

ELECTRONIC SUPPORTING INFORMATION

Heterogeneous and Recoverable Palladium Catalyst to access Regioselective C–H Alkenylation of Quinoline N–oxides.

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LIST OF ABBREVIATION:

CPME	Cyclopentyl methyl ether
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
ETP	Petroleum ether
EtOAc	Ethyl Acetate
GVL	γ -valerolactone
NMP	N-methylpyrrolidone
SolFC	Solvent-Free Conditions

1. General Remarks.

All chemicals were used without any further purification unless otherwise noted. GLC analyses were performed by using Agilent 6850 Series GC System equipped with a capillary column DB-5MS (30 m, 0.32 mm), a FID detector and helium as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (^1H at 400 MHz and ^{13}C at 100.6 MHz). Chemical shifts are reported in ppm and coupling constants in Hertz. Flash chromatography was carried out on a Büchi Reveleris® X2-UV system. Elemental Analysis (EA) were conducted on Elementar UNICUBE® elemental analyzer. XRD analysis were conducted on a Bruker D8 VENTURE in a glass capillary. This diffractometer uses a $1\mu\text{S}$ 3.0 microfocus Mo-K α X-ray source (0.71073 Å) and a PHOTON II detector with CPAD technology. TEM images were obtained using a FEI Tecnai 10 system with an operating voltage of 80 kV. Samples were prepared by depositing the suspension of materials in ethanol on a carbon coated copper grid. Palladium content was measured by using an Agilent 4210 MP-AES instrument. Melting points were measured on a Büchi 510 apparatus.

Synthesis of **SP-Cl**,¹ 3,3-di(1H-imidazol-1-yl)propan-1-ol (**L1**),² 3,3-di(1H-1,2,4-triazol-1-yl)propan-1-ol (**L2**)¹ and quinoline-d7³ have been performed as described in literature.

Characterization data of the ^1H and ^{13}C NMR are reported below.

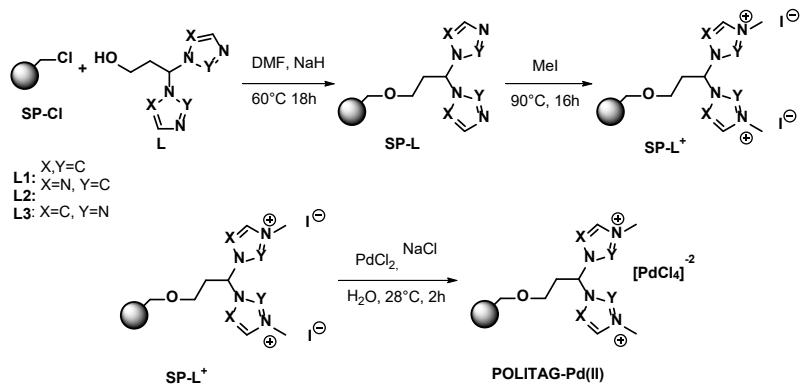
2. General Procedures

2.1 General procedure for functionalization of SP-Cl. In a 25 mL two-neck round bottom flask equipped with a magnetic stirrer ligand **L** (2 mmol, 1.2 eq.), NaH (3 eq, 60% oil dispersion) in 10 mL dry DMF were placed at 0 °C under nitrogen atmosphere. The mixture was heated to room temperature and **SP-Cl** (0.870 g) was added. After 1 h the temperature was increased to 60 °C and the mixture was left under stirring for 16 h. The solid was filtered and washed with DMF, milli-Q water, THF, MeOH and acetone and dried under vacuum for 24 h. Loading of ligands per gram of support were determined by elemental analysis (**SP-L1**: C: 76.61; H: 7.202; N: 7.96; **L1** 1.42 mmol/g; **SP-L2**: C: 73.49; H: 7.32; N: 12.98; **L2** 1.56 mmol/g; **SP-L3**: C: 75.92, H: 6.59, N: 12.06; **L3** 1.44 mmol/g).

2.2 General procedure for synthesis of POLITAG (SP-L⁺). In a stainless-steel vessel equipped with a magnetic stirrer, 5 mL of iodomethane were added to **SP-L** (1 g), and the reaction mixture was stirred at 90 °C for 20 h. After cooling to room temperature, the mixture was filtered and the polymer **SP-L⁺** washed with MeOH

and acetone, and finally dried under vacuum to afford a yellow solid. Ionic tags loading were determined by elemental analysis (**SP-L1⁺**: C: 54.65; H: 5.79; N: 5.05; **L1⁺** 0.90 mmol/g; **SP-L2⁺**: C: 49.83; H: 4.97; N: 7.82; **L2⁺** 0.93 mmol/g; **SP-L3⁺**: C: 52.16; H: 5.43; N: 7.53; **L3⁺** 0.90 mmol/g).

2.3 General procedure for synthesis of POLITAG-Pd(II). In a 20 mL round bottom flask equipped with a magnetic stirrer **SP-L⁺** (600 mg) was placed in 5 mL of water. A solution of Na₂PdCl₄ (1.2 eq), prepared in situ from PdCl₂ (1.2 eq) and NaCl (20 eq) in 10 mL water at 80°C until complete dissolution of palladium, was added dropwise at 28°C to the suspension and the mixture was kept under stirring for 2h. The final catalyst was filtered under reduced pressure and washed with water and methanol and finally dried under vacuum. Palladium loading in POLITAG-Pd(II) were measured by MP-AES analysis (**POLITAG-Pd(II)-1**: 8.0 wt%; **POLITAG-Pd(II)-2**: 8.5 wt%; **POLITAG-Pd(II)-3**: 8.5 wt%).



Scheme S1: synthesis of POLITAGs-Pd(II) tested in this work

2.4 General procedure for synthesis of quinoline *N*-oxide. In a 100 mL round bottom flask equipped with a magnetic stirrer quinoline (5mmol) was placed in 50 mL DCM. The solution was cooled to 0°C and m-CPBA (1.3 eq, 6.5 mmol, 1.121 g) was added portion wise. The reaction was heated at 28°C and kept under stirring. After 24h the reaction crude was washed with aqueous KOH [1M] (3x30 mL). The organic phase was dried over sodium sulphate and concentrated under reduced pressure. Silica plug purification (DCM) afforded the desired quinolines *N*-oxide in yields range 60-70%

2.5 General procedure for *N*-oxides alkenylation. Catalyst (5 mol%) and quinoline *N*-oxide (**1a**) (1mmol) were added in a 2mL screw-capped vial equipped with a magnetic stirrer. Toluene (50 µL) followed by acrylate (**2**) or styrene (**5**) (2 eq) were added. The resulting mixture was sealed with a Teflon lined cap and stirred at 110°C for 4h. After this time, the crude mixture was diluted with toluene (2 mL) and the catalyst was recovered by centrifugation (2 mL x 3 times, 5000 rpm, 10' at 10°C). The supernatant was concentrated under reduced pressure and the crude purified by column chromatography (ETP/EtOAc).

2.6 Catalyst regeneration. After the work-up the catalyst was dried under vacuum at 120°C for 2 hours. Then it was stirred in saturated aqueous solution of NH₄Cl (2 mL) at 25 °C for 1 hour. After this time the regenerated catalytic system was rinsed with water and dried under vacuum at 120°C for 16 hours.

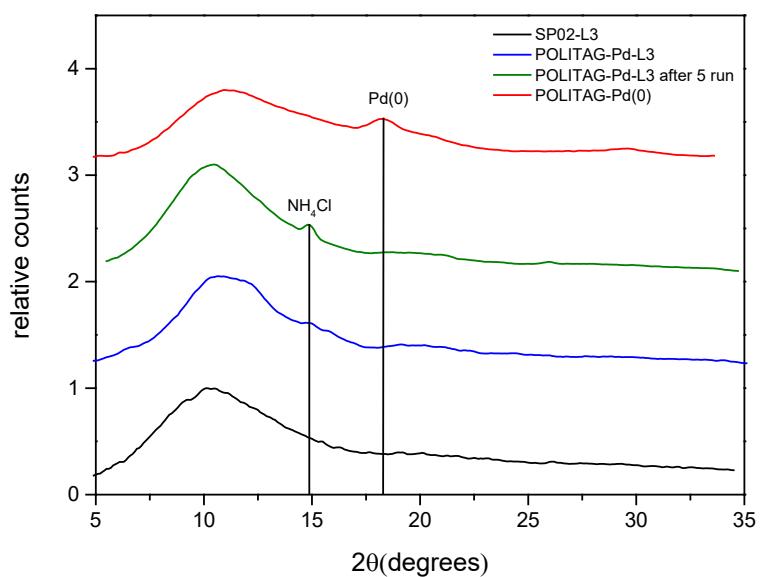


Figure S1: XRD spectra of support (black line), fresh catalyst (blue line), catalyst used for 5 consecutive runs (green line) and POLITAG-Pd(0) as reference (red line)

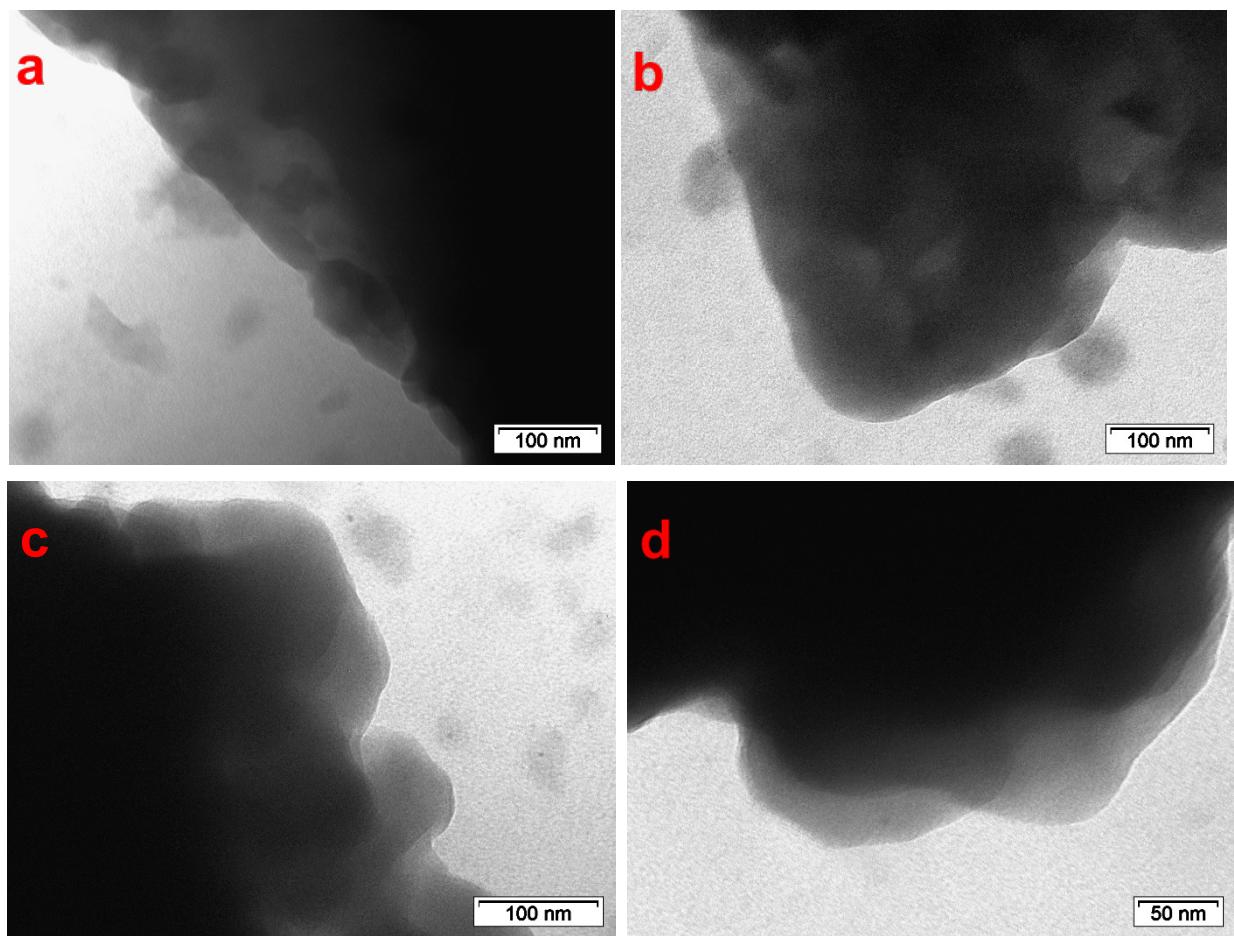


Figure S2: a) TEM images of fresh catalyst. b-d) TEM of the catalyst used for 5 consecutive runs at different enlargements.

2.7 General procedure for leaching measurement. The crude reaction mixture after separation and regeneration of **POLITAG-Pd(II)-3** catalyst, was dried under reduced pressure and digested in 2 mL of *aqua regia* for 1 h. Subsequently the digested material was diluted in milli-Q water to a final volume of 10 mL. The residual organic solid was filtered off and the solution analyzed with MP-AES 4210.

3. Optimization of reaction conditions:

3.1 Catalyst selection and acrylate stoichiometry.

Table S1. Optimization of reaction conditions for alkenylation of **1a** with **2a**.^a

	1a	2a	3a	4a
entry	catalyst	2a (eq)	Conv (%)	3a:4a
1^{b,c}	POLITAG-Pd(II)-L1	9	70	45:55
2^{b,c}	POLITAG-Pd(II)-L3	9	85	53:47
3^c	POLITAG-Pd(II)-L1	2	75	59:41
4^c	POLITAG-Pd(II)-L2	2	>99	70:30
5	POLITAG-Pd(II)-L3	2	>99	92:8

^aReaction conditions: **1a** (1 mmol), **2a** (2mmol), Pd(II) catalyst (5 mol%), toluene (50 μ L, 20 M), 110 °C, 4h. ^bSolvent-free conditions; ^cquinoline and 2-methyl quinoline were detected as degradation products.

3.2 Screening of reaction medium.

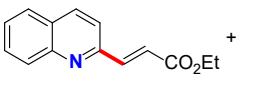
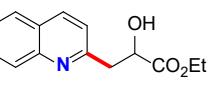
Table S2. Reaction medium screening for alkenylation of **1a** with **2a**.^a

	1a	2a	3a	4a
entry	Reaction medium		Conv (%)	3a:4a
1	DMF	(5 mol%) medium[20M] 110 °C, 4h	47	68:32
2	NMP		49	74:26
3	DMSO		47	78:22
4	Anisole		52	78:22
5	GVL		50	81:19
6	p-xylene		27	74:26
7	p-cymene		45	70:30
8	Ethanol		61	69:31
9	CPME		50	80:20
10	Propylene carbonate		41	72:28

^aReaction conditions: **1a** (1 mmol), **2a** (2 mmol), **POLITAG-Pd(II)-L3** catalyst (5 mol%), reaction medium (50 μ L, 20 M), 110 °C, 4h.

3.3 Summary of the results obtained with small deviations from the standard conditions

Table S3. Optimization of reaction conditions for C-2 selective alkenylation of quinoline N-oxide.^[a]

					
Entry	Deviation from standard optimized conditions		Conv (%) ^[b]	3a:4a	
1	none		>99 (85) ^[c]	92:8	
2	No Catalyst, no support		28	2:98	
3	POLITAG-L3 (support/no Pd)		50	90:10	
4	80 °C		30	3:97	
5	PhMe [2M]		67	30:70	
6	9 equiv of 2a		85	53:47	

[a] Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), Pd(II) (5 mol%), toluene (20 M), 110 °C, 4h. [b] Conversion to products, determined using samples of pure compounds as references. [c] Isolated yield in parenthesis.

4. Additional experiments for the mechanism investigation

4.1 KIE Determination

Method 1 (one pot competition experiment): Catalyst (5 mol%), Quinoline N-oxide (**1a**) (1 mmol) and Quinoline N-oxide-d7 (**1e**) (1 mmol) were added in a 2mL screw capped vial equipped with magnetic stirrer. Toluene (50µL) followed by ethyl acrylate (**2a**) (2 eq) were added and the resulting mixture was sealed with a Teflon lined cap and stirred at 110°C for 2h. After this time catalyst was filtered under vacuum. The crude mixture was concentrated under reduced pressure and the ratio between the products from quinoline/quinoline-d7 was determined by NMR spectroscopy (figure S2).

Method 2 (independent reactions): Catalyst (5mol%) and quinoline N-oxide (**1a**) or Quinoline N-oxide-d7 (**1e**) (1 mmol) were added in a 2mL screw capped vial equipped with magnetic stirrer. Toluene (50µL) followed by ethyl acrylate (**2a**) (2 eq) were added and the resulting mixture was sealed with a Teflon lined cap and stirred at 110°C. The reaction progresses were monitored by GLC Chromatography at 20 minutes, 40 minutes and 60 minutes. Kinetic constants k_H and k_D were measured by plotting the negative logarithm of the concentration at specific time against the time.

Quinoline N-oxide: $y = 0,0055x - 1,919$ $R^2 = 0,9964$

Quinoline N-oxide-d7: $y = 0,0037x - 1,9153$ $R^2 = 0,9954$

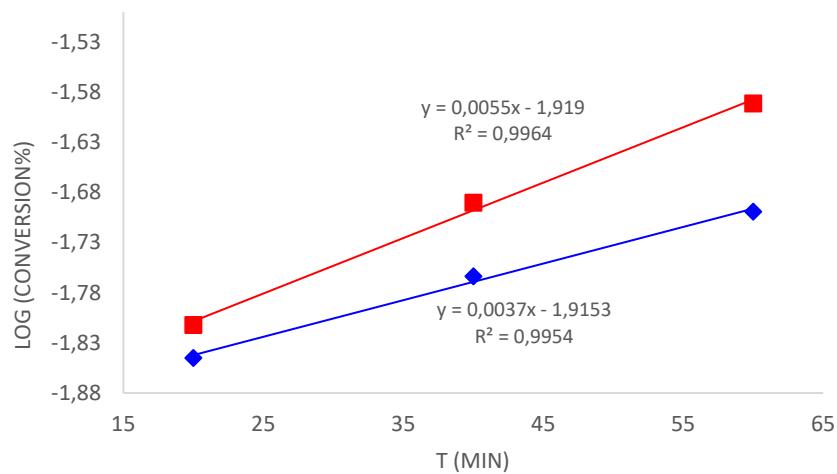


Figure S3: plot for determination of kinetic constant for the reaction conducted on **1a** (red line) and **1e** (blue line).

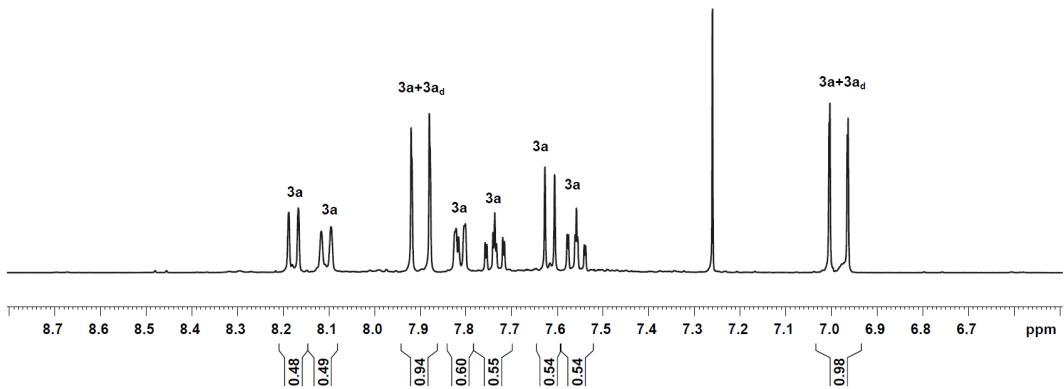
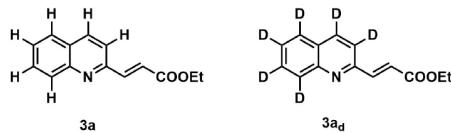


Figure S4: ^1H -NMR spectrum of the competition experiment between **1a** and **1ad** with **2a** in presence of **POLITAG-Pd(II)-L3**

4.2 POLITAG-Pd(II)-L3 recovery and reuse

Table S4. Recovery and reuse of POLITAG-Pd(II)-L3 catalyst in the reaction of **1a** and **2a** after 4h.^[a]

Run	Conv (%) ^[b]	3a:4a	Leaching (%)
1	>99	92:8	1.4
2	>99	92:8	1.4
3	>99	92:8	1.2
4	>99	92:8	1
5	>99	92:8	1

^aReaction conditions: **1a** (1 mmol), **2a** (2 mmol), **POLITAG-Pd(II)-L3** (5 mol%), toluene (50 µL, 20 M), 110 °C, 4h. ^b Conversion to products, determined using samples of pure compounds as references ^c loss of palladium has been determined using MP-AES.

4.3 Investigation regarding heterogeneous nature of the catalysis

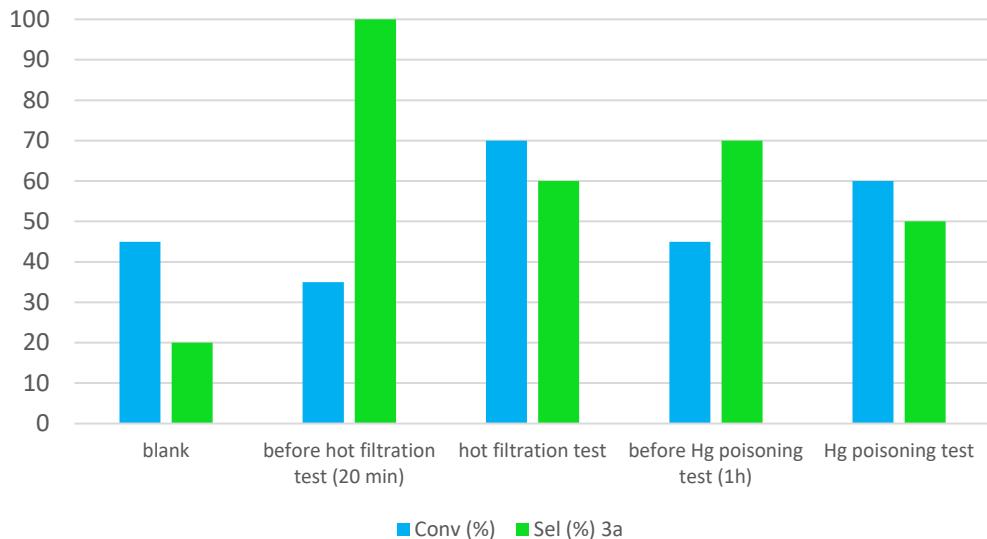
Hot filtration test. Catalyst (5 mol%) and quinoline *N*-oxide (**1a**) (1mmol) were added in a 2mL screw-capped vial equipped with a magnetic stirrer. Toluene (50 µL) followed by ethyl acrylate (**2a**) (2 eq) were added. The resulting mixture was sealed with a Teflon lined cap and stirred at 110°C. After 20 min the **POLITAG-Pd(II)-3** was filtered off and mixture was kept under stirring at 110°C for additional 3h and 40 min. The products distribution has been analyzed by GC analysis.

Hg poisoning test. Catalyst **POLITAG-Pd(II)-3** (5 mol%) and quinoline *N*-oxide (**1a**) (1mmol) were added in a 2mL screw-capped vial equipped with a magnetic stirrer. Toluene (50 µL) followed by ethyl acrylate (**2a**) (2 eq) were added. The resulting mixture was sealed with a Teflon lined cap and stirred at 110°C. After 20 min, 40 µL of Hg (100 eq respect to the catalyst) has been added and the mixture kept under stirring until the established final time. The products distribution has been analyzed by GC analysis.

Table S5. catalytic tests in the alkenylation of **1a** with **2a** for mechanism investigation.^a

entry	catalytic test	Conv (%)	3a:4a
1 ^b	blank experiment	28	2:98
2	before hot filtration test (20 min)	35	10:0
3	hot filtration test	70	6:4
4	before Hg poisoning test (1h)	45	7:3
5	Hg poisoning test	60	5:5

[a] Reaction conditions: **1a** (1 mmol), **2a** (2 eq), **POLITAG-Pd(II)-L3** (5 mol%), toluene (50 µL, 20 M), 110 °C, 4h; [b] without catalyst.



4.4 Investigation on the role of POLITAG catalyst in the regioselectivity of the C–H alkenylation

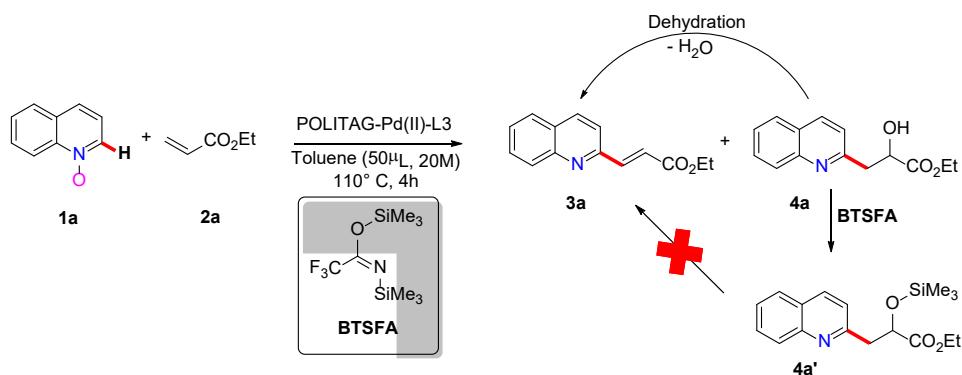
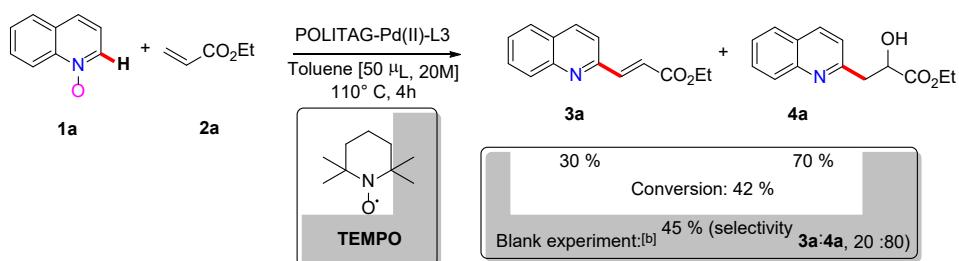


Table S6. catalytic tests in the alkenylation of **1a** with **2a** for mechanism investigation. [a]

entry	catalytic test	Conv (%)	3a : 4a : 4a'
1	No addition	>99	92:8:0
2^b	blank experiment, no catalyst	28	2:98:0
3^{b,c}	No catalyst, with BTSFA	70	10:0: 90
4	with BTSFA	60	90:0:10

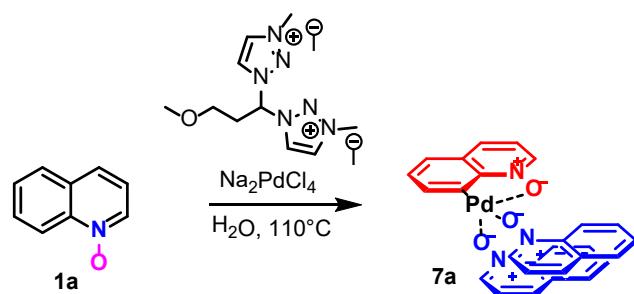
[a] Reaction conditions: **1a** (1 mmol), **2a** (2 eq), **POLITAG-Pd(II)-L3** (5 mol%), toluene ($50\mu\text{L}$, 20M), 110°C , 4h; [b] without catalyst; [c] 24h

4.5 Reaction with radical trapping (TEMPO)^[a]



[a] Reaction conditions: **1a** (1 mmol), **2a** (2 eq), POLITAG-Pd(II)-L3 (5 mol%), toluene (50 μ L, 20 M), 110 °C, 4h; [b] without catalyst

4.6 Homogeneous complex **7a** synthesis and NMR spectra



In a 4 mL screw capped vial equipped with magnetic stirring bar, PdCl_2 (1 equiv. 0.5 mmol, 88.7 mg), NaCl (22 equiv. 11 mmol, 642.8 mg) and H_2O 2.5 mL have been consecutively added and vigorously stirred during 30 min at 80 °C. After this time, quinoline *N*-oxide (**1a**) (1 equiv. 0.5 mmol, 72,5 mg) and quaternized-**L3** (1 equiv. 0.5 mmol, 246 mg) have been added and the resulting mixture has been stirred at 110 °C for 2h. The stirring has been stopped and a yellow precipitate has been observed.

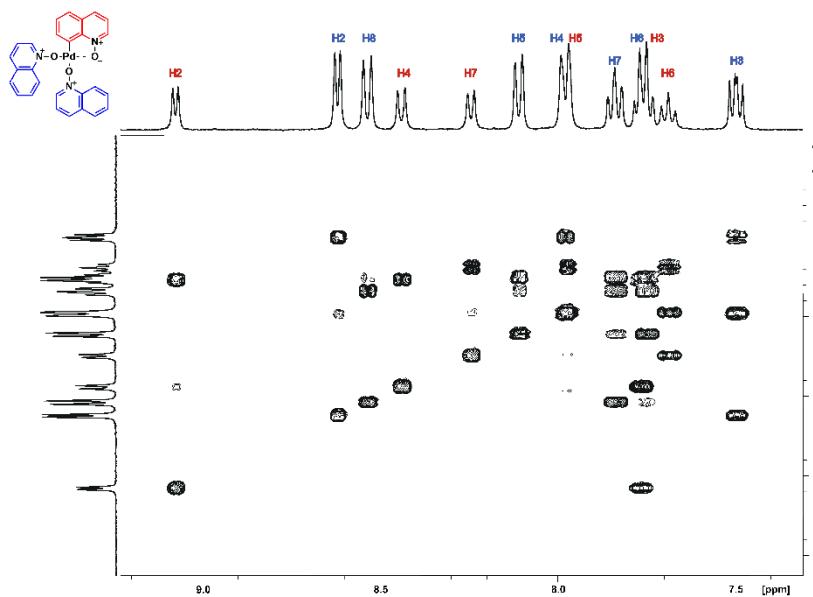
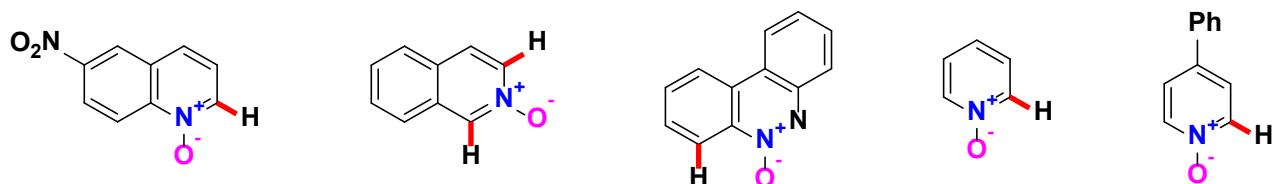


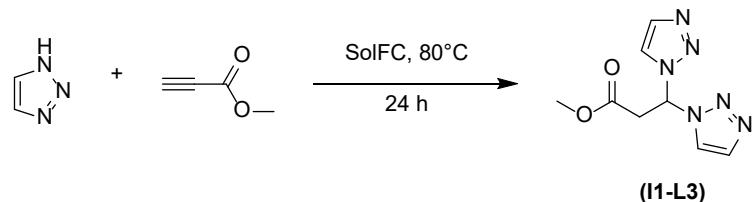
Figure S5: COESY of supposed palladacycle complex **7a**.

5. Substrates in which the optimized reaction conditions failed.



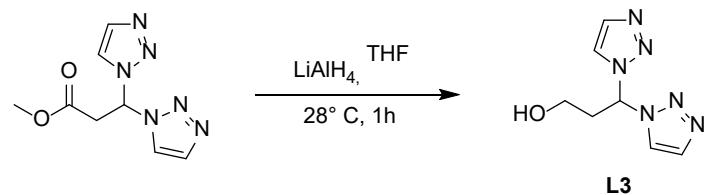
6. Characterization Data

Synthesis of L3:



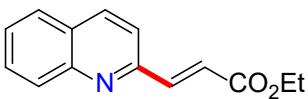
In a 4 mL screw capped vial, equipped with a magnetic stirrer, were placed methyl propiolate (0.9 mL, 10.4 mmol) and 1-H-1,2,3-triazole (1.8 mL, 3 eq). The mixture was kept under stirring at 80°C. After 24h, the solid was washed several times with diethyl ether to afford pure methyl 3,3-di(1H-1,2,3-triazol-1-yl)propanoate as a white solid (1.4 g, 6.5 mmol, 63% yield). M.p. 136-138 °C.

¹H NMR (400 MHz CDCl₃) δ: 7.86 (s, 2H), 7.74 (s, 2H), 7.56 (t, J = 8 Hz, 1H), 3.86 (d, J = 8 Hz, 2H), 3.70 (s, 3H). **¹³C NMR (100.6 MHz, CDCl₃) δ :** 168.0, 135.0, 123.4, 68.8, 52.9, 38.7. **GC-EIMS (m/z, %):** 162 (33), 140 (16), 125 (27), 121 (100), 94 (22), 84 (39), 68 (25), 67 (46), 66 (19), 59 (67), 57 (34), 54 (34), 53 (27), 52 (24)



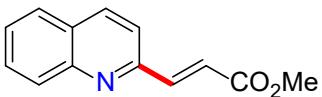
A 100 mL two-neck round bottom flask equipped with a magnetic stirrer was charged with LiAlH₄ (0.428 g, 11.3 mmol) in 20 mL of dry THF under nitrogen atmosphere. The mixture was cooled down to 0 °C and Methyl 3,3-di(1H-1,2,3-triazol-1-yl)propanoate (0.800 g, 3.6 mmol) in 50 mL of dry THF was added dropwise over 15 min. The reaction mixture was stirred for 1 h at 28 °C and 0.6 mL of water was added dropwise until the complete neutralization of the excess of LiAlH₄ at 0 °C. The mixture was filtrated and the remaining solid washed with warm THF (3 x 50 mL). The solvent was removed under vacuum and the residue was washed with diethyl ether, affording 3,3-di(1H-1,2,3-triazol-1-yl)propan-1-ol (L3) as a white solid (0.569 g, 2.9 mmol, 81 % yield). M. p. 117-119 °C.

¹H NMR (400 MHz CDCl₃) δ: 7.90 (s, 2H), 7.74 (s, 2H), 7.46 (t, J= 8 Hz, 1H), 3.64 (m, 2H), 3.00-2.96 (m, 2H), 2.03 (s, 1H). **¹³C NMR (101 MHz, CDCl₃) δ :** 134.7, 123.4, 69.7, 57.2, 36.8. **GC-EIMS (m/z, %):** 136 (19), 123 (35), 122 (24), 121 (58), 110 (21), 97 (40), 96 (30), 82 (27), 80 (29), 70 (17), 69 (16), 68 (43), 67 (25), 66 (24), 54 (100), 53 (33), 52 (44).



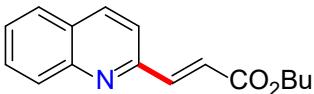
Ethyl (E)-3-(quinolin-2-yl)acrylate (3a).⁴

General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and ethyl acrylate (2 mmol, 200 mg, 218 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3a** (193 mg, 85%) as white solid. M. p. 80-81. **¹H NMR** (400 MHz, CDCl₃) δ = 8.18 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 16.0 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 153.3, 148.3, 144.1, 136.8, 130.1, 129.9, 128.1, 127.6, 127.3, 123.8, 120.3, 60.8, 14.3. **GC-EIMS (m/z, %)**: 227 (100), 199 (40), 155 (65), 143 (70), 129 (55).



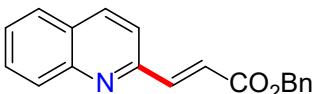
Methyl (E)-3-(quinolin-2-yl)acrylate (3b).⁵

General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and methyl acrylate (172 mg, 180 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3b** (160 mg, 75%) as white solid. M. p. 85-88. **¹H NMR** (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 15.9 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 167.2, 153.3, 148.4, 144.5, 136.9, 130.2, 130.0, 128.2, 127.7, 127.5, 123.4, 120.5, 52.1. **GC-EIMS (m/z, %)**: 213 (100), 199 (75), 185 (45), 143 (60), 129 (45).



Butyl (E)-3-(quinolin-2-yl)acrylate (3c).⁴

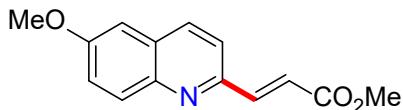
General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and butyl acrylate (256 mg, 287 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3c** (186 mg, 73%) as white solid. M. p. 75-77. **¹H NMR** (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.51 – 1.43 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.8, 153.4, 148.4, 144.2, 136.9, 130.2, 130.0, 128.2, 127.7, 127.5, 124.0, 120.4, 64.8, 30.9, 19.3, 13.9. **GC-EIMS (m/z, %)**: 255 (100), 226 (75), 183 (45), 143 (65), 129 (45).



Benzyl (E)-3-(quinolin-2-yl)acrylate (3d).⁶

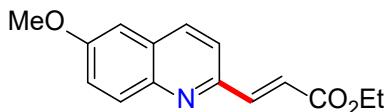
General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and benzyl acrylate (324 mg, 306 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3d** (197 mg, 68%) as white solid. M. p. 80-82. **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz,

1H), 7.94 (d, J = 15.9 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.74 (t, J = 7.7 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.05 (d, J = 15.9 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 153.3, 148.4, 144.7, 136.9, 136.0, 130.2, 130.0, 128.7, 128.4, 128.2, 127.7, 127.5, 123.5, 120.4, 66.7. GC-EIMS (m/z, %): 289 (10), 244 (100), 182 (50), 155 (45), 128(40).



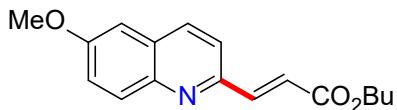
Methyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3e).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and methyl acrylate (172 mg, 180 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3e** (180 mg, 74%) as white solid. M. p. 80-81. ^1H NMR (400 MHz, CDCl_3) δ 8.06 – 7.98 (m, 2H), 7.87 (d, J = 15.8 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.06 (m, 1H), 6.94 (d, J = 15.9 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.4, 158.7, 150.9, 144.6, 144.6, 135.4, 131.5, 129.5, 123.2, 122.1, 120.9, 105.1, 55.8, 52.0. GC-EIMS (m/z, %): 243 (100), 212 (60), 185 (75), 169 (30), 141(25).



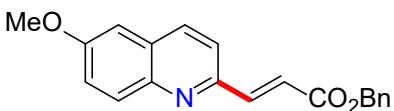
Ethyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3f).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and ethyl acrylate (2 mmol, 200 mg, 218 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **3f** (187 mg, 73%) as white solid. M. p. 78-80. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 15.9 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.39 (dd, J = 9.2, 2.8 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.92 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 158.7, 151.0, 144.6, 144.4, 135.5, 131.5, 129.4, 123.2, 122.7, 120.8, 105.1, 60.8, 55.8, 14.5. GC-EIMS (m/z, %): 257 (95), 212 (10), 185 (100), 141 (30), 115 (10).



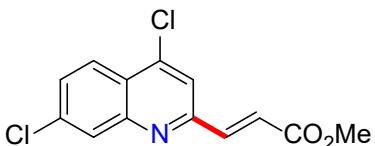
Butyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3g).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and butyl acrylate (256 mg, 287 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **3g** (222 mg, 78%) as white solid. M. p. 74-75. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 9.2 Hz, 1H), 7.84 (d, J = 15.9 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.36 (dd, J = 9.2, 2.7 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.91 (d, J = 15.9 Hz, 1H), 4.23 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 1.73 – 1.66 (m, 2H), 1.47 – 1.41 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 158.6, 151.0, 144.5, 144.3, 135.4, 131.4, 129.4, 123.1, 122.6, 120.7, 105.0, 64.7, 55.7, 30.9, 19.3, 13.9. GC-EIMS (m/z, %): 285 (60), 242 (5), 212 (10), 185 (100), 141 (25).



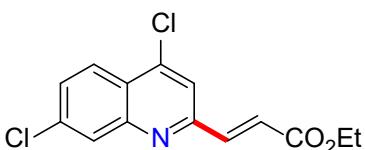
Benzyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3h).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and benzyl acrylate (324 mg, 306 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 5/95) yielded **3h** (214 mg, 67%) as pale yellow solid. M. p. 85-87. **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 7.90 (d, *J* = 15.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.34 (m, 6H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 5.29 (s, 2H), 3.92 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 158.6, 150.8, 144.9, 144.5, 136.1, 135.4, 131.4, 129.4, 128.7, 128.4, 123.2, 122.2, 120.8, 105.0, 66.6, 55.7. **GC-EIMS (m/z, %):** 319 (65), 274 (60), 212 (50), 185 (100), 169 (25).



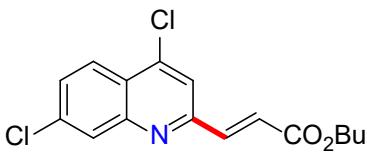
Methyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3i).

General procedure has been followed using 4,7-dichloroquinoline *N*-oxide (1 mmol, 214 mg) and methyl acrylate (172 mg, 180 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **3i** (225 mg, 80%) as pale yellow solid. M. p. 127-129. **¹H NMR** (400 MHz, CDCl₃) δ 8.18 – 8.10 (m, 2H), 7.78 (d, *J* = 15.9 Hz, 1H), 7.65 (s, 1H), 7.60 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.02 (d, *J* = 15.8 Hz, 1H), 3.86 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.7, 154.3, 149.5, 143.4, 142.8, 137.3, 129.4, 129.2, 125.6, 124.9, 124.8, 120.9, 52.2. **GC-EIMS (m/z, %):** 281 (60), 266 (20), 250 (95), 223 (100), 196 (40), 186 (25), 161 (45).



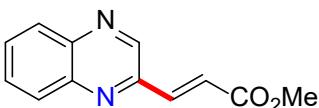
Ethyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3j).

General procedure has been followed using 4,7-dichloroquinoline *N*-oxide (1 mmol, 214 mg) and ethyl acrylate (2 mmol, 200 mg, 218 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **3j** (242 mg, 82%) as pale yellow solid. M. p. 115-116. **¹H NMR** (400 MHz, CDCl₃) δ 8.18 – 8.07 (m, 2H), 7.77 (d, *J* = 15.8 Hz, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 15.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.3, 154.4, 149.5, 143.4, 142.5, 137.3, 129.3, 129.2, 125.6, 125.5, 124.8, 120.8, 61.1, 14.4. **GC-EIMS (m/z, %):** 295 (50), 266 (20), 250 (100), 223 (100), 196 (40), 161 (45), 125 (20).



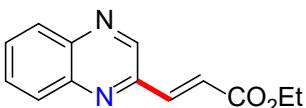
Butyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3k).

General procedure has been followed using 4,7-dichloroquinoline *N*-oxide (1 mmol, 214 mg) and butyl acrylate (256 mg, 287 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **3k** (265 mg, 82%) as white solid. M. p. 110-113. **¹H NMR** (400 MHz, CDCl₃) δ 8.18 – 8.08 (m, 2H), 7.77 (d, *J* = 15.9 Hz, 1H), 7.67 (s, 1H), 7.60 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.49 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.4, 154.5, 149.5, 143.4, 142.5, 137.3, 129.4, 129.2, 125.6, 125.5, 124.8, 120.9, 65.1, 30.8, 19.3, 13.9. **GC-EIMS (m/z, %)**: 326 (28), 324 (100), 322 (32), 288 (65), 268 (40), 254 (25), 252 (35).



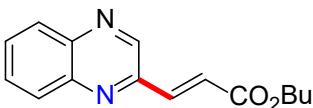
Methyl (E)-3-(quinoxalin-2-yl)acrylate (3l).

General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and methyl acrylate (172 mg, 180 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 15/85) yielded **3l** (139 mg, 65%) as pale orange solid. M. p. 75-76. **¹H NMR** (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.10 – 8.01 (m, 2H), 7.90 (d, *J* = 15.9 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.15 (d, *J* = 15.9 Hz, 1H), 3.86 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 148.0, 144.9, 142.7, 142.6, 140.7, 130.9, 130.9, 130.0, 129.4, 125.1, 52.3. **GC-EIMS (m/z, %)**: 214 (100), 199 (90), 183 (80), 155 (65), 129 (50).



Ethyl (E)-3-(quinoxalin-2-yl)acrylate (3m).

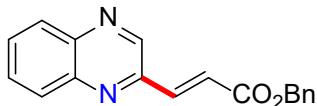
General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and ethyl acrylate (2 mmol, 200 mg, 218 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 15/85) yielded **3m** (155 mg, 68%) as pale orange solid. M. p. 77-78. **¹H NMR** (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.09 – 8.06 (m, 2H), 7.88 (d, *J* = 15.9 Hz, 1H), 7.79 – 7.77 (m, 2H), 7.13 (d, *J* = 15.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.1, 148.2, 144.8, 142.6, 142.5, 140.4, 130.9, 130.8, 129.9, 129.4, 125.7, 61.2, 14.4. **GC-EIMS (m/z, %)**: 228 (100), 199 (80), 183 (70), 155 (50), 129 (70).



Butyl (E)-3-(quinoxalin-2-yl)acrylate (3n).

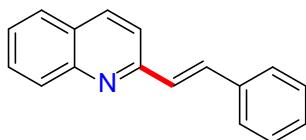
General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and butyl acrylate (256 mg, 287 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **3n** (159 mg, 62%) as pale orange solid. M. p. 72-74. **¹H NMR** (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.11 – 8.08 (m, 2H), 7.89

(d, $J = 15.9$ Hz, 1H), 7.80 – 7.78 (m, 2H), 7.14 (d, $J = 15.9$ Hz, 1H), 4.27 (t, $J = 6.6$ Hz, 2H), 1.75 – 1.68 (m, 2H), 1.51 – 1.41 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 166.3, 148.2, 144.8, 142.7, 142.6, 140.4, 130.9, 130.9, 129.9, 129.4, 125.7, 65.1, 30.8, 19.3, 13.9. **GC-EIMS (m/z, %)**: 256 (100), 241 (35), 213 (48), 199 (85), 183 (75), 155 (65), 129 (30).



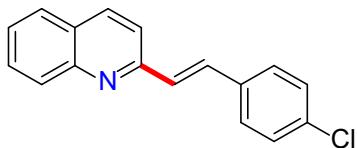
Benzyl (E)-3-(quinoxalin-2-yl)acrylate (3o).

General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and benzyl acrylate (324 mg, 306 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 → 20/80) yielded **3o** (208 mg, 72%) as pale orange solid. M. p. 78-80. **^1H NMR** (400 MHz, CDCl_3) δ 8.99 (s, 1H), 8.11 – 8.07 (m, 2H), 7.92 (d, $J = 15.9$ Hz, 1H), 7.79 – 7.77 (m, 2H), 7.45 – 7.28 (m, 5H), 7.19 (d, $J = 15.9$ Hz, 1H), 5.30 (s, 2H). **^{13}C NMR** (101 MHz, CDCl_3) δ 166.0, 148.1, 144.9, 142.7, 142.6, 141.0, 135.9, 131.0, 130.9, 130.0, 129.5, 128.8, 128.6, 128.6, 125.3, 67.0. **GC-EIMS (m/z, %)**: 290 (100), 274 (85), 199 (90), 183 (70), 155 (65), 129 (50).



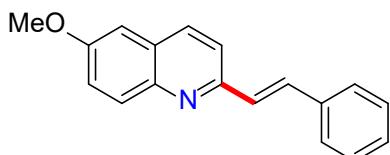
(E)-2-styrylquinoline (6a).⁵

General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and styrene (208 mg, 230 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 → 10/90) yielded **6a** (173 mg, 75%) as pale orange solid. M. p. 98-99. **^1H NMR** (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.6$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.73 – 7.64 (m, 5H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.48 – 7.39 (m, 3H), 7.33 (t, $J = 7.3$ Hz, 1H). **^{13}C NMR** (101 MHz, CDCl_3) δ 156.2, 148.4, 136.7, 136.5, 134.6, 129.9, 129.4, 129.2, 129.0, 128.8, 127.7, 127.5, 127.4, 126.3, 119.4. **GC-EIMS (m/z, %)**: 231 (100), 169 (40), 155 (20), 143 (40), 129 (45).



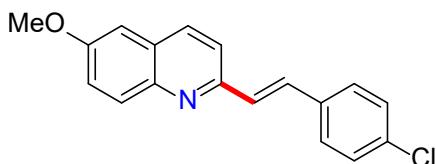
(E)-2-(4-chlorostyryl)quinoline (6b).⁷

General procedure has been followed using quinoline *N*-oxide (**1a**) (1 mmol, 145 mg) and 4-chlorostyrene (277 mg, 240 μL). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 → 10/90) yielded **6b** (195 mg, 73%) as pale orange solid. M. p. 143-144. **^1H NMR** (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.6$ Hz, 1H), 8.08 (dd, $J = 8.4, 1.0$ Hz, 1H), 7.79 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.71 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H), 7.67 – 7.63 (m, 2H), 7.57 – 7.55 (m, 2H), 7.51 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 1H), 7.39 – 7.34 (m, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 155.7, 148.4, 136.6, 135.2, 134.4, 133.2, 130.0, 129.7, 129.4, 129.2, 128.5, 127.7, 127.5, 126.5, 119.5. **GC-EIMS (m/z, %)**: 267 (75), 265 (100), 231 (60), 229 (55), 143 (80), 129 (30).



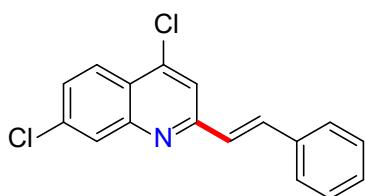
(E)-6-methoxy-2-styrylquinoline (6c).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and styrene (208 mg, 230 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6c** (216 mg, 83%) as pale orange solid. M. p. 148-151. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.02 – 7.97 (m, 2H), 7.64 – 7.59 (m, 4H), 7.41 – 7.29 (m, 5H), 7.04 (d, J = 2.8 Hz, 1H), 3.92 (s, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 157.8, 153.8, 144.3, 136.8, 135.2, 133.4, 130.7, 129.1, 128.9, 128.5, 128.4, 127.3, 122.4, 119.7, 105.4, 55.7. **GC-EIMS (m/z, %)**: 261 (100), 247 (35), 231 (40), 173 (25), 159 (60).



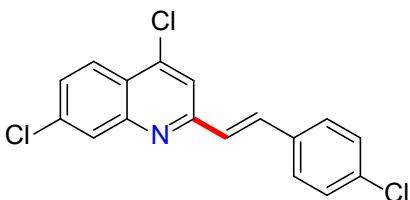
(E)-2-(4-chlorostyryl)-6-methoxyquinoline (6d).

General procedure has been followed using 6-methoxyquinoline *N*-oxide (1 mmol, 175 mg) and 4-chlorostyrene (277 mg, 240 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6d** (229 mg, 78%) as pale orange solid. M. p. 158-160. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.01 – 7.96 (m, 2H), 7.59 – 7.52 (m, 4H), 7.38 – 7.30 (m, 4H), 7.04 (d, J = 2.8 Hz, 1H), 3.92 (s, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 157.9, 153.4, 144.4, 135.4, 135.3, 134.1, 131.9, 130.8, 129.7, 129.1, 128.5, 128.4, 122.6, 119.8, 105.4, 55.7. **GC-EIMS (m/z, %)**: 294 (100), 280 (65), 251 (25), 216 (15), 189 (25), 163 (33).



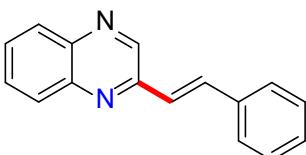
(E)-4,7-dichloro-2-styrylquinoline (6e).

General procedure has been followed using 4,7-dichloroquinoline *N*-oxide (1 mmol, 214 mg) and styrene (208 mg, 230 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **6e** (208 mg, 70%) as pale orange solid. M. p. 128-129. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.12 – 8.08 (m, 2H), 7.71 (t, J = 8.1 Hz, 2H), 7.63 (d, J = 7.3 Hz, 2H), 7.52 (dd, J = 8.9, 2.1 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 16.3 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 157.2, 149.6, 142.8, 136.8, 136.2, 136.1, 129.3, 129.0, 128.6, 128.1, 127.6, 127.6, 125.6, 124.1, 119.8. **GC-EIMS (m/z, %)**: 298 (100), 264 (60), 228 (15), 201 (15), 162 (30), 113 (20).



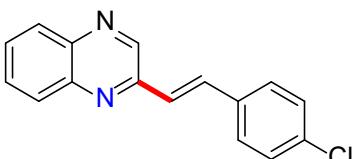
(E)-4,7-dichloro-2-(4-chlorostyryl)quinoline (6f).

General procedure has been followed using 4,7-dichloroquinoline *N*-oxide (1 mmol, 214 mg) and 4-chlorostyrene (277 mg, 240 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 20/80) yielded **6f** (257 mg, 77%) as pale orange solid. M. p. 136-138. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.14 – 8.09 (m, 2H), 7.71 – 7.67 (m, 2H), 7.58 – 7.54 (m, 3H), 7.40 (d, J = 8.1 Hz, 2H), 7.28 (s, 1H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 156.8, 149.5, 142.9, 137.0, 135.0, 134.8, 134.6, 129.3, 128.7, 128.6, 128.2, 128.0, 125.6, 124.1, 119.9. **GC-EIMS (*m/z*, %)**: 334 (100), 298 (75), 263 (15), 227 (25), 200 (15), 162 (15), 131 (20).



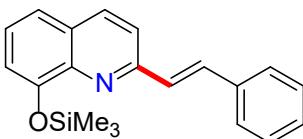
(E)-2-styrylquinoxaline (6g).⁸

General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and styrene (208 mg, 230 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6g** (167 mg, 72%) as pale orange solid. M. p. 105-107. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 9.05 (s, 1H), 8.08 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 16.3 Hz, 1H), 7.78 – 7.66 (m, 4H), 7.45 – 7.35 (m, 4H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 150.8, 144.6, 142.6, 141.7, 136.6, 136.1, 130.5, 129.4, 129.3, 129.3, 129.3, 129.1, 127.6, 125.5. **GC-EIMS (*m/z*, %)**: 232 (100), 203 (25), 176 (15), 128 (25), 102 (40).



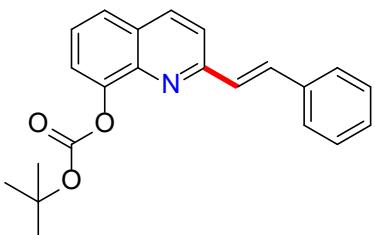
(E)-2-(4-chlorostyryl)quinoxaline (6h).⁹

General procedure has been followed using quinoxaline *N*-oxide (1 mmol, 146 mg) and 4-chlorostyrene (277 mg, 240 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6h** (180 mg, 68%) as pale orange solid. M. p. 118-120. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 9.02 (s, 1H), 8.08 – 8.05 (m, 2H), 7.83 (d, J = 16.3 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.40 – 7.32 (m, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 150.4, 144.6, 142.6, 141.8, 135.1, 134.7, 130.6, 129.6, 129.3, 129.3, 128.9, 128.7, 125.9. **GC-EIMS (*m/z*, %)**: 265 (100), 231 (35), 203 (15), 176 (15), 128 (20), 102 (35).



(E)-2-styryl-8-((trimethylsilyl)oxy)quinoline (6i).

General procedure has been followed using 8-((trimethylsilyl)oxy)quinoline *N*-oxide (1 mmol, 233 mg) and styrene (208 mg, 230 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6i** (268 mg, 84%) as pale orange solid. M. p. 98–101. **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 16.3 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 3H), 7.44 – 7.29 (m, 6H), 7.18 (d, *J* = 7.5 Hz, 1H), 0.08 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 153.8, 152.2, 138.2, 136.6, 136.5, 134.5, 129.0, 128.9, 128.3, 127.6, 127.4, 127.4, 120.5, 117.8, 110.3, 1.2. **GC-EIMS (m/z, %):** 319 (100), 247 (75), 246 (50), 230 (35), 171 (45), 154 (15).



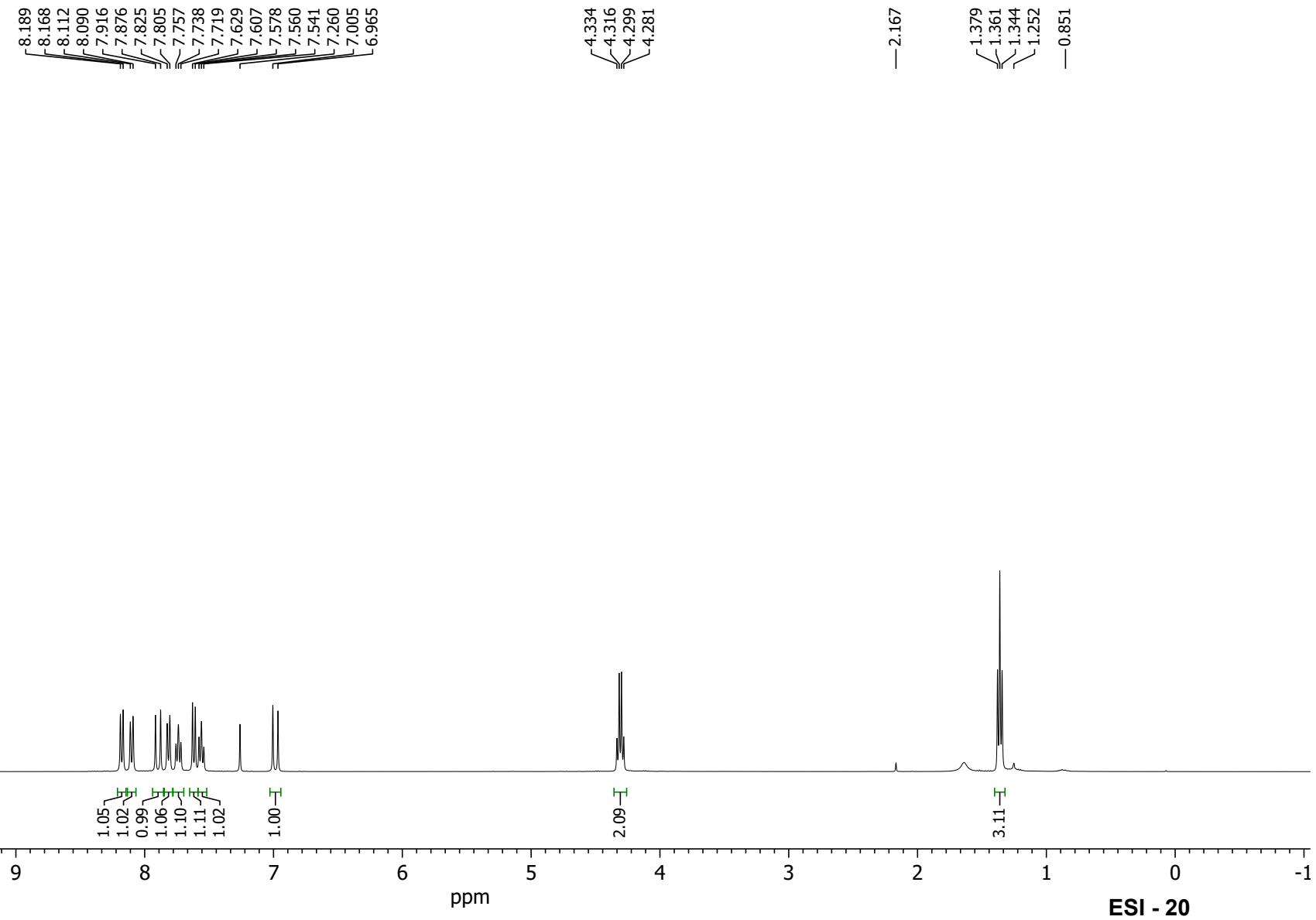
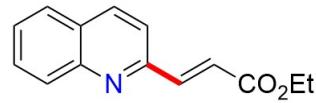
(E)-tert-butyl (2-styrylquinolin-8-yl) carbonate (6j).

General procedure has been followed using 8-((tert-butoxycarbonyl)oxy)quinoline *N*-oxide (1 mmol, 261 mg) and styrene (208 mg, 230 μ L). Isolation by column chromatography (EtOAc/Petroleum Ether 1/99 \rightarrow 10/90) yielded **6j** (270 mg, 78%) as white crystals. M. p. 107–109. **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 16.2 Hz, 1H), 7.67 – 7.59 (m, 4H), 7.52 – 7.33 (m, 6H), 1.65 (s, 9H).. **¹³C NMR** (101 MHz, CDCl₃) δ 155.8, 152.2, 147.5, 141.3, 136.7, 136.4, 134.8, 129.0, 128.8, 128.7, 127.4, 125.8, 125.6, 121.2, 120.7, 83.5, 27.9. **GC-EIMS (m/z, %):** 347 (100), 290 (15), 247 (80), 271 (40), 246 (35), 154 (25).

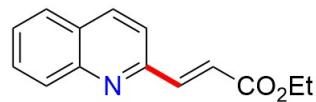
References:

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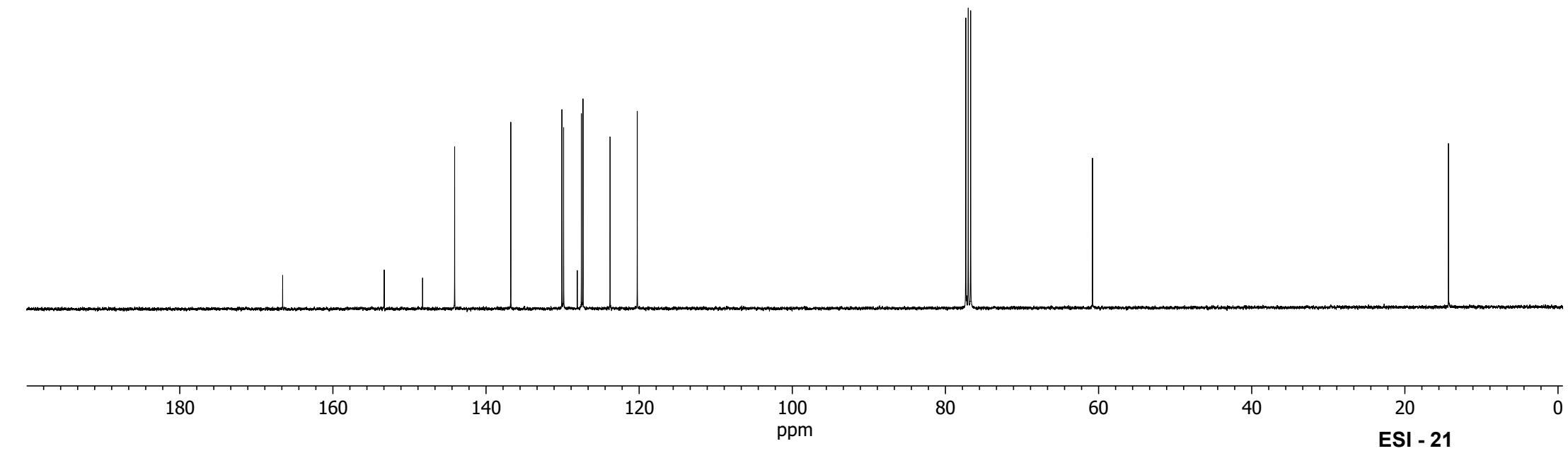
Ethyl (E)-3-(quinolin-2-yl)acrylate (3a).



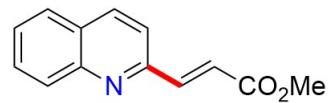
Ethyl (E)-3-(quinolin-2-yl)acrylate (3a).



—166.563
—153.296
—148.289
—144.099
—136.767
—130.092
—129.866
—128.083
—127.547
—127.338
—123.802
—120.251
—60.794
—14.303

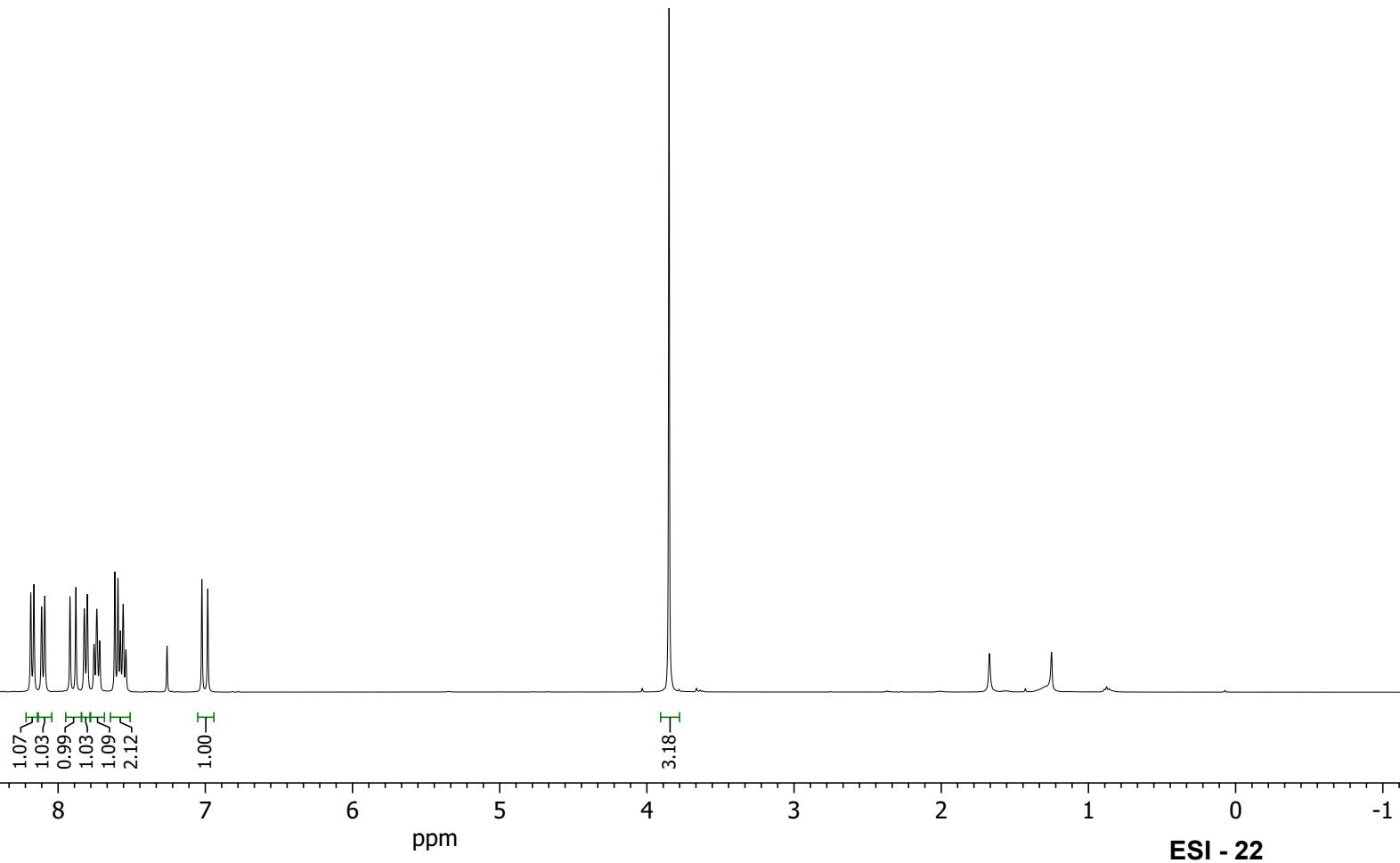


Methyl (E)-3-(quinolin-2-yl)acrylate (3b).

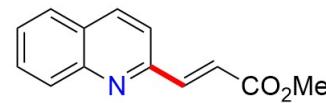


8.186
8.165
8.112
8.091
7.919
7.879
7.822
7.802
7.756
7.737
7.717
7.615
7.593
7.577
7.558
7.539
7.023
6.983

—3.850



Methyl (E)-3-(quinolin-2-yl)acrylate (3b).



—167.166

—153.273

—148.419

—144.481

—136.909

—130.232

—130.015

—128.238

—127.673

—127.497

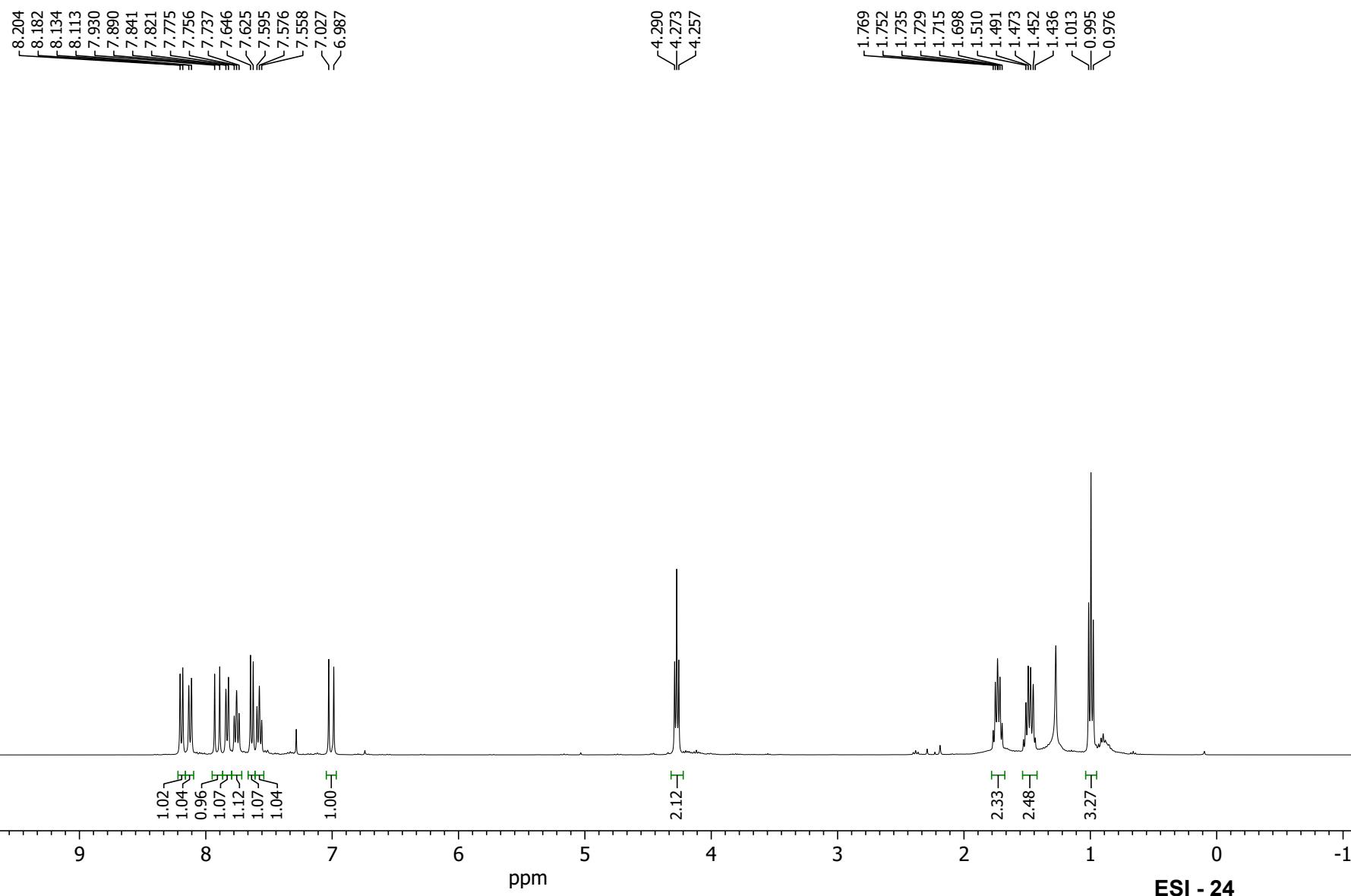
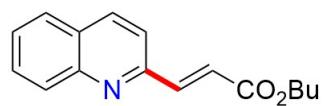
—123.383

—120.517

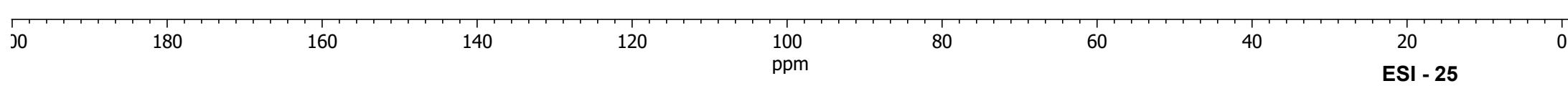
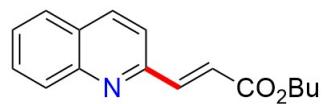
—52.078



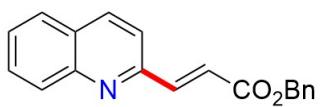
Butyl (E)-3-(quinolin-2-yl)acrylate (3c).



Butyl (E)-3-(quinolin-2-yl)acrylate (3c).



Benzyl (E)-3-(quinolin-2-yl)acrylate (3d).



8.181
8.159
8.107
8.086
7.955
7.915
7.820
7.799
7.754
7.735
7.716
7.614
7.593
7.576
7.557
7.538
7.452
7.434
7.399
7.380
7.367
7.350
7.332
7.068
7.028

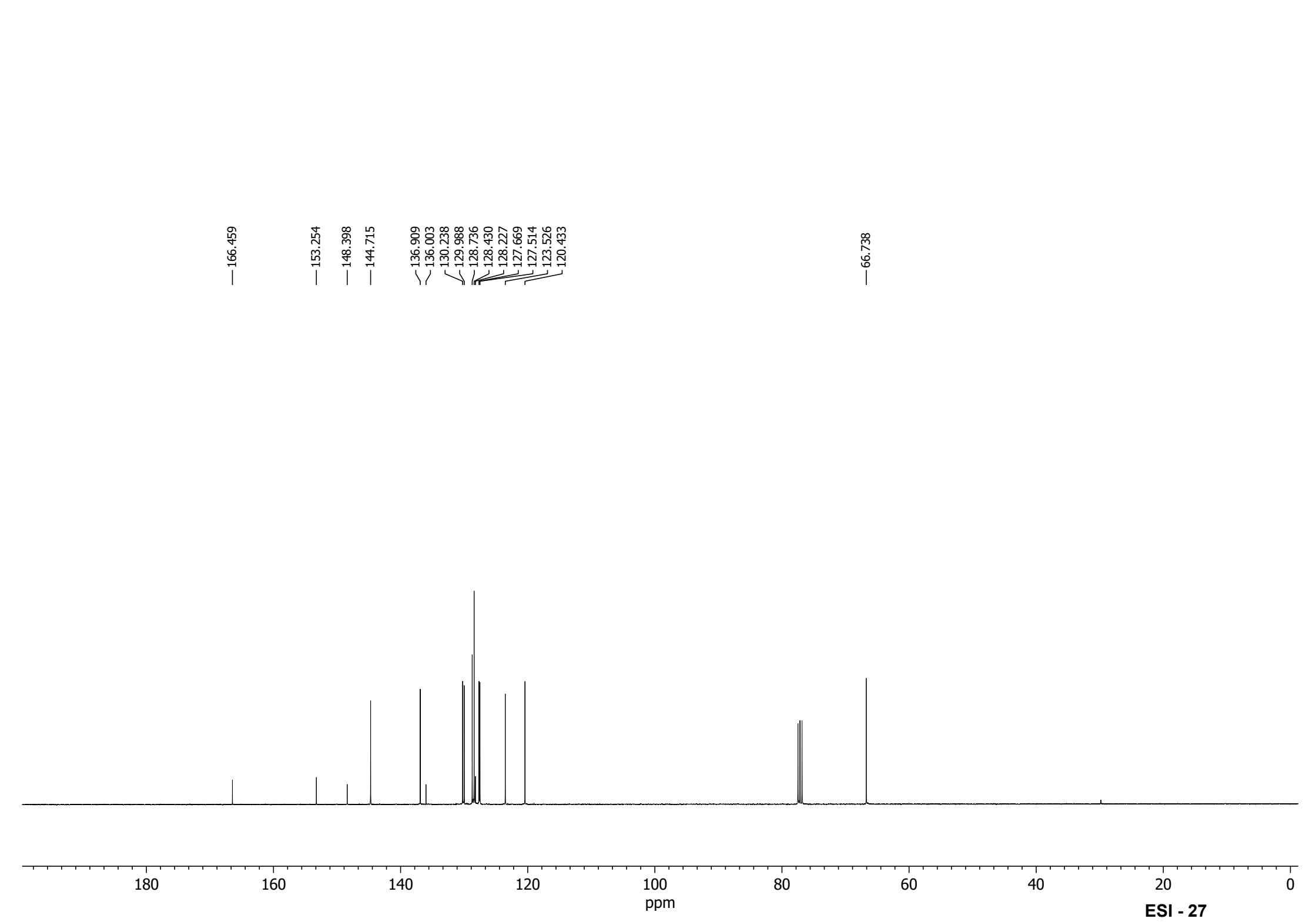
—5.299

1.05
1.02
0.99
1.06
1.11
2.17
4.97
1.00

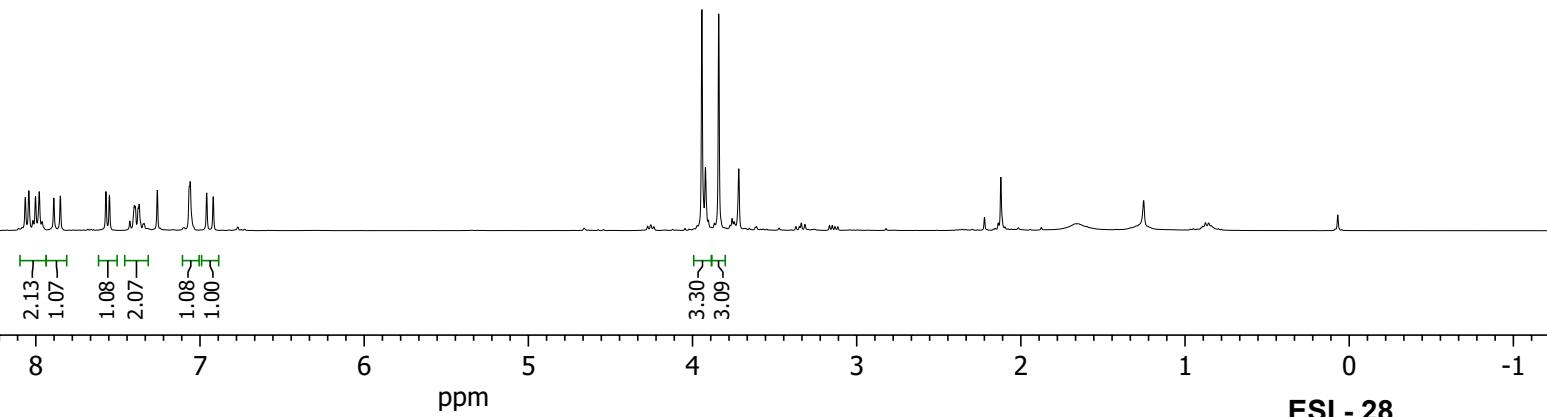
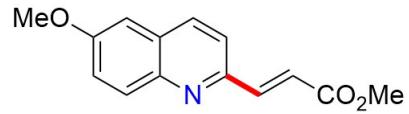
2.02

11 10 9 8 7 6 5 4 3 2 1 0 -1

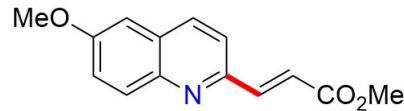
ppm



Methyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3e).



Methyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3e).



—167.352

—158.679

—150.857

—144.639

—144.579

—135.445

—131.490

—129.457

—123.187

—122.134

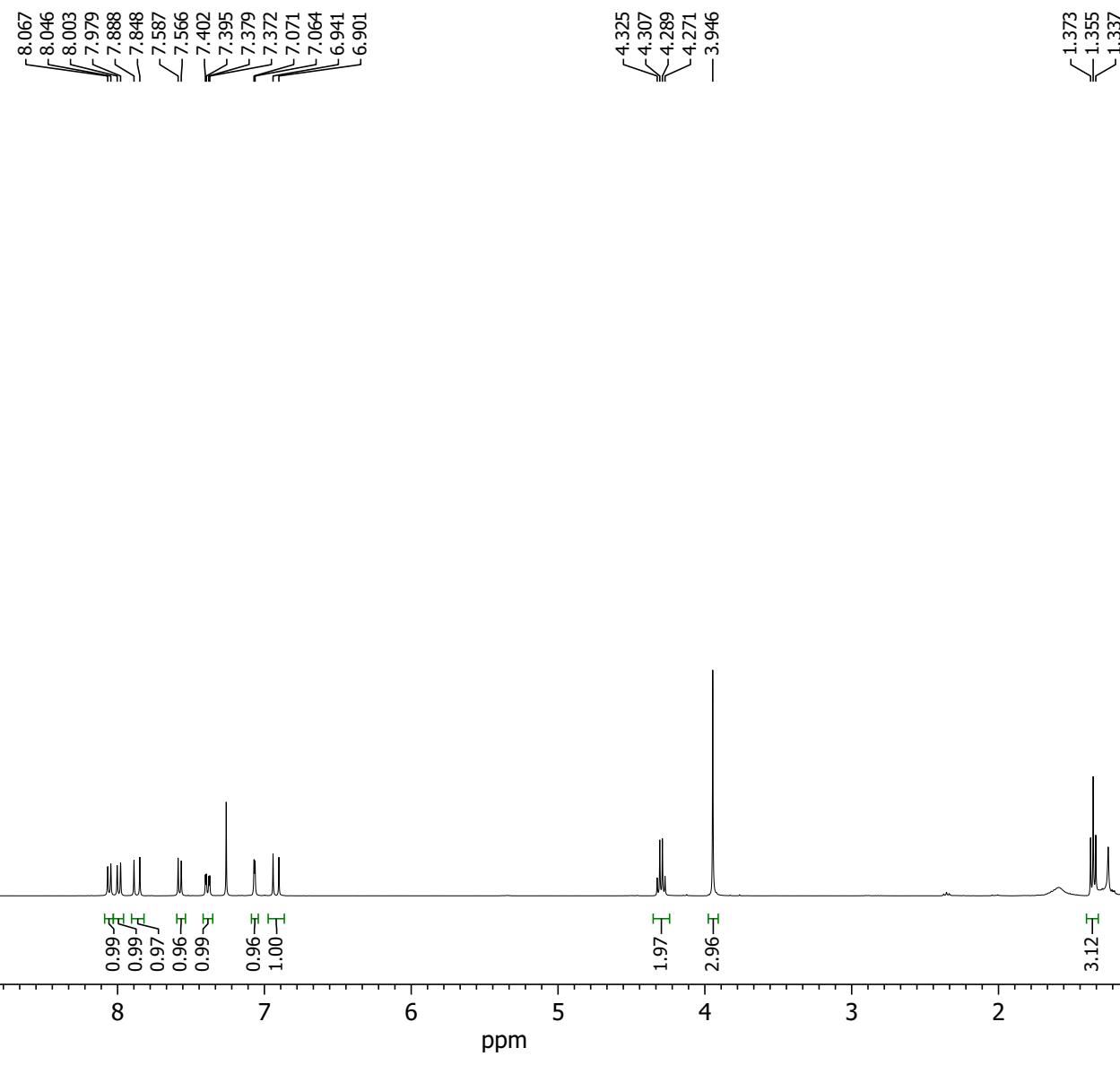
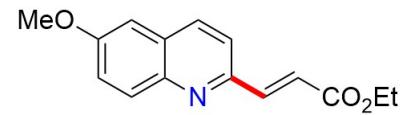
—120.932

—105.062

—55.751

—52.013

Ethyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3f).

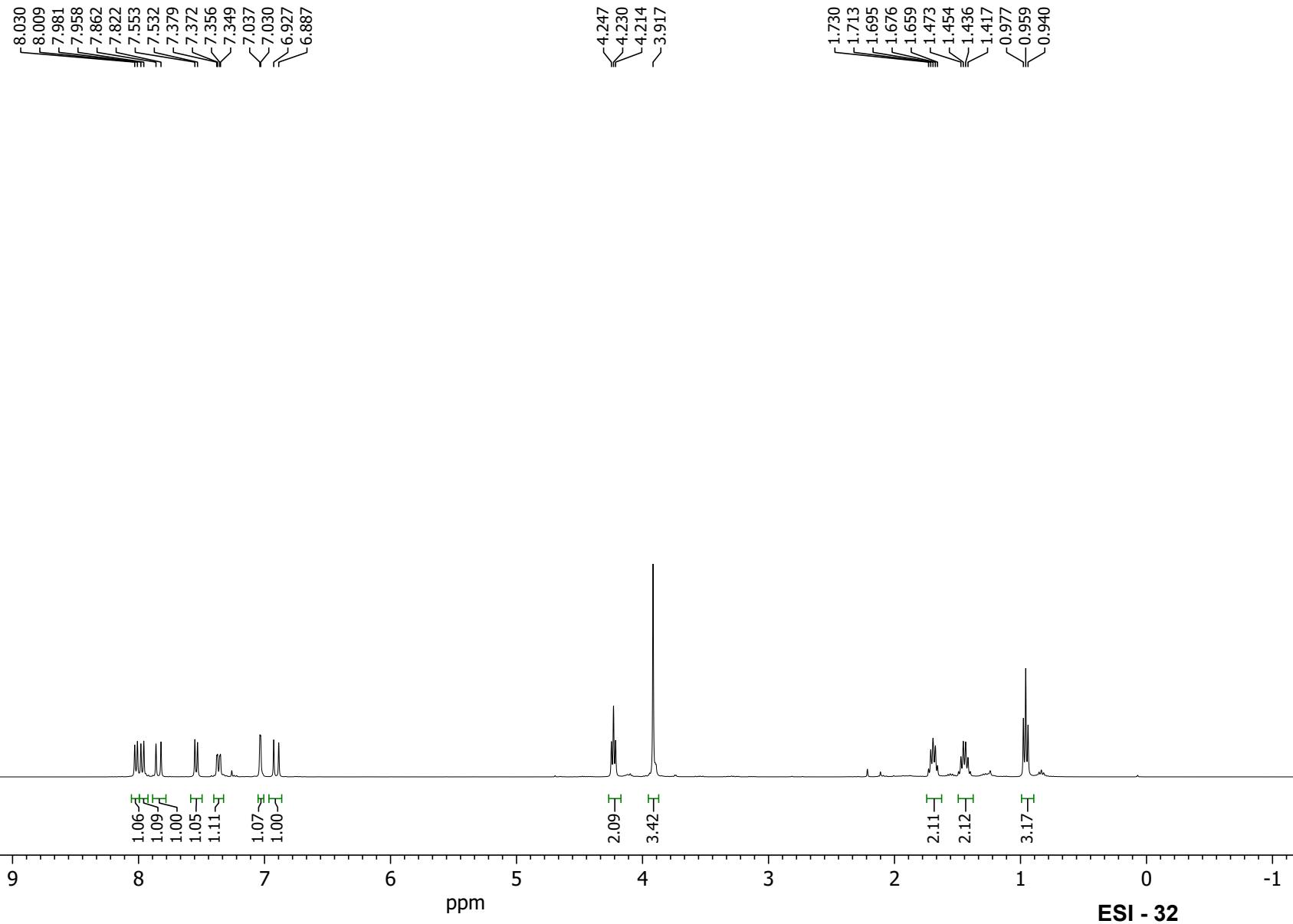
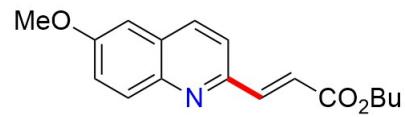


Ethyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3f).

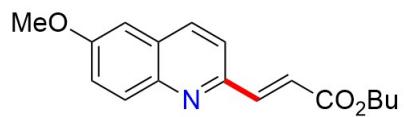


—166.886
—158.664
—151.020
—144.579
—144.391
—135.446
—131.475
—129.428
—123.160
—122.693
—120.792
—105.090
—60.837
—55.761
—14.453

Butyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3g).



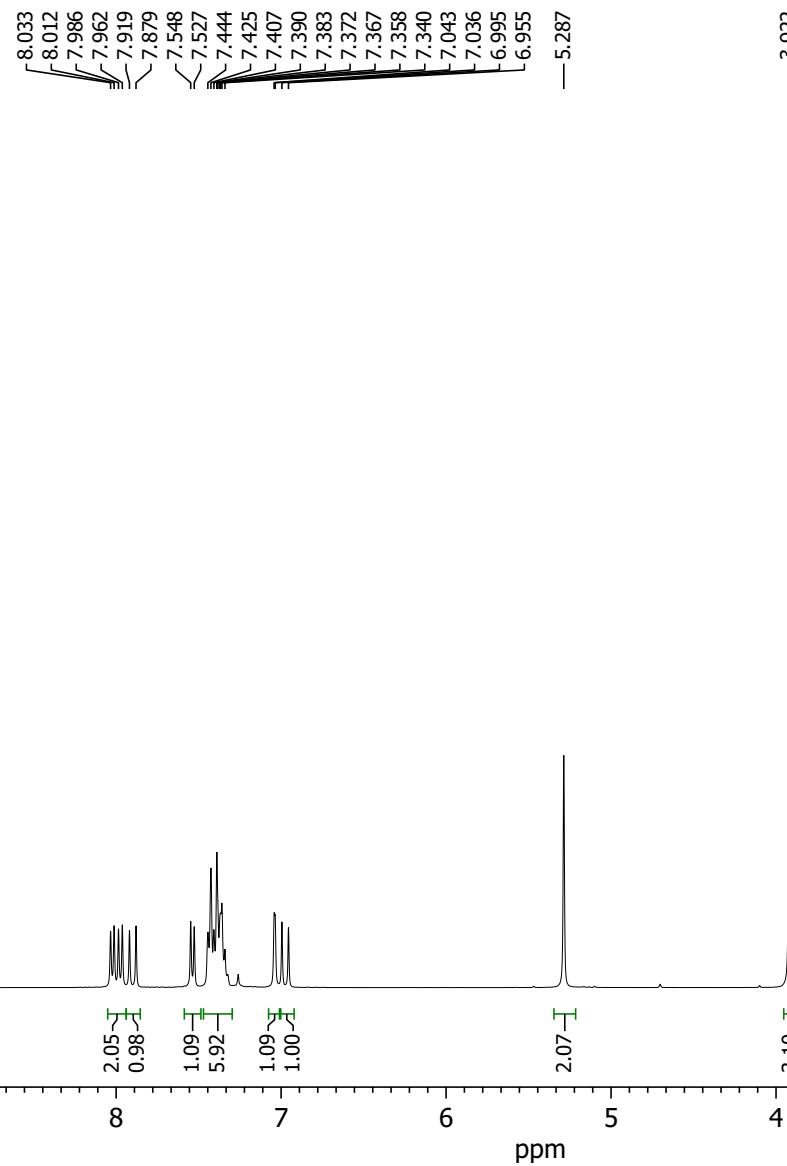
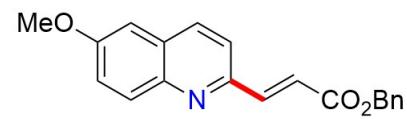
Butyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3g).



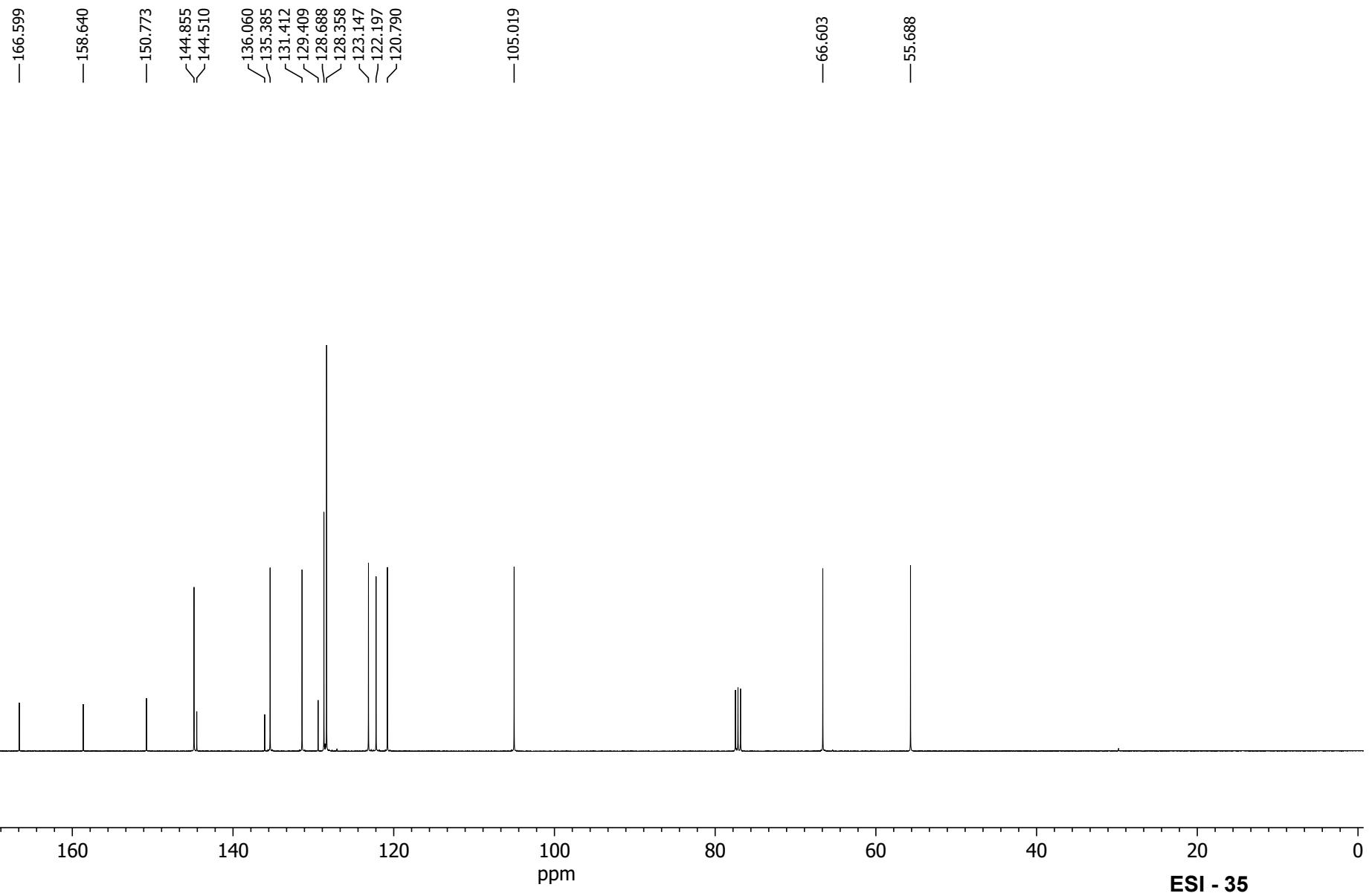
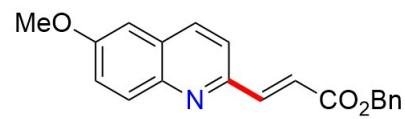
— 166.918
— 158.594
— 150.948
— 144.500
— 144.274
— ~135.380
— ~131.378
— ~129.364
— <123.102
— <122.642
— <120.731
— 105.032
— 64.697
— 55.686
— 30.850
— 19.307
— 13.847



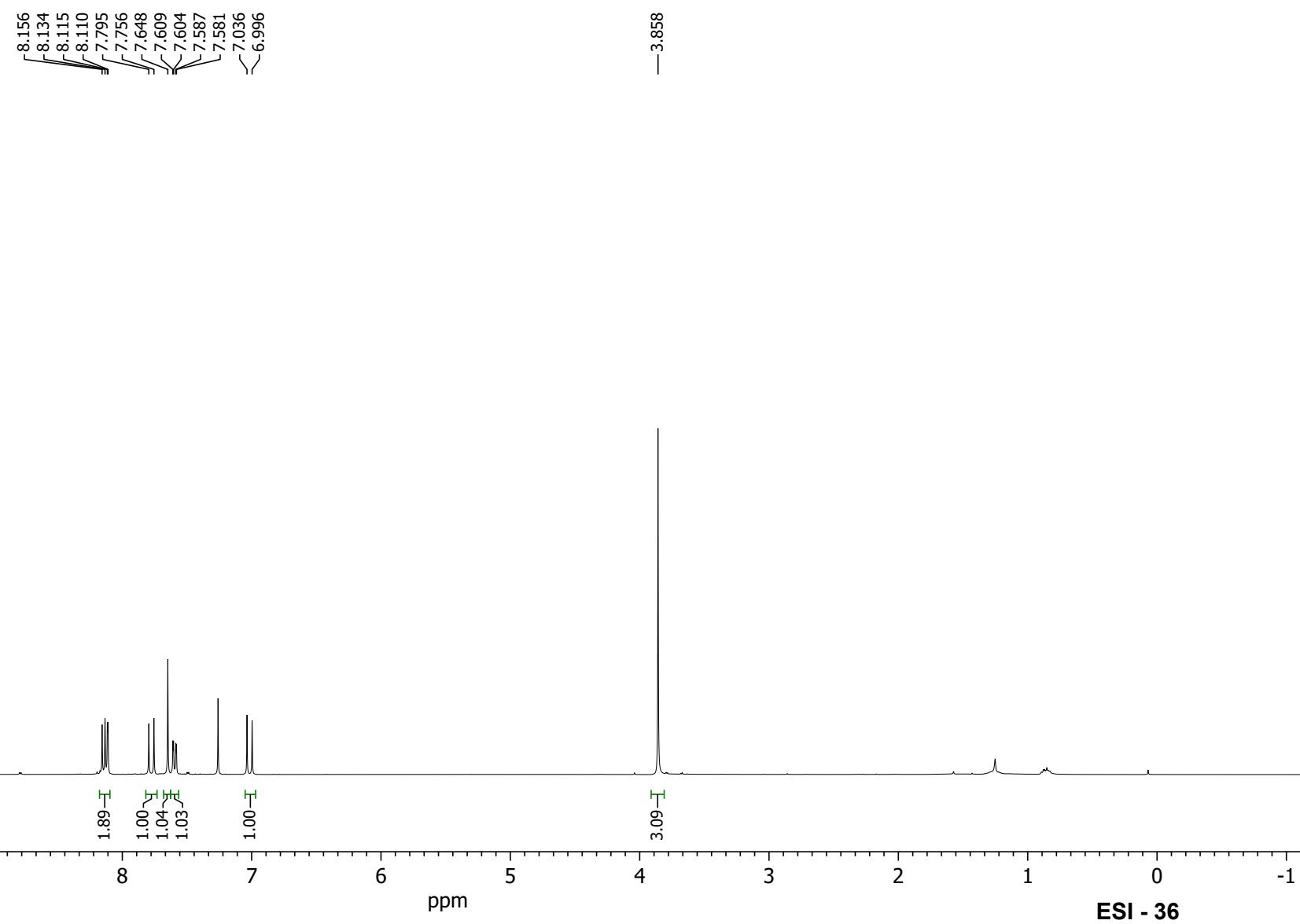
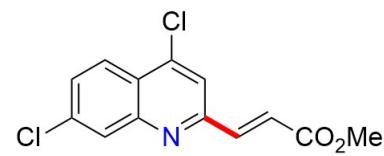
Benzyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3h).



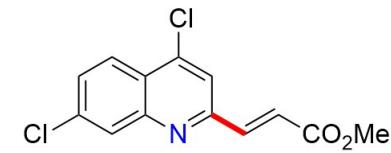
Benzyl (E)-3-(6-methoxyquinolin-2-yl)acrylate (3h).



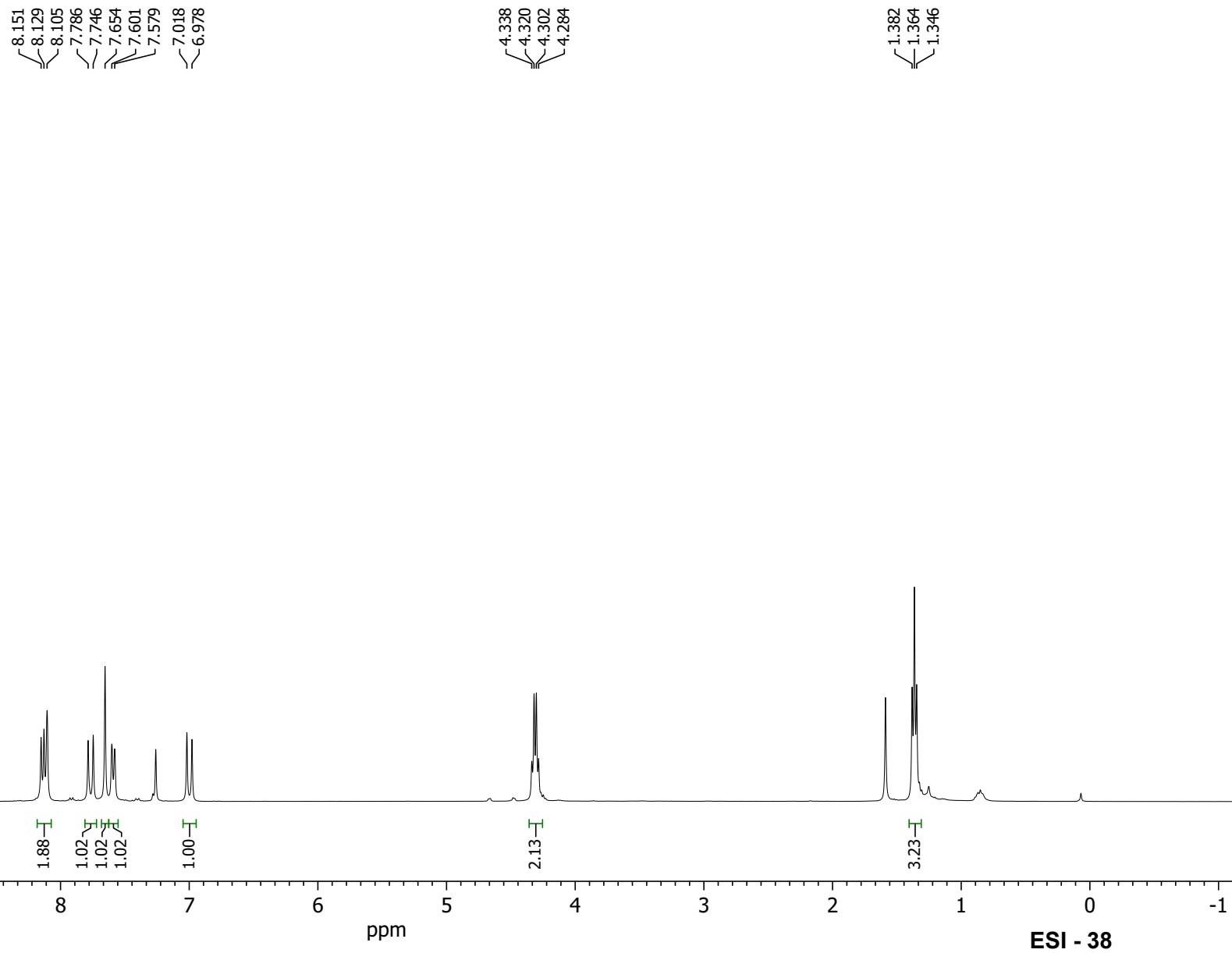
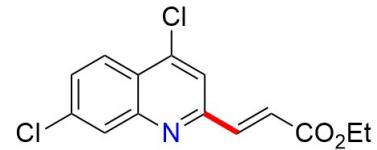
Methyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3i).



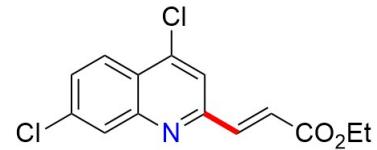
Methyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3i).



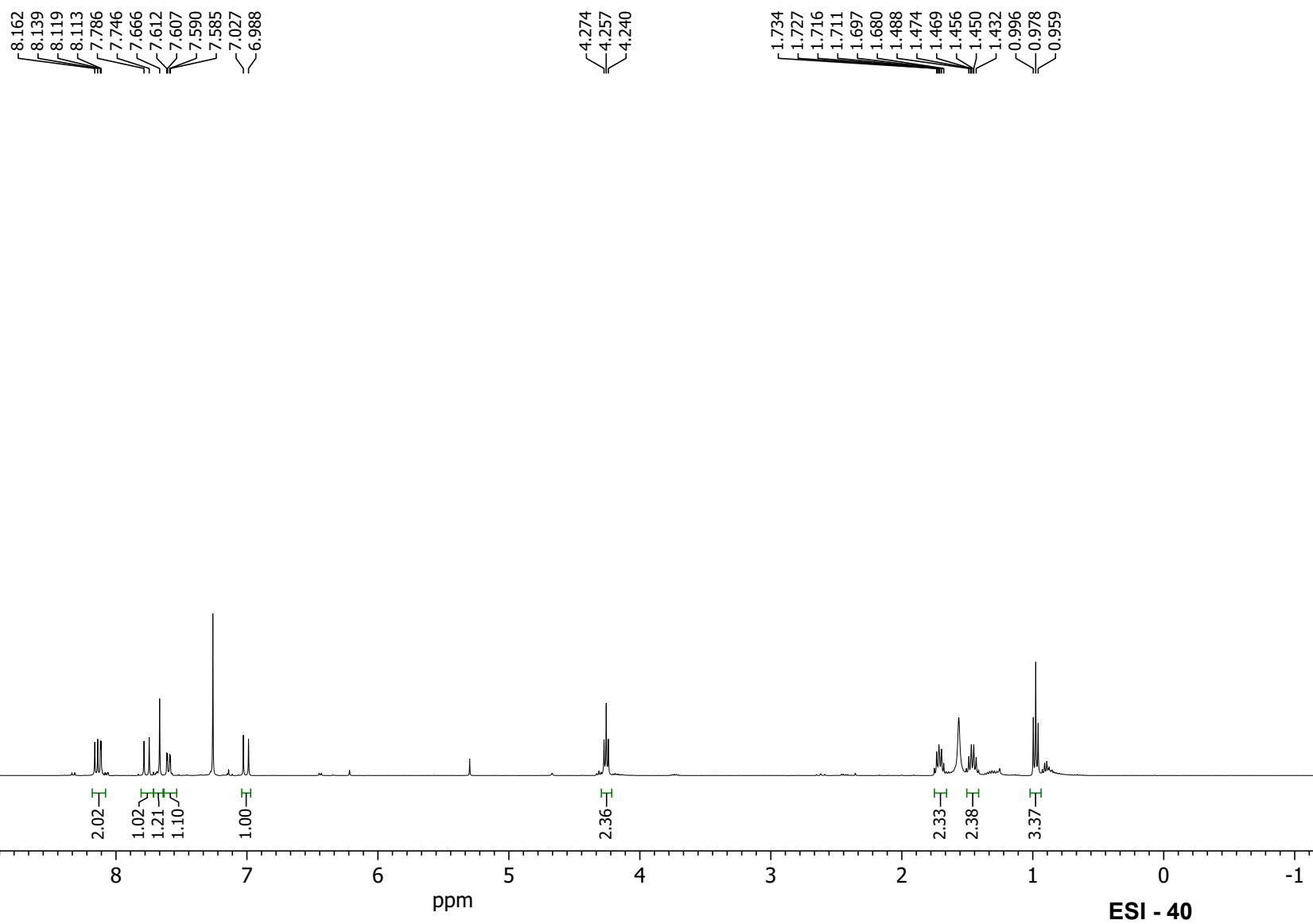
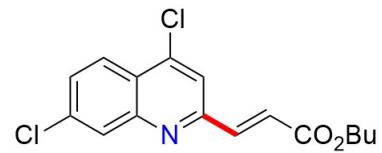
Ethyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3j).



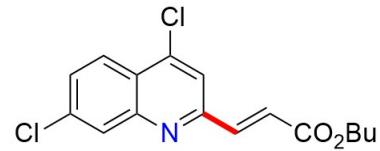
Ethyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3j).



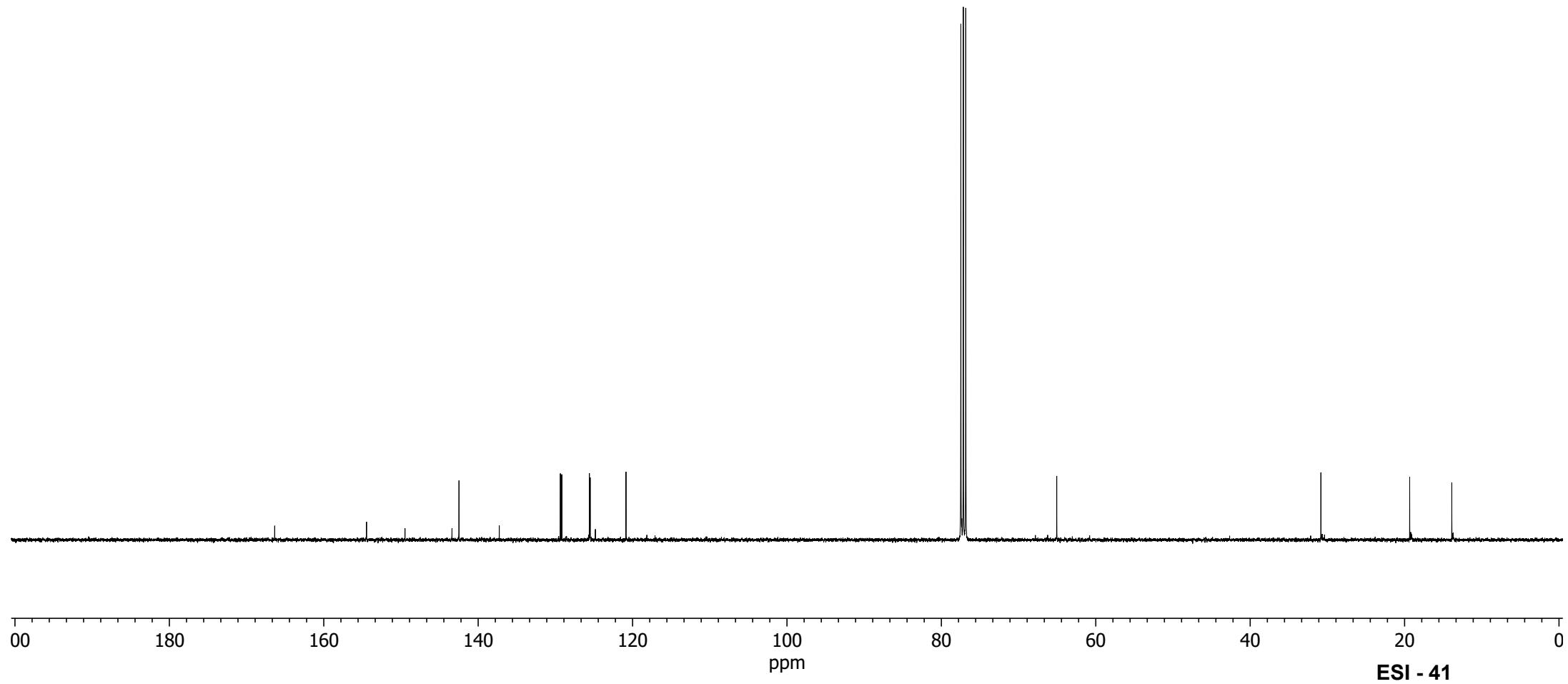
Butyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3k).



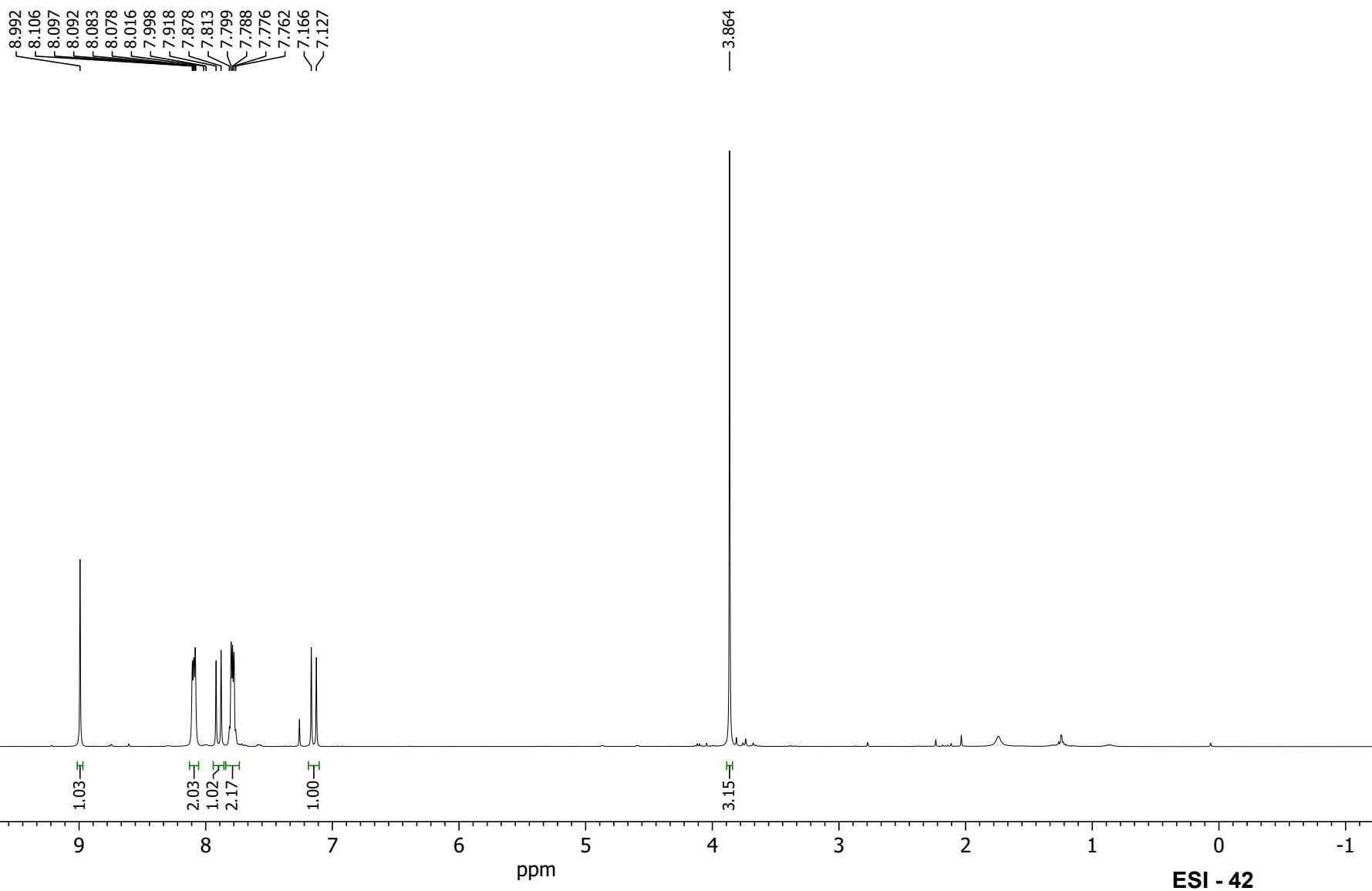
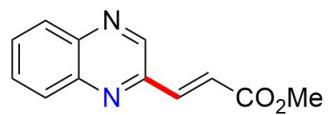
Butyl (E)-3-(4,7-dichloroquinolin-2-yl)acrylate (3k).



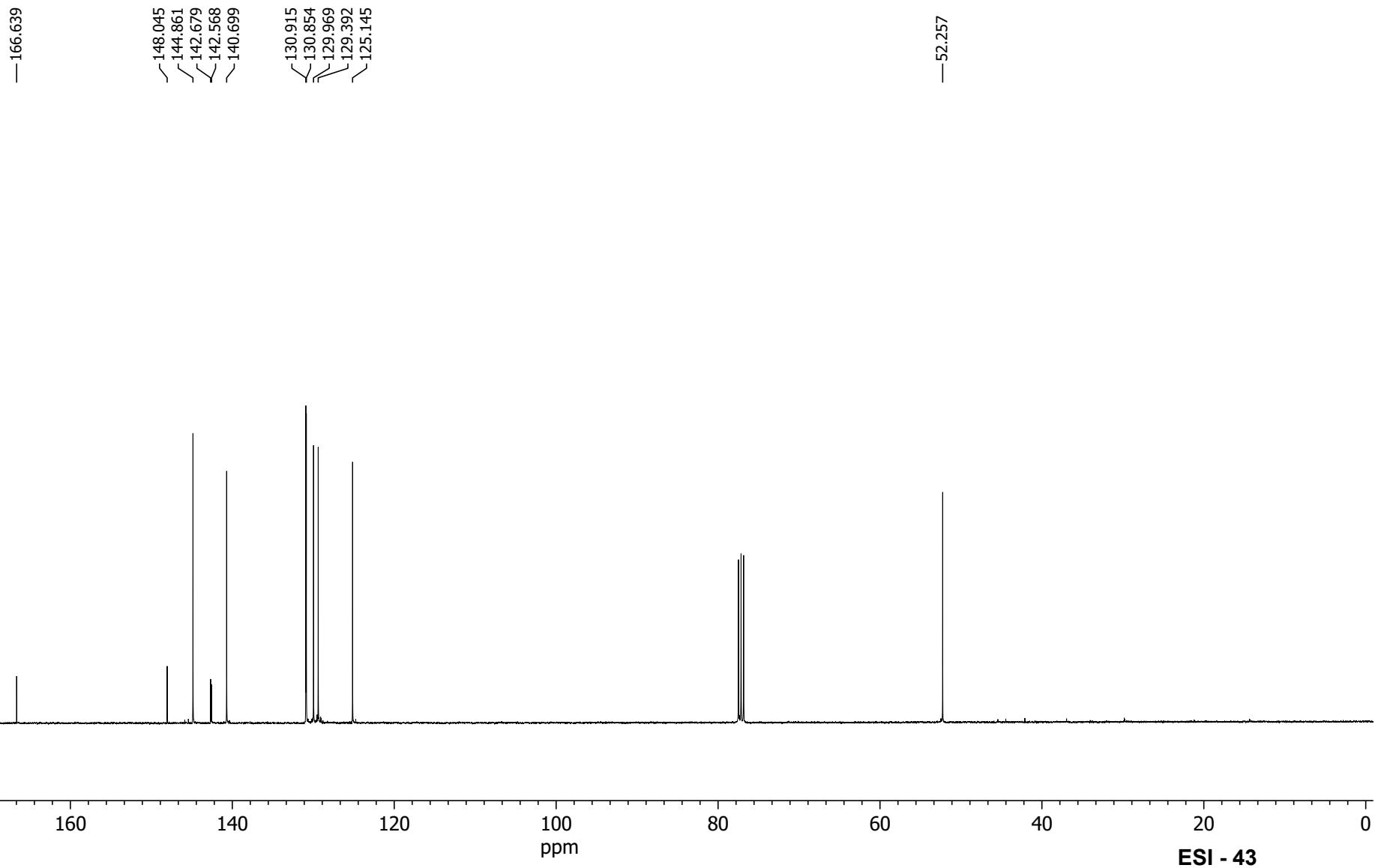
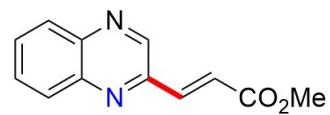
— 166.357
— 154.462
— 149.478
— 143.394
— 142.486
— 137.267
— 129.351
— 129.172
— 125.595
— 125.490
— 124.818
— 120.853
— 65.058
— 30.840
— 19.339
— 13.883



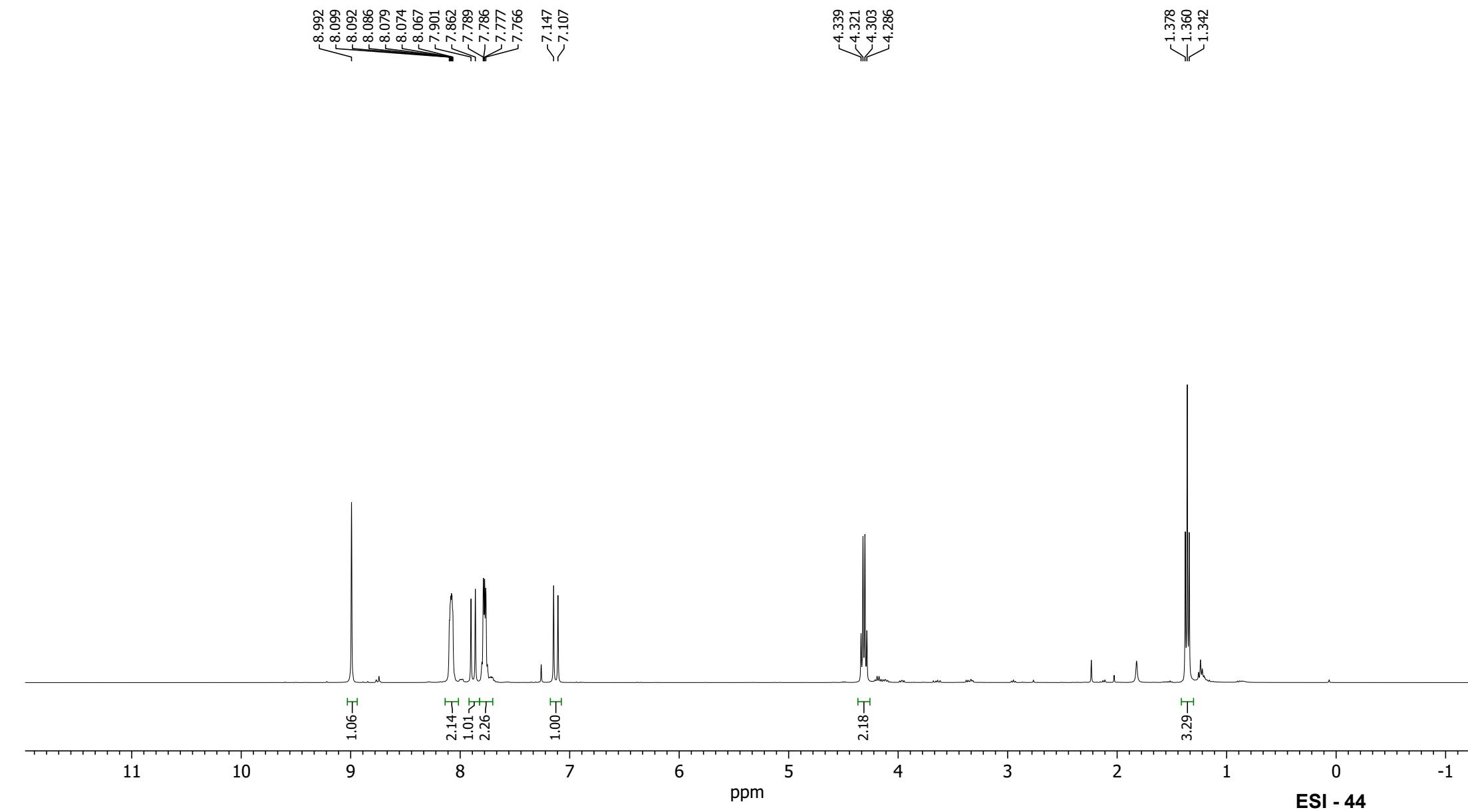
Methyl (E)-3-(quinoxalin-2-yl)acrylate (3l).



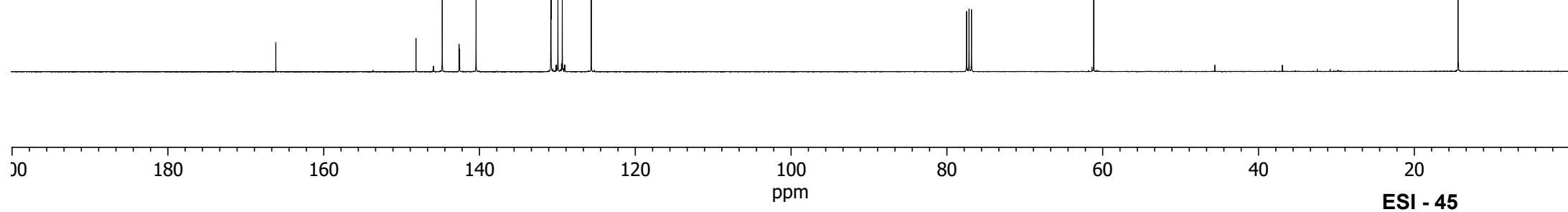
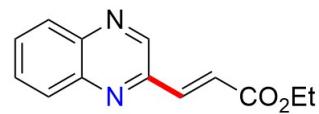
Methyl (E)-3-(quinoxalin-2-yl)acrylate (3l).



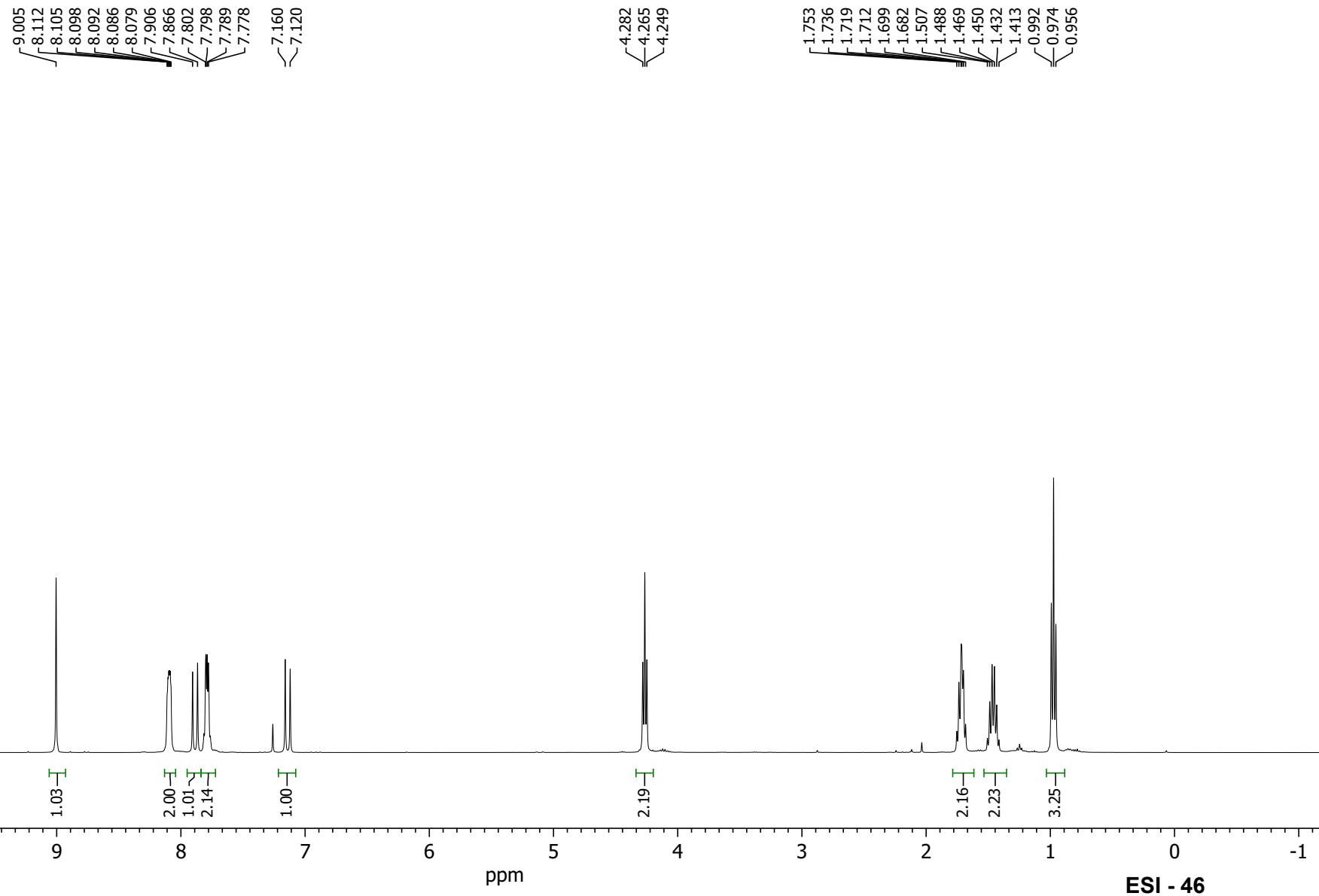
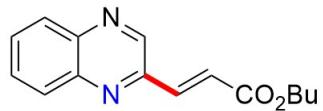
Ethyl (E)-3-(quinoxalin-2-yl)acrylate (3m).



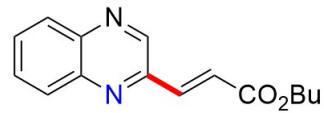
Ethyl (E)-3-(quinoxalin-2-yl)acrylate (3m).



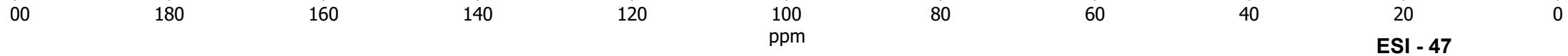
Butyl (E)-3-(quinoxalin-2-yl)acrylate (3n).



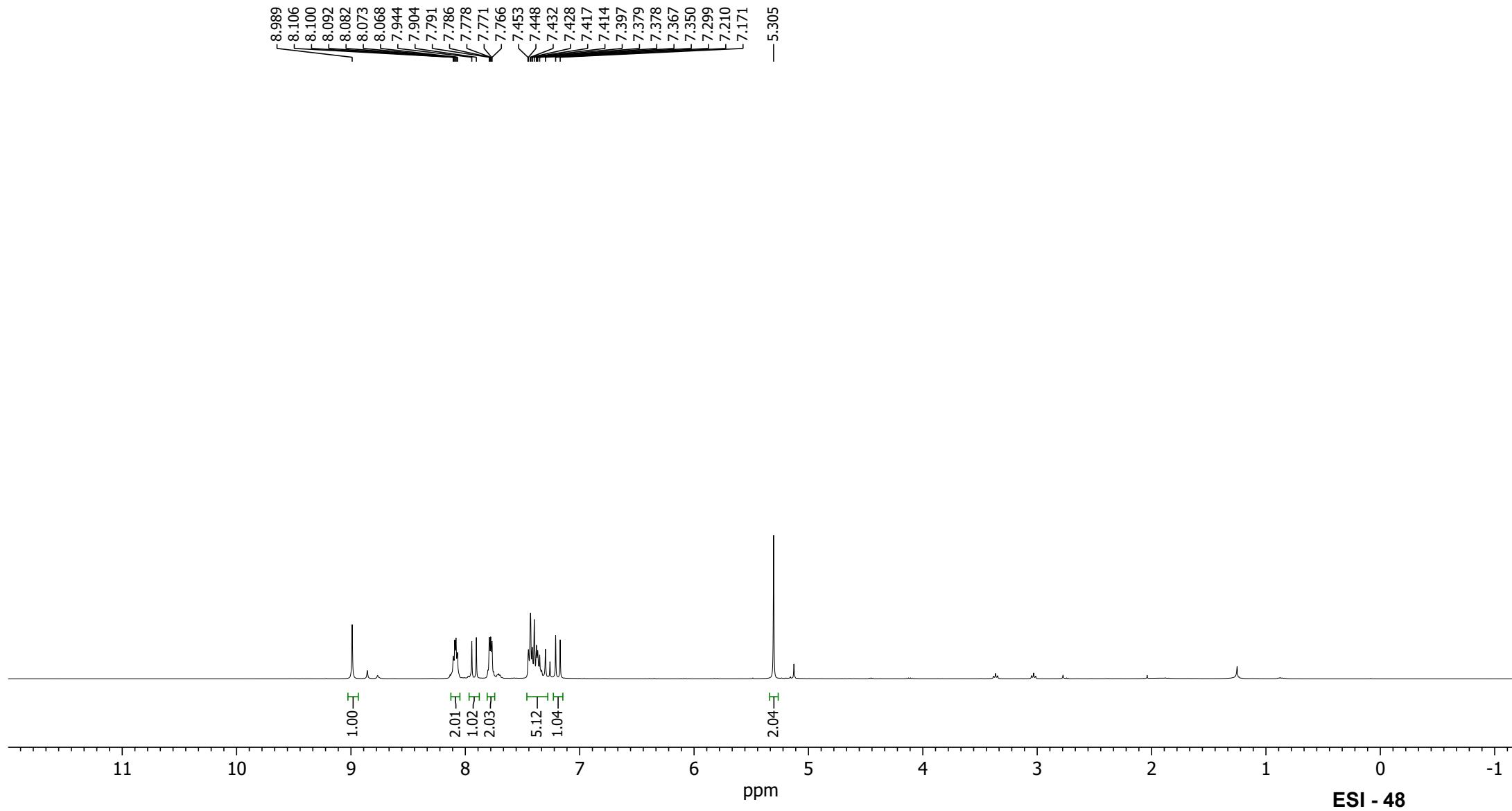
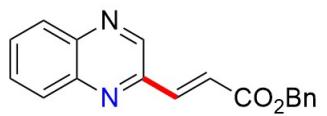
Butyl (E)-3-(quinoxalin-2-yl)acrylate (3n).



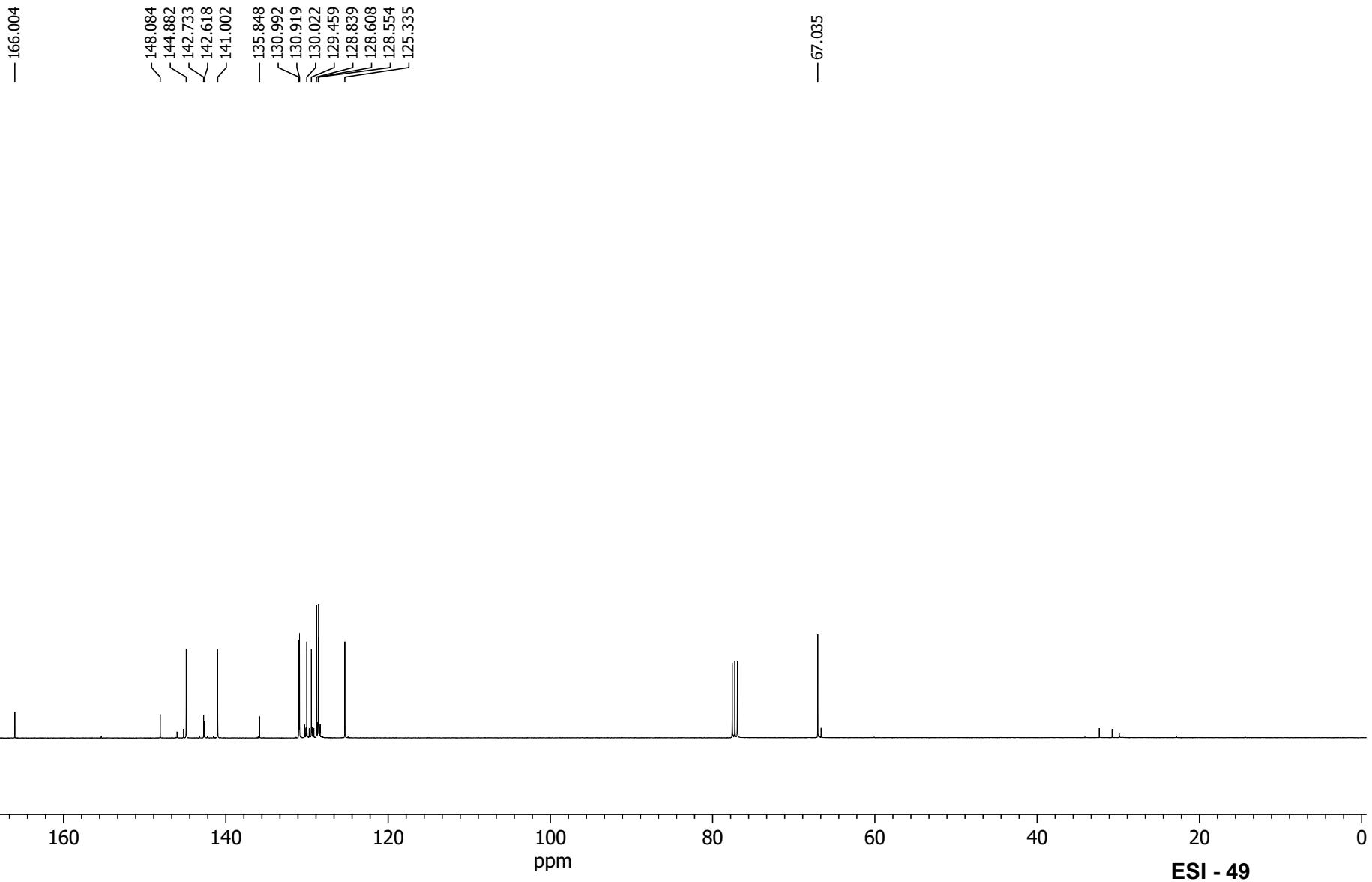
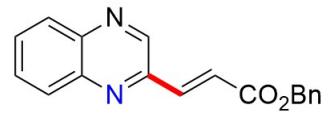
— 166.271
— 148.188
— 144.815
— 142.649
— 142.566
— 140.423
— 130.869
— 130.846
— 129.939
— 129.404
— 125.709
— 65.080
— 30.826
— 19.322
— 13.867



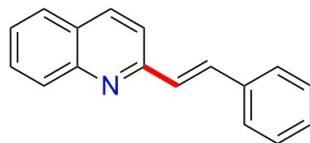
Benzyl (E)-3-(quinoxalin-2-yl)acrylate (3o).



Benzyl (E)-3-(quinoxalin-2-yl)acrylate (3o).

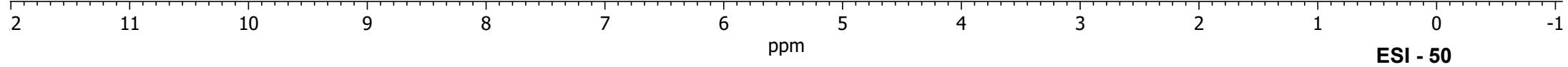


(E)-2-styrylquinoline (6a).

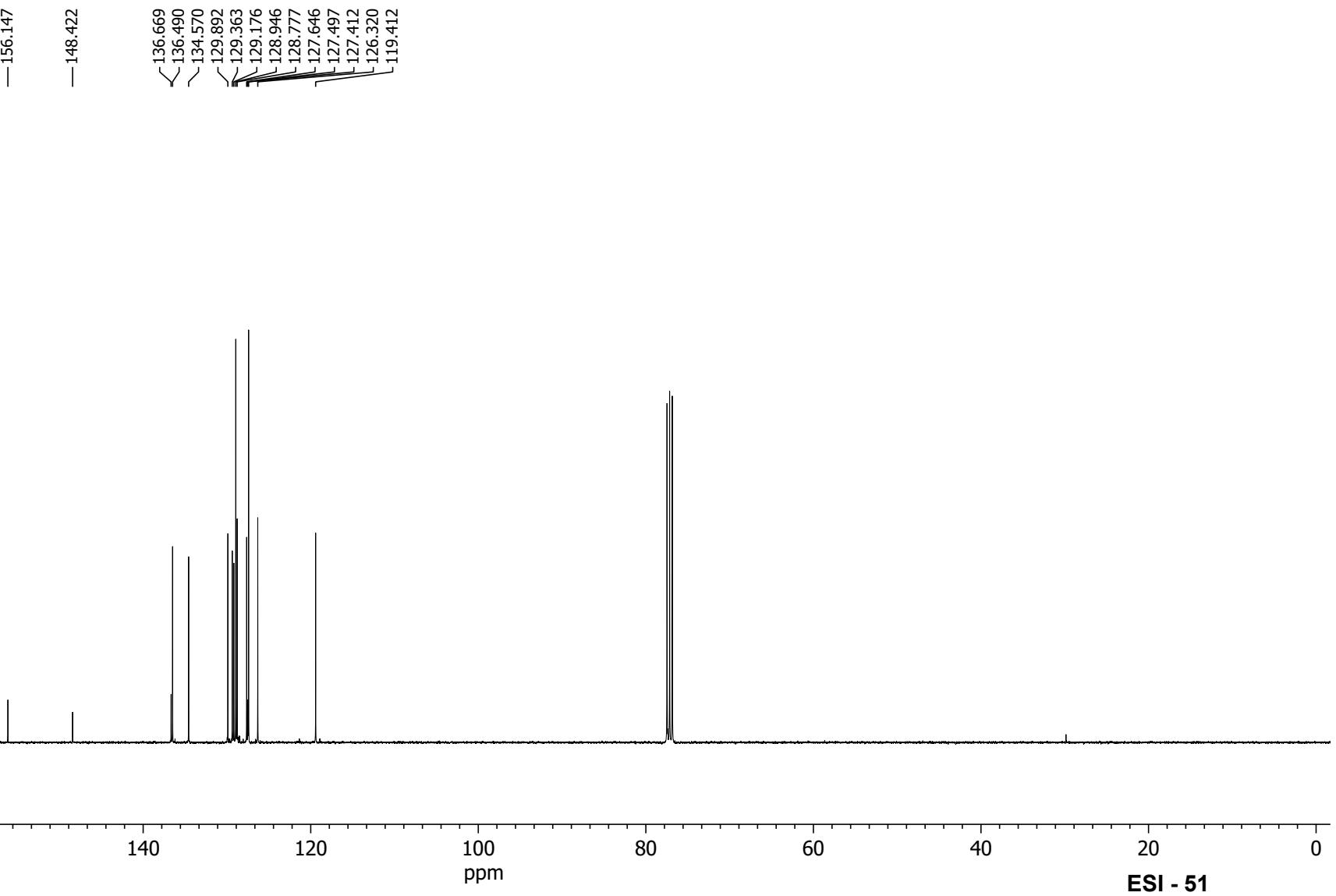


8.143
8.122
8.097
8.075
7.799
7.779
7.730
7.713
7.693
7.673
7.659
7.640
7.519
7.501
7.482
7.438
7.428
7.409
7.397
7.390
7.349
7.331
7.312

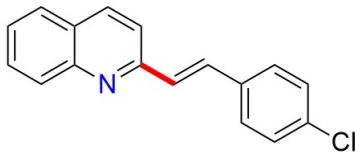
0.98
0.97
1.00
4.87
1.04
2.92
1.09



(E)-2-styrylquinoline (6a).



(E)-2-(4-chlorostyryl)quinoline (6b).



8.142
8.121
8.090
8.087
8.069
8.066
8.066
7.800
7.796
7.779
7.776
7.734
7.730
7.717
7.713
7.713
7.709
7.696
7.692
7.667
7.651
7.630
7.626
7.573
7.568
7.557
7.552
7.526
7.523
7.509
7.506
7.503
7.489
7.486
7.387
7.379
7.357
7.346

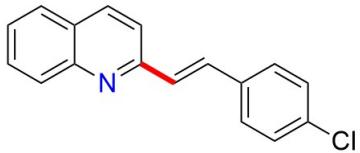
1.00
0.96
1.00
1.03
2.01
2.05
0.98
2.92

2 11 10 9 8 7 6 5 4 3 2 1 0 -1

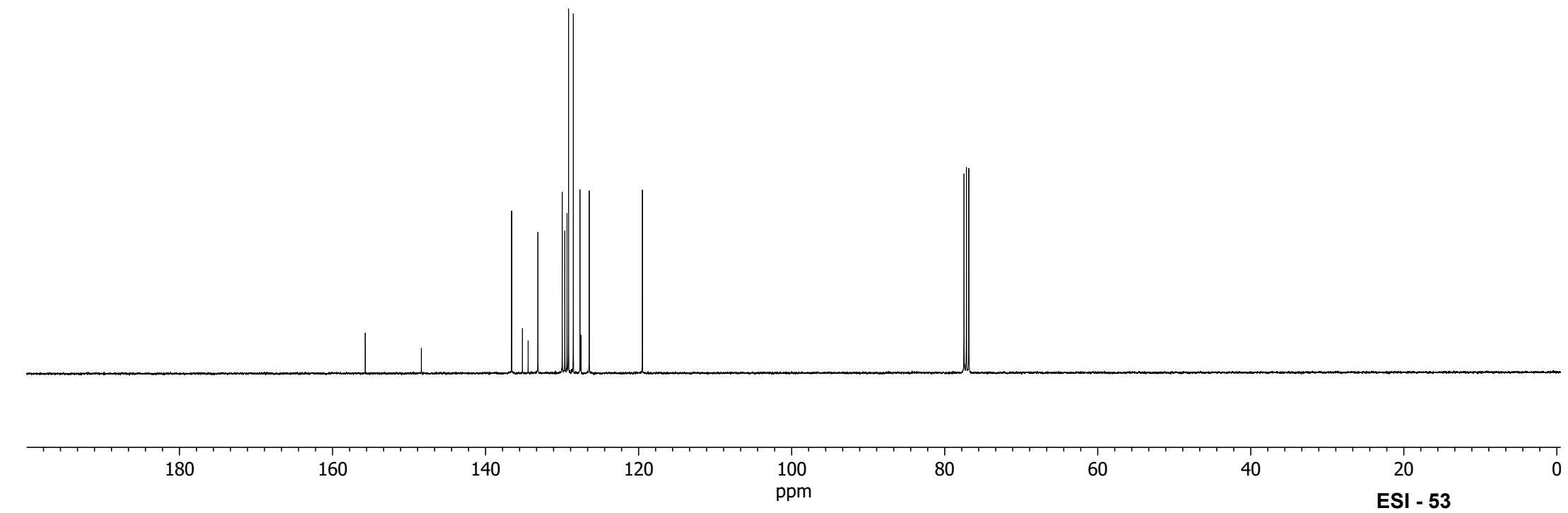
ppm

ESI - 52

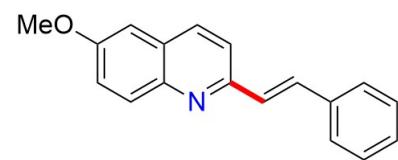
(E)-2-(4-chlorostyryl)quinoline (6b).



— 155.734
— 148.390
— 136.596
— 135.184
— 134.439
— 133.163
— 129.983
— 129.645
— 129.358
— 129.153
— 128.536
— 127.663
— 127.544
— 126.455
— 119.504



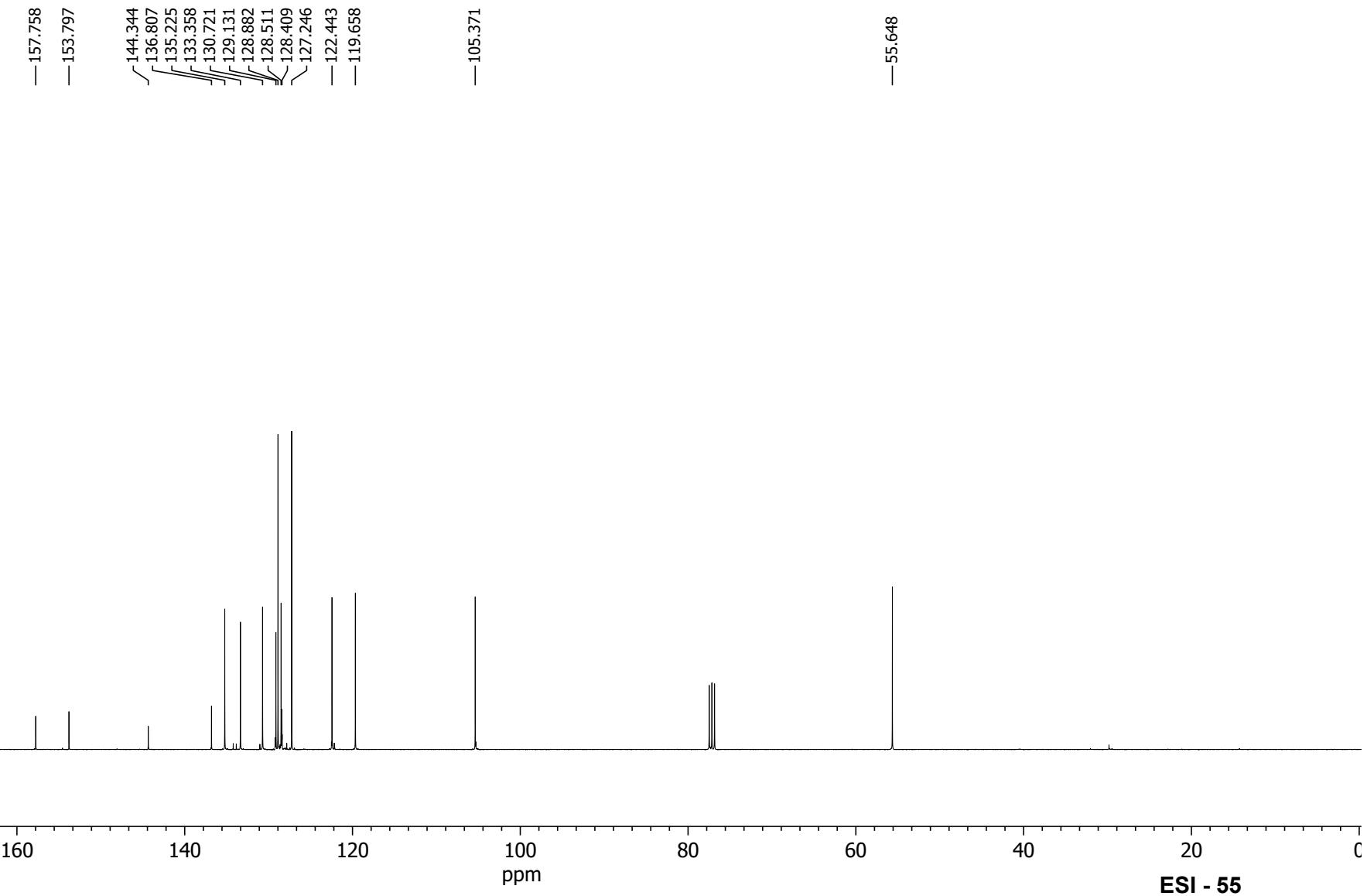
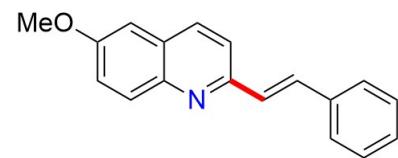
(E)-6-methoxy-2-styrylquinoline (6c).



ppm

ESI - 54

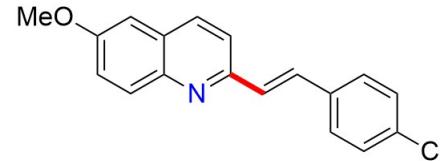
(E)-6-methoxy-2-styrylquinoline (6c).



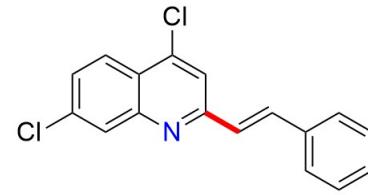
(E)-2-(4-chlorostyryl)-6-methoxyquinoline (6d).



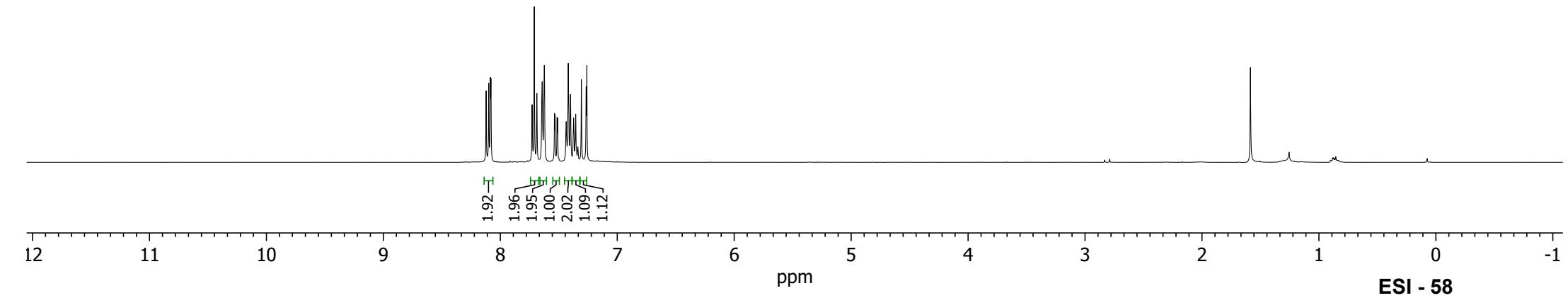
(E)-2-(4-chlorostyryl)-6-methoxyquinoline (6d).



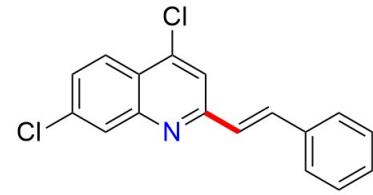
(E)-4,7-dichloro-2-styrylquinoline (6e).



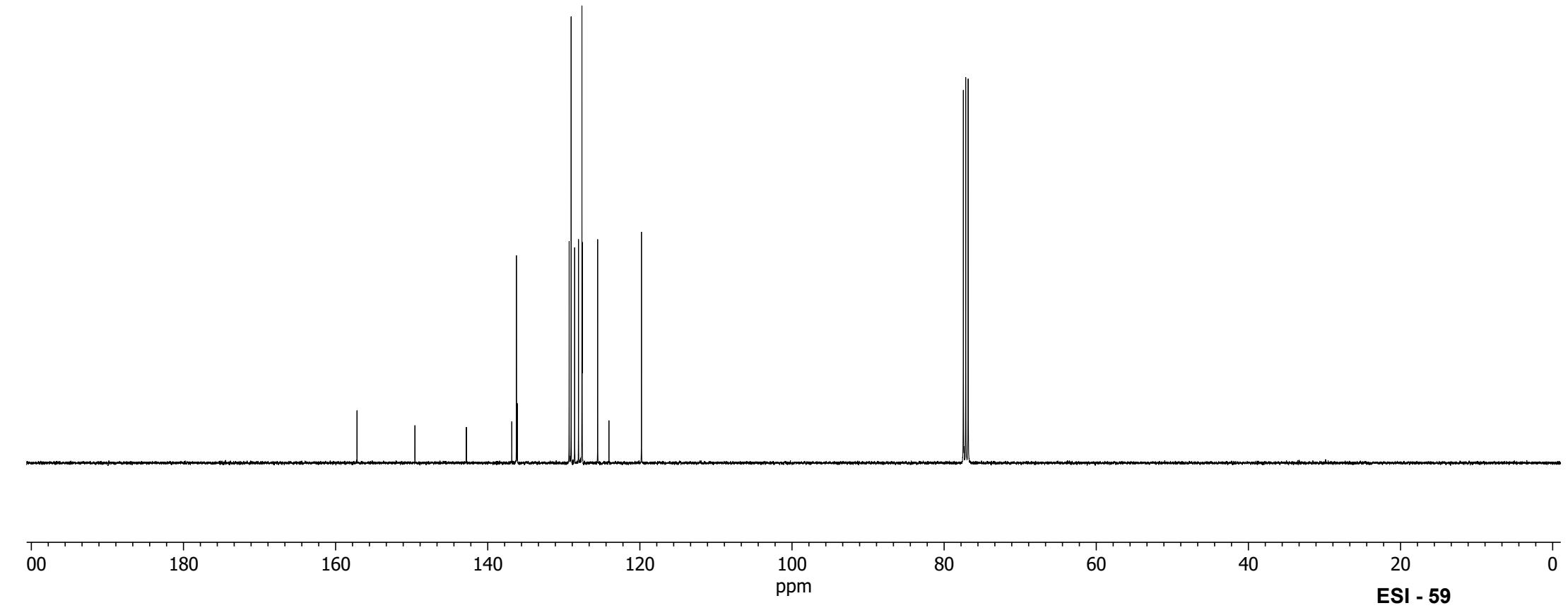
8.121
8.099
8.085
8.080
7.728
7.710
7.687
7.642
7.624
7.537
7.532
7.515
7.509
7.436
7.419
7.414
7.404
7.400
7.373
7.355
7.340
7.337
7.333
7.307
7.266



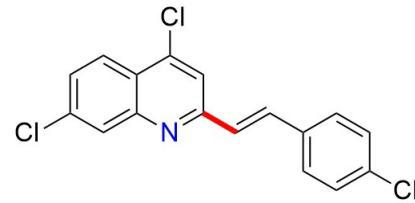
(E)-4,7-dichloro-2-styrylquinoline (6e).



— 157.187
— 149.573
— 142.812
136.840
136.228
136.108
129.300
129.039
128.577
128.066
127.615
127.563
125.550
124.063
119.790

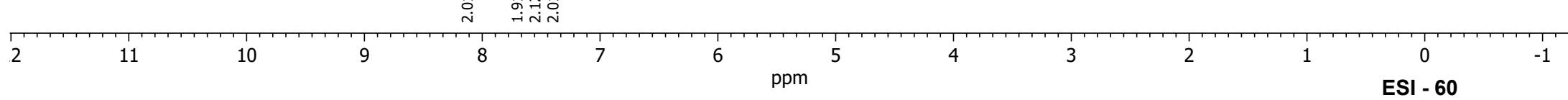


(E)-4,7-dichloro-2-(4-chlorostyryl)quinoline (6f).

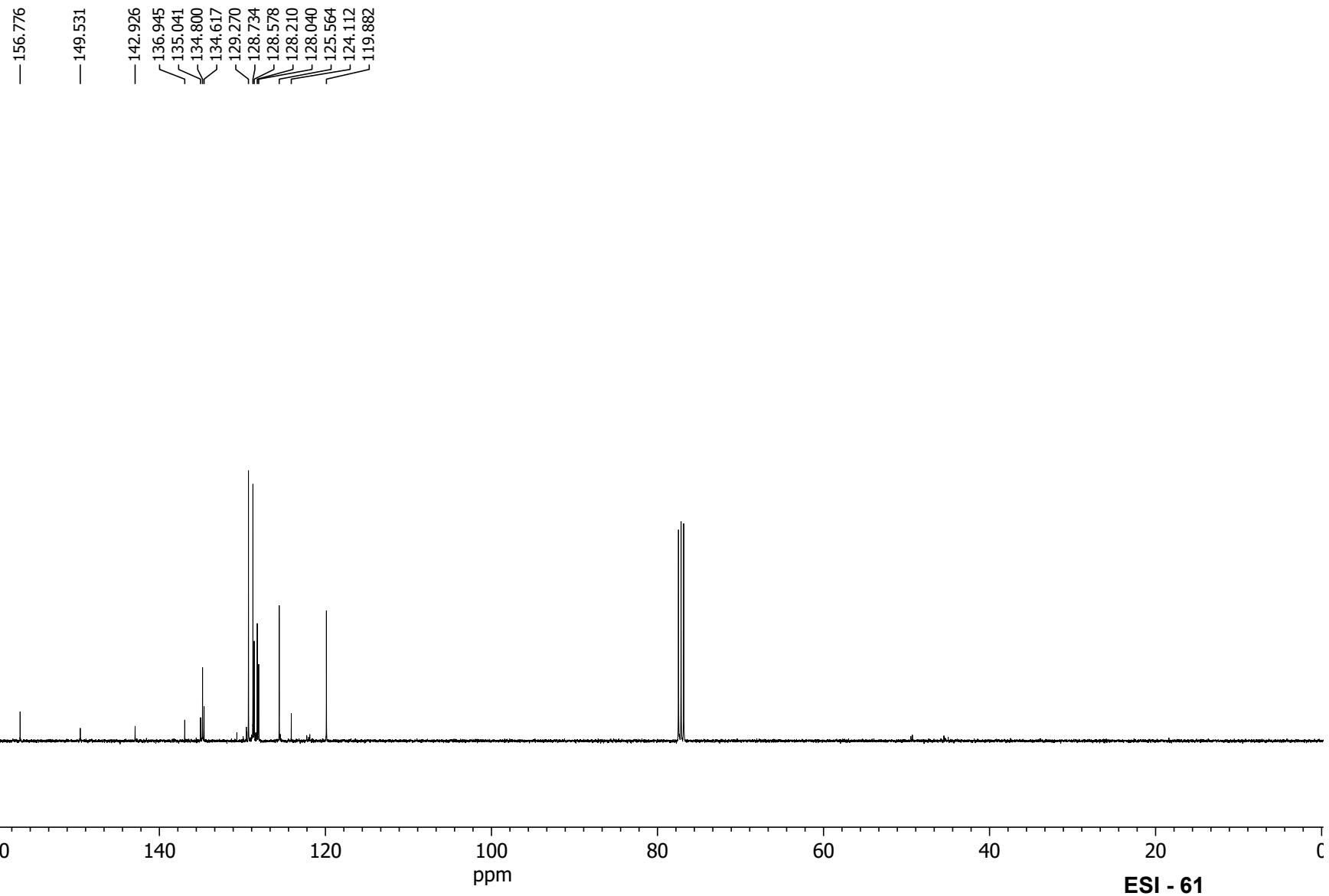
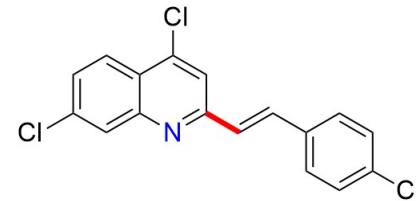


8.142
8.120
8.099
8.094
7.705
7.696
7.665
7.583
7.562
7.542
7.537
7.414
7.393

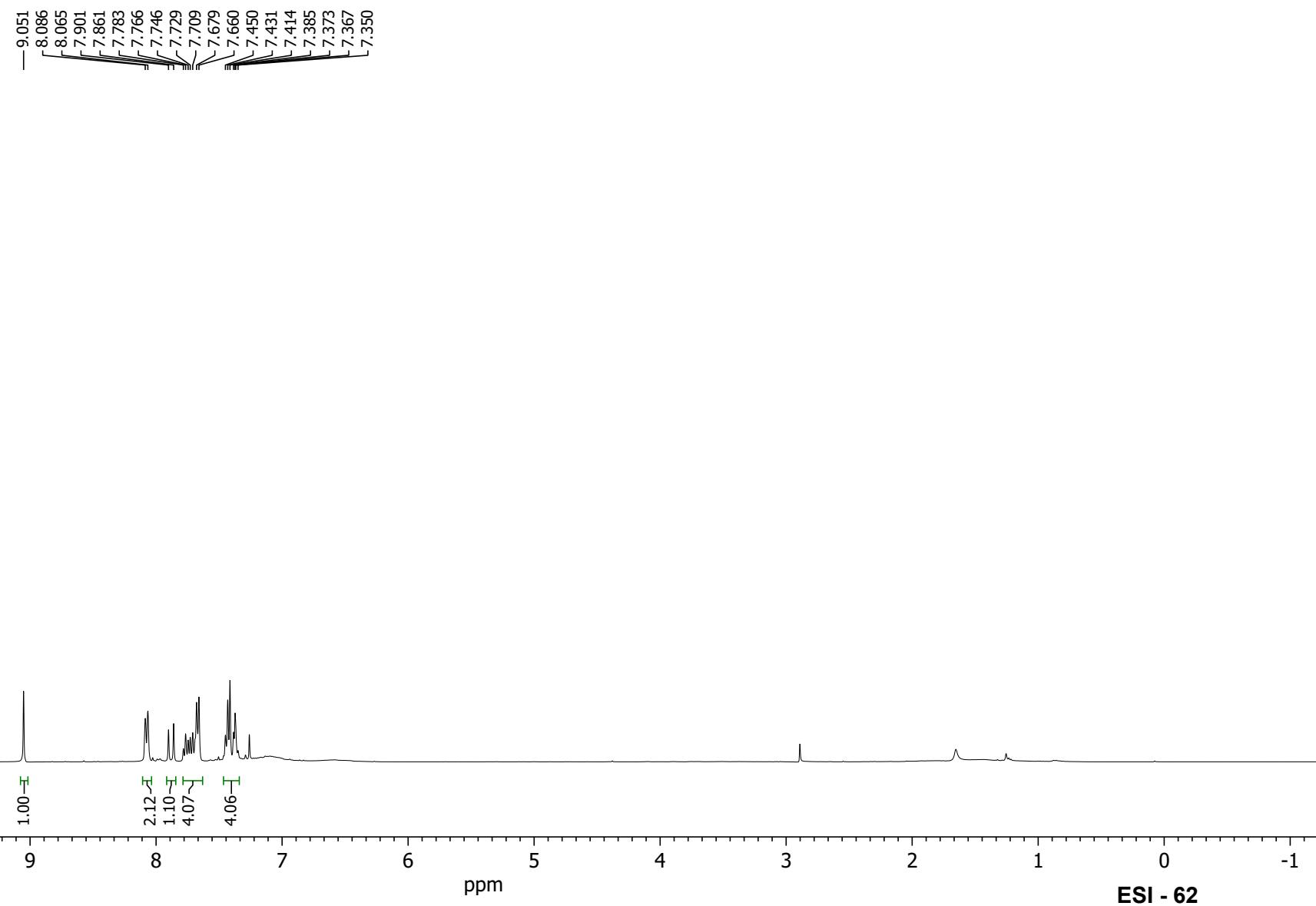
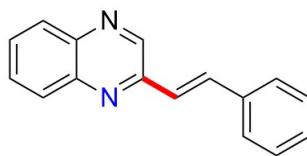
2.01
1.91
2.12
2.01



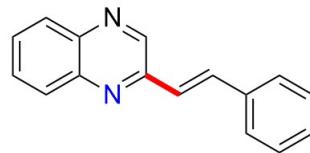
(E)-4,7-dichloro-2-(4-chlorostyryl)quinoline (6f).



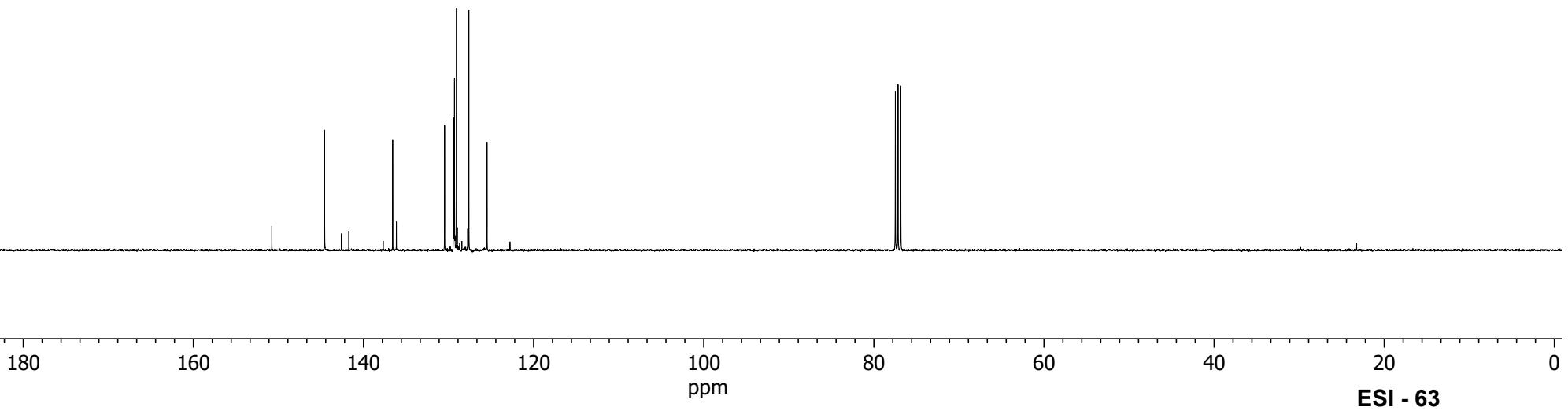
(E)-2-styrylquinoxaline (6g).



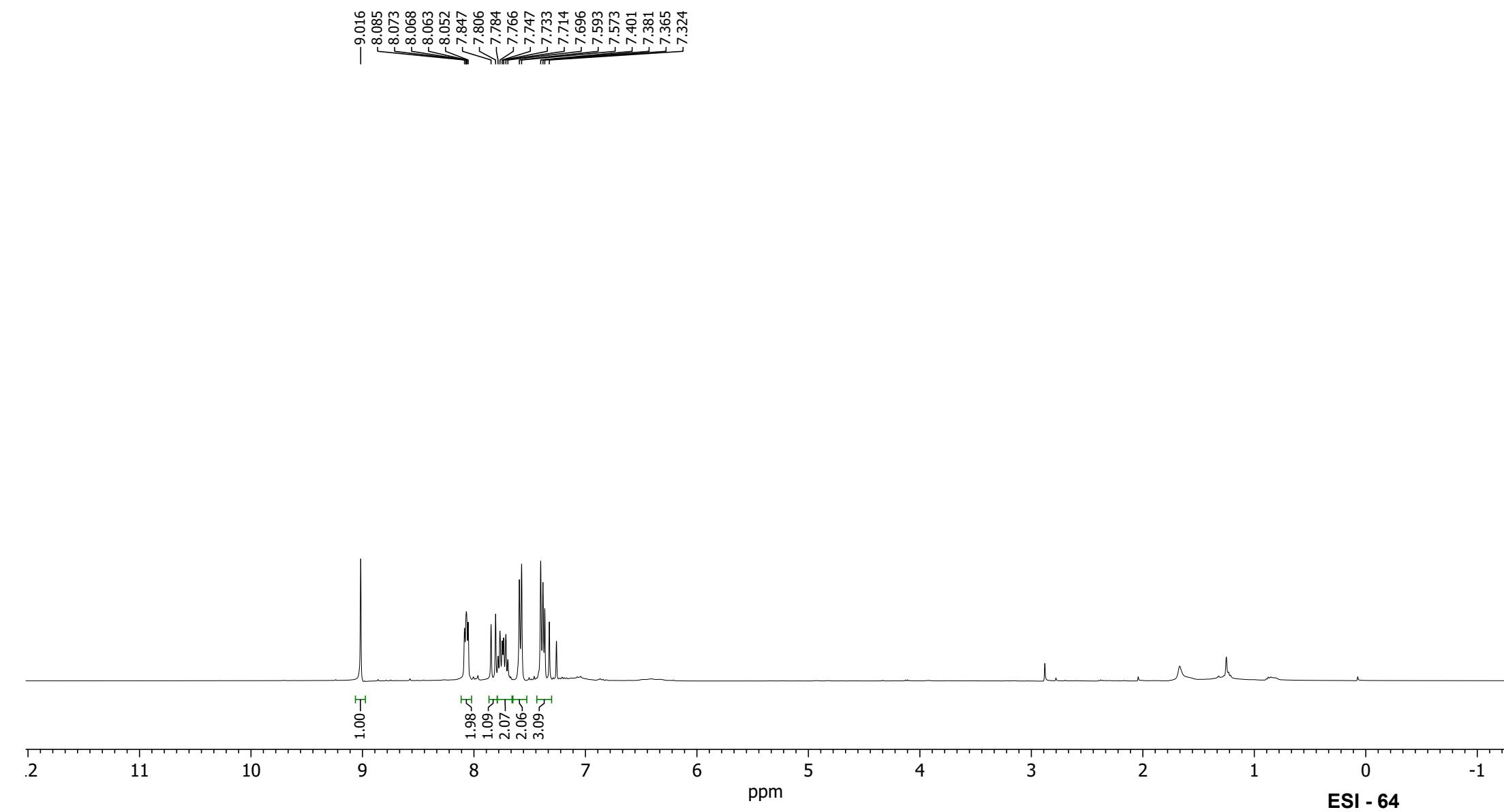
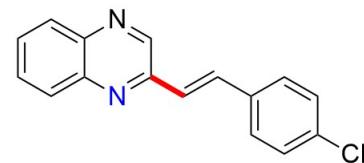
(E)-2-styrylquinoxaline (6g).



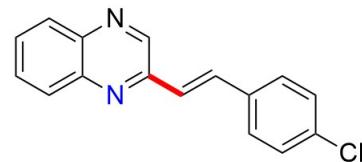
— 150.775
~ 144.575
~ 142.603
~ 141.722
136.572
~ 136.136
130.470
129.431
129.394
129.311
129.305
129.058
127.614
125.477



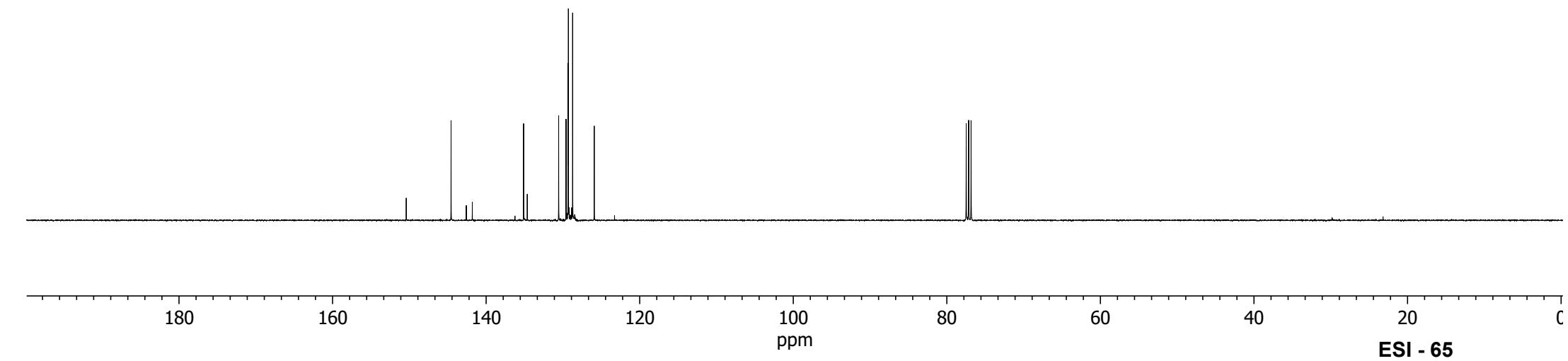
(E)-2-(4-chlorostyryl)quinoxaline (6h).



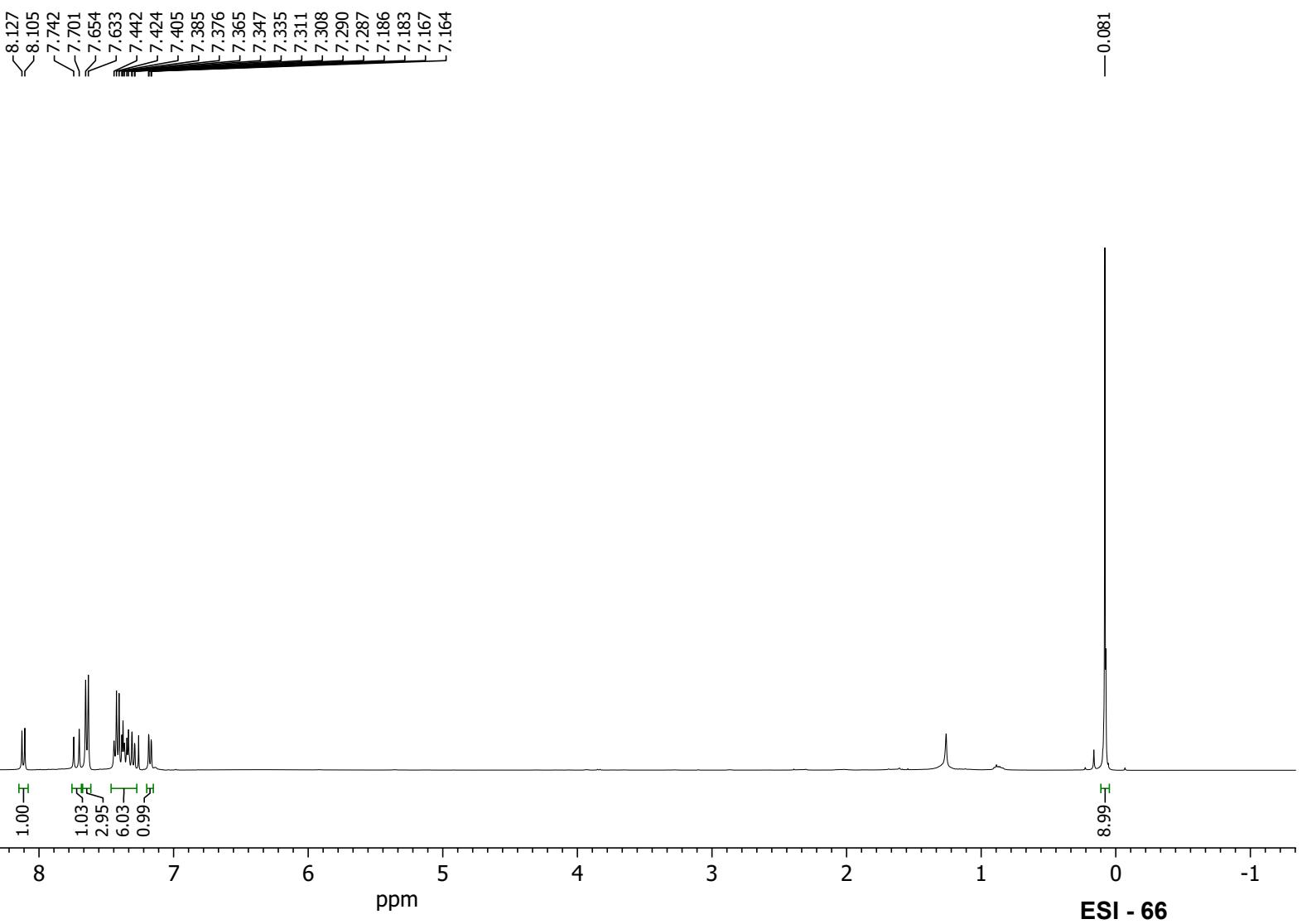
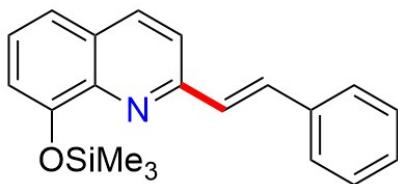
(E)-2-(4-chlorostyryl)quinoxaline (6h).



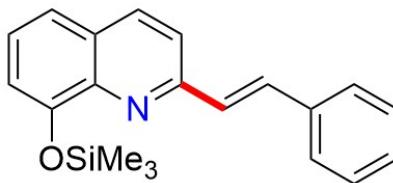
— 150.407
— 144.566
— 142.384
— 141.802
— 135.122
— 134.646
— 130.555
— 129.590
— 129.325
— 129.291
— 128.884
— 128.736
— 125.920



(E)-2-styryl-8-((trimethylsilyl)oxy)quinoline (6i)



(E)-2-styryl-8-((trimethylsilyl)oxy)quinoline (6i)

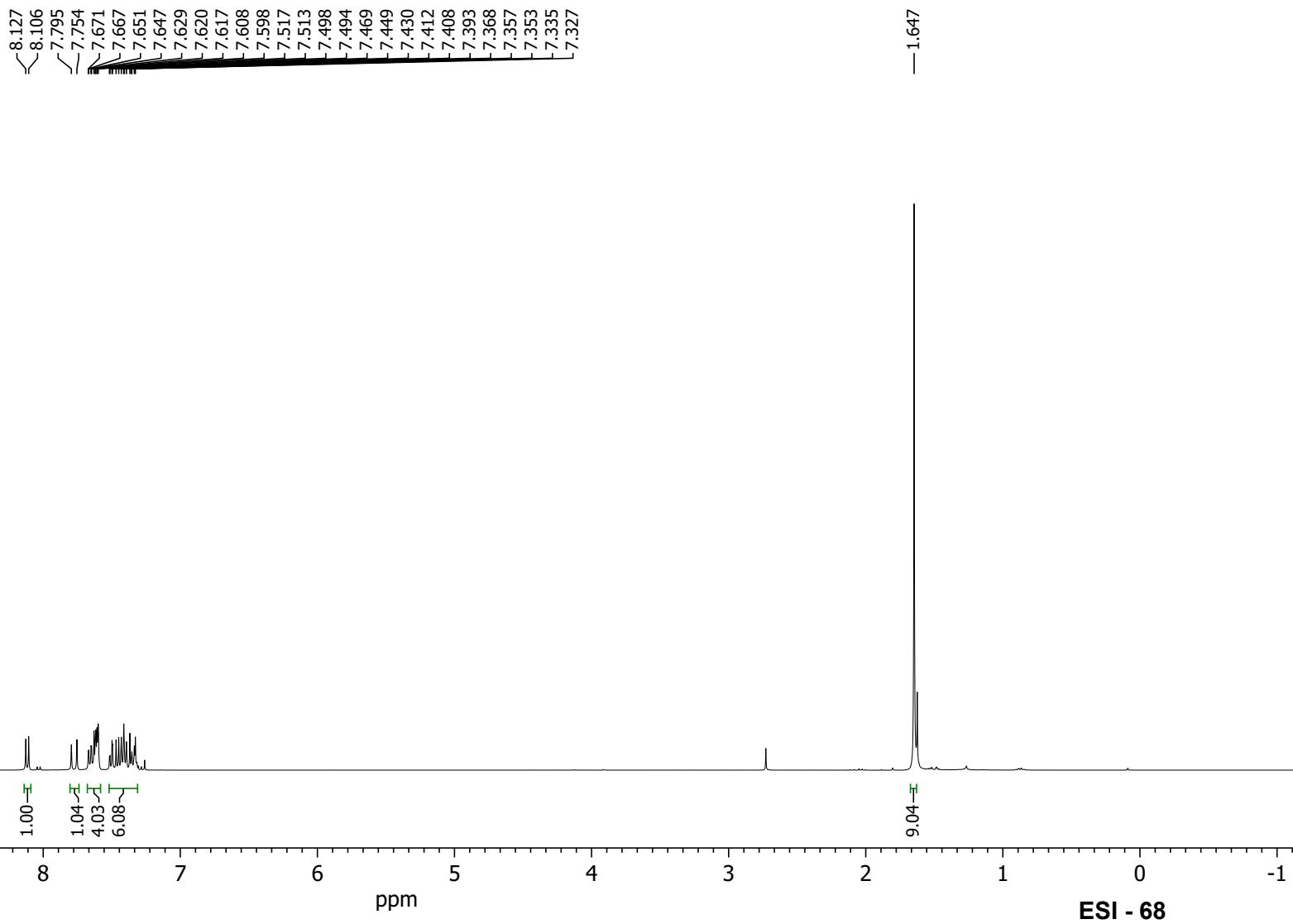
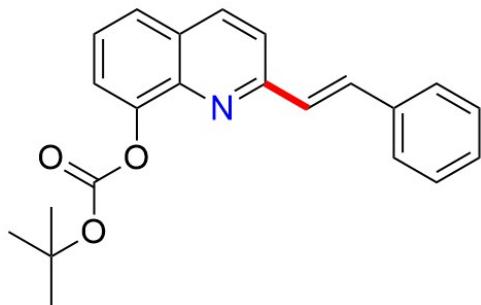


180 160 140 120 100 80 60 40 20 0

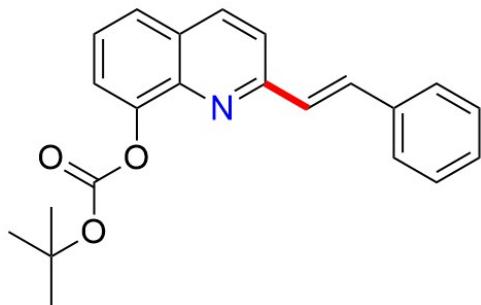
ppm

ESI - 67

(E)-tert-butyl (2-styrylquinolin-8-yl) carbonate (6j)



(E)-tert-butyl (2-styrylquinolin-8-yl) carbonate (6j)



—155.760
—152.171
—147.499
—141.299
—136.697
—136.357
—134.766
—128.949
—128.768
—128.654
—127.346
—125.772
—125.577
—121.172
—120.654
—83.471
—27.945

