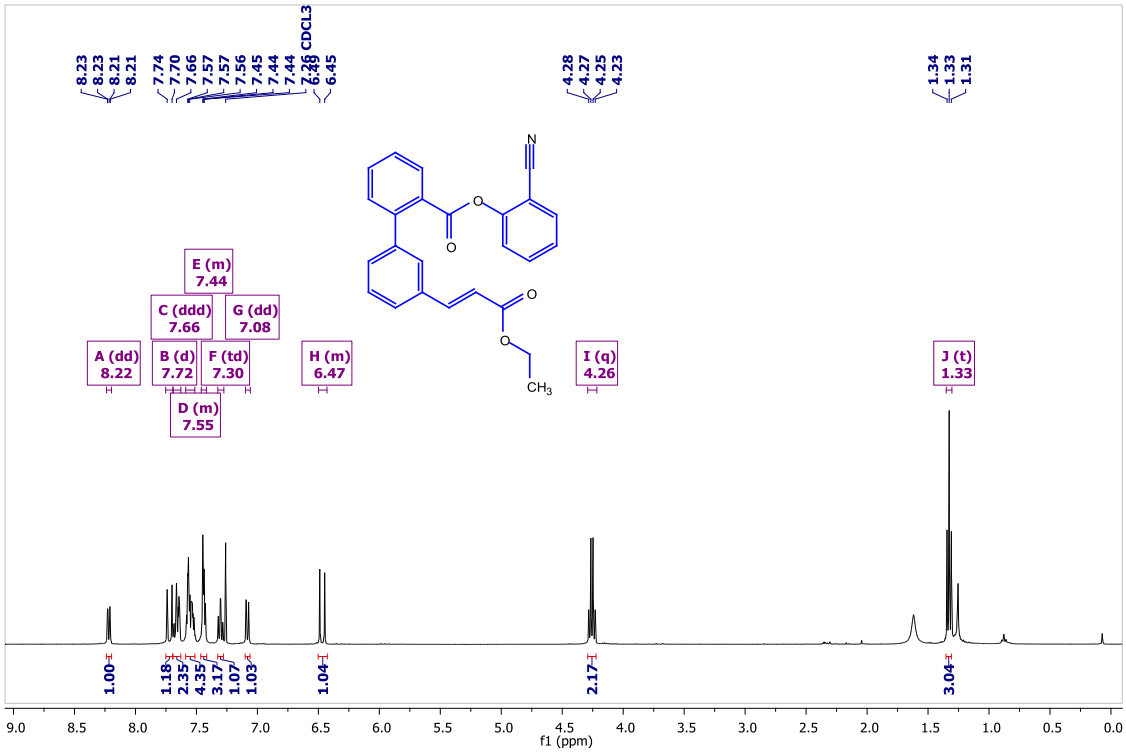


(2E,2'E)-dimethyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

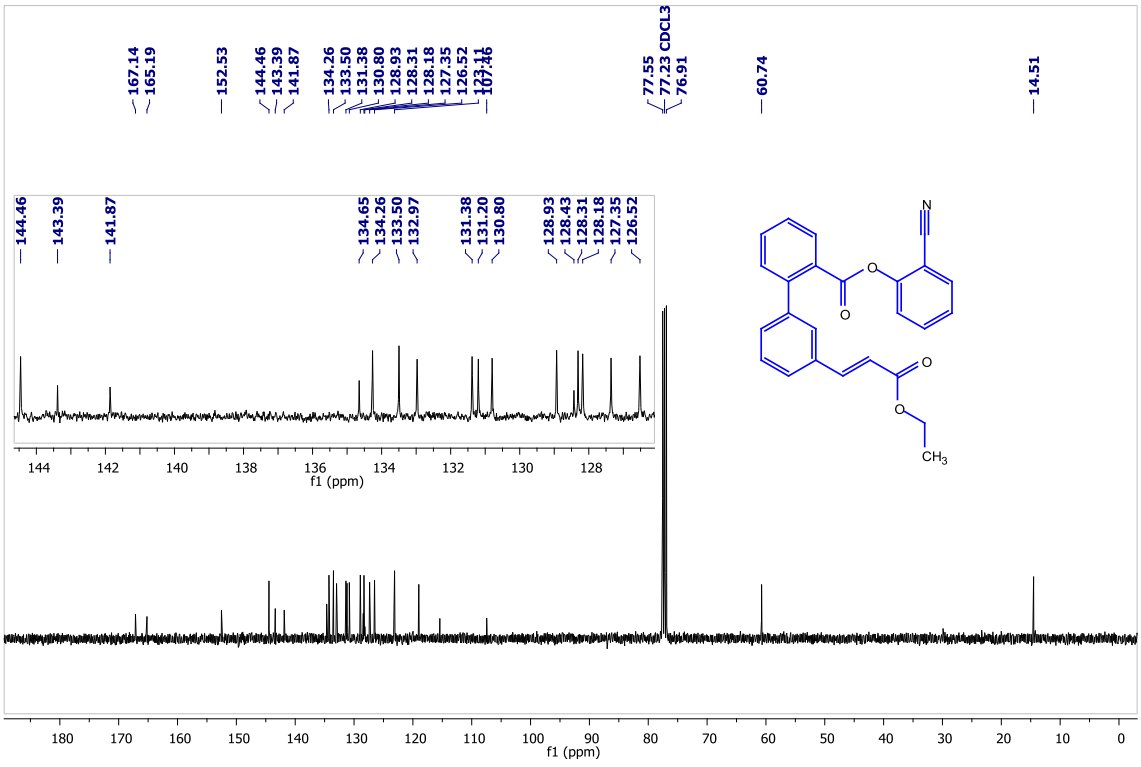


(**Scheme 3, 3b**)

(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

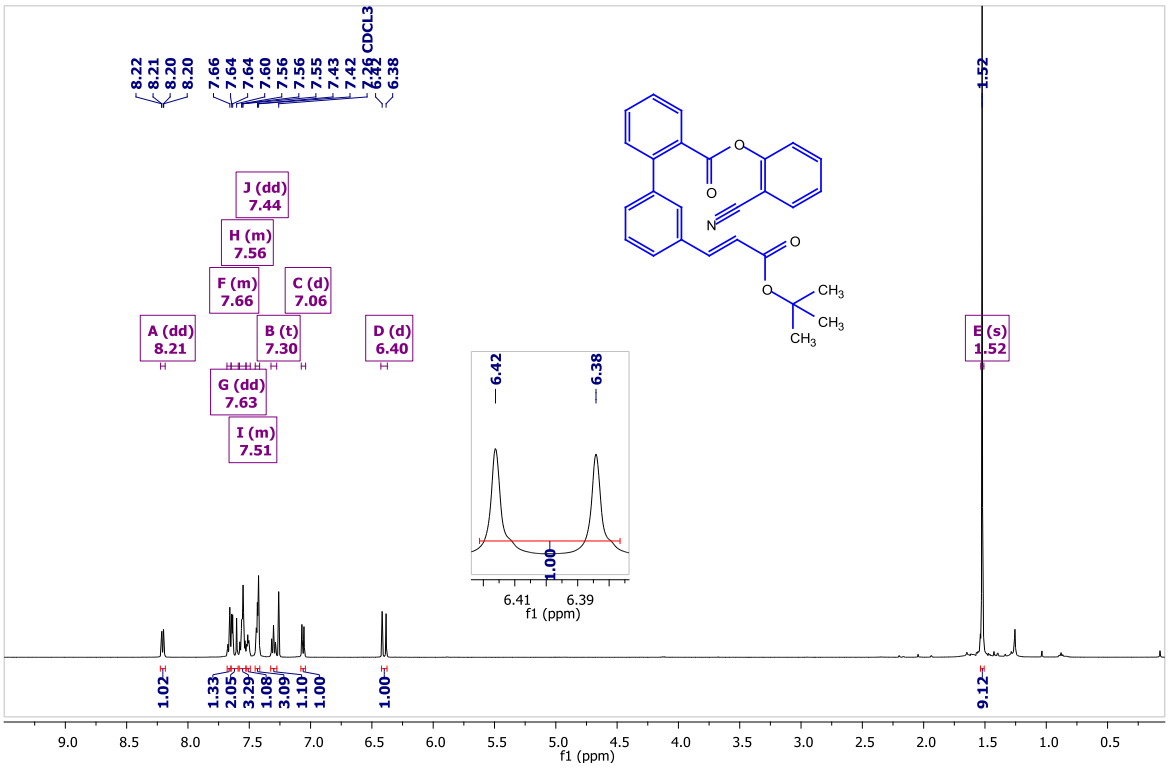


(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

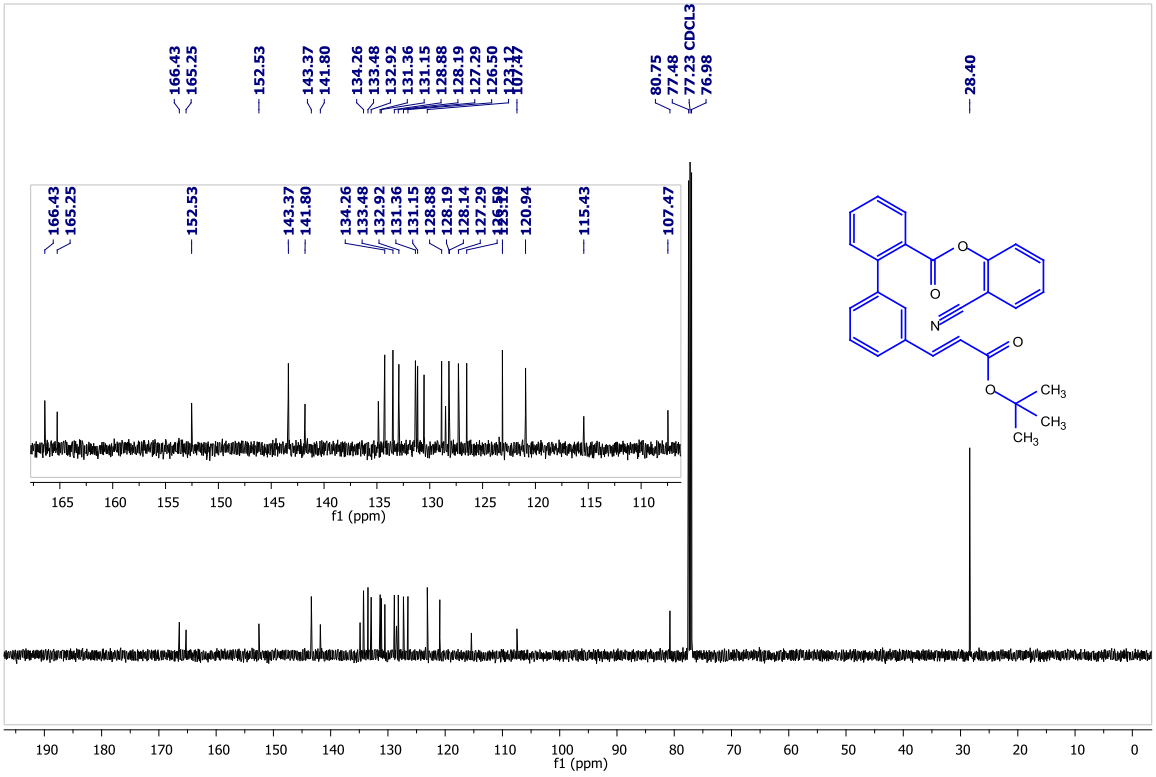


(**Scheme 3, 3c**)

(E)-2-cyanophenyl 3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

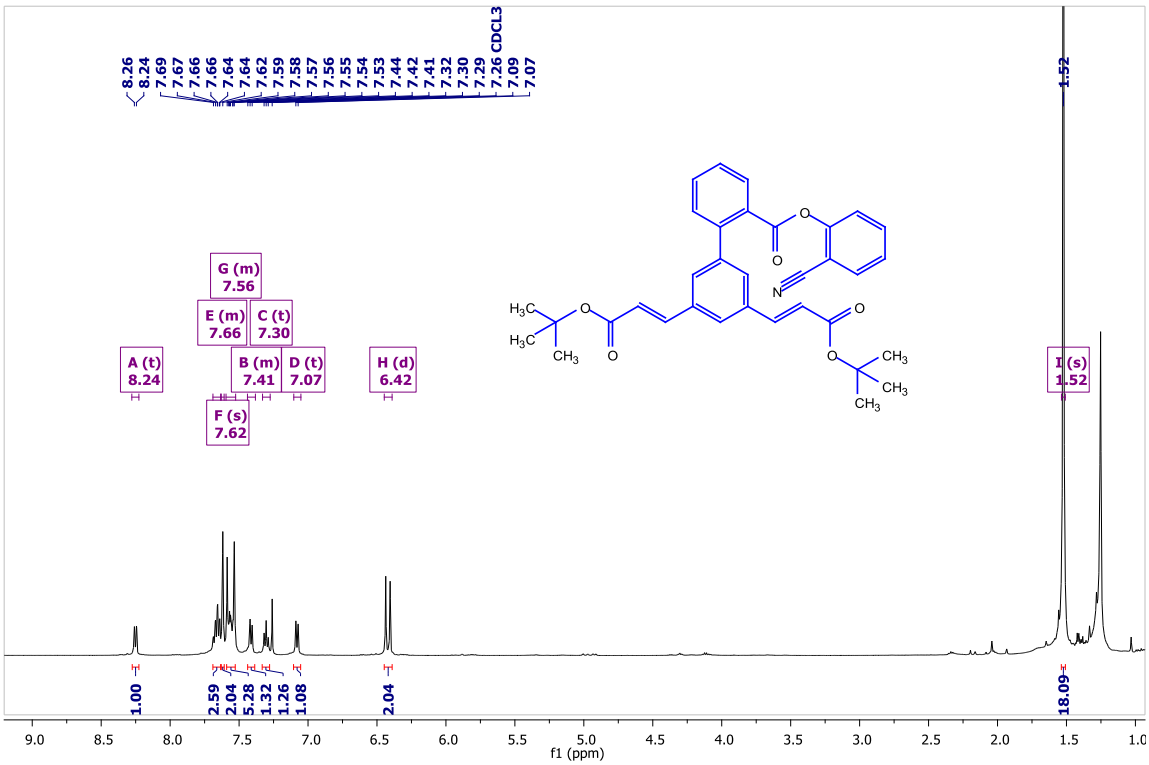


(E)-2-cyanophenyl 3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

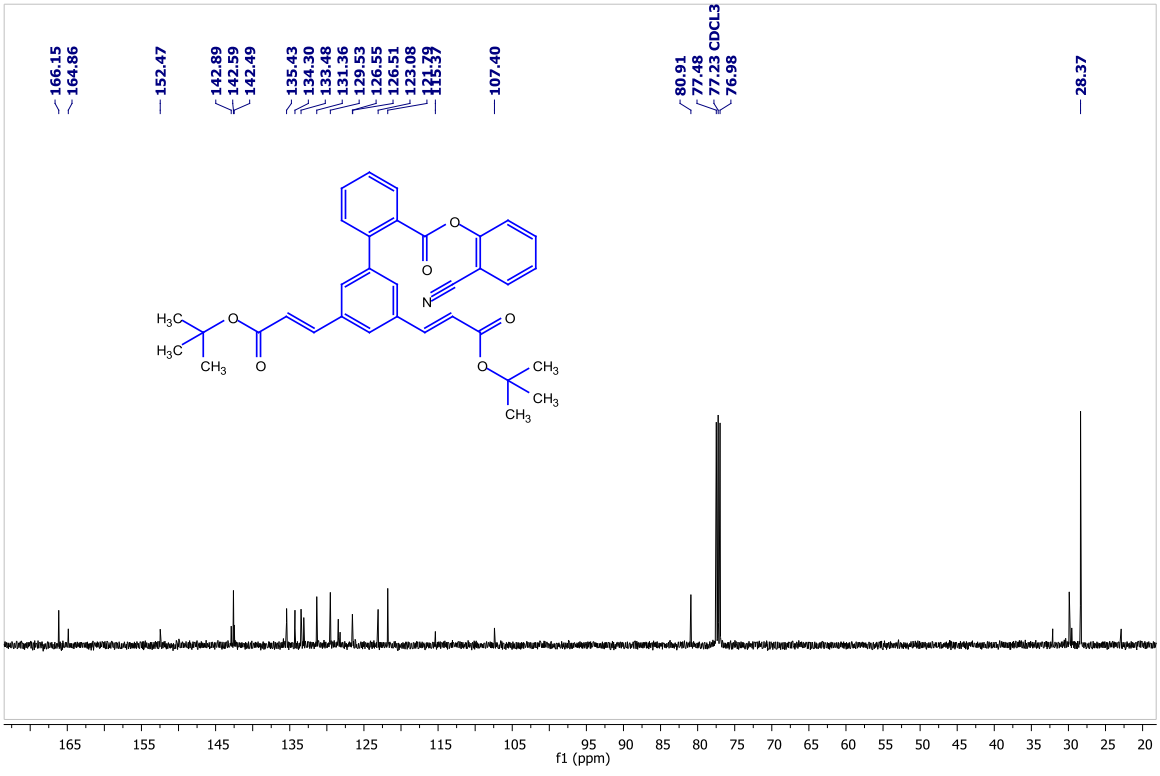


(**Scheme 3, 3c'**)

(2E,2'E)-di-tert-butyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

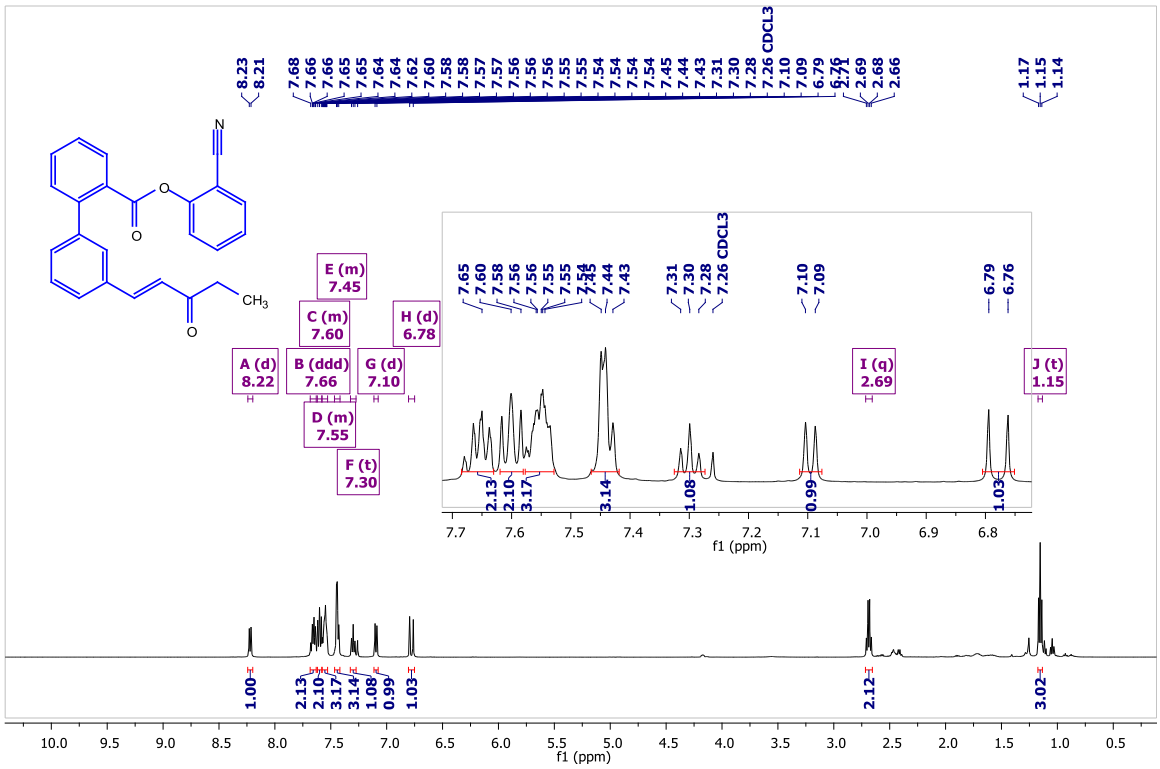


(2E,2'E)-di-tert-butyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

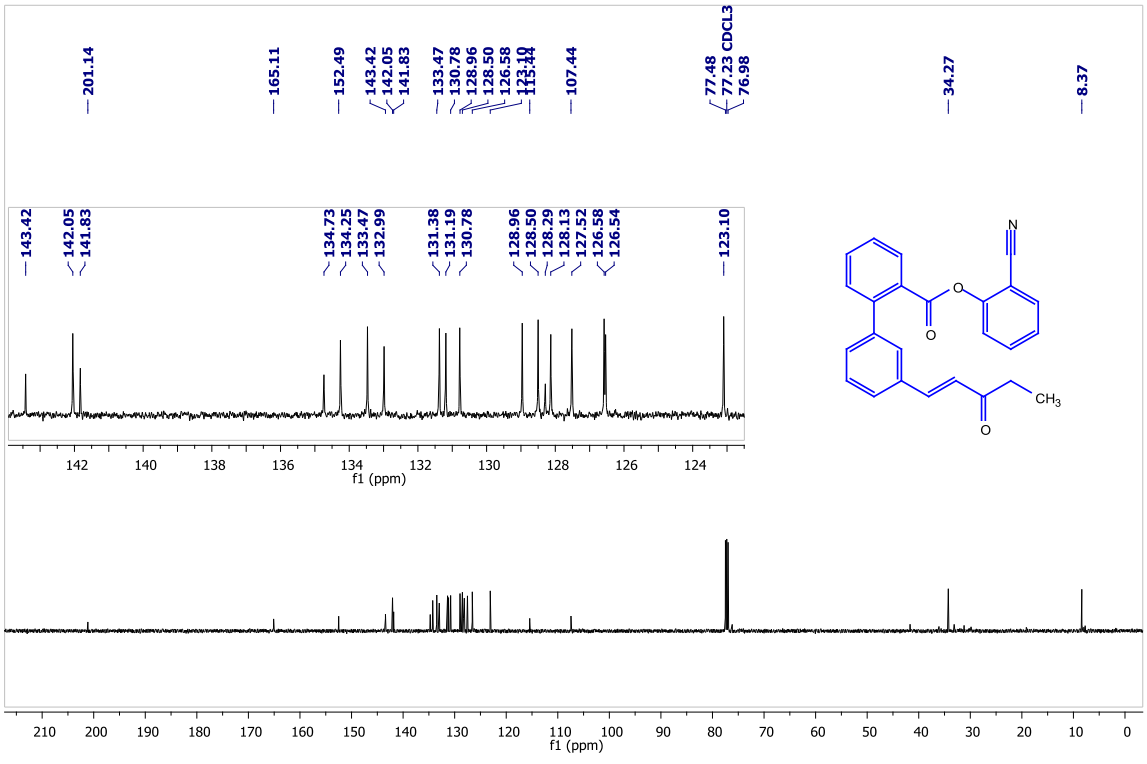


(**Scheme 3, 3d**)

(E)-2-cyanophenyl 3'-(3-oxopent-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

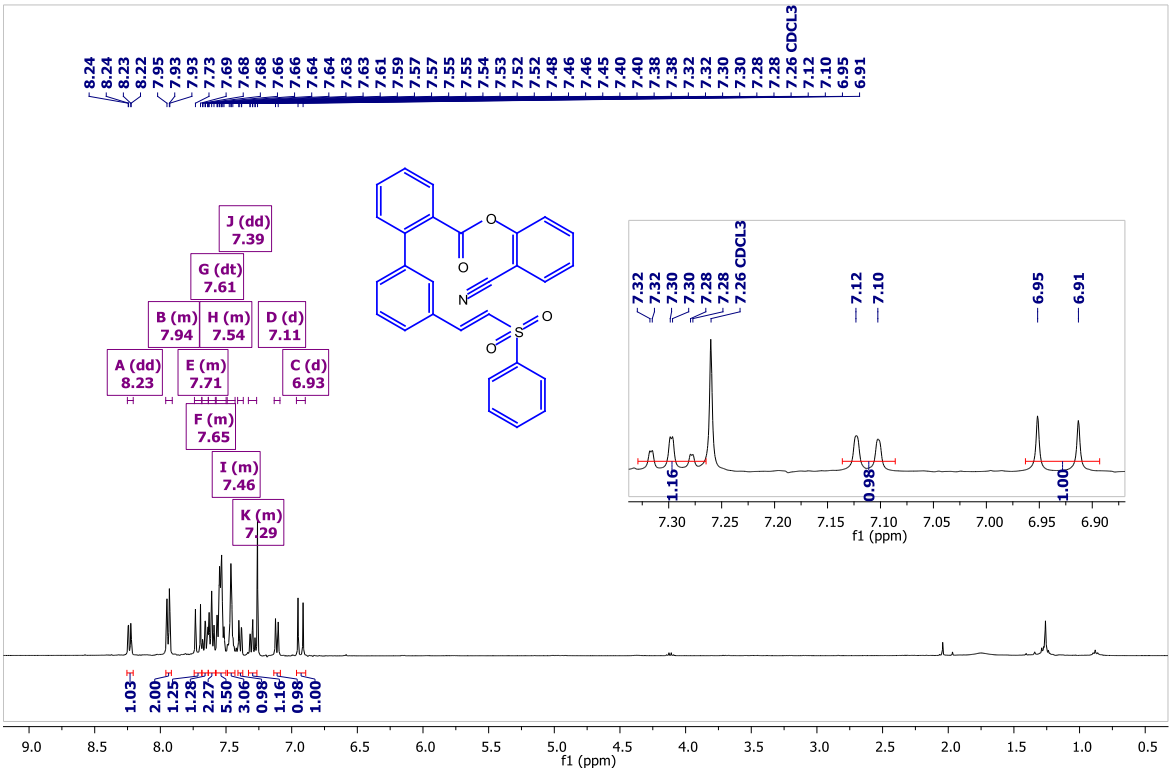


(E)-2-cyanophenyl 3'-(3-oxopent-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

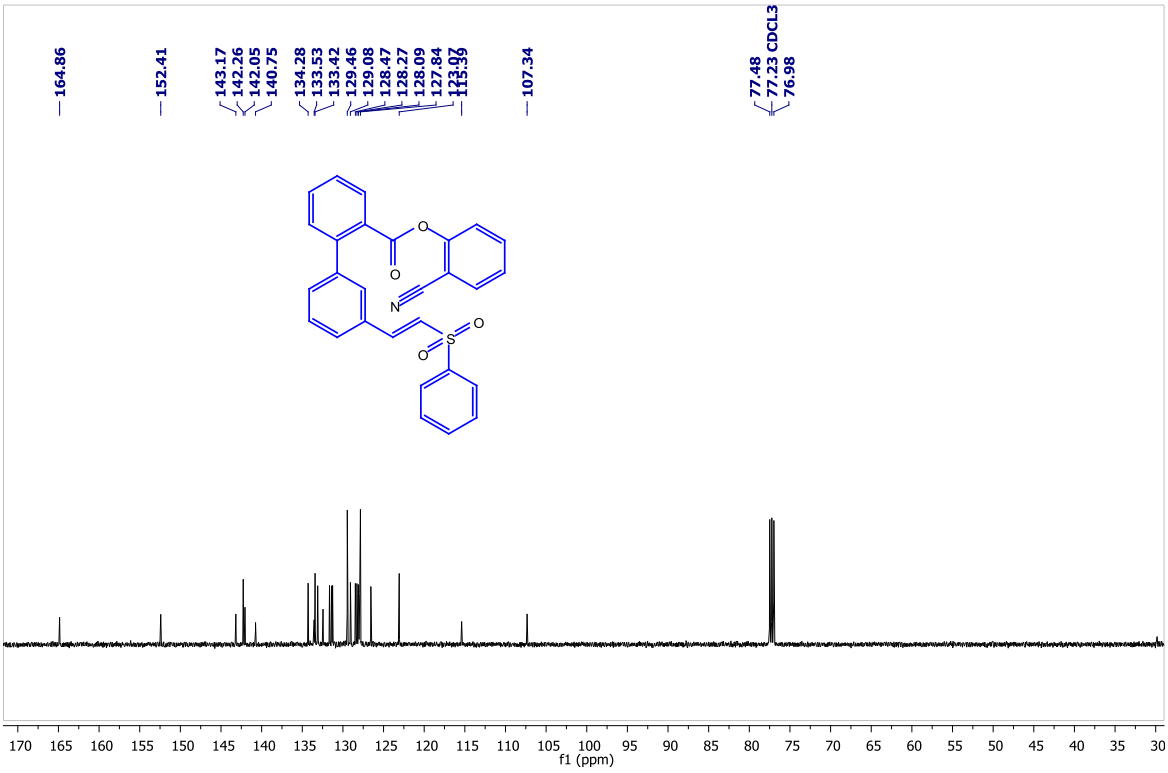


(**Scheme 3, 3e**)

(E)-2-cyanophenyl 3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-carboxylate

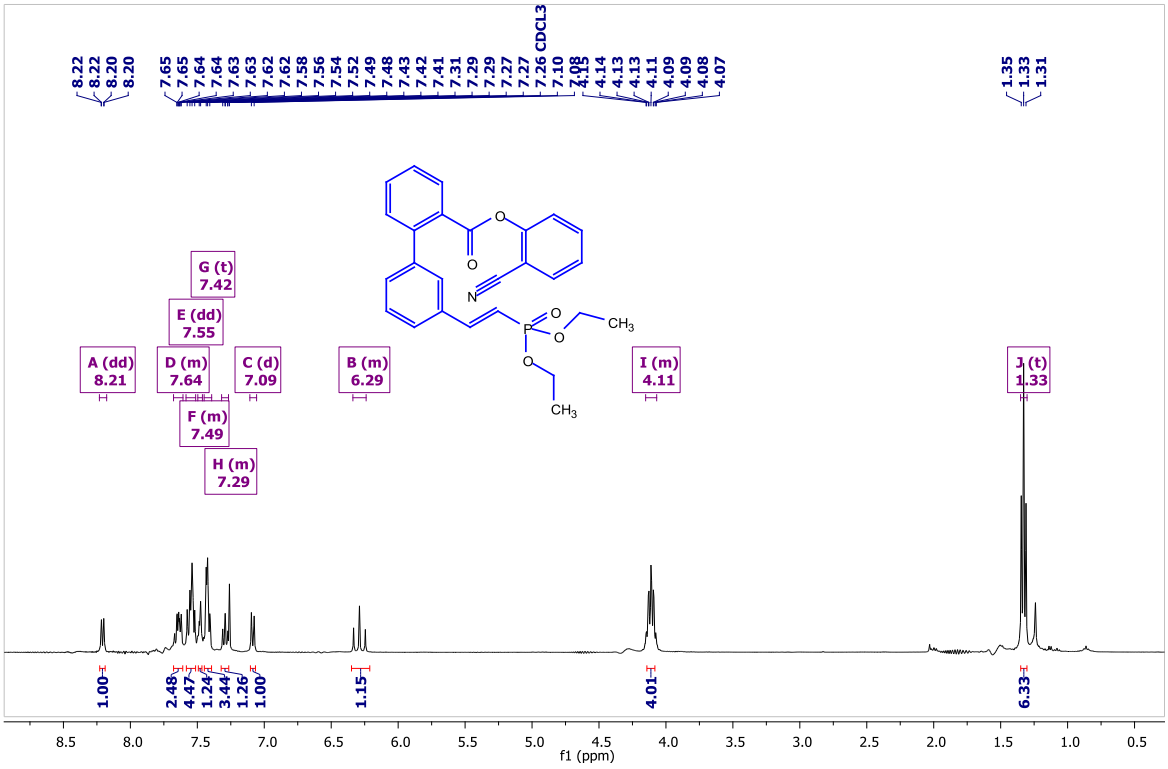


(E)-2-cyanophenyl 3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-carboxylate

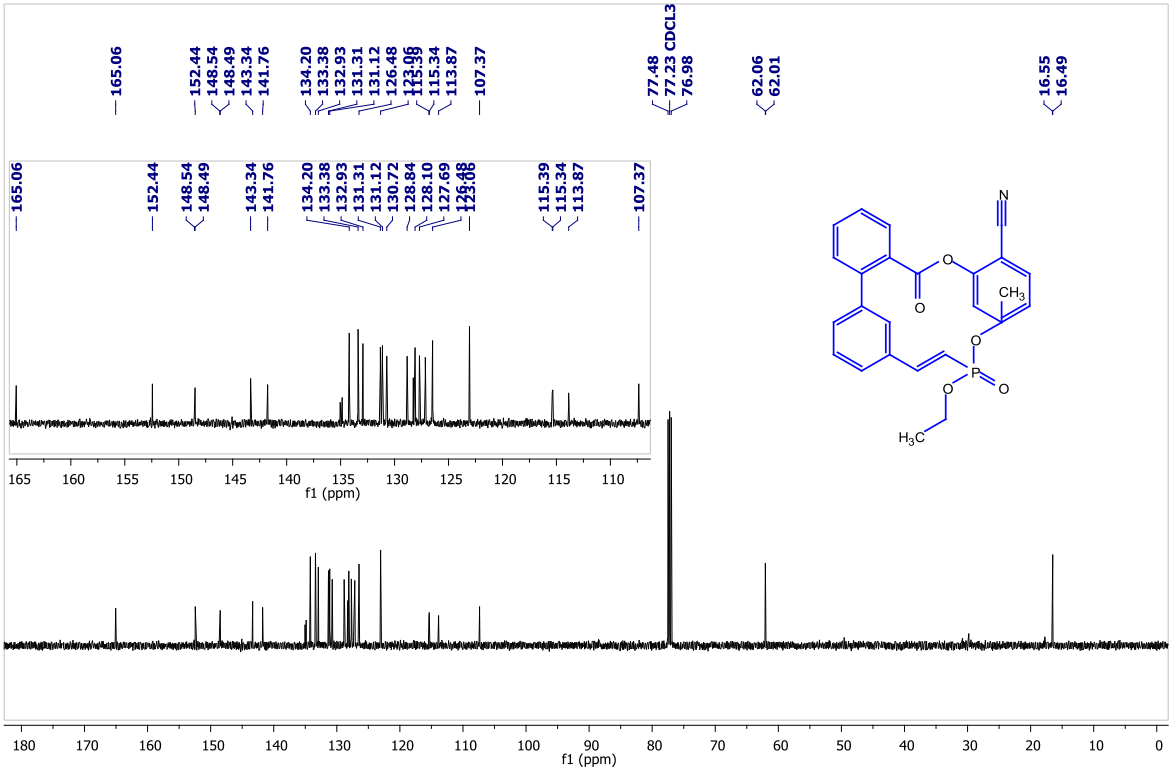


(**Scheme 3, 3f**)

(E)-2-cyanophenyl 3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-carboxylate

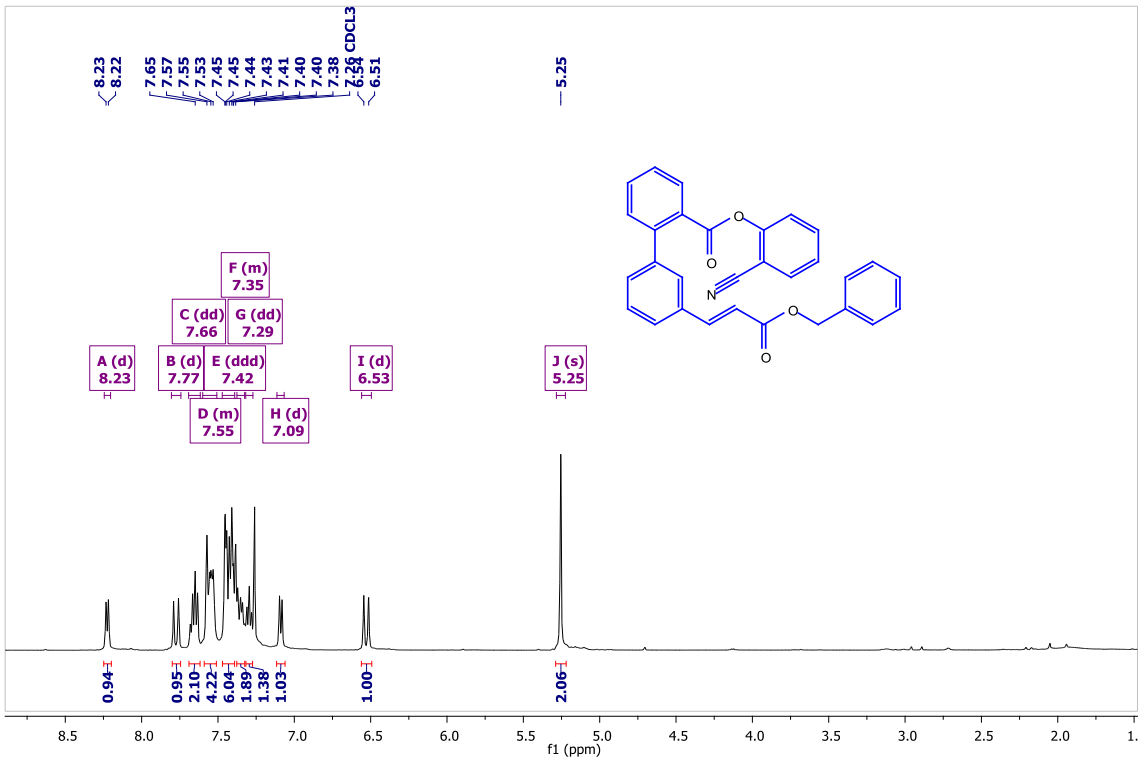


(E)-2-cyanophenyl 3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-carboxylate

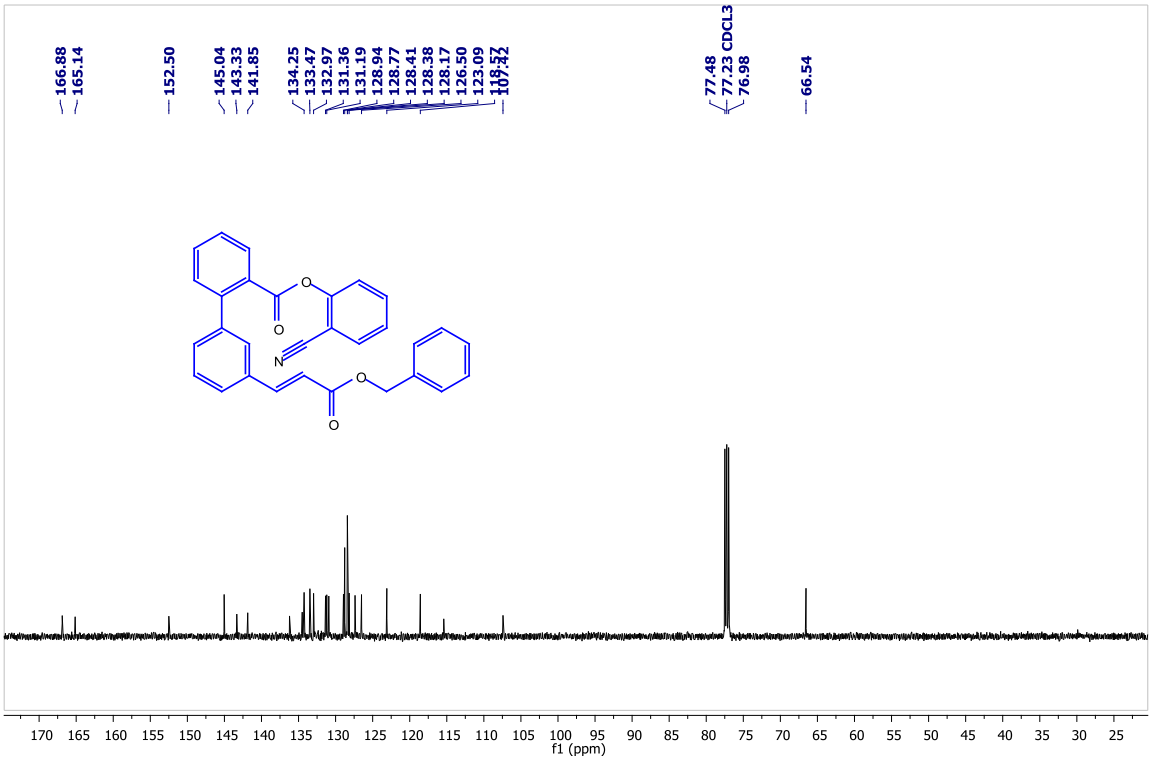


(**Scheme 3, 3g**)

(E)-2-cyanophenyl 3'-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

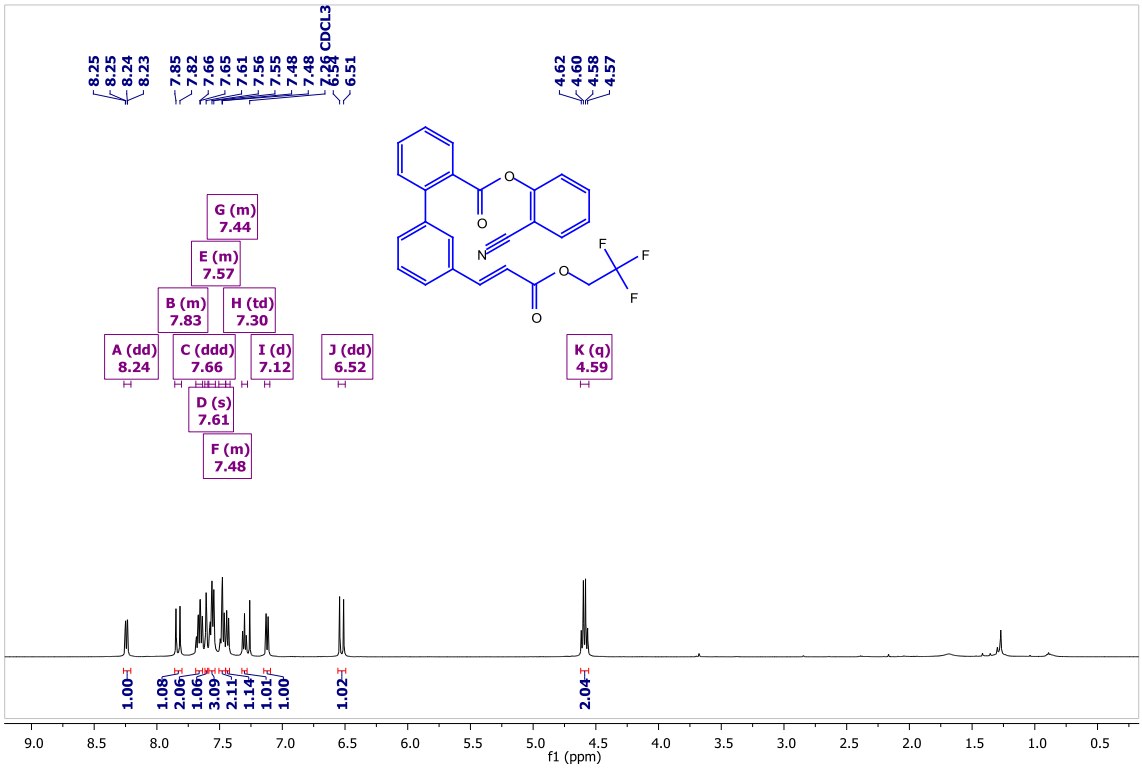


(E)-2-cyanophenyl 3'-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

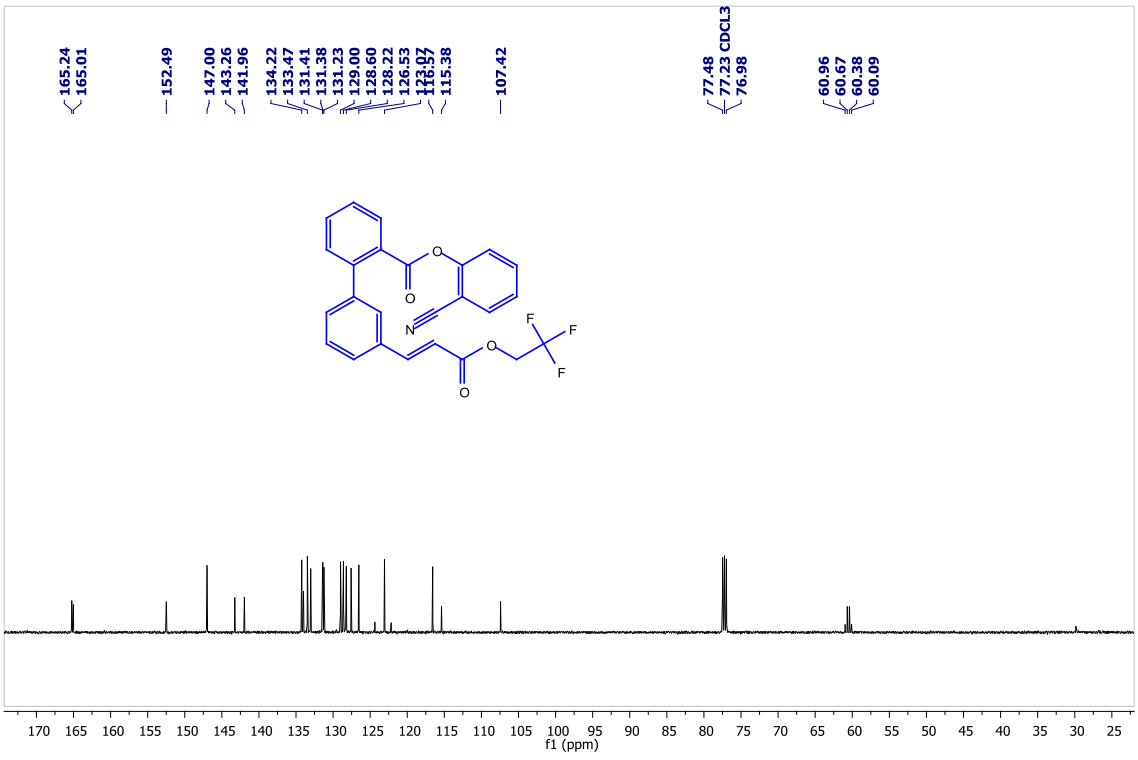


(**Scheme 3, 3h**)

(E)-2-cyanophenyl 3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

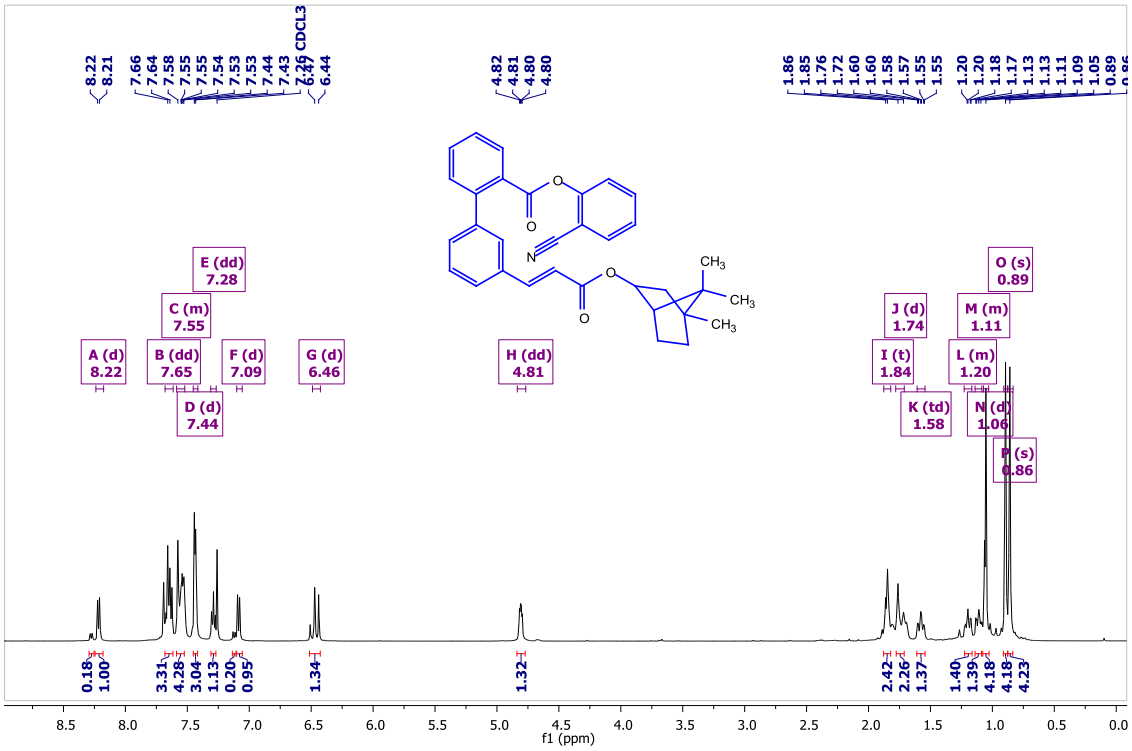


(E)-2-cyanophenyl 3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

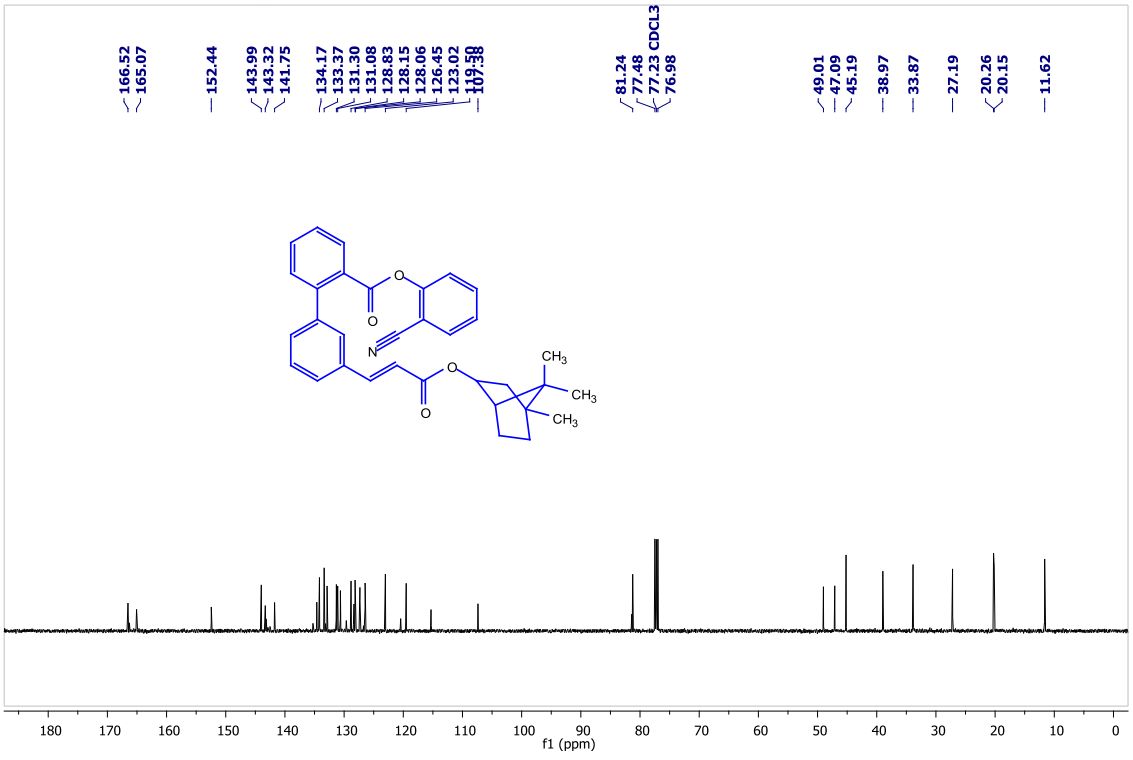


(Scheme 3, 3i)

2-cyanophenyl 3'-((E)-3-oxo-3-(((1R,4R)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

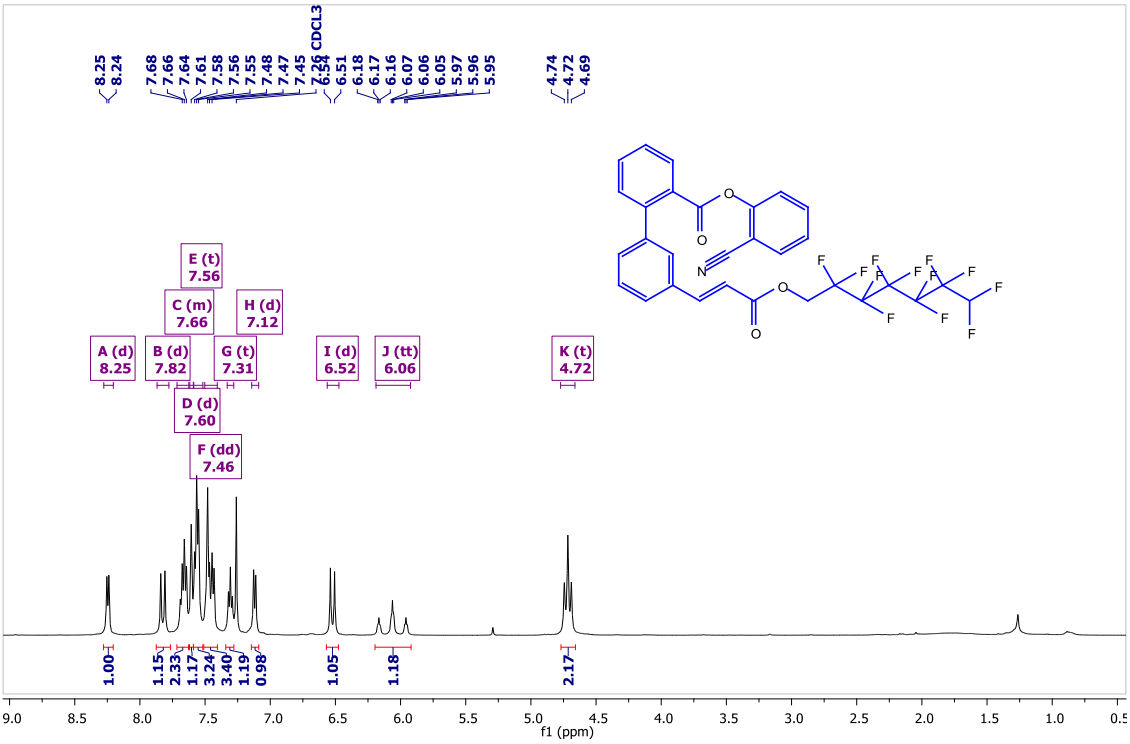


2-cyanophenyl 3'-((E)-3-oxo-3-(((1R,4R)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

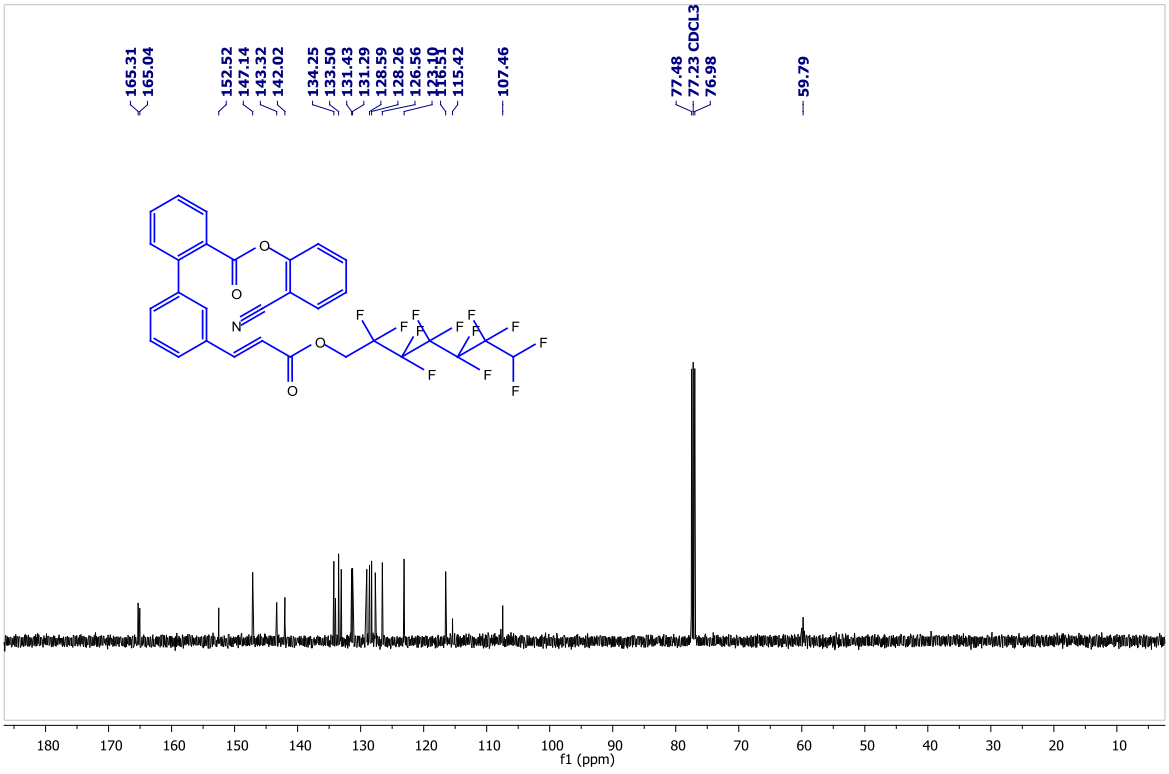


(**Scheme 3, 3j**)

(E)-2-cyanophenyl 3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

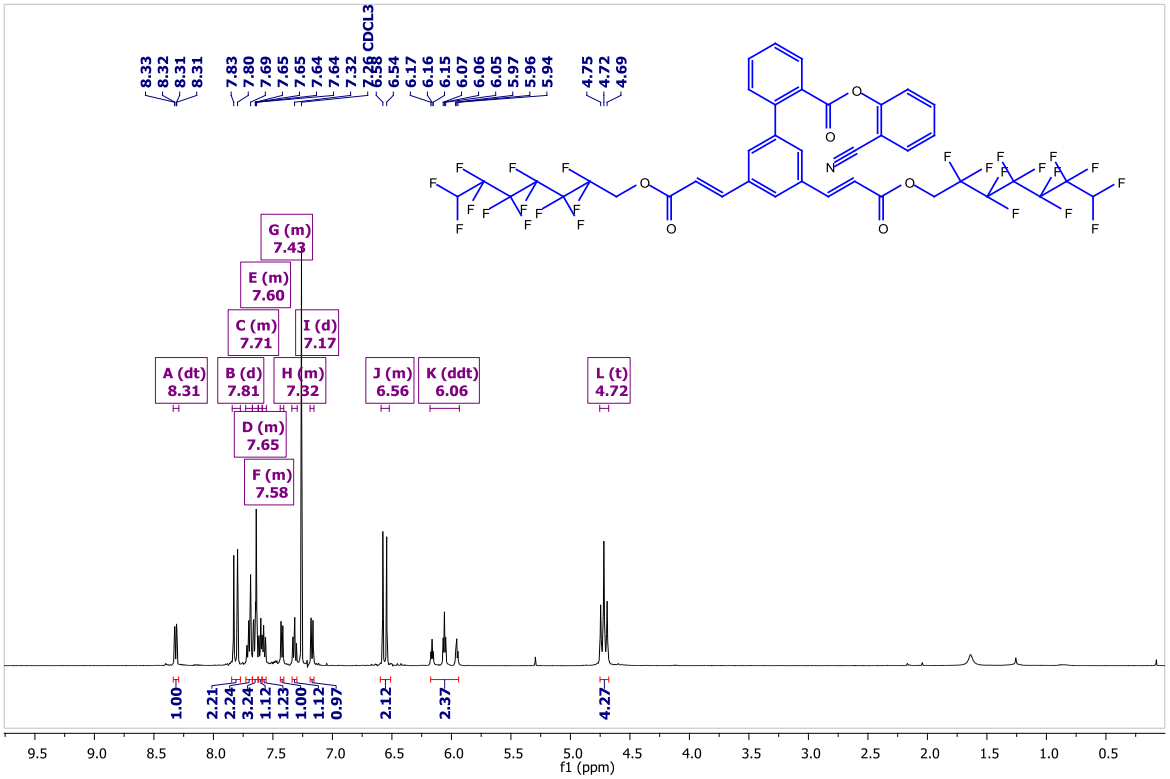


(E)-2-cyanophenyl 3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

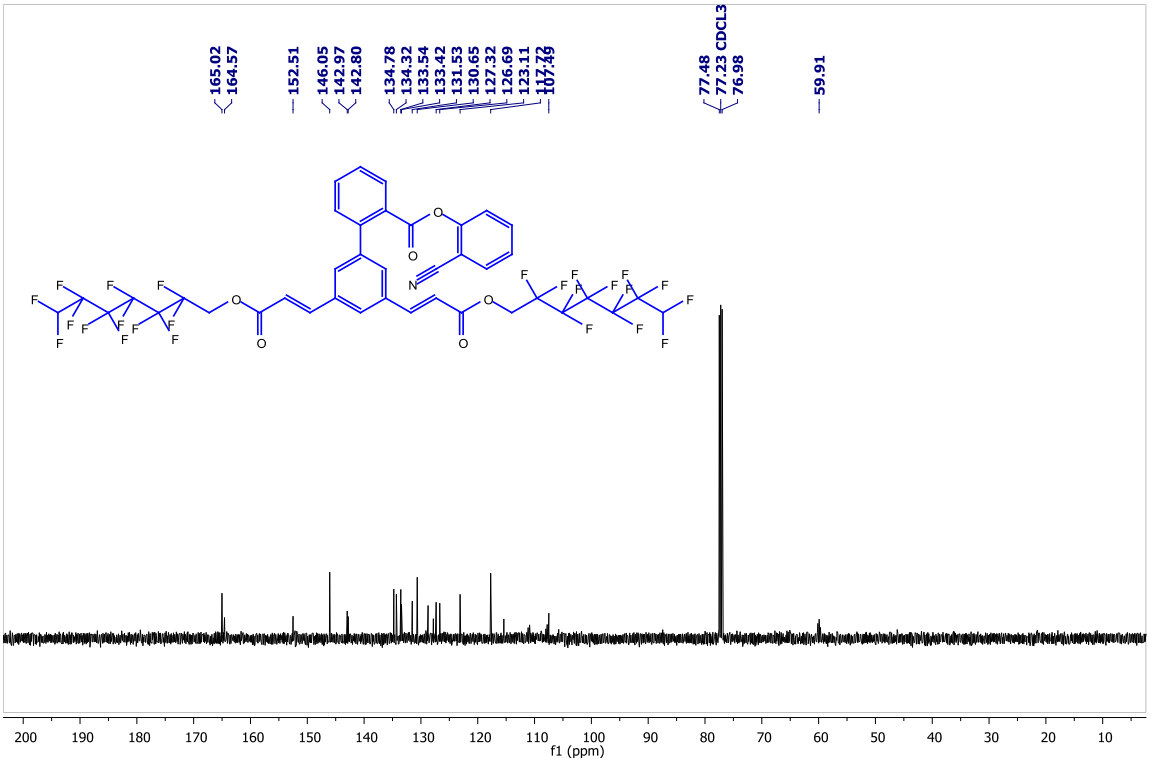


(Scheme 3, 3j')

(2E,2'E)-bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

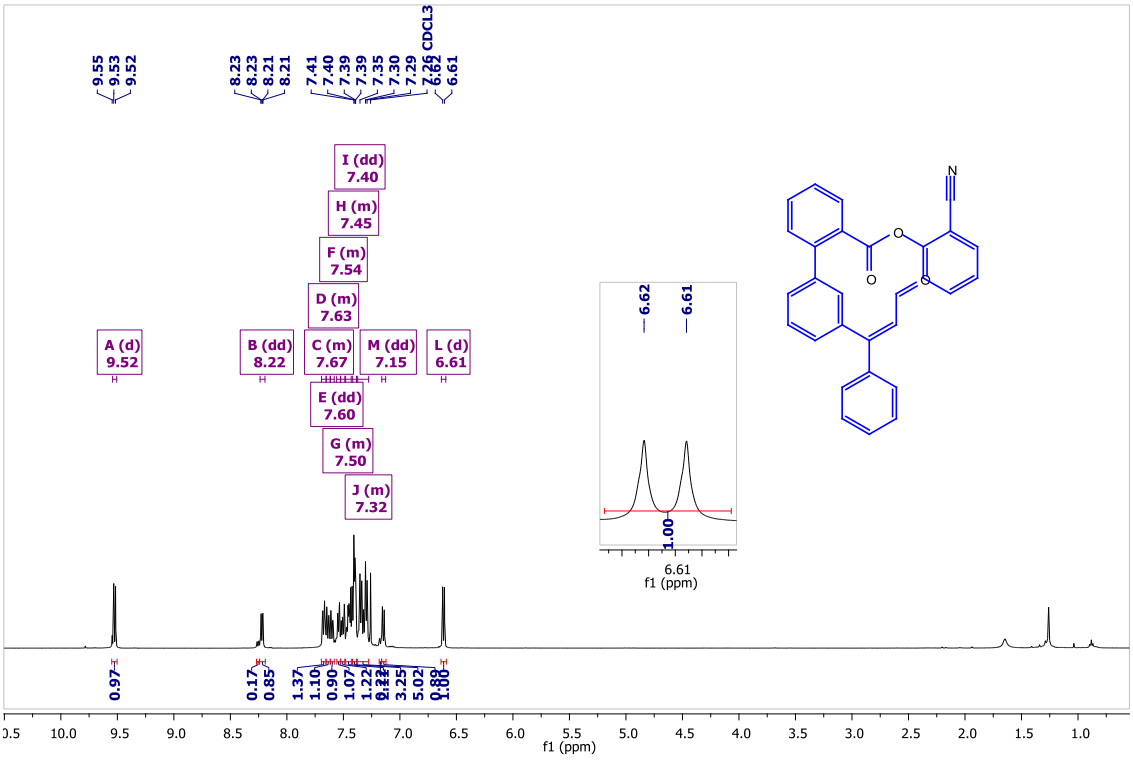


(2E,2'E)-bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

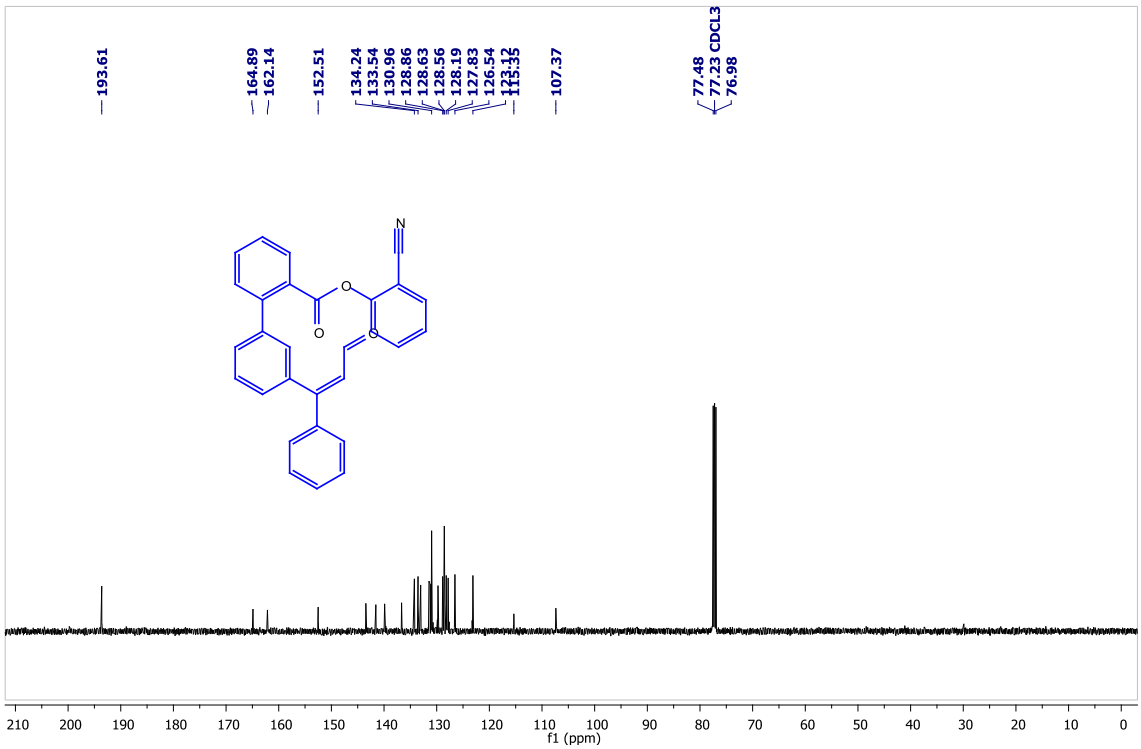


(**Scheme 3, 3k**)

(E)-2-cyanophenyl 3'-(3-oxo-1-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

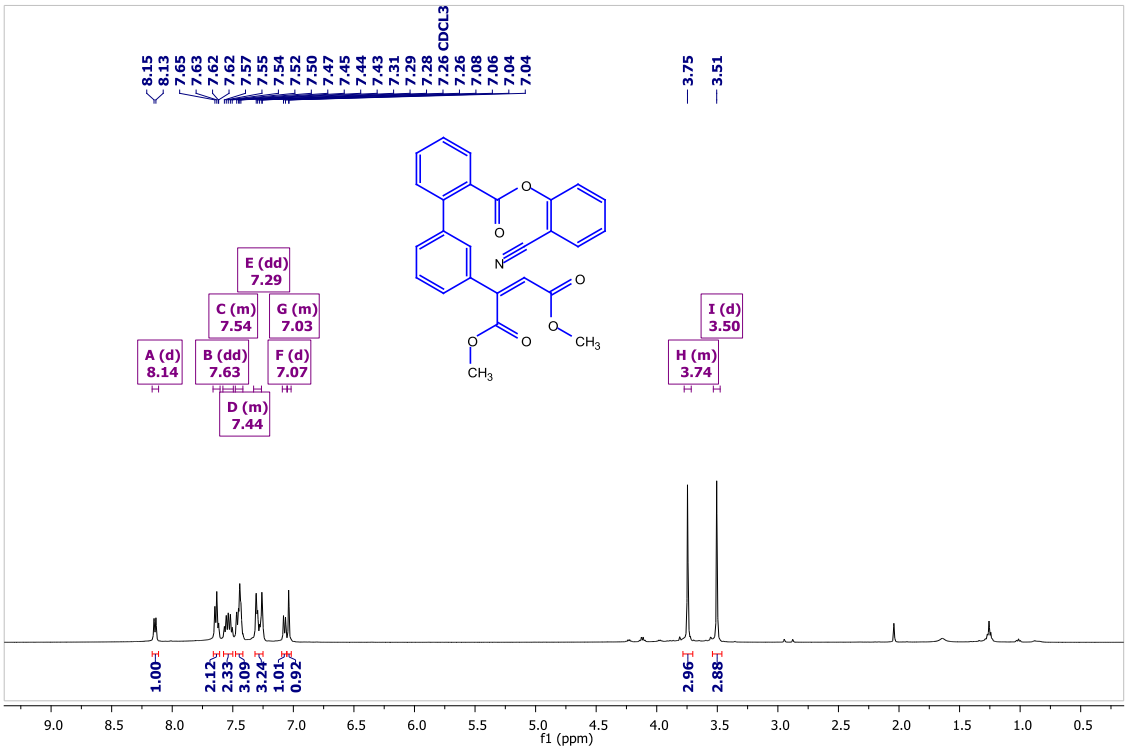


(E)-2-cyanophenyl 3'-(3-oxo-1-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

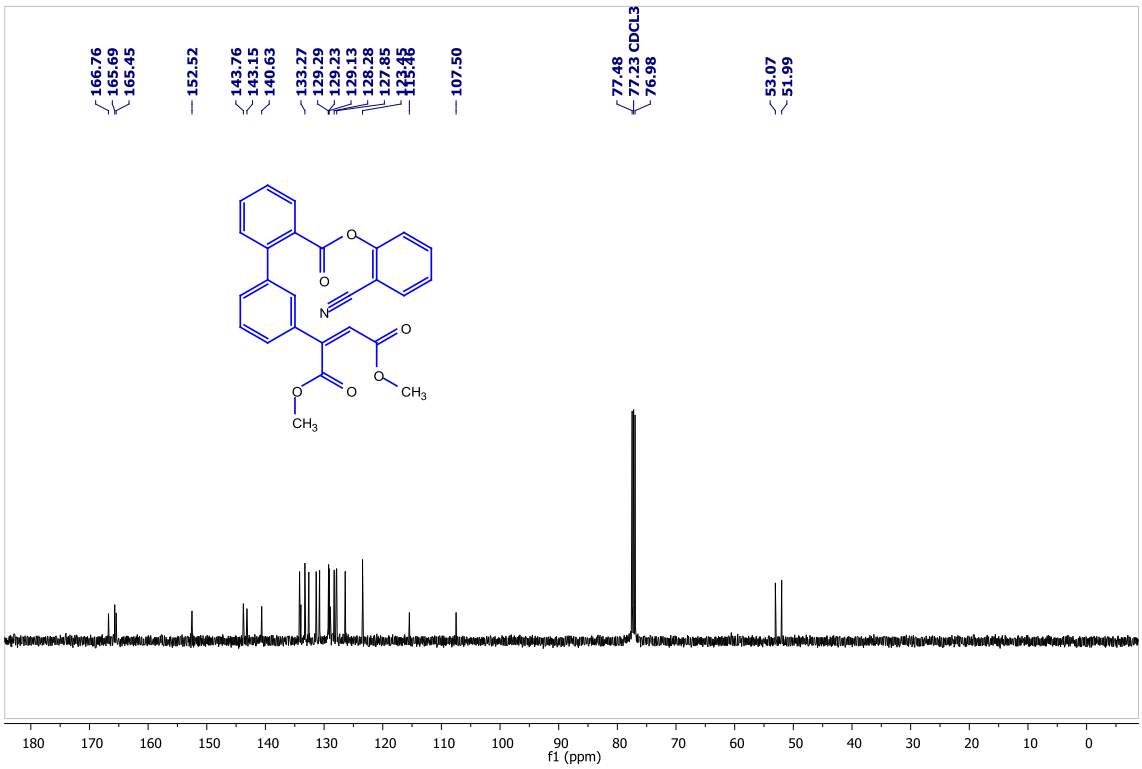


(Scheme 3, 3l)

dimethyl 2-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3-yl)maleate

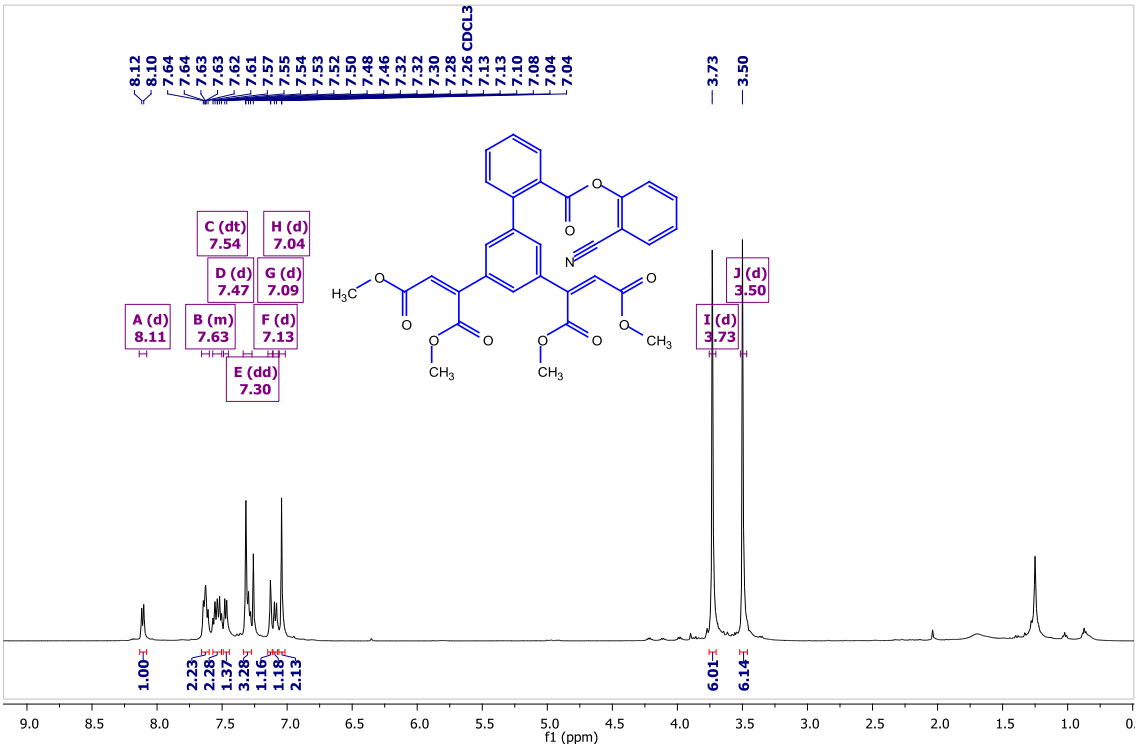


dimethyl 2-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3-yl)maleate

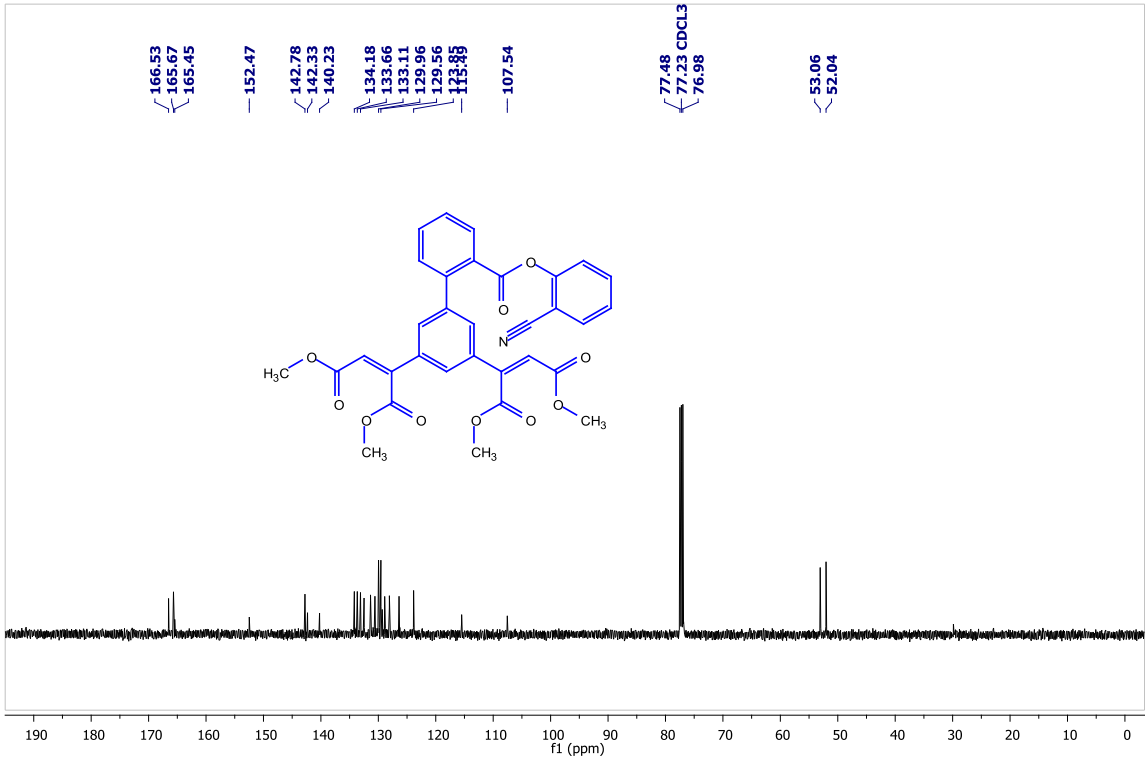


(**Scheme 3, 3l'**)

(Z)-tetramethyl 2,2'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)dimaleate

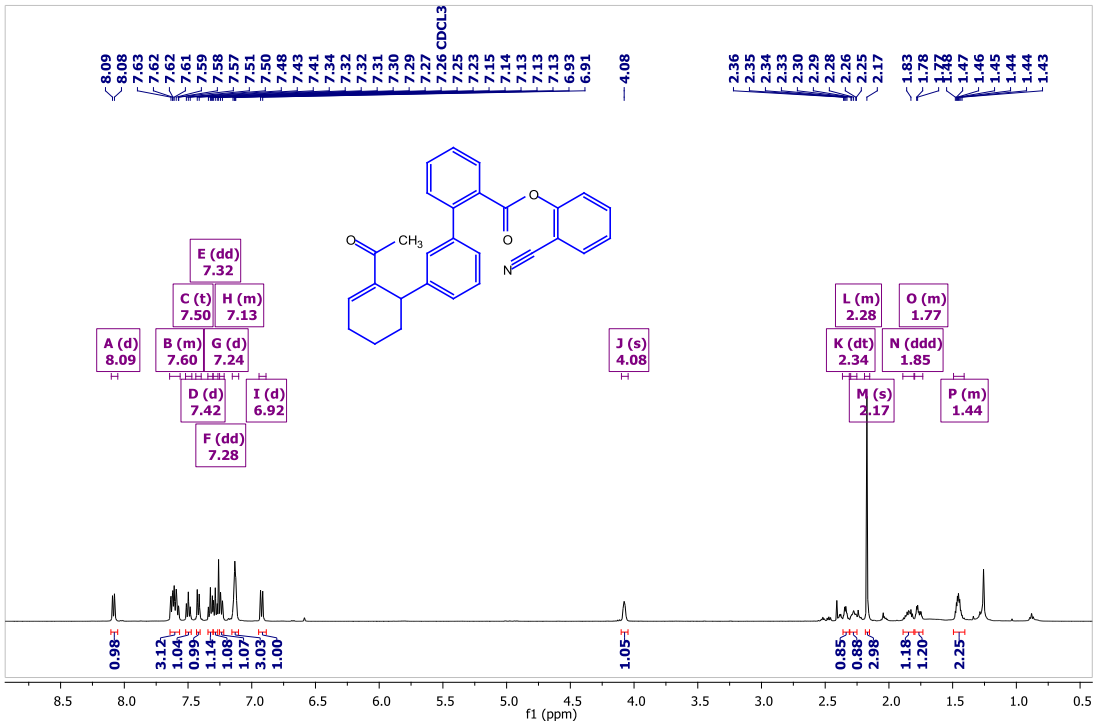


(Z)-tetramethyl 2,2'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)dimaleate

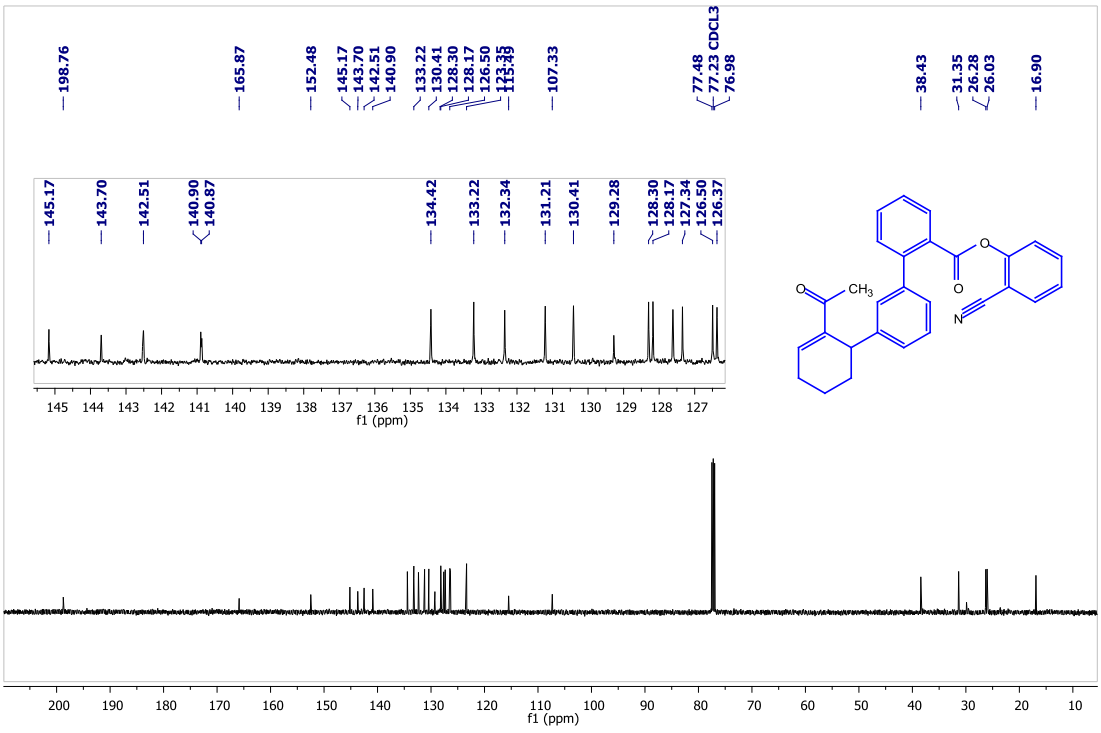


(**Scheme 3, 3m**)

2-cyanophenyl 6''-acetyl-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate

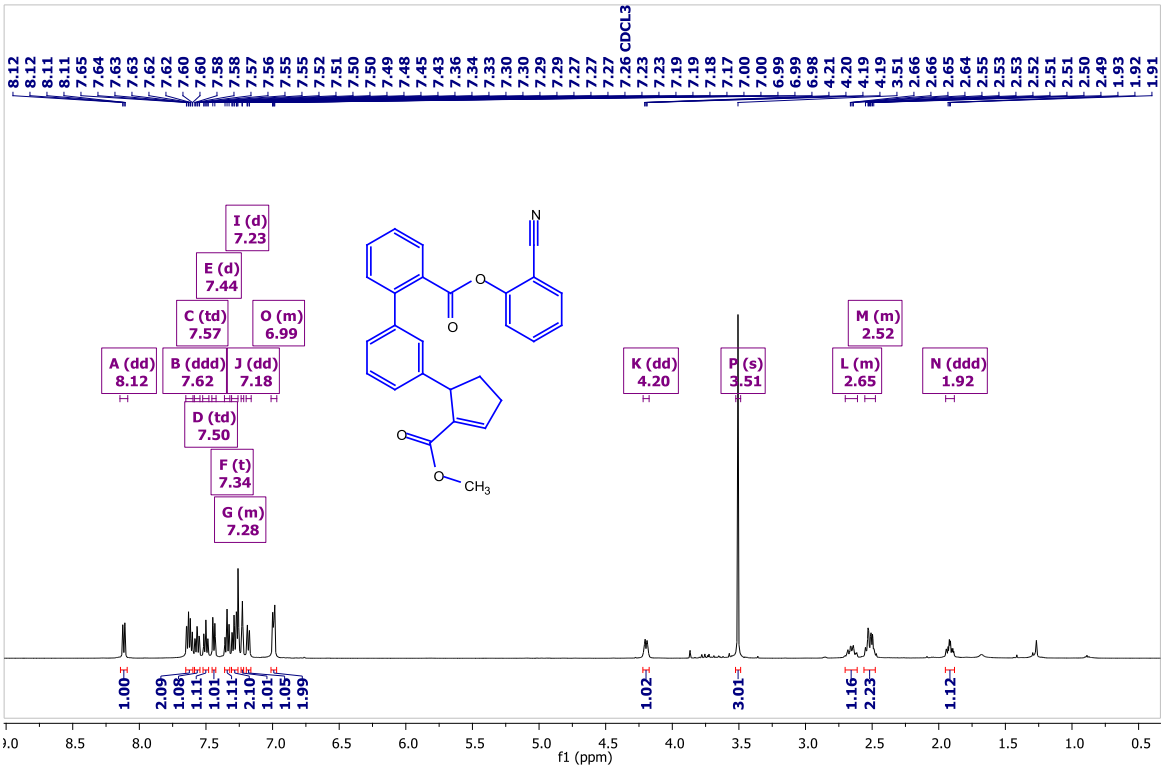


2-cyanophenyl 6''-acetyl-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate

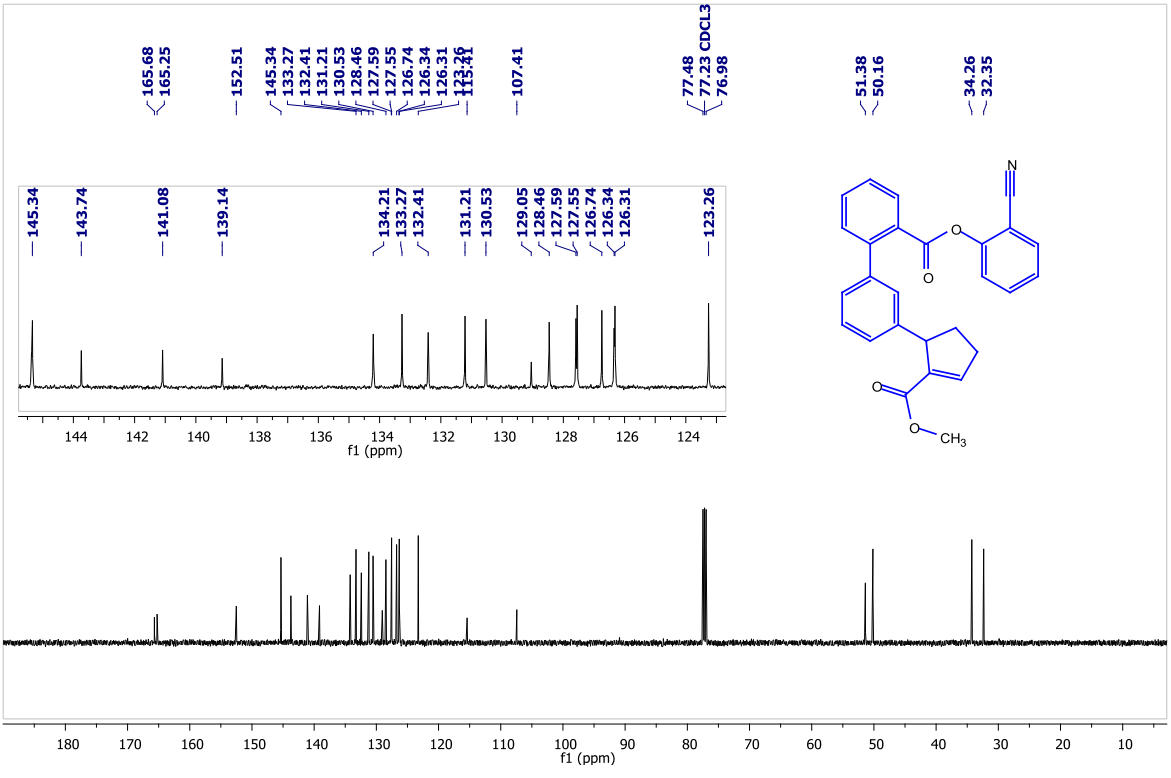


(**Scheme 3, 3n**)

2-cyanophenyl 3'-(2-(methoxycarbonyl)cyclopent-2-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

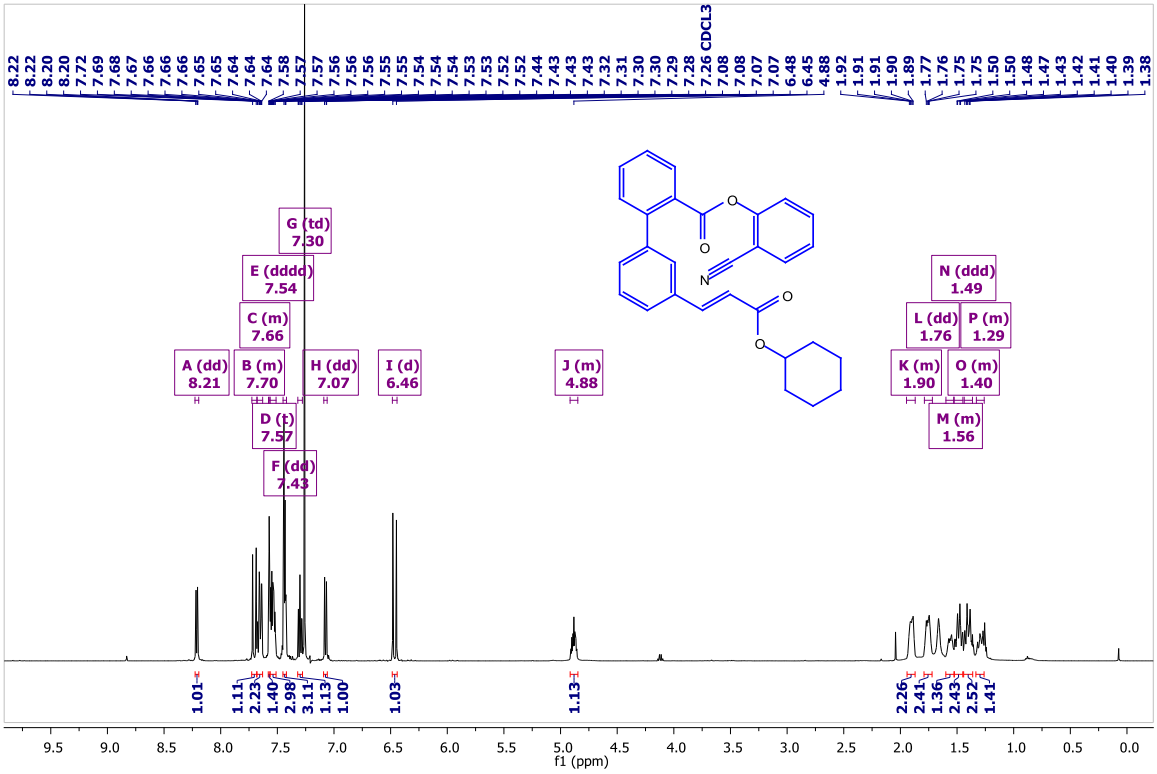


2-cyanophenyl 3'-(2-(methoxycarbonyl)cyclopent-2-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

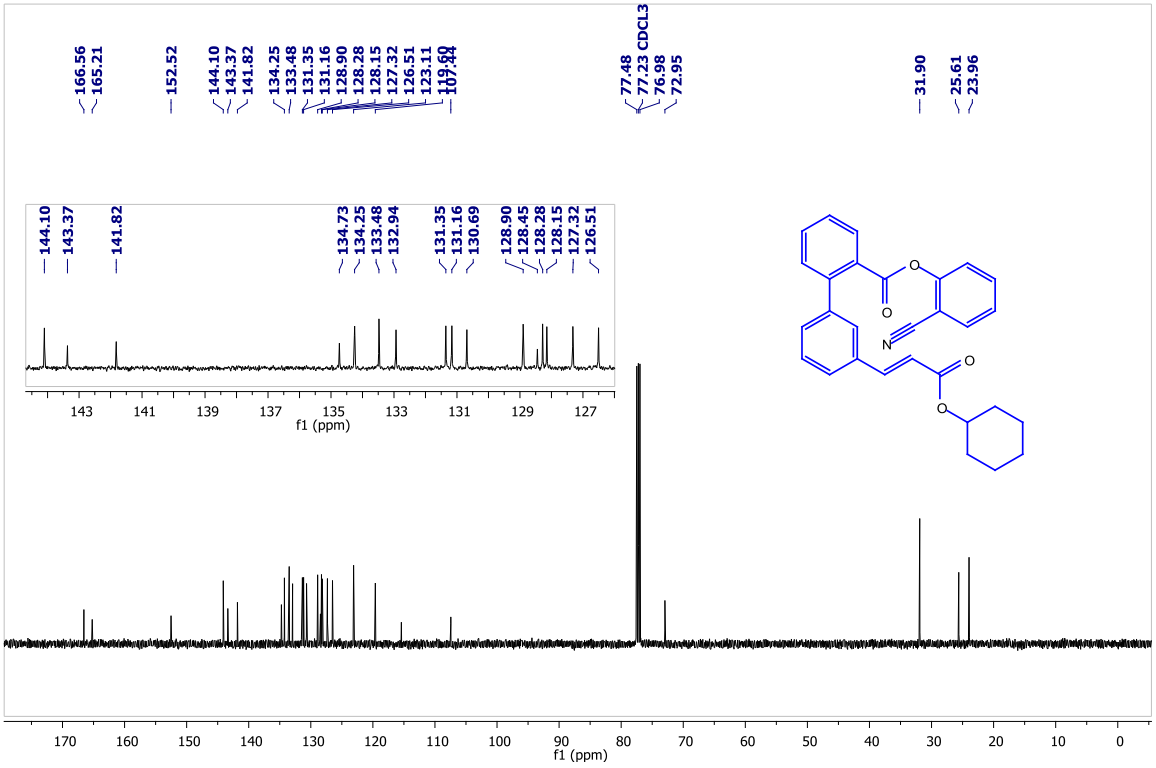


(**Scheme 3, 3o**)

(E)-2-cyanophenyl 3'-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

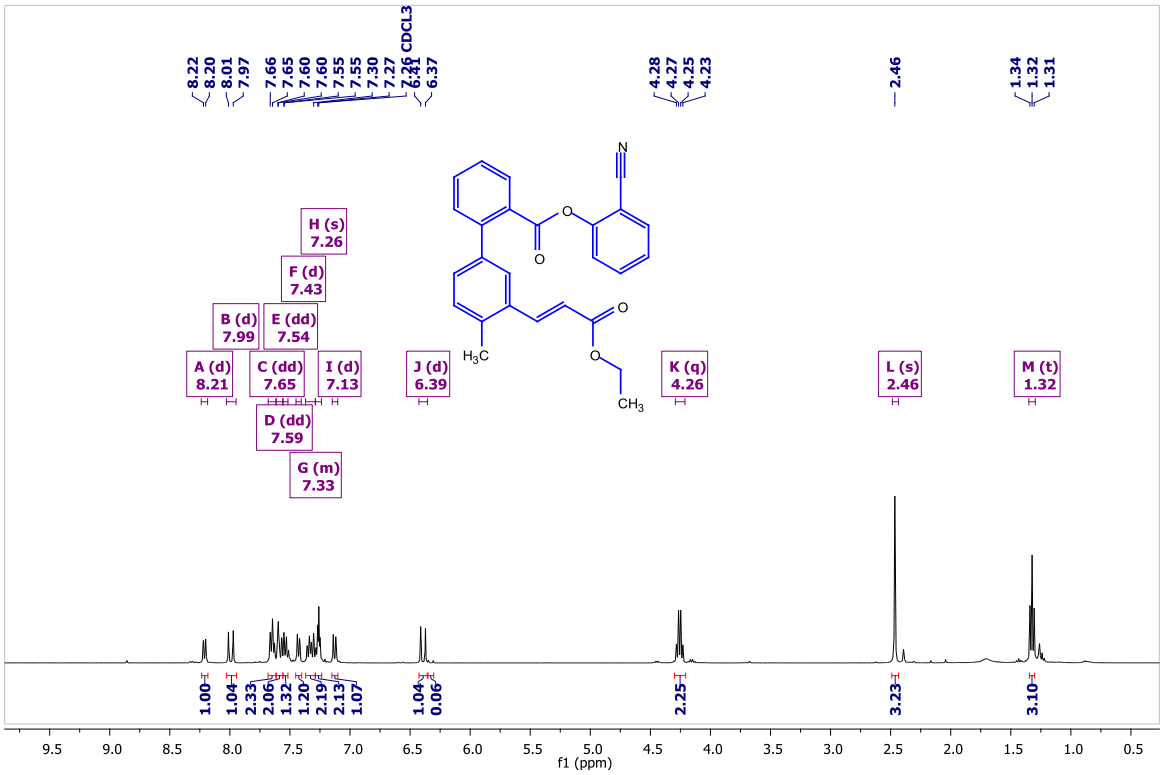


(E)-2-cyanophenyl 3'-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

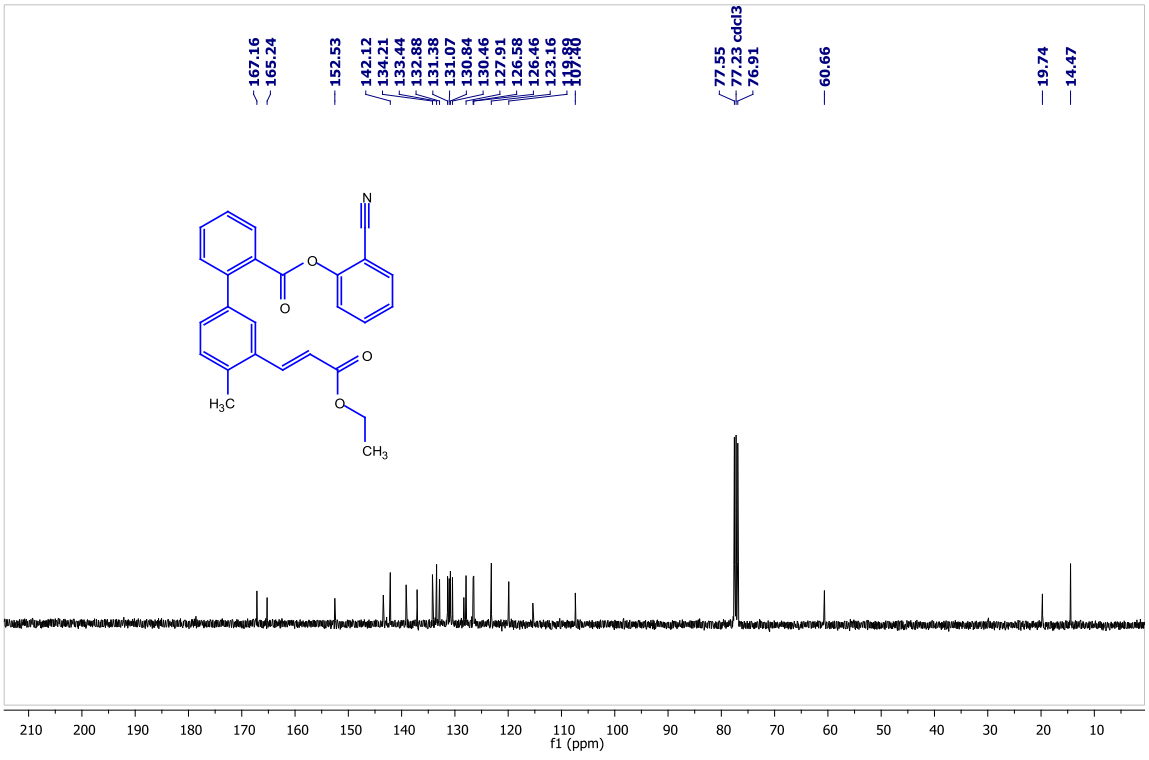


(**Scheme 4, 4a**)

(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-methyl-[1,1'-biphenyl]-2-carboxylate

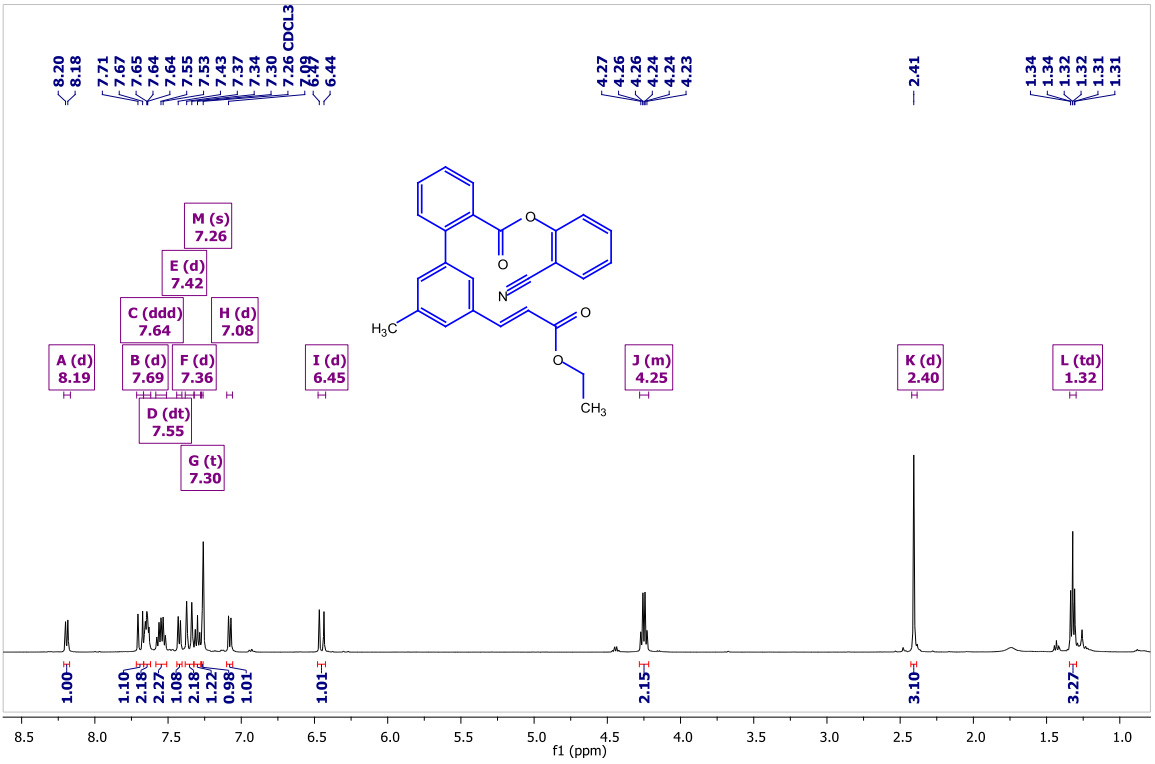


(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-methyl-[1,1'-biphenyl]-2-carboxylate

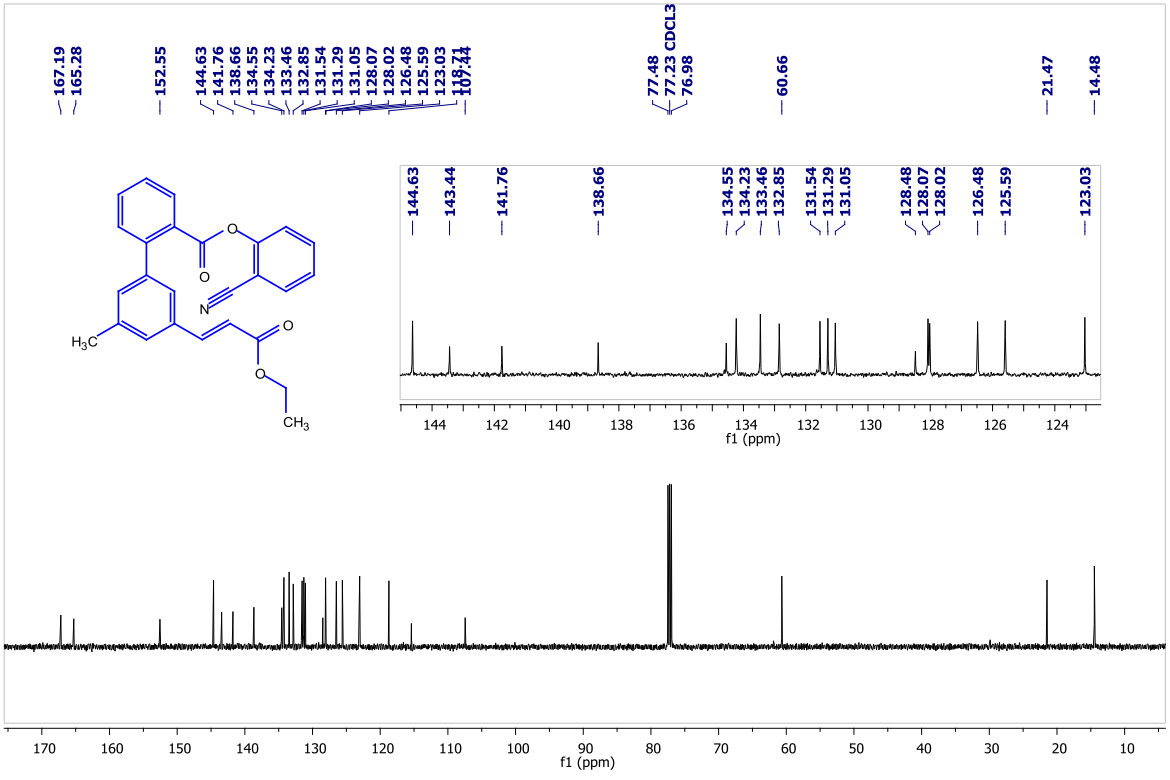


(**Scheme 4, 4b**)

(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate

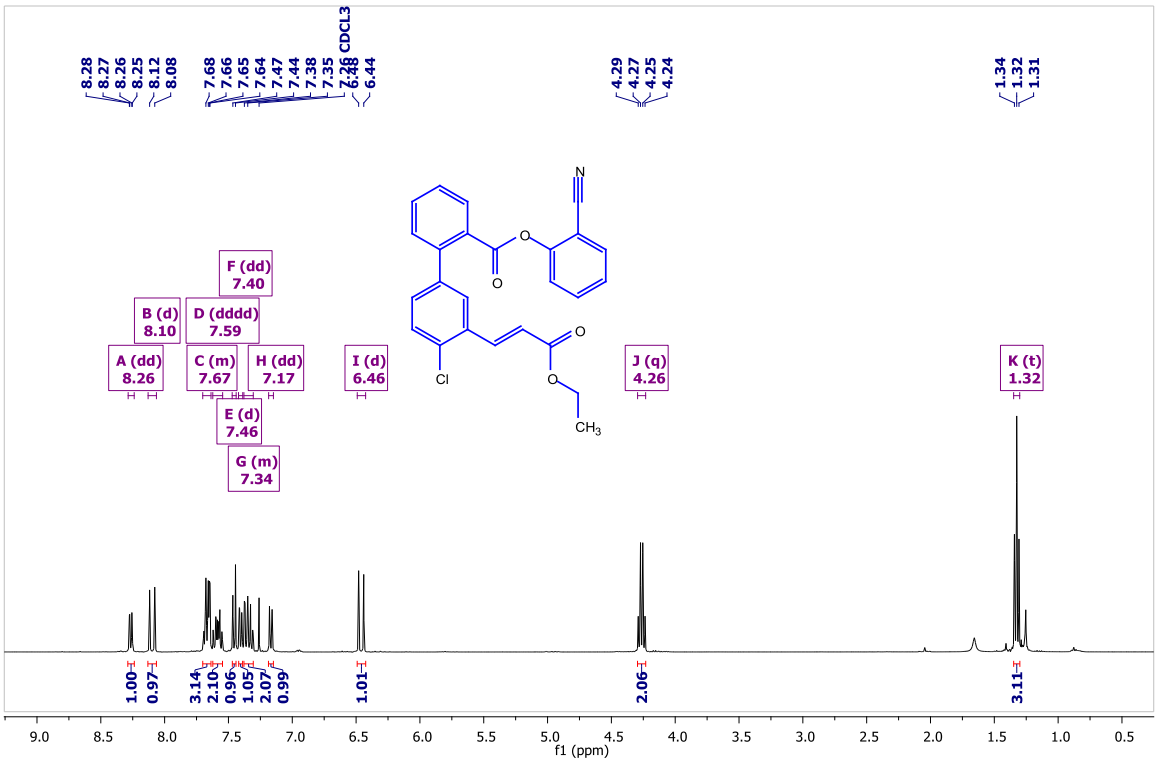


(E)-2-cyanophenyl 3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate

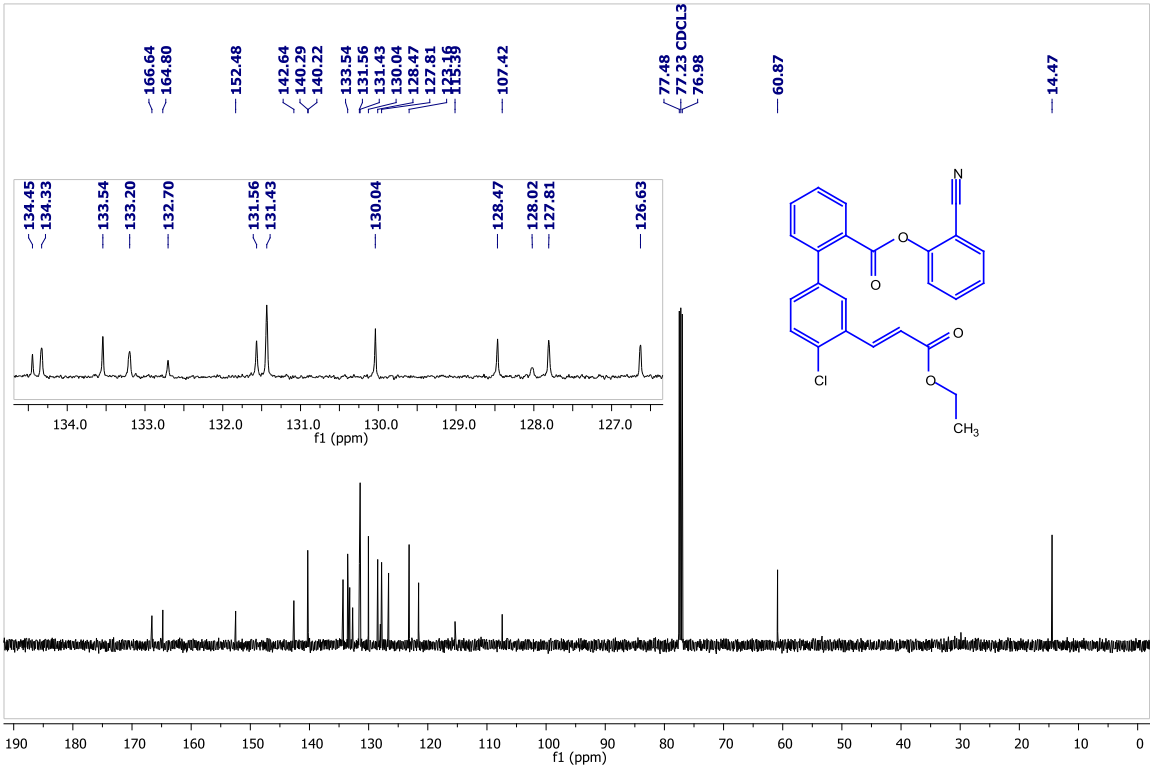


(**Scheme 4, 4c**)

(E)-2-cyanophenyl 4'-chloro-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

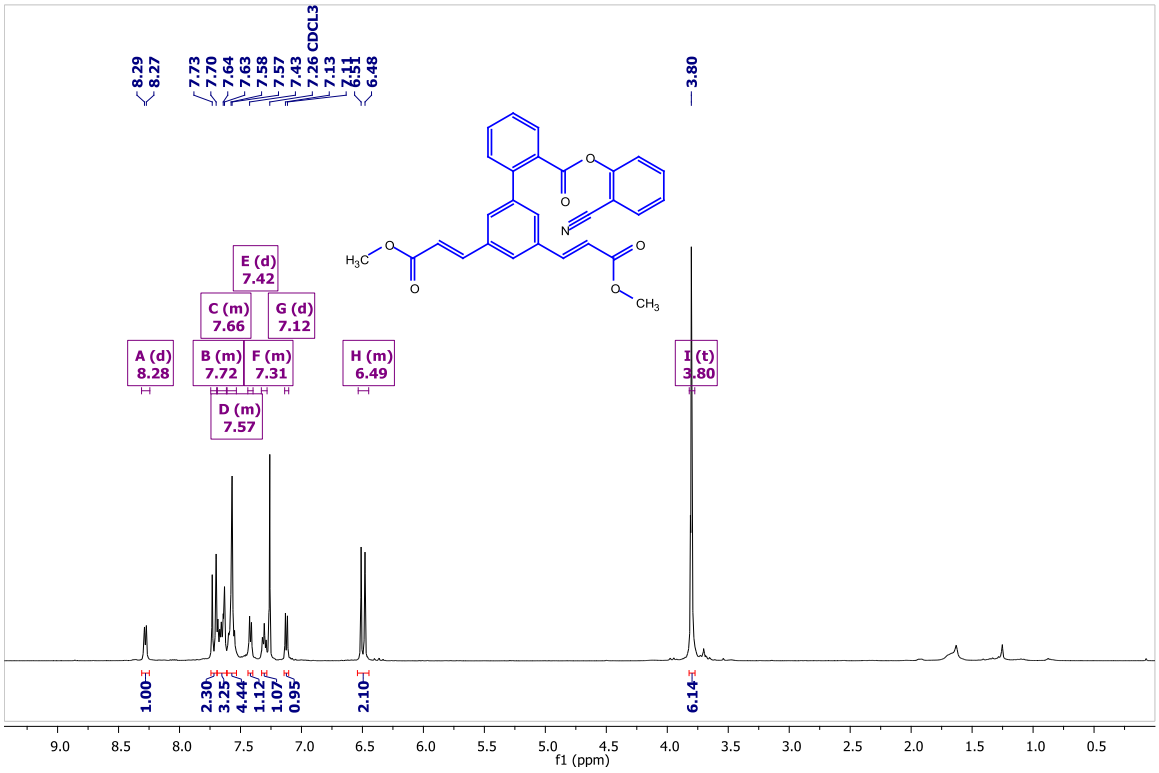


(E)-2-cyanophenyl 4'-chloro-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

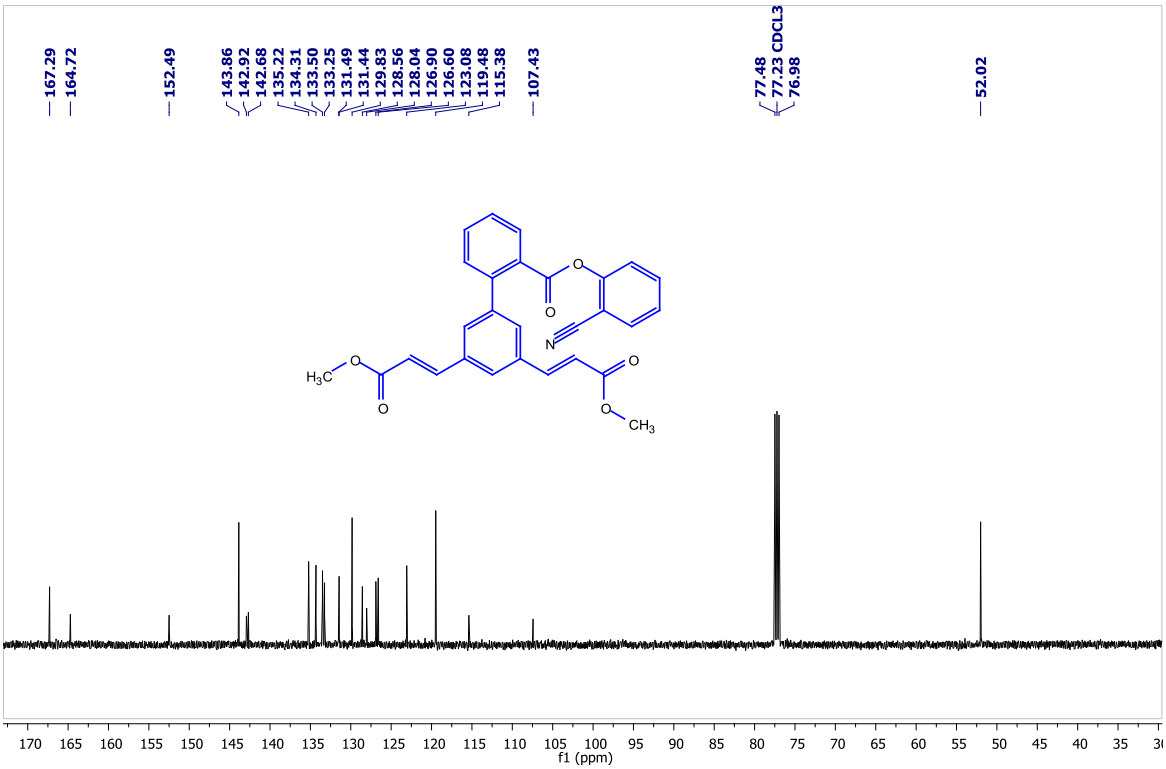


(**Scheme 4, 4d**)

(2E,2'E)-dimethyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

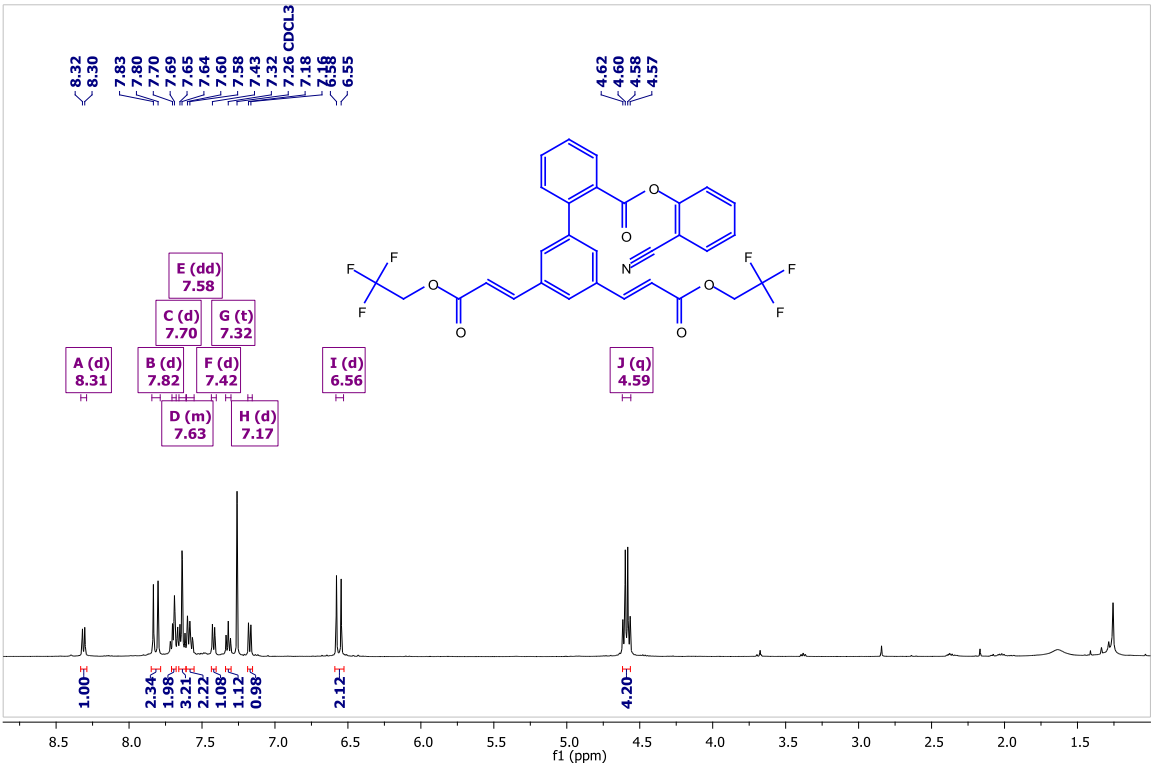


(2E,2'E)-dimethyl 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

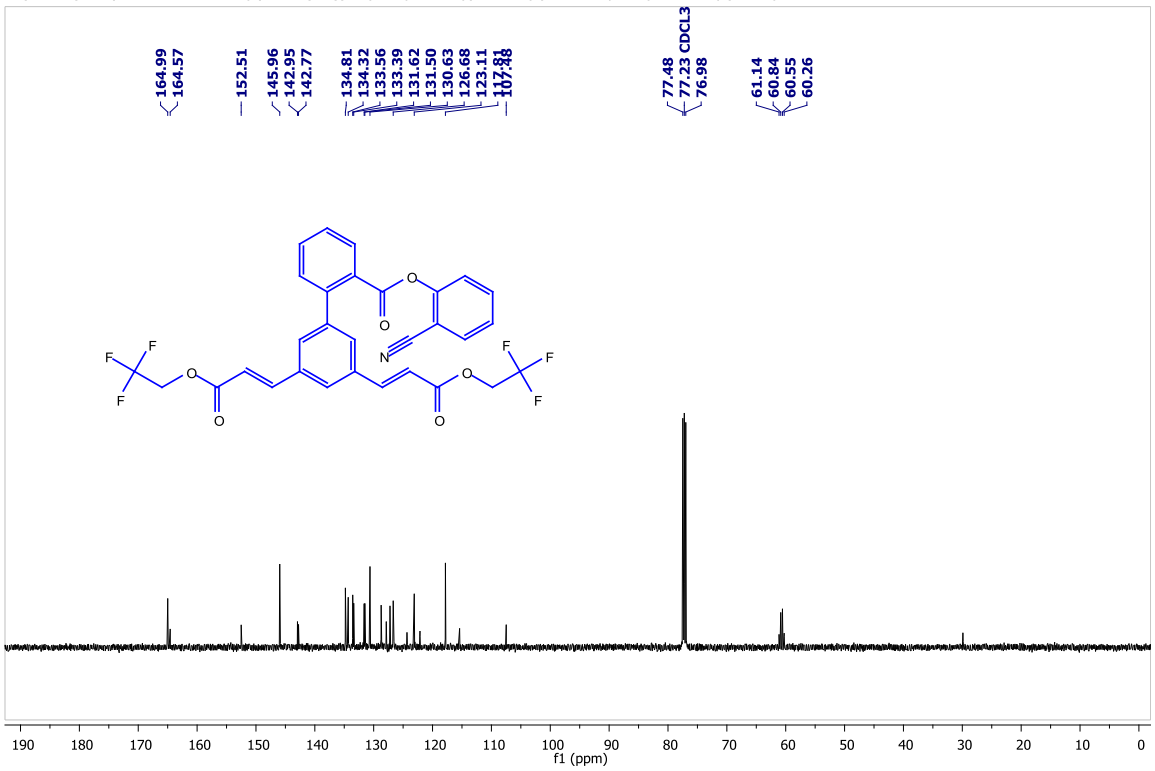


(**Scheme 4, 4e**)

(2E,2'E)-bis(2,2,2-trifluoroethyl) 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

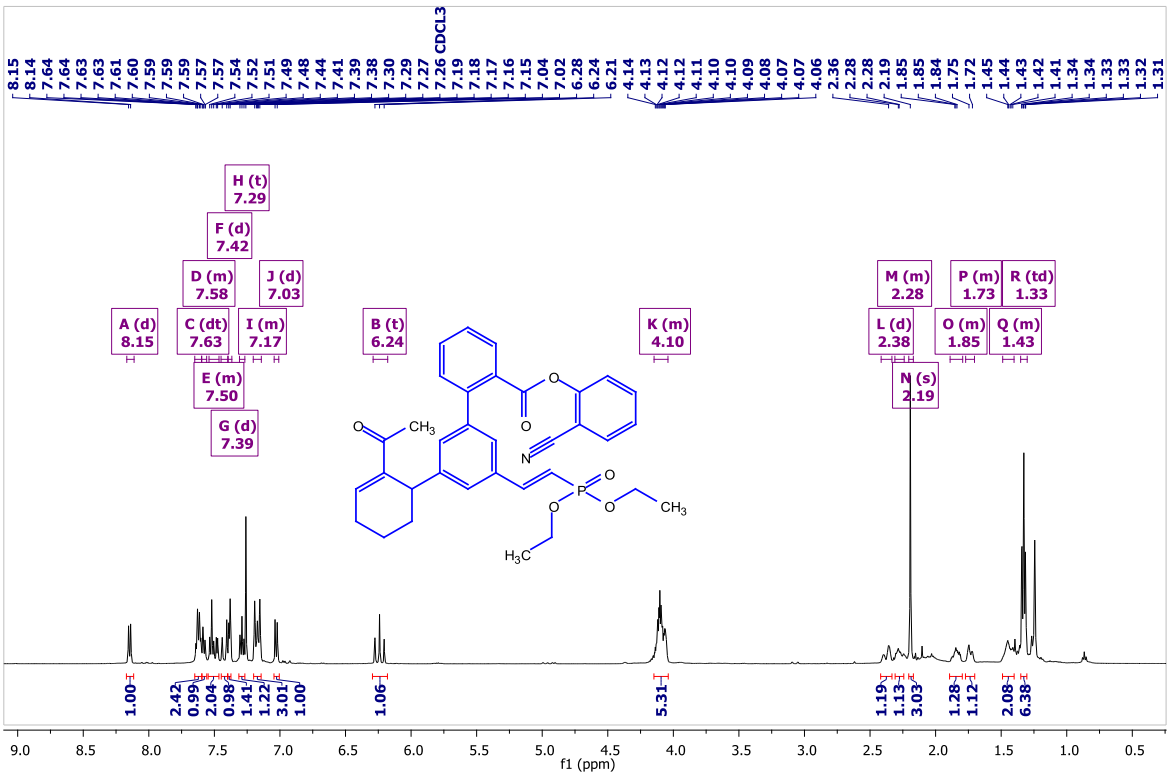


(2E,2'E)-bis(2,2,2-trifluoroethyl) 3,3'-(2'-((2-cyanophenoxy)carbonyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate

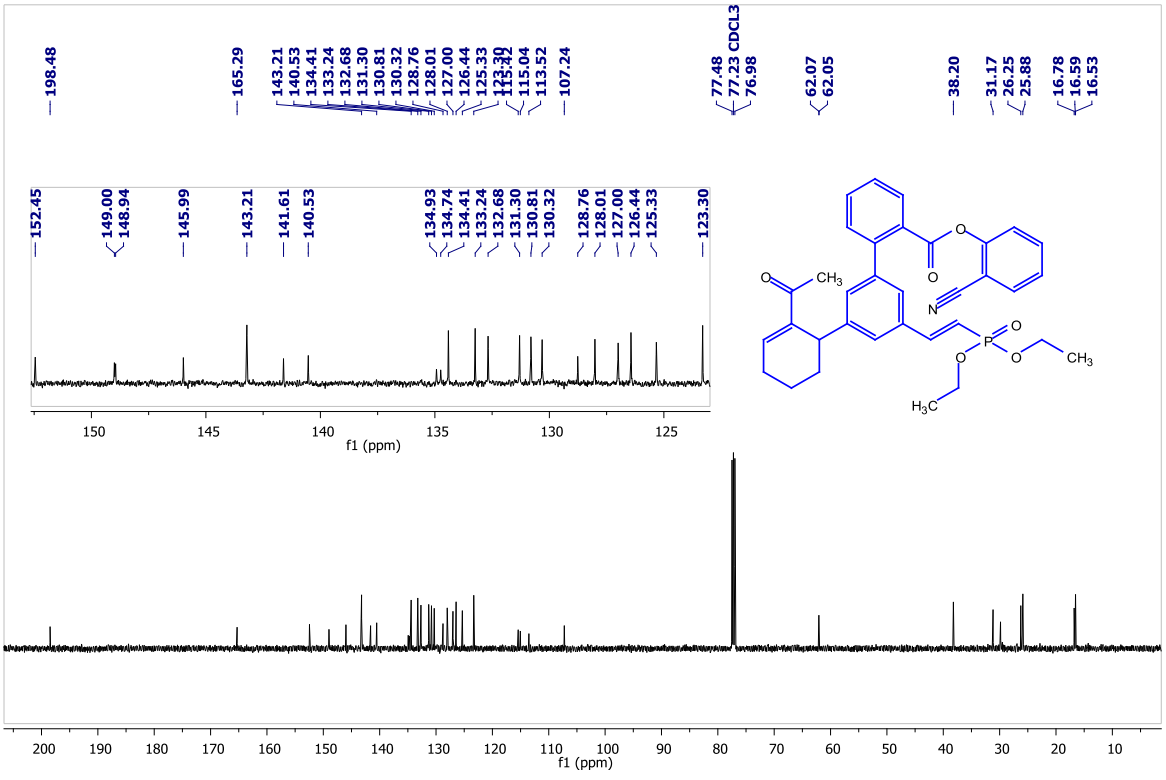


(**Scheme 4, 4f**)

(E)-2-cyanophenyl 6''-acetyl-5'-(2-(diethoxyphosphoryl)vinyl)-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate

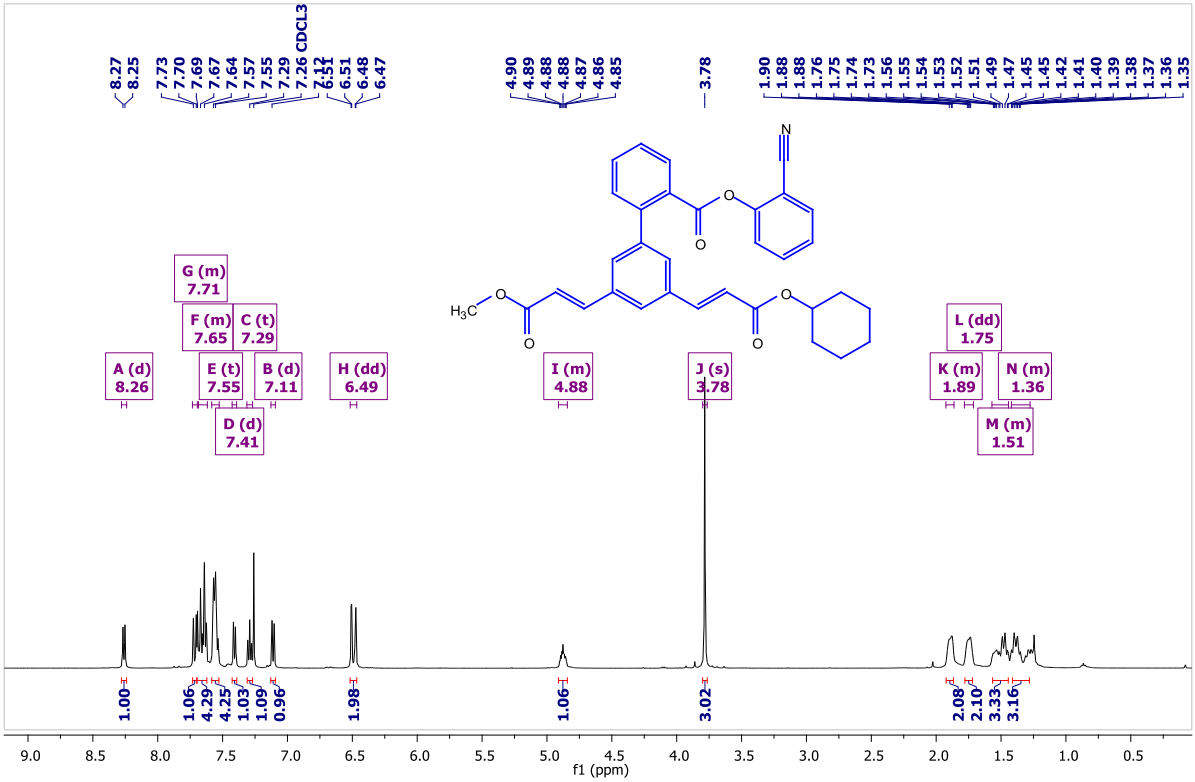


(E)-2-cyanophenyl 6''-acetyl-5'-(2-(diethoxyphosphoryl)vinyl)-1'',2'',3'',4''-tetrahydro-[1,1':3',1''-terphenyl]-2-carboxylate

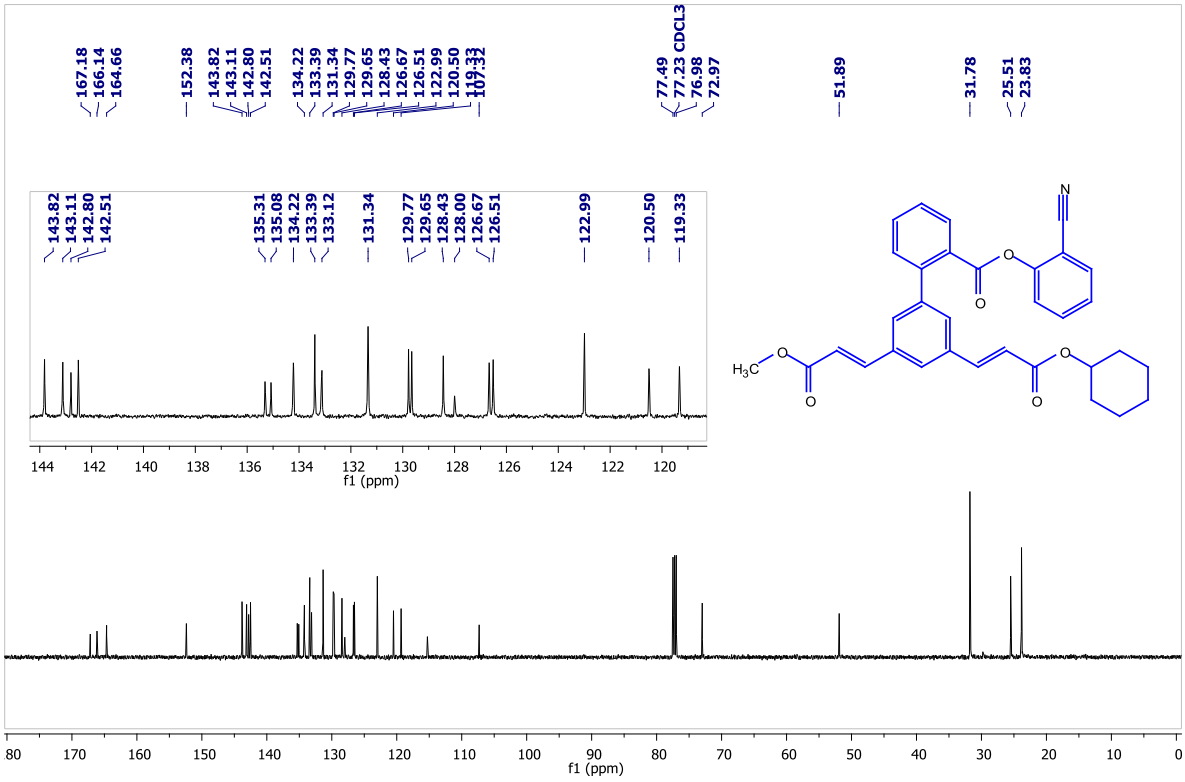


(**Scheme 4, 4g**)

2-cyanophenyl 3'-((E)-3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-5'-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

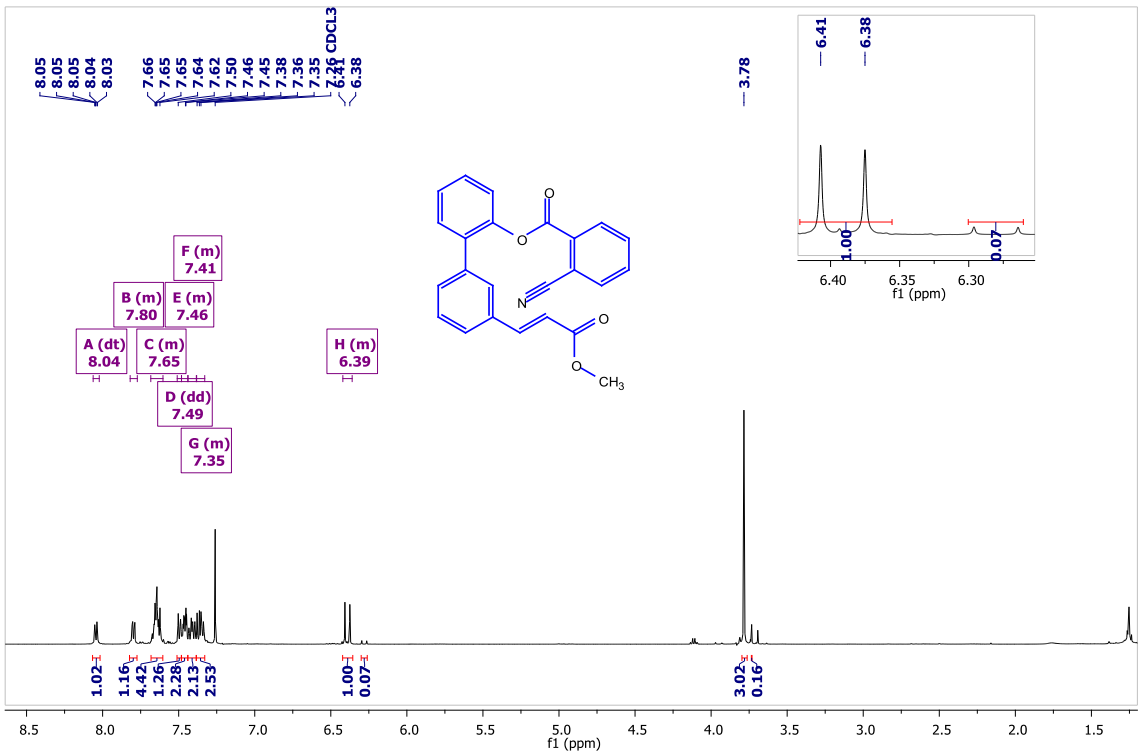


2-cyanophenyl 3'-((E)-3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-5'-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate

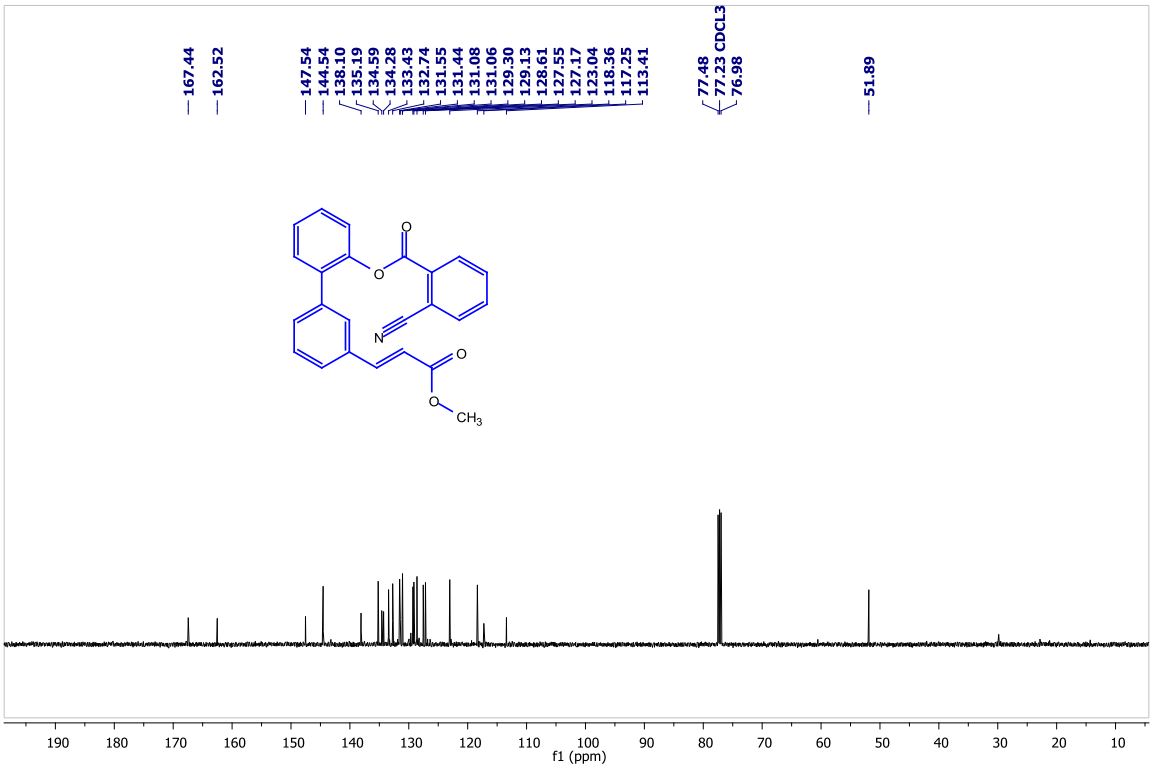


(Scheme 5, 5a)

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

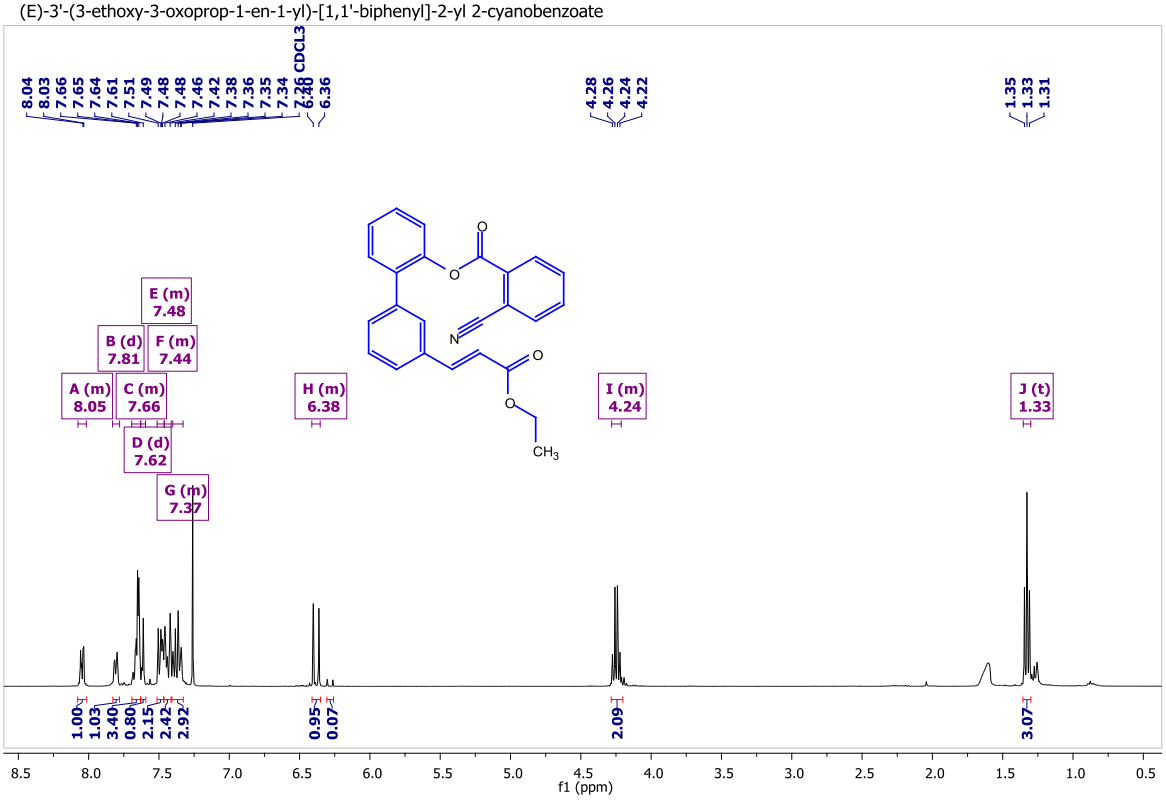


(E)-3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

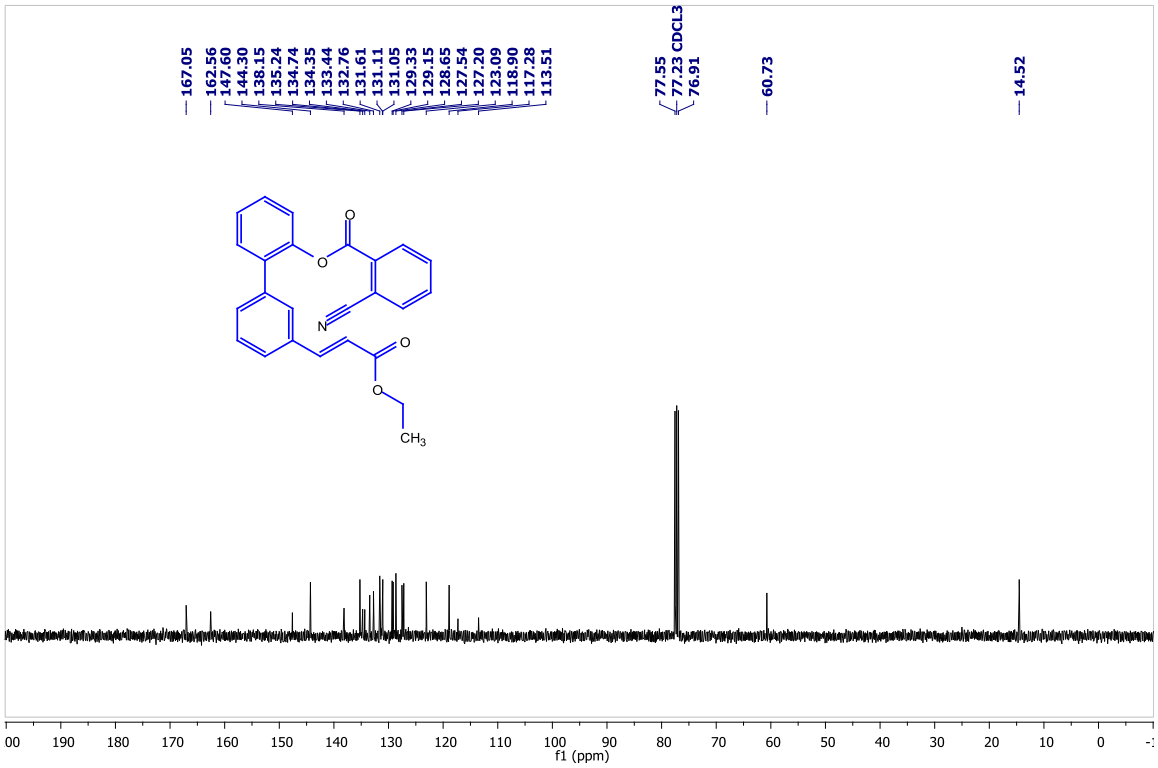


(**Scheme 5, 5b**)

(E)-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

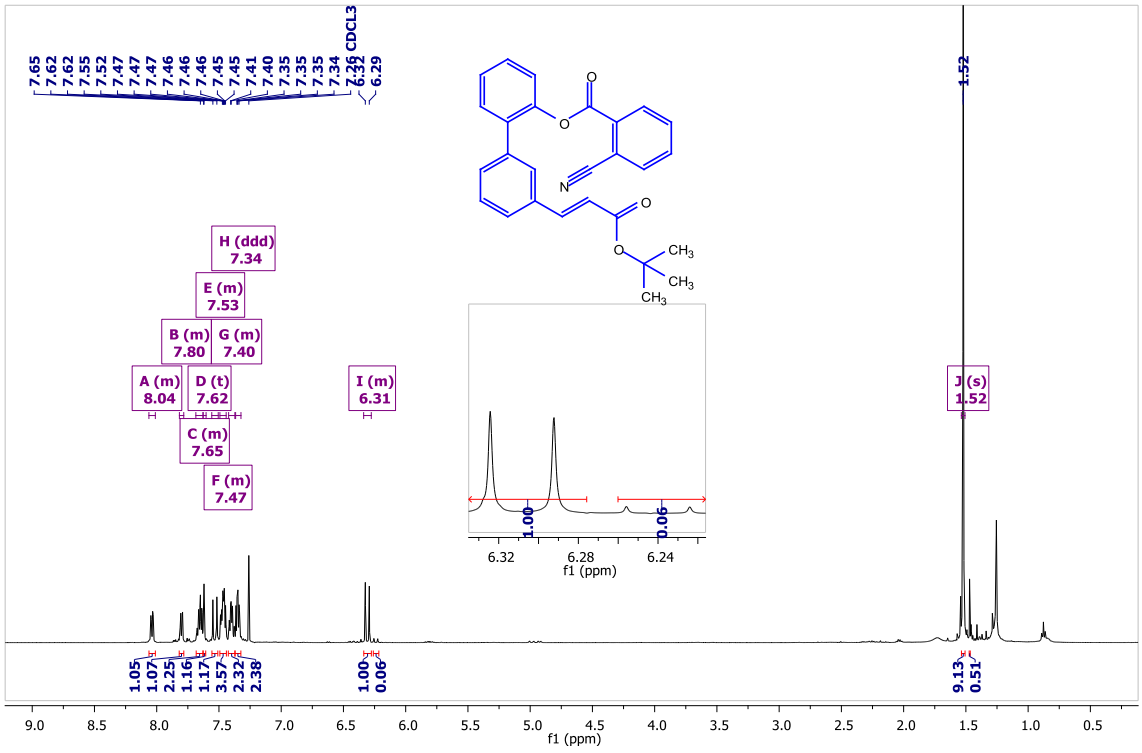


(E)-3'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

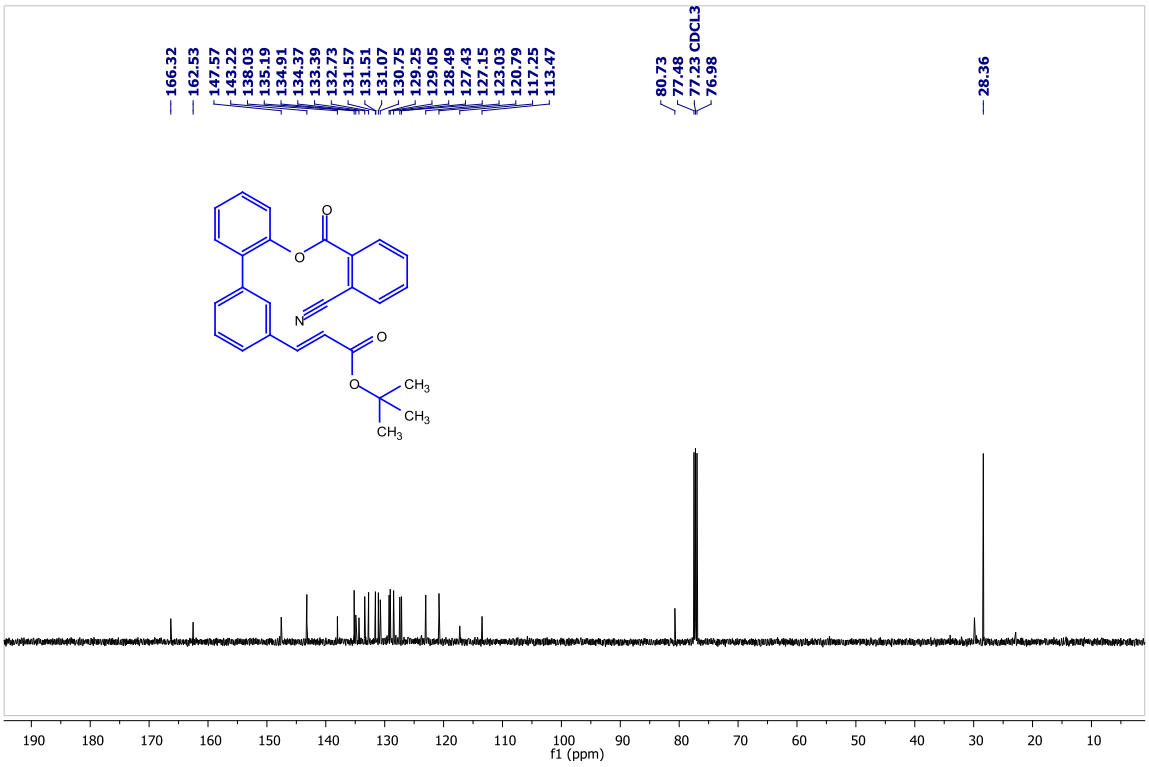


(**Scheme 5, 5c**)

(E)-3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

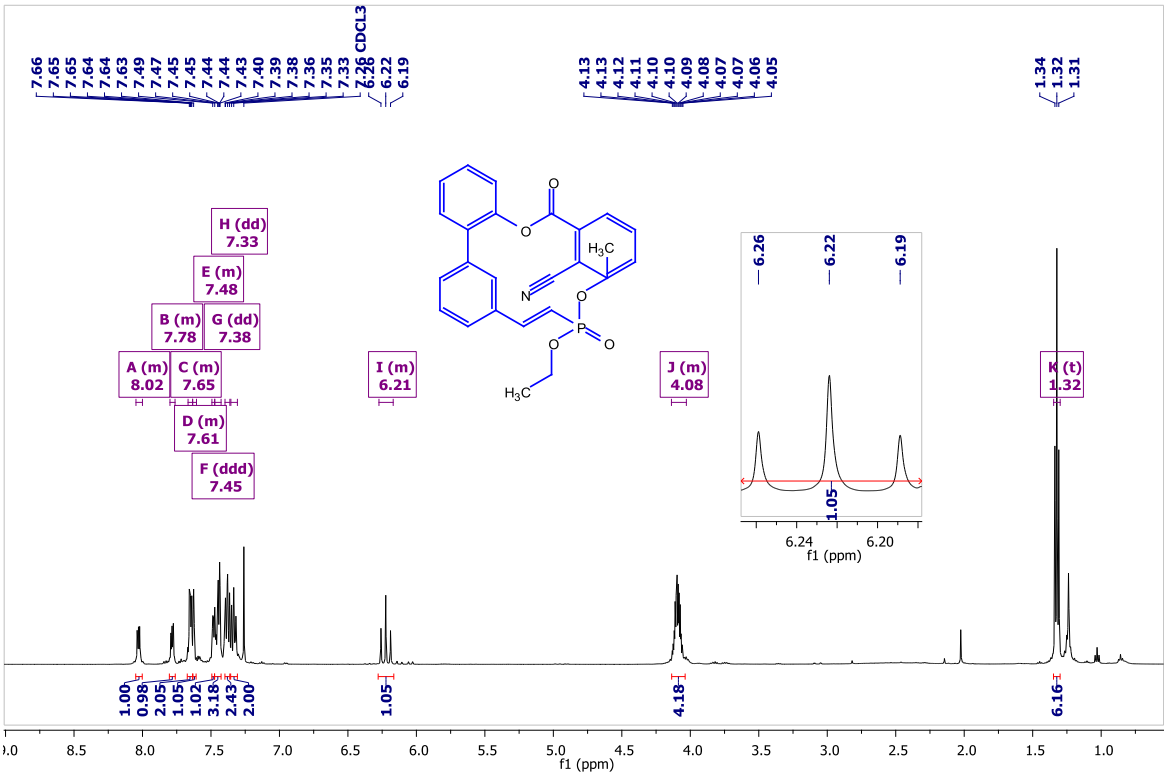


(E)-3'-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

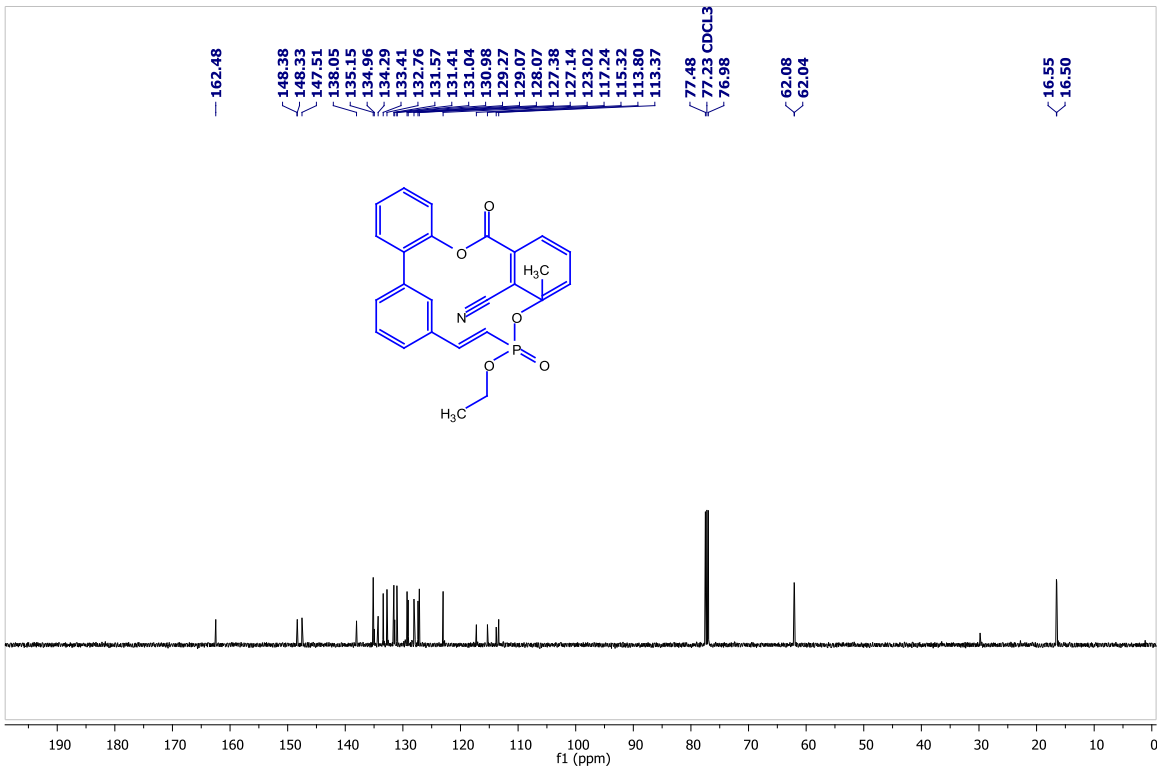


(Scheme 5, 5d)

(E)-3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

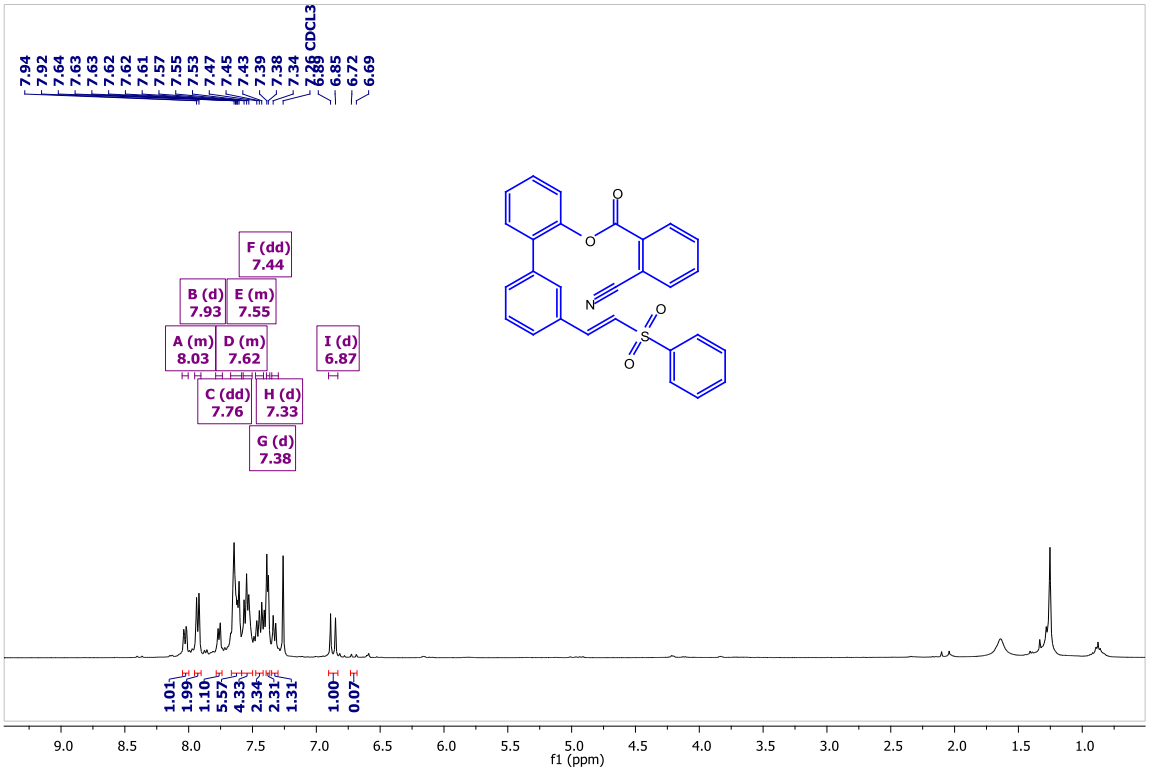


(E)-3'-(2-(diethoxyphosphoryl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

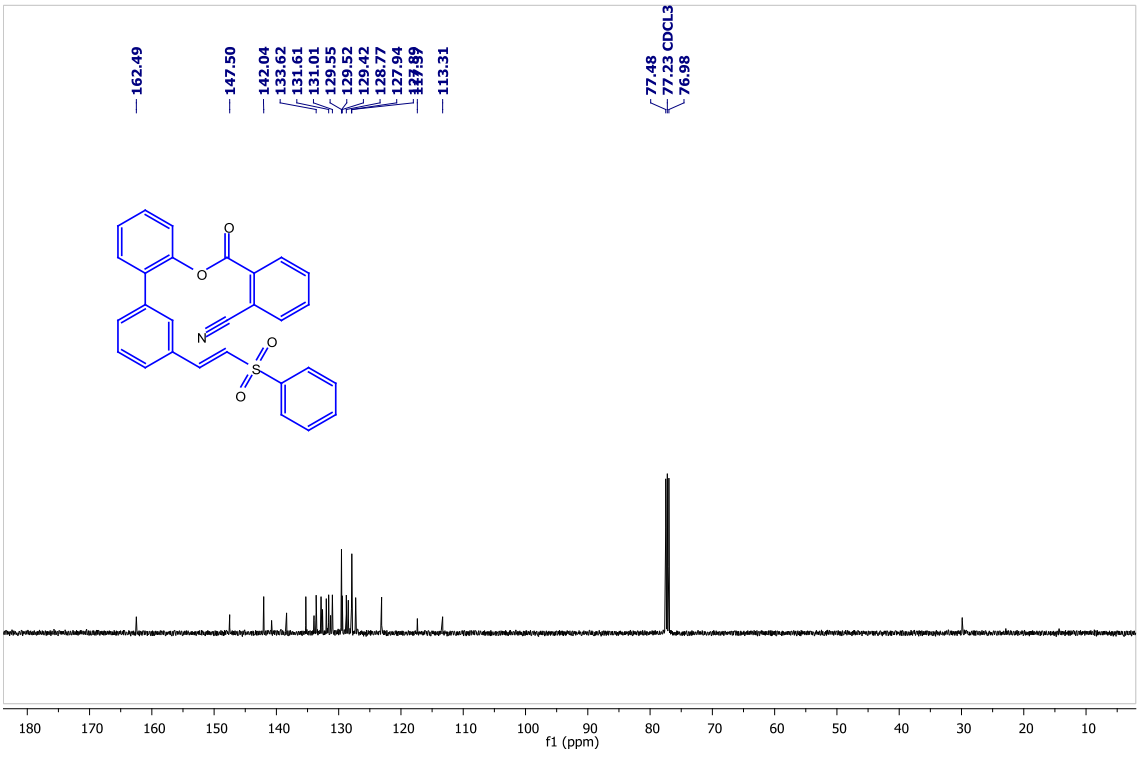


(**Scheme 5, 5e**)

(E)-3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

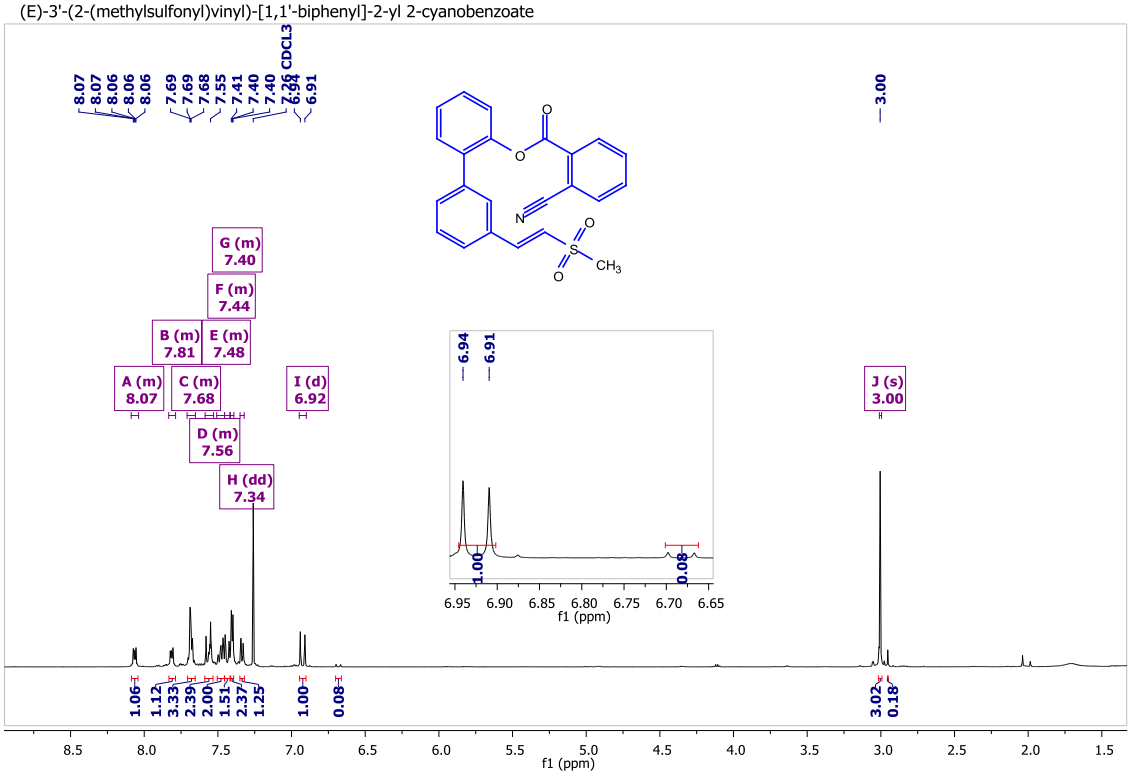


(E)-3'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

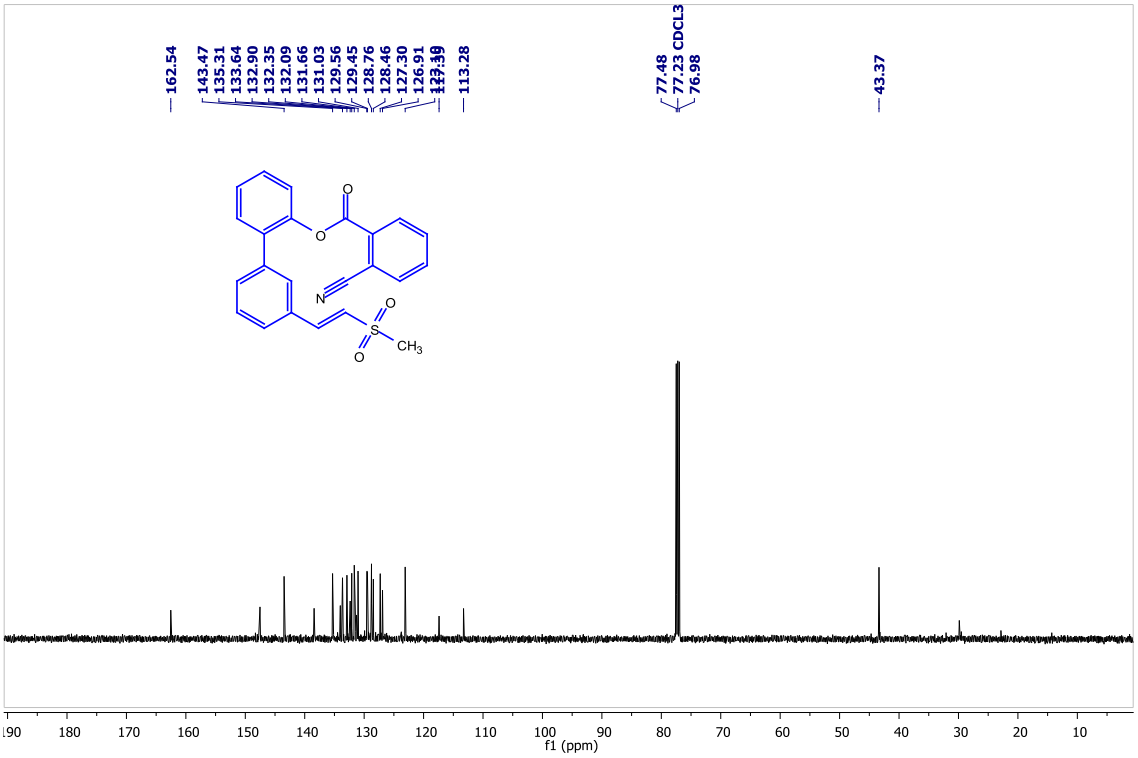


(**Scheme 5, 5f**)

(E)-3'-(2-(methylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

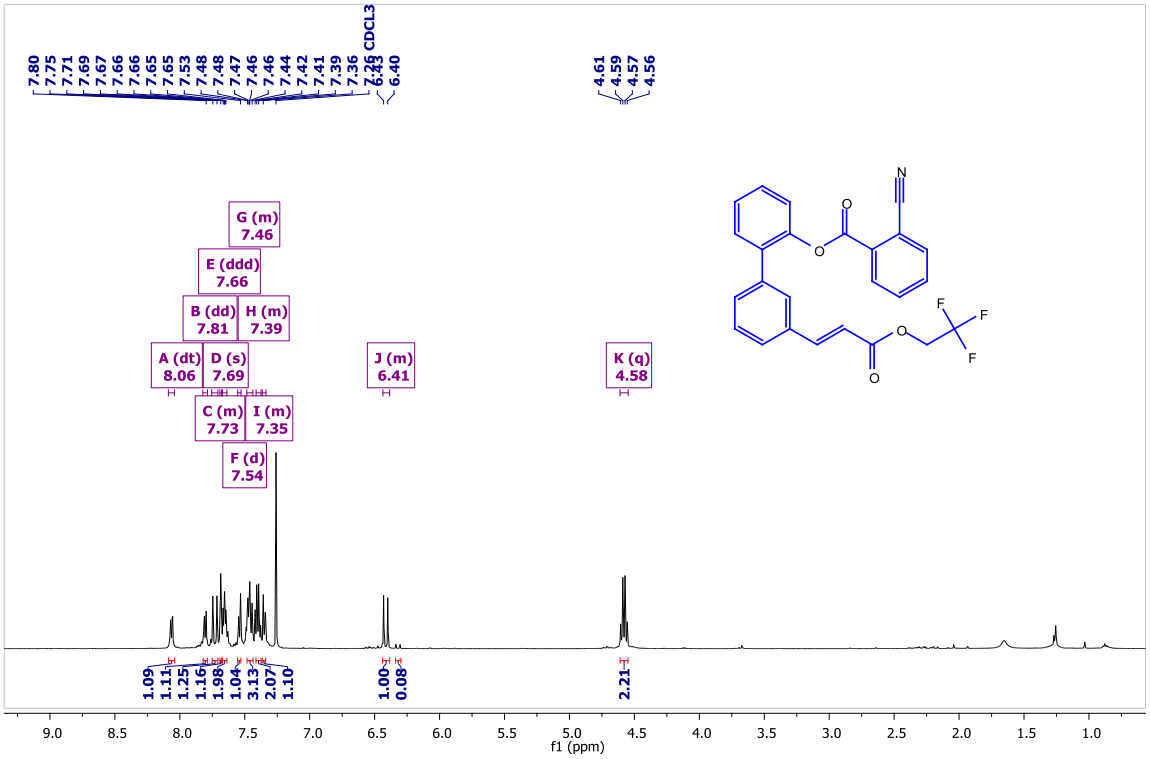


(E)-3'-(2-(methylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

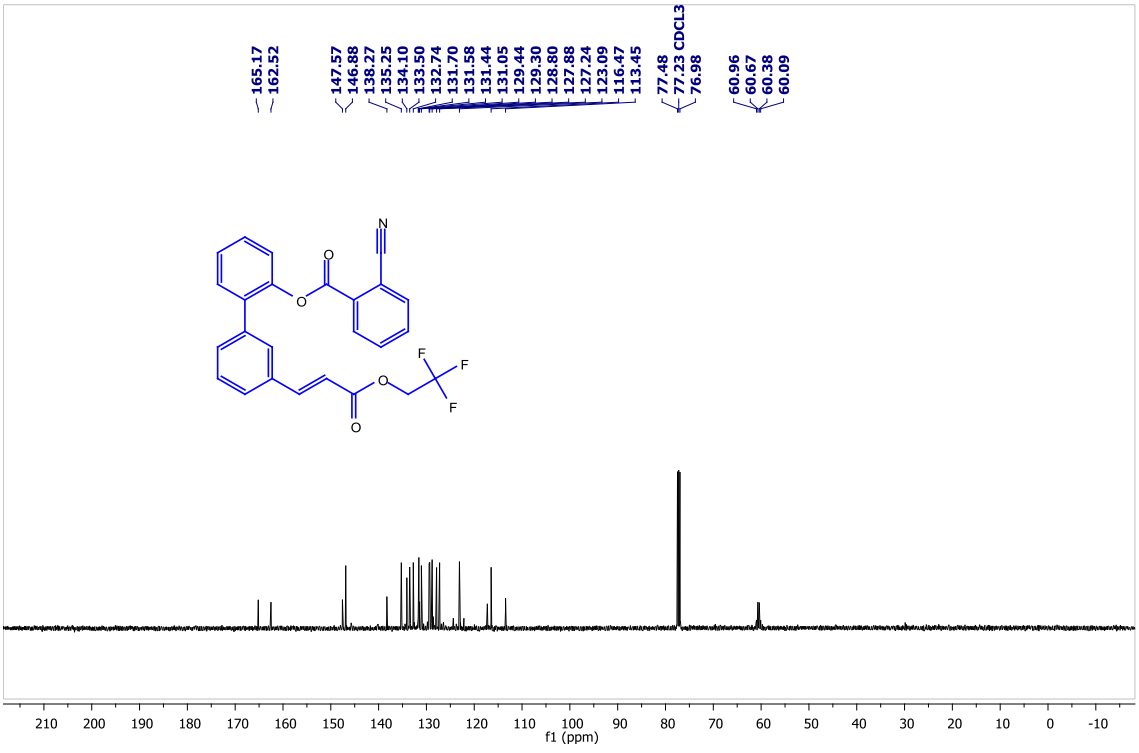


(Scheme 5, 5g)

(E)-3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

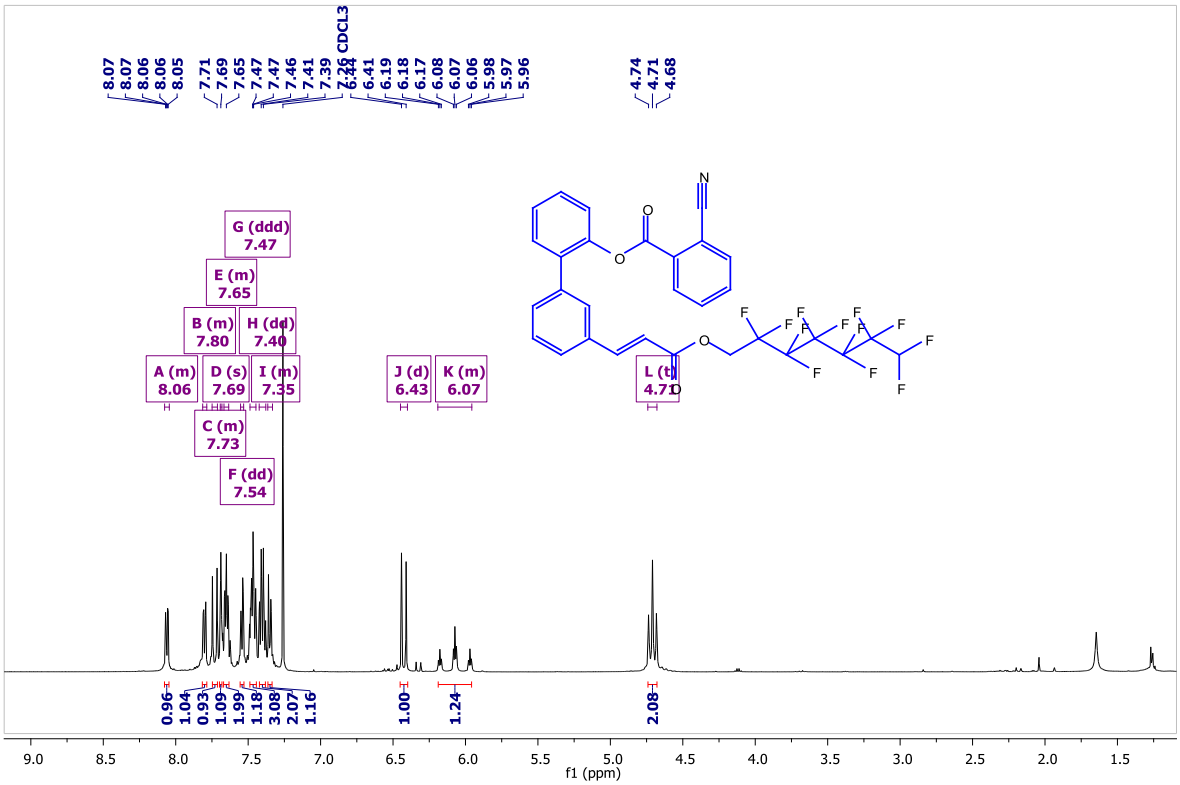


(E)-3'-(3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate

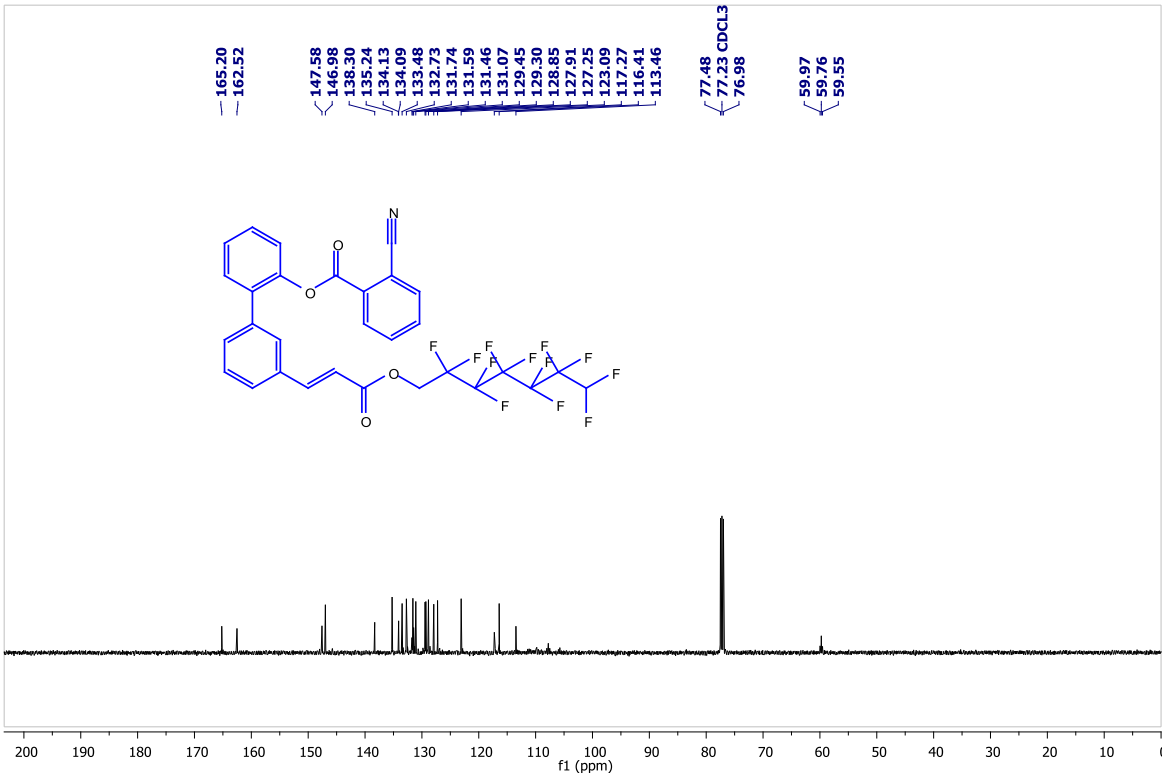


(**Scheme 5, 5h**)

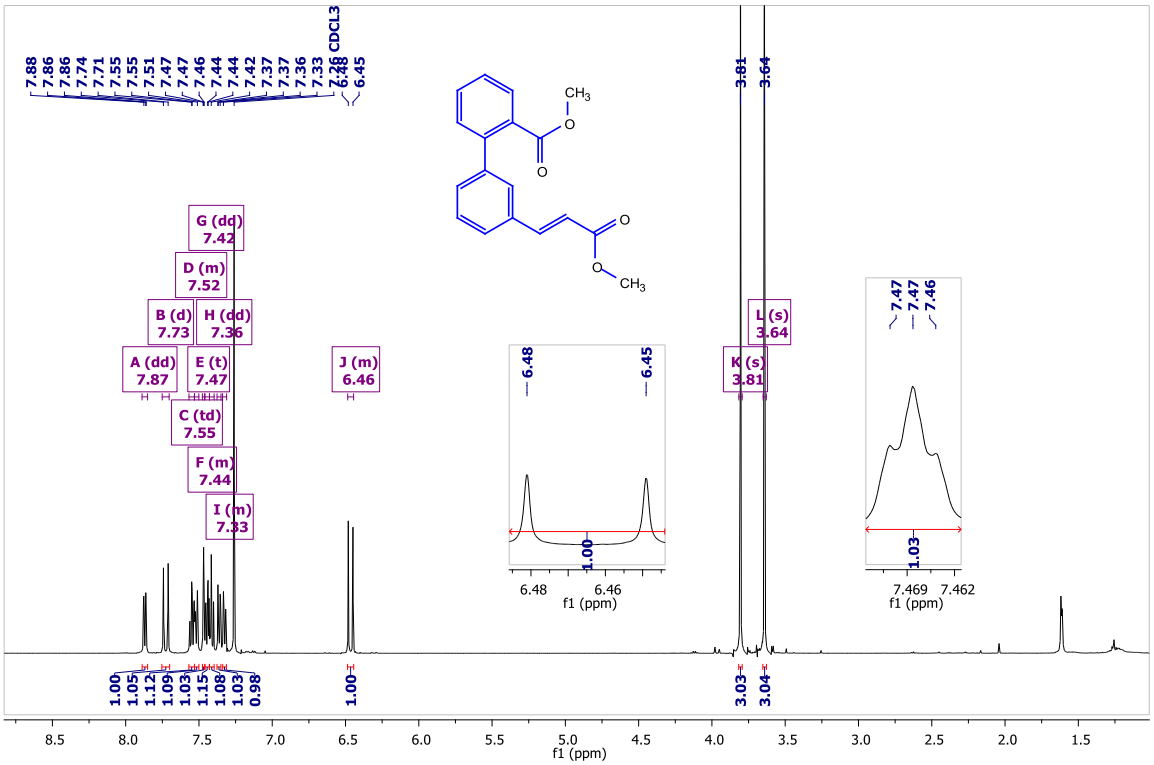
(E)-3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate



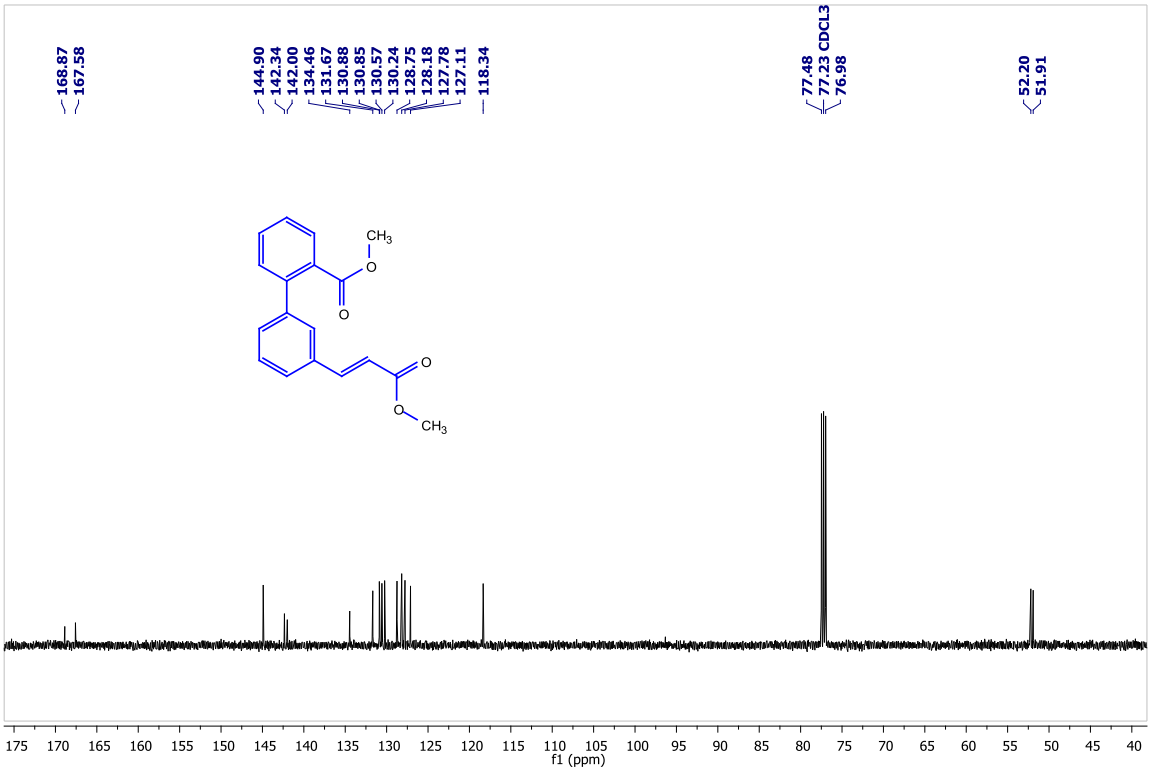
(E)-3'-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate



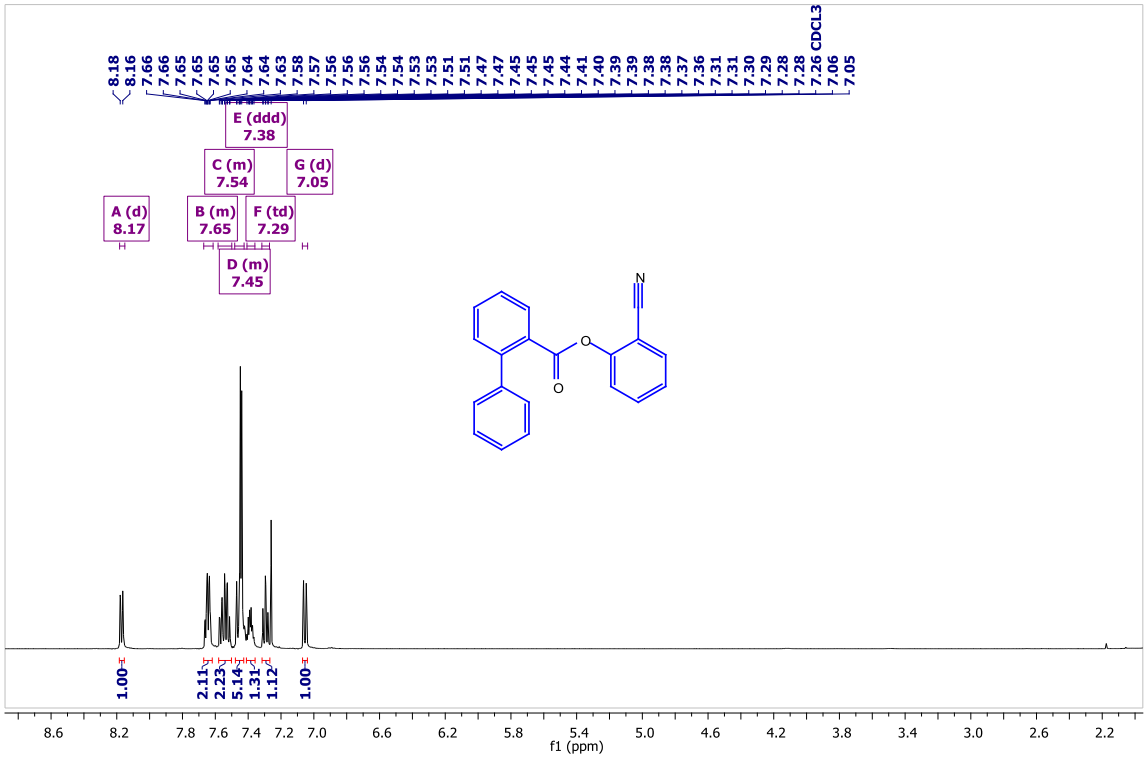
(E)-methyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate



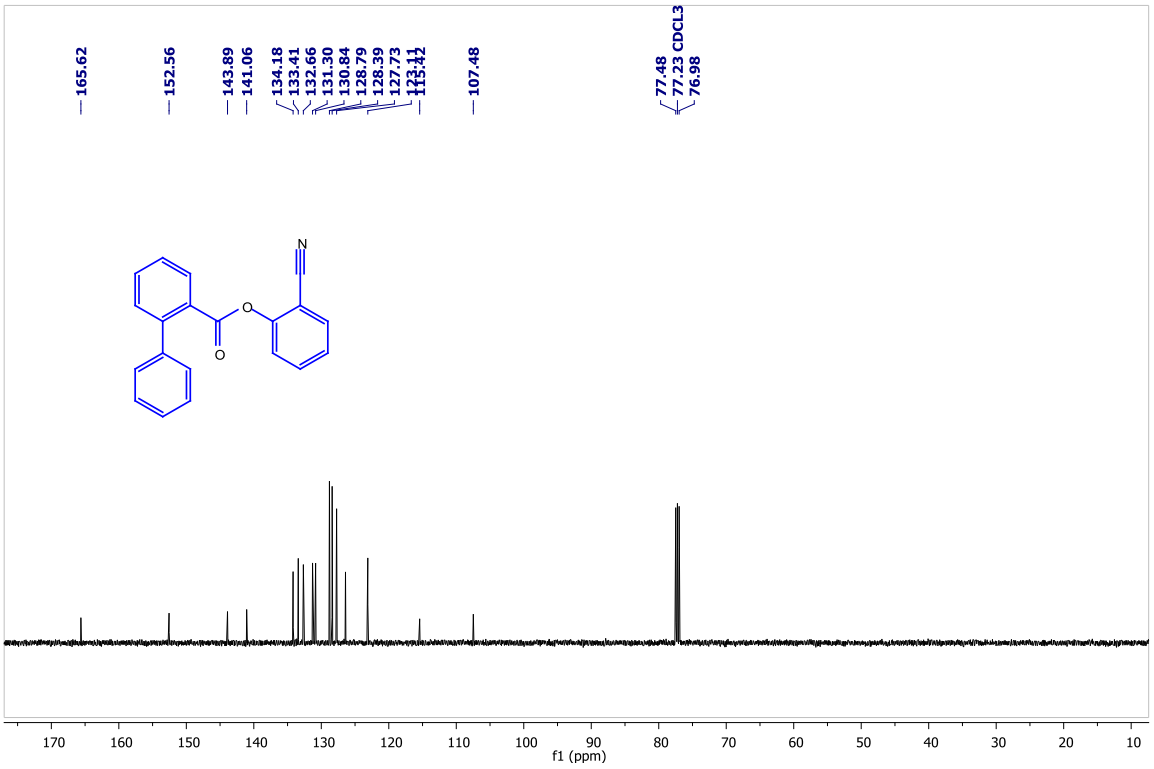
(E)-methyl 3'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate



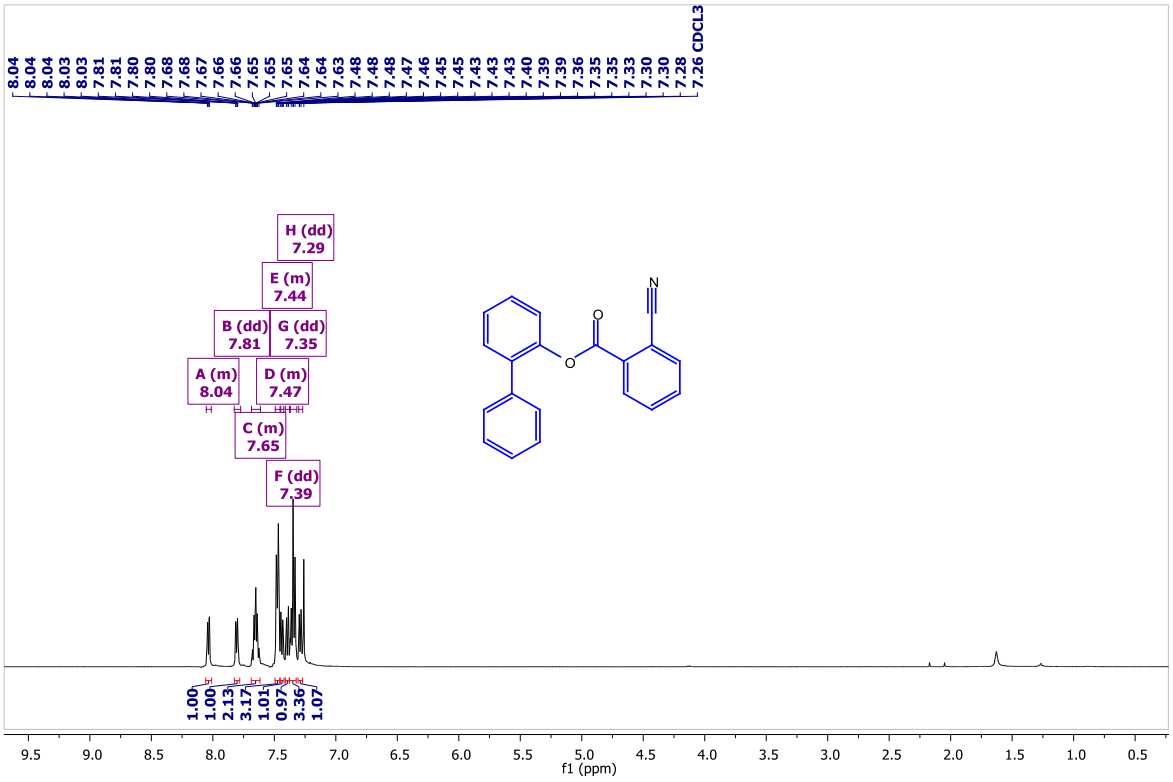
2-cyanophenyl [1,1'-biphenyl]-2-carboxylate



2-cyanophenyl [1,1'-biphenyl]-2-carboxylate



[1,1'-biphenyl]-2-yl 2-cyanobenzoate



[1,1'-biphenyl]-2-yl 2-cyanobenzoate