Electronic Supplementary Information (ESI)

Palladium-Catalysed Remote *meta*-C–H Olefination of Cinnamates

Manickam Bakthadoss,* Mir Ashiq Hussain, Tadiparthi Thirupathi Reddy

Department of Chemistry, Pondicherry University, Puducherry 605014, India.

E-mail: bhakthadoss@yahoo.com

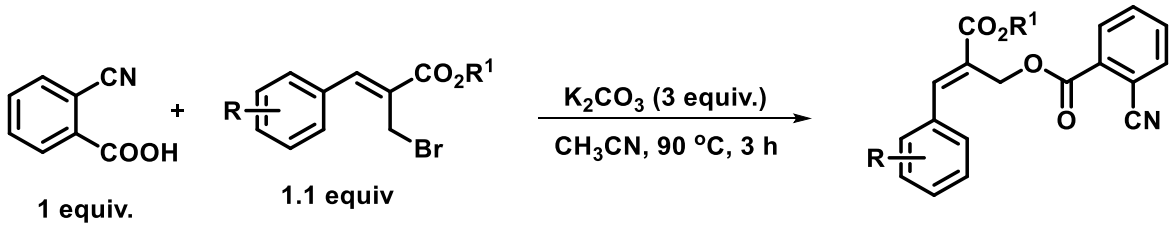
Contents

1. **General information:**

Commercial reagents were used without further purification. For compounds ^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (100 MHz, $CDCl_3$) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectra were recorded on Agilent 1200 LC/MS-6110 mass spectrometer. The structures of all compounds were confirmed by ^{1}H-NMR, ^{13}C-NMR spectrometry and ESI-HRMS spectrometry. Spectral data of ^{1}H, ^{13}C NMR and ESI-HRMS of all compounds are listed below.

2. **Experimental section:**

(a) General procedure for the synthesis of starting materials:



To a stirred solution of 2-cyanobenzoic acid (1 equiv.) in acetonitrile solvent in a round bottom flask K_2CO_3 (3equiv.) was added. The reaction mixture was stirred at 90 ^{o}C for 15 minutes then Baylis-Hillman[1] bromo compound (1.1 equiv.) was added and stirred under reflux temperature for 3 h. After the completion of the reaction as indicated by TLC, the reaction mixture was extracted twice with the ethyl acetate (2x20 mL) and water (20 mL). The combined organic layers were washed with brine solution (20 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue thus obtained was purified by column chromatography (silica gel 100-200 mesh, EtOAc in hexane) to provide the desired *O*- allylated products in very good yields (81-93 %).

(b) General experimental procedure for *meta*-C-H olefination of cinnamates:

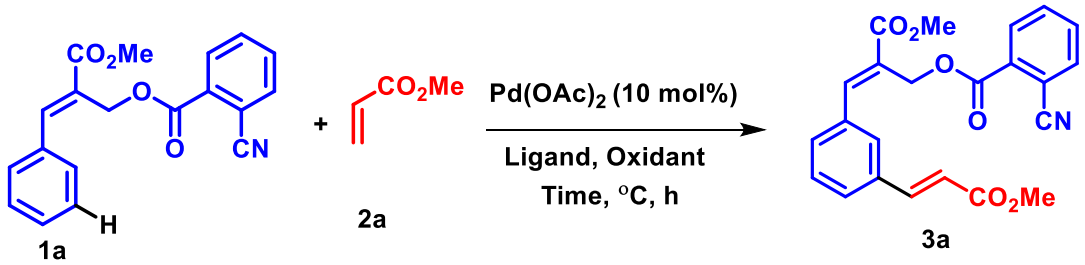
In an oven dried reaction test tube containing a magnetic stir-bar, was charged with cinnamate (1 equiv.), $Pd(OAc)_2$ (10 mol %), Ac-Gly-OH (40 mol%) and Ag_2CO_3 (2 equiv.) in 1,1,1,3,3,3-Hexafluoro-2-propanol (1 mL) followed by the addition of alkenes (3 equiv.) under N_2. The reaction mixture was stirred vigorously on a pre-heated oil bath at 80 ^{o}C for 24 h. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and diluted with DCM. The reaction mixture was filtered through celite pad. The filtrate was concentrated in vacuo to afford the crude mixture, the obtained crude

product was purified by column chromatography using silica gel (100-200 mesh size) and hexane/ ethyl acetate as the eluent to afford the *meta*-coupled products in very good yields.

3. Optimization studies for *meta*-C-H activation of cinnamates:

To optimize the reaction conditions, a series of optimization experiments were performed by screening various parameters such as mono protected amino acid as ligand, silver salts as oxidants and reaction time for a representative reaction of (*E*)-2-(methoxycarbonyl)-3-phenylallyl-2-cyanobenzoate (**1a**) as the model substrate containing nitrile as the directing group with methyl acrylate(**2a**). The best yield was obtained by using $Pd(OAc)_2$ (10 mol%) as catalyst in combination with N-Ac-Gly-OH (40 mol%) as the ligand and Ag_2CO_3 (2 equiv.) as an oxidant in 1,1,1,3,3,3-hexafluoro-2-propanol (l mL) solvent at 80 ^oC for 24 h afforded a desired *meta*-olefinated product (*E*)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl) allyl 2-cyanobenzoate (**3a**) in 85% yield with very good selectivity (*m*:others 90:10, entry 9).

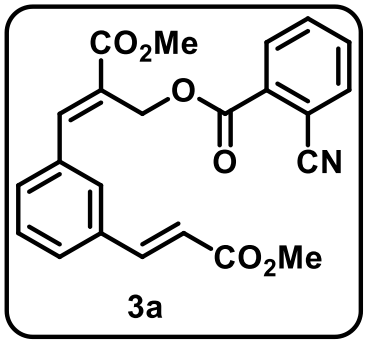
Table 1. Screening of the Reaction Parameters



Entry	Oxidant (2equiv.)	Ligand (40 mol%)	Solvent	Time (h)	Yield (%)	Selectivity (*meta*:others)
01	AgOAc	TFA-Gly-OH	HFIP	24	11	80:20
02	AgOAc	Boc-Alanine	HFIP	24	22	72:28
03	AgOAc	Boc-Valine	HFIP	24	18	63:37
04	AgOAc	N-Ac-Phenyl-Gly-OH	HFIP	24	28	70:30
05	Ag_2CO_3	N-Ac-Phenyl- Gly-OH	HFIP	24	32	76:24
06	AgOAc	N-Ac-Gly-OH	HFIP	24	35	84: 16
07	AgOAc	Boc-Phenyl-Ala-OH	HFIP	24	8	75:25
08	Ag_2CO_3	Boc-Phenyl Ala-OH	HFIP	24	15	70:30
09	**Ag_2CO_3**	**N-Ac-Gly-OH**	**HFIP**	**24**	**85**	**90:10**
10	Ag_2CO_3	N-Ac-Gly-OH	HFIP	12	64	90:10
11	Ag_2CO_3	N-Ac-Gly-OH	HFIP	16	72	90:10
12	Ag_2CO_3	N-Ac-Gly-OH	HFIP	20	78	90:10

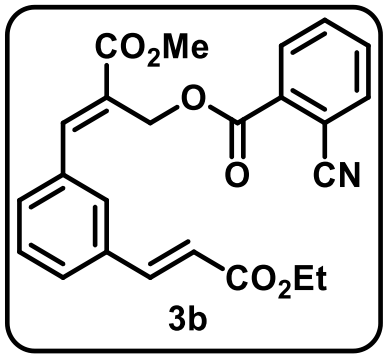
4. ^{1}H, ^{13}C NMR and ESI-HRMS spectral data for all the compounds:

(*E*)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3a)



White solid; Yield 85%; M.P (110-112 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.05 (dd, *J* = 9.3, Hz, 1H), 7.81 – 7.74 (m, 2H), 7.66 – 7.60 (m, 3H), 7.40 – 7.38 (m, 2H), 7.35 – 7.33 (m, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 5.10 (s, 2H), 3.88 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 163.6 , 144.1, 141.6, 134.9, 134.2, 133.4, 132.9, 132.5, 132.0, 131.4, 130.3, 129.6, 129.64, 128.9, 127.3, 120.8, 117.5, 113.1, 60.9, 52.6, 51.9; HRMS (ESI): calc. for [($C_{23}H_{19}NO_6$)] $(M+H)^+$ 406.1290, measured 406.1317.

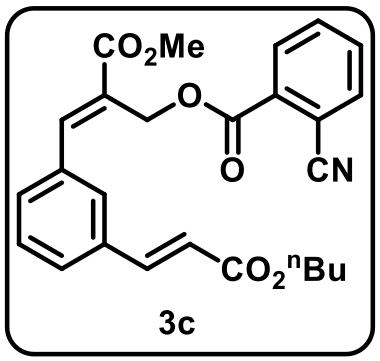
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl2-cyanobenzoate (3b)



White solid; Yield 78%; M.P (114-116 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.06 (t, *J* = 8.0 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.70 – 7.57 (m, 3H), 7.39-7.37 (m,2H), 7.36 (d, 4 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 5.10 (s, 2H), 4.22 (q, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 1.33 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.4, 163.6, 144.1, 141.4, 134.9, 134.4, 133.5, 132.8, 132.5, 132.1, 131.45, 130.2, 129.6, 129.6, 128.9, 127.3, 121.3, 117.4, 113.1, 60.9,

60.8, 52.6, 14.3; HRMS (ESI): calc. for $[(C_{24}H_{21}NO_6)]$ $(M+H)^+$ 420.1447, measured 420.1447.

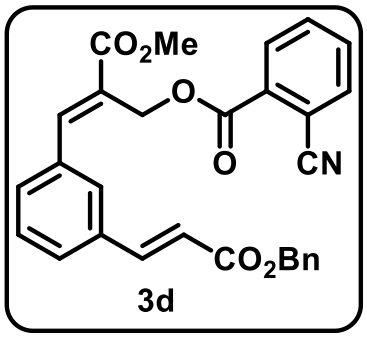
(*E*)-3-(3-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3c)



3c

Yellow colour liquid; Yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.09 – 8.03 (m, 1H), 7.82 – 7.73 (m, 2H), 7.69 – 7.59 (m, 3H), 7.39-7.37 (m, 2H), 7.34 (d, *J* = 3.7 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 5.10 (s, 2H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 1.70 – 1.62 (m, 2H), 1.46 – 1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.4, 163.6, 144.11, 141.3, 134.9, 134.3, 133.5, 132.8, 132.5, 132.0, 131.4, 130.2, 129.66, 129.6, 128.9, 127.2, 121.2, 117.4, 113.1, 64.7, 60.9, 52.6, 30.7, 19.2, 13.8; HRMS (ESI): calc. for $[(C_{26}H_{25}NO_6)]$ $(M+H)^+$ 448.1760, measured 448.1753.

(*E*)-3-(3-((*E*)-3-(benzyloxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3d)

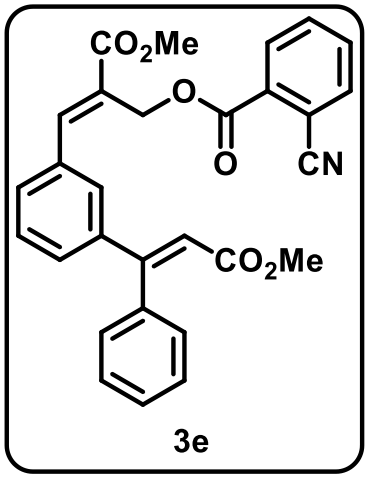


3d

Yellow colour liquid; Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.09 – 8.02 (m, 1H), 7.84 (d, *J* = 15.9 Hz, 1H), 7.78 (d, *J* = 4.8 Hz, 1H), 7.64-7.62 (m,3H), 7.40-7.38 (m, 5H), 7.37-7.34 (m,4H), 6.42 (d, *J* = 15.9 Hz, 1H), 5.22 (s, 2H), 5.11 (s, 2H), 3.87 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2,163.5,144.0, 142.0, 135.9, 134.9, 134.5, 133.4, 132.8, 132.5, 132.0, 131.4, 130.3, 129.6, 129.6, 129.0, 128.7, 128.4, 128.3, 127.31, 120.7, 117.5, 113.1, 66.6, 60.9, 52.7; HRMS (ESI): calc. for $[(C_{29}H_{23}NO_6)]$ $(M+H)^+$ 482.1603, measured 482.1599.

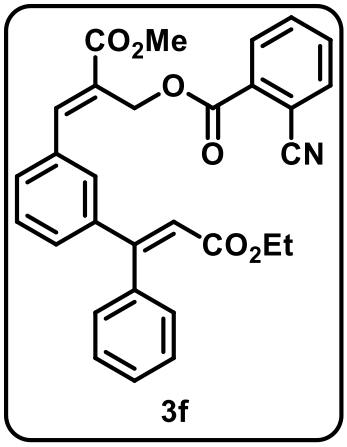
(*E*)-3-(3-((*E*)-3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3e)



3e

Yellow liquid; Yield 76%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.80 (s, 1H), 7.71 – 7.64 (m, 3H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.16 – 7.04 (m, 4H), 6.26 (s, 1H), 5.02 (s, 2H), 3.84 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 163.2, 155.1, 142.5, 140.1, 137.9, 135.6, 134.9, 133.0, 132.9, 132.5, 131.9, 131.6, 130.5, 130.2, 130.0, 129.1, 128.6, 128.4, 128.0, 117.9, 113.4, 96.2, 60.8, 52.7, 51.4; HRMS (ESI): calc. for $[(C_{29}H_{23}NO_6)]$ $(M+H)^+$ 482.1595 measured 482.1583

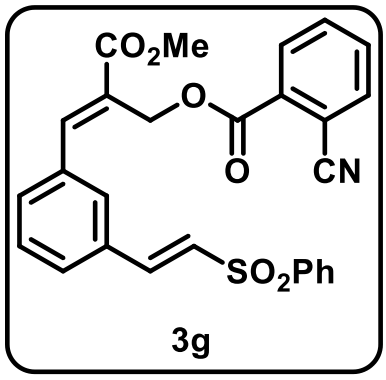
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3f)



3f

Yellow liquid; Yield 77%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.02 – 7.99 (m, 1H), 7.82 – 7.79 (m, 1H), 7.70 – 7.66 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 2.2 Hz, 2H), 7.28 (d, *J* = 2.2 Hz, 1H), 7.11 – 7.04 (m, 5H), 6.27 (s, 1H), 5.02 (s, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.6, 163.1, 154.3, 142.3, 140.0, 137.9, 135.4, 134.8, 132.9, 132.8, 132.3, 131.8, 131.5, 130.4, 129.9, 129.8, 128.9, 128.3, 128.3, 127.8, 118.5, 117.2, 113.2, 96.1, 60.6, 60.1, 13.9; HRMS (ESI): calc. for [($C_{30}H_{25}NO_6$)] $(M+H)^+$ 496.1752, measured 496.1746

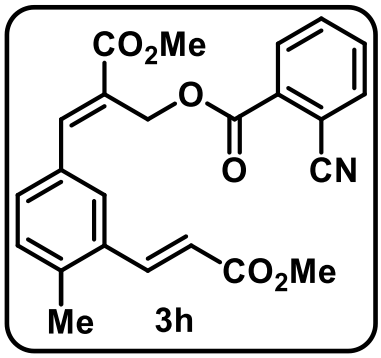
(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)allyl-2 cyanobenzoate (3g)



3g

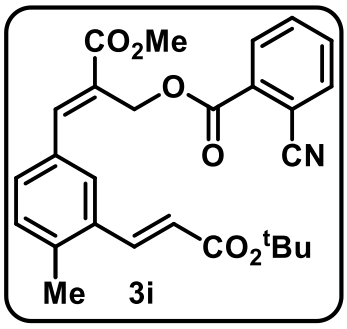
Colourless liquid; Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 – 7.89 (m, 3H), 7.79 – 7.73 (m, 2H), 7.67 – 7.60 (m, 4H), 7.57 – 7.51 (m, 4H), 7.40 – 7.33 (m, 2H), 6.83 (d, J=4 Hz, 1H), 5.08 (s, 2H), 3.87 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.4, 143.0, 140.2, 139.0, 134.8, 134.7, 133.6, 132.8, 132.5, 131.8, 131.4, 131.2, 131.0, 130.3, 129.8, 129.7, 129.6, 129.5, 129.4, 129.4, 117.4, 112.9, 60.6, 52.6; HRMS (ESI): calc. for [($C_{27}H_{21}NO_6S$)] $(M+H)^+$ 488.1162, measured 488.1180.

(*E*)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3h)



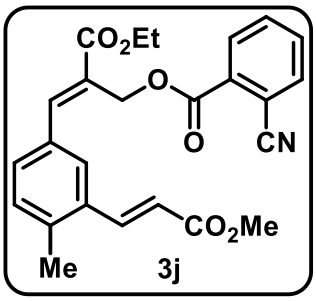
Colourless liquid; Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.08 – 8.03 (m, 1H), 7.83 – 7.77 (m, 2H), 7.69 – 7.62 (m, 2H), 7.42 (s, 1H), 7.25 – 7.19 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.11 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.5, 163.6, 144.2, 141.88, 139.8, 134.9, 133.4, 132.8, 132.5, 132.1, 131.63, 131.4, 131.1, 129.6, 128.4, 128.0, 120.6, 117.5, 113.1, 61.0, 52.6, 51.9, 21.4; HRMS (ESI): calc. for $[(C_{24}H_{21}NO_6)]$ $(M+H)^+$ 420.1447, measured 420.1472.

(*E*)-3-(3-((*E*)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2(methoxycarbonyl) allyl-2-cyanobenzoate (3i)



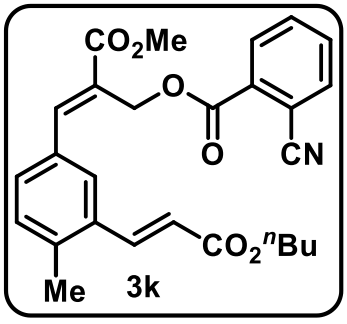
Yellow colour liquid; Yield 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 – 8.06 (m, 1H), 7.82 – 7.78 (m, 1H), 7.72 – 7.63 (m, 3H), 7.44 (s, 1H), 7.22 (s, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.11 (s, 2H), 3.86 (s, 3H), 2.36 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.0, 163.6, 144.3, 140.4, 139.8, 134.9, 133.7, 132.8, 132.5, 132.2, 131.5, 131.4, 130.9, 129.6, 128.3, 122.8, 117.5, 113.2, 96.2, 80.9, 61.1, 52.5, 28.3, 21.41. HRMS (ESI): calc. for $[(C_{27}H_{27}NO_6)]$ $(M+H)^+$ 462.1916, measured 462.1906.

(*E*)-2-(ethoxycarbonyl)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)allyl 2-cyanobenzoate (3j)



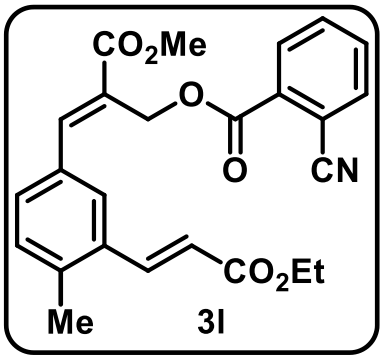
White solid; Yield 70%; M.P (116-119 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.10 – 8.04 (m, 1H), 7.84 – 7.74 (m, 2H), 7.69 – 7.62 (m, 2H), 7.42 (s, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.12 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.77 (s, *J* = 3.1 Hz, 3H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.1, 163.6, 143.9, 141.9, 139.8, 134.9, 133.5, , 132.8, 132.5, 132.3, 131.8, 131.4, 131.2, 129.7, 128.8, 128.1, 120.6, 113.2, 96.1, 61.6, 61.1, 51.9, 21.4, 14.4; HRMS (ESI): calc. for [($C_{25}H_{23}NO_6$)] $(M+H)^+$ 434.1603, measured 434.1588.

(*E*)-3-(3-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3k)



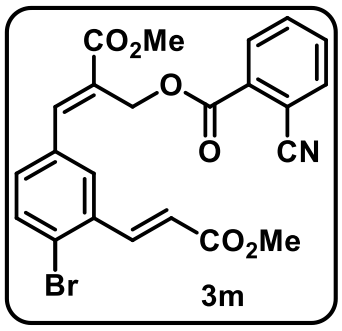
Colourless liquid; Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.10 – 8.05 (m, 1H), 7.81 – 7.74 (m, 2H), 7.68 – 7.63 (m, 2H), 7.43 (s, 1H), 7.23 – 7.18 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.11 (s, 2H), 4.16 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.36 (s, 3H), 1.68-1.64 (m, 2H), 1.41-1.44 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.5, 163.6, 144.2, 141.5, 139.8, 134.9, 134.4, 133.5, 132.8, 132.5, 132.1, 131.6, 131.4, 131.1, 129.6, 128.3, 127.9, 121.0, 117.5, 113.1, 64.6, 61.1, 52.8, 30.8, 19.3, 13.8; HRMS (ESI): calc. for [($C_{27}H_{27}NO_6$)] $(M+H)^+$ 462.1916, measured 462.1913.

(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3l)



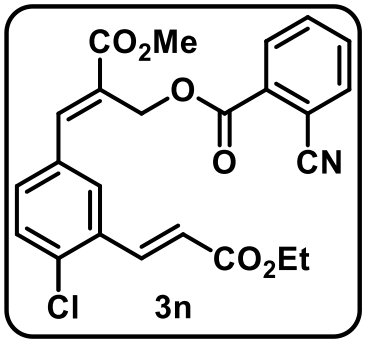
White solid; Yield 77%; M. P (108-111 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.08-8.06 (m, 1H), 7.81-7.79 (m, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.64-7.67 (m, 2H), 7.43 (s, 1H), 7.26-7.19 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.12 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.5, 163.6, 144.2, 141.62, 139.8, 134.9, 133.5, 132.8, 132.5, 132.2, 131.6, 131.4, 131.1, 129.6, 128.4, 127.9, 121.1, 117.5, 113.1, 61.1, 60.7, 52.5, 21.40, 14.41; HRMS (ESI): calc. for $[(C_{25}H_{23}NO_6)]$ $(M+H)^+$ 434.1603, measured 434.1599.

(*E*)-3-(4-bromo-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3m)



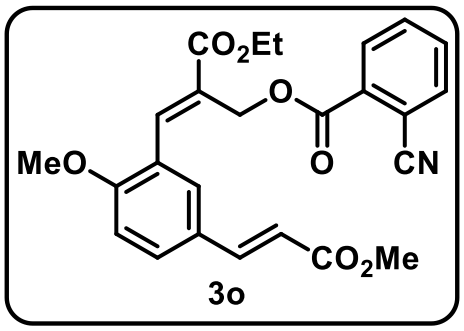
White solid; Yield 60%; M. P (112-115 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.06 (t, J=8 Hz,1H), 7.83 – 7.76 (m, 2H), 7.68 – 7.61 (m, 2H), 7.42 – 7.32 (m, 3H), 7.35 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.35 (d, J=12 Hz,1H), 5.14 (s, 2H), 3.88 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 163.6 , 144.1, 141.7, 134.9, 134.4, 133.4, 132.9, 132.5, 132.0, 131.4, 130.3, 129.7, 129.6, 128.9, 127.3, 120.8, 117.5, 113.1, 60.9, 52.6, 51.9; HRMS (ESI): calc. for $[(C_{23}H_{18}BrNO_6)]$ $(M+H)^+$ 484.0395, measured 484.0404.

(*E*)-3-(4-chloro-3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3n)



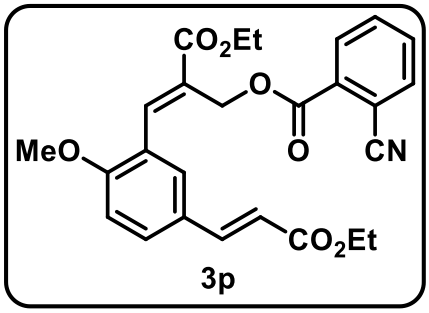
Yellow colour liquid; Yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.06 (t, *J* = 8 Hz 1H), 7.79 – 7.75 (m, 2H), 7.65 – 7.62 (m, 2H),, 7.39-7.33 (m, 3H), 6.36 (d, *J* = 8 Hz, 1H), 5.20 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.13 (t, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.5, 164.3, 142.9, 139.9, 136.4, 133.5, 133.1, 131.5, 131.4, 131.1, 130.7, 130.0, 129.5, 128.8, 127.6, 127.3, 126.4, 125.7, 121.0, 111.7, 60.88, 60.72 14.25; HRMS (ESI): calc. for [($C_{24}H_{20}ClNO_6$)] $(M+H)^+$454.1057, measured 454.1042.

(*E*)-2-(ethoxycarbonyl)-3-(2-methoxy-5-((*E*)-3-methoxy-3-oxoprop-1-en-1yl)phenyl)allyl 2-cyanobenzoate (3o)



White solid, Yield 80%; M. P (110-112 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.94 – 7.85 (m, 1H), 7.80 (dt, *J* = 6.8, 3.2 Hz, 1H), 7.67-7.65 (m, 2H), 7.60-7.57 (m, 2H), 7.53 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 5.20 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.69 (s, 3H), 1.31 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.3, 163.6, 159.2, 143.7, 142.0, 141.3, 134.9, 132.8, 132.3, 132.0, 131.3, 130.8, 129.5, 127.3, 127.0, 124.0, 117.4, 116.2, 113.1, 111.0, 61.3, 55.9, 51.6, 14.3; HRMS (ESI): calc. for [($C_{25}H_{23}NO_7$)] $(M+H)^+$ 450.1547, measured 450.1555.

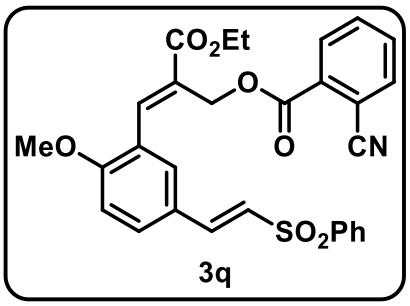
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-methoxyphenyl)-2-(ethoxycarbonyl)allyl 2-cyanobenzoate (3p)



3p

White solid; Yield 83%; M. P (118-120 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 – 7.88 (m, 1H), 7.80 (s, 1H), 7.67 (dt, *J* = 5.3, 2.0 Hz, 2H), 7.58 (s, 1H), 7.54 (s, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 5.22 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 4.2 Hz, 3H), 1.26 (t, *J* = 3.8 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 163.6, 159.2, 143.6, 141.8, 141.4, 135.0, 132.8, 132.6, 132.1, 131.3, 129.7, 127.4,127.21, 124.0, 117.5, 116.8, 113.20, 111.1, 61.4, 61.4, 60.4, 55.9, 14.4, 14.3 HRMS (ESI): calc. for [($C_{26}H_{25}NO_7$)] $(M+H)^+$ 464.1631, measured 464.1636.

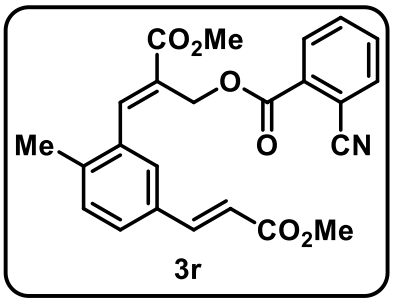
(*E*)-2-(ethoxycarbonyl)-3-(2-methoxy-5-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)allyl-2-cyanobenzoate (3q)



3q

White solid; Yield 70%; M. P (110-112 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m,1H) 8.06 (s, 1H), 7.88 (dd, *J* = 6.7, 2.5 Hz, 1H),7.83-7.81 (m, 2H), 7.77 (d, *J* = 6.7 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.57-7.55 (m, 2H), 7.54 – 7.44 (m, 5H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.68 (d, *J* = 15.3 Hz, 1H), 5.18 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.28 (q, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.6, 159.8, 141.5, 140.8, 140.2, 139.4, 138.1, 134.8, 133.6, 133.3, 132.9, 132.7, 132.4, 131.8, 131.3, 130.1, 129.3, 127.6, 125.5, 124.9, 124.2, 117.4, 112.8, 111.2, 61.3, 55.9, 14.3; HRMS (ESI): calc. for [($C_{29}H_{25}NO_7S$)] $(M+H)^+$ 532.1422, measured 532.1432.

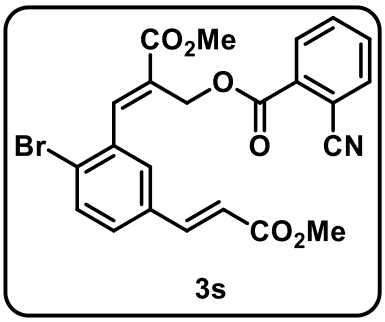
(*E*)-3-(5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-2-methylphenyl)-2(methoxycarbonyl)allyl -2-cyanobenzoate (3r)



3r

White solid; Yield 74%; M. P (118-121 ^{o}C) ^{1}H NMR (400 MHz, $CDCl_3$) 8.11 (s, 1H), 7.82-7.80 (m, 1H), 7.70 – 7.66 (m, 2H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.43 – 7.39 (m, 2H),7.24 (d, *J* = 7.9 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.15 (s, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.7, 163.6, 144.7, 144.0, 139.6, 135.0, 134.3, 132.9, 132.5, 132.1,132.0, 131.4, 131.0, 128.9, 128.2, 127.8, 117.8, 117.4, 113.1, 60.9, 52.6, 51.7, 20.1; HRMS (ESI): calc. for [($C_{24}H_{21}NO_6$)] $(M+H)^+$ 420.1442, measured 420.1453.

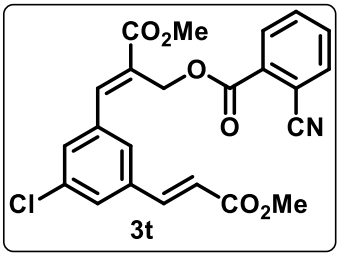
(*E*)-3-(2-bromo-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3s)



3s

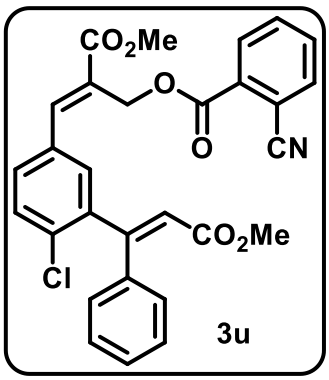
White solid; Yield 66%; M. P (113-117 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.11 (m, 1H), 8.09 – 8.05 (m, 1H), 8.04 (s, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.35 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.15 (s, 2H), 3.88 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 163.6, 144.1, 141.7, 134.9, 134.4, 133.5, 132.9, 132.6, 132.0, 131.4, 130.3, 129.7, 129.6, 128.9, 127.3, 120.8, 117.5, 113.1, 60.9, 52.7, 51.9; HRMS (ESI): calc. for [($C_{23}H_{18}BrNO_6$)] $(M+H)^+$484.0395, measured 484.0404.

(*E*)-3-(3-chloro-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3t)



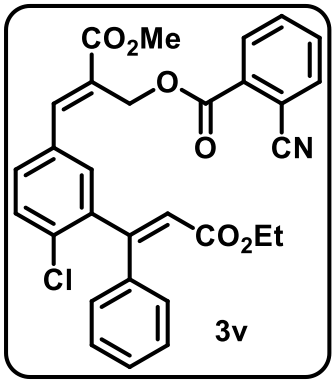
Colourless liquid; Yield 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.11 – 8.12 (m, 2H), 8.07 (s, 1H), 8.00-8.02 (m, 3H), 7.73 – 7.69 (m, 1H), 7.57 – 7.50 (m, 4H), 7.46 – 7.42 (m, 6H), 7.29 – 7.27 (m, 3H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.12 (s, 1H), 5.10 (s, 2H), 5.07 (s, 1H), 3.89 (s, 3H), 3.88 (s,3H), 3.83 (S, 3H), 3.82 (s, 1H), 3.79 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (10O MHz, $CDCl_3$) δ 166.8, 166.5, 165.9, 166.67, 142.6, 141.6, 135.7, 134.7, 133.7, 133.3, 133.1, 130.9, 130.6, 129.8, 129.5 128.4, 128.00, 121.52 (s), 120.8, 119.2, 60.2, 59.6, 51.7, 51.8; HRMS (ESI): calc. for [($C_{23}H_{18}ClNO_6$)] $(M+H)^+$ 415.0943, measured 415.0940.

(*E*)-3-(4-chloro-3-((1*E*,3*E*)-5-methoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3u)



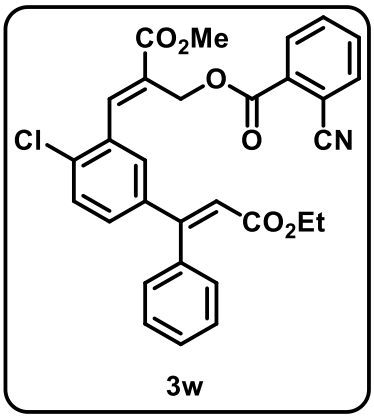
Colourless liquid; Yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 (d, *J* = 0.5 Hz, 1H), 7.80 (s, 1H), 7.71 – 7.64 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.15 – 7.12 (m, 2H), 7.10 – 7.06 (m, 3H), 6.26 (s, 1H), 5.02 (s, 2H), 3.84 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 163.3, 155.1, 142.5, 140.1, 137.9, 135.6, 134.9, 133.0, 132.9, 132.5, 131.9, 131.6, 130.5, 130.2, 130.0, 129.1, 128.6, 128.4, 128.0, 117.9, 113.4, 96.2, 60.8, 52.7, 51.4; HRMS (ESI): calc. for [($C_{29}H_{22}ClO_6$)] $(M+H)^+$ 516.1206, measured 516.1198.

(*E*)-3-(4-chloro-3-((1*E*,3*E*)-5-ethoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3v)



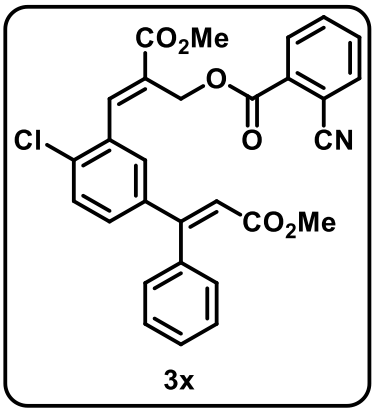
Colouless liquid,Yield 78% , ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.80 (s, 1H), 7.71 – 7.64 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 2.3, 0.5 Hz, 3H), 7.14 – 7.02 (m, 5H), 6.27 (s, 1H), 5.01 (s, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.9, 163.3, 158.0, 154.3142.6, 140.2, 138.2, 135.6, 135.0, 133.1, 133.0, 132.6, 131.0, 130.7, 130.2, 130.1, 129.2, 128.6, 128.5, 128.1, 118.8, 113.5, 96.4, 60.9, 60.4, 52.8, 29.9; HRMS (ESI): calc. for [($C_{30}H_{24}ClNO_6$)] $(M+H)^+$ 530.1362, measured 530.1358.

(*E*)-3-(2-chloro-5-((1*E*,3*E*)-5-ethoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3w)



Colourless liquid; Yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.80 (s, 1H), 7.82 – 7.80 (m, 1H), 7.69-7.66 (m, 2H), 7.43 (d, *J* = 8, 1H), 7.38 – 7.35 (m, 1H), 7.27 (d, J= 4 Hz, 1H), 7.14 – 7.02 (m, 5H), 6.27 (s, 1H), 5.01 (s, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.9, 163.3, 142.6, 140.3, 138.2, 135.6, 135.1, 133.1, 133.0, 132.6, 131.7, 130.7, 130.2, 130.1, 129.2, 128.6, 128.5, 128.1, 127.9,117.8, 117.2 113.5, 96.4, 60.9, 60.4, 52.8, 13.9, HRMS (ESI): calc. for [($C_{30}H_{24}ClNO_6$)] $(M+H)^+$ 530.1362, measured 530.1367.

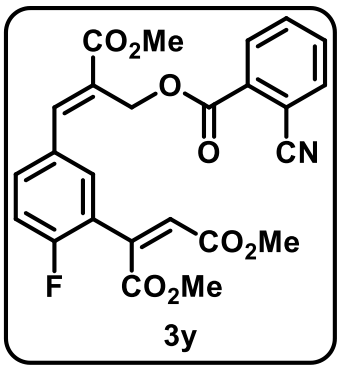
(*E*)-3-(2-chloro-5-((1*E*,3*E*)-5-methoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3x)



3x

Colourless liquid; Yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.03-8.01 (m, 1H), 8.02-8.0 (m, 1H), 7.69-7.66 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.14 – 7.12 (m, 2H), 7.10 – 7.06 (m, 2H), 6.26 (s, 1H), 5.02 (s, 2H), 3.84 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.9 163.6, 144.1, 142.1, 135.9, 134.9, 134.5, 133.4, 132.9, 132.5, 132.1 131.4, 130.4, 129.7, 129.0, 128.7, 128.9, 127.3, 123.7, 120.8, 117.8,117.3 113.1, 66.6, 52.6, 51.3 HRMS (ESI): calc. for HRMS (ESI): calc. for $[(C_{29}H_{22}ClO_6)]$ $(M+H)^+$ 516.1206, measured 516.1211.

Dimethyl-2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3y)

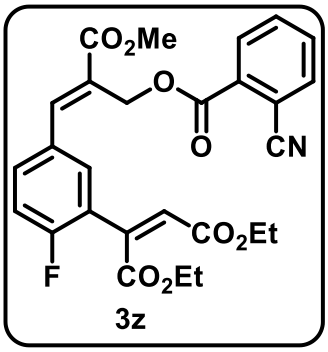


3y

Colourless liquid; Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 1H), 8.03 (s, 1H), 7.80 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.48 (ddd, *J* = 7.4, 4.7, 2.1 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.15 (d, *J* = 9.0 Hz, 1H), 7.11 (s, 1H), 5.27 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.4, 163.5, 162.6, 143.7,

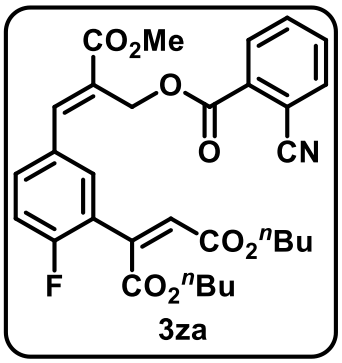
137.1, 133.8, 131.7, 131.6, 131.3, 131.0, 130.3, 129.9, 128.8,128.7, 125.1, 116.3, 115.0, 114.8, 111.9, 59.7, 52.1, 51.3, 51.1; HRMS (ESI): calc. for [($C_{25}H_{20}FNO_8$)] $(M+H)^+$ 482.1246, measured 482.1235.

Diethyl-2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3z)



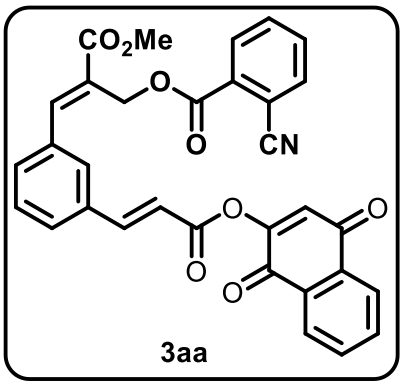
Colourless liquid; Yield 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 1H), 8.03 (s, 1H), 7.82 – 7.79 (m, 1H), 7.69 – 7.65 (m, 2H), 7.51 – 7.45 (m, 1H), 7.35 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.13 (t, *J* = 8.9 Hz, 1H), 7.10 (s, 1H), 5.28 (s, 2H), 4.27 – 4.23 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.80 (d, *J* = 5.7 Hz, 1H), 1.25 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.1, 164.4, 163.7, 144.8, 138.1, 134.9, 132.9, 132.8, 132.7, 131.8, 131.4, 129.8, 126.2, 122.9, 122.8, 117.4, 116.1, 115.8, 113.1, 62.4, 61.3, 61.3, 60.8, 52.5, 14.1,14.0; HRMS (ESI): calc. for [($C_{27}H_{24}FNO_8$)] $(M+H)^+$ 510.1086, measured 510.1078.

Dibutyl-2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3za)



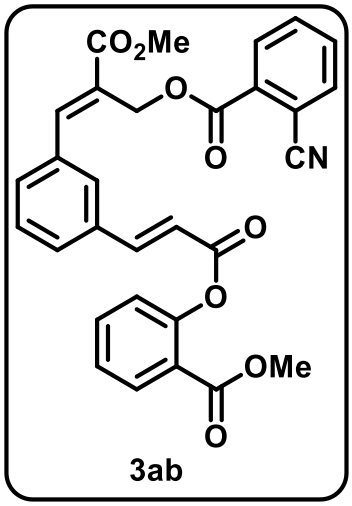
White solid; Yield 75%; M. P (110-112 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 1H), 8.03 (s, 1H), 8.02-8.00 (m, 1H), 7.68 – 7.65 (m, 2H), 7.50-7.46 (m, 1H), 7.35 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.14 (d, *J* = 12 Hz, 1H), 7.10 (s, 1H), 5.28 (s, 2H), 4.19 – 4.16 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 1.65 – 1.59 (m, 2H), 1.47 – 1.41 (m, 2H), 1.37 (ddd, *J* = 17.7, 11.5, 4.7 Hz, 2H), 1.25 – 1.18 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.0, 165.2, 160.3, 146.2, 143.4, 134.7, 134.3, 133.9, 133.8, 130.4, 130.3, 129.5, 129.4, 128.3, 126.9, 121., 116.38, 113.6, 102.8, 66.0, 64.9, 64.1, 52.5, 30.5, 30.4, 19.2, 19.05, 13.7, 13.7; HRMS (ESI): calc. for [($C_{31}H_{32}FNO_8$)] $(M+H)^+$ 566.2185, measured 566.2177.

(*E*)-3-(3-((*E*)-3-((1,4-dioxo-1,4-dihydronaphthalen-2-yl)oxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3aa)



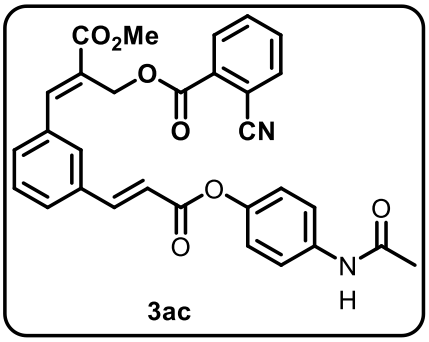
Yellow colour liquid; Yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.91 (d, *J* = 15.9 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.64 – 7.62 (m, 3H), 7.59 (d, *J* = 5.4 Hz, 2H), 7.55 – 7.53 (m, 3H), 7.40 – 7.37 (m, 3H), 7.34 – 7.32 (m, 4H), 7.17 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 16 Hz, 1H), 5.09 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 166.2, 164.7, 163.5, 145.4, 143.9, 143.7, 134.9, , 132.8, 132.6, 132.5, 132.4, 132.0, 131.4, 130.7, 130.7, 130.0, 129.6, 129.6, 129.2, 129.1, 129.0, 128.5, 127.4, 126.2, 125.5, 123.5, 119.6, 117.4, 113.0, 60.8, 52.6; HRMS (ESI): calc. for [($C_{32}H_{21}NO_8$)] $(M+H)^+$ 548.1317, measured 548.1314.

(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-3-(2-(methoxycarbonyl)phenoxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ab)



Yellow solid; Yield 63%, M. P (106-108 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.10 – 7.96 (m, 4H), 7.77 (d, *J* = 5.5 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.61 – 7.56 (m, 2H), 7.48 – 7.32 (m, 2H), 7.16 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 5.14 (s, 2H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.0, 163.6, 150.5, 143.8, 143.4, 134.8, 134.8, 134.6, 133.8, 133.2, 132.8, 132.5, 132.4, 132.0, 131.9, 131.4, 130.6, 129.7, 129.2, 127.5, 126.1, 123.9, 123.4, 119.9, 117.4, 113.1, 60.9, 52.6, 52.3; [($C_{30}H_{23}NO_8$)] $(M+H)^+$ 526.1547, measured 526.1541.

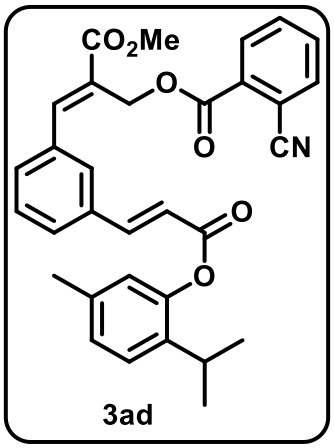
(*E*)-3-(3-((*E*)-3-(4-acetamidophenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl) allyl- 2-cyanobenzoate (3ac)



Light yellow solid; Yield 60%; M. P (148-152 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.03-8.05 (m,2H), 7.94 (d, *J* = 15.8 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.70 – 7.61 (m, 2H), 7.52 – 7.47 (m, 2H), 7.44 – 7.39 (m, 2H), 7.26 (s, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 5.11 (s, 2H), 3.85 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.3, 165.2, 163.5, 146.6, 143.7, 143.3, 136.0, 134.8, 134.6, 133.0, 132.9, 132.6, 131.8, 131.36, 130.6, 129.7, 129.6, 129.1, 128.8, 127.5, 121.8, 120.9, 120.9, 120.1, 117.4, 112.9,

60.8, 52.6, 24.3; HRMS (ESI): calc. for [($C_{30}H_{24}N_2O_7$)] $(M+H)^+$ 525.1684, measured 525.1680

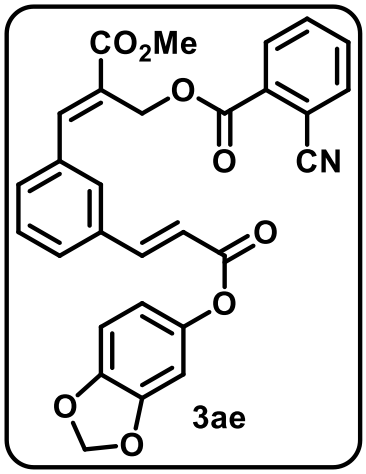
(*E*)-3-(3-((*E*)-3-(2-isopropyl-5-methylphenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3ad)



3ad

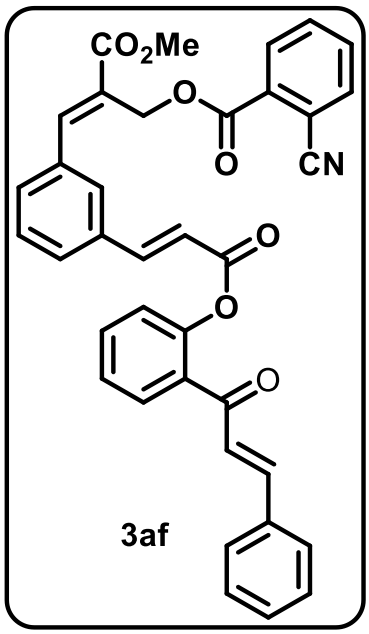
Yellow colour liquid; Yield 65% ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.07 (s, 1H), 7.99 (d, *J* = 15.9 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.73-7.75 (m, 1H), 7.69 – 7.60 (m, 2H), 7.48 – 7.37 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 1.0 Hz, 1H), 6.88 (d, *J* = 1.0 Hz, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 5.15 (s, 2H), 3.86 (s, 3H), 3.06 – 2.97 (m, 1H), 2.33 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.2, 163.6, 147.9, 143.8, 143.1, 137.1, 136.6, 134.9, 134.6, 134.3, 133.1, 132.8, 132.5, 132.0, 131.4, 130.6, 129.7, 129.1, 127.3, 126.5, 123.6, 122.81, 120.2, 117.4, 113.0, 60.8, 52.6, 27.3, 23.1, 20.9; HRMS (ESI): calc. for [($C_{32}H_{29}NO_6$)] $(M+H)^+$ 524.2068, measured 524.2069.

(*E*)-3-(3-((*E*)-3-(benzo[d][1,3]dioxol-5-yloxy)-3-oxoprop-1-en-1-yl)phenyl)-2 (methoxycarbonyl)allyl 2-cyanobenzoate (3ae)



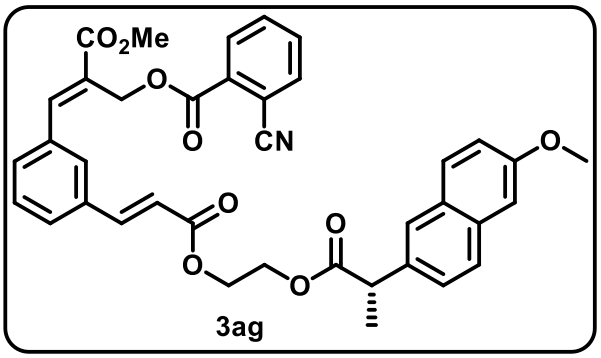
Yellow colour liquid; Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.09 – 8.06 (m, 1H), 7.94 (d, *J* = 15.9 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.71 – 7.68 (m, 1H), 7.64 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.38 – 7.36 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 6.59 – 6.55 (m, 2H), 6.00 (s, 2H), 5.12 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.3, 163.6, 148.0, 145.4, 145.0, 143.8, 143.3, 134.9, 134.7, 133.2, 132.9, 132.5, 132.0, 131.4, 130.7, 129.7, 129.2, 127.5, 127.2, 120.1, 117.5, 114.0, 113.1, 108.0, 103.8, 101.8, 60.9, 52.7; HRMS (ESI): calc. for $[(C_{29}H_{21}NO_8)]$ $(M+H)^+$ 512.1337, measured 512.1330.

(*E*)-3-(3-((*E*)-3-(2-cinnamoylphenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2(methoxycarbonyl) allyl-2-cyanobenzoate (3af)



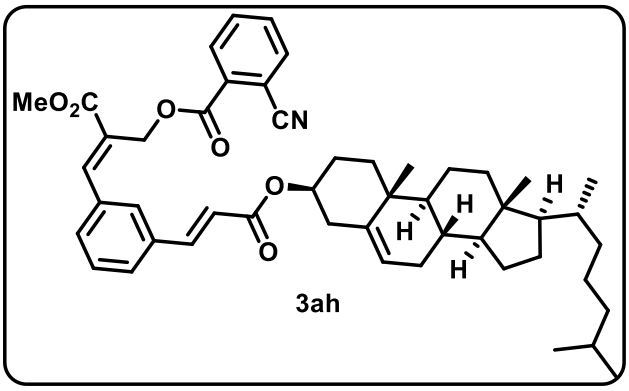
Yellow colour liquid; Yield 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.06-8.03 (m, 1H), 7.91 (d, *J* = 15.8 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.64 – 7.61 (m, 2H), 7.58 (d, *J* = 4Hz, 1H), 7.55 – 7.51 (m, 4H), 7.39 (d, *J* = 7.5 Hz, 3H), 7.35 – 7.28 (m, 4H), 7.17 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 5.09 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 164.7, 163.5, 148.7, 145.4, 143.9, 143.7, 134.8, 134.7, 134.6, 132.9, 132.8, 132.5, 132.5, 132.4, 132.0, 131.4, 130.7, 130.7, 130.0, 129.6, 129.5, 129.2, 129.1, 129.0, 128.5, 127.4, 126.2, 125.5, 123.5, 119.6, 117.4, 113.0, 60.8, 52.6; HRMS (ESI): calc. for $[(C_{37}H_{27}NO_7)]$ $(M+H)^+$ 598.1866, measured 598.1817.

(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-3-(2-(((S)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)ethoxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ag)



Yellow colour liquid; Yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.07 – 8.03 (m, 1H), 7.77 (dd, *J* = 8.1, 4.0 Hz, 1H), 7.69-7.61 (m, 6H), 7.47 (d, *J*= 8 Hz, 1H), 7.40-7.35 (m, 4H), 7.08 – 7.01 (m, 2H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.10 (s, 2H), 4.34 (m, 5H), 3.87 (s, 3H), 3.84 (s, 3H), 1.58 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 166.4,166.1, 163.6, 157.6, 143.9, 142.0, 135.4, 134.9, 134.4, 133.7, 133.3, 132.8, 132.5, 132.0, 131.4, 130.3, 129.6, 129.3, 129.0, 128.9,127.3, 127.2, 126.2, 126.0, 120.3, 119.0, 117.4, 113.1, 105.6, 62.4, 62.3, 60.9, 55.3, 52.6, 45.4, 18.4; HRMS (ESI): calc. for $[(C_{38}H_{33}NO_9)]$ $(M+H)^+$ 648.2155, measured 648.2218.

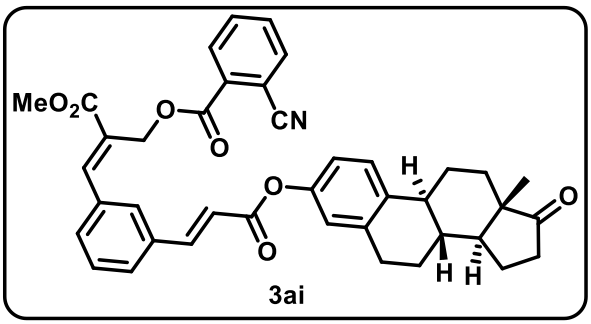
(*E*)-3-(3-((*E*)-3-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3ah)



3ah

White solid; Yield 64%; M. P (132-135 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.07 (s, 1H), 7.80 (s, 2H), 7.66 – 7.45 (m, 4H), 7.43 – 7.32 (m, 3H), 6.35 (d, *J* = 15.3 Hz, 1H), 5.40 (s, 1H), 5.11 (s, 2H), 4.71 (s, 1H), 3.88 (s, 3H), 2.38 (d, *J* = 7.3 Hz, 2H), 2.00 (t, *J* = 13.1 Hz, 2H), 1.89 (d, *J* = 10.2 Hz, 2H), 1.62 (s, 4H), 1.49 (dd, *J* = 16.9, 8.8 Hz, 4H), 1.34 (d, *J* = 6.7 Hz, 3H), 1.25 (s, 3H), 1.19 – 1.10 (m, 6H), 1.02 (d, *J* = 14.7 Hz, 5H), 0.92 (d, *J* = 5.4 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 163.6, 144.1, 141.2, 139.7, 134.9, 134.4, 133.6, 132.8, 132.5, 132.1, 131.5, 130.2, 129.6, 128.9, 127.3, 122.9, 121.7, 117.5, 113.1, 74.5, 61.0, 56.8, 56.2, 52.6, 50.1, 42.4, 39.8, 39.6, 38.2, 37.13, 36.9, 36.3, 35.9, 32.0, 28.3, 28.1, 27.9, 24.4, 23.9, 22.9, 22.8, 21.9, 19.9, 18.8, 12.0; HRMS (ESI): calc. for [($C_{49}H_{61}NO_6$)] $(M+H)^+$ 760.4572, measured 760.4587.

(E)-2-(methoxycarbonyl)-3-(3-((E)-3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ai)

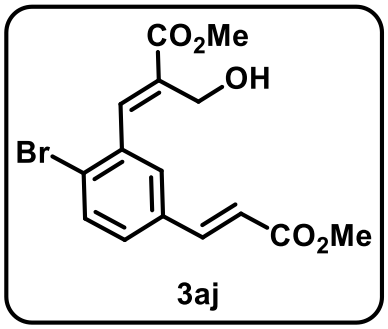


3ai

Yellow colour solid; Yield 67%, M. P (102-104 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.11 – 8.04 (m, 1H), 7.95 (d, *J* = 15.9 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.72 – 7.68 (m, 1H), 7.65 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.53 – 7.40 (m, 3H), 7.40 – 7.36 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 5.14 (s, 2H), 3.87 (s, 3H), 2.93 (d, *J* = 5.0 Hz, 2H), 2.56 – 2.48 (m, 1H), 2.43 (d, *J* = 16.5 Hz, 1H), 2.31 (t, *J* = 10.6 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.05 (dd, *J* = 5.7, 3.4 Hz, 2H), 2.00 – 1.96 (m, 1H), 1.67 (s, 2H), 1.61 (s, 2H), 1.53 (s, 2H), 1.25 (s,

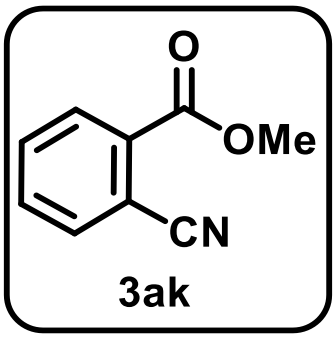
1H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.3, 163.6, 148.7, 143.9, 143.2, 138.1, 137.5, 134.9, 134.7, 133.3, 132.9, 132.6, 132.1, 131.5, 130.6, 129.8, 129.2, 127.5, 126.5, 121.7, 120.4, 118.8, 117.5, 113.2, 60.9, 52.7, 50.6, 48.1, 44.3, 38.1, 35.9, 31.7, 29.5, 26.5, 25.9, 21.7, 13.9; HRMS (ESI): calc. for [($C_{40}H_{37}NO_7$)] $(M+H)^+$ 644.2648, measured 644.2673.

Methyl(*E*)-3-(2-bromo-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(hydroxymethyl)acrylate (3aj)



White colour solid; Yield 76%, M. P (124-126 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.67 – 7.64 (m, 2H), 7.63 (d, *J* = 2.9 Hz, 1H), 7.38 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 4.35 (s, 2H), 3.90 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.0, 142.9, 140.6, 135.7, 133.9, 133.4, 132.9, 130.2, 129.4, 125.9, 119.4, 58.0, 52.4, 51.9; HRMS (ESI): calc. for [($C_{15}H_{15}BrO_5$)] $(M+H)^+$ 355.0176, measured 355.0169.

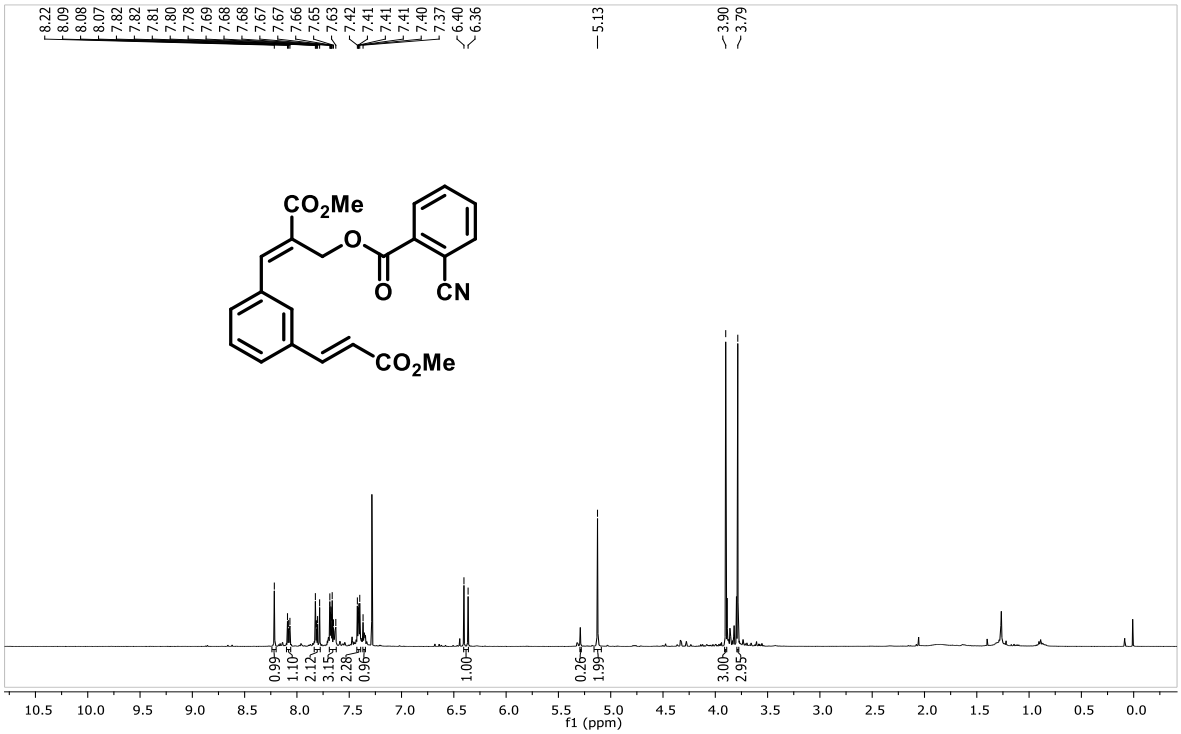
Methyl 2-cyanobenzoate (3ak)

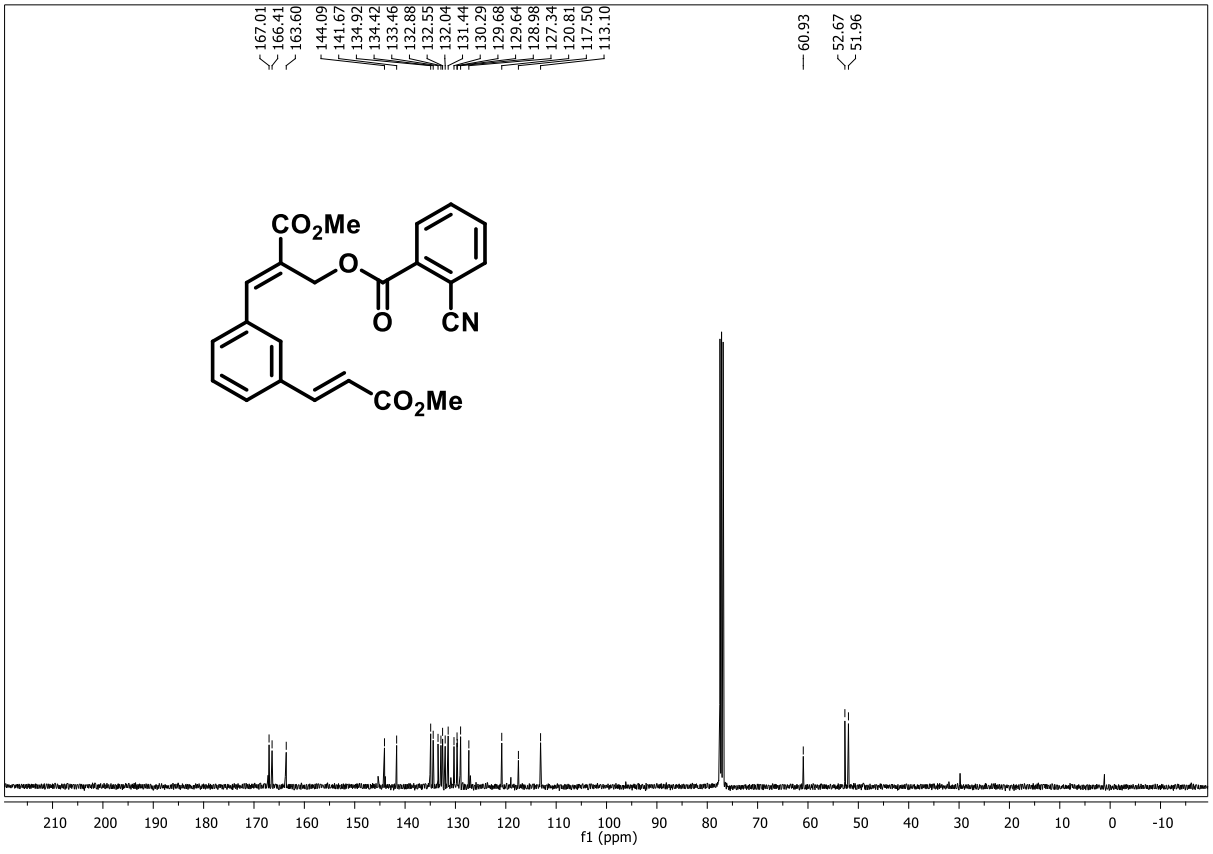


White colour solid; Yield 76%, M. P (106-108 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 1H), 7.83 – 7.78 (m, 1H), 7.70 – 7.63 (m, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 133.8, 131.7, 131.4, 130.1,130.1, 116.5, 111.9, 51.8; HRMS (ESI): calc. for [($C_9H_7NO_2$)] $(M+H)^+$ 162.0547, measured 162.0552.

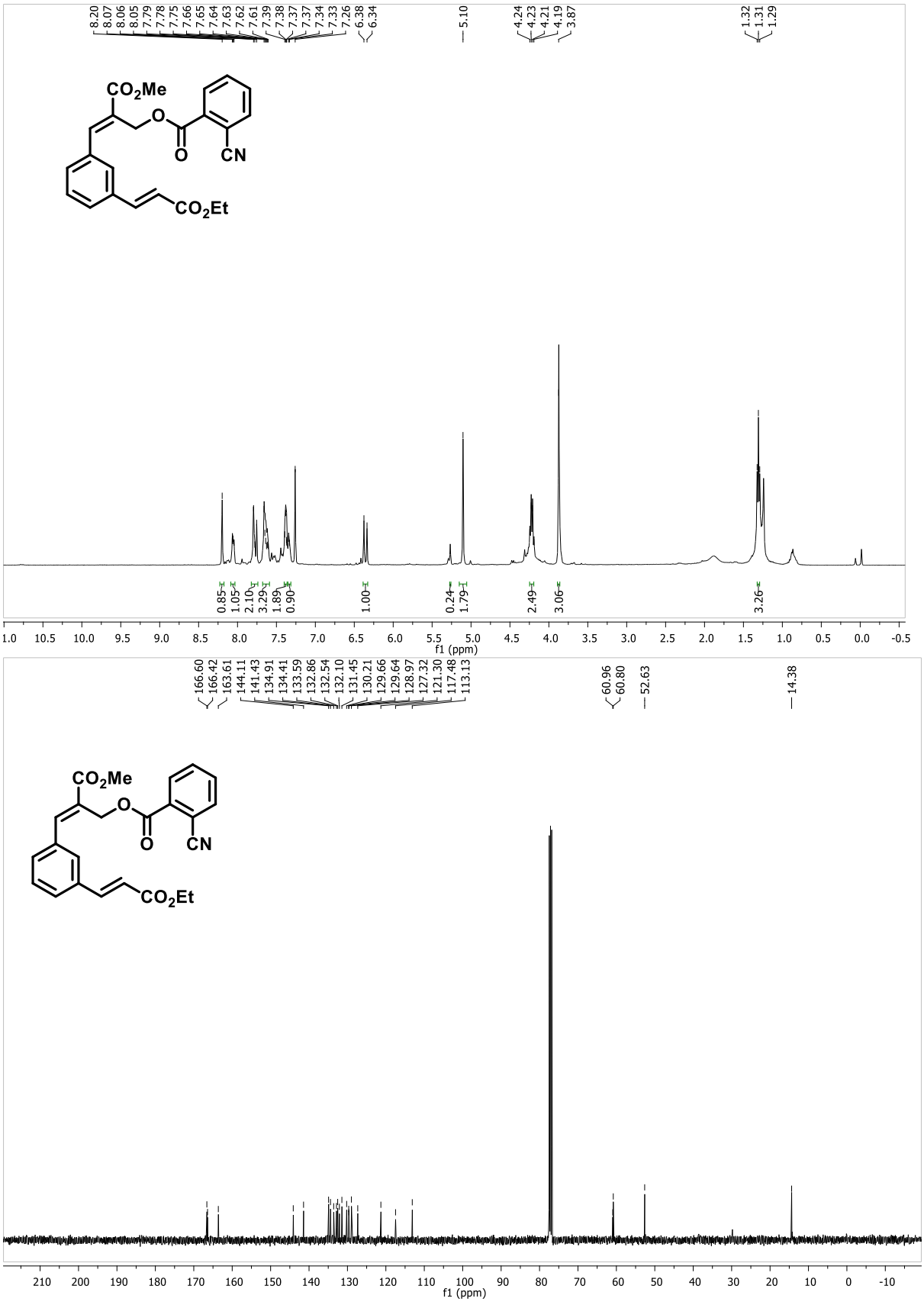
5. ^{1}H and ^{13}C NMR spectra of all the compounds:

(*E*)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl) phenyl)-2-(methoxycarbonyl)allyl-2-cyanobenzoate (3a)

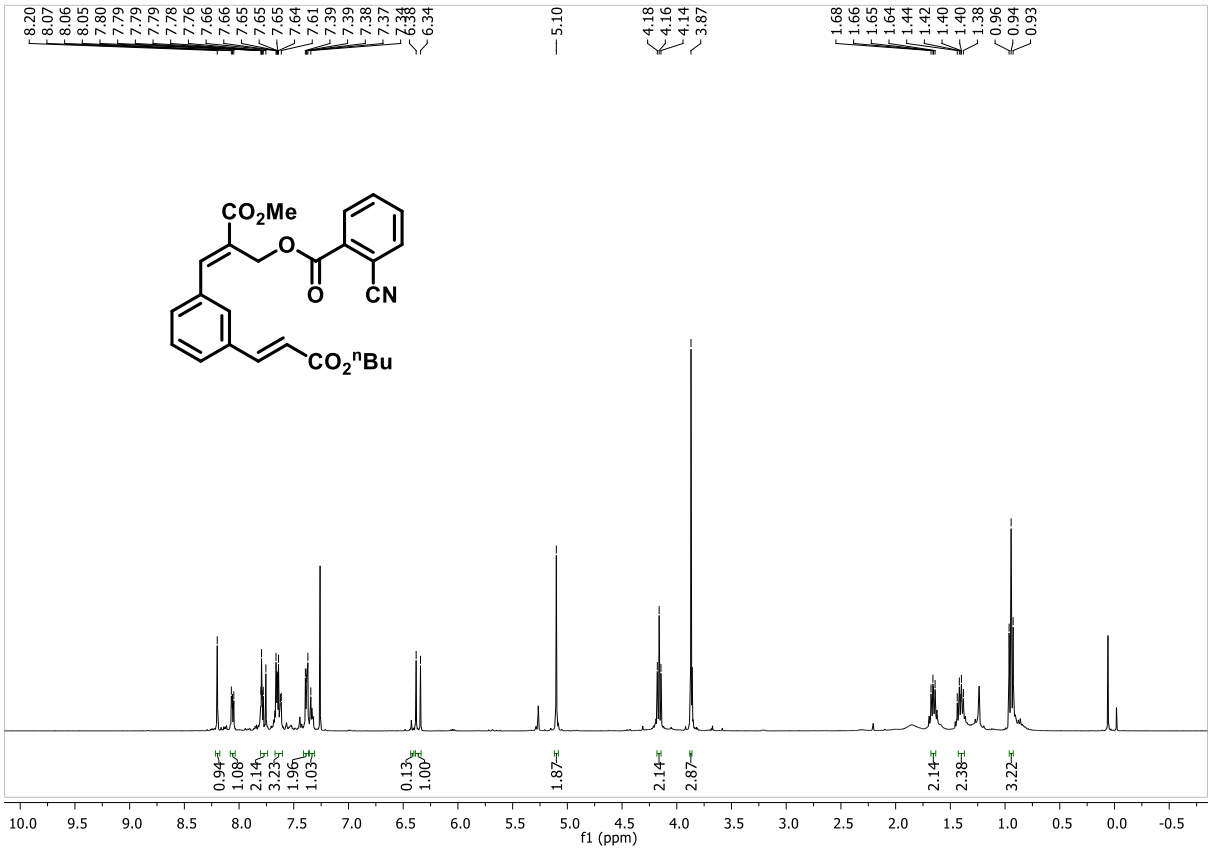


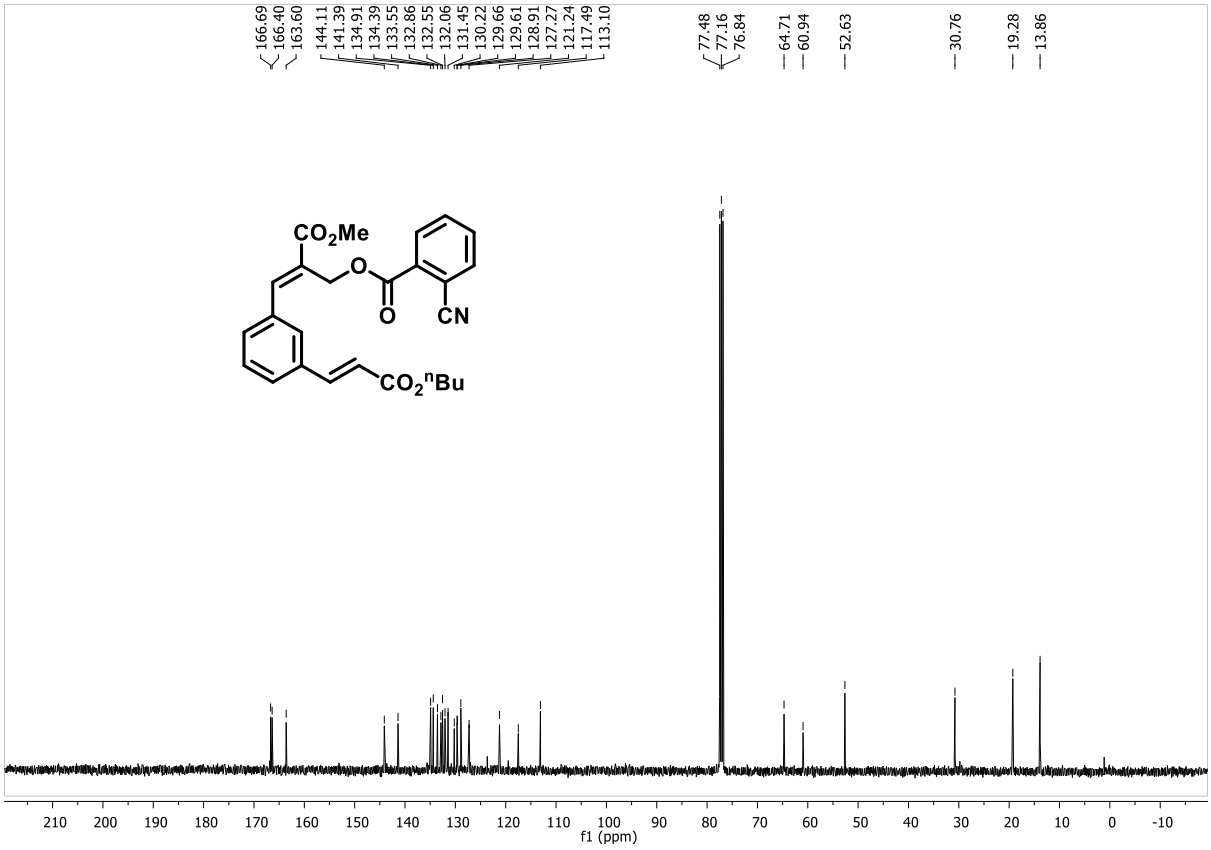


(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyano benzoate (3b)

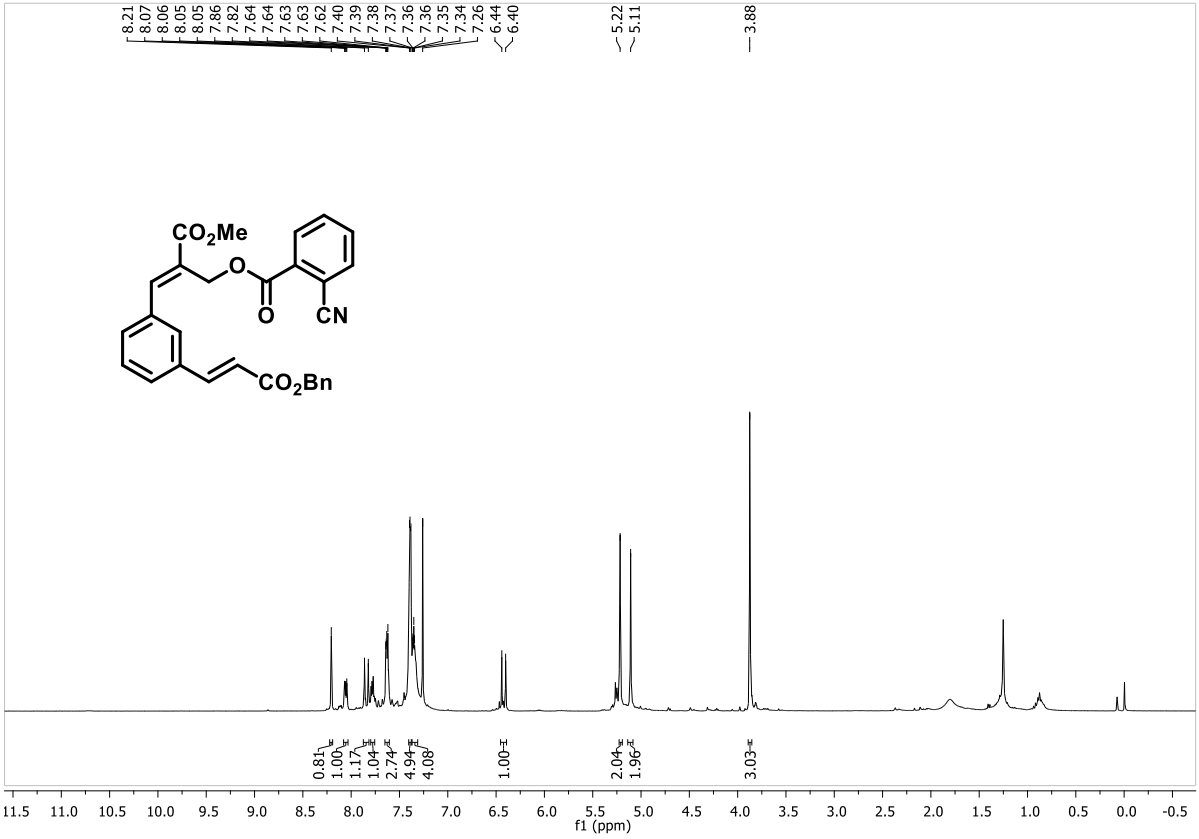


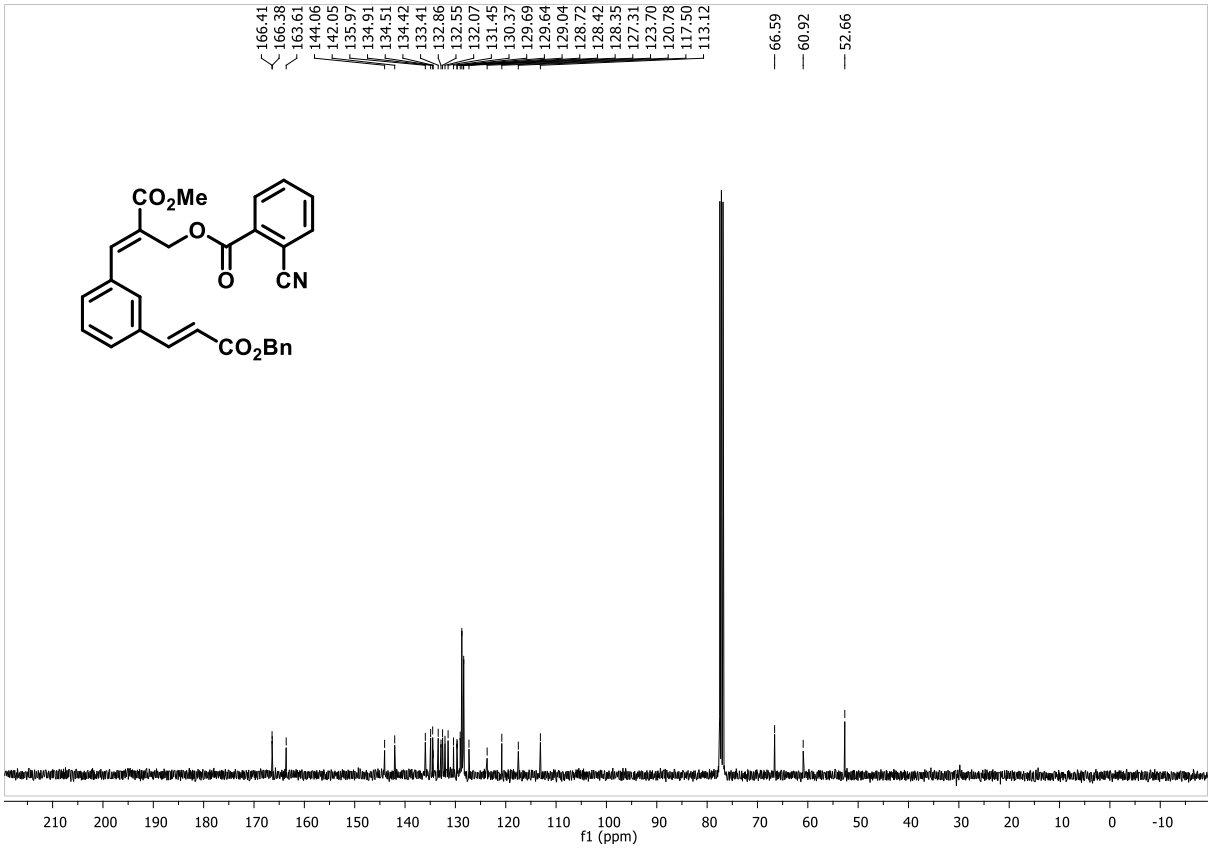
(*E*)-3-(3-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl-2-cyano benzoate (3c)



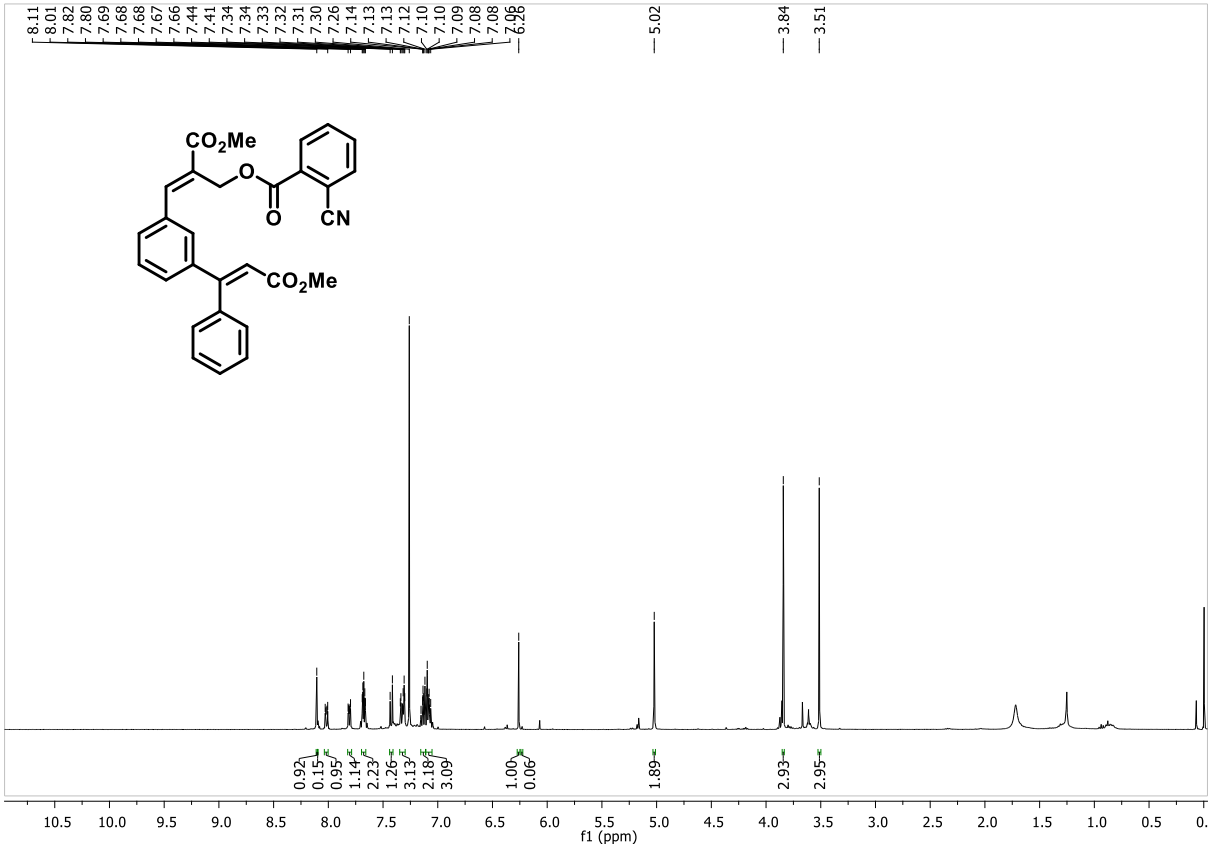


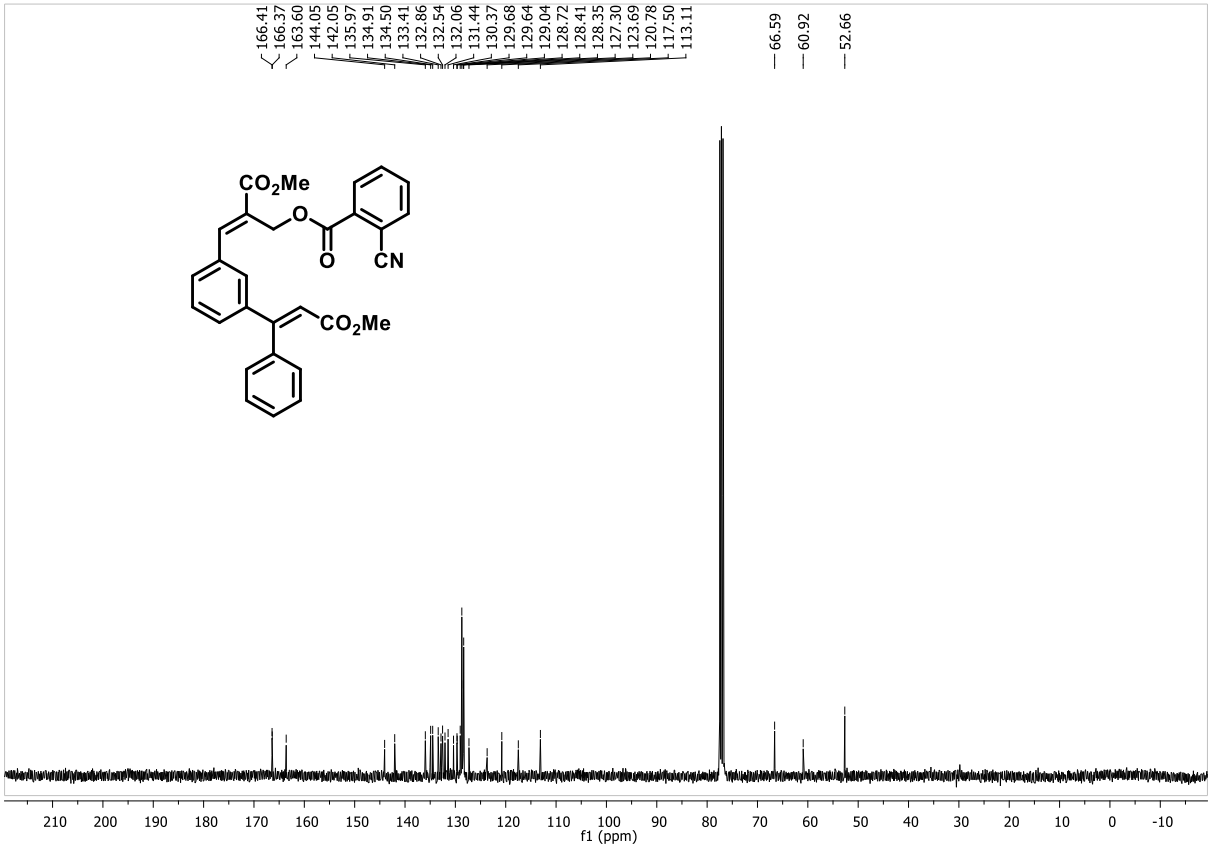
(*E*)-3-(3-((*E*)-3-(benzyloxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyano benzoate (3d)



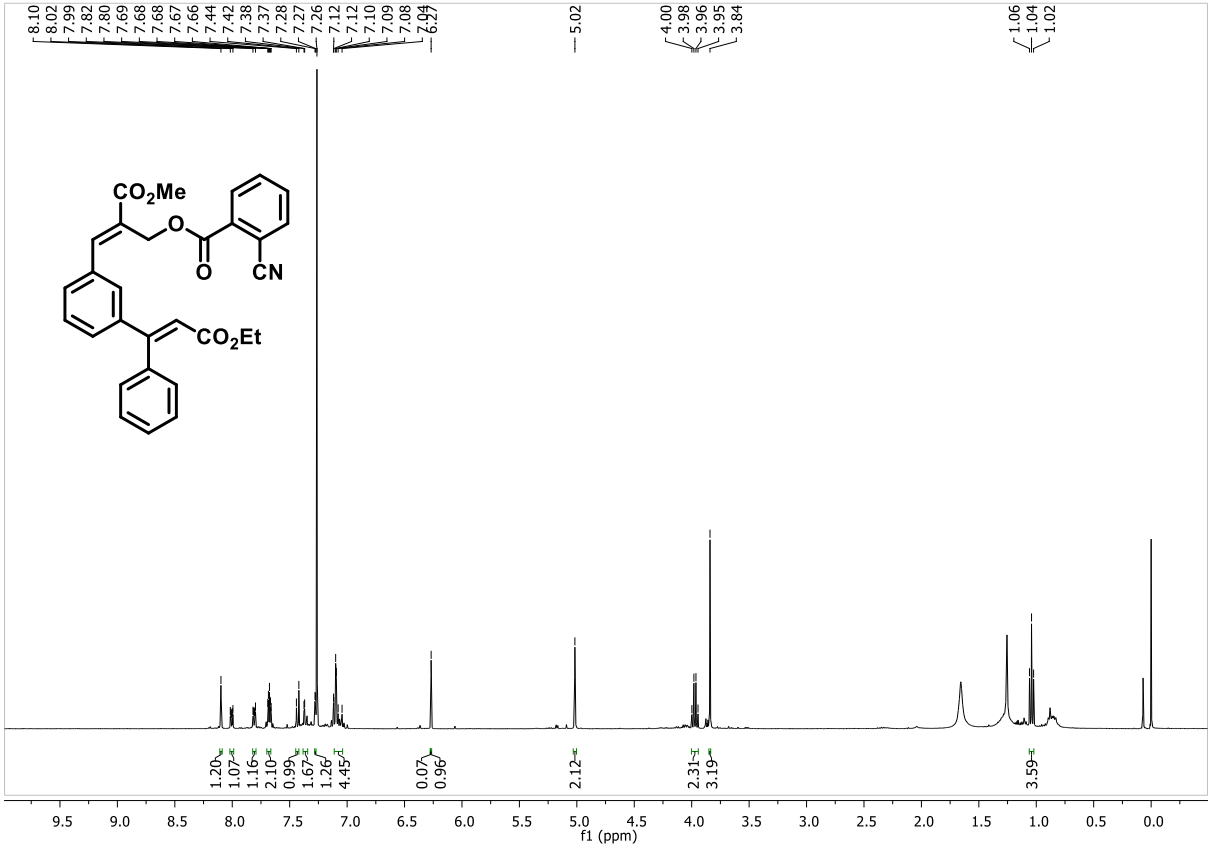


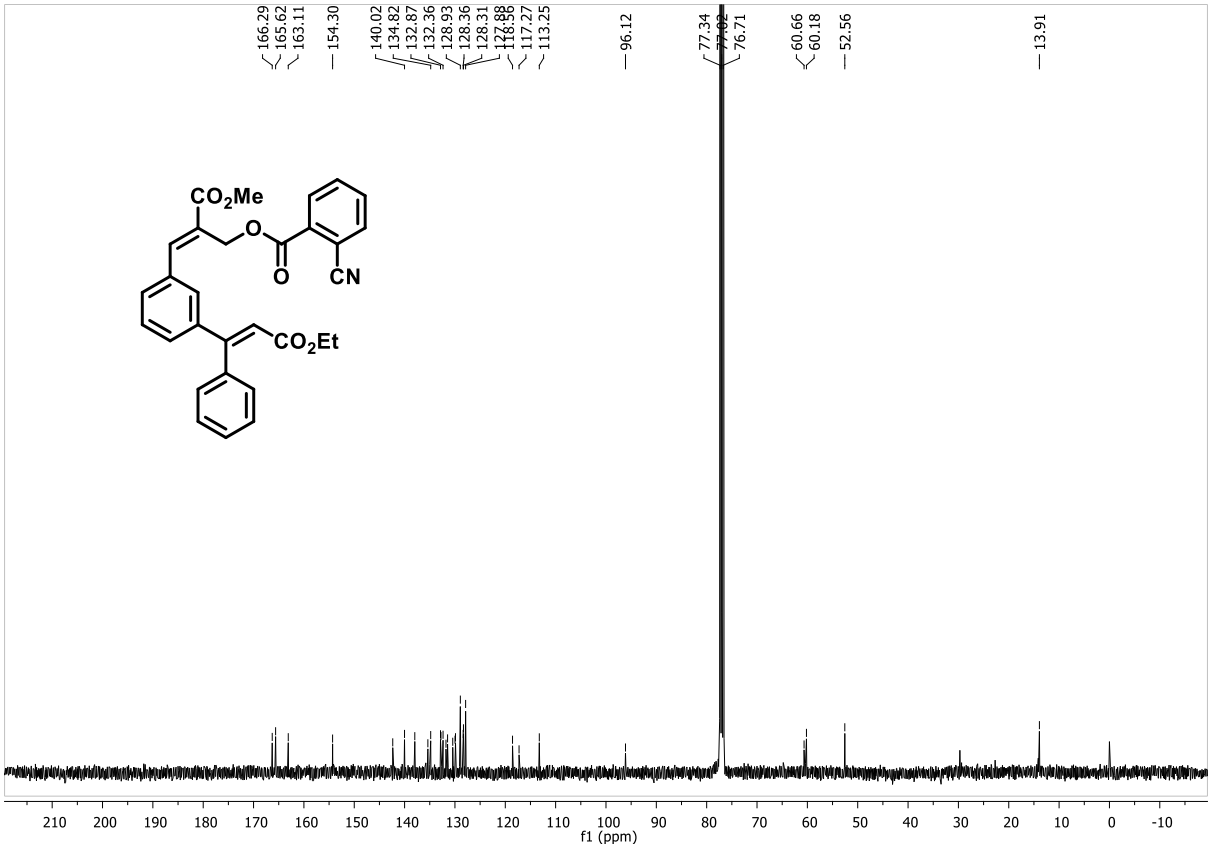
(*E*)-3-(3-((*E*)-3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3e)



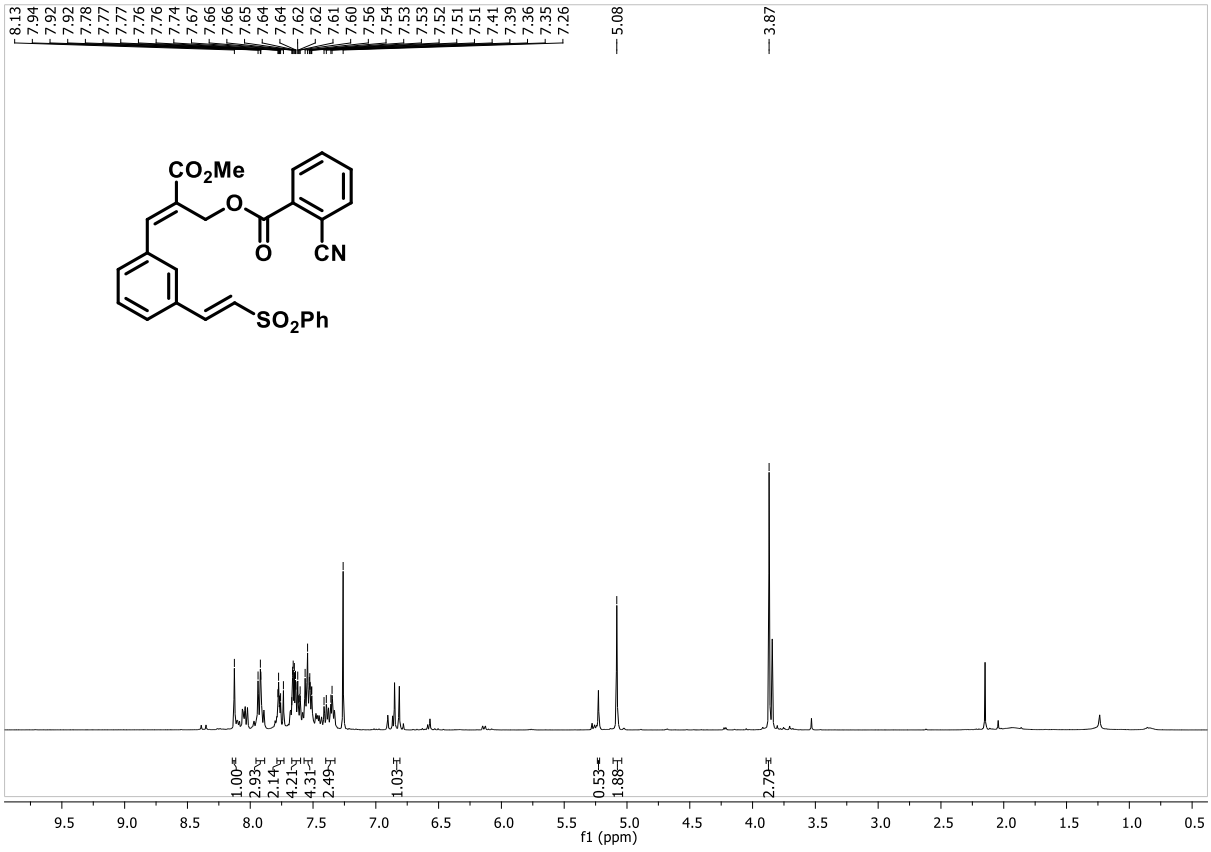


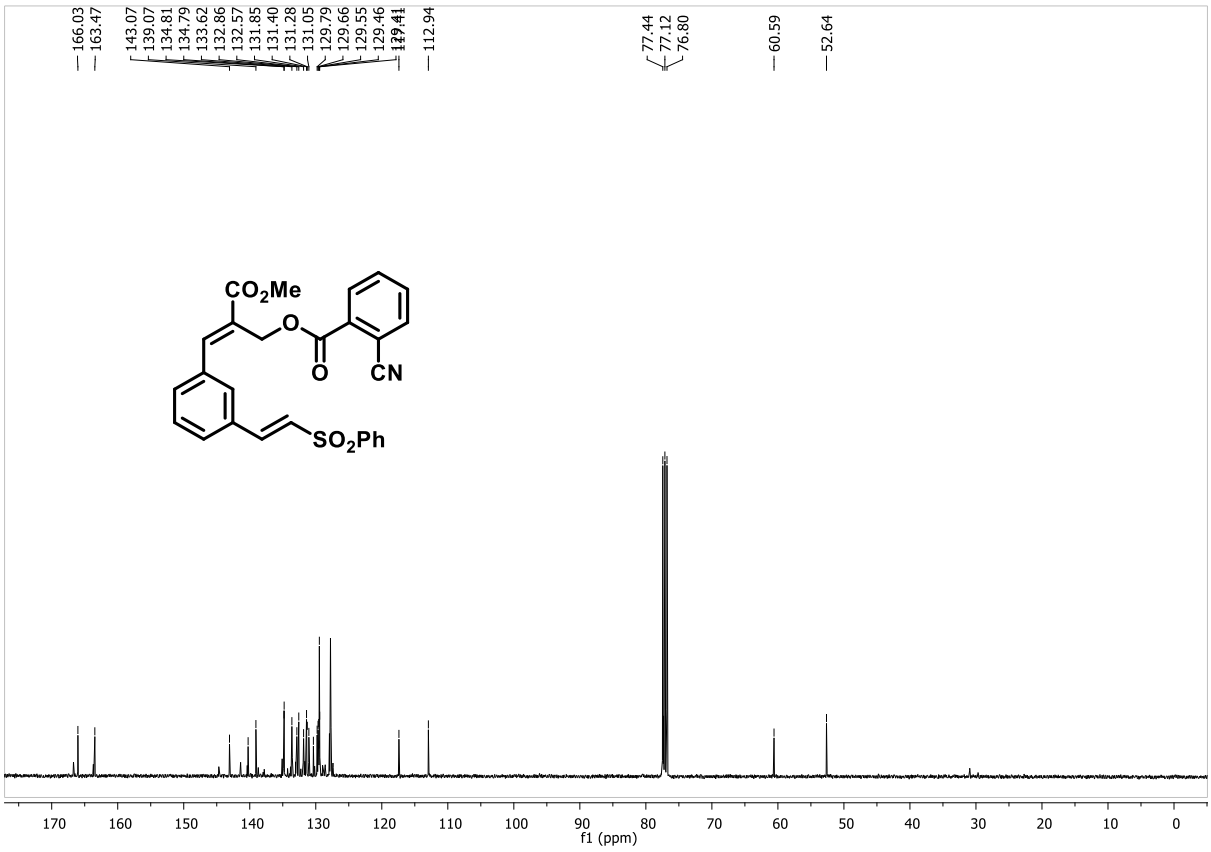
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)phenyl)-2-(methoxycarbonyl)allyl -2-cyanobenzoate (3f)



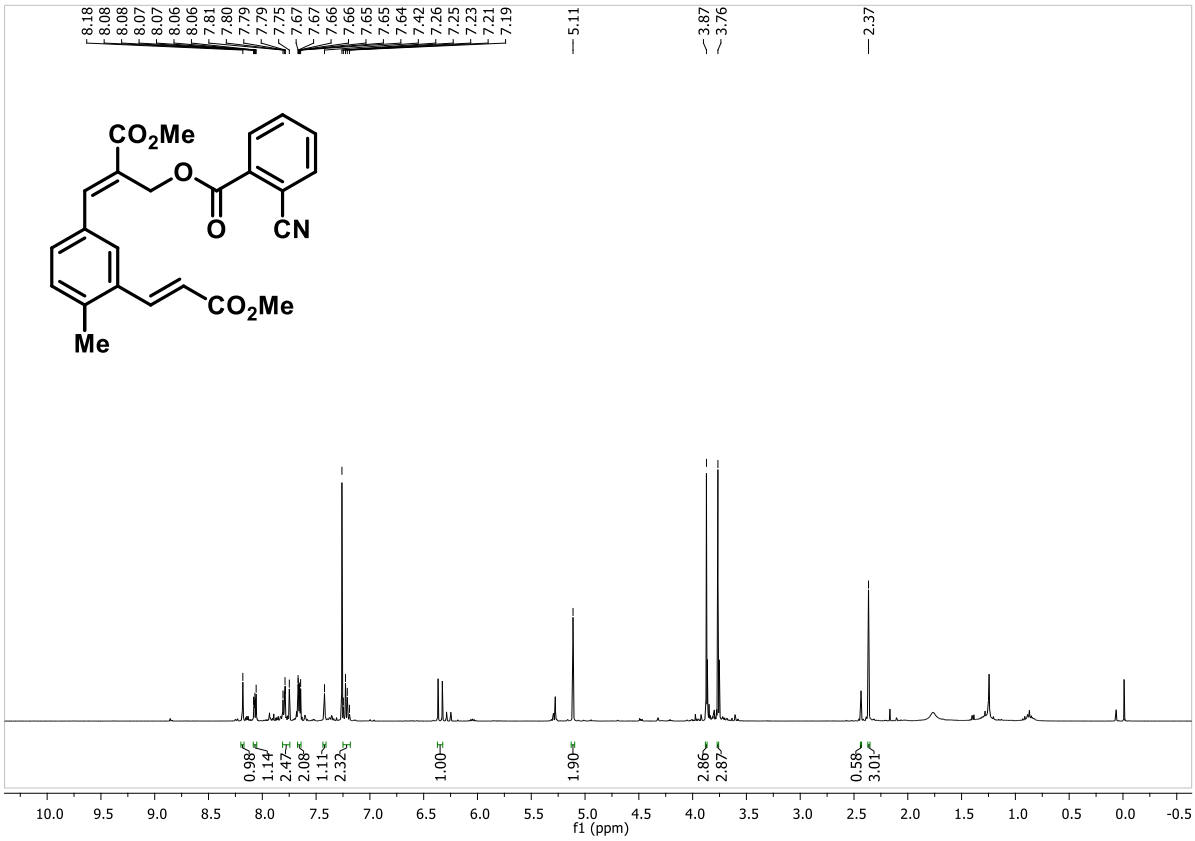


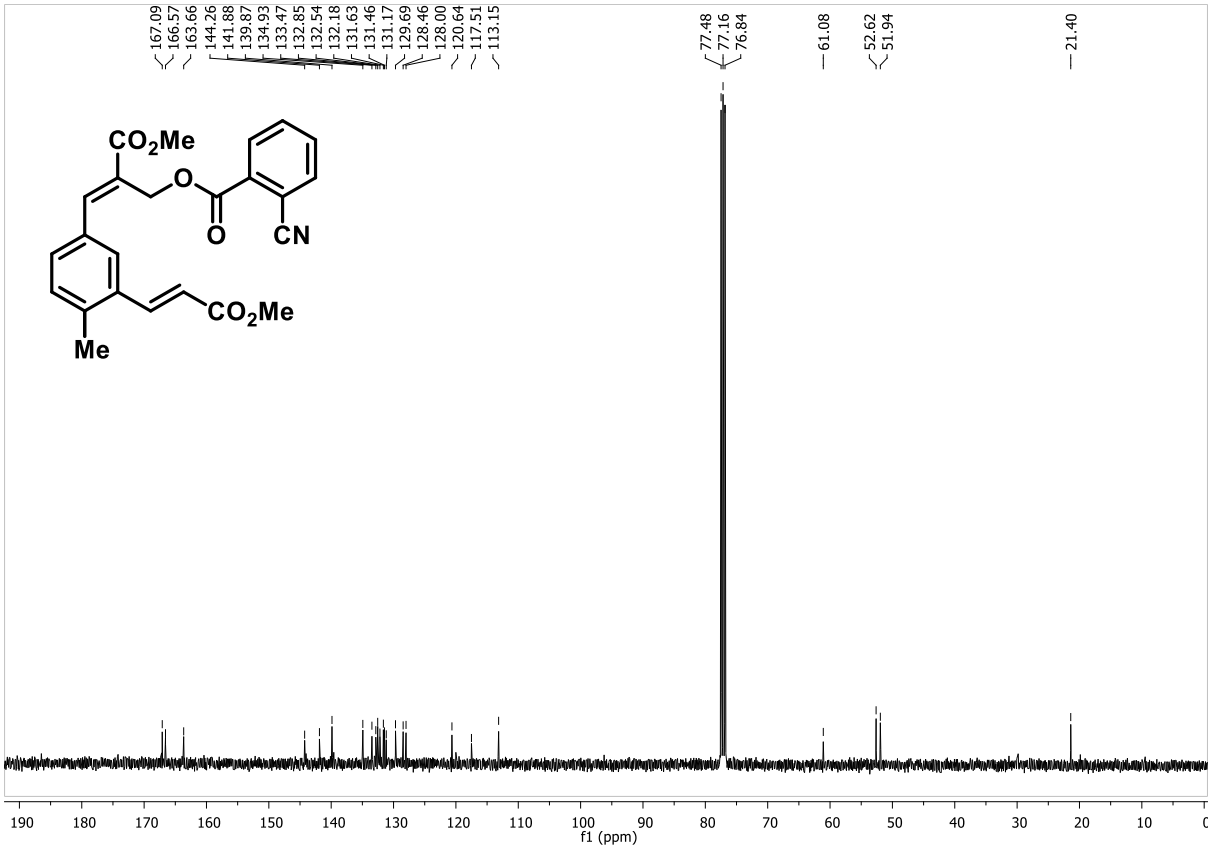
(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)allyl-2-cyano benzoate (3g)



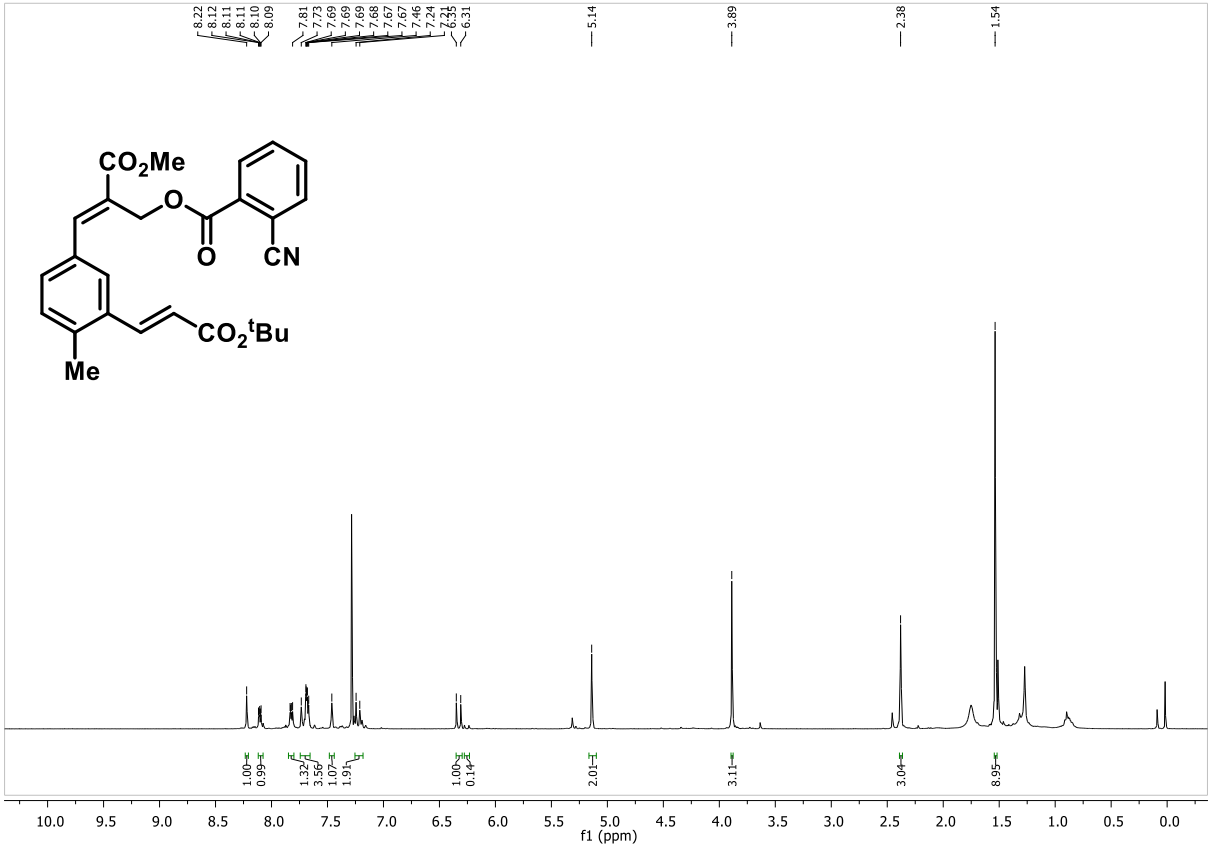


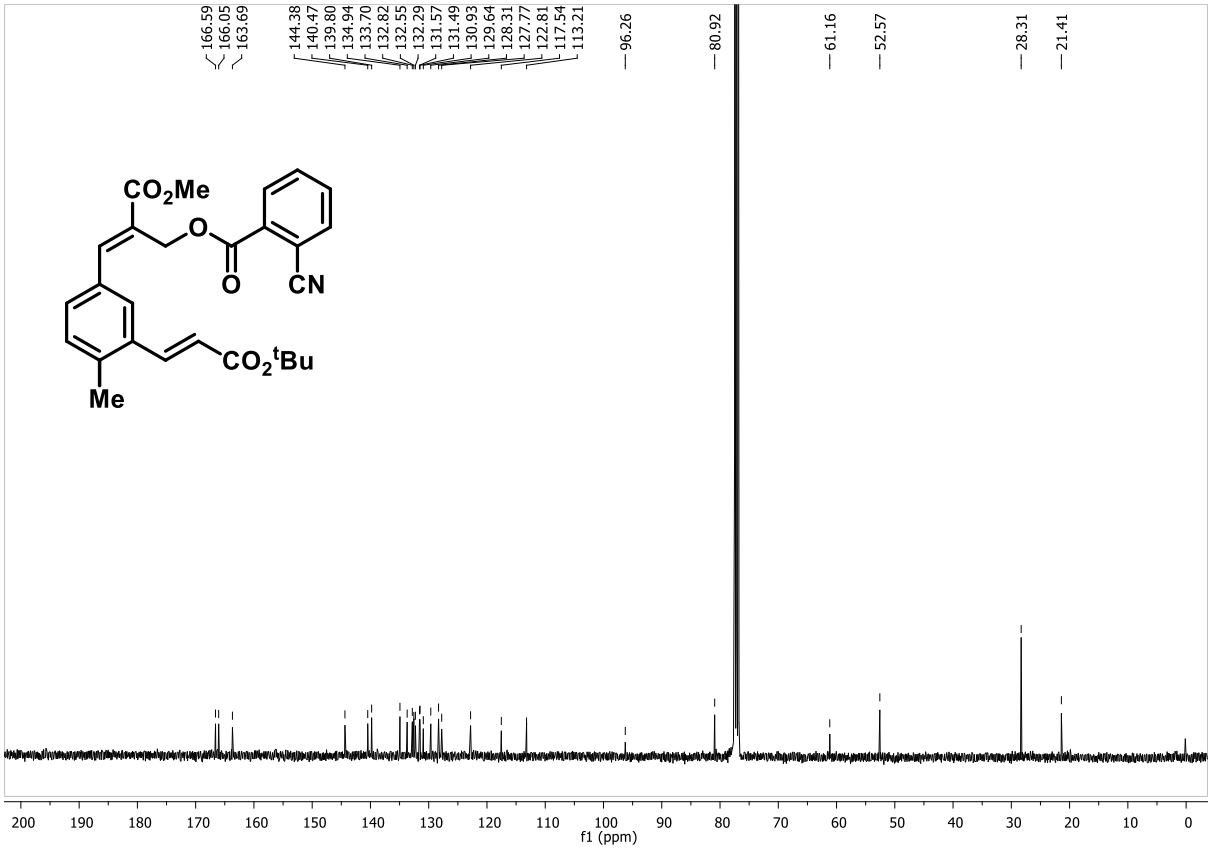
(*E*)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3h)



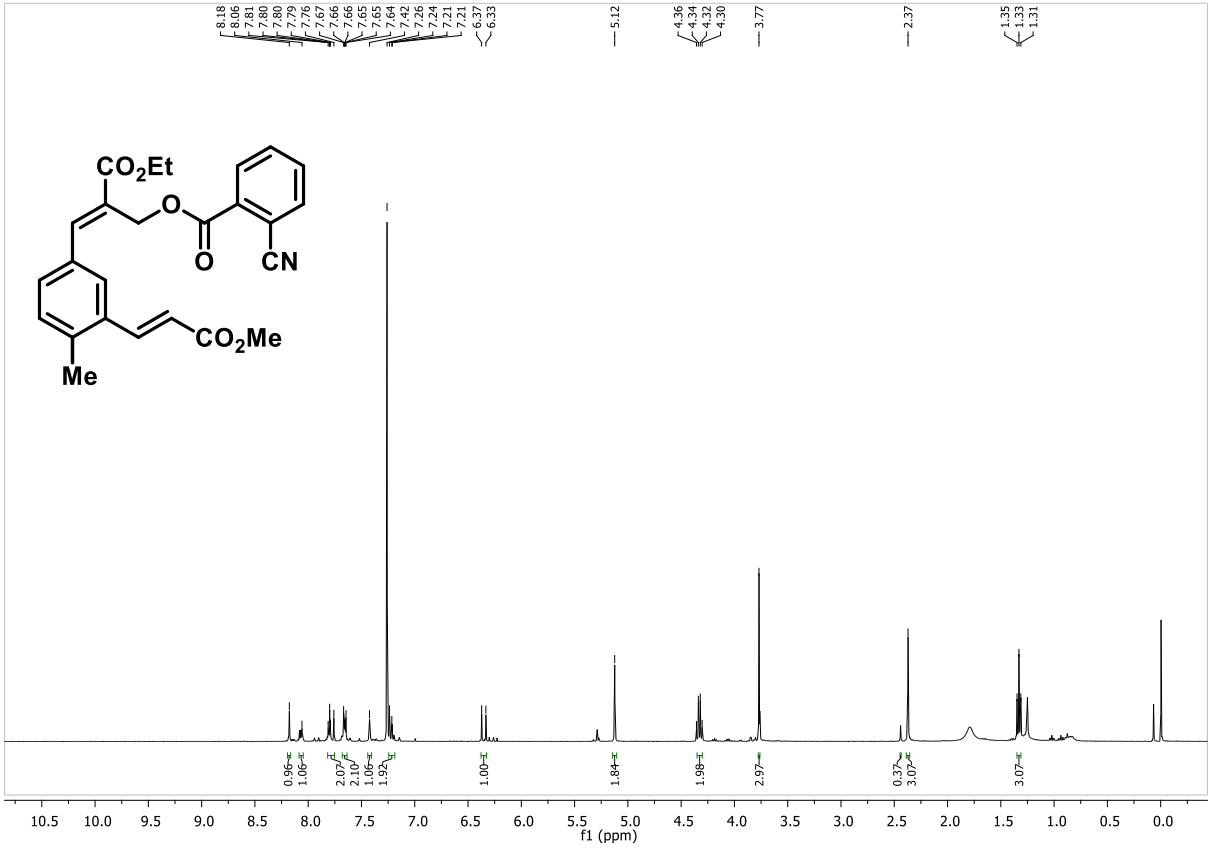


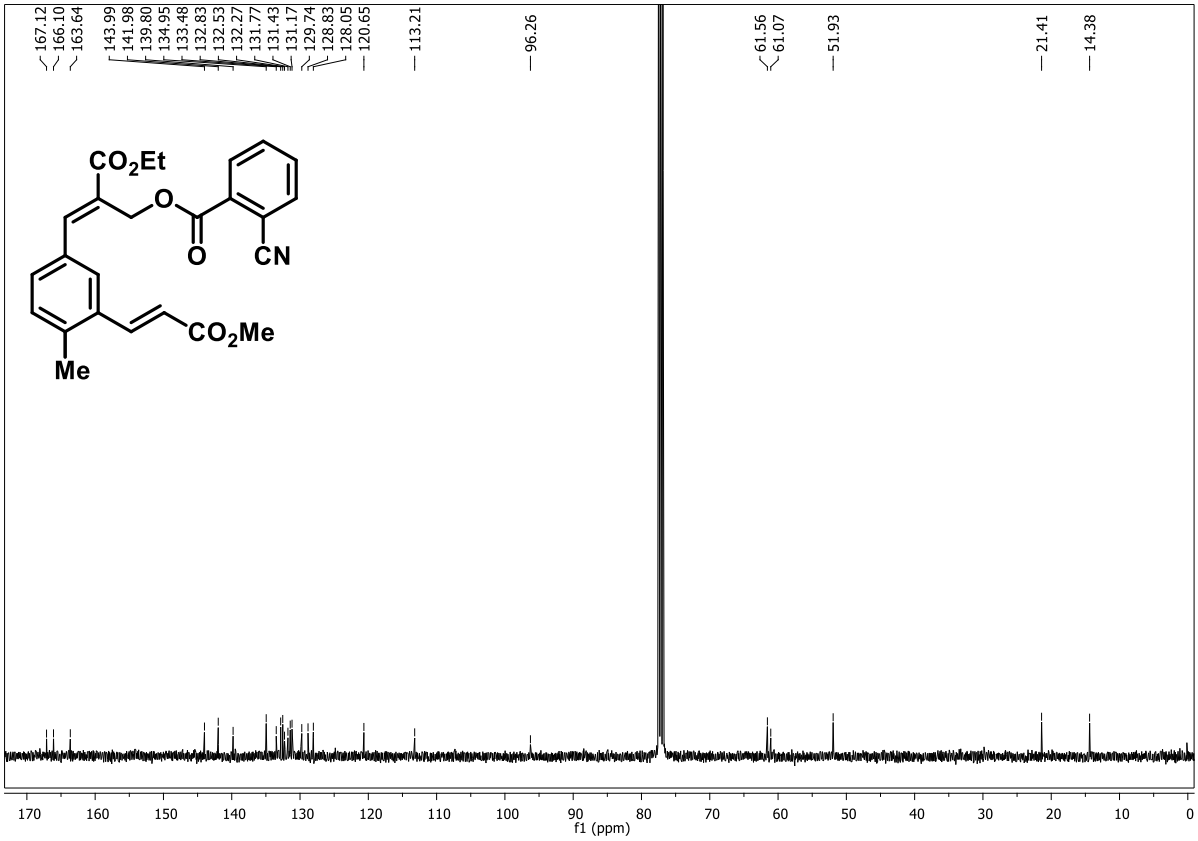
(E)-3-(3-((E)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2(methoxycarbonyl) allyl 2-cyanobenzoate (3i)



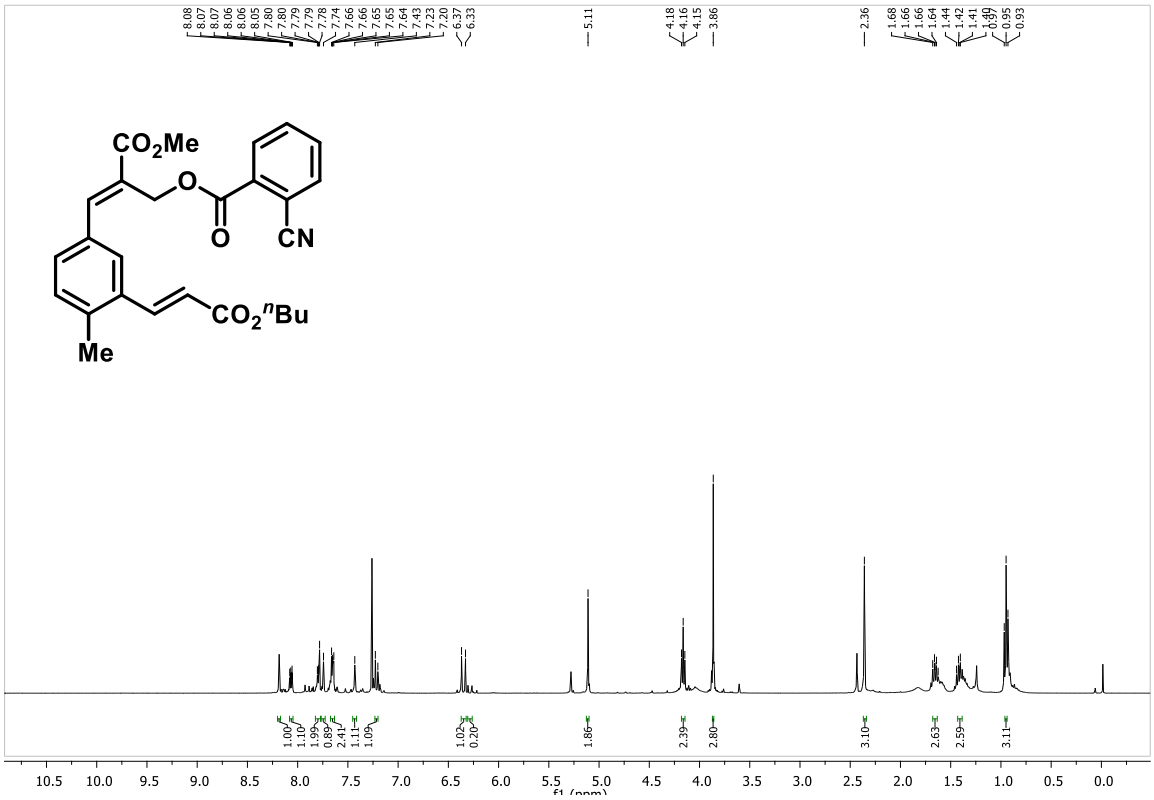


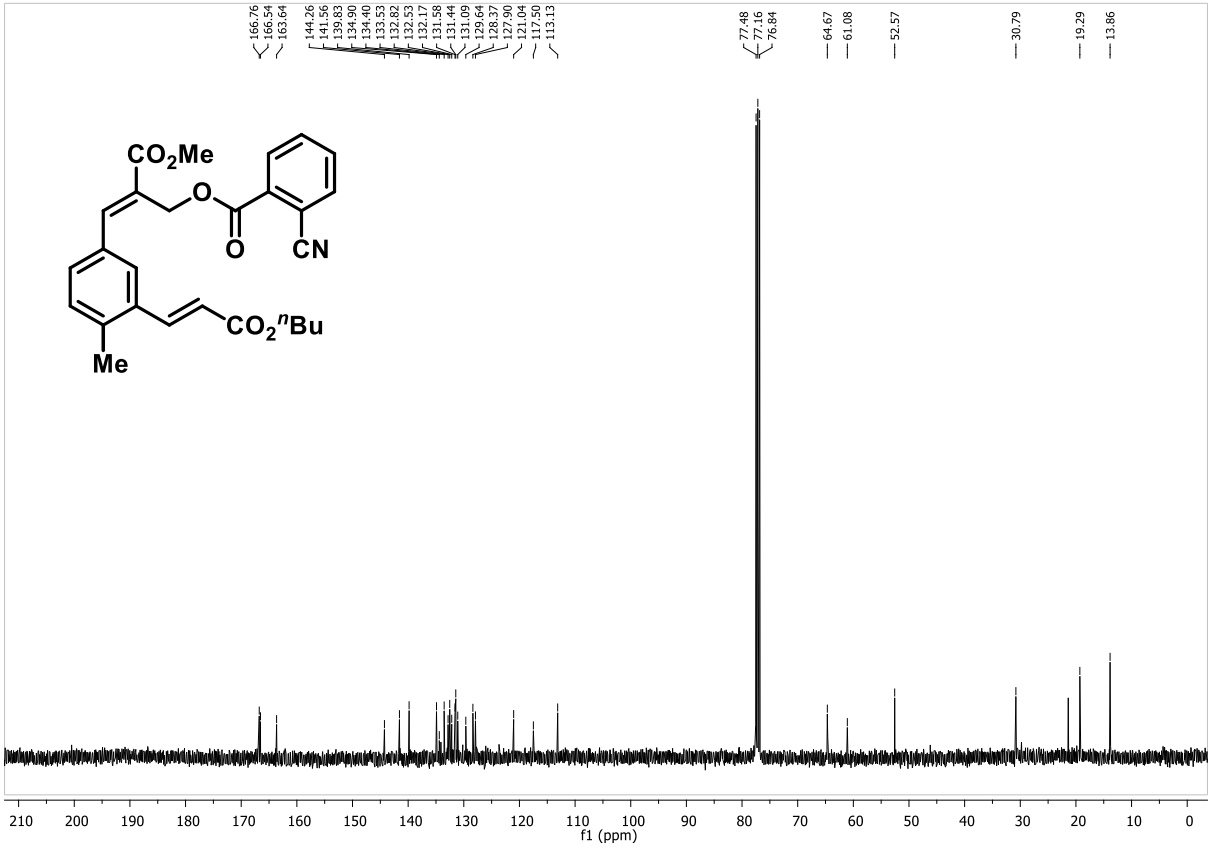
(*E*)-2-(ethoxycarbonyl)-3-(3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)allyl 2-cyanobenzoate (3j)



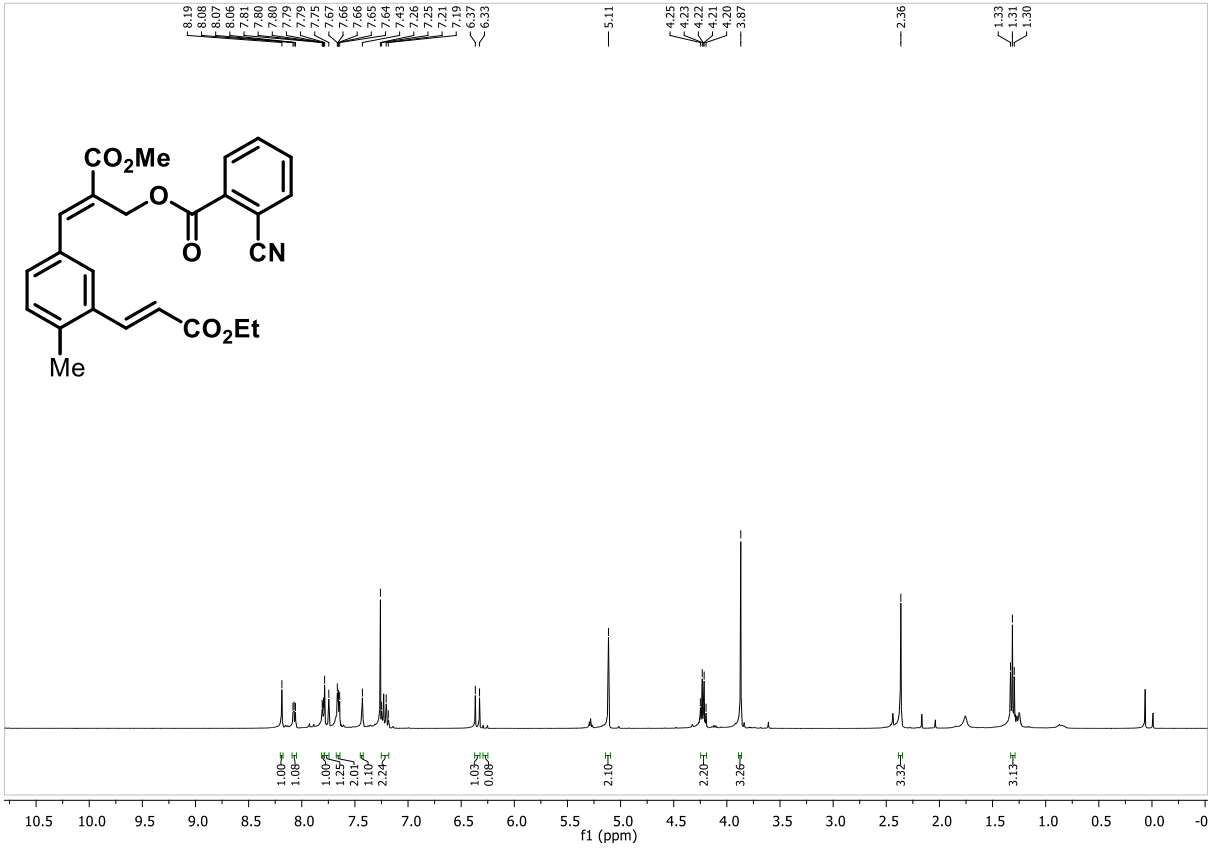


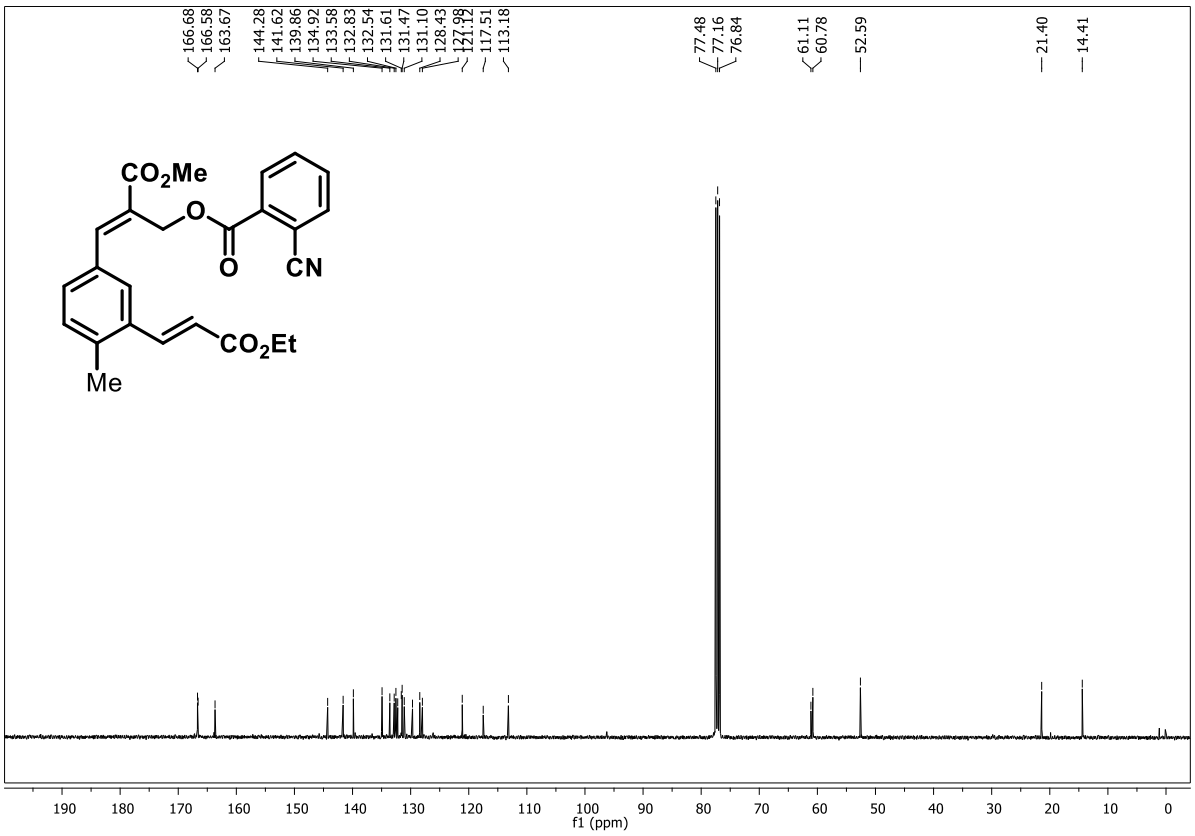
(*E*)-3-(3-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3k)



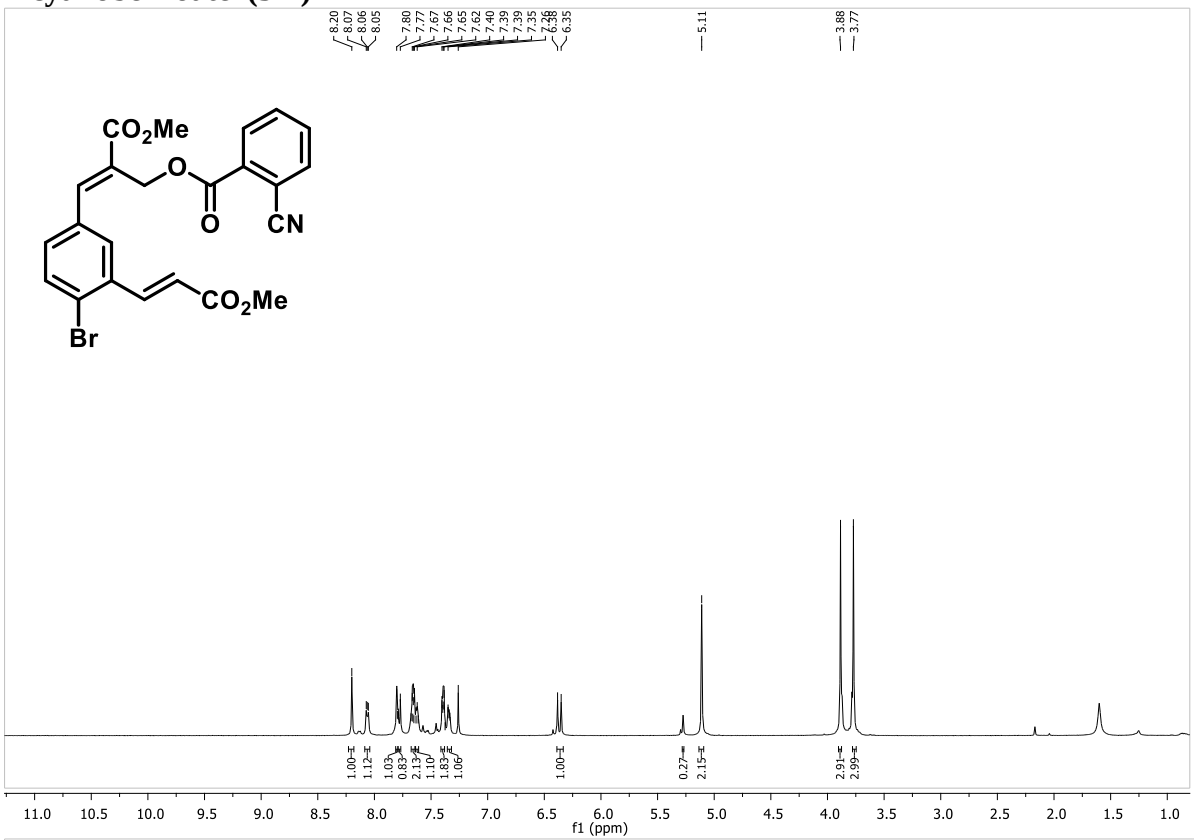


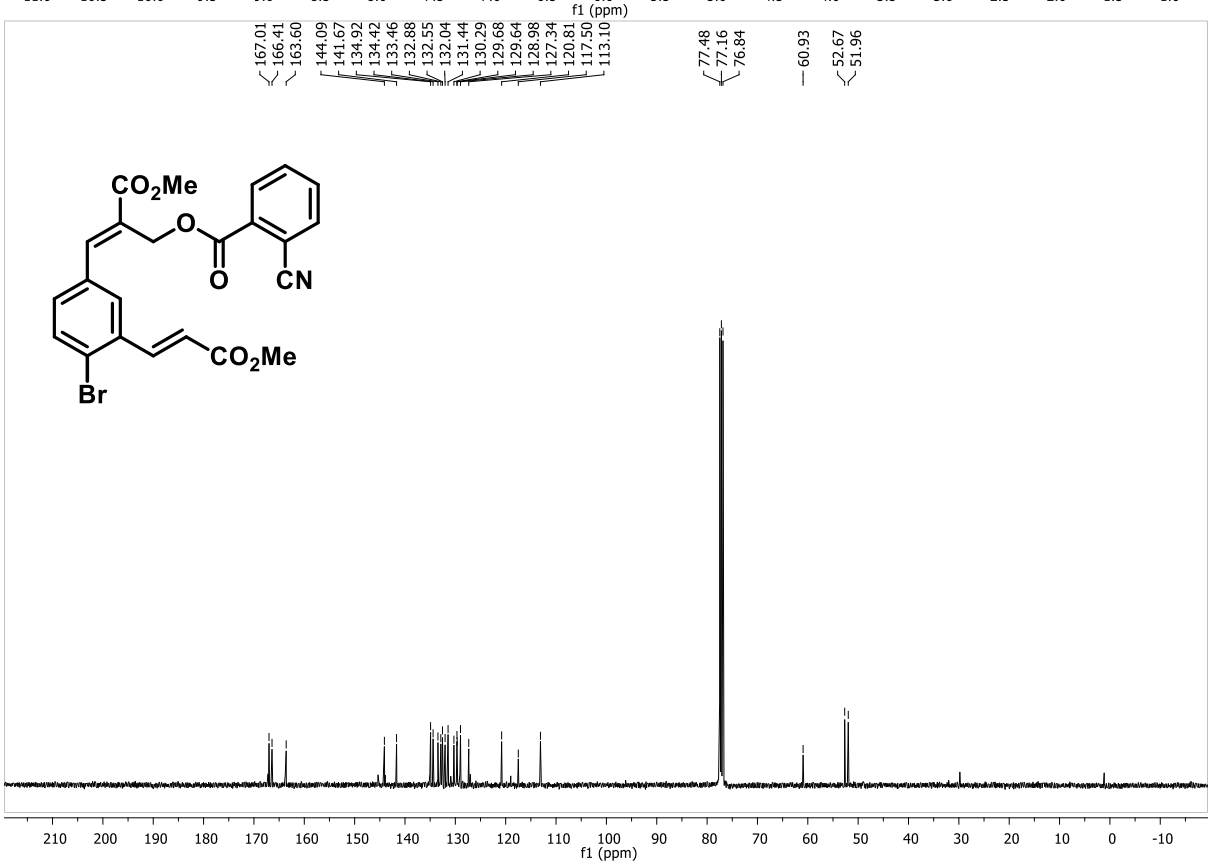
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3l)



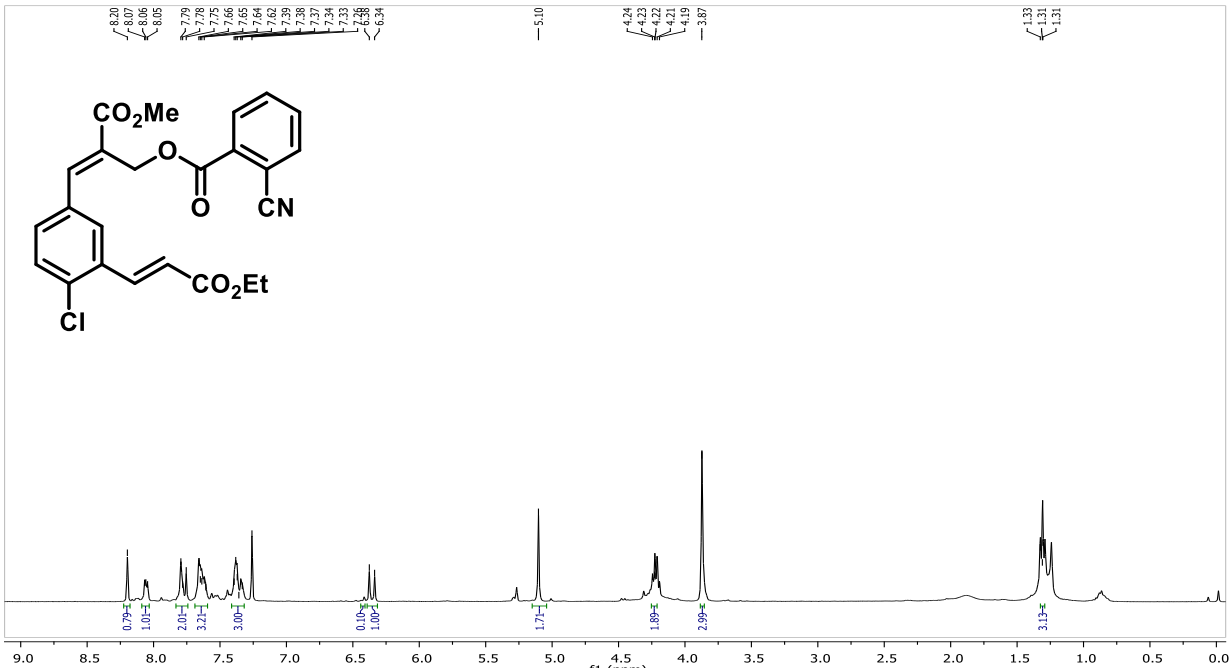


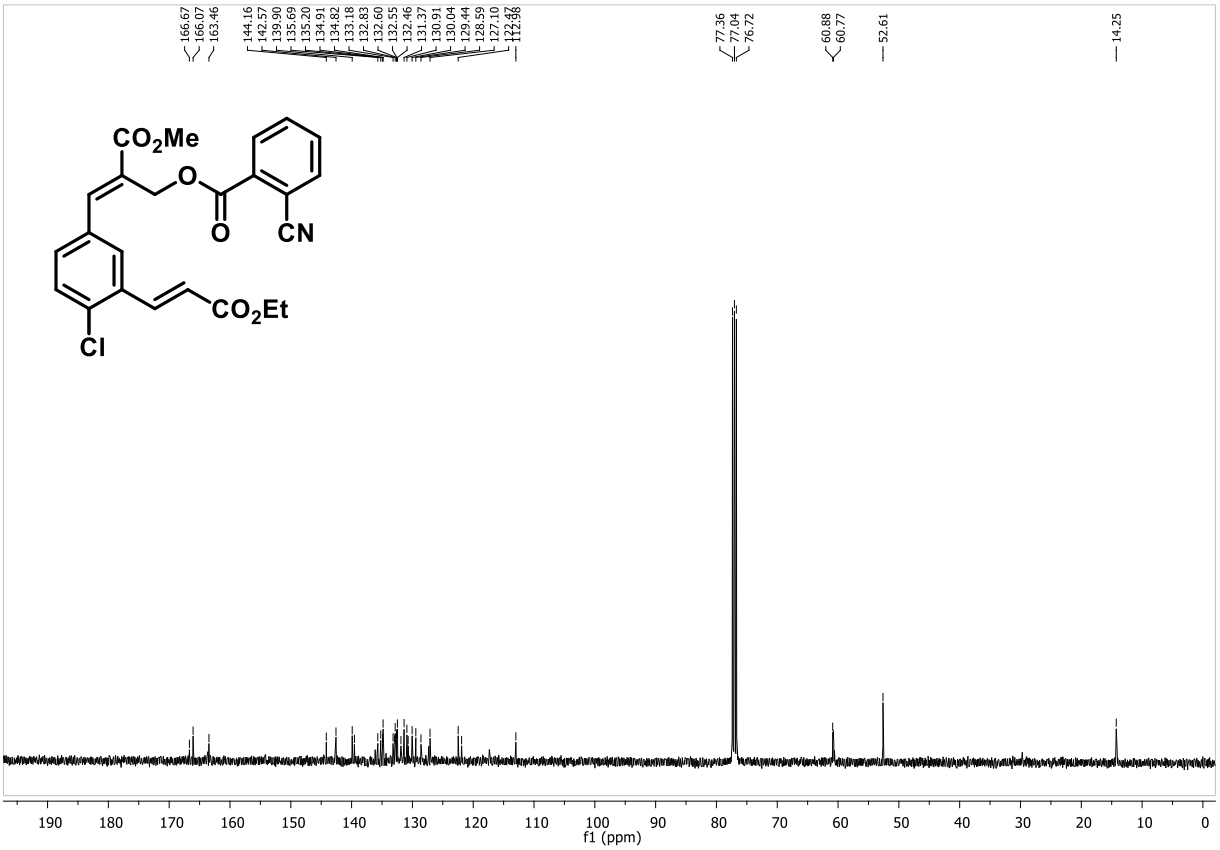
(*E*)-3-(4-bromo-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3m)



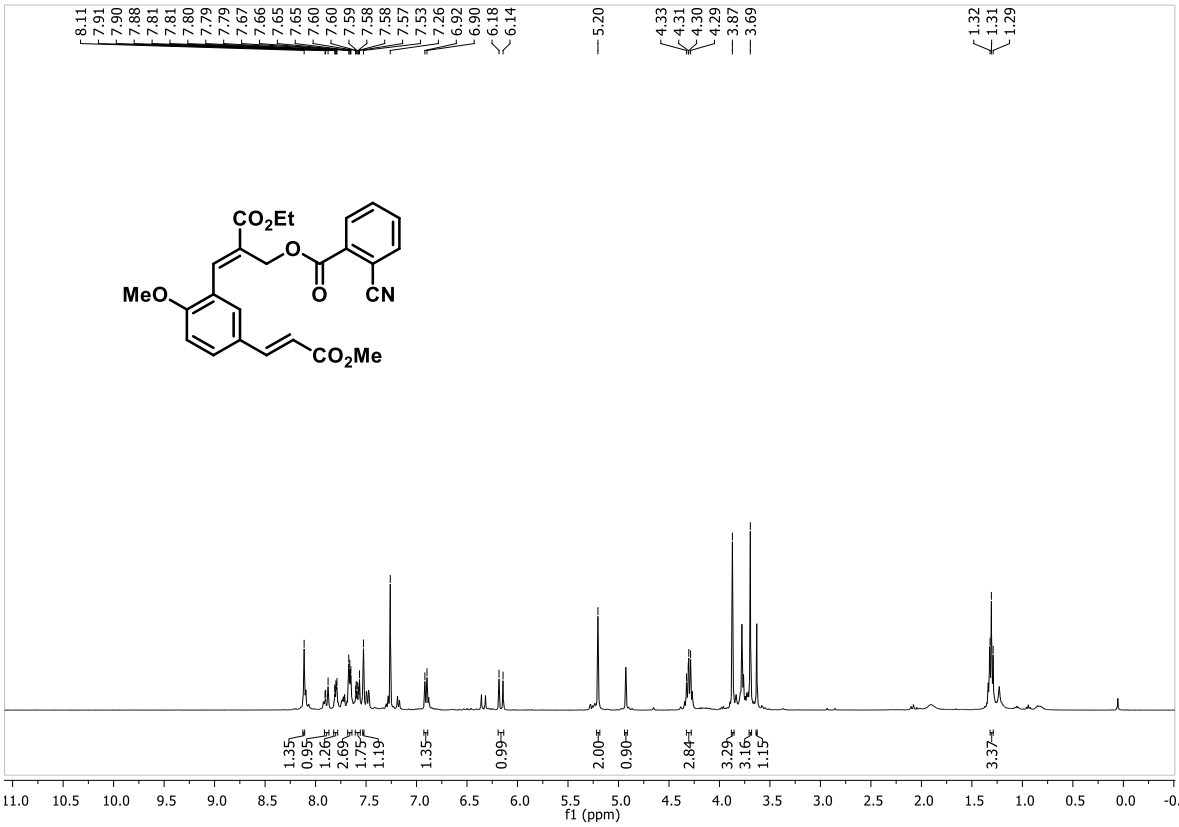


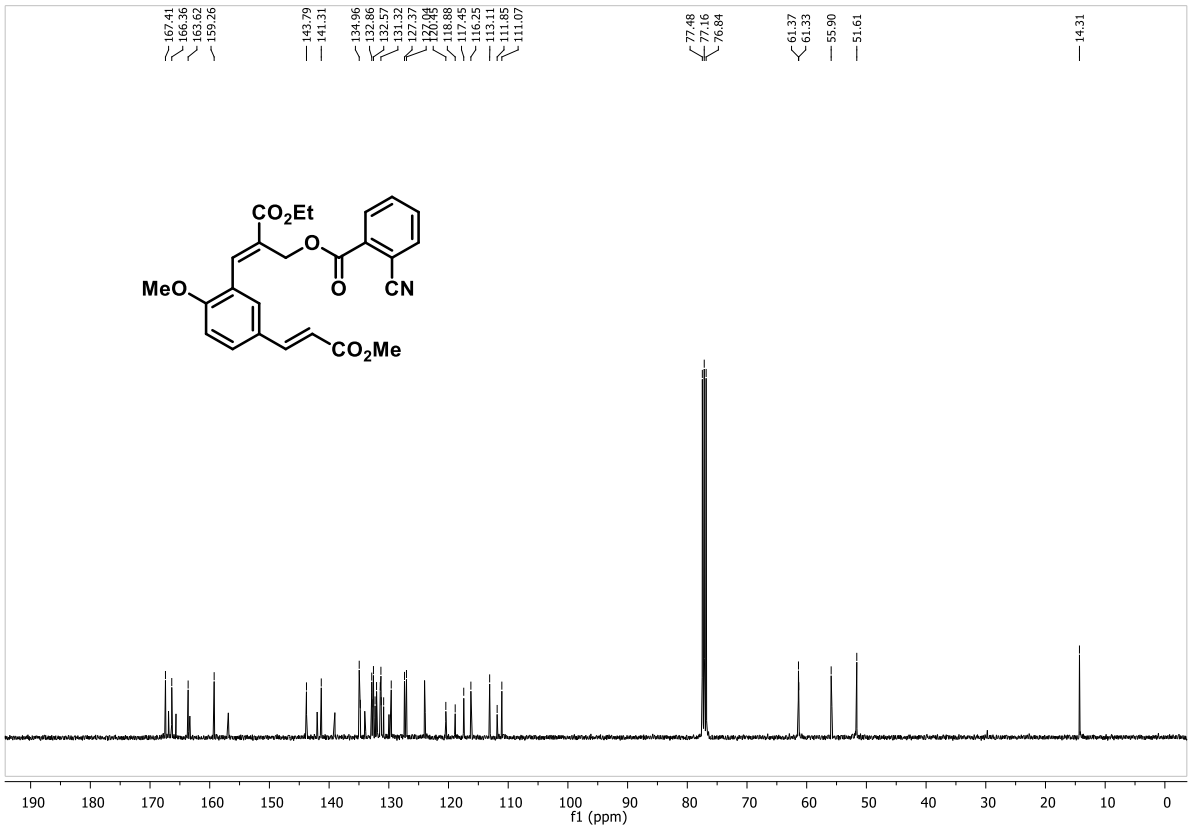
(*E*)-3-(4-chloro-3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3n)



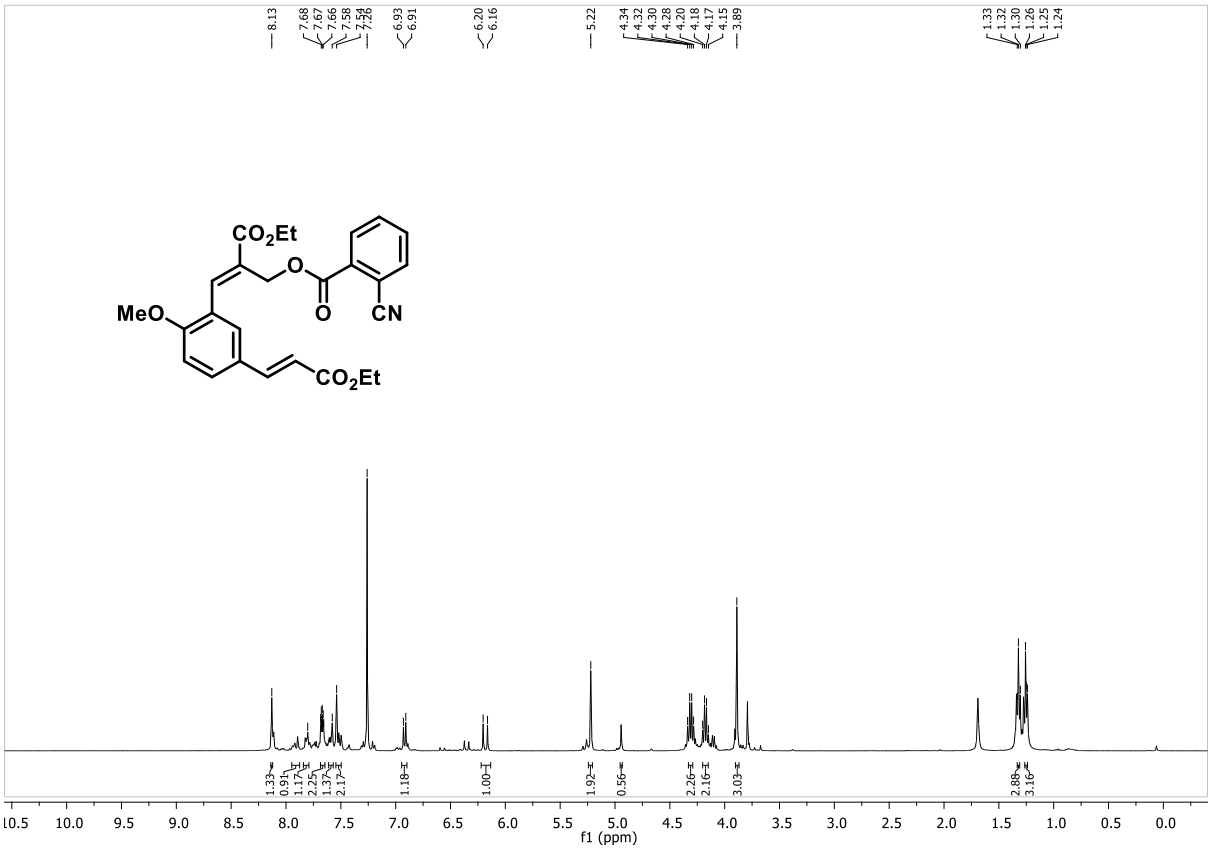


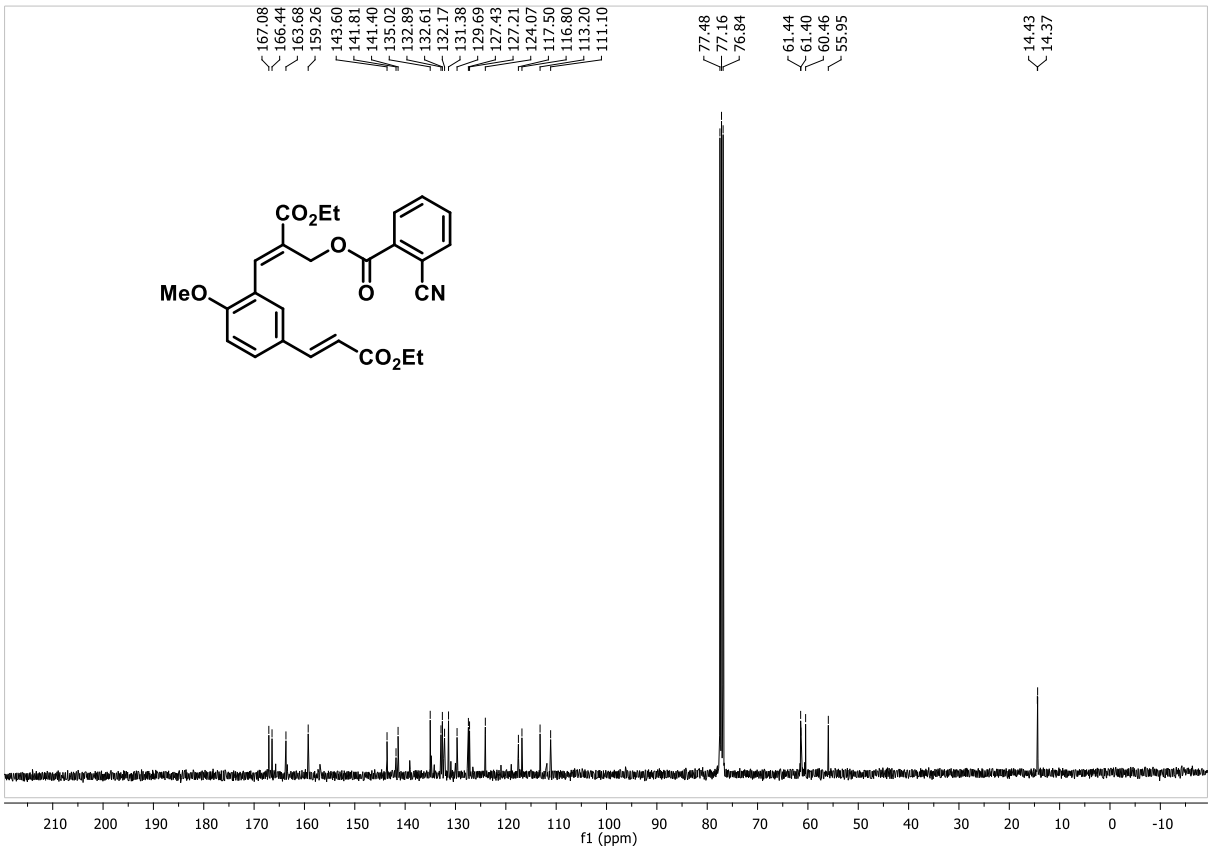
(*E*)-2-(ethoxycarbonyl)-3-(2-methoxy-5-((*E*)-3-methoxy-3-oxoprop-1-en-1yl)phenyl)allyl 2-cyanobenzoate (3o)



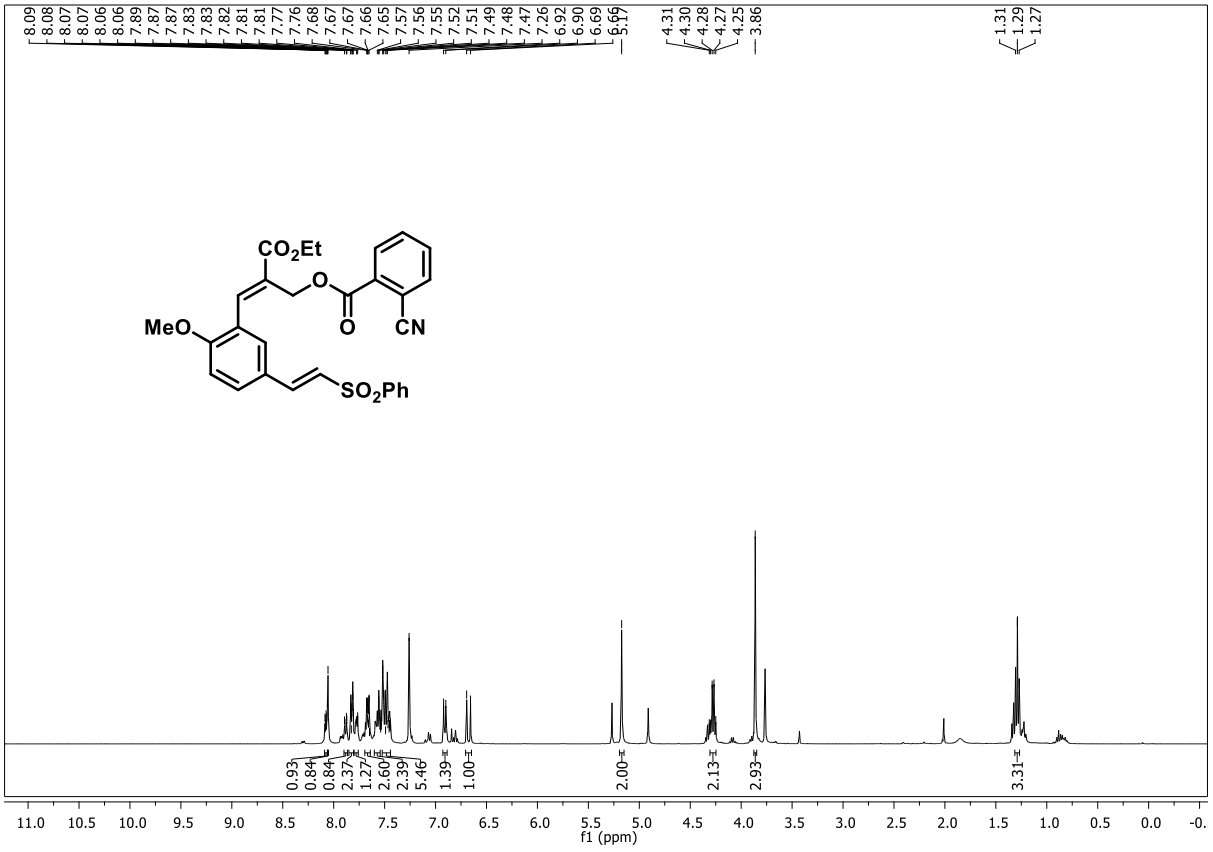


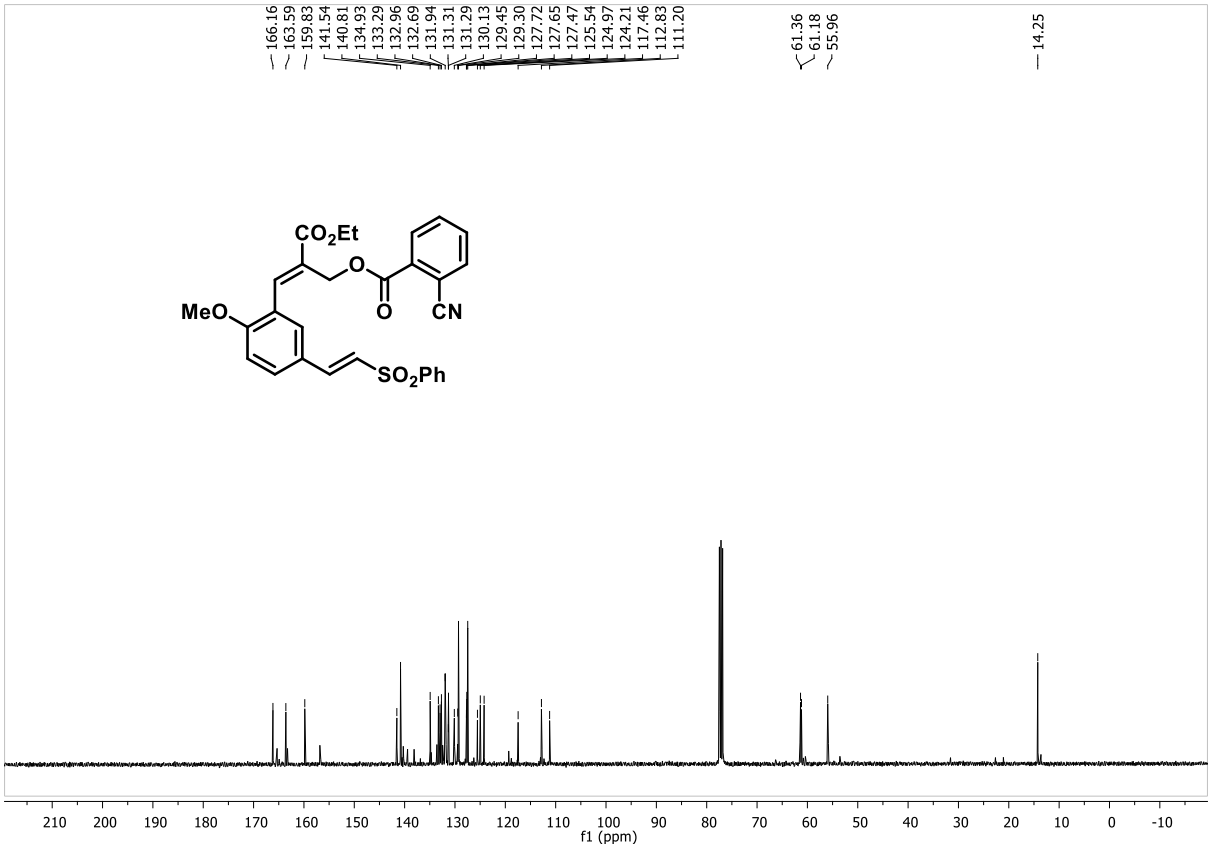
(*E*)-3-(3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-methoxyphenyl)-2-(ethoxycarbonyl)allyl 2-cyanobenzoate (3p)



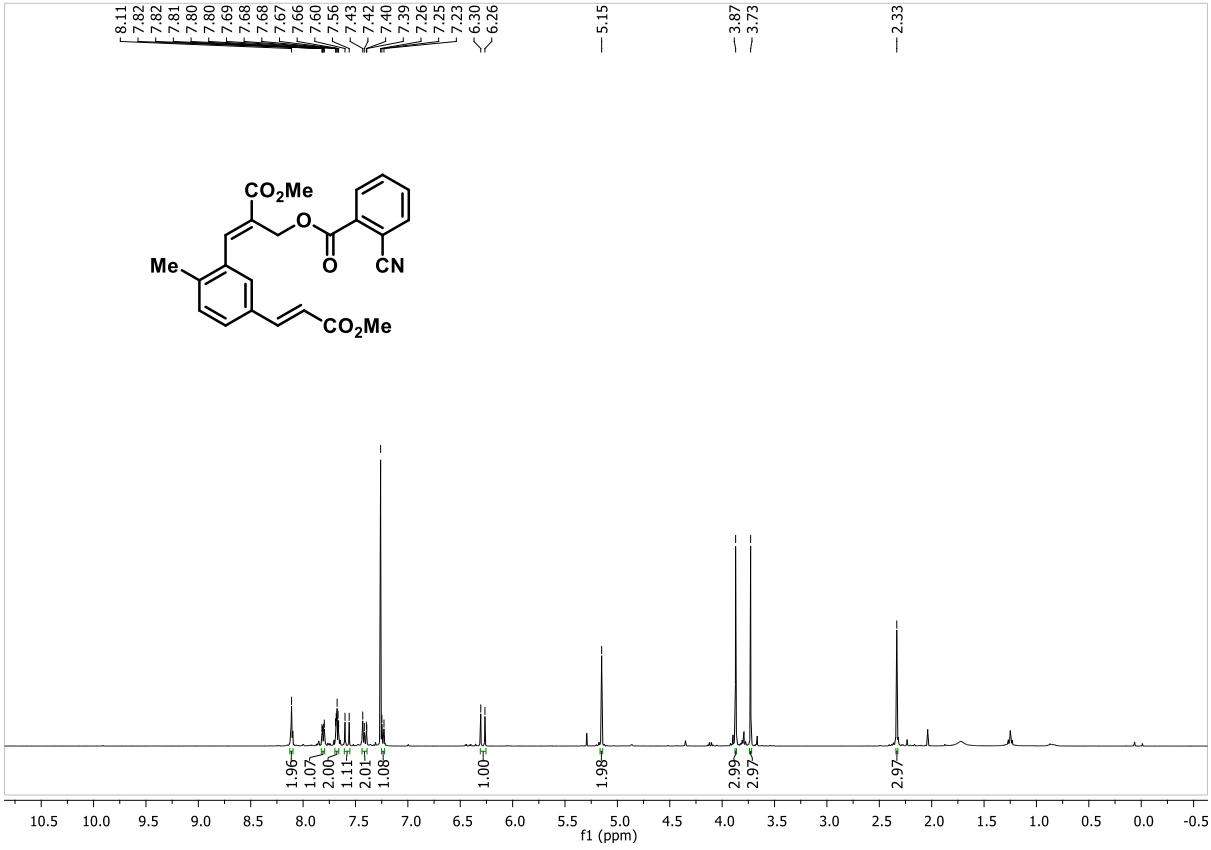


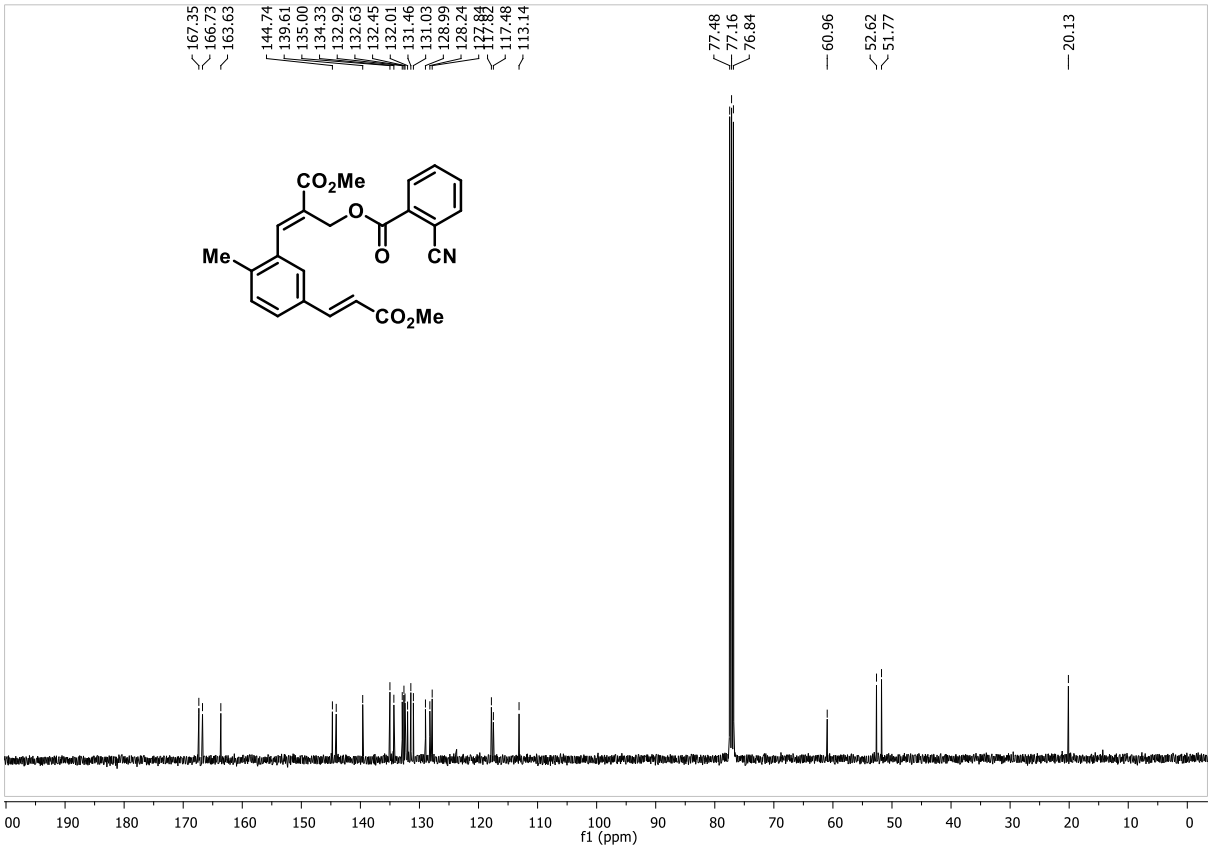
(*Z*)-2-(ethoxycarbonyl)-3-(3-methoxy-5-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)allyl 2-cyanobenzoate (3q)



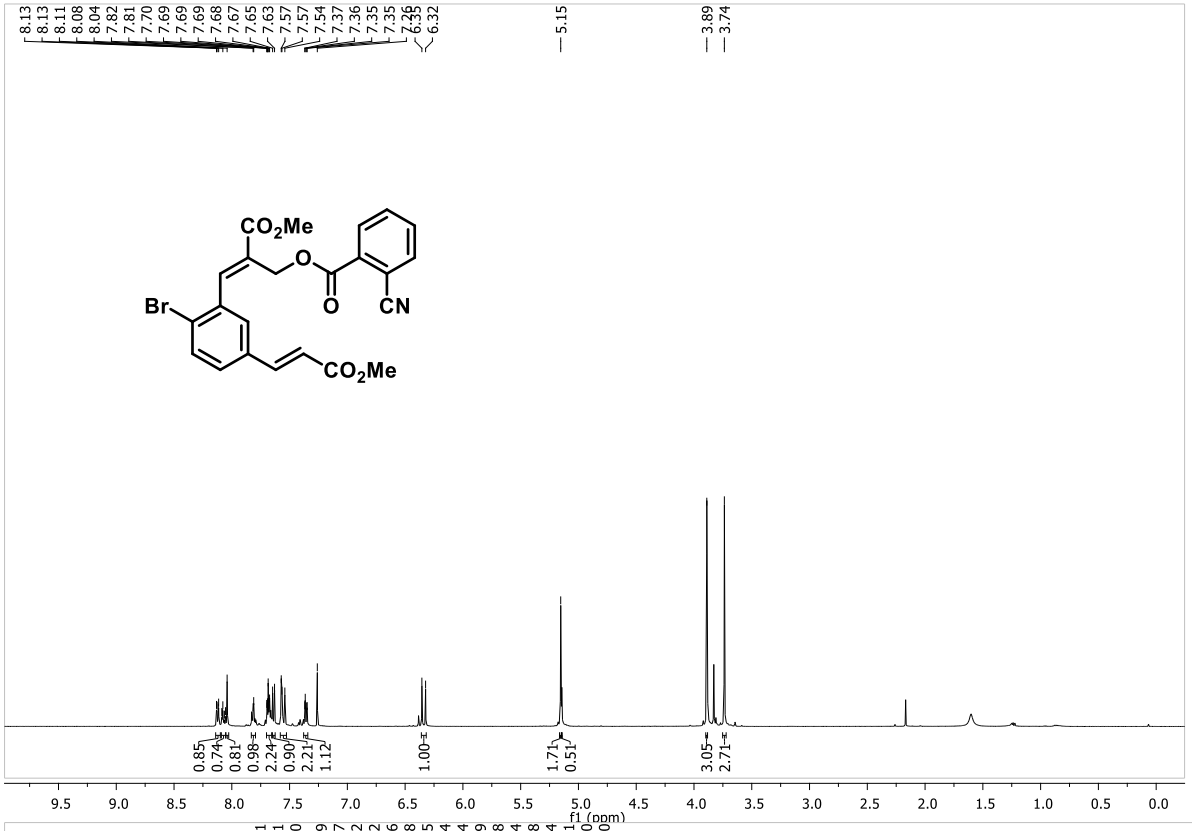


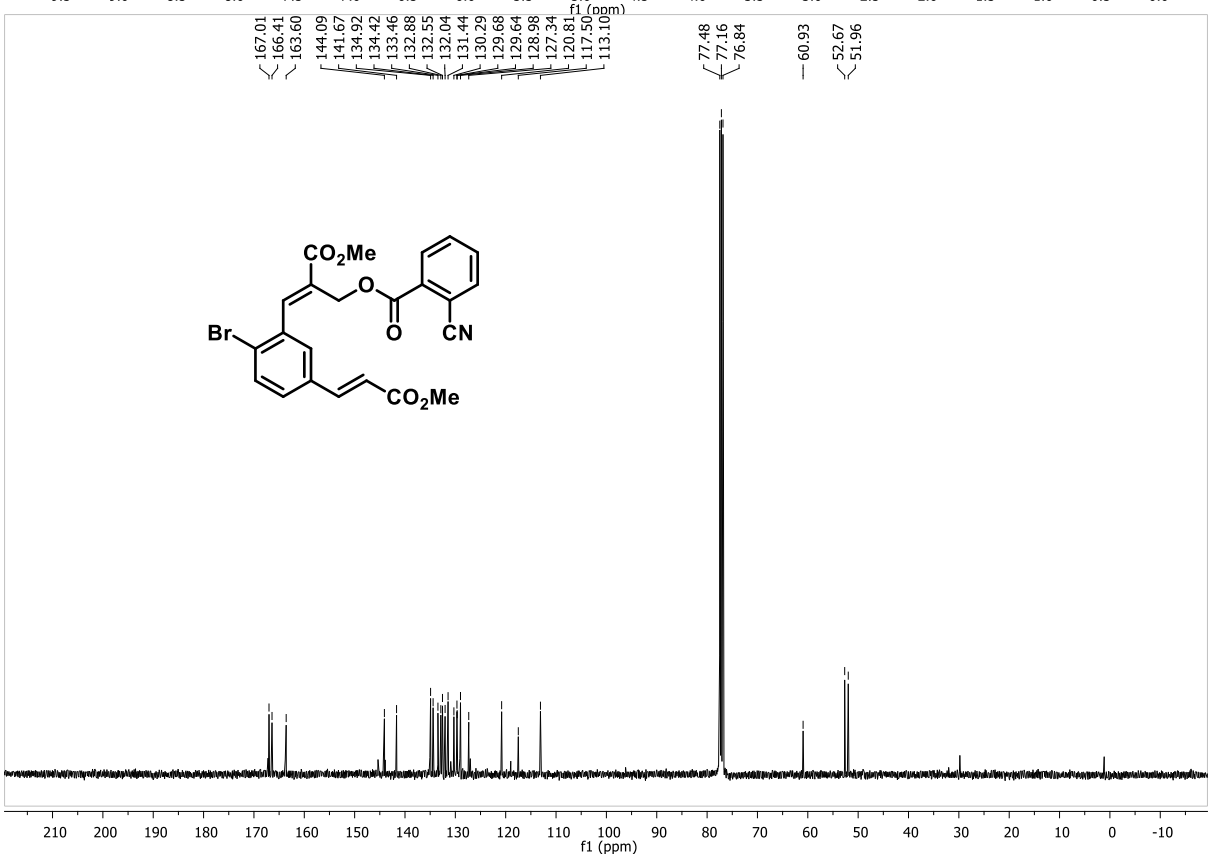
(*E*)-3-(5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-2-methylphenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3r)



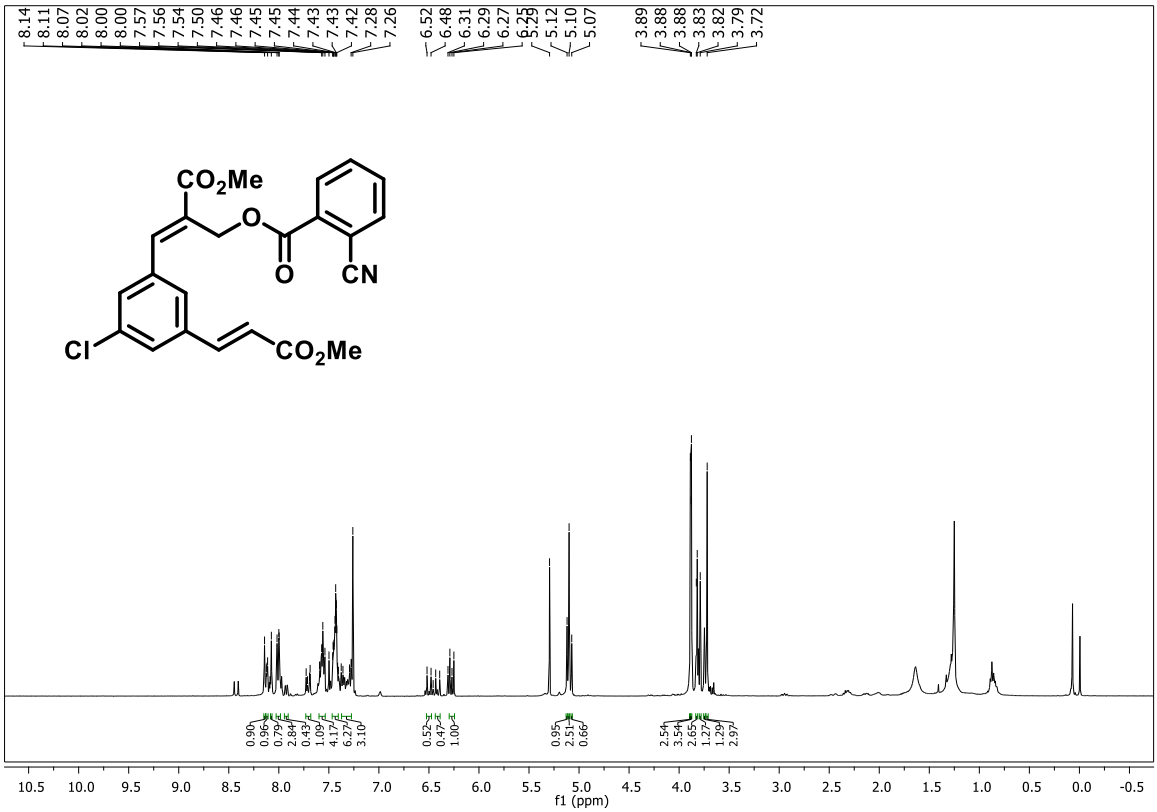


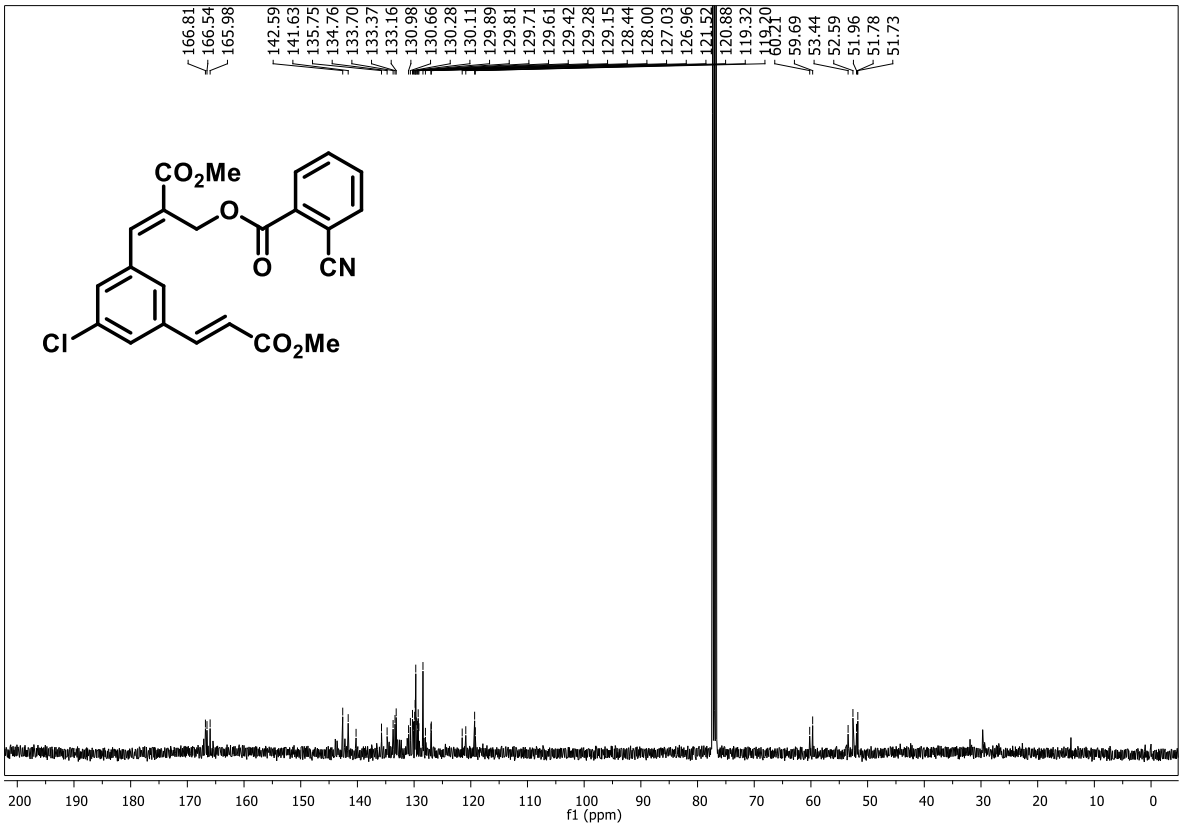
(*E*)-3-(2-bromo-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2(methoxycarbonyl)allyl 2-cyanobenzoate (3s)



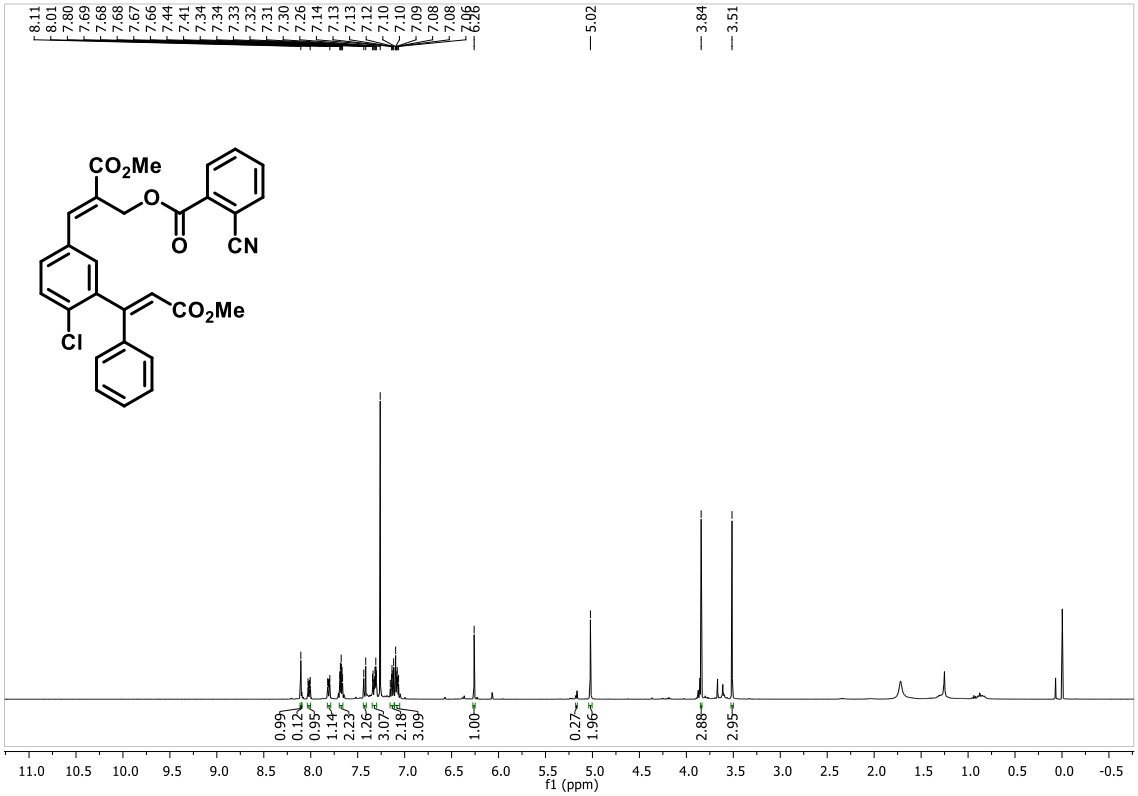


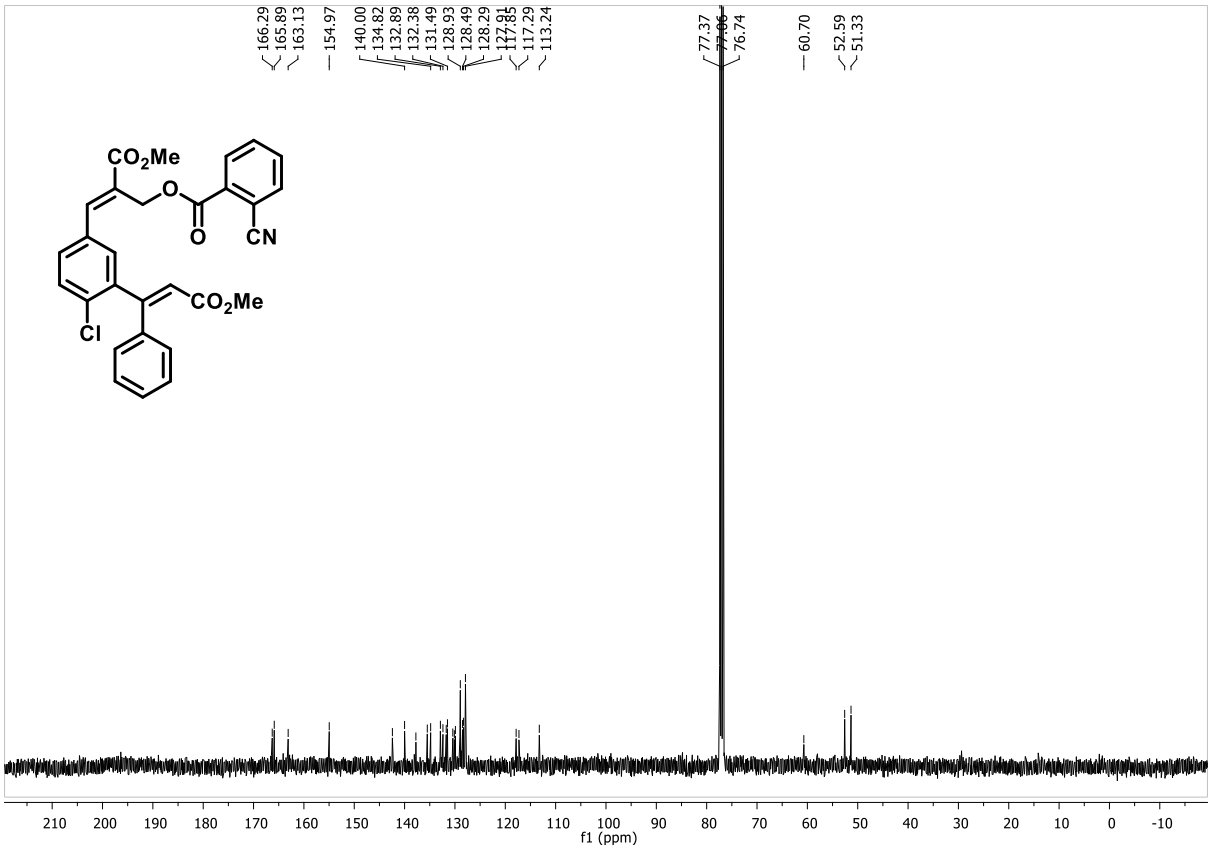
(*E*)-3-(3-chloro-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3t)



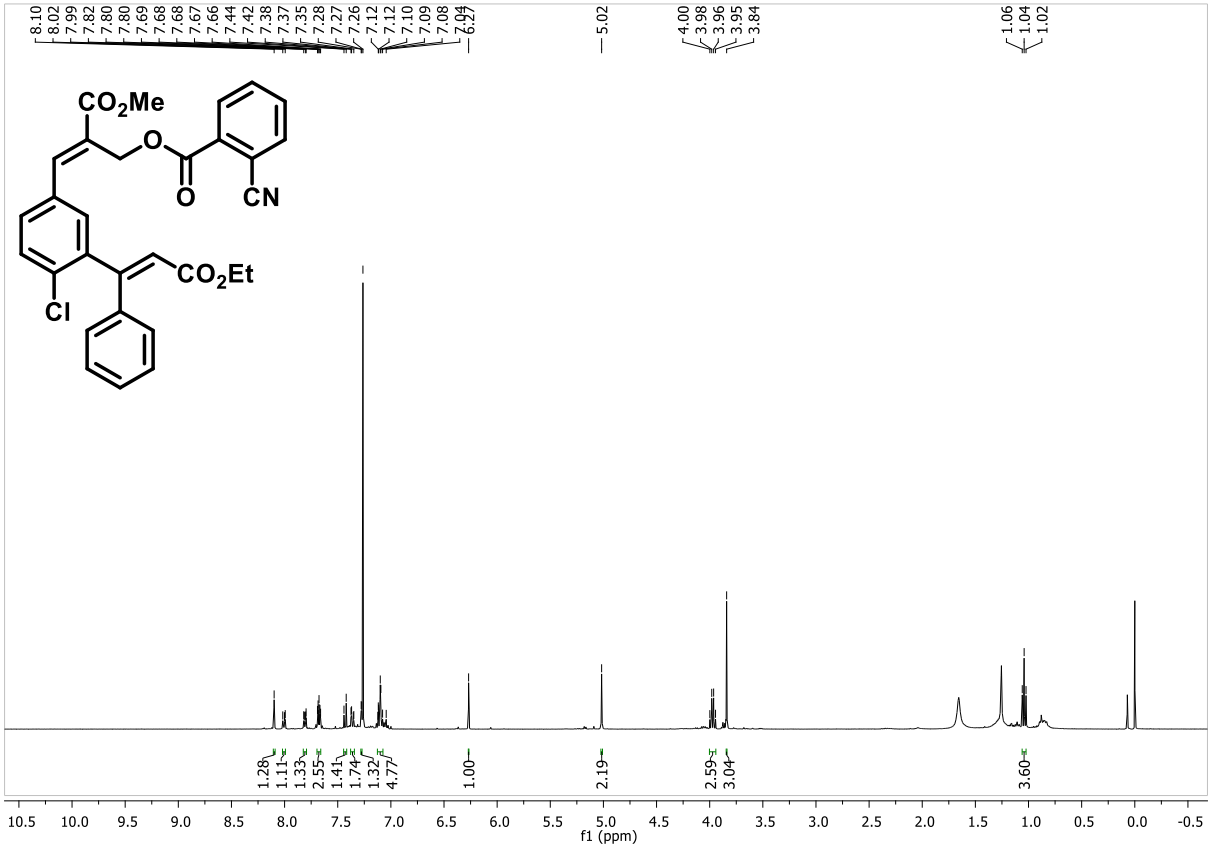


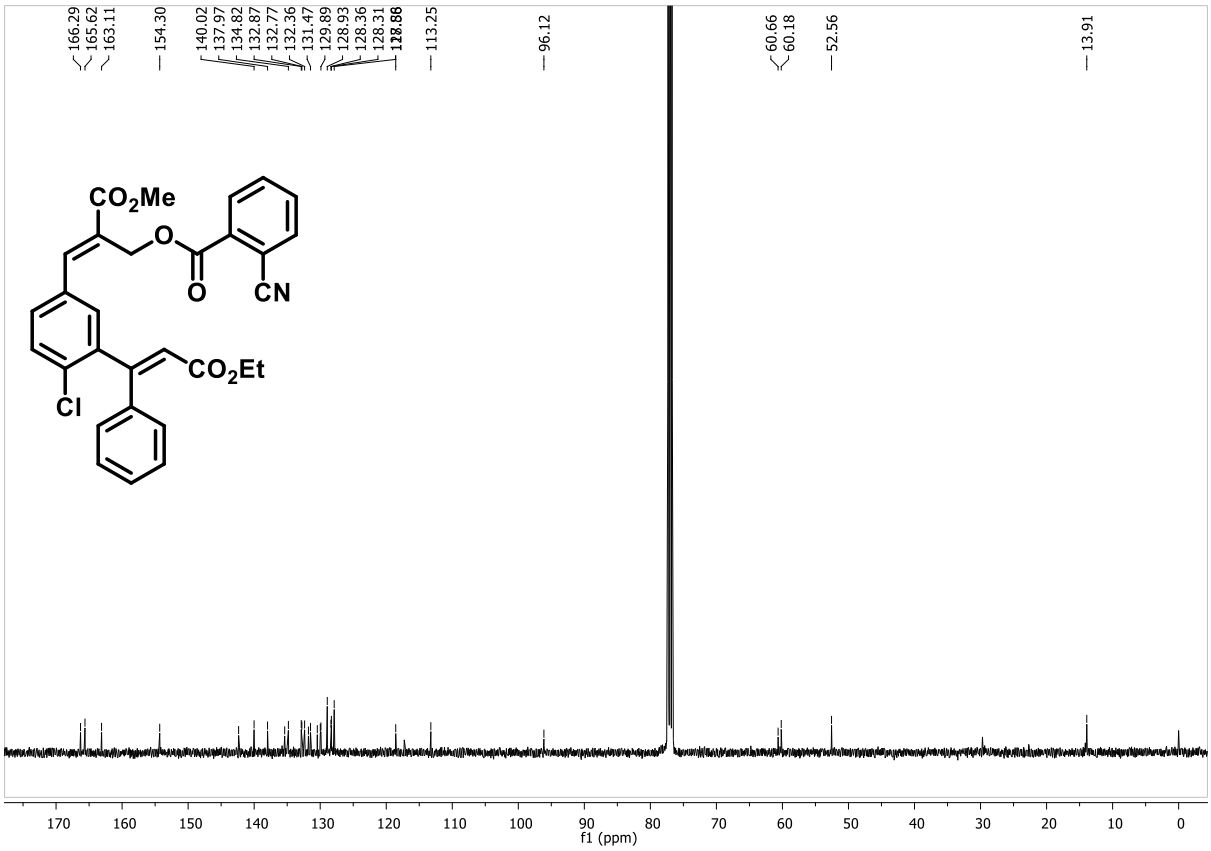
(*E*)-3-(4-chloro-3-((*E*)-3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl) allyl 2-cyanobenzoate (3u)



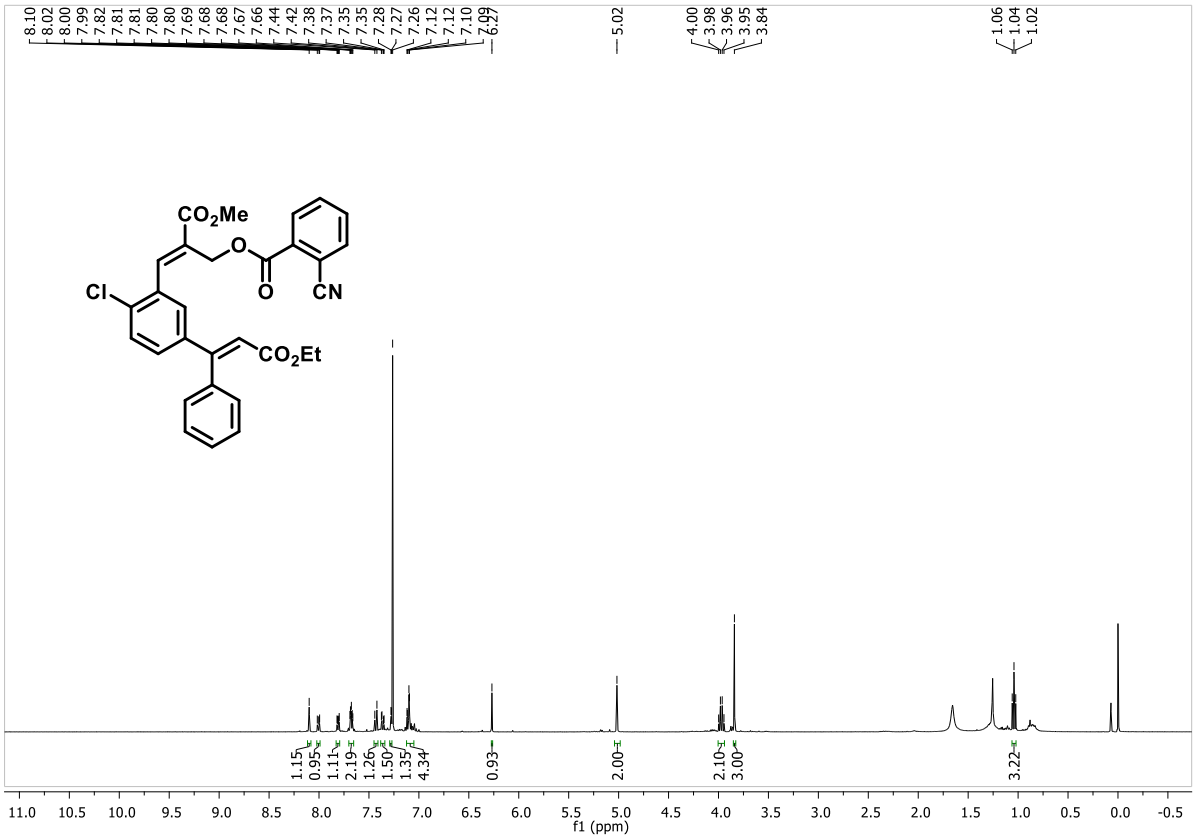


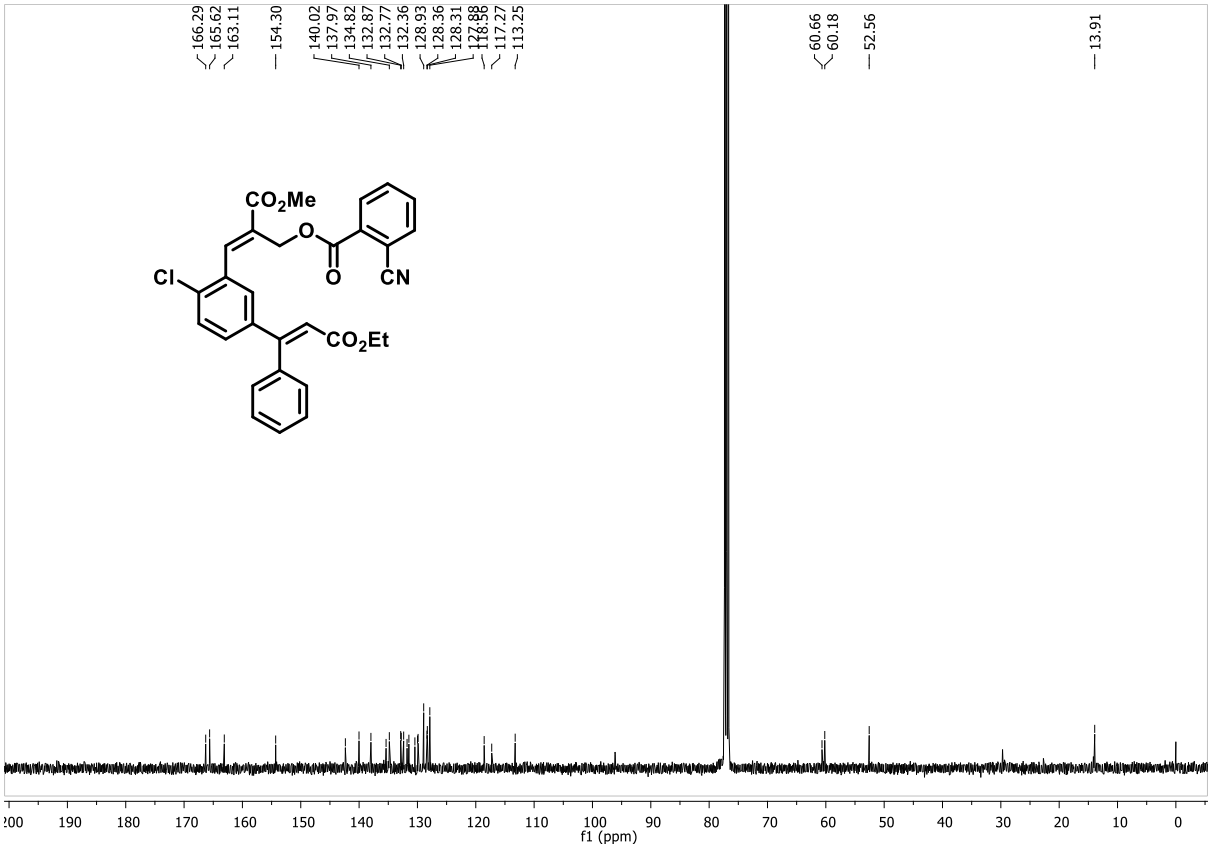
(*E*)-3-(4-chloro-3-((1*E*,3*E*)-5-ethoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3v)



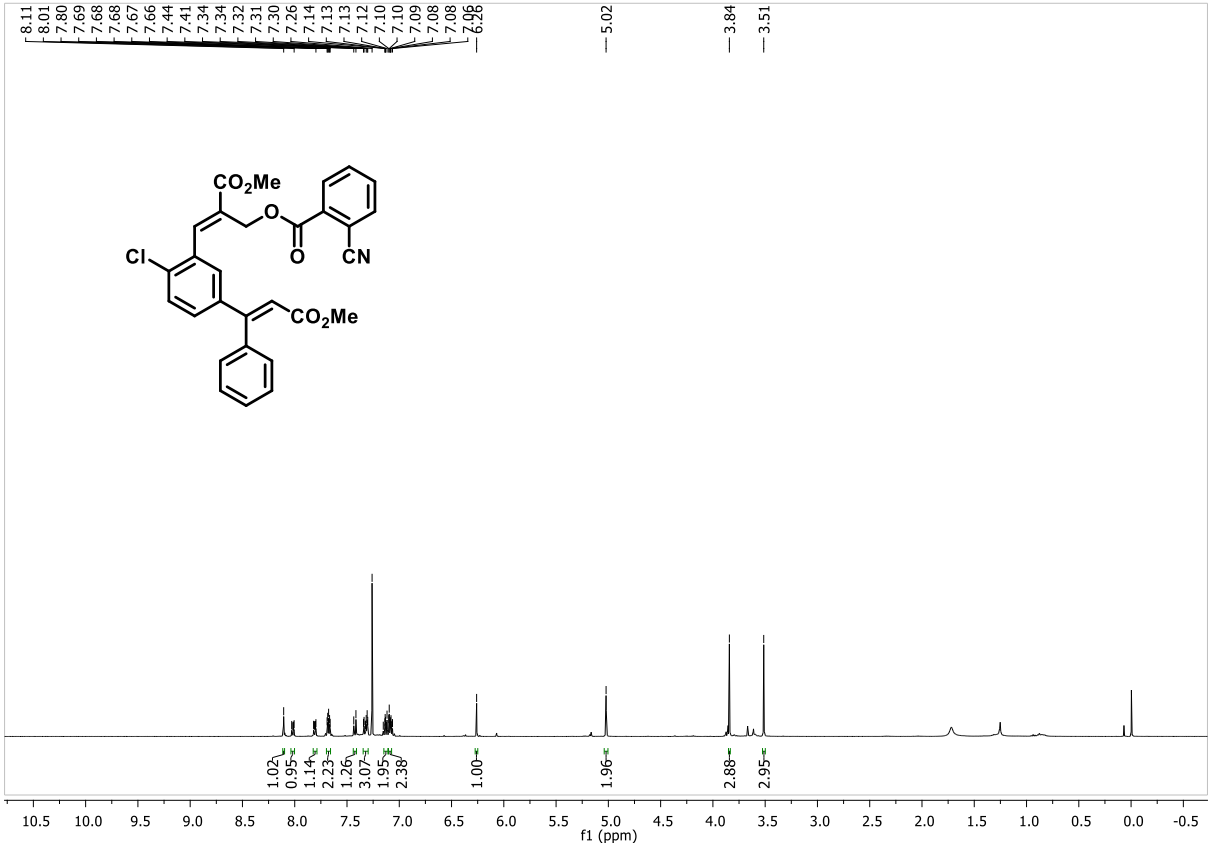


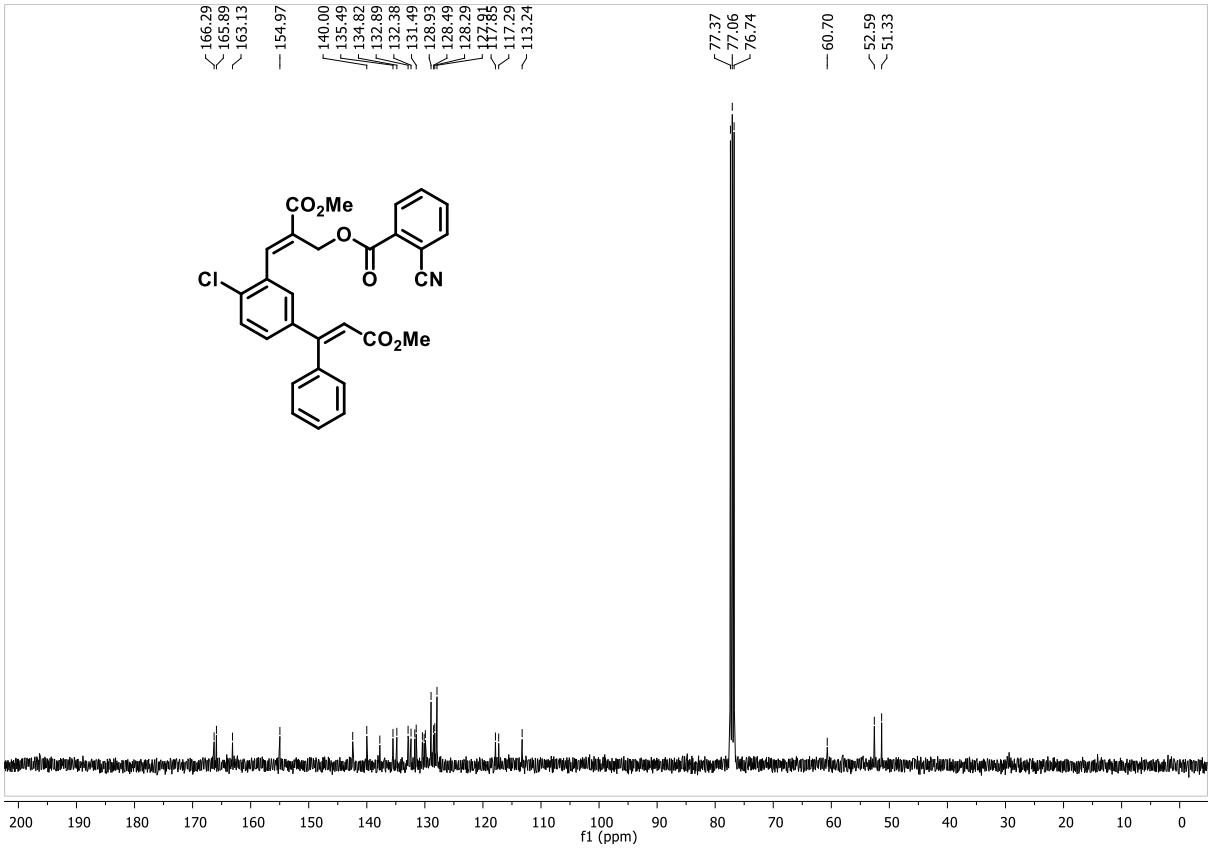
(*E*)-3-(2-chloro-5-((Z)-3-ethoxy-3-oxo-1-phenylprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3w)



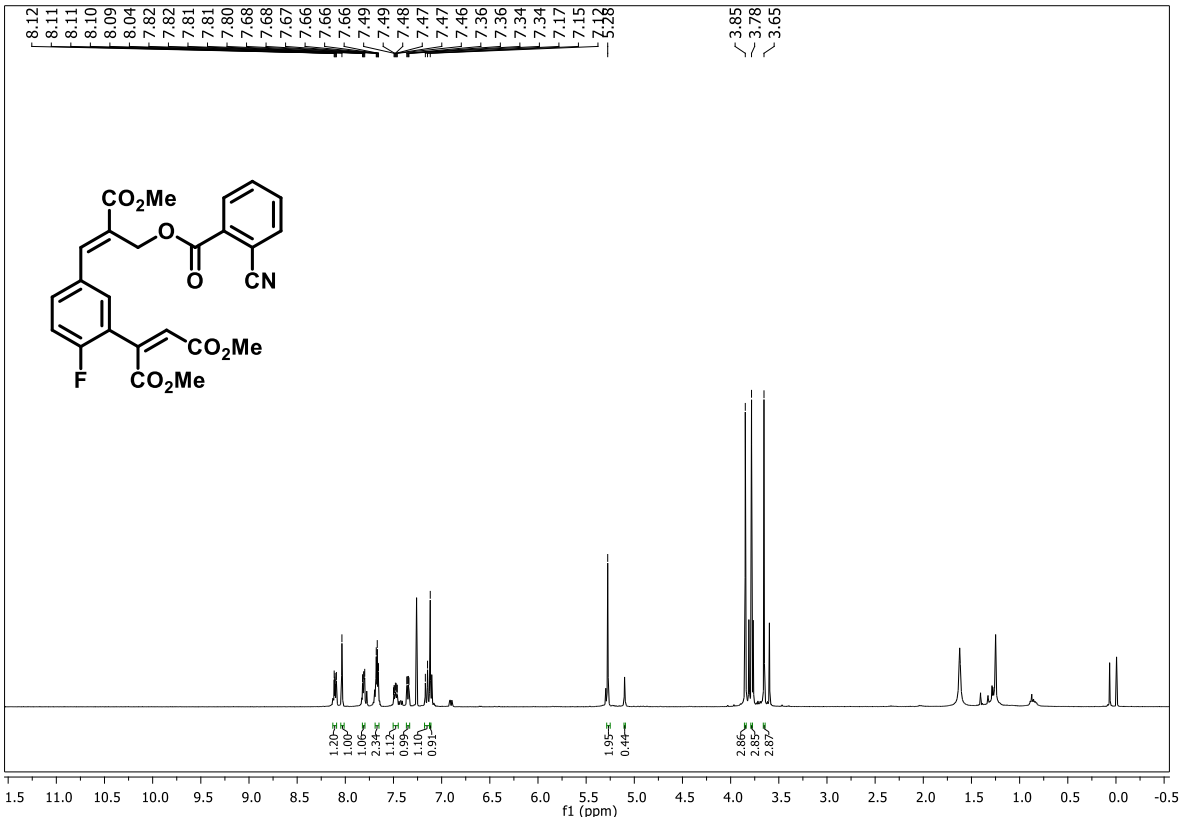


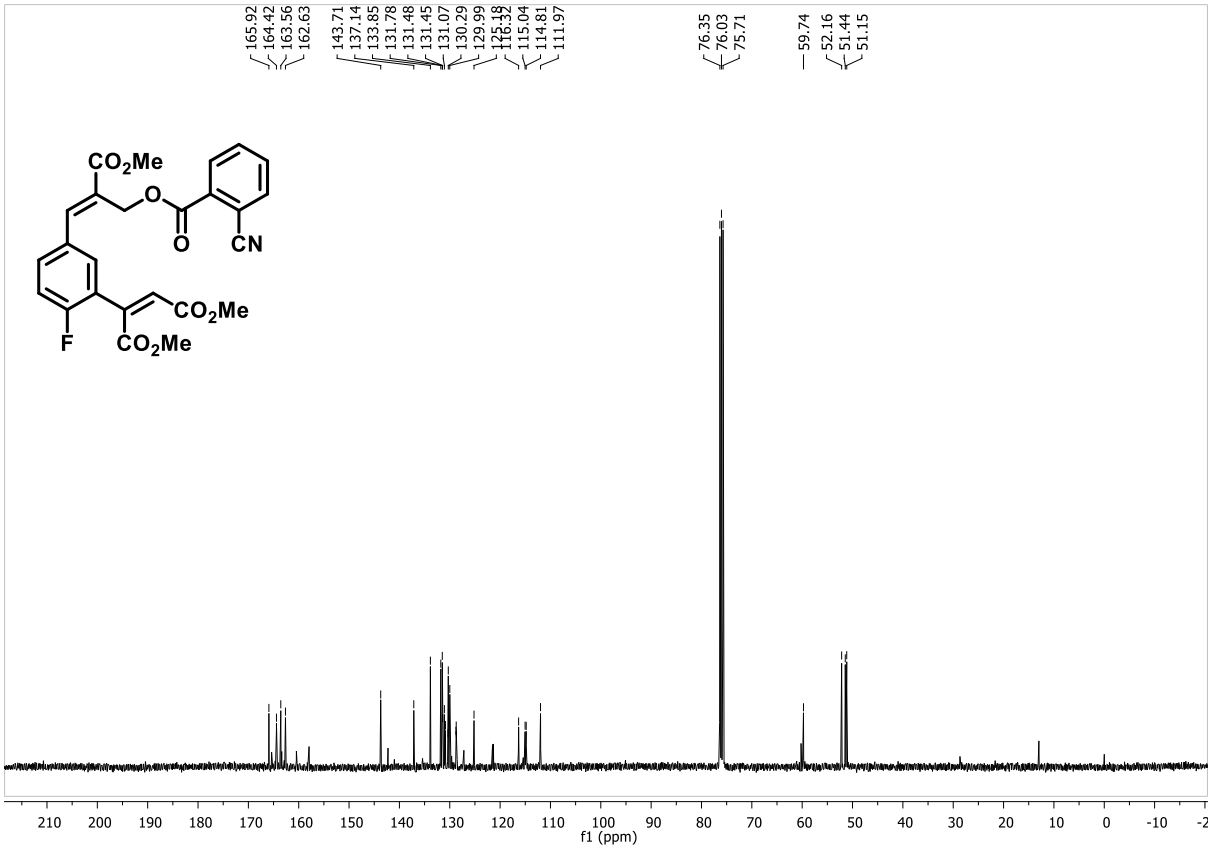
(*E*)-3-(2-chloro-5-((1*E*,3*E*)-5-methoxy-5-oxo-3-phenylpenta-1,3-dien-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3x)



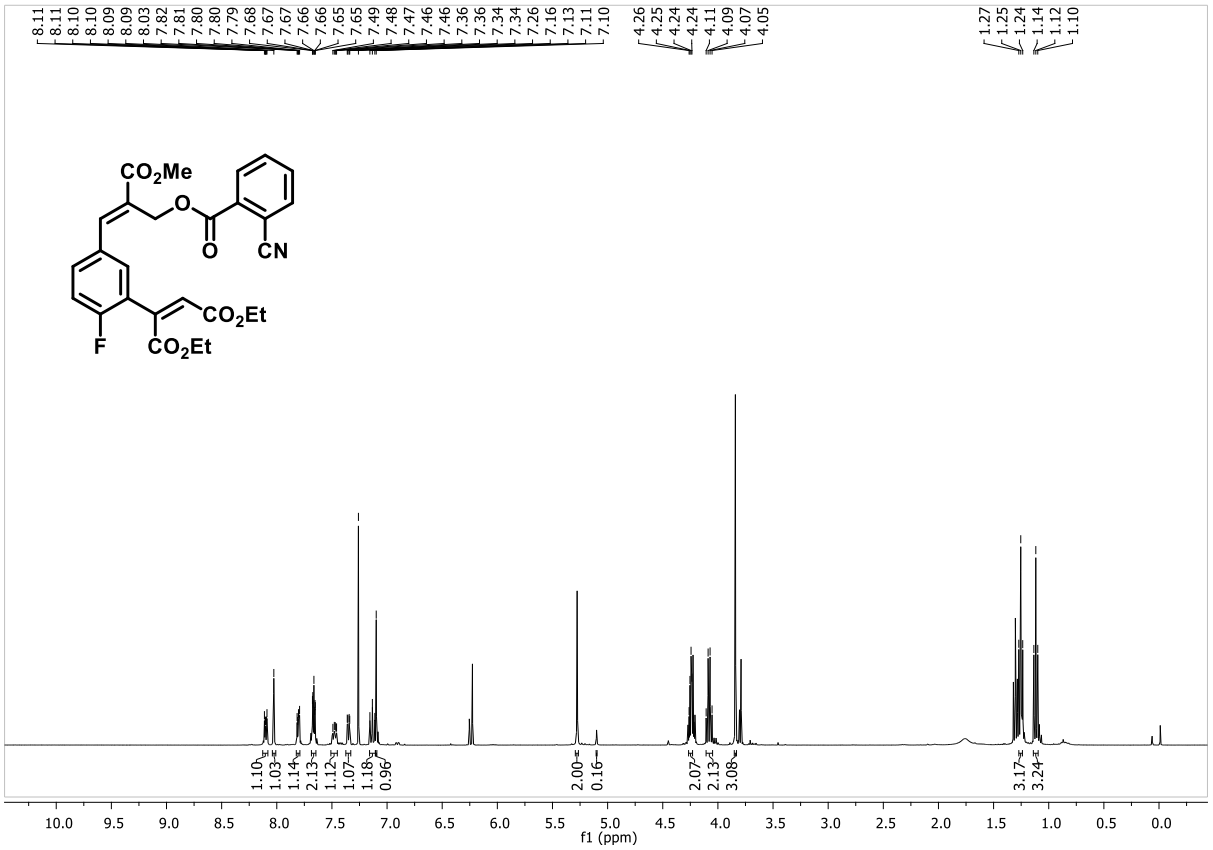


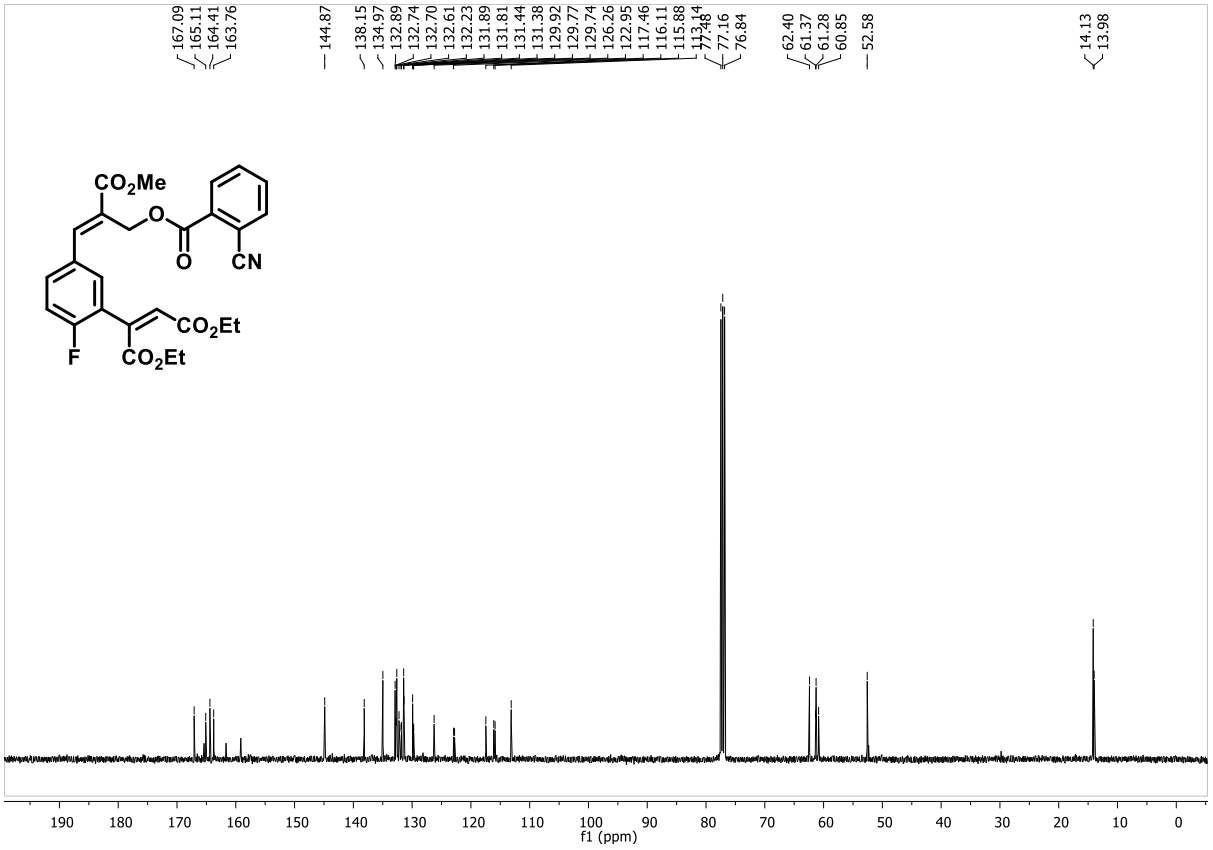
Dimethyl-2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3y)



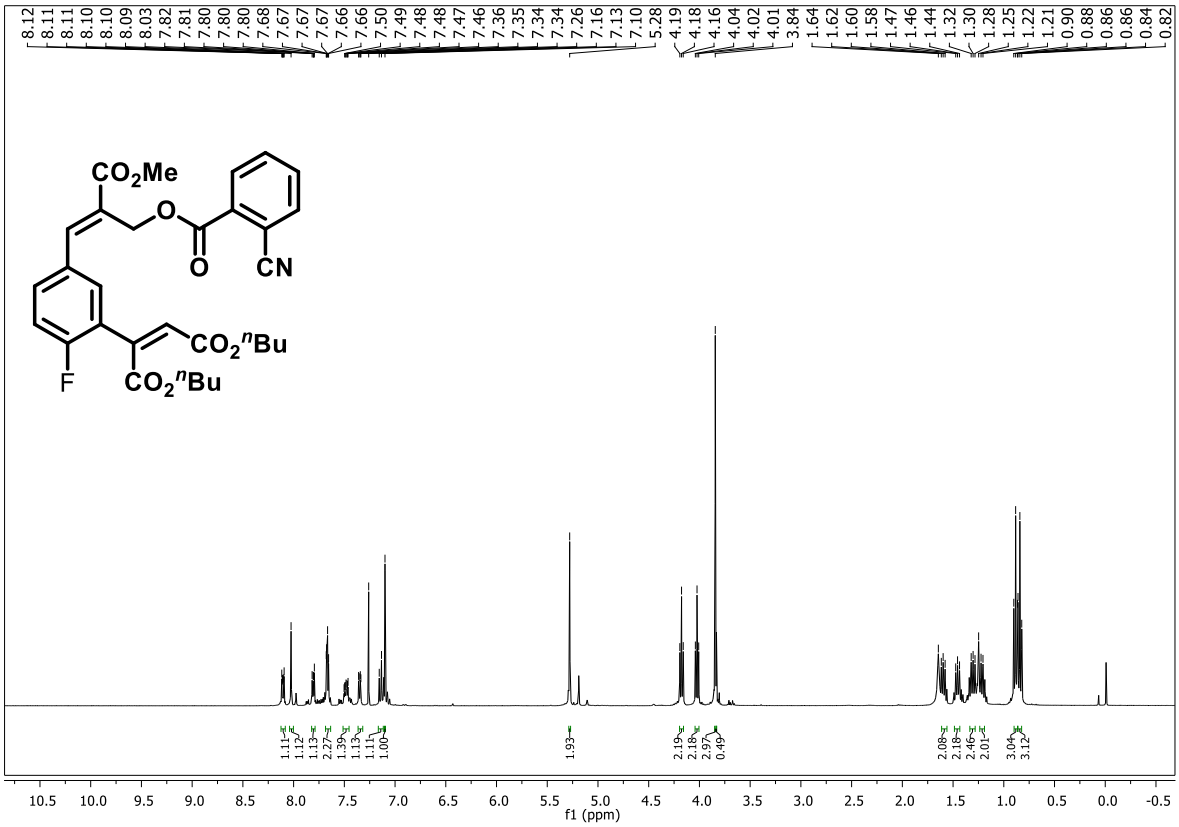


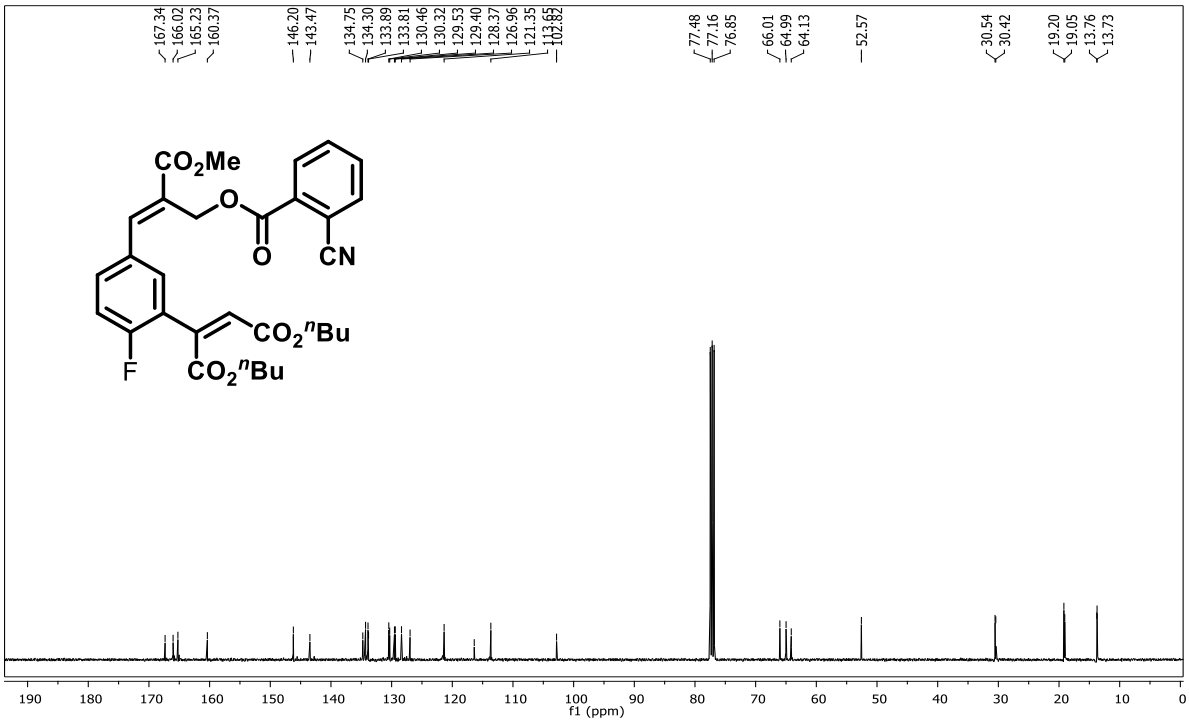
Diethyl-2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3z)



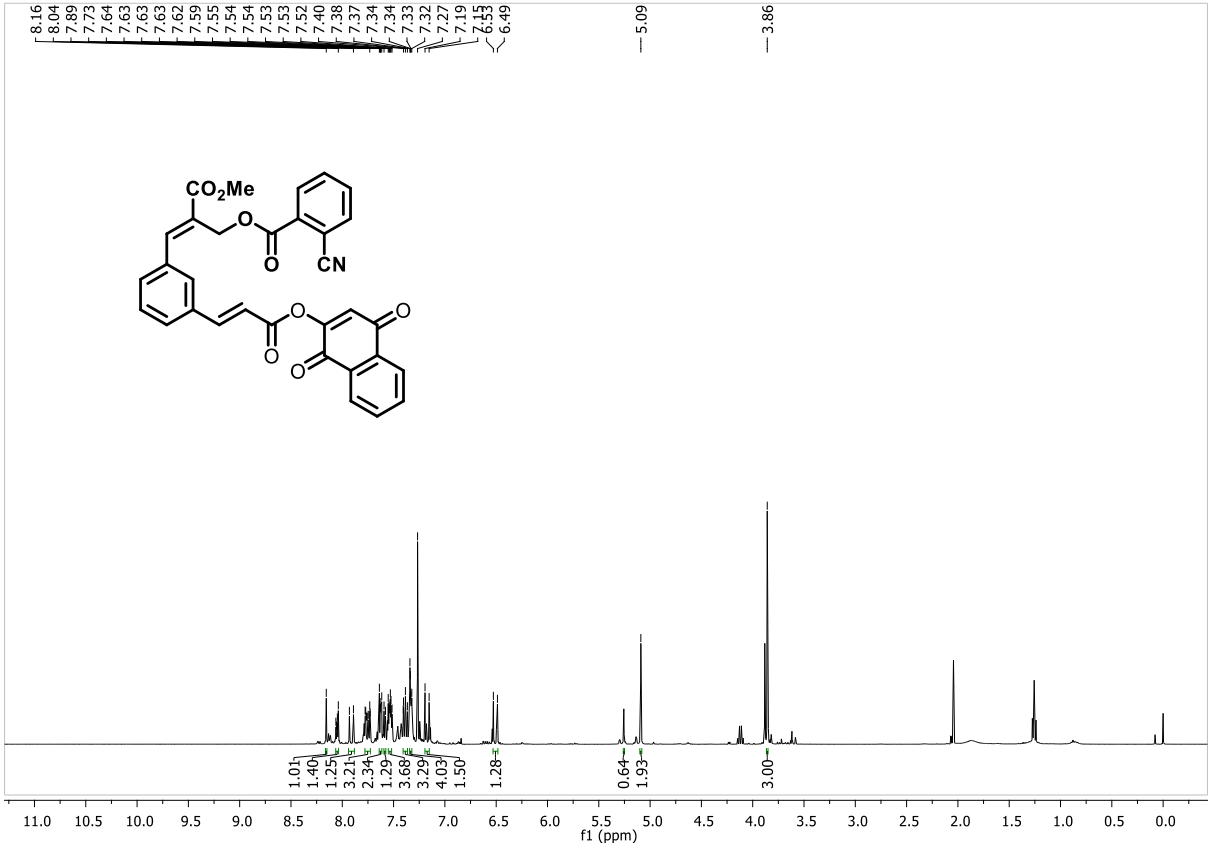


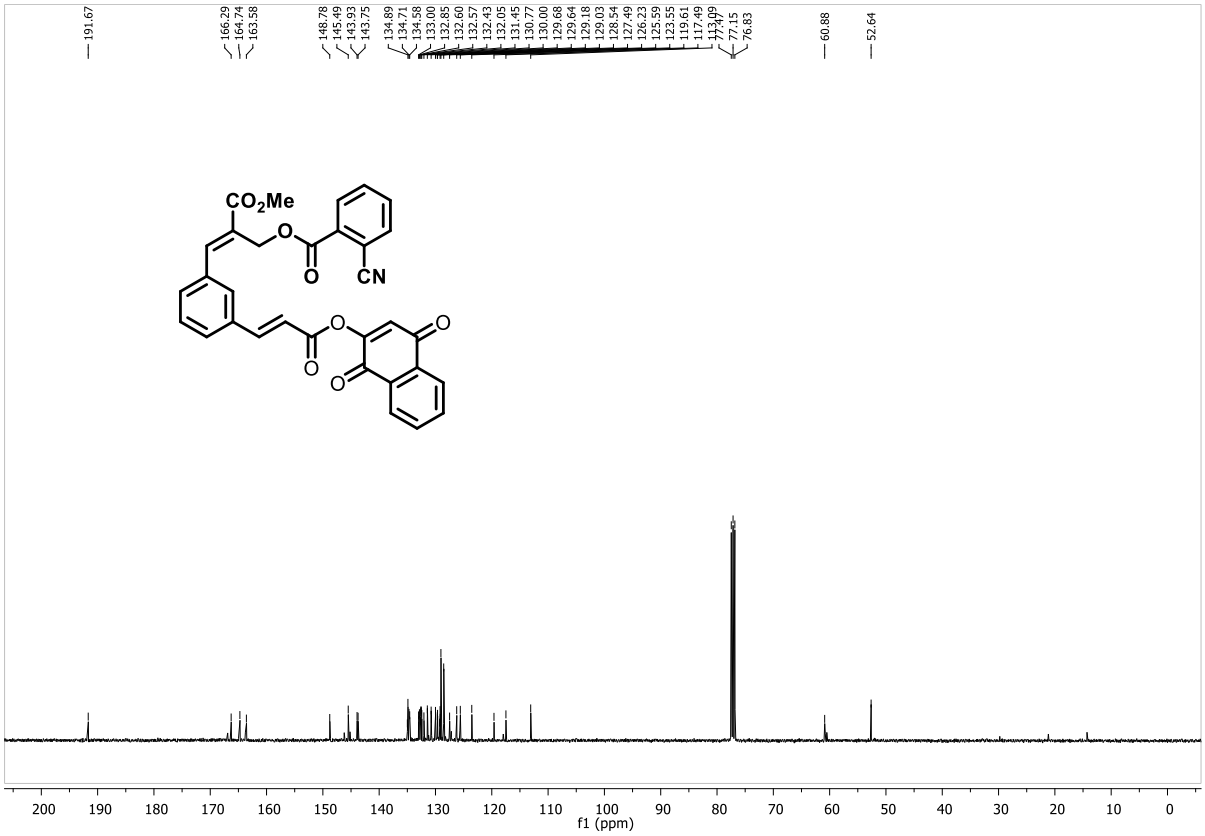
Dibutyl2-(5-((*E*)-2-(((2-cyanobenzoyl)oxy)methyl)-3-methoxy-3-oxoprop-1-en-1-yl)-2-fluorophenyl)maleate (3za)



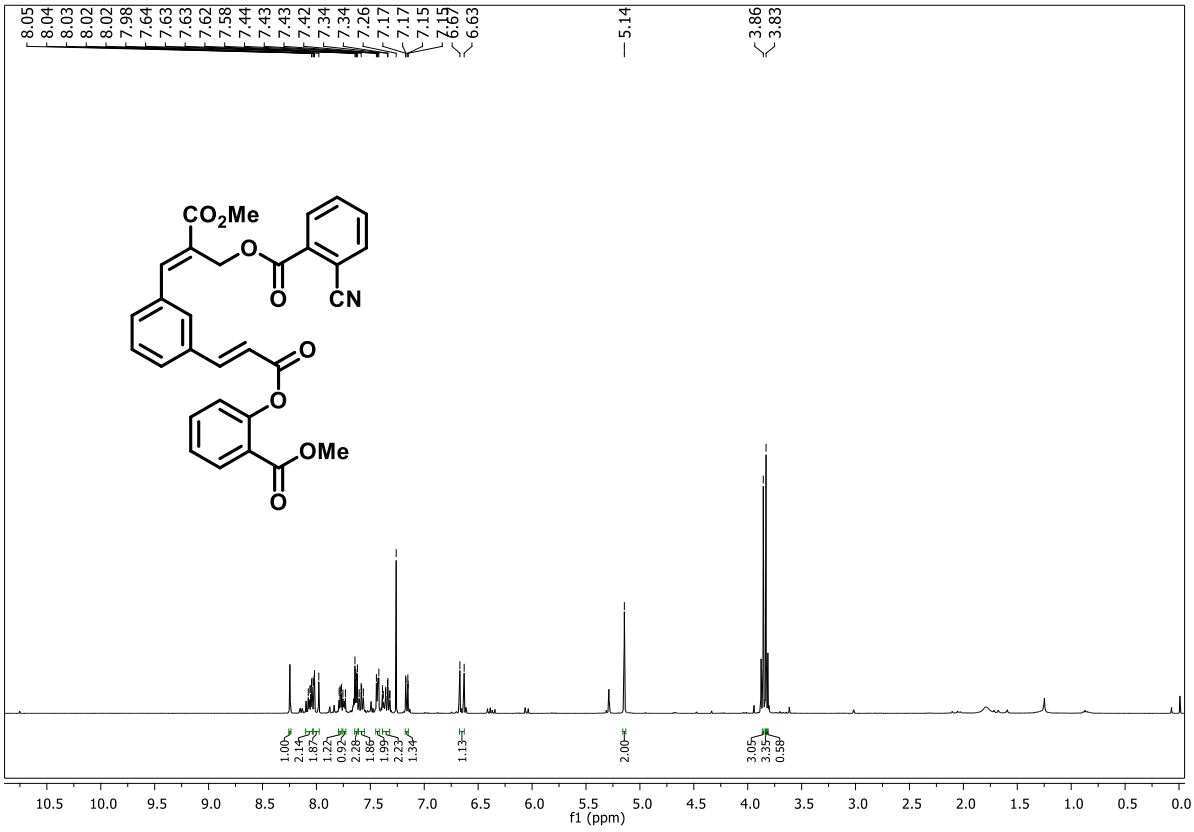


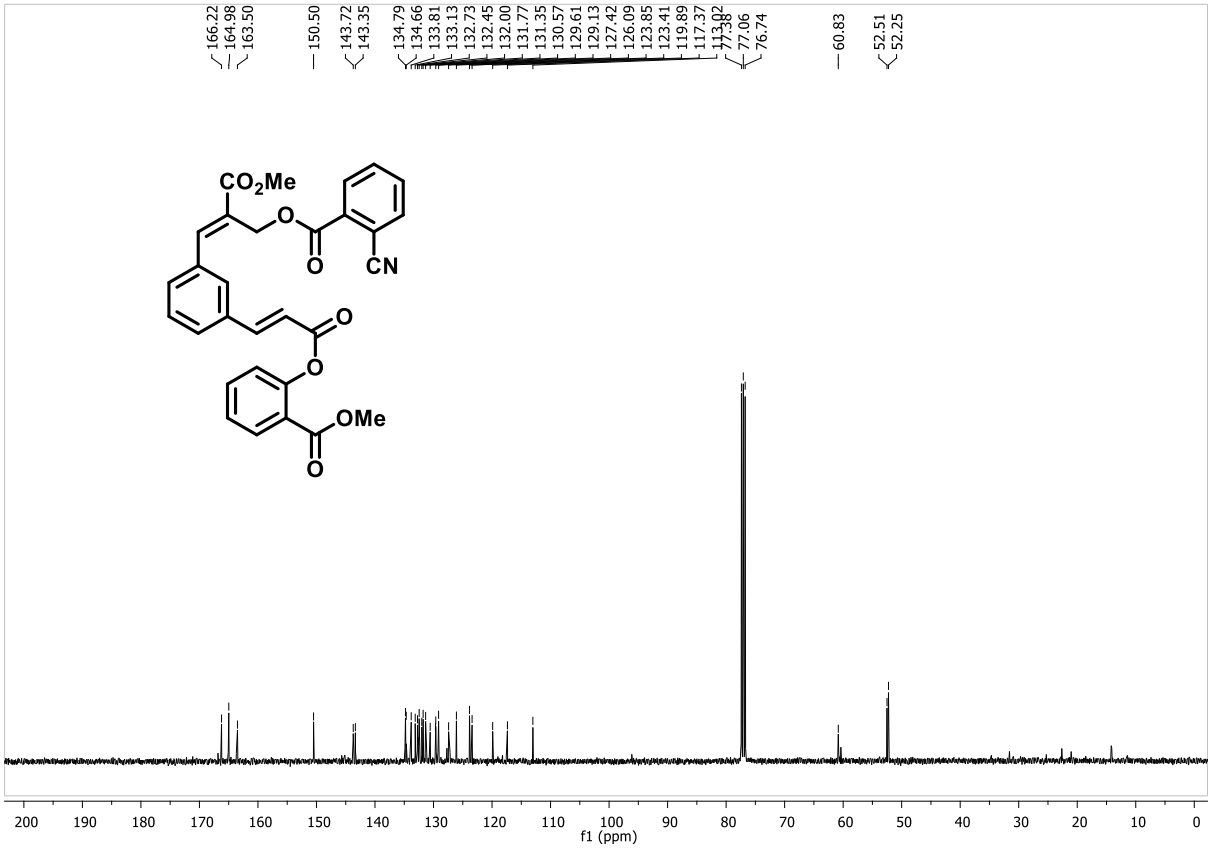
(*E*)-3-(3-((*E*)-3-((1,4-dioxo-1,4-dihydronaphthalen-2-yl)oxy)-3-oxoprop-1-en-1-yl) phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3aa)



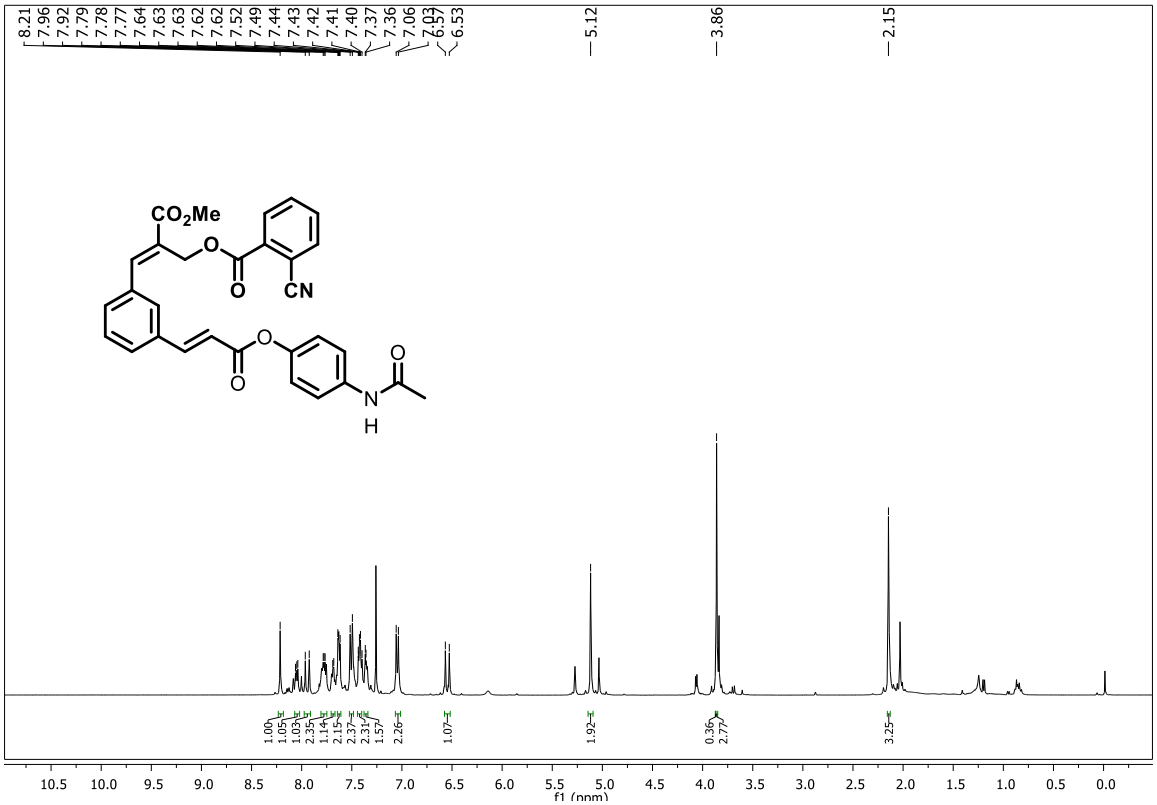


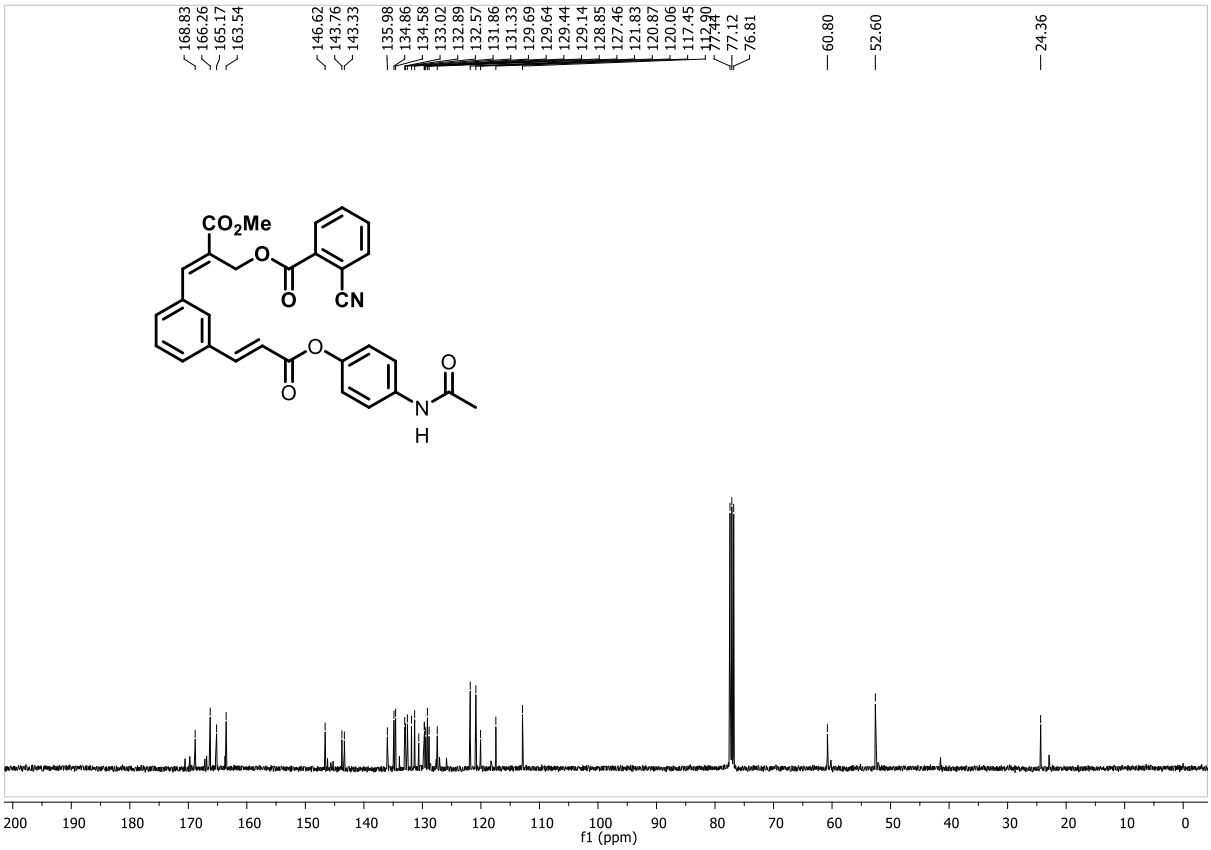
(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-3-(2-(methoxycarbonyl)phenoxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ab)



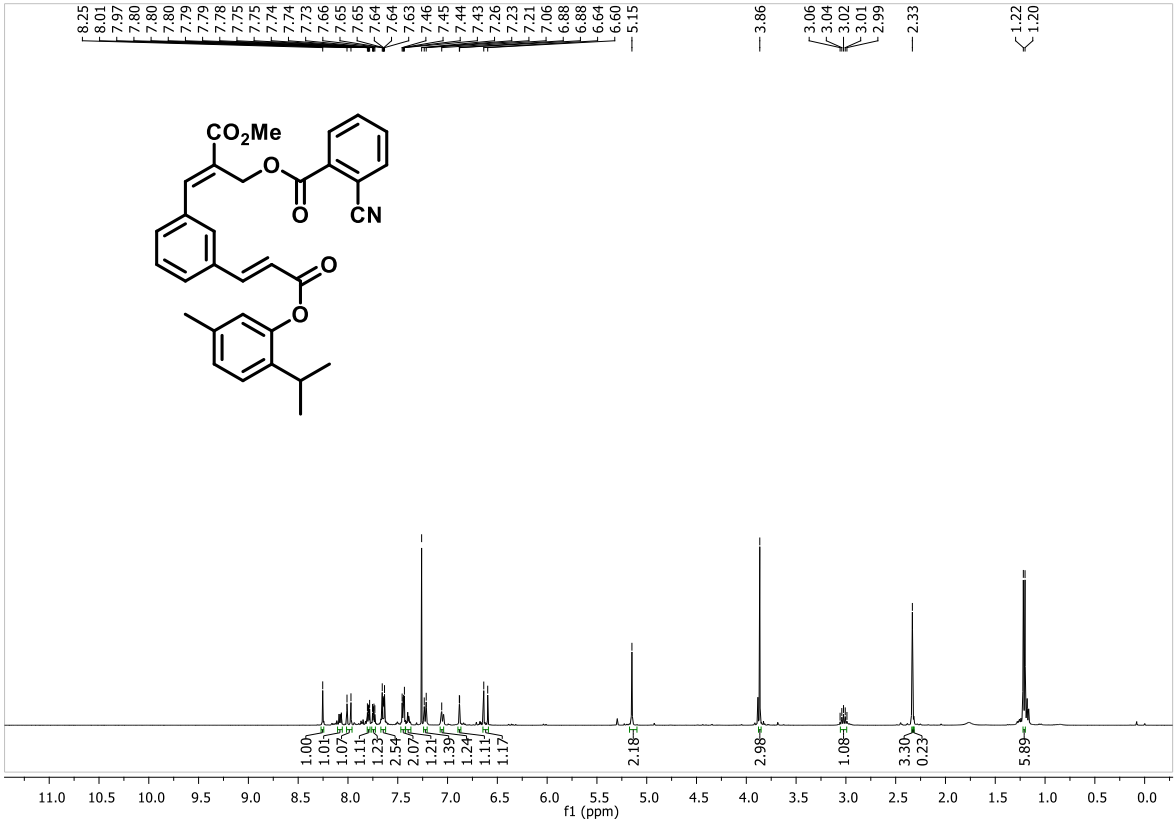


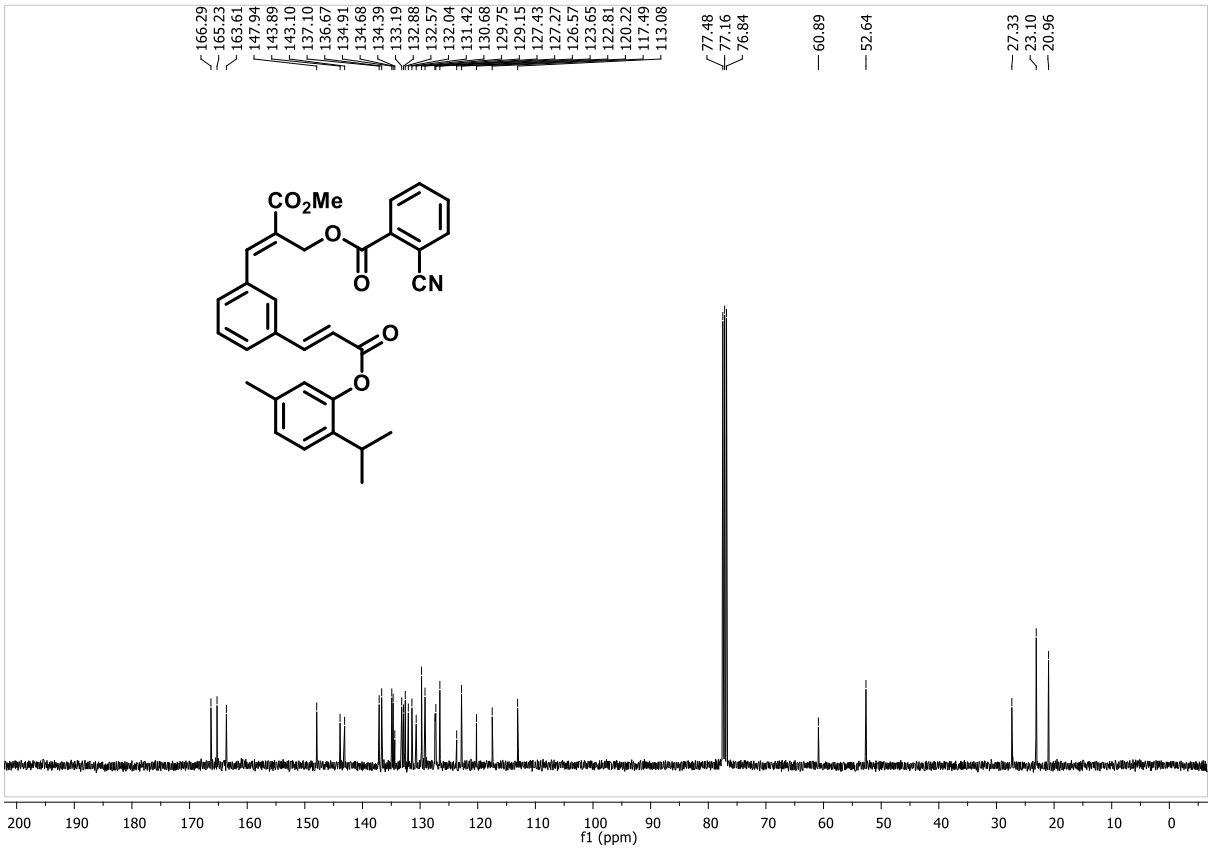
(*E*)-3-(3-((*E*)-3-(4-acetamidophenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl) allyl 2-cyanobenzoate (3ac)



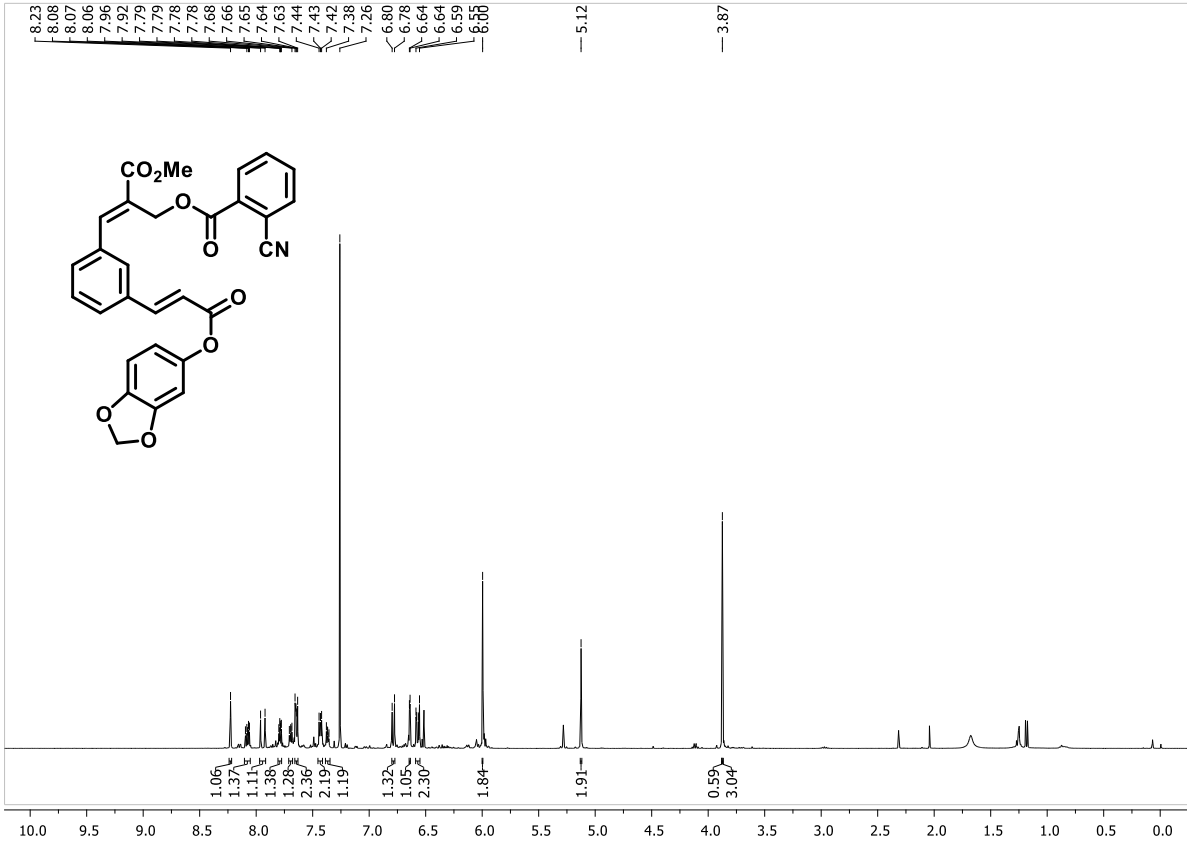


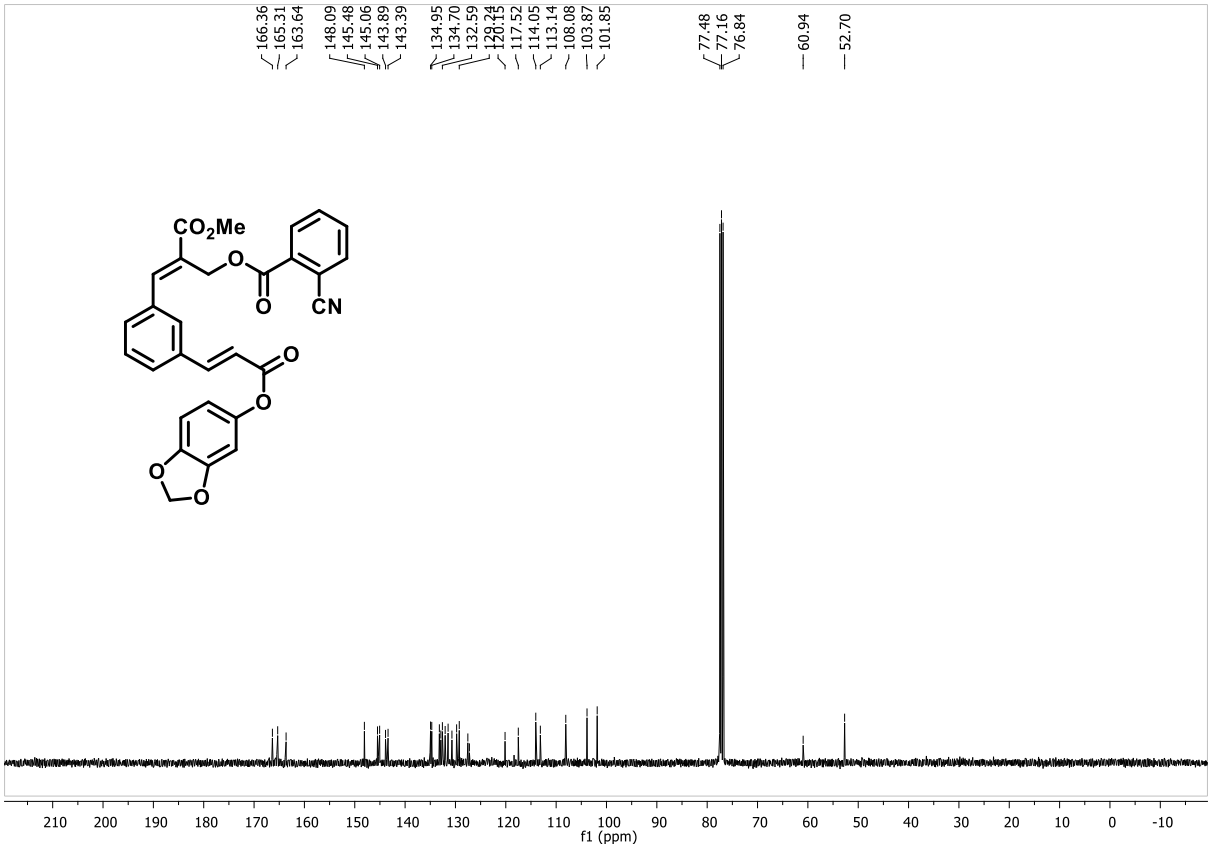
(*E*)-3-(3-((*E*)-3-(2-isopropyl-5-methylphenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3ad)



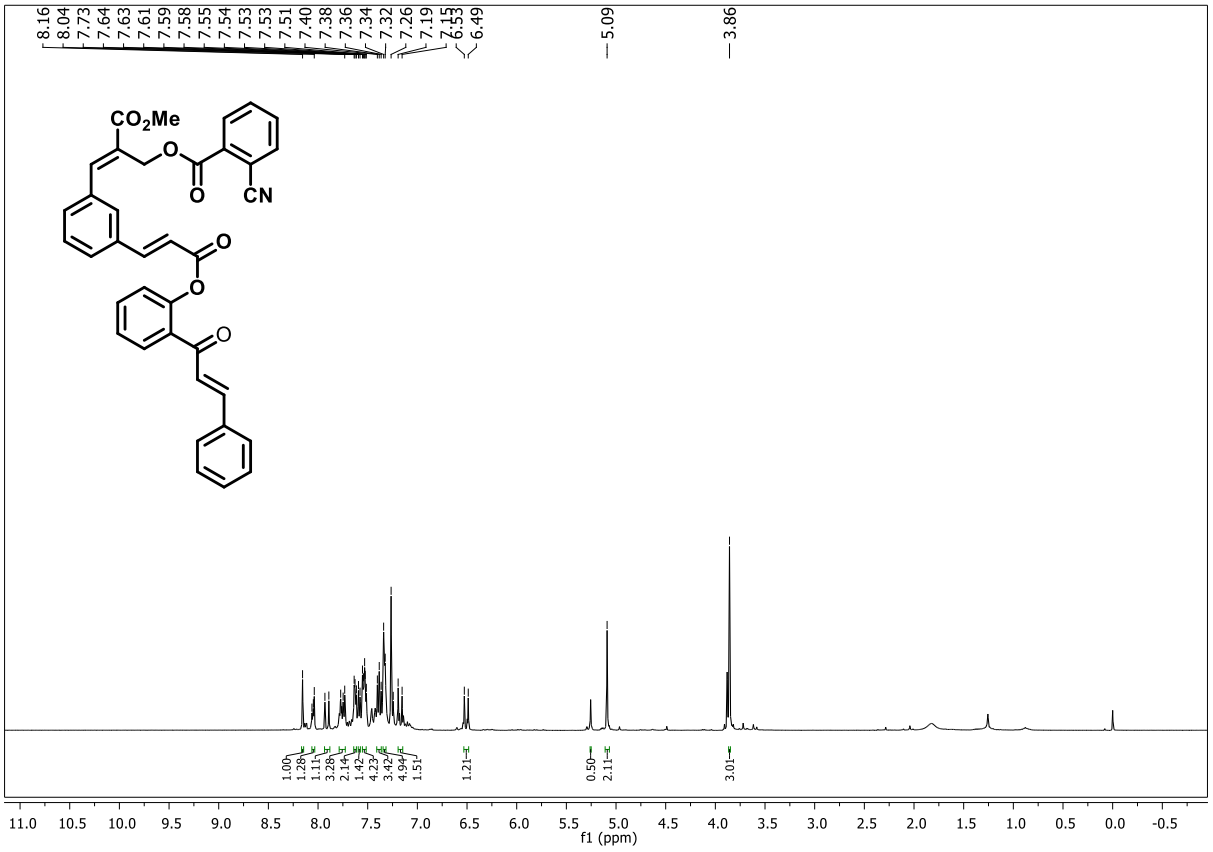


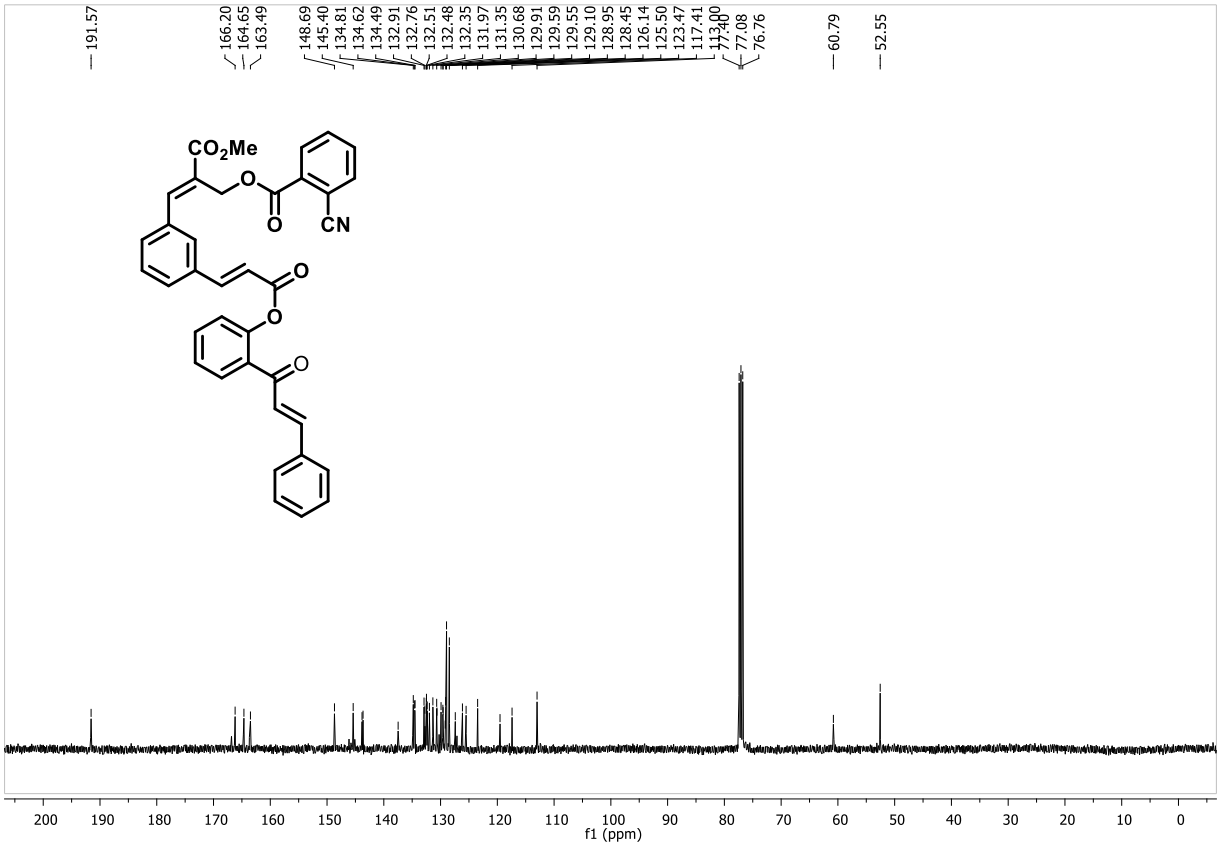
(*E*)-3-(3-((*E*)-3-(benzo[d][1,3]dioxol-5-yloxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3ae)



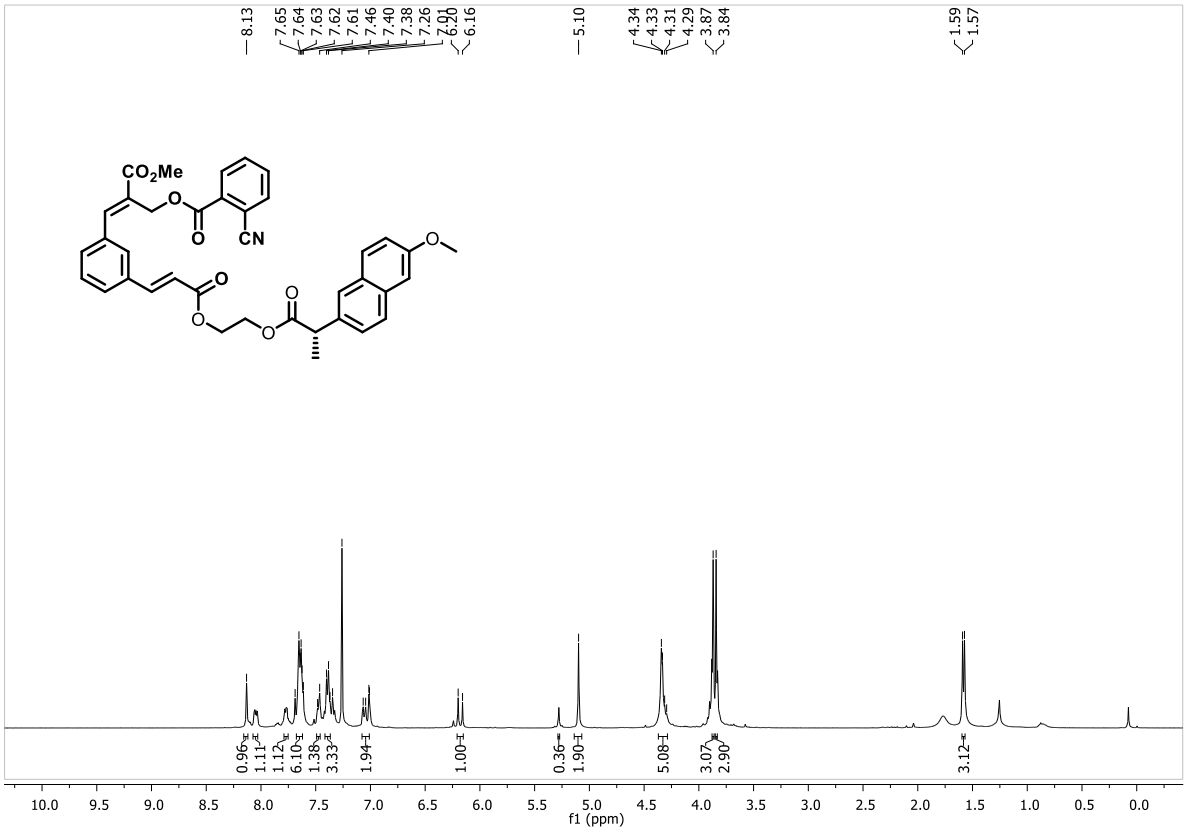


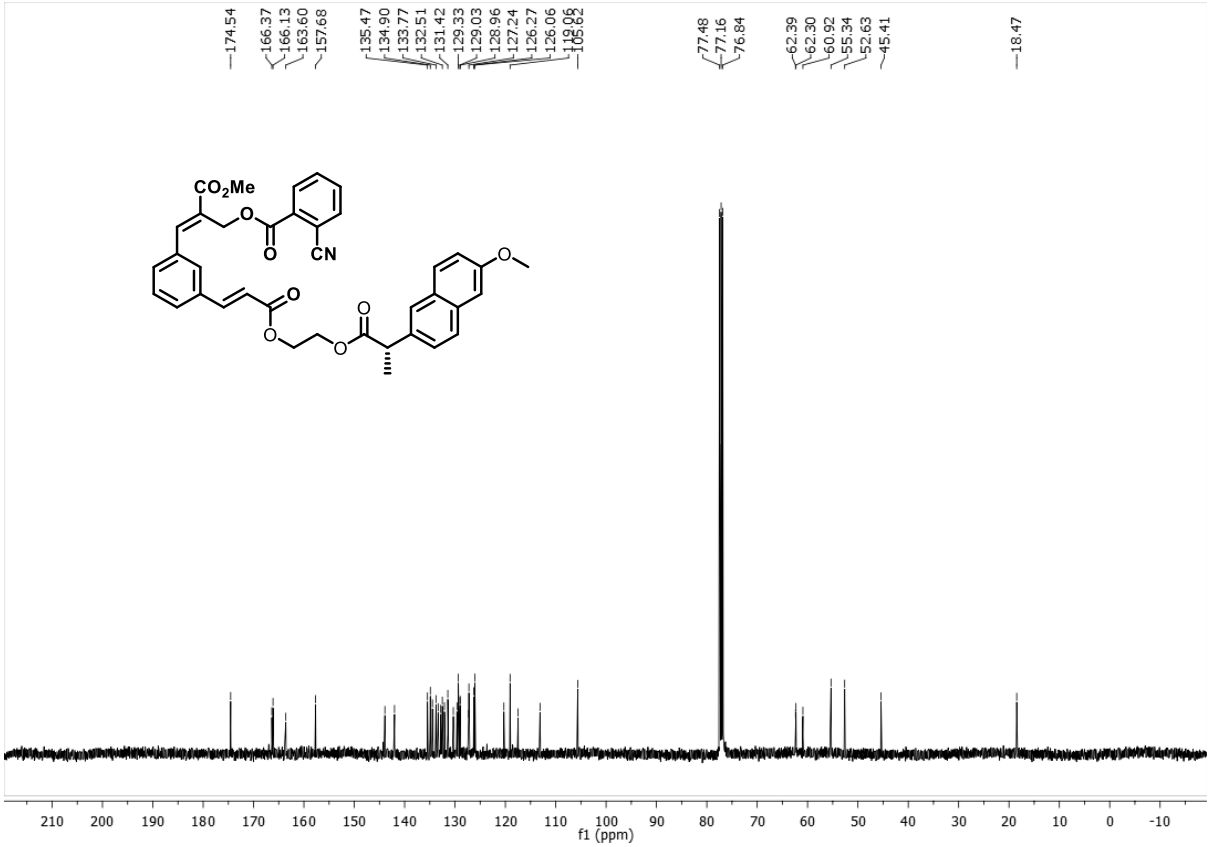
(*E*)-3-(3-((*E*)-3-(2-cinnamoylphenoxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3af)



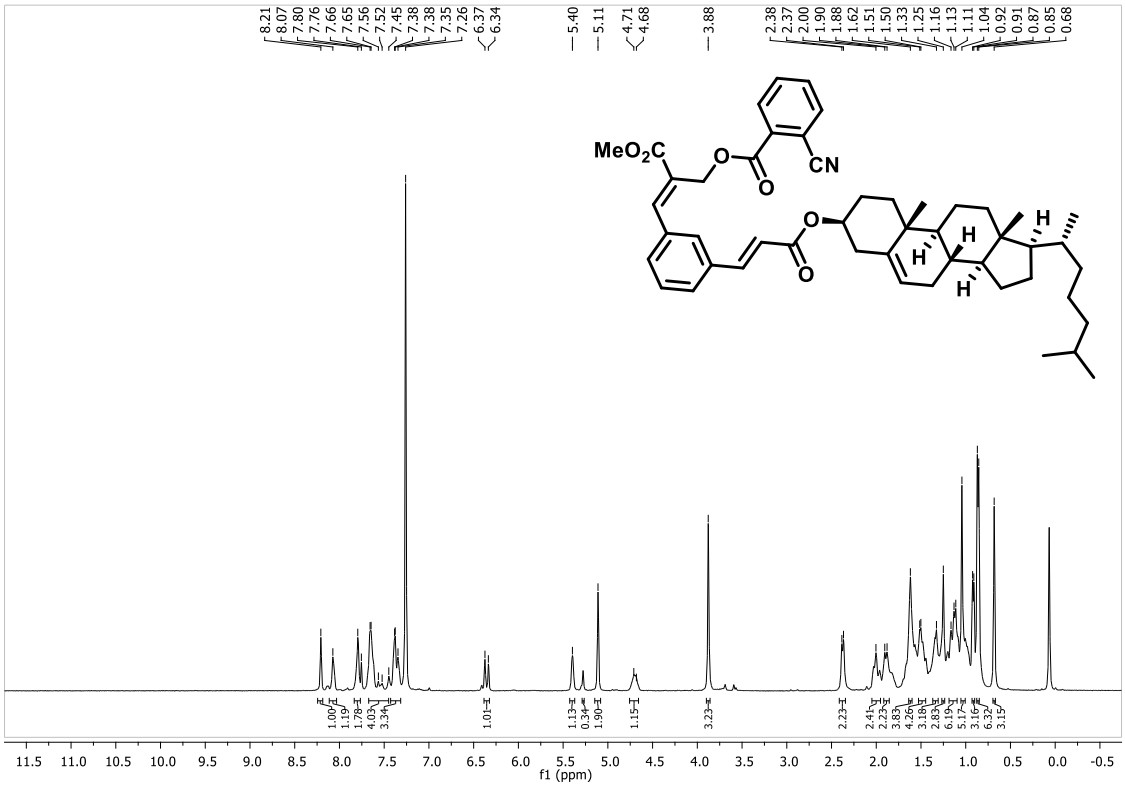


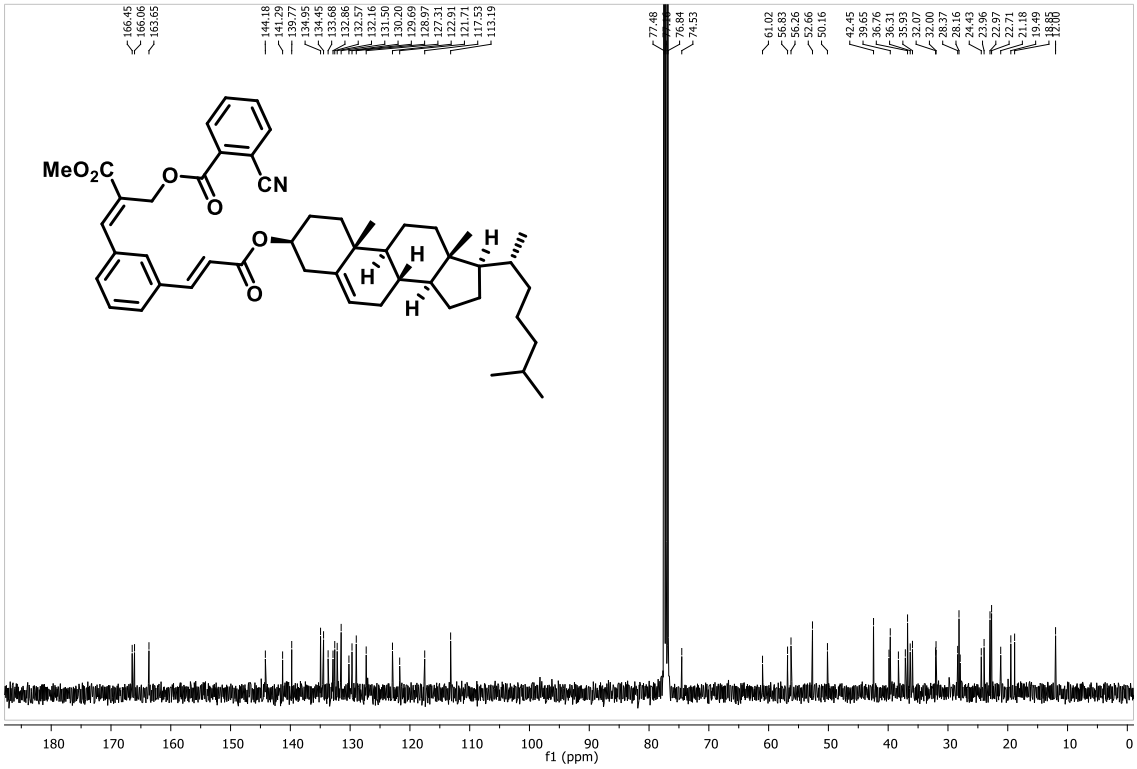
(*E*)-2-(methoxycarbonyl)-3-(3-((*E*)-3-(2-(((S)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)ethoxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ag)



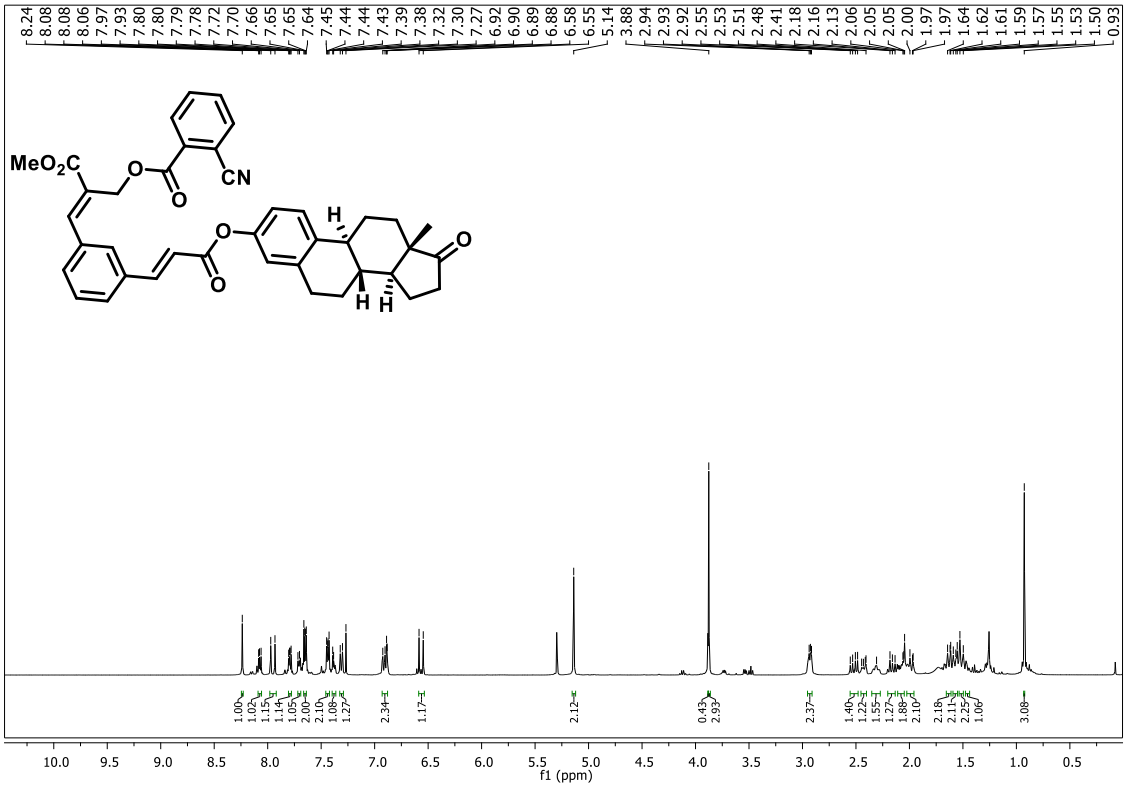


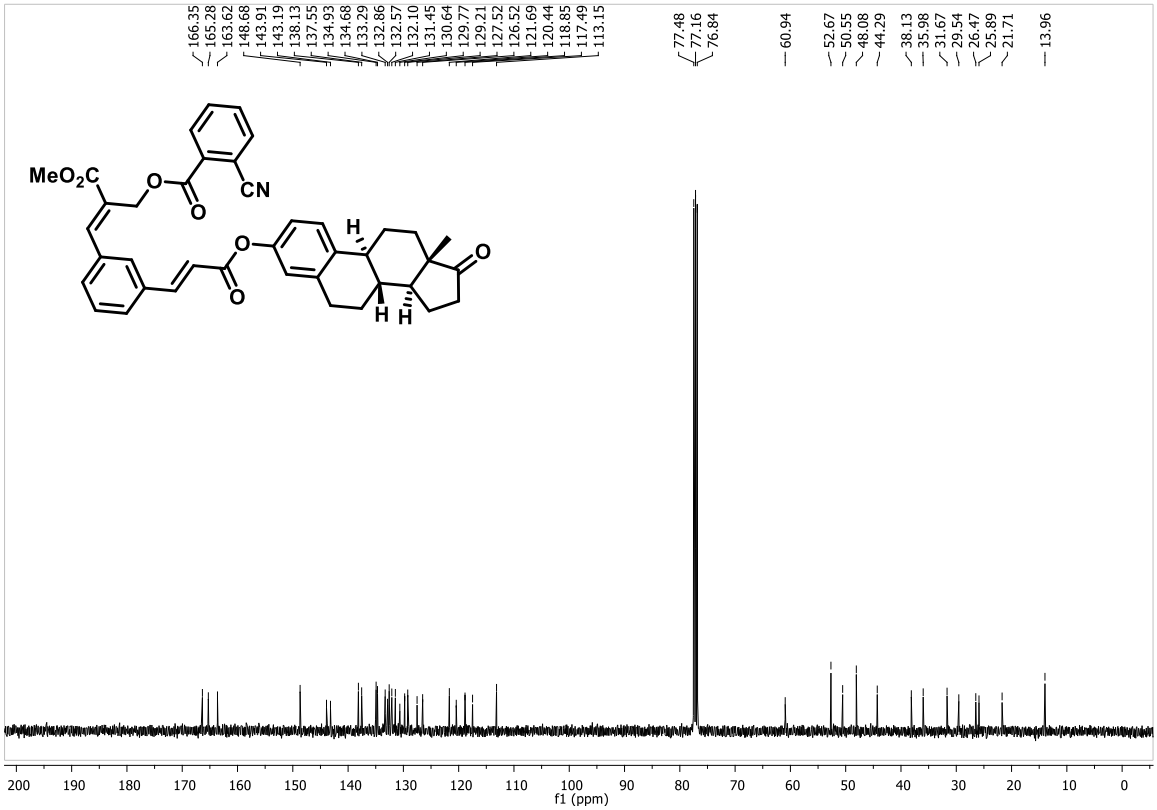
(*E*)-3-(3-((*E*)-3-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxoprop-1-en-1-yl)phenyl)-2-(methoxycarbonyl)allyl 2-cyanobenzoate (3ah)



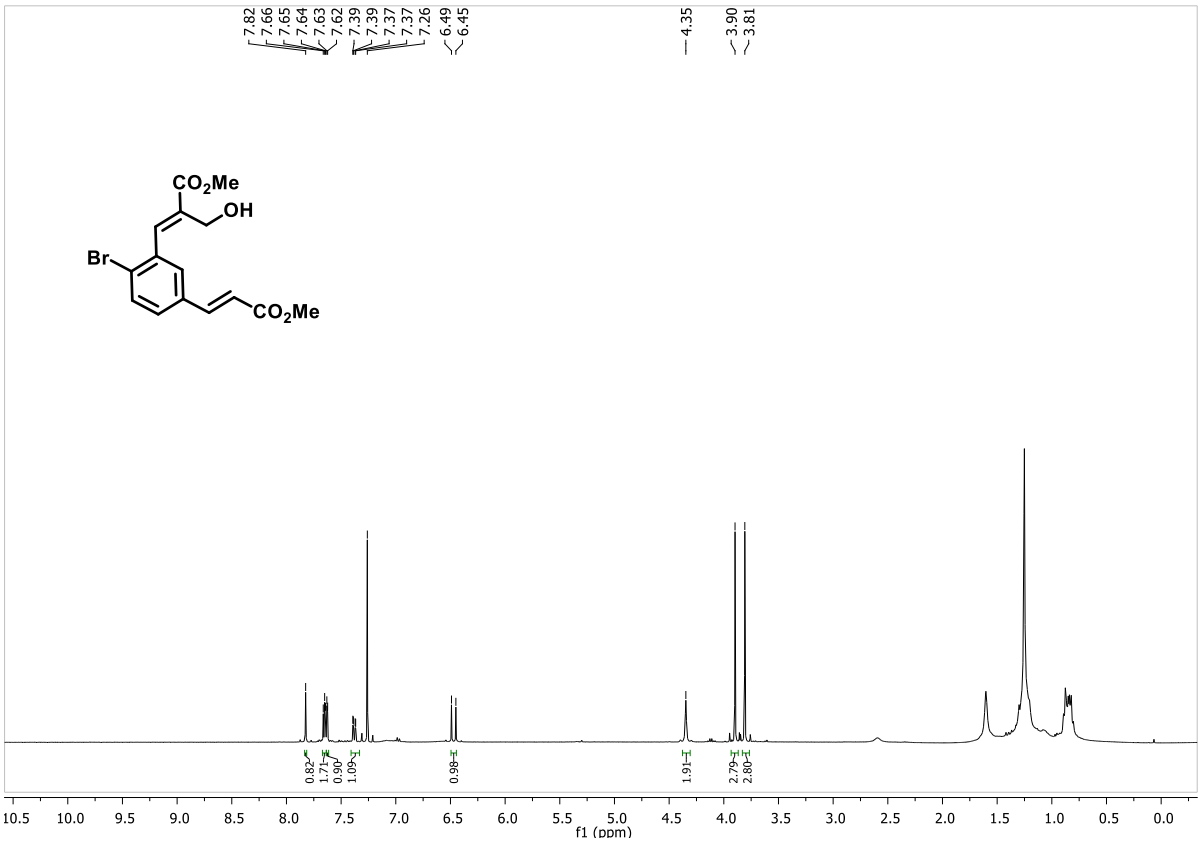


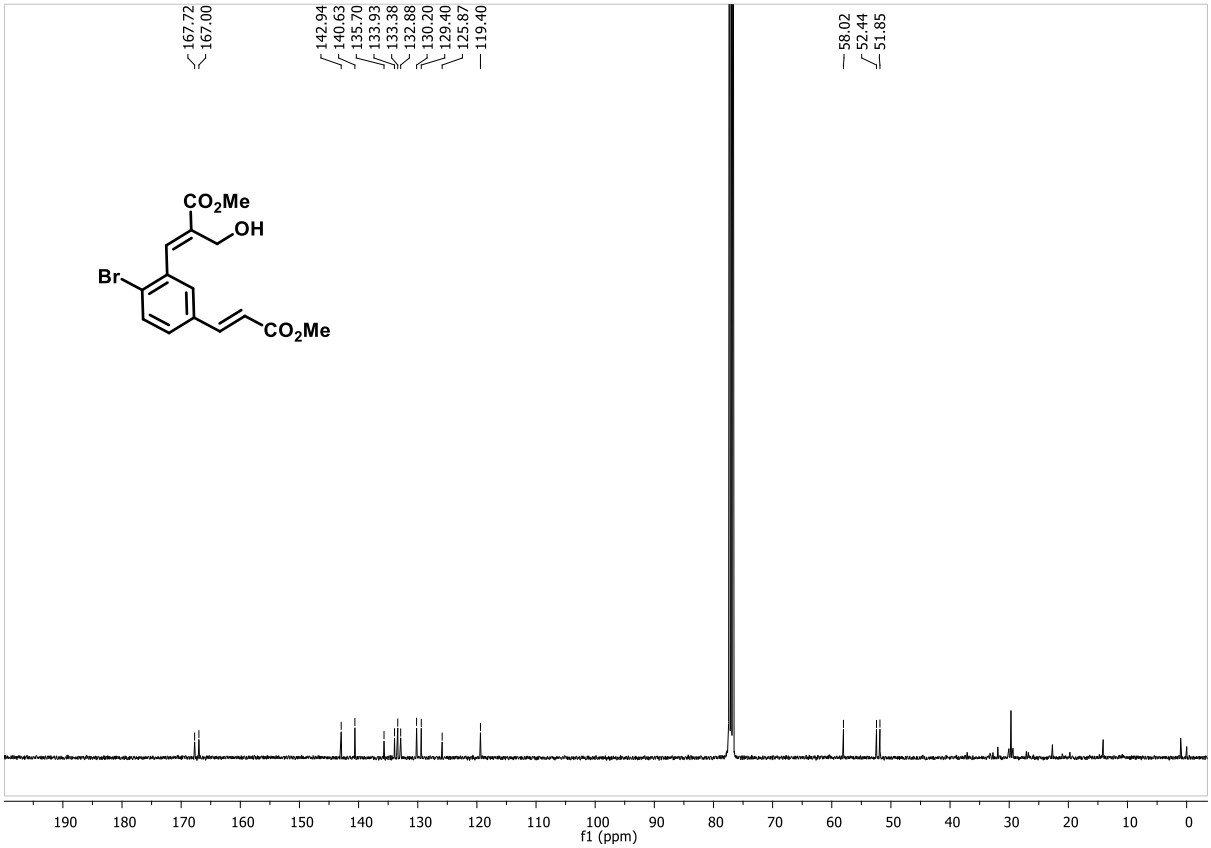
(E)-2-(methoxycarbonyl)-3-(3-((E)-3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxoprop-1-en-1-yl)phenyl)allyl 2-cyanobenzoate (3ai)



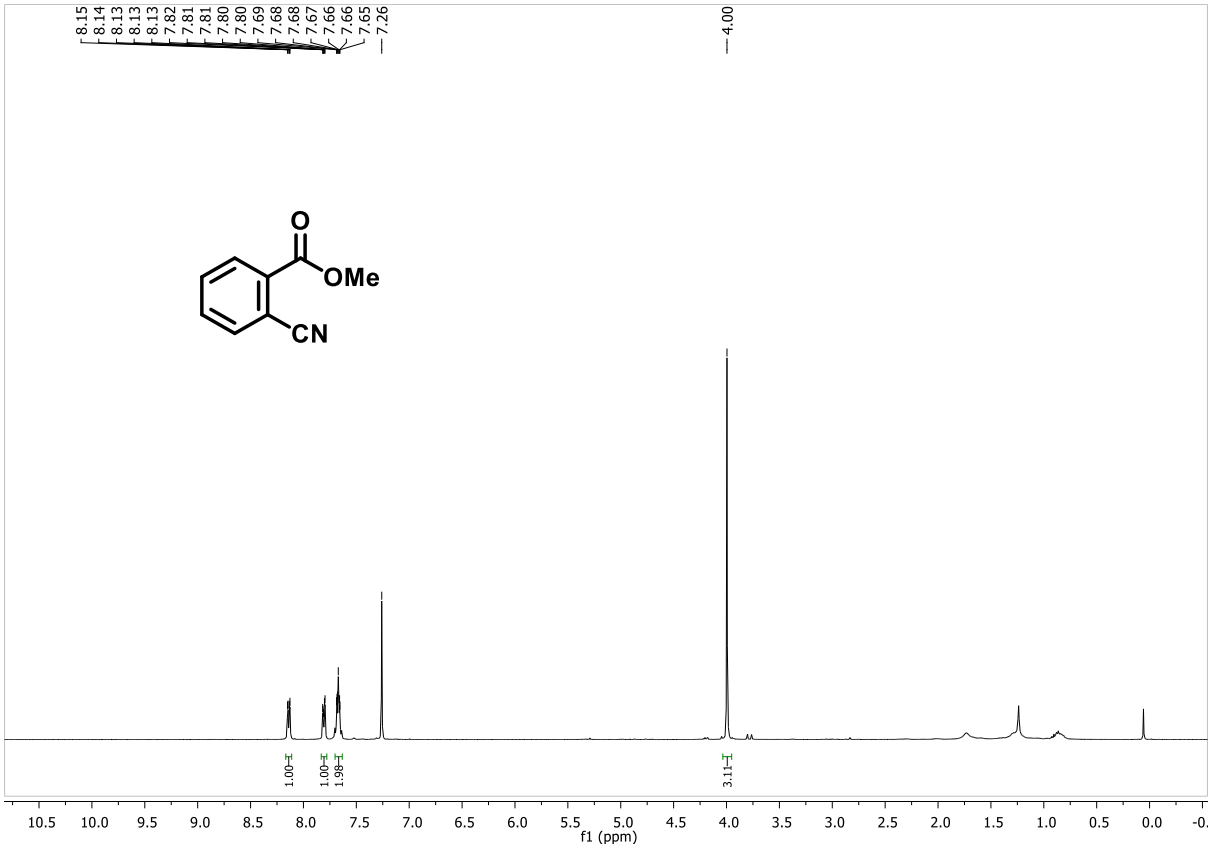


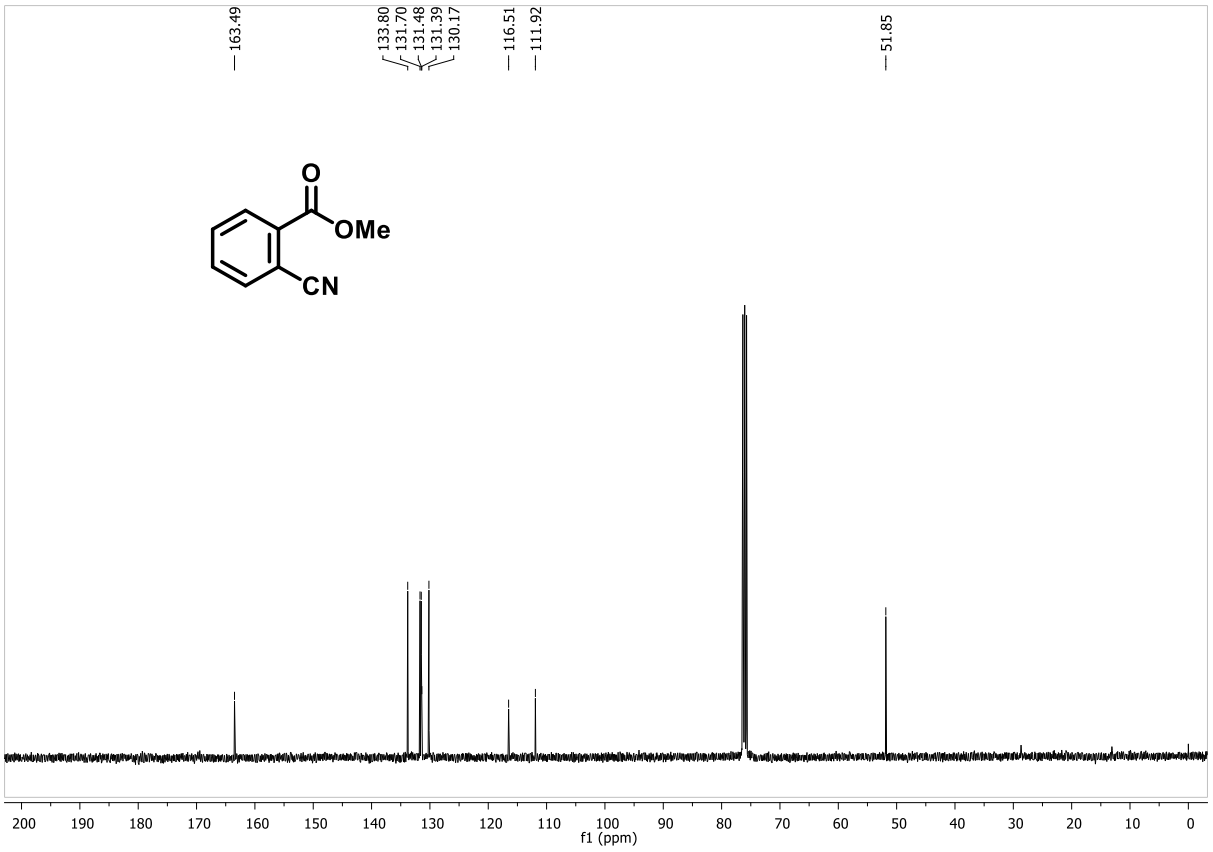
Methyl(*E*)-3-(2-bromo-5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-(hydroxymethyl)acrylate (3aj)





Methyl-2-cyanobenzoate (3ak)

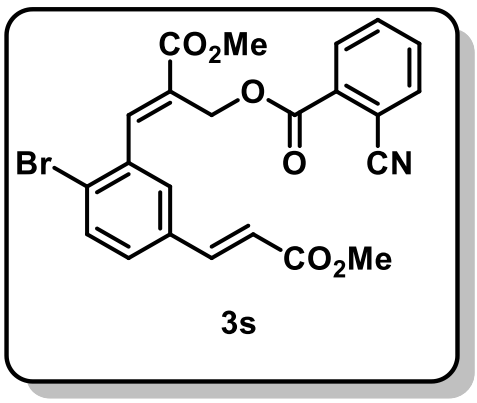




6. Crystallographic Data of Compounds 3s and 3x:

a) **Sample Preparation for Crystal Growth:** The compound 3s and 3x was dissolved in 1ml of 1,2-dichloromethane (DCM) in a 3ml vail and added 2ml of 20% (Hexane/Ethyl acetae) in each vial and kept for slow evaporation at room temperature. The formation of crystals was observed after 5 day. The single crystals were then subjected to X-ray diffraction analysis.

Crystal data and structure refinement for 3s:



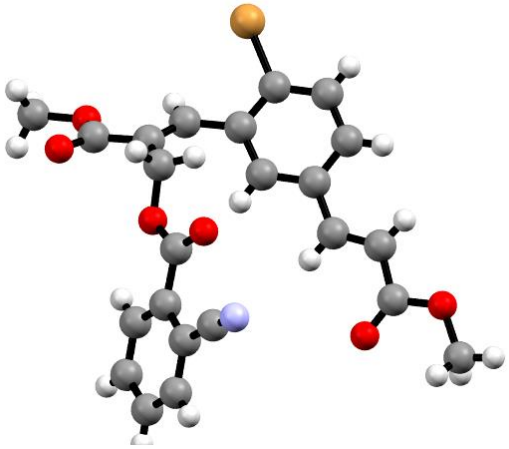


Figure 2. Molecular structure of compound 3s **CCDC : 2235298**

Table. Crystal data and structure refinement for 3s

Identification code: MA-CY-361

Empirical formula: C23 H18 Br N O6

Formula weight: 484.28

Temperature (K): 100 K

Wavelength= 1.54184

Crystal system: Monoclinic

Space group: P 21/c

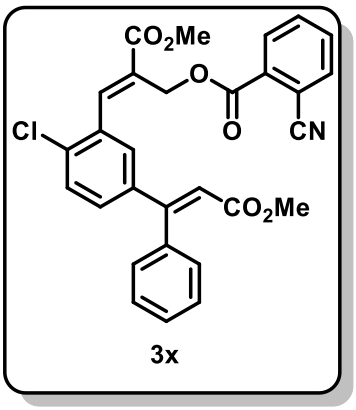
Unit cell dimensions

a=7.9904(1) b=22.6800(2) c=11.9133(1)

α/° 90.00

β/° 95.679(1) , γ/° 90.00, Volume : 2148.36(4)

Crystal data and structure refinement for 3x:



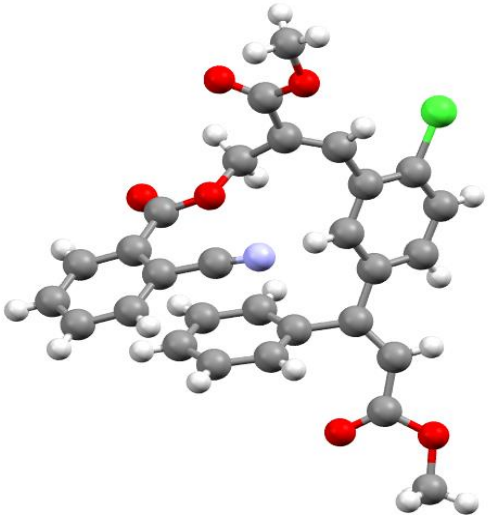


Figure 2. Molecular structure of compound 3x **CCDC : 2235316**

Table. Crystal data and structure refinement for 3x.

Identification code: MA-CY-103

Empirical formula: C29 H22 Cl N O6

Formula weight: 515.93

Temperature (K): 100 K

Wavelength (A^o): 0.71073

Crystal system: Monoclinic

Space group: P 21/c

Unit cell dimensions

a=11.1628(5) b=20.3645(10) c=10.9319(5)

α/° 90.00

β/° 95.967(2)

γ/° 90.00,

Volume: 2471.6(2)

7) References:

1. a) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev*. **2003**, *103*, 811; b) b) D. Basavaiah, K. V. Rao, R. J. Reddy, *Chem. Soc. Rev.* **2007**, *36*, 1581.