Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Overriding *Ortho* Selectivity by Template Assisted *Meta*-C–H Activation of Benzophenone

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Section	Table of Contents	Page Numbers

1. General remarks:

Reagent information:

All commercial reagents were purchased from Sigma-Aldrich, AlfaAesar, TCI, Merck and Spectrochem and were used without further purification. Palladium catalysts were obtained from AlfaAesar. All solvents were bought from Merck and Spectrochem and were used as received. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254}$) visualized under UV illumination at 254 nm.

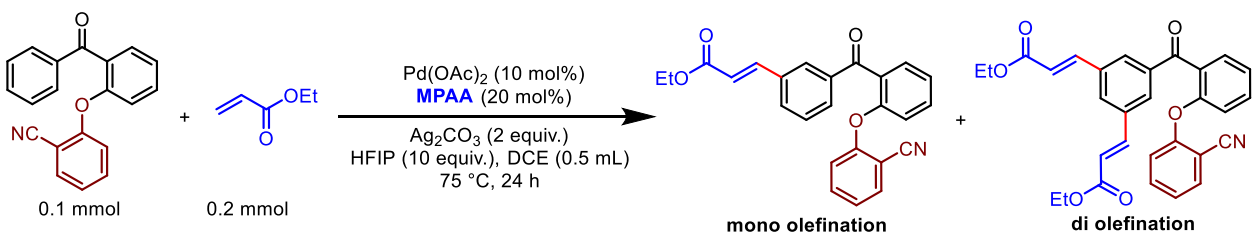
Analytical information:

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 (400 MHz and 100 MHz respectively) and 500 (500 MHz and 125 MHz respectively) instrument. All NMR spectra were reported in parts per million (ppm) downfield of TMS and were internally referenced to TMS (0 ppm) or residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.23 ppm for ^{13}C). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, m = multiplet. Yield and selectivity for optimization were determined from NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene (TMB) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

2. Optimization details for *meta*-olefination:

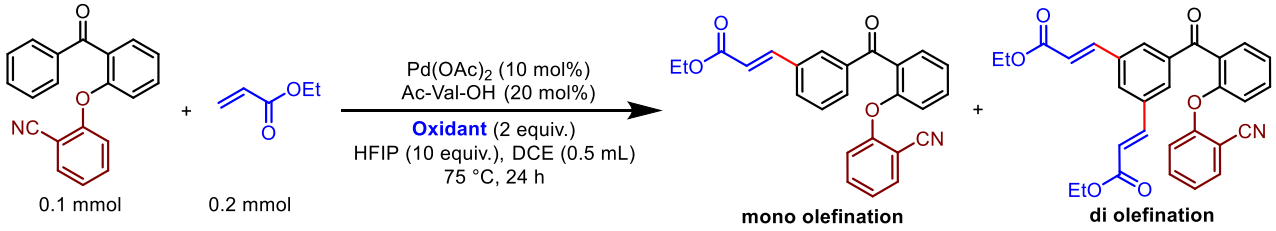
General procedure for optimization of *meta*-C-H olefination: In a clean, oven-dried screw cap reaction tube containing magnetic stir–bar, the substrate (0.1 mmol), Pd catalyst. (10 mol%), ligand (20 mol%) and oxidant (2 equiv.) were weighed. The solvent or their combination (as metioned) and the olefin (2 equiv., 0.2 mmol), were added sequentially by syringes. The cap was sealed and this reaction tube was placed in a preheated oil bath at specific temperature for 24 h with vigorous stirring. Then the reaction mixture was cooled to room temperature and trimethoxybenzene (TMB, 0.1 mmol, 1 equiv.) was added as internal standard. The crude reaction misture was filtered through celite with aid of ethyl acetate (5 mL) and the solvent was removed under reduced pressure. The yield and regioselectivity was determined from ^{1}H NMR of this crude reaction mixture.

Table S1: Optimization of ligand



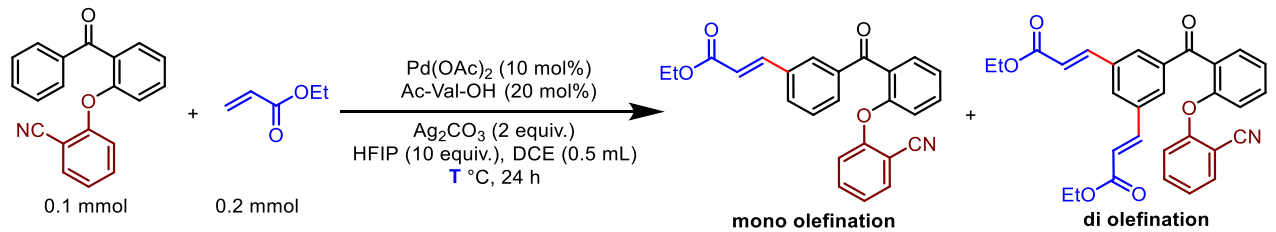
Entry	MPAA ligand	Yield (mono: di)	Conv.
1	Ac-Gly-OH	67 (3:1)	85
2	Boc-Phe-OH	38 (5:1)	49
3	**Ac-Val-OH**	**77 (7:1)**	**89**
4	Boc-Val-OH	23(3:1)	38
5	Cbz-Leu-OH	18 (4:1)	31
6	Ac-Leu-OH	33 (3.5:1)	45
7	Boc-Ala-OH	15 (2:1)	36

Table S2: Optimization of oxidant



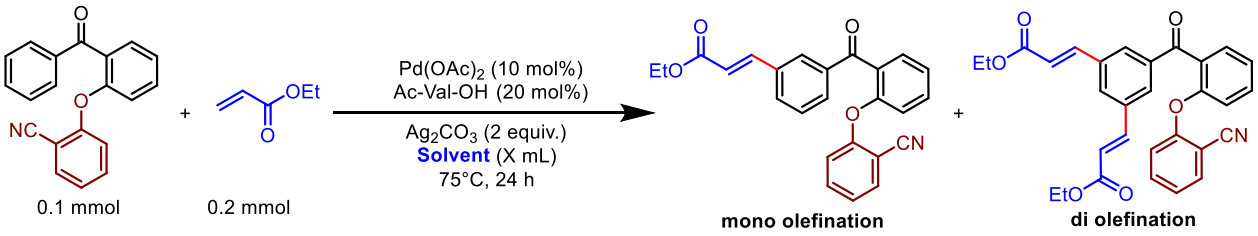
Entry	Oxidant	Yield (mono: di)	Conv.
1	AgOAc	66 (2:1)	81
2	**Ag_2CO_3**	**77 (7:1)**	**89**
3	Ag_2O	15 (2.5:1)	21
4	$AgBF_4$	17(3:1)	25

Table S3: Optimization of temperature



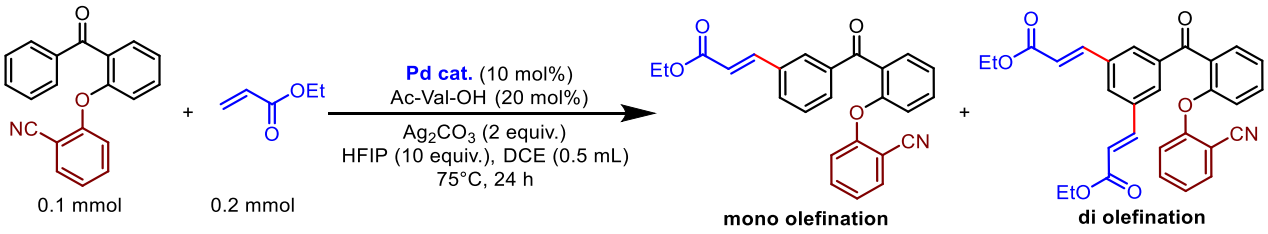
Entry	Temperature	Yield (mono: di)	Conv.
1	90 °C	65 (5:1)	90
2	80 °C	73 (6:1)	92
3	**75 °C**	**77 (7:1)**	**89**
4	70 °C	70 (5:1)	87
5	65 °C	61 (5.5:1)	76

Table S4: Optimization of solvent



Entry	Solvent	Yield (mono: di)	Conv.
1	DCE (0.5 mL)	13 (11:1)	29
2	**DCE (0.5 mL), HFIP (10 equiv.)**	**77 (7:1)**	**89**
3	DCE (0.5 mL), HFIP (5 equiv.)	53 (5:1)	70
4	DCE (0.5 mL), HFIP (15 equiv.)	70 (6:1)	91
5	HFIP (0.5 mL)	75 (1:1)	95

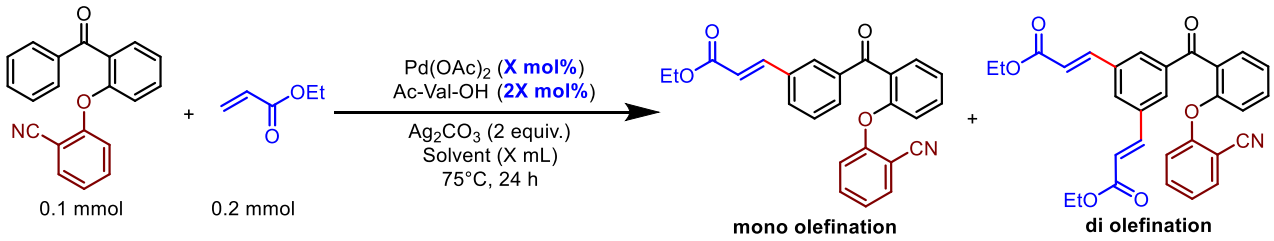
Table S5: Optimization of Palladium catalyst



Entry	Pd salt	Yield (mono: di)	Conv.
1	**$Pd(OAc)_2$**	**77(7:1)**	**89**
2	$PdCl_2$	16(1:1)	28

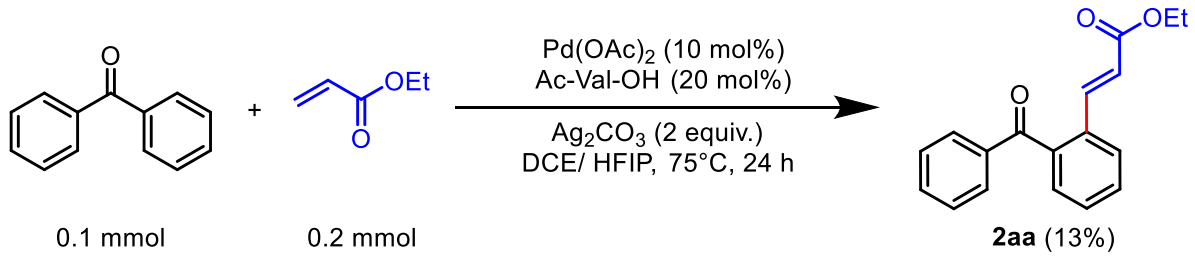
3	$Pd(OPiv)_2$	64 (5:1)	81
4	$Pd(OTf)_2$	18 (1.5:1)	31
5	$Pd(PPh_3)_4$	09 (1:1)	20
6	$Pd(acac)_2$	26 (2:1)	37
7	$PdSO_4$	21 (1.5:1)	34
8	$Pd(MeCN)_2Cl_2$	45 (4:1)	59

Table S6: Optimization of catalyst loading



Entry	Catalyst loading (mol%)	Yield (mono: di)	Conv.
1	2.5	24 (3:1)	35
2	5.0	53 (5:1)	61
3	7.5	70 (5.5:1)	85
4	**10**	**77 (7:1)**	**89**
5	12.5	73 (7:1)	92

3. Control reaction for *meta*-olefination in absence of directing template:



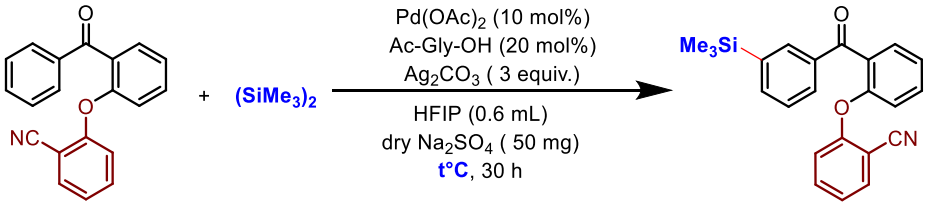
ethyl (*E*)-3-(2-benzoylphenyl)acrylate (2aa): A clean, oven-dried screw cap reaction tube containing magnetic stir–bar was charged with benzophenone (2.7 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Val-OH (20 mol%) and Ag_2CO_3 (2.0 equiv.). DCE (13 mL), HFIP (10 equiv.) and ethyl acrylate (2.0 equiv., 5.4 mmol) were added sequentially by syringes. The cap was sealed and this reaction tube was

placed in a preheated oil bath at 75 °C to stir vigorously for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (30 mL). Regioselectivity was determined from ^{1}H NMR of this crude reaction mixture filtrate. Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to obtain pure **2aa** (13% yield). **^{1}H NMR (200 MHz, $CDCl_3$)** δ 7.83 – 7.71 (m, 3H), 7.64 – 7.38 (m, 7H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.19 (q, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 8.0 Hz, 3H).

4. Optimization details for *meta*-silylation:

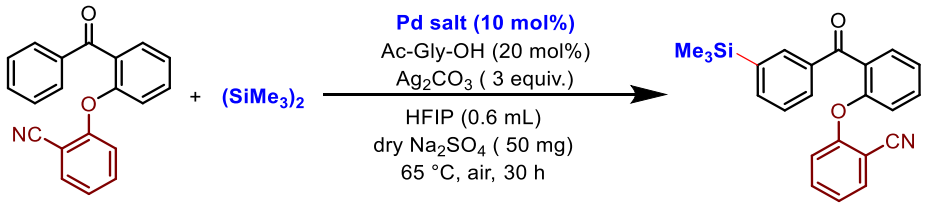
General procedure for optimization of *meta*-C–H silylation: In a clean, oven-dried screw cap reaction tube containing magnetic stir–bar, the substrate (0.1 mmol), Pd catalyst. (10 mol%), ligand (20 mol%) and oxidant (2 equiv.) were weighed. The reaction tube was dried using a hot gun and sealed with a cap. Subsequently, corresponding solvent and hexamethyldisilane (2 equiv.) were added sequentially by syringes. The reaction tube was placed in a preheated oil bath at specific temperature for 24 h with vigorous stirring. Then the reaction mixture was cooled to room temperature and trimethoxybenzene (TMB, 0.1 mmol, 1 equiv.) was added as internal standard. The crude reaction misture was filtered through celite with aid of ethyl acetate (5 mL) and the solvent was removed under reduced pressure. The yield and regioselectivity was determined from ^{1}H NMR of this crude reaction mixture.

Table S7: Optimization of temperature



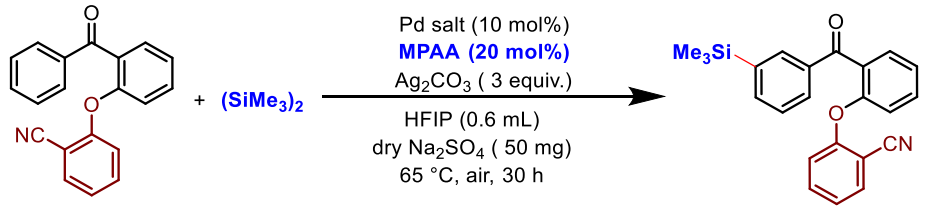
Entry	Temperature (°C)	Yield (mono + di) (%)
1	55	38
2	60	35
3	**65**	**51**
4	70	27
5	80	21
6	90	18

Table S8: Optimization of Palladium salts



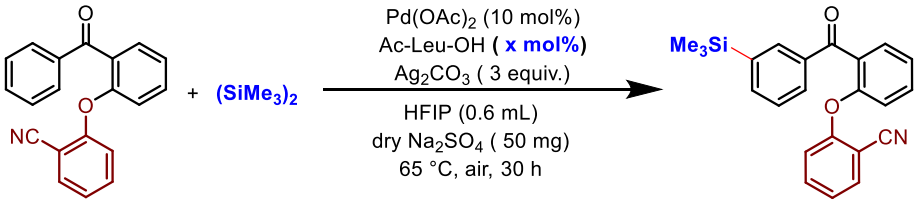
Entry	Pd salt	Yield (mono+di) (%)
1	**$Pd(OAc)_2$**	**51**
2	$PdCl_2$	<5
3	$Pd(OPiv)_2$	22
4	$Pd_2(dba)_3$	<5
5	$(PPh_3)_2PdCl_2$	<5
6	$PdCl_2(PhCN)_2$	<5
7	$Pd(MeCN)_2Cl_2$	<5

Table S9: Optimization of ligands



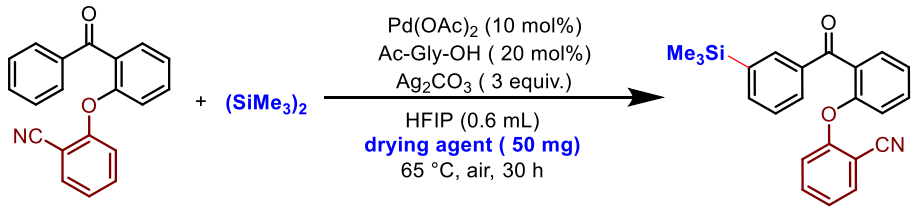
Entry	Ligand	Yield (mono+di) (%)
1	Ac-Ala-OH	43
2	Ac-Leu-OH	50
3	Ac-NorLeu-OH	45
4	Ac-Phe-OH	38
5	Boc-Gly-OH	--
6	Carbobenzoxy-Leu-OH	21
7	Boc-Val-OH	<5
8	**Ac-Gly-OH**	**51**

Table S10: Optimization of ligand amount



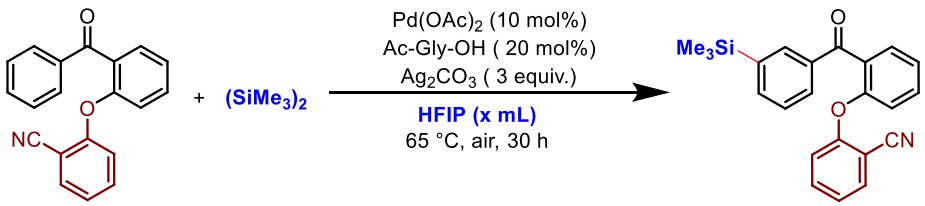
Entry	Ligand amount (mol%)	Yield (mono + di) (%)
1	10	39
2	**20**	**51**
3	30	46
4	No Ligand	No product

Table S11: Optimization of drying agent



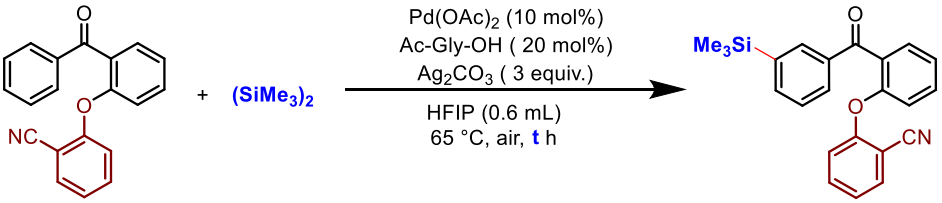
Entry	Drying agent	Yield (mono+di) (%)
1	Molecular Sieves (4 Å)	--
2	$MgSO_4$	<5
3	SiO_2	Very Less
4	Al_2O_3	10
5	**...**	**57**
6	Na_2SO_4	50

Table S12: Optimization of solvent amount



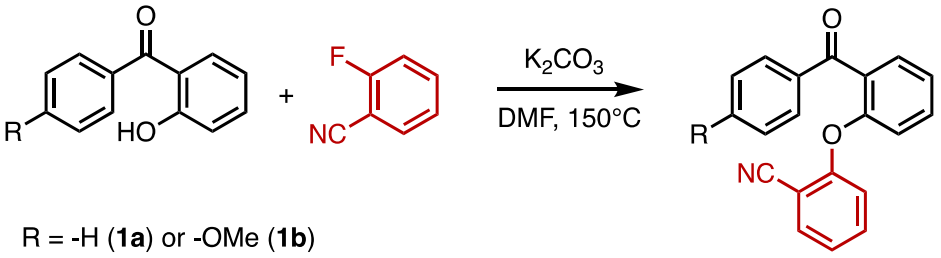
Entry	HFIP amount (mL)	Yield (mono+di) (%)
1	0.4	35
2	**0.6**	**57**
3	0.8	45
4	1.0	51
5	1.2	49
6	1.5	34
7	1.8	20

Table S13: Optimization of time



Entry	Time	Yield (mono+di) (%)
1	18	46
2	24	46
3	**30**	**57**
4	36	49
5	48	35

5. Experimental procedures:



R = -H (**1a**) or -OMe (**1b**)

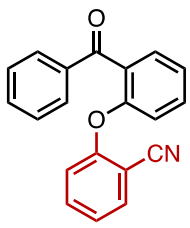
General procedure A for starting material preparations: 2-fluorobenzonitrile was refluxed with the corresponding 2-hydroxybenzophenone in presence of potassium carbonate in DMF for 12 h. Then aqueous workup followed by purification by column chromatography using petroleum ether/ethyl acetate as eluent provided the desired products **1a** and **1b**.[1]

General procedure B for *meta*-C–H olefination: In a clean, oven-dried screw cap reaction tube containing magnetic stir–bar, the substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Val-OH (20 mol%), Ag_2CO_3 (2 equiv.) were weighed. DCE (0.5 mL), HFIP (10 equiv.) and the corresponding olefin (2 equiv., 0.2 mmol) were added sequentially by syringes. The cap was sealed and this reaction tube was placed in a preheated oil bath at 75 °C to stir vigorously for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Regioselectivity was determined from ^{1}H NMR of this crude reaction mixture filtrate. Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petroleum ether/ethyl acetate as eluent.

General procedure C for *meta*-C–H diolefination: In a clean, oven-dried screw cap reaction tube containing magnetic stir–bar, substrate **2i** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Val-OH (20 mol%), Ag_2CO_3 (2 equiv.) were weighed. HFIP (0.5 mL) and the corresponding olefin (2 equiv., 0.2 mmol) were added sequentially by syringes. The cap was sealed and this reaction tube was placed in a preheated oil bath at 75 °C with vigorous stirring for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Regioselectivity was determined from ^{1}H NMR of this crude reaction mixture filtrate. The filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petroleum ether/ethyl acetate as eluent.

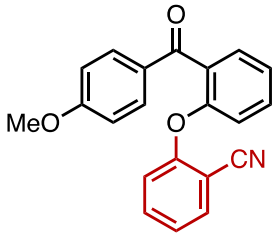
General procedure D for *meta*-C–H silylation: In a clean, oven-dried screw cap reaction tube containing magnetic stir–bar, the substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Gly-OH (20 mol%), Ag_2CO_3 (3 equiv., 0.3 mmol) were weighed. The reaction tube was dried using a hot gun and capped. Subsequently, HFIP (0.6 mL) and hexamethyldisilane (2 equiv.) were added sequentially by syringes. This reaction tube was placed in a preheated oil bath at 65 °C to stir vigorously for 30 h. Then the reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Regioselectivity was determined using Gas Chromatography of this crude reaction mixture filtrate. Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petroleum ether/ethyl acetate as eluent.

6. Characterisation data:



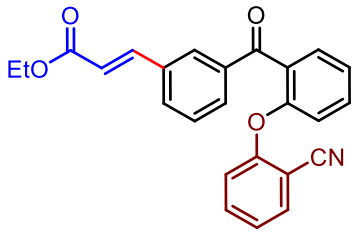
2-(2-benzoylphenoxy)benzonitrile (1a): General procedure A was followed and the titled compound was obtained as white solid (86%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.68 – 7.53 (m, 3H), 7.51 – 7.34 (m, 5H), 7.19 – 7.02 (m, 2H), 6.81 (dd, *J* = 8.5, 1.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.86, 159.18, 152.37, 137.05, 134.20, 133.74, 133.52, 132.64, 132.03, 130.84, 129.76, 128.53, 125.44, 123.04, 120.84, 116.84, 115.40, 103.38. **HRMS (ESI):** m/z calculated for [$C_{20}H_{13}O_2N$] [M+H$^+$]: 300.1019, measured: 300.1025.



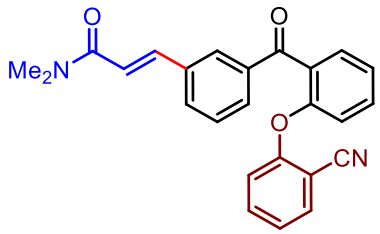
2-(2-(4-methoxybenzoyl)phenoxy)benzonitrile (1b): General procedure A was followed and the titled compound was obtained as white solid (75%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 2H), 7.62 – 7.47 (m, 3H), 7.42 (td, *J* = 7.5, 1.7 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.14 – 7.02 (m, 2H), 6.95 – 6.89 (m, 2H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.22, 164.01, 159.27, 152.11, 134.20, 133.67, 132.48, 132.29, 132.15, 130.52, 129.86, 125.36, 122.98, 120.74, 117.02, 115.50, 113.85, 103.37, 55.56. **HRMS (ESI):** m/z calculated for [$C_{21}H_{15}NO_3$] [M+H$^+$]: 330.1125, measured: 330.1121.



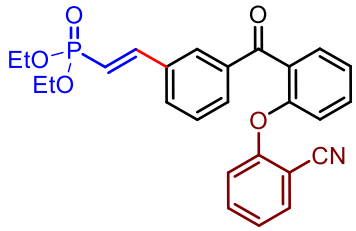
ethyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (2a): General procedure B was followed and the titled compound was obtained as colourless oil (77%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79 – 7.74 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.49 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.06 (td, *J* = 7.6, 0.9 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.57, 166.85, 159.18, 152.55, 143.53, 138.04, 135.05, 134.38, 133.98, 133.19, 132.68, 131.73, 131.47, 131.11, 129.43, 128.96, 125.79, 123.29, 121.12, 119.84, 116.84, 115.41, 103.54, 60.83, 14.49. **HRMS (ESI):** m/z calculated for [$C_{25}H_{19}O_4NNa$] [M+Na$^+$]: 420.1206, measured: 420.1194.



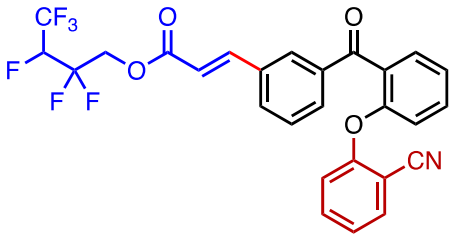
(*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)-*N*,*N*-dimethylacrylamide (2b): General procedure B was followed and the titled compound was obtained as colourless oil (83%) after the elution with 80:20 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.68 (d, *J* = 9.4 Hz, 2H), 7.63 – 7.56 (m, 3H), 7.47 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.37 (td, *J* = 7.5, 0.9 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.05 (td, *J* = 7.6, 0.7 Hz, 1H), 6.90 (d, *J* = 15.5 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.15 (s, 3H), 3.05 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.76, 166.54, 159.20, 152.62, 141.22, 137.85, 136.01, 134.37, 133.94, 133.06, 132.78, 131.79, 131.03, 129.22, 128.27, 125.64, 123.27, 121.02, 119.18, 116.97, 115.48, 103.53, 37.67, 36.13. **HRMS (ESI):** m/z calculated for [$C_{25}H_{20}O_3N_2Na$] [M+Na^+]: 419.1366, measured: 419.1372.



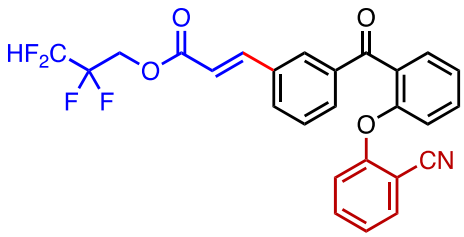
diethyl (*E*)-(3-(2-(2-cyanophenoxy)benzoyl)styryl)phosphonate (2c): General procedure for olefination was followed and the titled compound was obtained as colourless oil (71%) after the elution with 85:15 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.32 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.26 (t, *J* = 16.9 Hz, 1H), 4.15 – 4.07 (m, 4H), 1.32 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.45, 159.08, 152.48, 147.61, 147.57, 137.88, 135.48, 135.24, 134.35, 133.89, 133.13, 132.35, 131.59, 131.44, 130.98, 129.33, 128.59, 125.69, 123.26, 120.99, 116.83, 115.36, 103.46, 62.14, 16.56, 16.51. **HRMS (ESI):** m/z calculated for [$C_{26}H_{25}O_5NP$] [M+H^+]: 462.1465, measured: 462.1459.



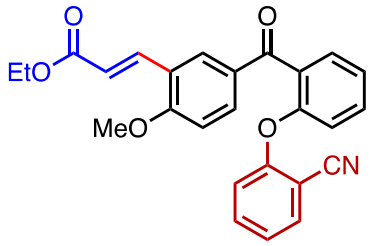
2,2,3,4,4,4-hexafluorobutyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (2d): General procedure B was followed and the titled compound was obtained as colourless oil (45%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 1H), 7.87 – 7.72 (m, 3H), 7.70 – 7.57 (m, 2H), 7.57 – 7.36 (m, 4H), 7.17 – 7.04 (m, 2H), 6.88 – 6.75 (m, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 5.22 – 4.90 (m, 1H), 4.71 – 4.52 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.11, 164.67, 158.67, 152.33, 145.81, 144.75, 137.88, 135.12, 134.13, 133.68, 132.96, 132.48, 131.73, 131.22, 130.83, 130.59, 129.24, 129.06, 125.45, 123.17, 120.45, 118.34, 117.16, 116.83, 115.09, 103.45, 60.86. **HRMS (ESI):** m/z calculated for [$C_{27}H_{17}F_6NO_4$] [M+H$^+$]: 534.1135, measured: 534.1138.



2,2,3,3-tetrafluoropropyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (2e): General procedure B was followed and the titled compound was obtained as colourless oil (55%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

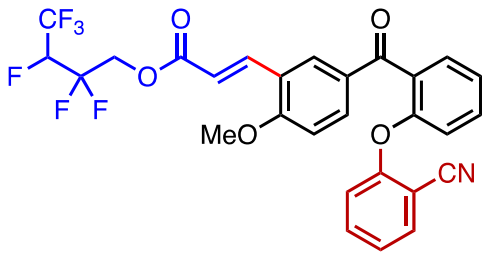
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.86 – 7.69 (m, 3H), 7.69 – 7.56 (m, 2H), 7.56 – 7.32 (m, 4H), 7.20 – 7.00 (m, 2H), 6.81 (d, 1H), 6.48 (d, *J* = 16.1 Hz, 1H), 5.96 (tt, *J* = 53.1, 4.0 Hz, 1H), 4.62 (t, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ194.11, 164.85, 158.73, 152.28, 145.62, 137.88, 134.17, 134.10, 133.68, 132.97, 132.49, 131.70, 131.27, 130.84, 129.24, 128.94, 125.49, 123.10, 120.61, 117.31, 116.66, 115.08, 114.09, 109.18, 103.35, 59.67. **HRMS (ESI):** m/z calculated for [$C_{26}H_{17}F_4NO_4$] [M+H$^+$]: 484.1166, measured: 484.1161.



ethyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (2f): General procedure for olefination was followed and the titled compound was obtained as colourless oil (43%) after the elution with 95:5 pet ether/ethyl acetate (v/v) from silica column.

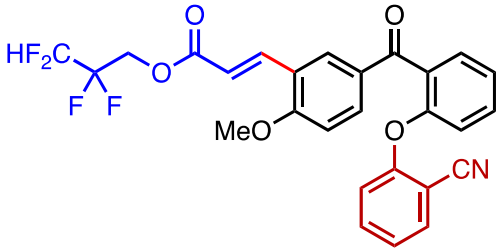
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.85 (m, 2H), 7.84 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.68 – 7.55 (m, 2H), 7.53 – 7.34 (m, 3H), 7.20 – 7.05 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.5, 1.0 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.09, 167.17, 162.20, 159.17, 152.10, 138.93, 134.21, 134.02, 133.73, 132.55, 132.04, 130.69, 130.48, 129.90, 125.59, 123.61, 123.02, 120.92, 120.16, 116.80, 115.41,

111.04, 103.31, 60.47, 56.02, 14.35. **HRMS (ESI):** m/z calculated for [$C_{26}H_{21}NO_5$] [M+H$^+$]: 428.1492, measured: 428.1496.



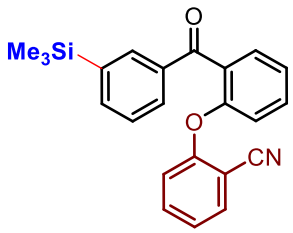
2,2,3,4,4,4-hexafluorobutyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (2g): General procedure B was followed and the titled compound was obtained as colourless oil (23%) after the elution with 95:5 petroleum ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.94 (m, 2H), 7.88 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.72 – 7.55 (m, 2H), 7.55 – 7.34 (m, 3H), 7.19 – 7.05 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 5.20 – 4.91 (m, 1H), 4.74 – 4.48 (m, 2H), 4.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.03, 165.39, 162.43, 159.02, 152.12, 141.72, 134.65, 134.29, 133.75, 132.66, 131.86, 131.52, 131.07, 130.72, 129.98, 126.38, 125.61, 123.17, 122.98, 120.68, 117.73, 117.00, 115.41, 114.47, 111.21, 103.45, 60.80, 56.12. **HRMS (ESI):** m/z calculated for [$C_{28}H_{19}F_6NO_5$] [M+H$^+$]: 564.1240, measured: 564.1243.



2,2,3,3-tetrafluoropropyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (2h): General procedure B was followed and the titled compound was obtained as colourless oil (39%) after the elution with 95:5 pet ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.93 (m, 2H), 7.87 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.55 – 7.34 (m, 3H), 7.18 – 7.04 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 8.5, 1.0 Hz, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 5.96 (tt, *J* = 53.1, 4.2 Hz, 1H), 4.61 (t, *J* = 11.4 Hz, 2H), 4.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.02, 193.02, 165.56, 162.40, 159.06, 152.10, 141.50, 134.61, 134.27, 133.75, 132.66, 131.89, 130.93, 130.73, 129.97, 125.63, 123.12, 123.03, 120.79, 117.85, 116.88, 115.40, 111.19, 109.25, 103.38, 59.76, 56.11. **HRMS (ESI):** m/z calculated for [$C_{27}H_{19}F_4NO_5$] [M+H$^+$]: 514.1272, measured: 514.1269.

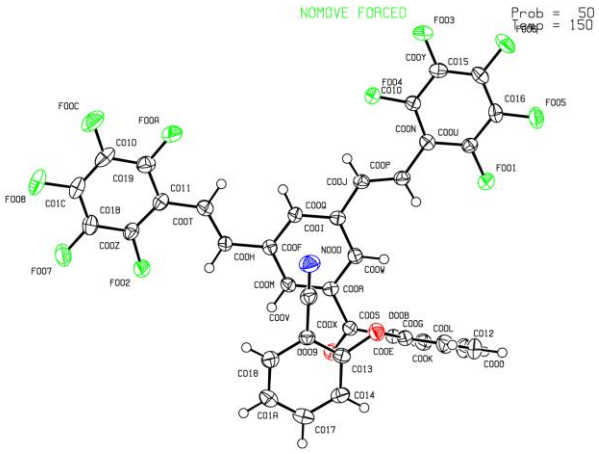


2-(2-(3-(trimethylsilyl)benzoyl)phenoxy)benzonitrile (4): General procedure D was followed and the titled compound was obtained as colourless oil (54%) after the elution with 97:3 pet ether/ethyl acetate (v/v) from silica column.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.61 – 7.56 (m, 2H), 7.46 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 0.26 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 195.52, 159.60, 152.54, 141.32, 138.64, 136.43, 134.30, 134.07, 133.88, 132.84, 132.40, 131.04, 130.87, 128.01, 125.63, 123.00, 121.38, 116.82, 115.56, 103.39, -1.06. **HRMS (ESI):** m/z calculated for [$C_{23}H_{21}O_2NSiNa$] [M+Na^+]: 394.1234, measured: 394.1221.

7. Crystal data for 3i

Crystals suitable for X-ray diffraction was obtained by slow evaporation from a saturated solution of **3i** in chloroform.



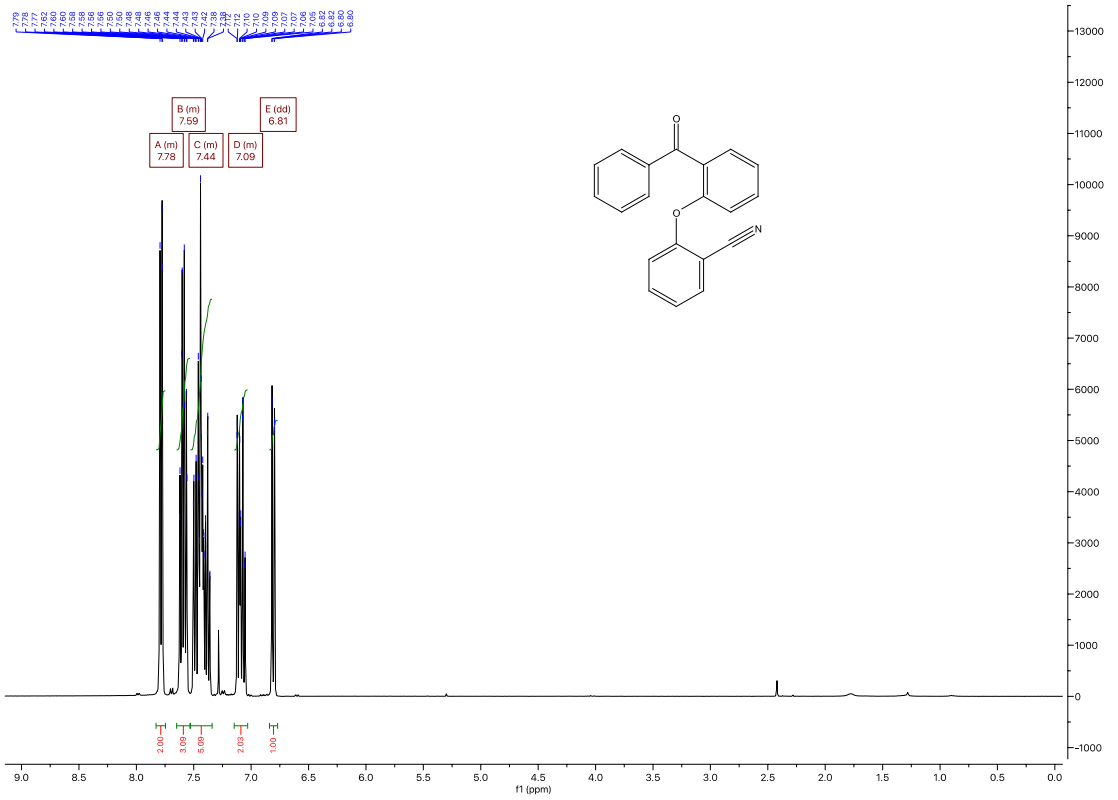
Crystal data, CCDC 1996646:

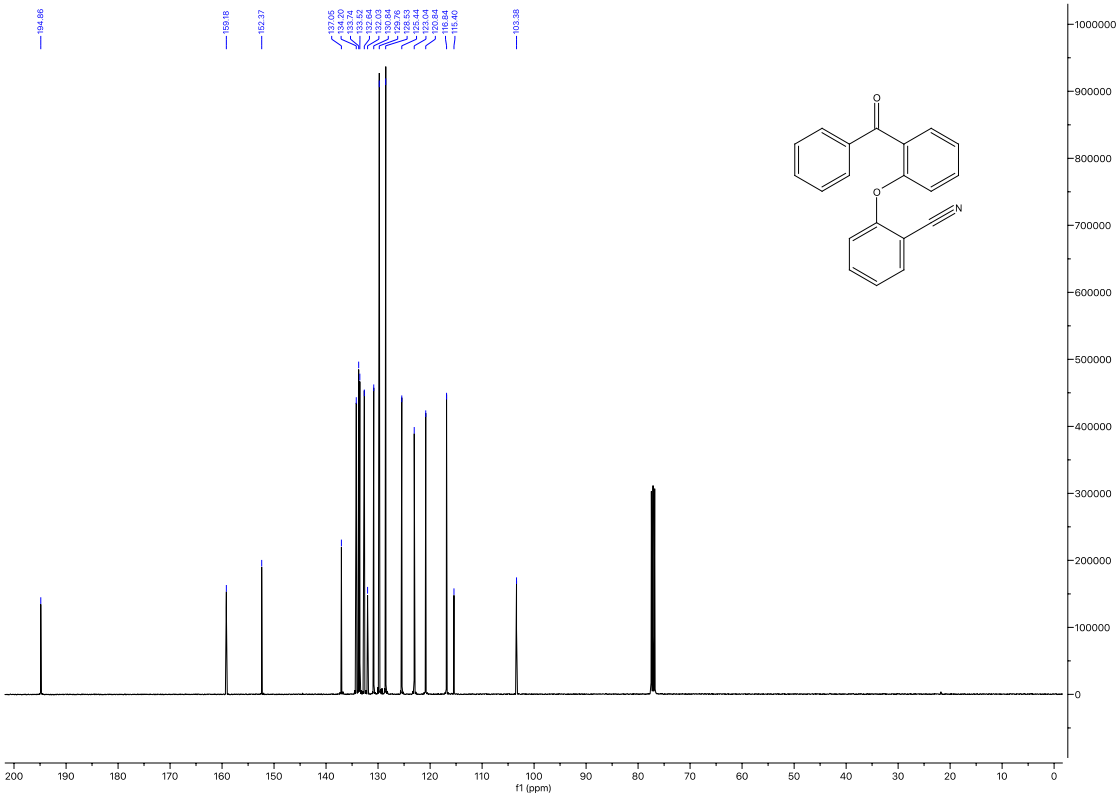
Crystal data and structure refinement for $C_{36}H_{15}F_{10}NO_2$	
Formula	$C_{36}H_{15}F_{10}NO_2$
Formula weight (g/mol)	227.83
Temperature/K	150 K
Crystal system	triclinic
Space group	P_{-1}
a/Å	10.3014(4)
b/Å	11.5202(5)
c/Å	12.2962(6)

α/ °	96.803(4)
β/ °	97.658(4)
γ/ °	98.459(4)
Volume/Å^3	1416.24(11)
Z	6
P_{calc} (g/cm^3)	1.603
μ/mm^{-1}	0.144
F(000)	688
Crystal size/mm^3	0.09 mm x 0.085 mm x 0.072 mm
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.805 to 24.995
Index ranges	-12≤h≤12, -13≤k≤12, -14≤l≤14
Reflections collected / unique	14956 / 5680 [R(int) = 0.0662]
Data / restraints / parameters	4983 / 0 / 442
Goodness-of-fit on F^2	1.050
Final R indices [I>2σ(I)]	0.0536 / 0.1175
R indices (all data)	0.0836 / 0.1462
Largest diff. peak and hole/ e Å^{-3}	0.366 and -0.351

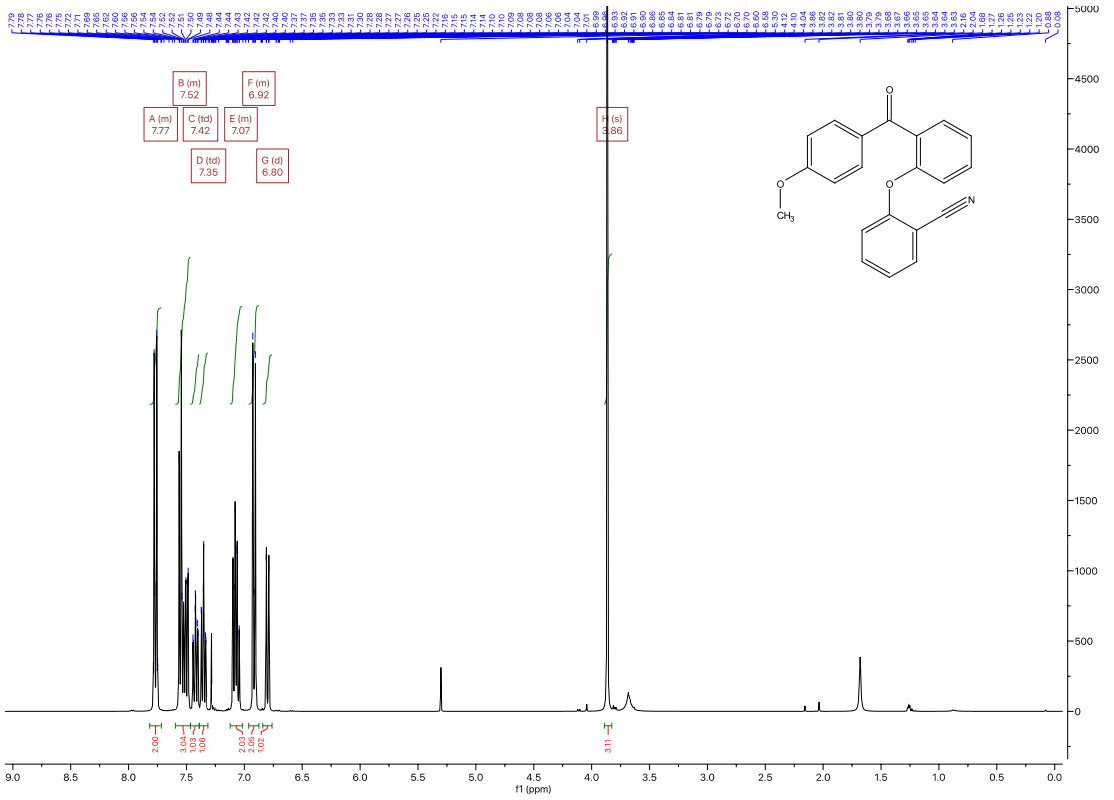
8. NMR Spectra

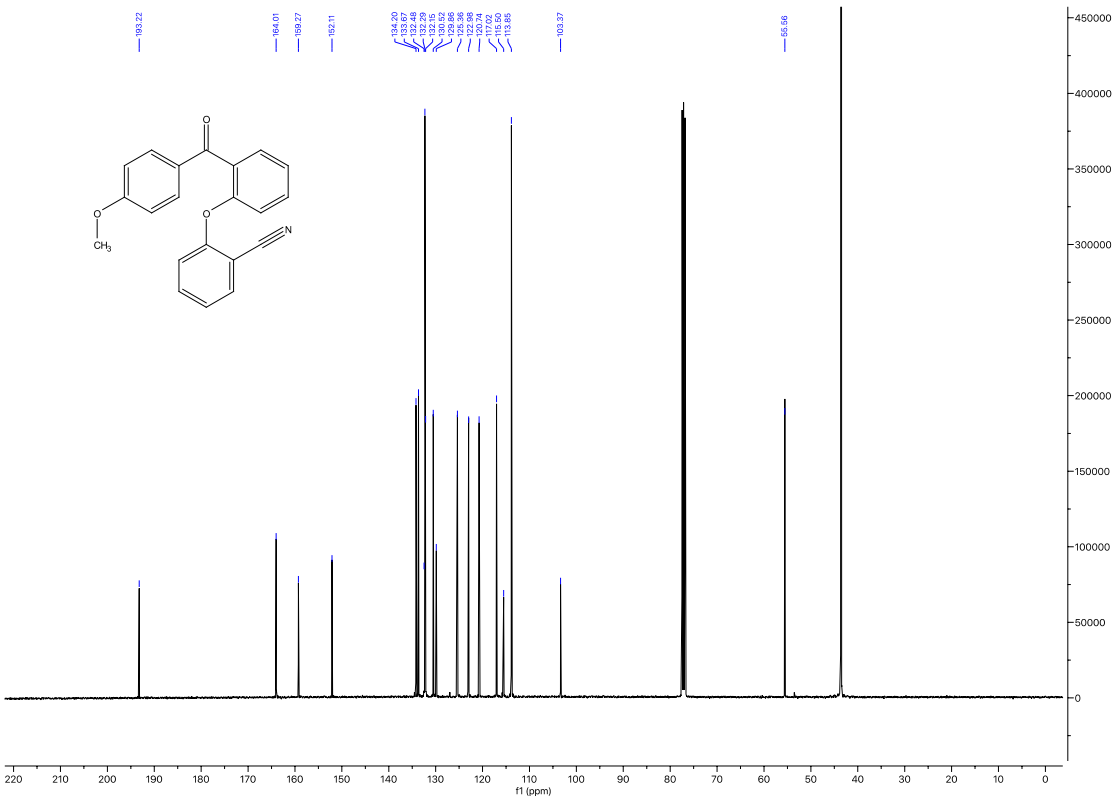
2-(2-benzoylphenoxy)benzonitrile (substrate 1a):



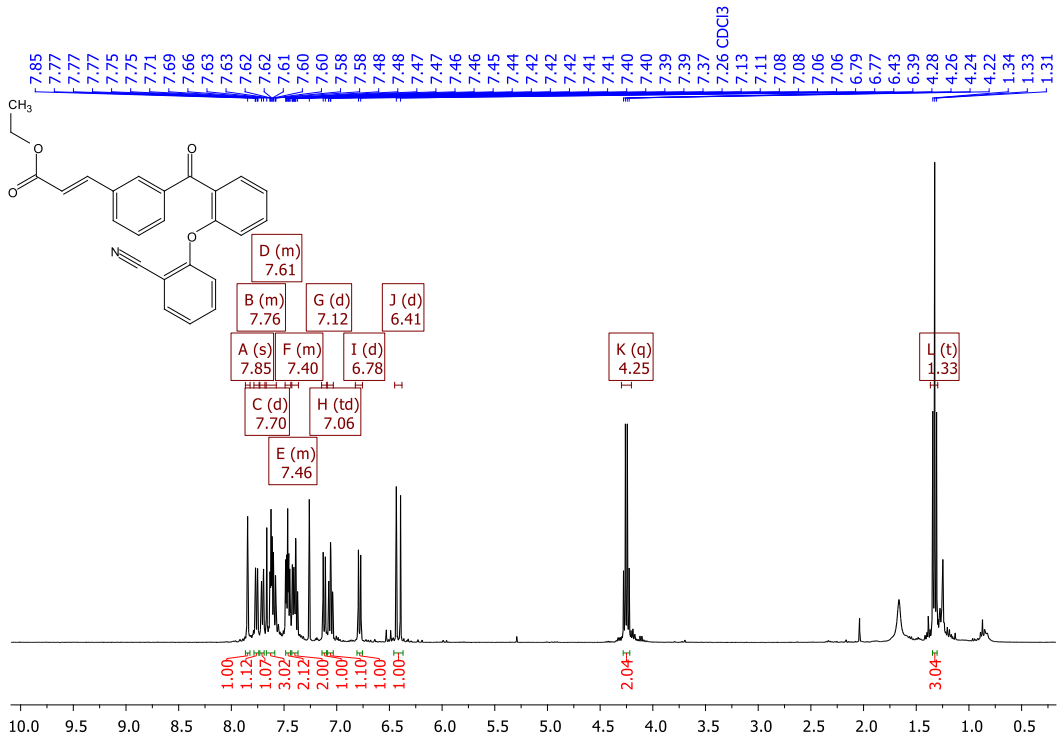


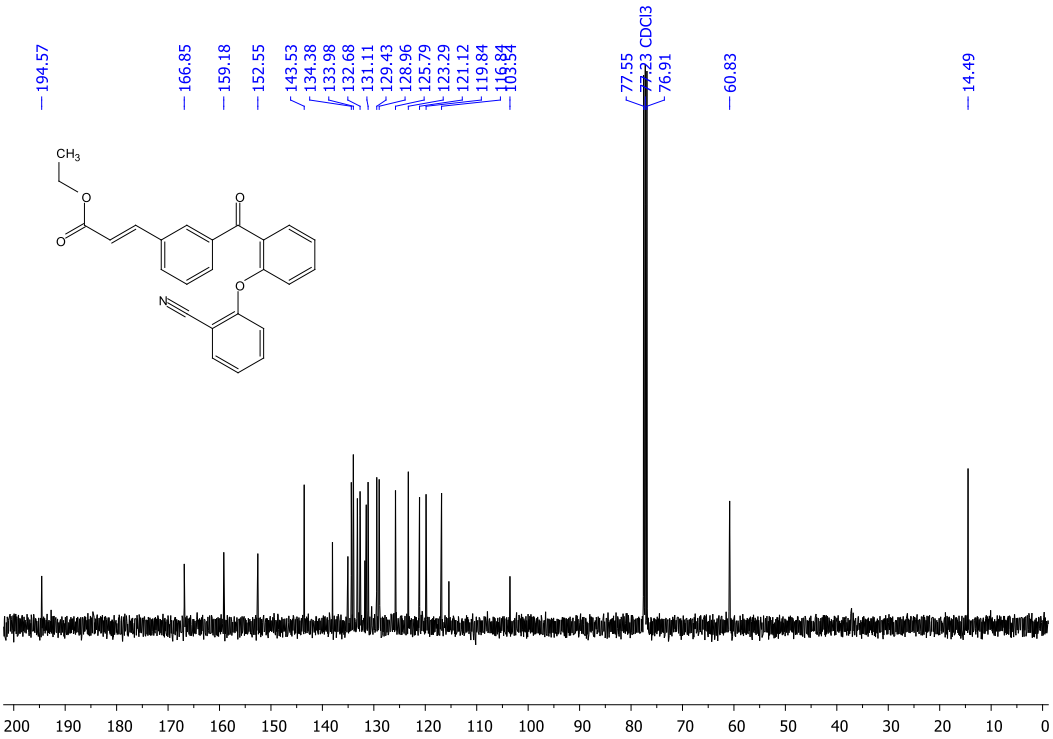
2-(2-(4-methoxybenzoyl)phenoxy)benzonitrile (substrate 1b):



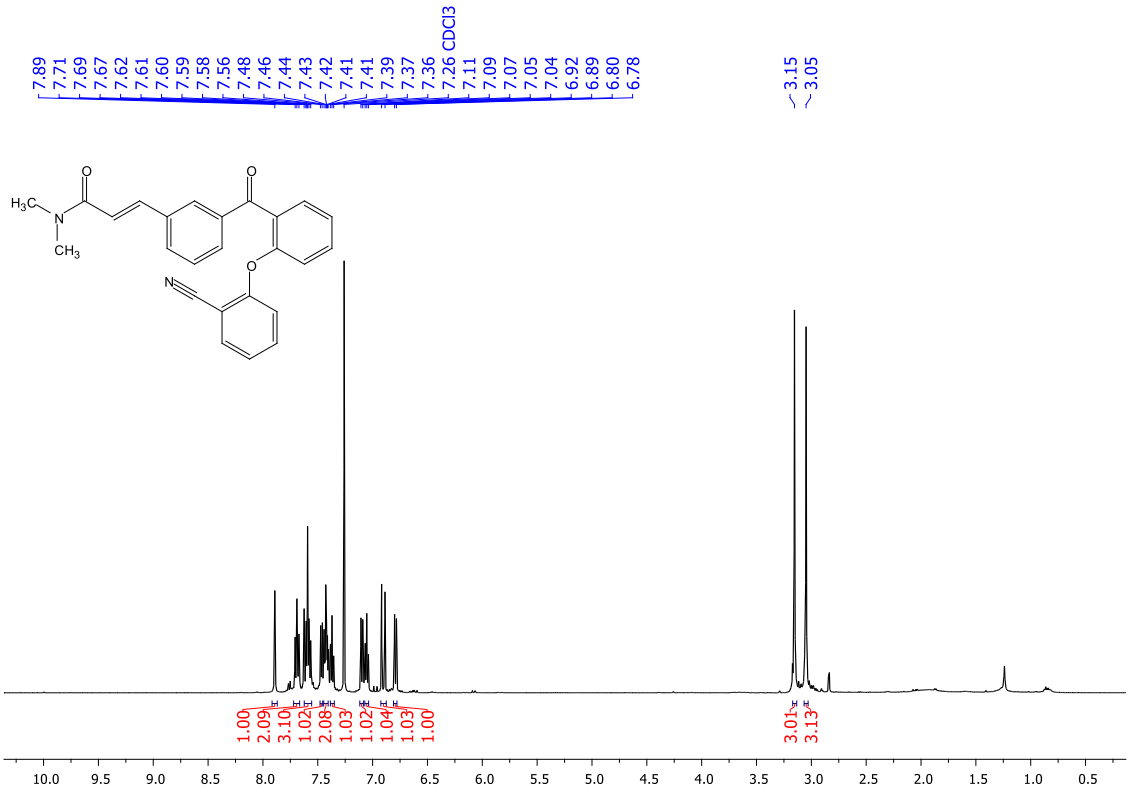


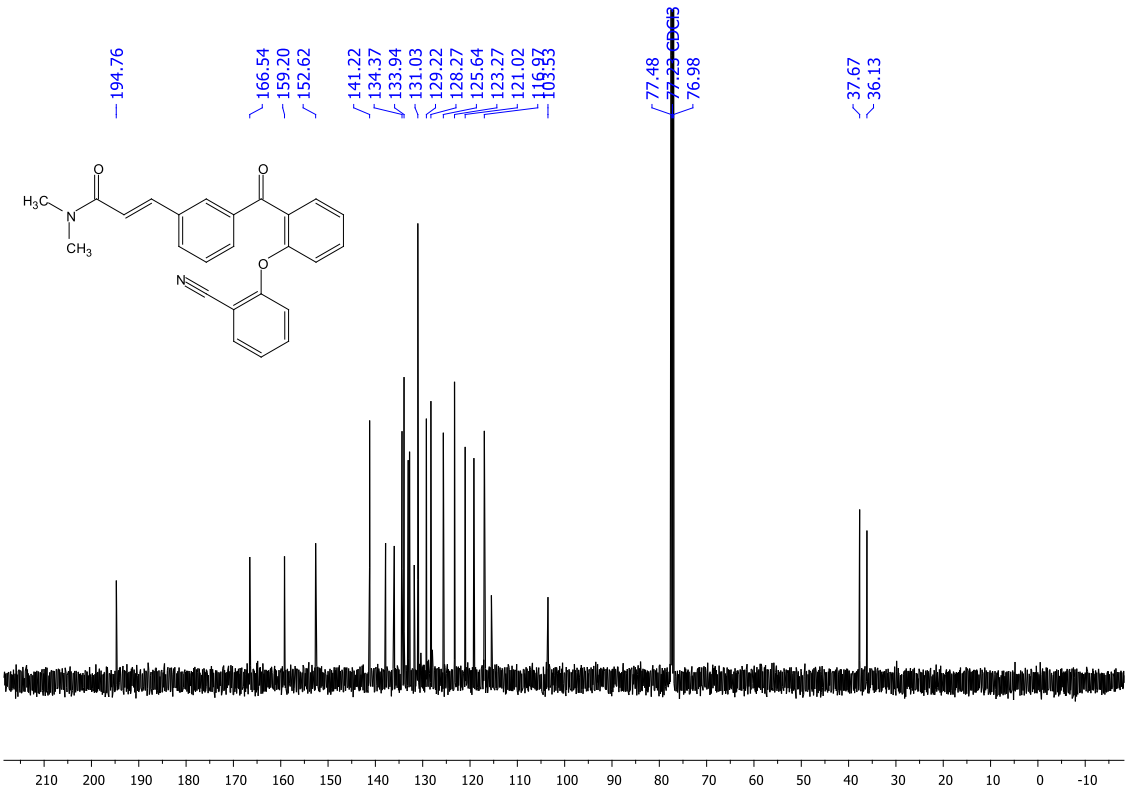
ethyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (entry 2a):



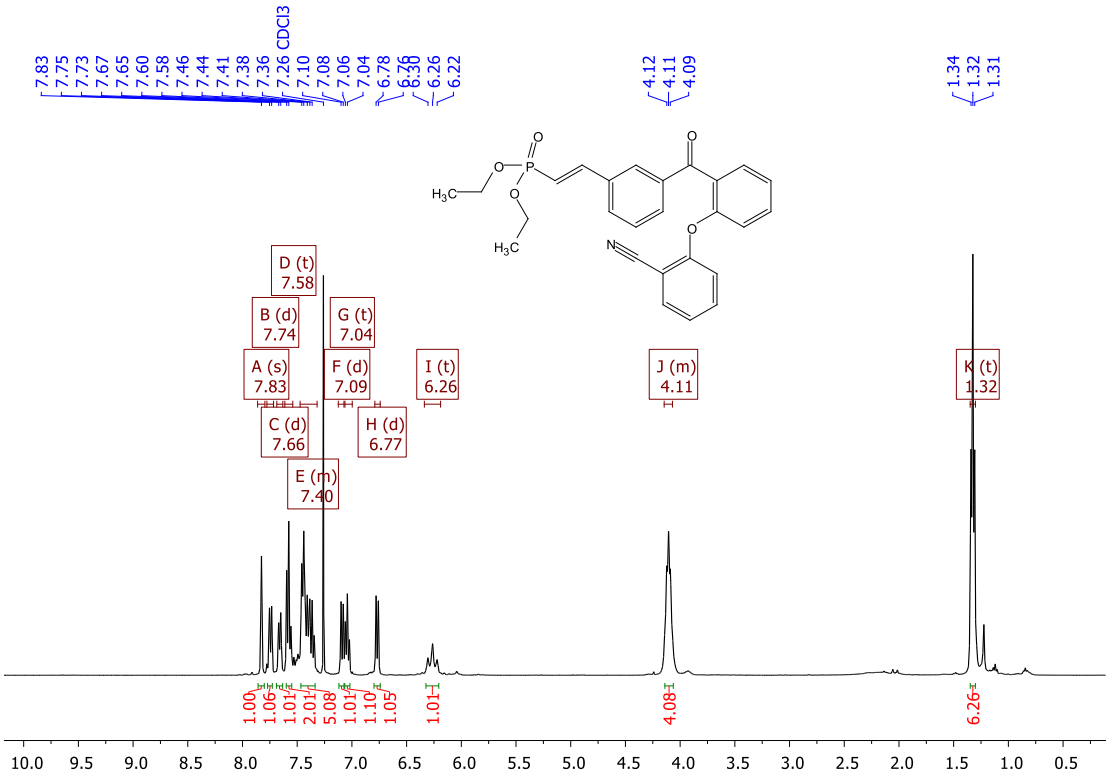


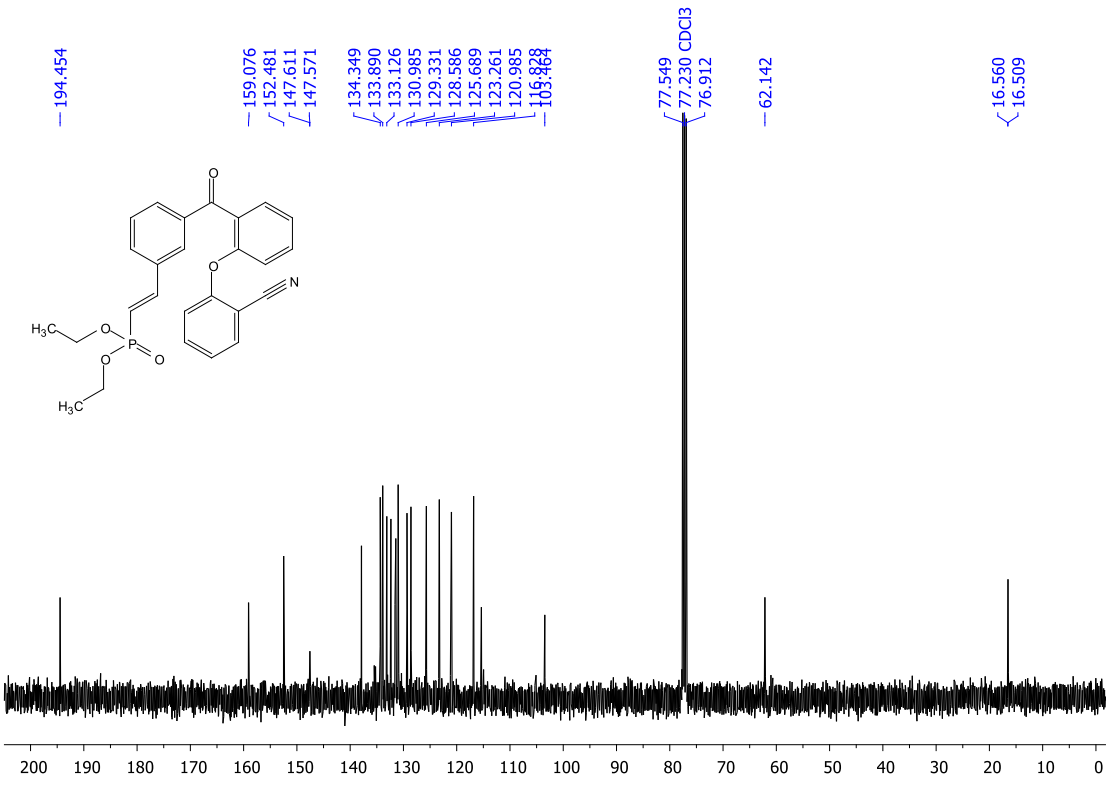
(*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)-*N*,*N*-dimethylacrylamide (entry 2b):



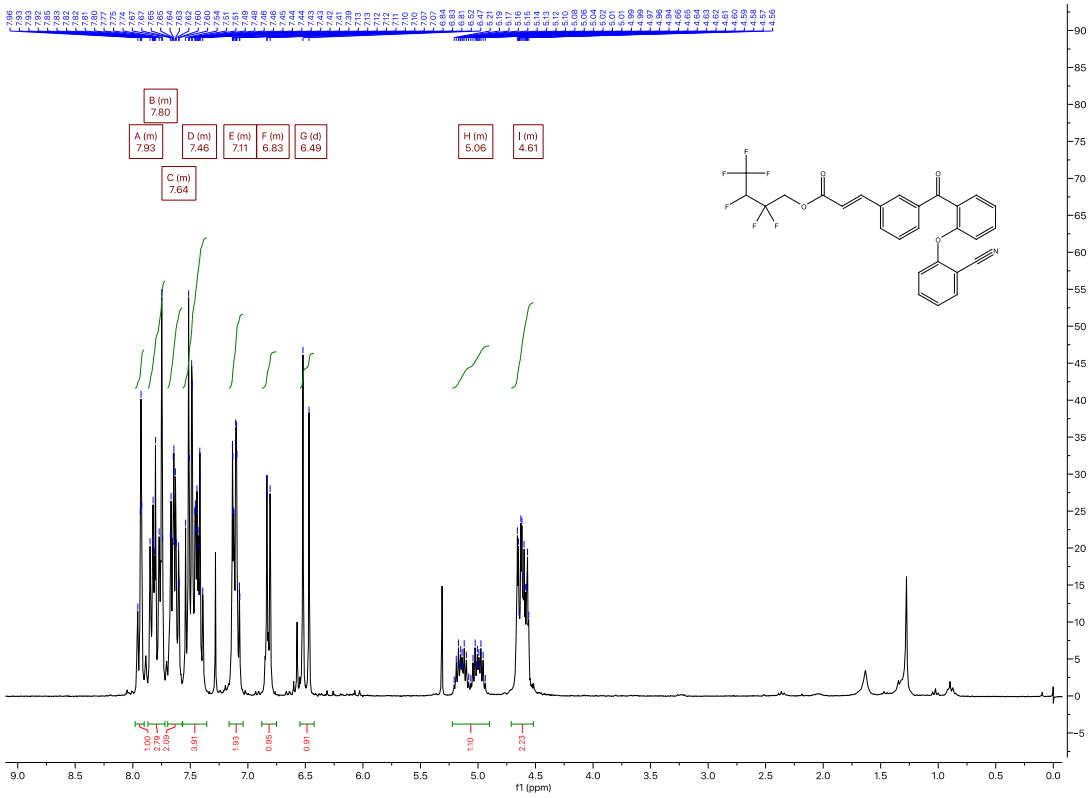


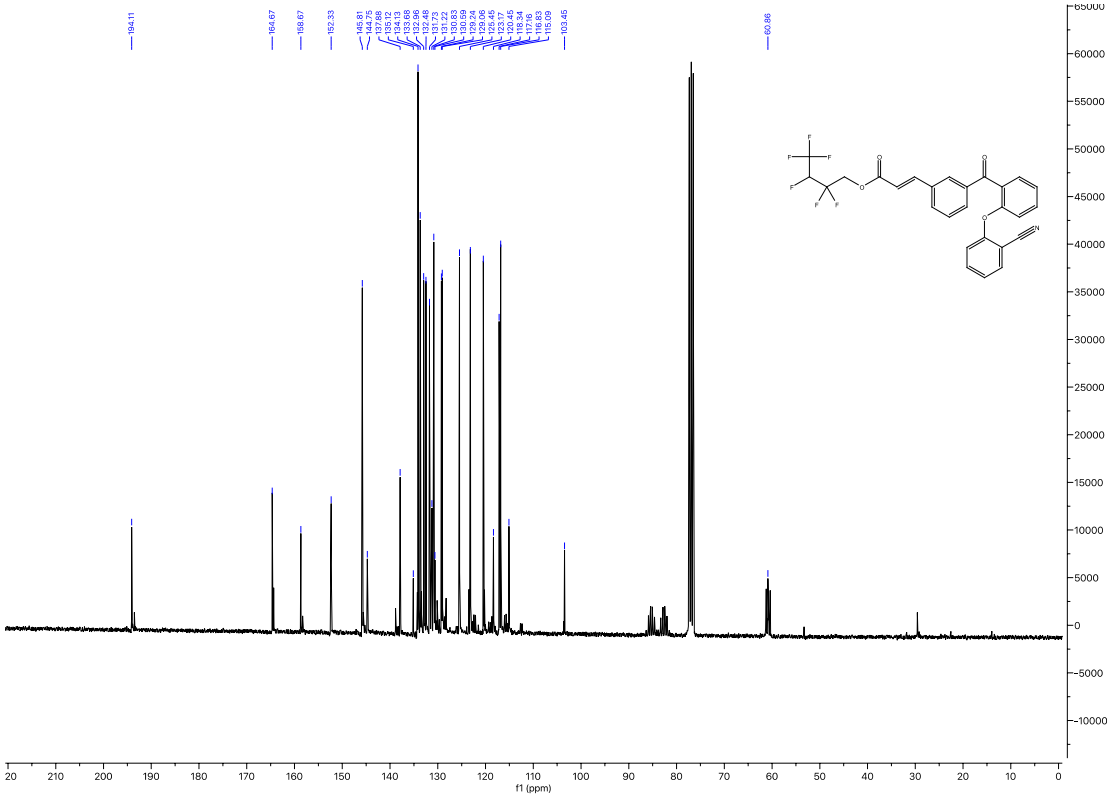
diethyl (*E*)-(3-(2-(2-cyanophenoxy)benzoyl)styryl)phosphonate (entry 2c):



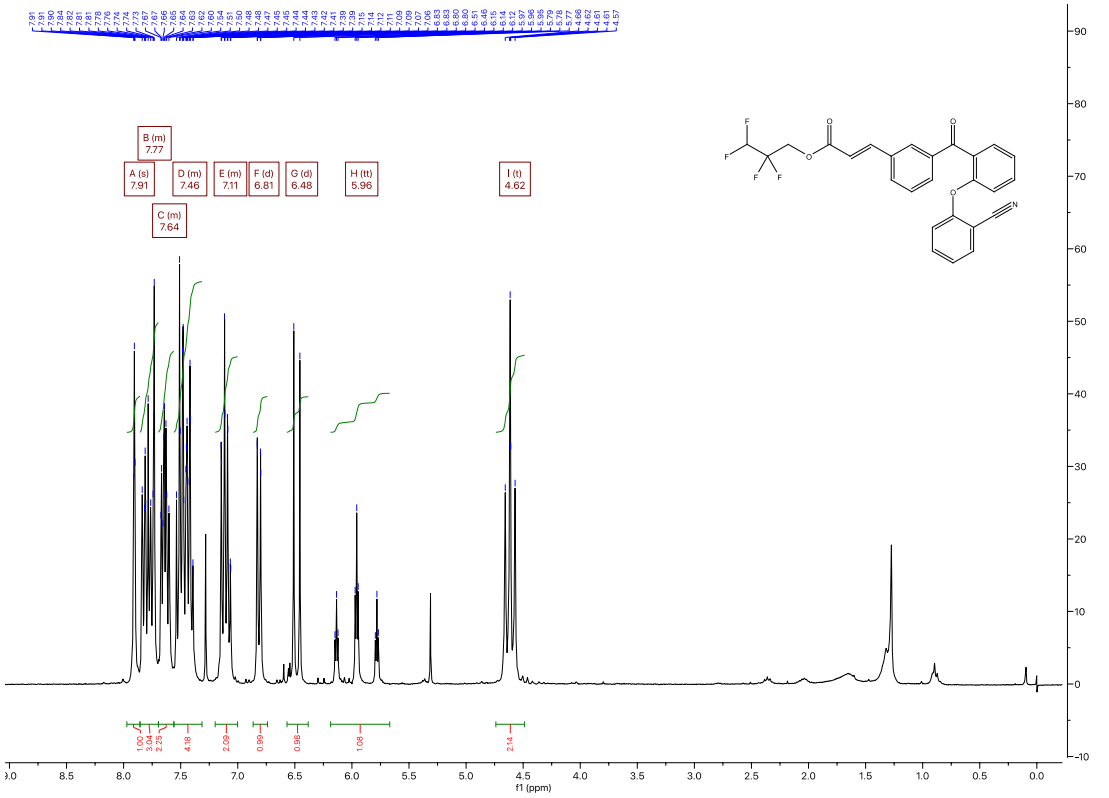


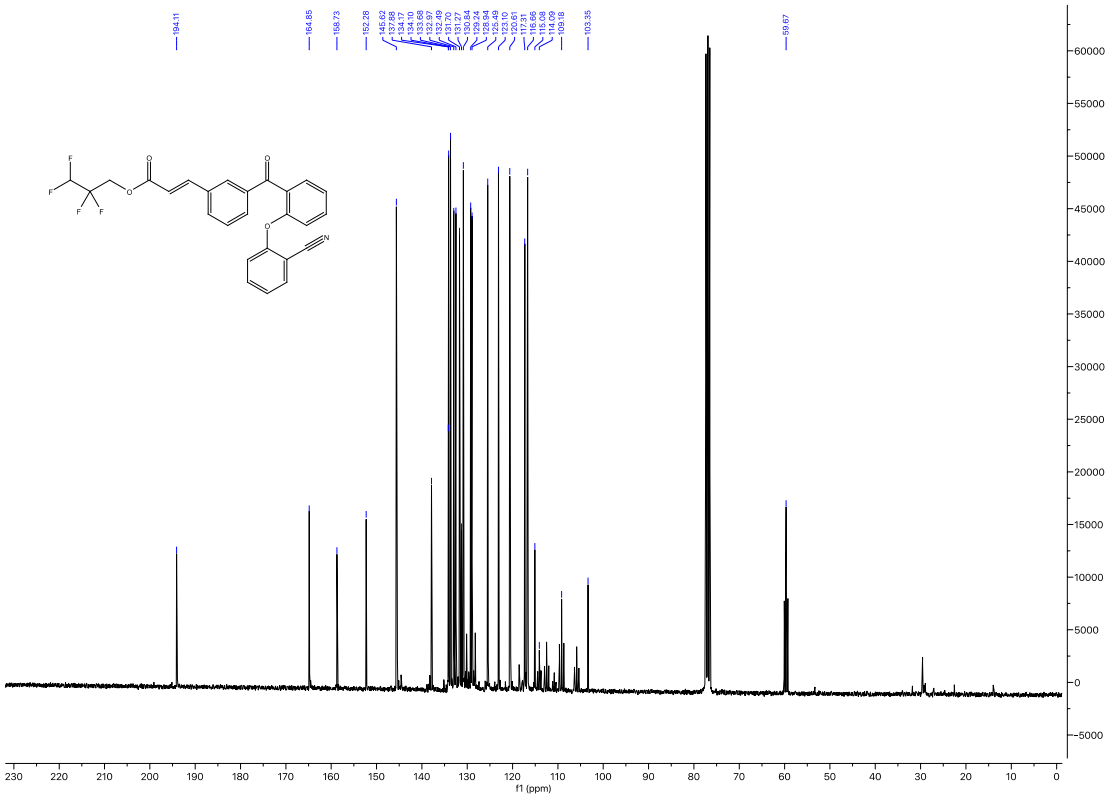
2,2,3,4,4,4-hexafluorobutyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (entry 2d):



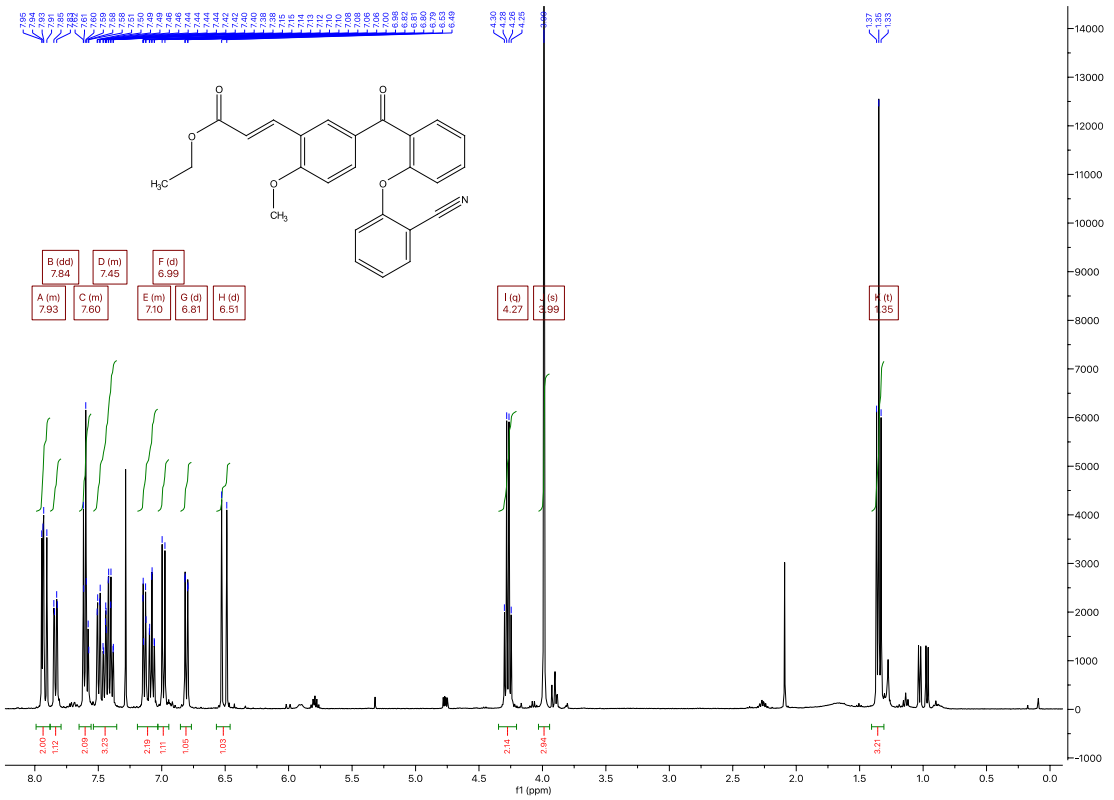


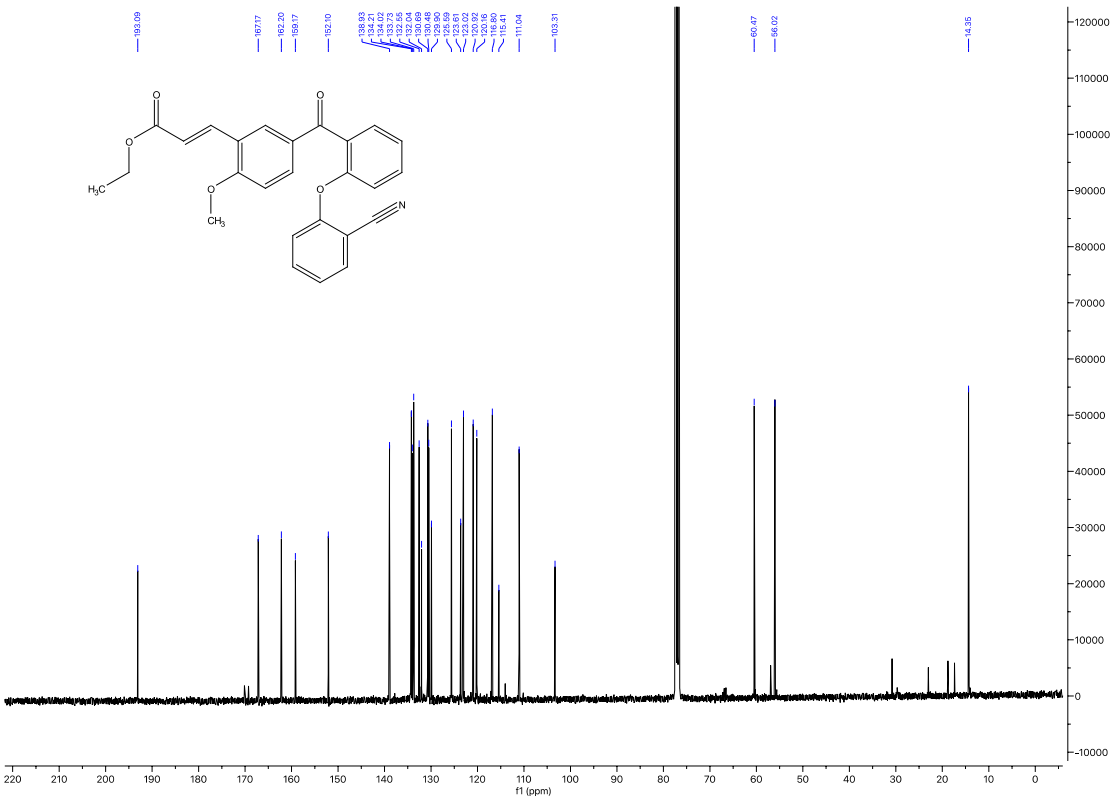
2,2,3,3-tetrafluoropropyl (*E*)-3-(3-(2-(2-cyanophenoxy)benzoyl)phenyl)acrylate (entry 2e):



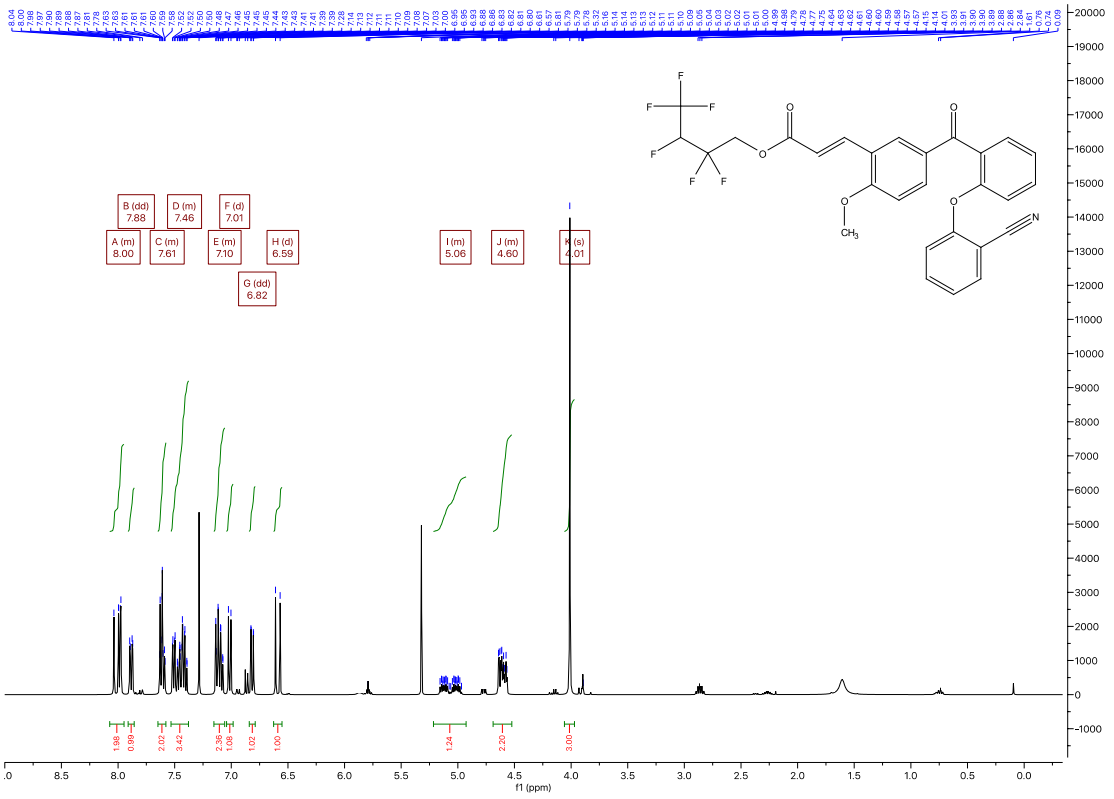


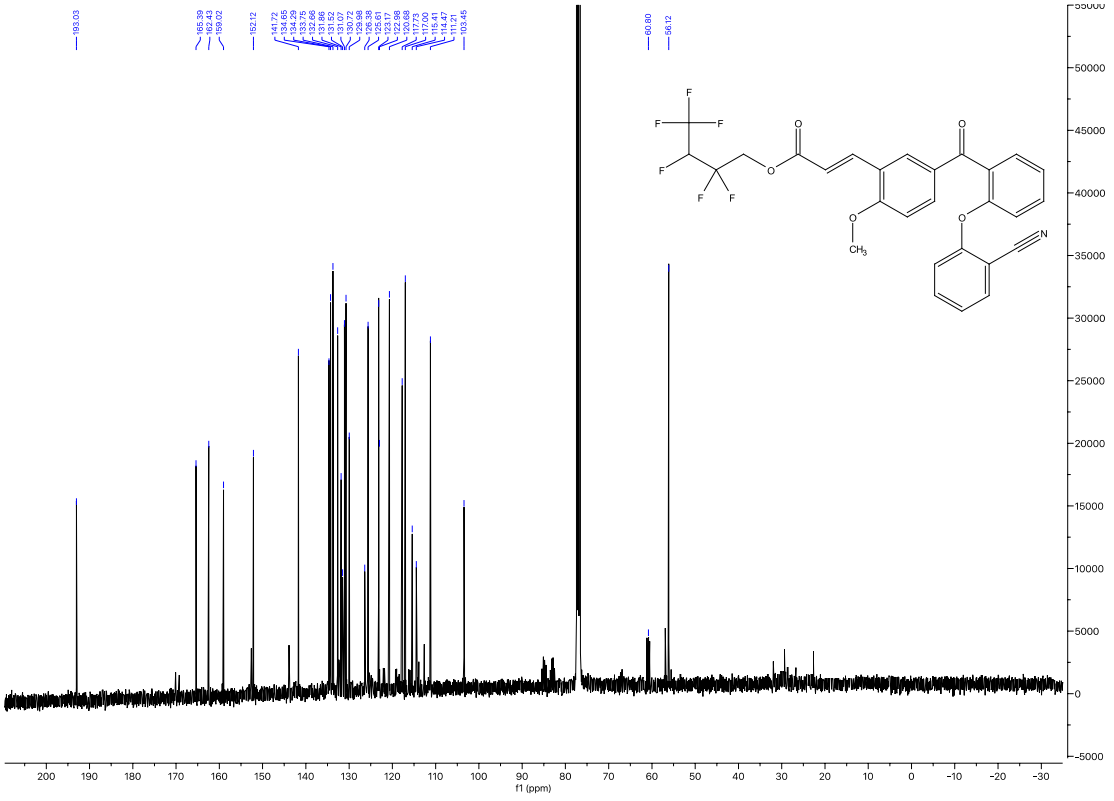
ethyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (entry 2f):



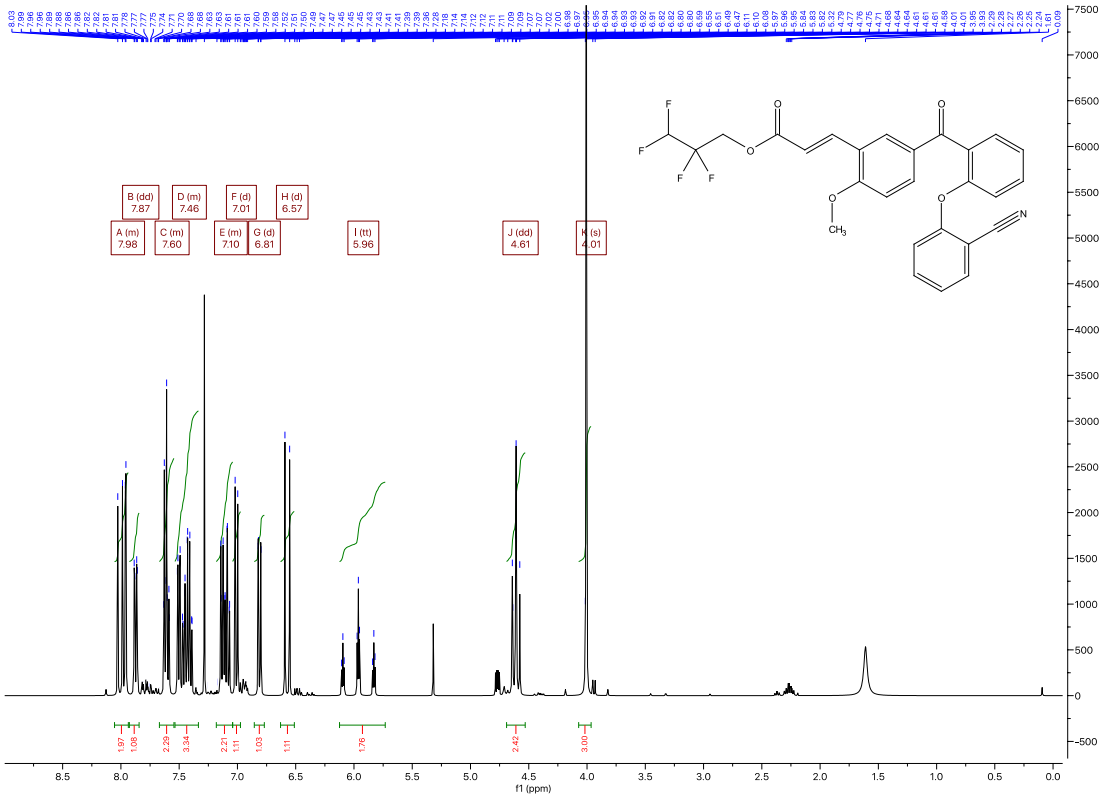


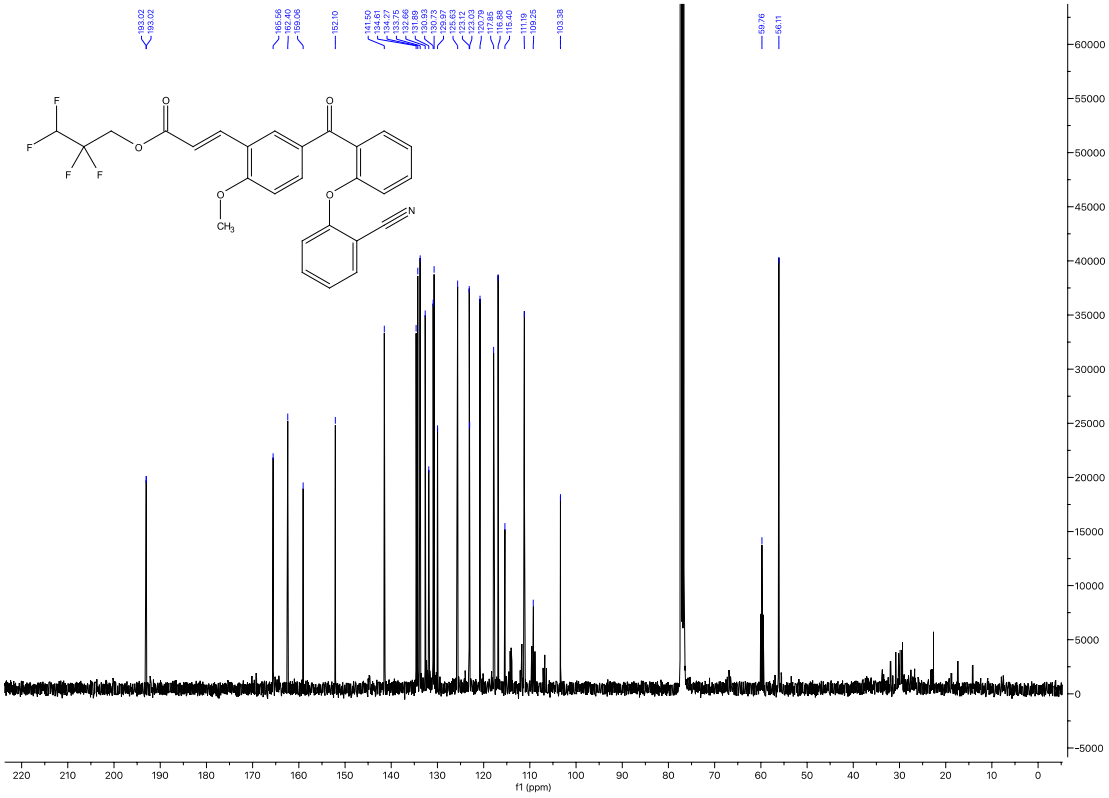
2,2,3,4,4,4-hexafluorobutyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (entry 2g):



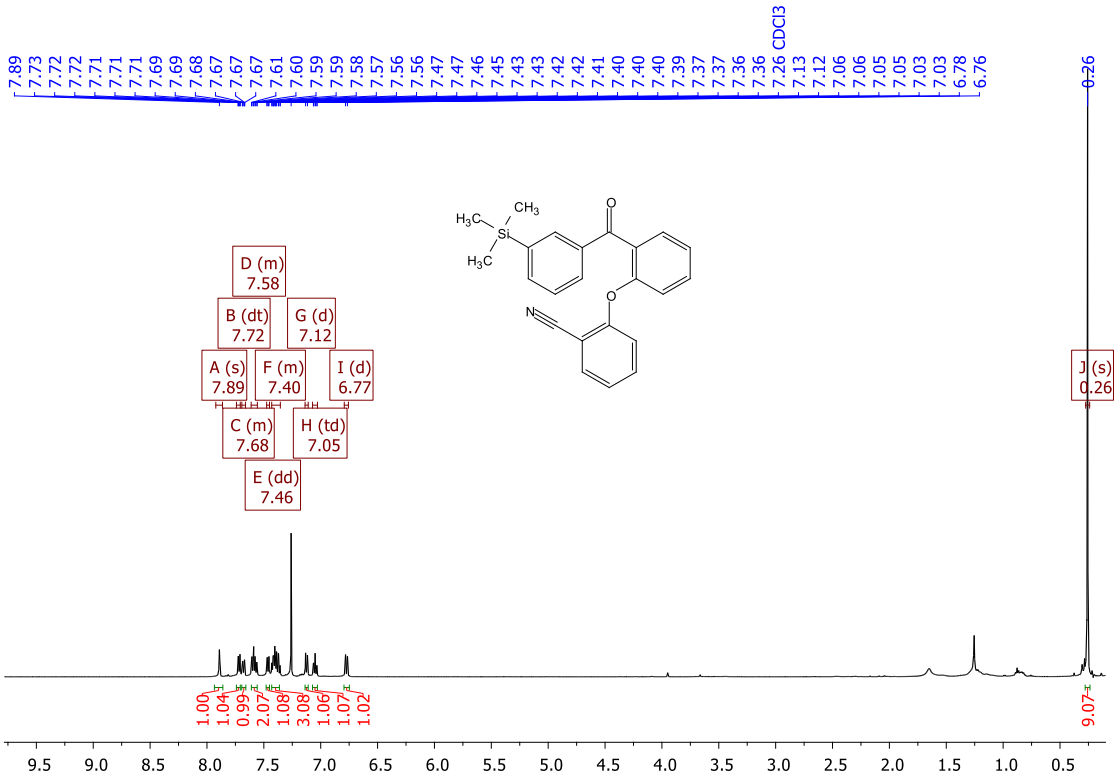


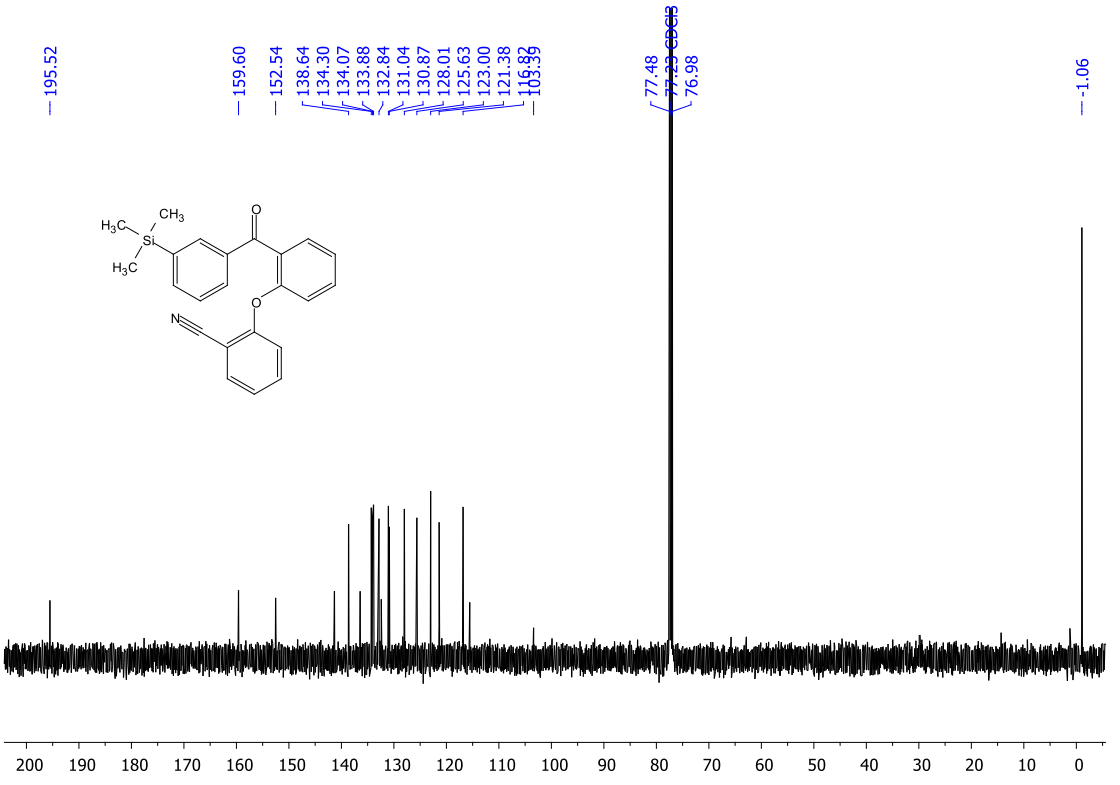
2,2,3,3-tetrafluoropropyl (*E*)-3-(5-(2-(2-cyanophenoxy)benzoyl)-2-methoxyphenyl)acrylate (entry 2h):



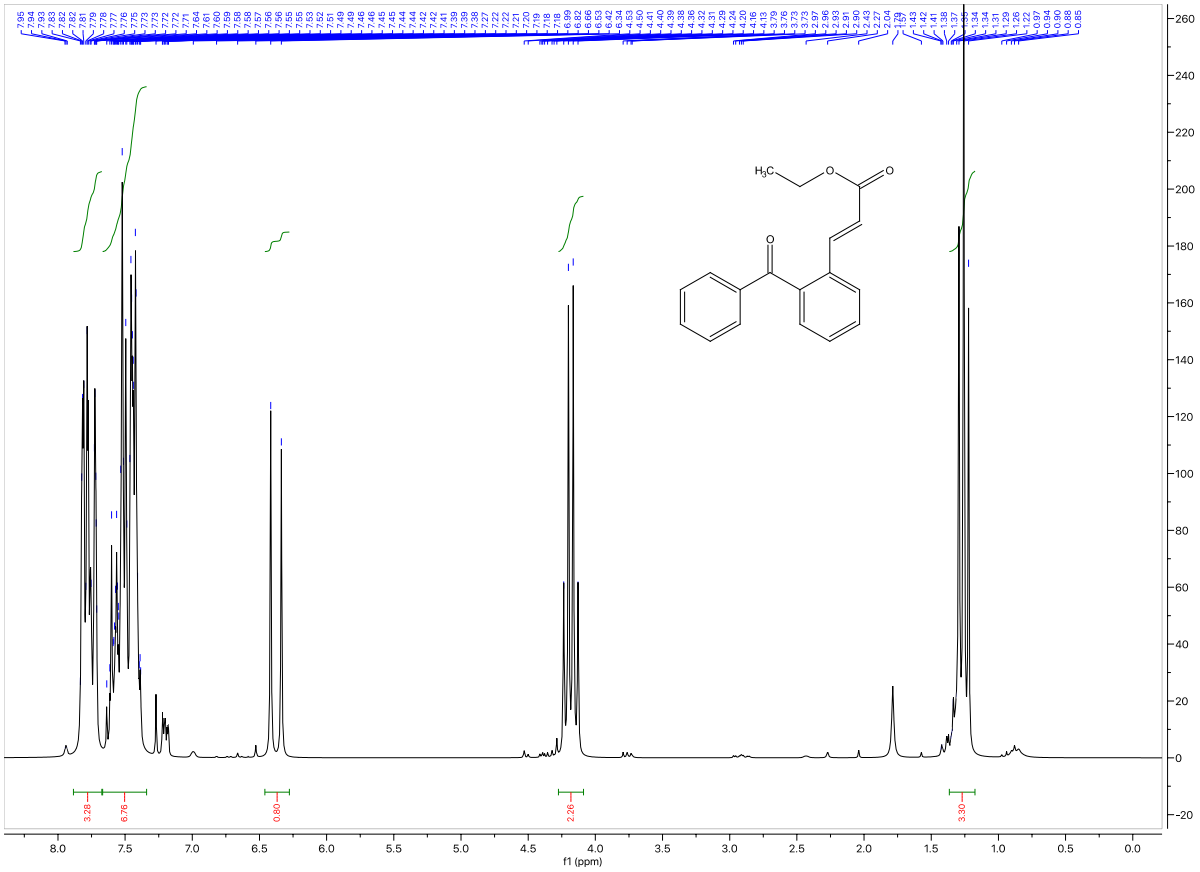


2-(2-(3-(trimethylsilyl)benzoyl)phenoxy)benzonitrile (entry 4):





ethyl (*E*)-3-(2-benzoylphenyl)acrylate (entry 2aa)



9. References

1) Feng, J. B.; Wu, X. F. Base-promoted synthesis of dibenzoxazepinamines and quinazolinimines under metal-free conditions, *Green Chem.*, **2015**, *17*, 4522-4526.