Supporting Information

Denitrative Mizoroki-Heck Reaction of Unactivated Alkenes

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I. General

^{1}H NMR spectra were acquired on Jeol 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvent ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C and ^{19}F NMR spectra.

Glassware was dried in an oven at 110 ^{o}C for at least 2 hours before use. Unless noted otherwise, commercially available chemicals were used without further purification. The GC standard, *n*-dodecane was degassed with argon bubbling and dried over activated 4 Å molecular sieve beads for a few days in the glove box before use.

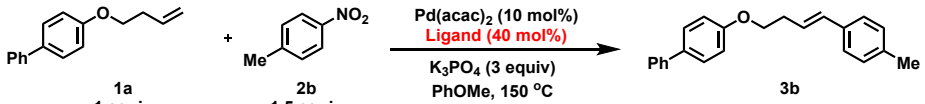
Thin-layer chromatography (TLC) was performed with Merck 60 F254 coated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm) or SiliCycle silica gel F60 (0.040-0.063 mm). The dilute solvents usually used Ethyl Acetate/Petroleum Ether, which was abbreviated as EA/PE.

GCMS analysis was performed on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was performed on a ThermoFinnigan LCQ Fleet MS spectrometer. Gas chromatographic (GC) analysis was performed on a SHIMADZU GC-2010 plus instrument equipped with an FID detector and an Agilent J & W GC column DB-5MS-UI.

II. Condition Optimization for the Model Reaction

Typical procedure for condition optimization: To a dry 10-mL Schlenk tube containing a magnetic stir bar was added alkene **1a** (1.0 equiv, 0.20 mmol, 44.8 mg), $Pd(acac)_2$ (10.0 mol%, 0.02 mmol, 6.1 mg), X-Phos (40 mol%, 0.08 mmol, 38.1 mg), K_3PO_4 (3.0 equiv, 0.60 mmol, 127.2 mg), nitroarene **2b** (1.5 equiv, 0.30 mmol, 41.1 mg), PhOMe (1.0 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a *pre*-warmed 150 °C oil bath. After 24 hours, 20 μL dodecane was added in the tube. After filtering, the filtrate was subjected to GC analysis to determine the conversion of alkene **1a**, calibrated GC yield of the coupling product. The major byproducts from alkene are the [1,1'-biphenyl]-4-ol and the isomer of olefin.

Table S1 Effect of Ligands



Entry	Ligand	Yield of 3b (%)
1	No ligand	0
2	$^{n}Bu_3P{\bullet}HBF_4$	0
3	BrettPhos	46
4	^{t}BuDavePhos	20
5	Cy-JohnPhos	0
6	MePhos	0
7	^{t}Bu-XPhos	10
8	**X-Phos**	**84**
9	^{t}Bu-MePhos	32
10	RuPhos	31
11	XantPhos	0
12	cataCXium®PCy	0
13	P(2-furyl)$_3$	0

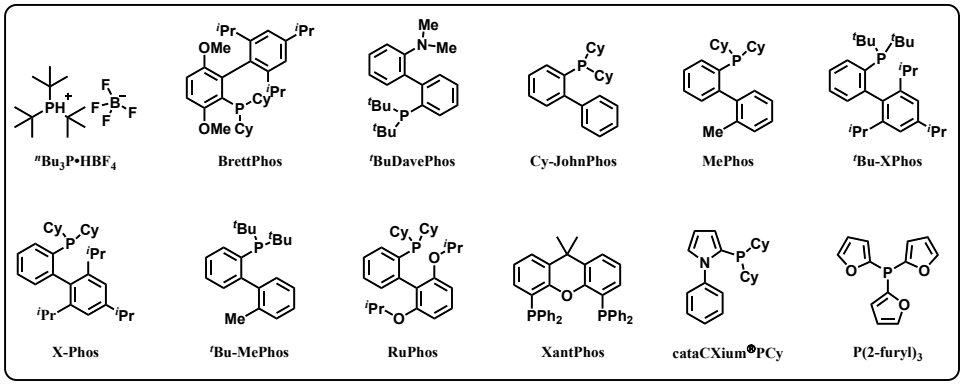
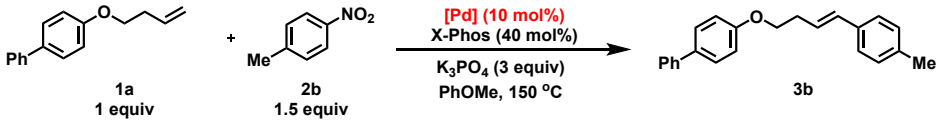
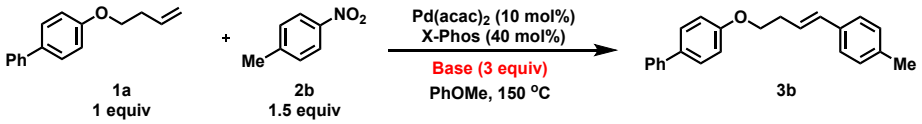


Table S2 Effect of Catalysts



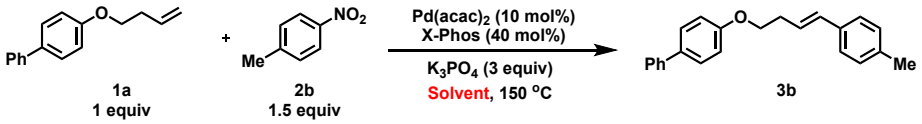
Entry	Catalyst	Yield of 3b (%)
1	No catalyst	0
2	$Pd(OAc)_2$	0
3	**$Pd(acac)_2$**	**84**
4	$Pd_2(dba)_3$	0
5	$PdCl_2$	0
6	Pd (COD)Cl_2	0
7	$[Pd(ally)Cl]_2$	0
8	$[(Cinnamyl)PdCl]_2$	0
9	$Pd(PPh_3)_4$	0

Table S3 Effect of Bases



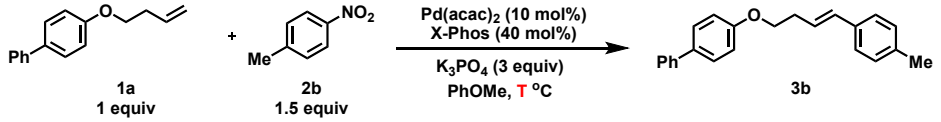
Entry	Base	Yield of 3b (%)
1	No base	30
2	**K_3PO_4**	**84**
3	Cs_2CO_3	60
4	K_2CO_3	66
5	^{t}BuOK	0
6	CH_3OK	15
7	Et_3N	0
8	Li_3PO_4	0
9	Na_2CO_3	0
10	K_2HPO_4	0
11	KOAc	0

Table S4 Effect of Solvents



Entry	Solvent	Yield of 3b (%)
1	**PhOMe**	**84**
2	Hexane	73
3	$PhCF_3$	60
4	^{i}PrOH	0
5	DMF	0
6	THF	38
7	DCE	0
8	CH_3CN	trace
9	PhMe	78

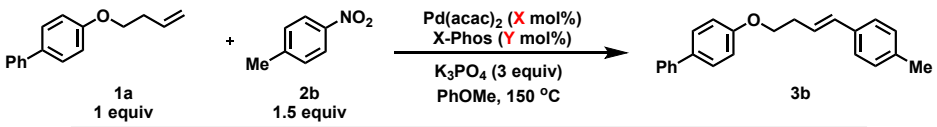
Table S5 Effect of Temperature



Entry	Temperature	Yield of 3b (%)

1	130	50
2	140	59
3	**150**	**84**

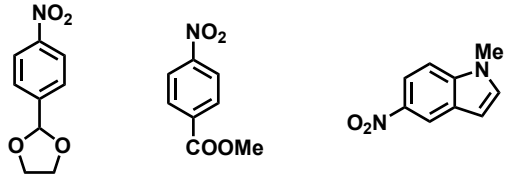
Table S6 Effect on ratio of $Pd(acac)_2$ / X-Phos.



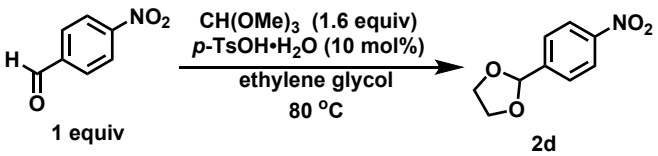
Entry	X	Y	Yield of 3b (%)
1	2.5	2.5	0
2	2.5	10	21
3	2.5	20	43
4	2.5	40	45
5	5	5	5
6	5	10	24
7	5	20	59
8	5	40	50
9	7.5	5	6
10	7.5	10	31
11	7.5	20	53
12	7.5	30	70
13	7.5	40	73
14	10	2.5	0
15	10	5	0
16	10	10	16
17	10	20	73
18	**10**	**40**	**84**

III. Synthesis of Nitroarenes and Alkene Substrates

Synthesis of Nitroarenes [1]



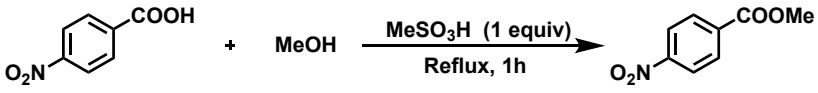
Synthesis of 2d



To a solution of 4-nitrobenzaldehyde (1.0 equiv, 5.0 mmol, 756.0 mg) and *p*-toluenesulfonic acid monohydrate (10 mol %, 0.50 mmol, 95.2 mg) in ethylene glycol (8.0 mL) were added trimethyl orthoformate (1.6 equiv, 8.0 mmol, 848.0 mg) at room temperature. Then the mixture was stirring at 80 ºC for 24 h with monitoring reaction

progress with TLC. Upon the completion of the reaction, the mixture was added $NaHCO_3$ aq. and extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography (PE/EA = 10:1) to afford **2d** as a pale-yellow solid (390.0mg, 40 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 5.90 (s, 1H), 4.15-4.05 (m, 4H). The spectra matched with those of compounds reported in the literature.

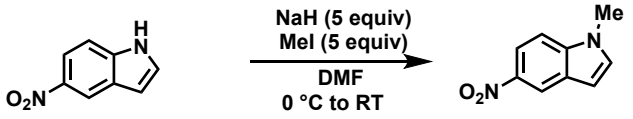
Synthesis of 2f



12 equive 10 equiv 2f

Methyl 4-nitrobenzoate (**2f**) was synthesized according to a procedure reported in the literature with a slight modification. Methane sulfonic acid (1.0 equiv, 0.50 mmol, 48.00 mg) was added to the solution of 4-nitrobenzoic acid (12.0 equiv, 6.0mmol, 1.0 g) in methanol (10.0quiv, 5.0mmol, 160.0 mg) and the mixture was refluxed for 1 h and down to room temperature. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography (PE/EA = 10:1) to afford **2f** as a white solid (724.0 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.28 (m, 2H), 8.23-8.20 (m, 2H), 3.98 (s, 3H).

Synthesis of 2o



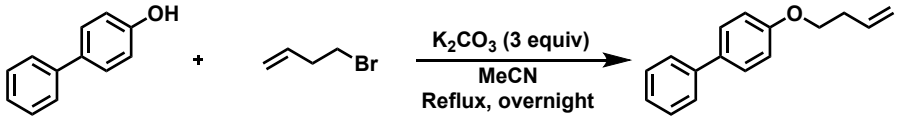
1 equiv 2o

1-Methyl-5-nitro-1*H*-indole (**2o**) was synthesized according to a procedure reported in the literature with a slight modification. To a solution of 5-nitro-1*H*-indole (1.0 equiv, 5.0 mmol, 810.0 mg) in DMF (20 mL) was added sodium hydride (60% oil dispersion; 5.0 equiv, 25.0 mmol, 1.0 g) at 0 °C. After stirring for 30 min at 0 °C, iodomethane (5.0 equiv, 25.0 mmol, 3.5 g) was added dropwise and then the mixture was stirred at room temperature for 12 h with monitoring reaction progress with TLC. Upon the

completion of the reaction, the mixture was added H_2O and extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography (Hexane/DCM = 30 :1) to afford **2o** as a yellow solid (736.0 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.0 Hz, 1H), 8.14 (dd, *J* = 9.0, 1.4 Hz, 1H), 7.35 (d, *J* = 12.0 Hz, 1H), 7.21 (d, *J* = 2.9 Hz, 1H), 6.68 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H).

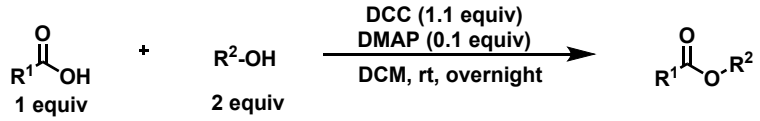
Synthesis of Starting Material Alkenes

General Producer A



To a solution of [1,1'-biphenyl]-4-ol (1.0 equiv, 5.0 mmol, 850.0 mg) in MeCN (15 mL), K_2CO_3 (3.**0** equiv, 15.0 mmol, 2.07 g), 4-bromo-1-butene (2.0 equiv, 10.0 mmol, 1 mL) were added at room temperature. The reaction mixture was refluxed overnight. After completion, it was then cooled to room temperature and the solvent was removed in vacuo. The reaction mixture was extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with brine, dried over Na_2SO_4, and the solvent was removed under vacuo. The crude product was then purified by silica gel column chromatography to afford the desired product **1a** (white soild, 896.0 mg, 80%). All the other compounds were prepared by following the same procedure.

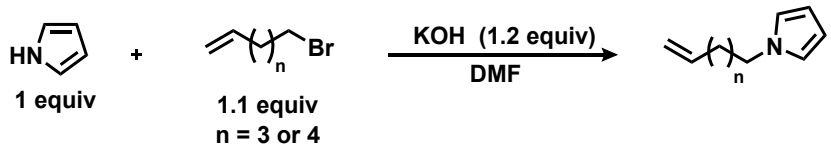
General Producer B



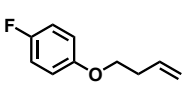
To a solution of carboxylic acid (1.0 equiv, 7.0 mmol) in 30 mL anhydrous DCM was added DMAP (0.1 equiv, 0.70 mmol) and alcohol (2.0 equiv, 14.0 mmol). DCC (1.1 equiv, 7.7 mmol) was then added to the reaction mixture at 0 ^{o}C, and then allowed to stir overnight at room temperature. Precipitated urea was then filtered off. The filtrate was evaporated and the residue was dissolved in DCM and washed twice with

$NaHCO_3$ solution, and then dried over Na_2SO_4. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel (eluent: PE/EA) to give the desired ester.

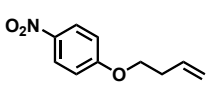
General Producer C



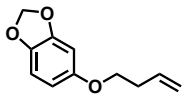
To a solution of *N*-heterocycle (1.0 equiv, 5.0 mmol) in DMF (8 mL), was added alkyl bromide (1.2 equiv, 6.0 mmol) and KOH (1.2 equiv, 6.0 mmol, 336.0 mg). The mixture was heated to 70 ^{o}C and stirred for 3 h. The solution was allowed to cool to room temperature and water (20 mL) was added to the solution. Then the solution was extracted with ethyl acetate (3 x 15 mL). The organic phase was combined, washed with water (6 x 30 mL), and dried over Na_2SO_4. The crude product obtained after filtration and concentration in vacuo was purified by column chromatography with hexanes and ethyl acetate as eluents to afford the pure product.



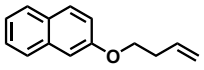
1c



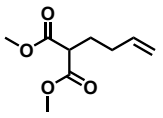
1e



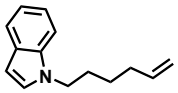
1f



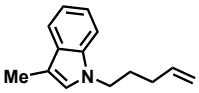
1g



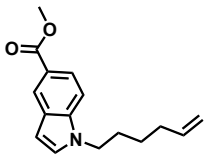
1h



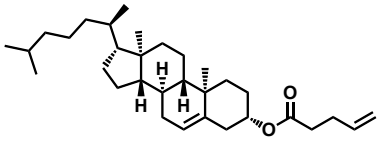
1j



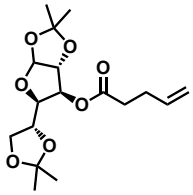
1k



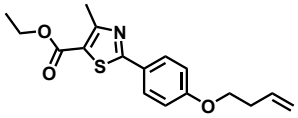
1l



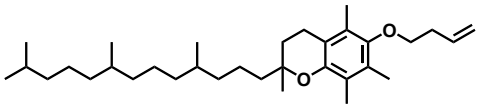
6a



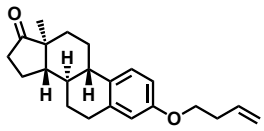
6b



6d



6c



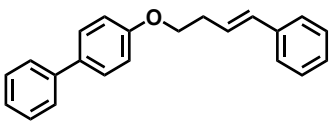
6e

1c,**1e**, **1f, 1g, 1h, 6c**,**6d**, **6e** was prepared by the general **producer A** [2]
6a, **6b** was prepared by the general **producer B** [3]
1j, **1k**, **1l** was prepared by the general **producer C** [4]

IV. Palladium-Catalyzed Heck Reaction of Various Nitroarenes.

General Procedure A: To a dry 10-mL Schlenk tube containing a magnetic stir bar was added alkene substrate **1a** (1.0 equiv, 0.20 mmol, 44.8 mg), $Pd(acac)_2$ (10 mol%, 0.01 mmol, 6.1 mg), X-Phos (40 mol%, 0.02 mmol, 38.1 mg), K_3PO_4 (3.0 equiv, 0.60 mmol, 127.2 mg), nitroarenes (1.5 equiv, 0.30 mmol), PhOMe (1.0 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a *pre*-warmed 150 ^oC oil bath. After 24 hours, the reaction mixture was cooled to room temperature, filtered, and concentrated *in vacuo*, the resulting residue was purified by preparative TLC to afford the desired product. The structure of the pure product was determined by ^1H and ^{13}C NMR spectroscopy.

General Procedure B: To a dry 10-mL Schlenk tube containing a magnetic stir bar was added alkene substrate **1a** (1.0 equiv, 0.20 mmol, 44.8 mg), $Pd(acac)_2$ (10 mol%, 0.02 mmol, 6.1 mg), X-Phos (40 mol%, 0.08 mmol, 38.1 mg), K_3PO_4 (3 equiv, 0.60 mmol, 127.2 mg), nitroarenes (1.5 equiv, 0.30 mmol), hexane (1.0 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a *pre*-warmed 150 ^oC oil bath. After 24 hours, the reaction mixture was cooled to room temperature, filtered, and concentrated *in vacuo*, the resulting residue was purified by preparative TLC to afford the desired product. The structure of the pure product was determined by ^1H and ^{13}C NMR spectroscopy.



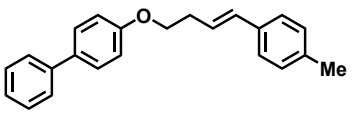
(*E*)-4-((4-phenylbut-3-en-1-yl)oxy)-1,1'-biphenyl (3a) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as yellow solid (48.6 mg, 81%). The E/Z value is 96:4 analysis by NMR.

^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 4H), 7.44-7.37 (m, 4H), 7.33-7.29 (m, 3H), 7.24-7.20 (m, 1H), 7.00 (d, J = 8.1 Hz, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.36-6.29 (m, 1H), 4.13 (t, J = 6.6 Hz, 2H), 2.76-2.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 140.9, 137.5, 133.9, 132.4, 128.9, 128.7, 128.3, 127.4, 126.9, 126.8, 126.2, 126.2, 115.0, 67.6,

33.1.

HRMS (ESI): Calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1412, Found: 323.1412.

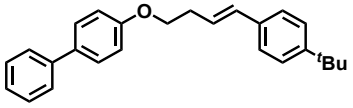


(*E*)-4-((4-(*p*-tolyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3b) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as yellow solid (52.7 mg, 84%). The E/Z value is 94:6 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.52 (m, 4H), 7.44-7.40 (m, 2H), 7.33-7.27 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.01-6.99 (m, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.31-6.24 (m, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 2.75-2.70 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 140.9, 137.1, 134.7, 133.9, 132.2, 129.4, 128.8, 128.3, 126.9, 126.8, 126.1, 125.1, 115.0, 67.7, 33.1, 21.3.

HRMS (ESI): Calcd for $C_{23}H_{23}O$ $[M+H]^+$: 315.1749, Found: 315.1746.

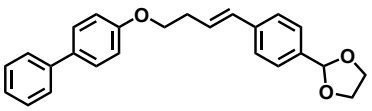


(*E*)-4-((4-(4-(*tert*-butyl)phenyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3c) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as pale-yellow solid (34.2 mg, 48%). The E/Z value is ＞99:1 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 4H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 5H), 7.04-7.01 (m, 2H), 6.55 (d, *J* = 15.8, 1H), 6.34-6.26 (m, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.77-2.72 (m, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 150.4, 140.9, 134.7, 133.9, 132.1, 128.8, 128.3, 126.9, 126.8, 125.9, 125.6, 125.3, 115.0, 67.7, 34.7, 33.1, 31.4.

HRMS (ESI): Calcd for $C_{26}H_{29}O$ $[M+H]^+$: 357.2218, Found: 357.2214.

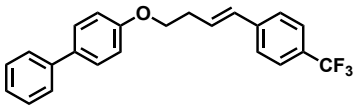


(*E*)-2-(4-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)phenyl)-1,3-dioxolane (3d) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as yellow solid (37.9 mg, 51%). The E/Z value is 94:6 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 4H), 7.44-7.38 (m, 6H), 7.32-7.28 (m, 1H), 7.01-6.98 (m, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.38-6.31 (m, 1H), 5.80 (s, 1H), 4.15-4.12 (m, 4H), 4.05-4.02 (m, 2H), 2.76-2.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 140.9, 138.4, 136.8, 133.9, 132.0, 128.8, 128.3, 126.9, 126.8, 126.8, 126.2, 115.0, 103.7, 67.5, 65.4, 33.1.

HRMS (ESI): Calcd for $C_{25}H_{25}O_3$ $[M+H]^+$: 373.1804, Found: 373.1799.



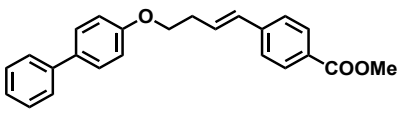
(*E*)-4-((4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3e) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as yellow solid (52.2 mg, 71%). The E/Z value is 99:1 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.0 Hz, 6H), 7.47-7.40 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.48-6.40 (m, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.79-2.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 140.9, 134.1 (d, *J* = 295.2 Hz), 129.2, 128.9, 128.3, 126.9, 126.8, 126.4, 125.7, 125.7, 125.6, 125.6, 115.0, 67.3, 33.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.30 .

HRMS (ESI): Calcd for $C_{23}H_{20}OF_3$ $[M+H]^+$: 369.1466, Found: 369.1458.

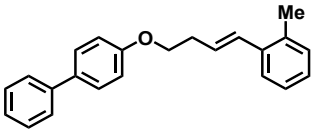


Methyl (*E*)-4-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)benzoate (3f) The reaction was conducted according to general procedure B. The product was purified by column chromatography (PE: EA = 10:1) as white solid (37.2 mg, 52%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.57-7.52 (m, 4H), 7.42 (t, *J* = 8.1 Hz, 4H), 7.33-7.29 (m, 1H), 7.02-6.98 (m, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.50-6.43 (m, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 3.91 (s, 3H), 2.79-2.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 158.4, 141.9, 140.9, 134.0, 131.5, 130.0, 129.3, 128.9, 128.8, 128.3, 126.9, 126.8, 126.1, 114.9, 67.3, 52.2, 33.2.

HRMS (ESI): Calcd for $C_{24}H_{23}O_3$ $[M+H]^+$: 359.1647, Found: 359.1650.

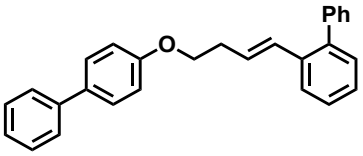


(*E*)-4-((4-(*o*-tolyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3g) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as white solid (41.4 mg, 66%). The E/Z value is 99:1 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.51 (m, 4H), 7.46-7.40 (m, 3H), 7.33-7.28 (m, 1H), 7.19-7.14 (m, 3H), 7.02-6.98 (m, 2H), 6.75 (d, *J* = 15.7 Hz, 1H), 6.23-6.15 (m, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.78-2.73 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 140.9, 136.6, 135.2, 133.9, 130.3, 130.3, 128.9, 128.3, 127.5, 127.3, 126.9, 126.8, 126.2, 125.6, 115.0, 67.7, 33.4, 20.0.

HRMS (ESI): Calcd for $C_{23}H_{23}O$ $[M+H]^+$: 315.1749, Found: 315.1743.



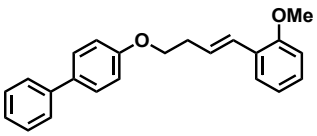
(*E*)-2-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)-1,1'-biphenyl (3h) The reaction was conducted according to general procedure A. The product was purified by

preparative TLC (PE: EA = 10:1) as yellow solid (44.4 mg, 59%). The E/Z value is 98:2 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 3H), 7.62-7.58 (m, 3H), 7.57-7.56 (m, 1H), 7.51-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.45-7.42 (m, 3H), 7.40-7.33 (m, 2H), 7.07-7.03 (m, 2H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.47-6.40 (m, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.82-2.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 141.6, 141.2, 140.9, 137.9, 133.9, 132.3, 129.1, 128.9, 128.8, 128.3, 127.4, 127.3, 126.8, 126.8, 126.6, 126.2, 125.2, 125.1, 115.0, 67.5, 33.1.

HRMS (ESI): Calcd for $C_{28}H_{25}O$ $[M+H]^+$: 377.1905, Found: 377.1906.

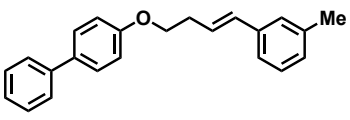


(*E*)-4-((4-(2-methoxyphenyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3i) The reaction was conducted according to general procedure B. The product was purified by preparative TLC (PE: EA = 30:1) as white solid (54.8 mg, 83%). The E/Z value is 94:6 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.51 (m, 4H), 7.46-7.40 (m, 3H), 7.32-7.28 (m, 1H), 7.24-7.19 (m, 1H), 7.01-6.99 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.87 (dd, *J* = 12.2, 3.0 Hz, 2H), 6.35-6.28 (m, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.78-2.72 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 156.4, 140.9, 133.8, 128.8, 128.4, 128.3, 127.0, 126.8, 126.8, 126.7, 126.5, 120.8, 115.0, 110.9, 67.8, 55.6, 33.6.

HRMS (ESI): Calcd for $C_{23}H_{23}O_2$ $[M+H]^+$: 331.1698, Found: 331.1704.

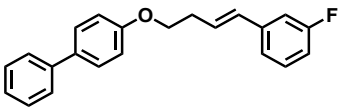


(*E*)-4-((4-(*m*-tolyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3j) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as yellow solid (40.2 mg, 64%). The E/Z value is 98:2 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 4H), 7.43-7.40 (m, 2H), 7.32-7.29 (m, 1H), 7.23-7.17 (m, 3H), 7.05-6.99 (m, 3H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.35-6.27 (m, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 2.75-2.70 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 140.9, 138.2, 137.4, 133.9, 132.4, 128.9, 128.6, 128.3, 128.2, 126.9, 126.9, 126.8, 125.9, 123.4, 115.0, 67.6, 33.1, 21.6.

HRMS (ESI): Calcd for $C_{23}H_{23}O$ $[M+H]^+$: 315.1749, Found: 315.1759.



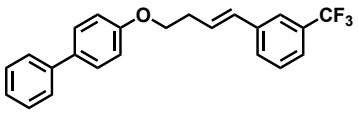
(*E*)-4-((4-(3-fluorophenyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3k) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as pale-yellow solid (59.2 mg, 93%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.51 (m, 4H), 7.44-7.39 (m, 2H), 7.33-7.28 (m, 1H), 7.27-7.24 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.10-7.06 (m, 1H), 7.01-6.98 (m, 2H), 6.94-6.89 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.38-6.30 (m, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 2.76-2.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5 (d, *J* = 243.1 Hz), 158.5, 140.9, 134.0 ,131.3 (d, *J* = 1.8 Hz), 130.1, 130.0, 128.9, 128.3, 127.8, 126.9, 126.8, 122.1 (d, *J* = 2.0 Hz), 115.0, 114.0 (dd, *J* = 148.0, 21.5 Hz), 67.4, 33.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.59 .

HRMS (ESI): Calcd for $C_{22}H_{20}OF$ $[M+H]^+$: 319.1498, Found: 319.1495.



(*E*)-4-((4-(3-fluorophenyl)but-3-en-1-yl)oxy)-1,1'-biphenyl (3l) The reaction was conducted according to general procedure A. The product was purified by preparative

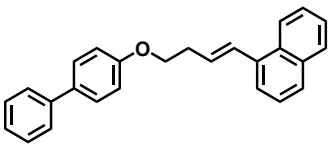
TLC (PE as eluent) as yellow solid (61.1 mg, 83%). The E/Z value is 98:2 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.58-7.53 (m, 5H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.45-7.41 (m, 3H), 7.34-7.30 (m, 1H), 7.03-6.99 (m, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.46-6.39 (m, 1H), 4.16 (t, *J* = 6.5 Hz, 2H), 2.79-2.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 140.8 (d, *J* = 268.0 Hz), 134.0, 131.0, 129.4, 129.1, 128.9, 128.4, 128.3, 126.8, 123.9 (d, *J* = 4.0 Hz), 122.9 (q, *J* = 4.0 Hz), 114.9, 67.3, 33.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.52 .

HRMS (ESI): Calcd for $C_{23}H_{20}OF_3$ $[M+H]^+$: 369.1466, Found: 369.1469.

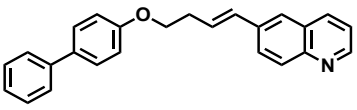


(*E*)-1-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)naphthalene (3m) The reaction was conducted according to general procedure B, X-Phos (20 mol%) was used. The product was purified by preparative TLC (PE: EA = 100:1) as yellow solid (56.0 mg, 80%). The E/Z value is 90:10 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (m, 1H), 7.87-7.84 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.60-7.55 (m, 4H), 7.54-7.49 (m, 3H), 7.47-7.41 (m, 3H), 7.33-7.27 (m, 2H), 7.05-7.02 (m, 2H), 6.38-6.31 (m, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 2.89-2.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 140.9, 135.3, 134.0, 133.7, 131.2, 129.7, 129.5, 128.9, 128.6, 128.3, 127.8, 126.9, 126.8, 126.1, 125.8, 125.8, 124.0, 123.9, 115.0, 67.6, 33.5.

HRMS (ESI): Calcd for $C_{26}H_{23}O$ $[M+H]^+$: 351.1749, Found: 351.1745.



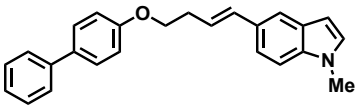
(*E*)-6-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)quinoline (3n) The reaction was conducted according to general procedure A. The product was purified by preparative

TLC (PE: EA = 30:1) as pale-yellow solid (42.1 mg, 60%). The E/Z value is 98:2 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.85 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.57-7.52 (m, 4H), 7.44-7.37 (m, 3H), 7.33-7.29 (m, 1H), 7.04-7.00 (m, 2H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.54-6.47 (m, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.83-2.78 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 150.1, 148.0, 140.9, 136.1, 135.7, 134.0, 131.7, 129.7, 128.9, 128.6, 128.3, 128.0, 127.3, 126.8, 126.8, 125.3, 121.6, 115.0, 67.4, 33.2.

HRMS (ESI): Calcd for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1701, Found: 352.1706.



(*E*)-5-(4-([1,1'-biphenyl]-4-yloxy)but-1-en-1-yl)-1-methyl-1*H*-indole (3o) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as yellow solid (22.6 mg, 32%). The E/Z value is 94:6 analysis by NMR.

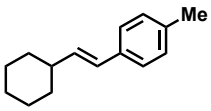
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.52 (m, 5H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 1H), 7.03-7.00 (m, 3H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.49-6.45 (m, 1H), 6.30-6.22 (m, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 2.78-2.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 141.0, 136.4, 133.8, 133.4, 129.4, 129.1, 128.8, 128.7, 128.3, 126.9, 126.7, 122.9, 119.9, 119.1, 115.0, 109.4, 101.2, 68.0, 33.2, 33.1.

HRMS (ESI): Calcd for $C_{25}H_{24}NO$ $[M+H]^+$: 354.1858, Found: 354.1864.

V. Palladium-Catalyzed Heck Reaction of Various Alkene Substrates.

General Procedure A: To a dry 10-mL Schlenk tube containing a magnetic stir bar was added alkene substrate (1 equiv, 0.2 mmol), $Pd(acac)_2$ (10 mol%, 0.01 mmol, 6.1 mg), X-Phos (40 mol%, 0.02 mmol, 38.1 mg), K_3PO_4 (3 equiv, 0.6 mmol, 127.2 mg), 4-nitrotoluene (1.5 equiv, 0.3 mmol, 44.1 mg), PhOMe (1.0 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a *pre*-warmed 150 ^{o}C oil bath. After 24 hours, the reaction mixture was cooled to room temperature, filtered, and concentrated *in vacuo*, the resulting residue was purified by preparative TLC to afford the desired product. The structure of the pure product was determined by ^{1}H and ^{13}C NMR spectroscopy.

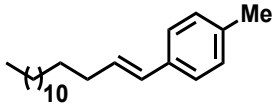


(*E*)-1-(2-cyclohexylvinyl)-4-methylbenzene (4a) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as colorless oil (24.8 mg, 62%). The E/Z value is 93:7 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.32 (d, J = 15.9 Hz, 1H), 6.13 (dd, J = 16.0, 6.9 Hz, 1H), 2.33 (s, 3H), 2.14-2.07 (m, 1H), 1.84-1.65 (m, 5H), 1.38-1.18 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 136.0, 135.4, 129.3, 127.1, 125.9, 41.3, 33.1, 26.3, 26.2, 21.3.

HRMS (ESI): Calcd for $C_{15}H_{21}$ $[M+H]^+$: 201.1643, Found: 201.1647.

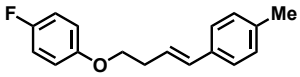


(*E*)-1-methyl-4-(pentadec-1-en-1-yl)benzene (4b) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as colorless oil (36.6 mg, 61%). The E/Z value is 94:6 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.14-7.11 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.24-6.17 (m, 1H), 2.35 (s, 3H), 2.25-2.19 (m, 2H), 1.50-1.45 (m, 2H), 1.29 (s, 20H), 0.92 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 135.3, 130.4, 129.6, 129.3, 125.9, 33.2, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 22.9, 21.3, 14.3.

HRMS (ESI): Calcd for $C_{22}H_{37}$ $[M+H]^+$: 301.2895, Found: 301.2892.



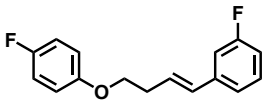
(*E*)-1-fluoro-4-((4-(*p*-tolyl)but-3-en-1-yl)oxy)benzene (4c) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 80:1) as pale-yellow solid (39.4 mg, 77%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H), 7.13-7.11 (m, 2H), 7.01-6.96 (m, 2H), 6.88-6.84 (m, 2H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.28-6.20 (m, 1H), 4.06-4.02 (m, 2H), 2.70-2.65 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5 (d, *J* = 236.2 Hz), 155.1, 137.1, 134.7, 132.2, 129.4, 126.1, 125.0, 116.0, 115.8, 115.7, 115.6, 68.3, 33.1, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.98.

HRMS (ESI): Calcd for $C_{17}H_{18}OF$ $[M+H]^+$: 257.1342, Found: 257.1342.



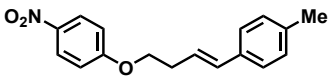
(*E*)-1-fluoro-3-(4-(4-fluorophenoxy)but-1-en-1-yl)benzene (4d) The reaction was conducted according to general procedure B. The product was purified by preparative TLC (PE: EA = 80:1) as pale-yellow solid (27.6 mg, 53%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.08-7.05 (m, 1H), 7.01-6.89 (m, 3H), 6.87-6.83 (m, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.35-6.27 (m, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 2.72-2.66 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4 (d, *J* = 243.1 Hz), 158.6 (d, *J* = 236.2 Hz), 155.0, 139.8, 139.8, 131.4, 130.1, 130.0, 127.7, 122.1, 116.1, 115.8, 115.7, 115.6, 114.3, 114.1, 112.8, 112.5, 68.0, 33.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.57, -123.86.

HRMS (ESI): Calcd for $C_{16}H_{15}OF_2$ $[M+H]^+$: 261.1091, Found: 261.1102.

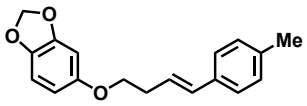


(*E*)-1-methyl-4-(4-(4-nitrophenoxy)but-1-en-1-yl)benzene (4e) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 60:1) as yellow solid (28.3mg, 50%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.19 (m, 2H), 7.28-7.26 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.98-6.96 (m, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.26-6.18 (m, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 2.76-2.71 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 141.6, 137.4, 134.4, 132.8, 129.4, 126.1, 126.1, 124.1, 114.6, 68.4, 32.8, 21.3.

HRMS (ESI): Calcd for $C_{17}H_{18}O_3N$ $[M+H]^+$: 284.1287, Found: 284.1287.



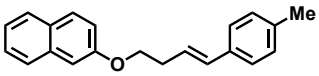
(*E*)-5-((4-(*p*-tolyl)but-3-en-1-yl) oxy)benzo [*d*] [1,3] dioxole (4f) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as pale-yellow solid (39.4 mg, 70%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* =

8.5, 2.5 Hz, 1H), 6.28-6.20 (m, 1H), 5.92 (s, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 2.69-2.64 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 148.3, 141.7, 137.1, 134.7, 132.1, 129.3, 126.1, 125.1, 108.0, 105.9, 101.2, 98.3, 68.6, 33.1, 21.3.

HRMS (ESI): Calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1334, Found: 283.1335.

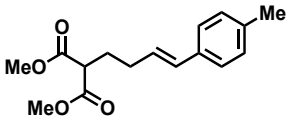


(*E*)-2-((4-(*p*-tolyl) but-3-en-1-yl)oxy)naphthalene (4g) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as colorless oil (31.6 mg, 55%). The E/Z value is 98:2 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.73 (m, 3H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.20-7.12 (m, 4H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.34-6.26 (m, 1H), 4.21 (t, *J* = 6.8 Hz, 2H), 2.80-2.74 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 137.1, 134.7, 132.2, 129.5, 129.4, 129.1, 127.8, 126.9, 126.5, 126.1, 125.1, 123.7, 119.1, 106.8, 106.8, 67.6, 33.1, 21.3.

HRMS (ESI): Calcd for $C_{21}H_{21}O$ $[M+H]^+$: 289.1592, Found: 289.1594.

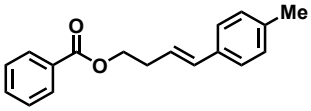


Dimethyl(*E*)-2-(4-(*p*-tolyl)but-3-en-1-yl)malonate (4h) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as pale-yellow oil (35.9 mg, 65%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.13-6.05 (m, 1H), 3.73 (s, 6H), 3.44 (t, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 2.27-2.22 (m, 2H), 2.12-2.07 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 137.0, 134.7, 131.3, 129.3, 127.5, 126.1, 52.7, 51.1, 30.8, 28.6, 21.3.

HRMS (ESI): Calcd for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1440, Found: 277.1442.

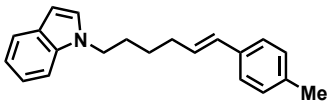


(*E*)-4-(p-tolyl)but-3-en-1-yl benzoate (4i) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as pale-yellow soild (23.9 mg, 45%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.58-7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.27-7.25 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.25-6.17 (m, 1H), 4.44 (t, *J* = 6.7 Hz, 2H), 2.71-2.66 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 137.2, 134.6, 133.0, 132.5, 130.4, 129.7, 129.4, 128.5, 126.1, 124.7, 64.4, 32.6, 21.3.

HRMS (ESI): Calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385, Found: 267.1397.

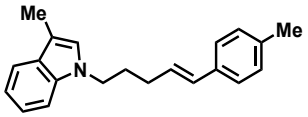


(*E*)-1-(6-(*p*-tolyl)hex-5-en-1-yl)-1*H*-indole (4j) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 20:1) as pale-yellow oil (38.1 mg, 66%). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 1H), 7.38-7.36 (m, 1H), 7.24-7.20 (m, 3H), 7.14-7.10 (m, 4H), 6.52 (dd, *J* = 3.1, 0.7 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.15-6.08 (m, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.26-2.20 (m, 2H), 1.95-1.87 (m, 2H), 1.53-1.47 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 136.0, 134.9, 130.4, 129.3, 129.1, 128.7, 127.9, 126.0, 121.5, 121.1, 119.3, 109.5, 101.0, 46.4, 32.7, 29.9, 26.9, 21.3.

HRMS (ESI): Calcd for $C_{21}H_{24}N$ $[M+H]^+$: 290.1909, Found: 290.1910.

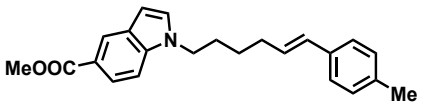


(*E*)-3-methyl-1-(5-(*p*-tolyl)pent-4-en-1-yl)-1*H*-indole (4k) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 20:1) as pale-yellow oil (32.3 mg, 56%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24-7.19 (m, 3H), 7.13-7.09 (m, 3H), 6.89 (s, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.16-6.09 (m, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 6H), 2.23-2.18 (m, 2H), 2.03-1.96 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 136.4, 134.8, 130.9, 129.4, 128.8, 128.3, 126.0, 125.6, 121.4, 119.1, 118.6, 110.3, 109.4, 45.4, 30.3, 30.0, 21.3, 9.8.

HRMS (ESI): Calcd for $C_{21}H_{24}N$ $[M+H]^+$: 290.1909, Found: 290.1908.

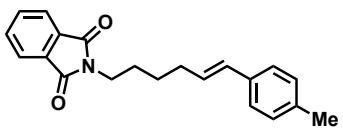


Methyl(*E*)-1-(6-(*p*-tolyl) hex-5-en-1-yl)-1*H*-indole-5-carboxylate (4l) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 20:1) as pale-yellow solid (41.7 mg, 60%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41-8.41 (m, 1H), 7.91 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.16-7.14 (m, 1H), 7.11-7.09 (m, 2H), 6.60 (dd, *J* = 3.2, 0.6 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.13-6.05 (m, 1H), 4.16 (t, *J* = 7.0 Hz, 2H), 3.94 (s, 3H), 2.33 (s, 3H), 2.24-2.19 (m, 2H), 1.92-1.86 (m, 2H), 1.53-1.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 138.5, 136.9, 134.8, 130.5, 129.3, 128.9, 128.2, 125.9, 124.2, 122.9, 121.4, 109.1, 102.8, 52.0, 46.6, 32.6, 29.8, 26.8, 21.3.

HRMS (ESI): Calcd for $C_{23}H_{26}NO_2$ $[M+H]^+$: 348.1964, Found: 348.1959.

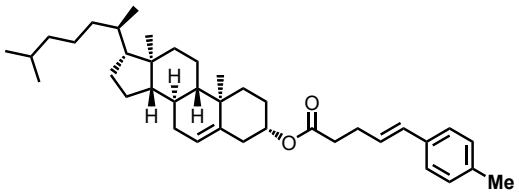


(*E*)-2-(6-(*p*-tolyl)hex-5-en-1-yl)isoindoline-1,3-dione (4m) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as yellow solid (38.3 mg, 60%). The E/Z value is 92:8 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.83 (m, 2H), 7.71-7.69 (m, 2H), 7.23-7.21 (m, 2H), 7.10-7.08 (m, 2H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.17-6.09 (m, 1H), 3.74-3.70 (m, 2H), 2.31 (s, 3H), 2.25-2.24 (m, 2H), 1.77-1.71 (m, 2H), 1.55-1.48 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 136.7, 135.0, 134.0, 132.2, 130.2, 129.3, 129.2, 126.0, 123.3, 38.0, 32.7, 28.3, 26.7, 21.3.

HRMS (ESI): Calcd for $C_{21}H_{22}O_2N$ $[M+H]^+$: 320.1651, Found: 320.1654.

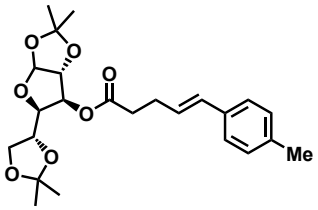


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*α*]phenanthren-3-yl (*E*)-5-(*p*-tolyl)pent-4-enoate (5a) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as white solid (89.3 mg, 80%). The E/Z value is 93:7 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.18-6.11 (m, 1H), 5.37-5.36 (m, 1H), 4.66-4.59 (m, 1H), 2.51 (t, *J* = 6.7 Hz, 2H), 2.47-2.43 (m, 2H), 2.32 (s, 3H), 2.31 (s, 1H), 2.02-1.93 (m, 2H), 1.86-1.81 (m, 3H), 1.63-1.38 (m, 9H), 1.38-1.24 (m, 4H), 1.17-1.04 (m, 7H), 1.01 (s, 3H), 0.98-0.95 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 139.8, 137.0, 134.8, 130.8, 129.3, 127.6, 126.1, 122.8, 74.1, 56.8, 56.2, 50.1, 42.4, 39.8, 39.7, 38.3, 37.1, 36.7, 36.3, 35.9, 34.6, 32.0, 32.0, 28.5, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.3, 21.2, 19.5, 18.9, 12.0.

HRMS (ESI): Calcd for $C_{39}H_{59}O_2$ $[M+H]^+$: 559.4515, Found: 559.4511.



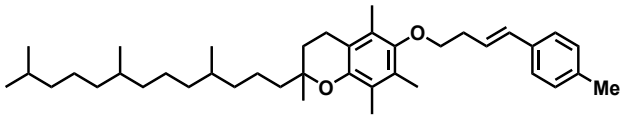
(5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl(*E*)-5-(*p*-tolyl)pent-4-enoate (5b)

The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 30:1) as red oil (51.9 mg, 60 %). The E/Z value is 97:3 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.17-6.10 (m, 1H), 5.78 (d, *J* = 3.6 Hz, 1H), 5.26 (d, *J* = 2.8 Hz, 1H), 4.43 (d, *J* = 3.7 Hz, 1H), 4.25-4.18 (m, 2H), 4.09-4.00 (m, 2H), 2.54-2.53 (m, 4H), 2.31 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 137.2, 134.4, 131.3, 129.4, 126.9, 126.0, 112.3, 109.5, 105.1, 83.4, 79.8, 76.2, 72.5, 67.3, 34.2, 28.5, 27.0, 26.8, 26.1, 25.4, 21.3.

HRMS (ESI): Calcd for $C_{24}H_{33}O_7$ $[M+H]^+$: 433.2226, Found: 433.2224.

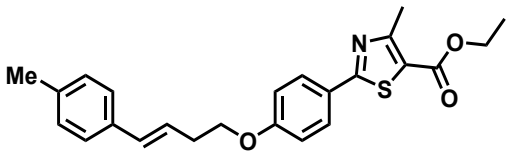


(*R*)-2,5,7,8-tetramethyl-6-(((*E*)-4-(*p*-tolyl)but-3-en-1-yl)oxy)-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chromane (5c) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 20:1) as yellow oil (70.1 mg, 61%). The E/Z value is 93:7 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.37-6.30 (m, 1H), 3.78 (t, *J* = 6.8 Hz, 2H), 2.73-2.68 (m, 2H), 2.60-2.57 (m, 2H), 2.35 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.85-1.74 (m, 2H), 1.59-1.51 (m, 4H), 1.44-1.38 (m, 3H), 1.31-1.27 (m, 7H), 1.25-1.23 (m, 1H), 1.18-1.07 (m, 7H), 0.90-0.86 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 147.9, 136.9, 135.0, 131.8, 129.3, 128.0, 126.1, 125.9, 122.9, 117.6, 74.9, 72.6, 40.2, 40.2, 39.5, 37.7, 37.6, 37.5, 37.4, 34.1, 32.9, 32.8, 31.4, 31.4, 28.1, 25.0, 24.6, 24.0, 22.9, 22.8, 21.3, 21.2, 20.8, 19.9, 19.8, 19.8, 19.8, 13.0, 12.1, 11.9.

HRMS (ESI): Calcd for $C_{40}H_{63}O_2$ $[M+H]^+$: 575.4828, Found: 575.4836.

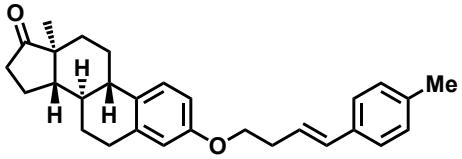


Ethyl(*E*)-4-methyl-2-(4-((4-(*p*-tolyl)but-3-en-1-yl)oxy)phenyl)thiazole-5-carboxylate (5d) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 10:1) as white solid (27.6 mg, 34%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.97-6.94 (m, 2H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.28-6.20 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.76 (s, 3H), 2.74-2.69 (m, 2H), 2.33 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 162.6, 161.4, 161.1, 137.2, 134.6, 132.4, 129.4, 128.5, 126.1, 125.9, 124.7, 120.9, 115.1, 67.8, 61.3, 33.0, 21.3, 17.7, 14.5.

HRMS (ESI): Calcd for $C_{24}H_{26}O_3NS$ $[M+H]^+$: 408.1633, Found: 408.1631.



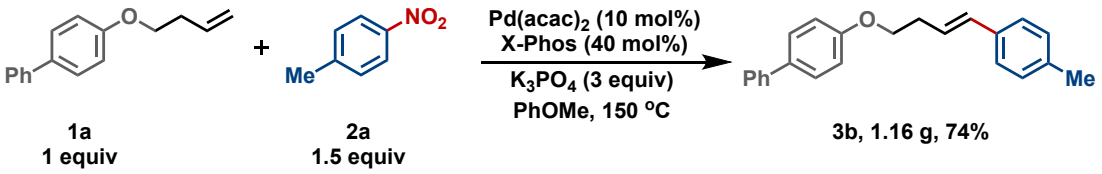
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(((*E*)-4-(*p*-tolyl)but-3-en-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (5e) The reaction was conducted according to general procedure A. The product was purified by preparative TLC (PE: EA = 10:1) as yellow solid (37.2 mg, 45%). The E/Z value is 96:4 analysis by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.67-6.66 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.27-6.20 (m, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.91-2.87 (m, 2H), 2.69-2.64 (m, 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.41-2.37 (m, 1H), 2.32 (s, 3H), 2.27-2.23 (m, 1H), 2.19-2.07 (m, 2H), 2.05-1.94 (m, 2H), 1.65-1.61 (m, 1H), 1.55-1.38 (m, 5H), 0.91 (s, 3H).

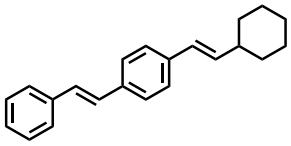
^{13}C NMR (100 MHz, $CDCl_3$): δ 221.2, 157.0, 137.9, 137.0, 134.7, 132.2, 132.0, 129.3, 126.5, 126.1, 125.2, 114.8, 112.3, 67.6, 50.5, 48.1, 44.1, 38.5, 36.0, 33.1, 31.7, 29.8, 26.7, 26.0, 21.7, 21.3, 14.0.

HRMS (ESI): Calcd for $C_{29}H_{35}O_2$ $[M+H]^+$: 415.2637, Found: 415.2639.

VI. Gram-scale denitrative Heck reaction and synthetic practicality



In an argon atmosphere, to a dry 100-mL Schlenk tube containing a magnetic stir bar was added alkene substrate 1a (1.0 equiv, 5.0 mmol, 1.12 g), $Pd(acac)_2$ (10 mol%, 0.5 mmol, 0.15 g), X-Phos (40 mol%, 2.0 mmol, 0.95 g), K_3PO_4 (3.0 equiv, 15.0 mmol, 3.18 g), 4-nitrotoluene (1.5 equiv, 7.5 mmol, 1.03g), PhOMe (20 mL), sequentially, the tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 150 °C oil bath. After 48 hours, the reaction mixture was cooled to room temperature, filtered, and concentrated in vacuo, the resulting residue was directly subjected to flash silica gel chromatography (1:50 EA/PE), product was obtained as yellow solid (1.16 g, 74%).



1-((*E*)-2-cyclohexylvinyl)-4-((*E*)-styryl)benzene (7a) To a dry 10-mL Schlenk tube containing a magnetic stir bar was added stryene (1.0 equiv, 0.50 mmol, 104.1 mg), $Pd(acac)_2$ (10 mol%, 0.10 mmol, 30.0 mg), K_2CO_3 (2.0 equiv, 2.0 mmol, 276.4 mg), **1-**bromo-4-nitrobenzene (1.0 equiv, 0.50 mmol, 101.1 mg), DMF (1 mL) sequentially. The reaction mixture was stirred at 120 °C for 16h[5]. After alkene was almost fully consumed (monitored by GCMS), the reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to flash silica gel chromatography to get the (*E*)-1-nitro-4-styrylbenzene (101.2 mg, 90%) as yellow soild. Then the (*E*)-1-nitro-4-styrylbenzene (1.5 equiv, 0.30 mmol, 76.5 mg) and vinylcyclohexane (1.0 equiv, 0.20 mmol, 22.04 mg) as the reaction subtract were

conducted according to general procedure A. The product was purified by preparative TLC (PE as eluent) as colorless oil (35.1 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.67 (m, 2H), 7.63-7.61 (m, 2H), 7.55-7.50 (m, 5H), 7.45-7.40 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 15.9, 6.9 Hz, 1H), 2.35-2.27 (m, 1H), 2.01-1.92 (m, 4H), 1.89-1.84 (m, 1H), 1.52-1.45 (m, 2H), 1.42-1.32 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.6, 137.1, 135.9, 128.8, 128.6, 128.1, 127.6, 127.0, 126.8, 126.6, 126.4, 41.4, 33.1, 26.3, 26.2.

HRMS (ESI): Calcd for $C_{22}H_{25}$ $[M+H]^+$: 289.1956, Found: 289.1953

VII. Reference

1. Okita, T.; Asahara, K. K.; Muto, K.; Yamaguchi, J., Palladium-catalyzed Mizoroki-Heck reaction of nitroarenes and styrene derivatives. *Org. Lett.* 2020, **22**, 3205-3208.

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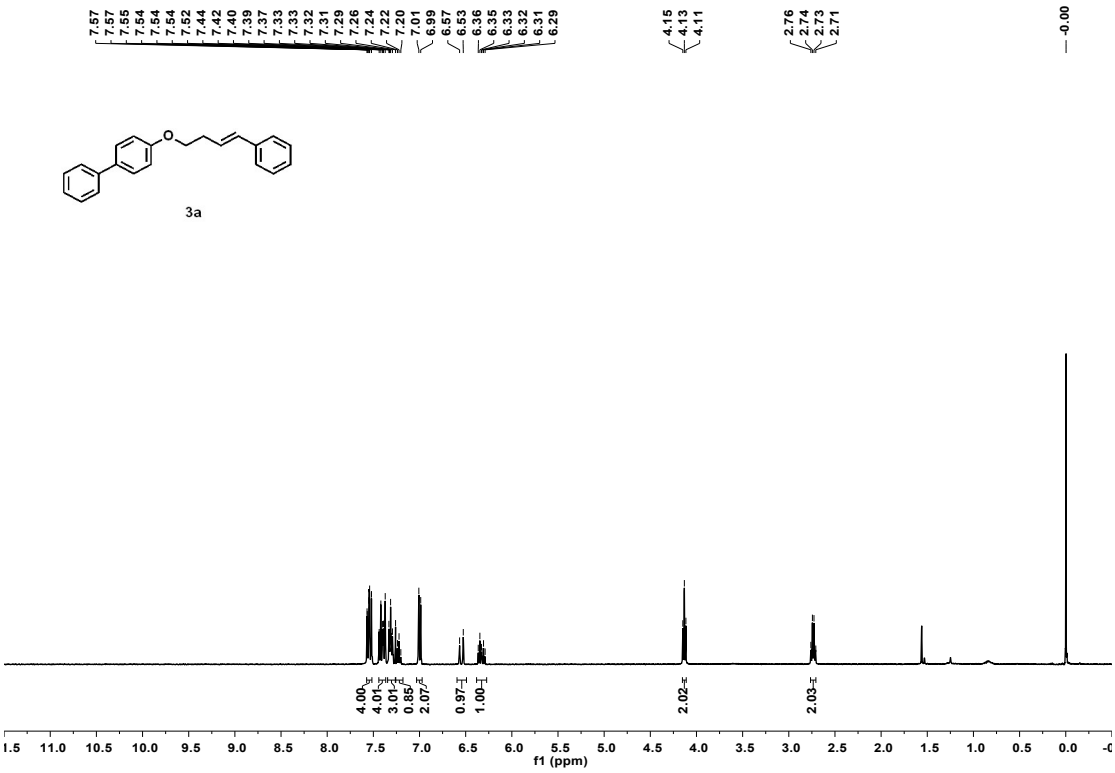
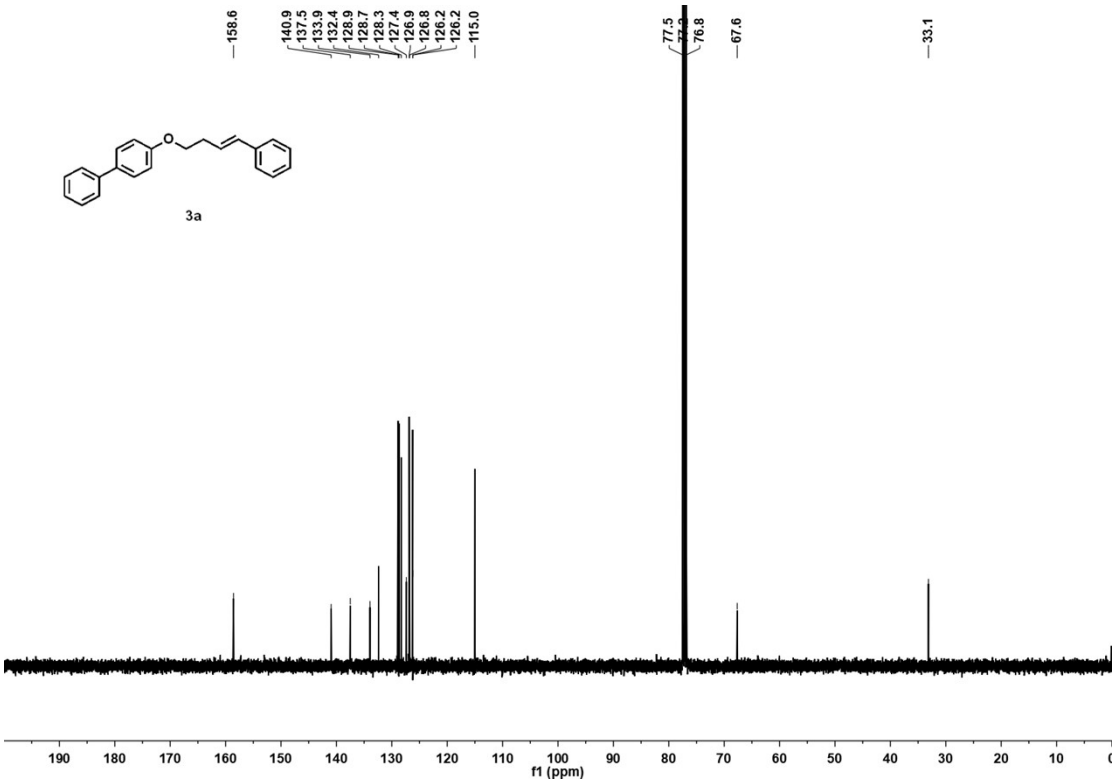
VIII. NMR spectra

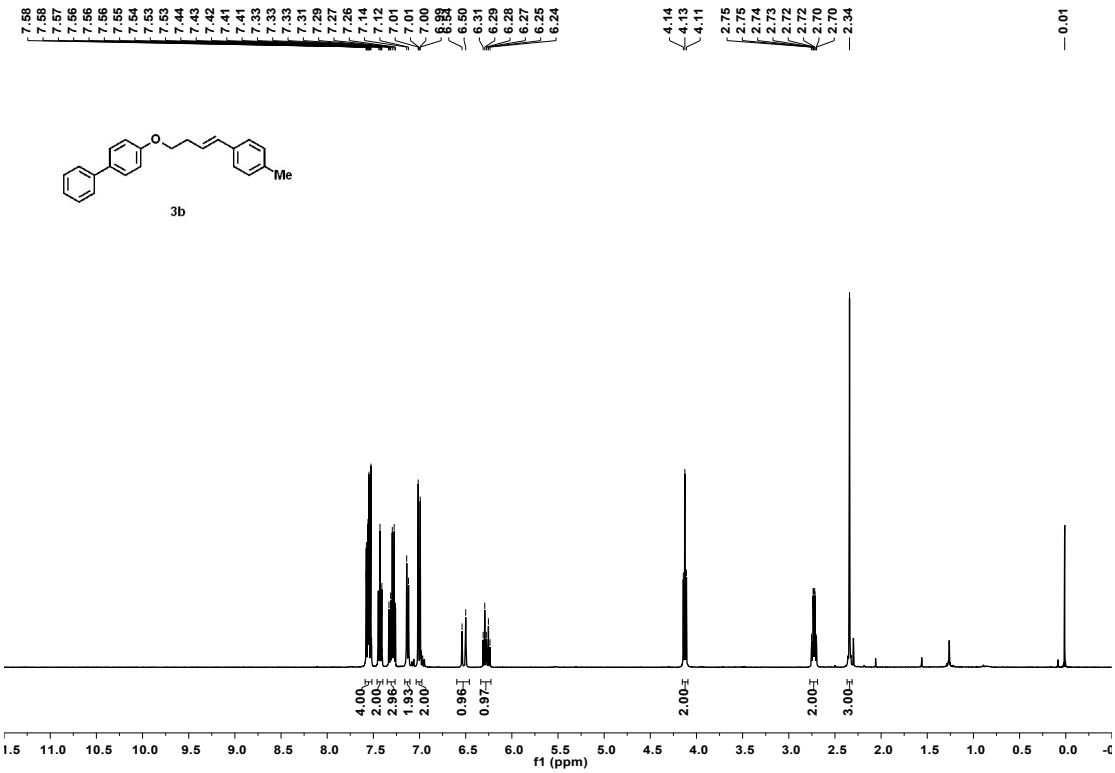
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**



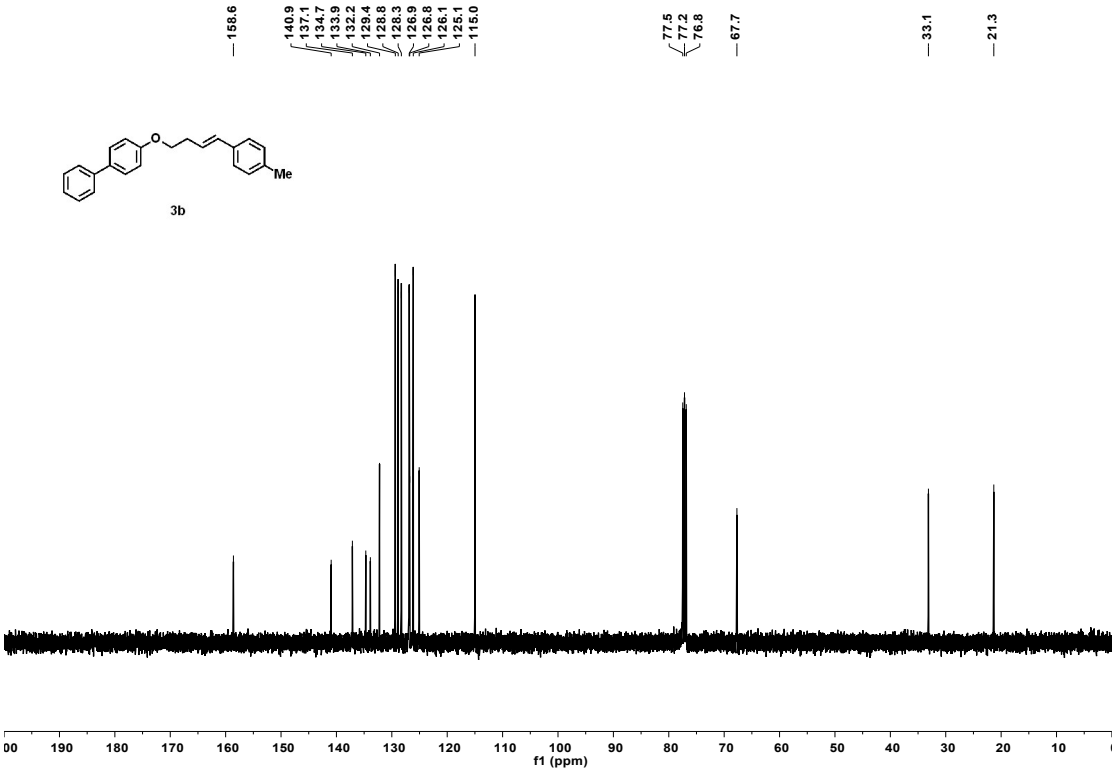
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3a**



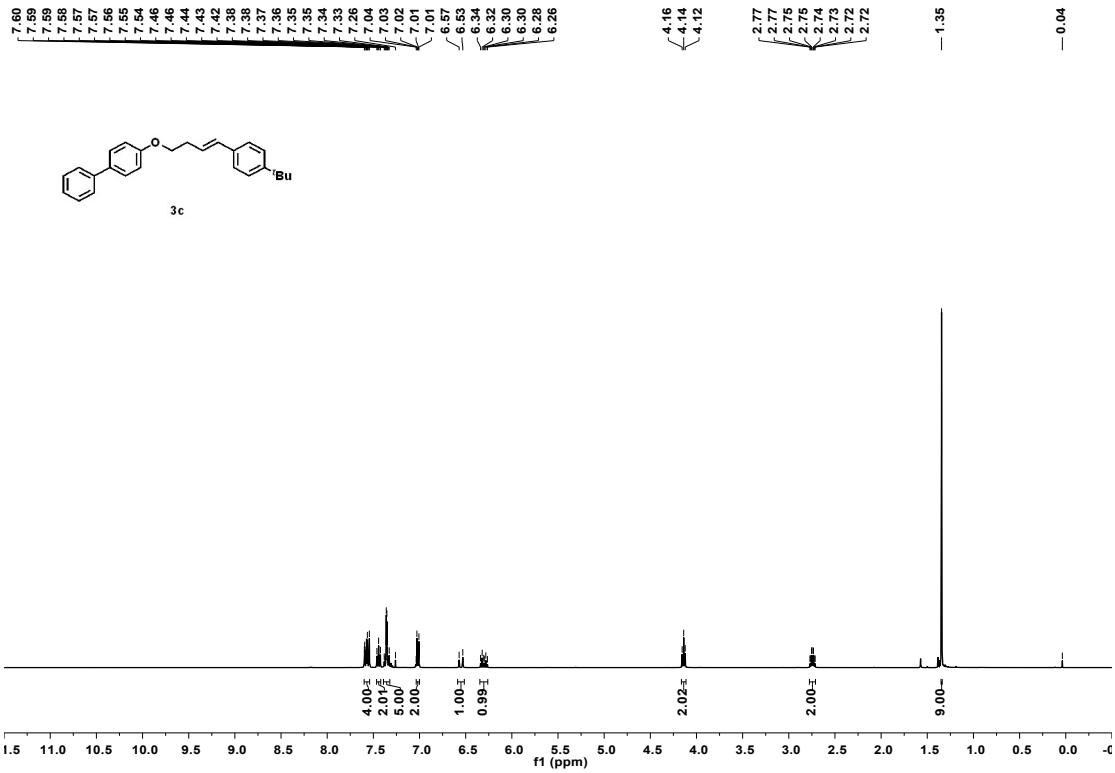
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3b**



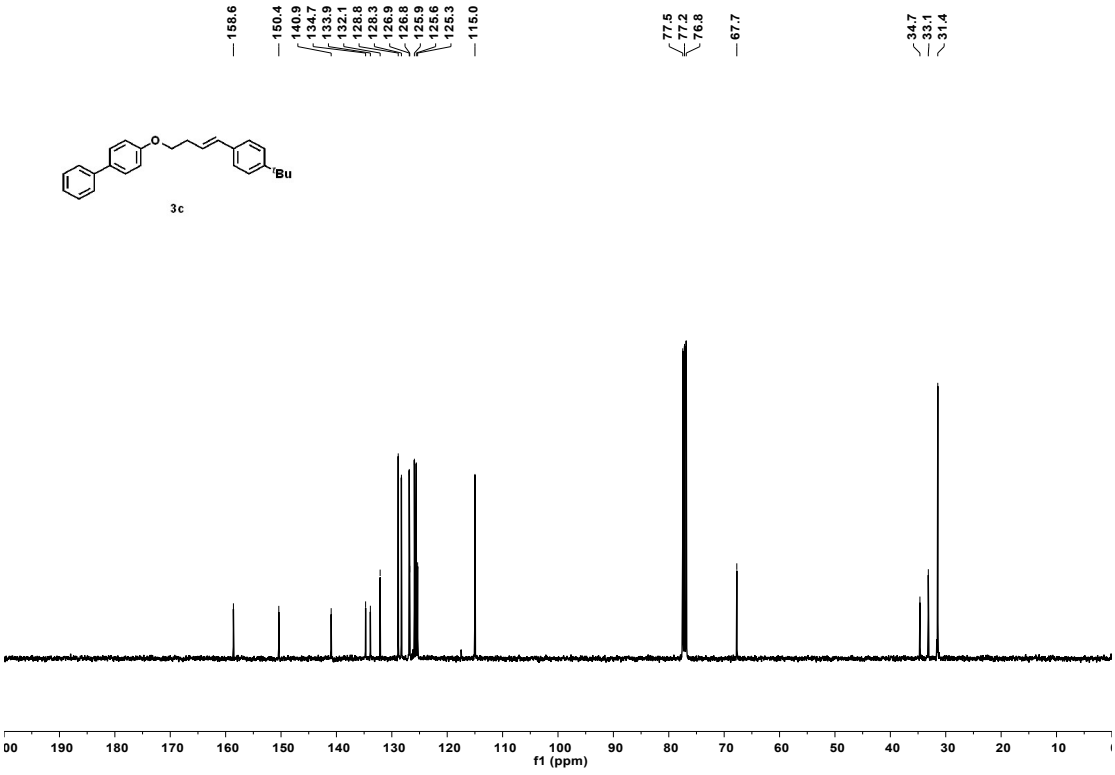
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3b**



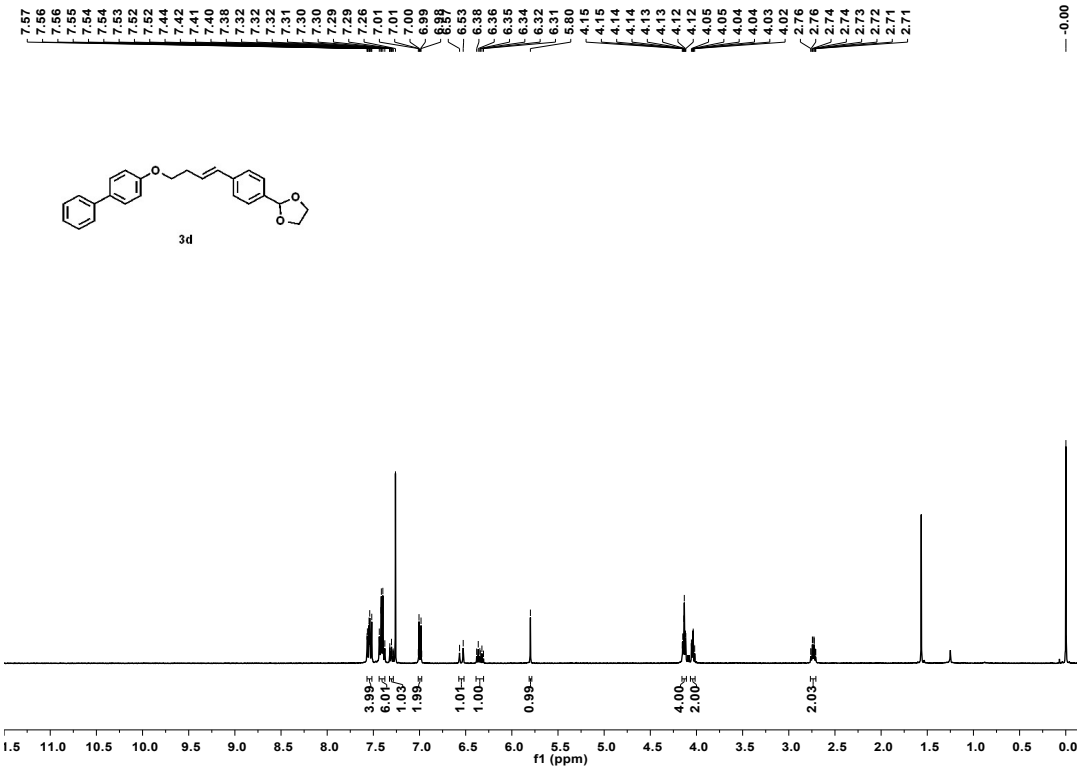
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**



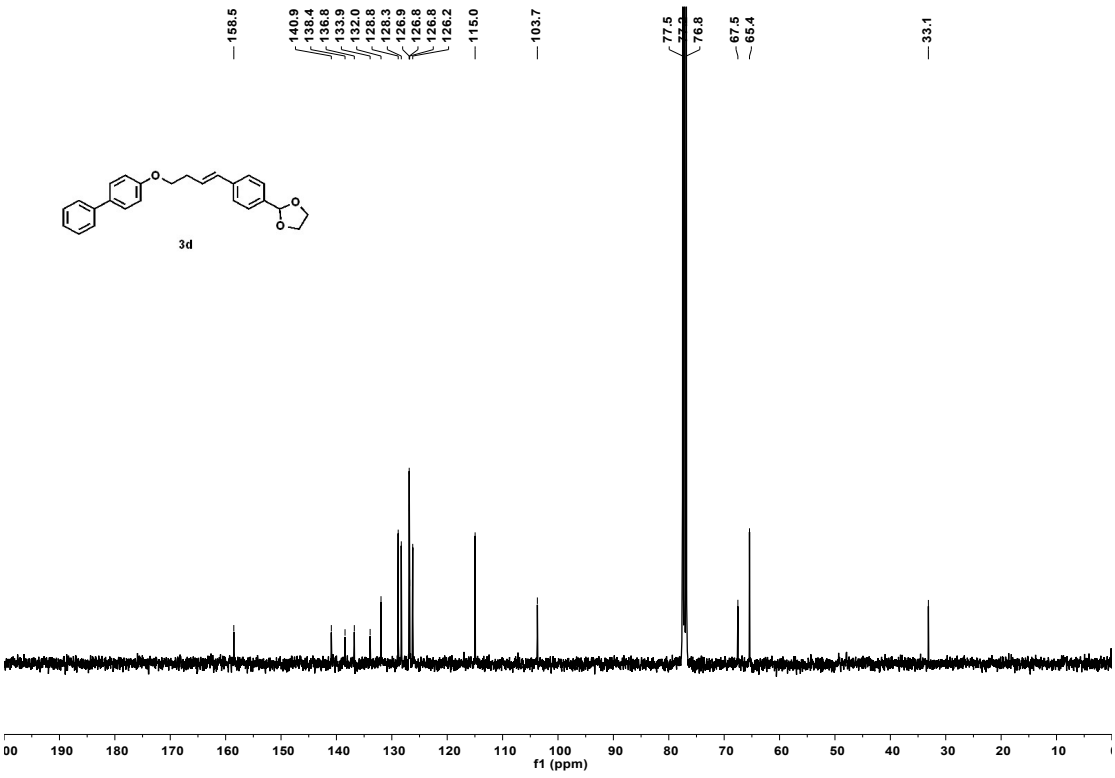
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3c**



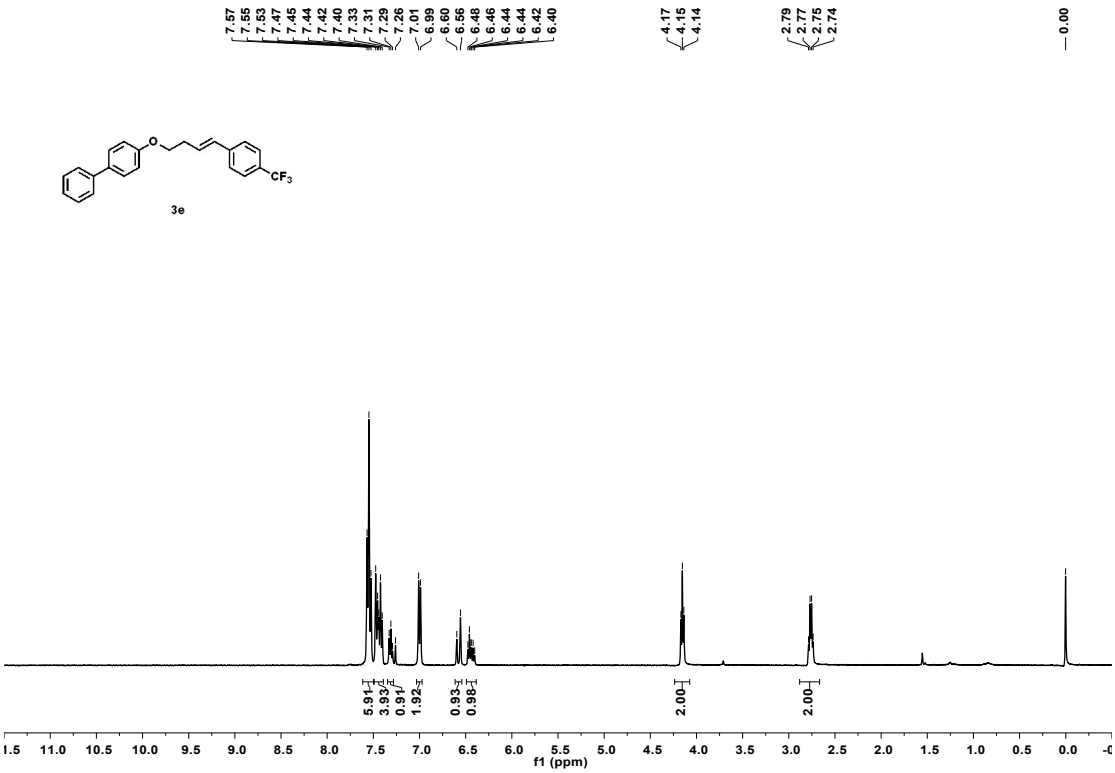
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d**



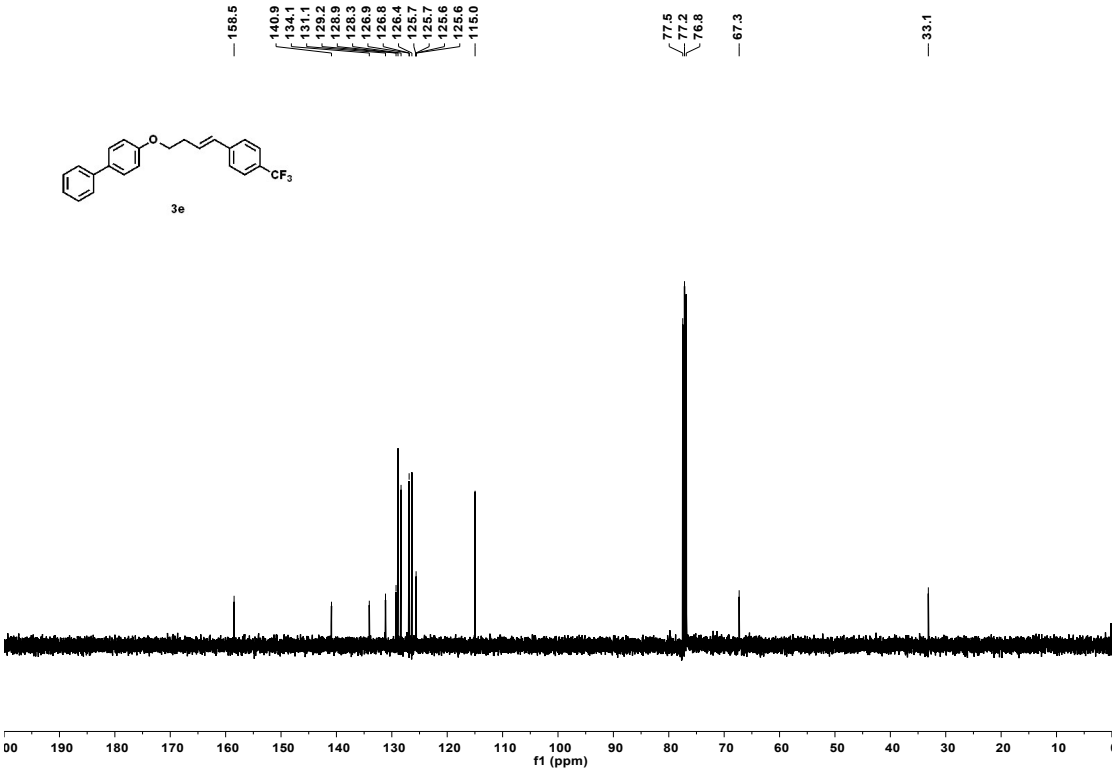
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3d**



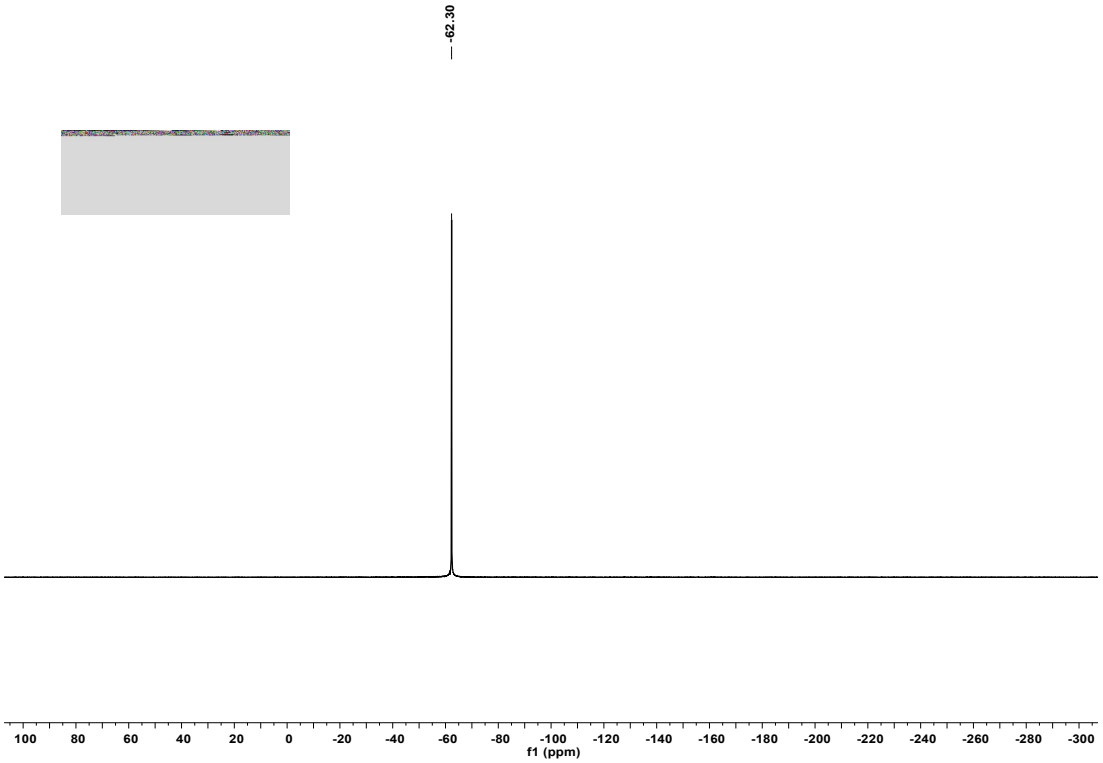
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e**



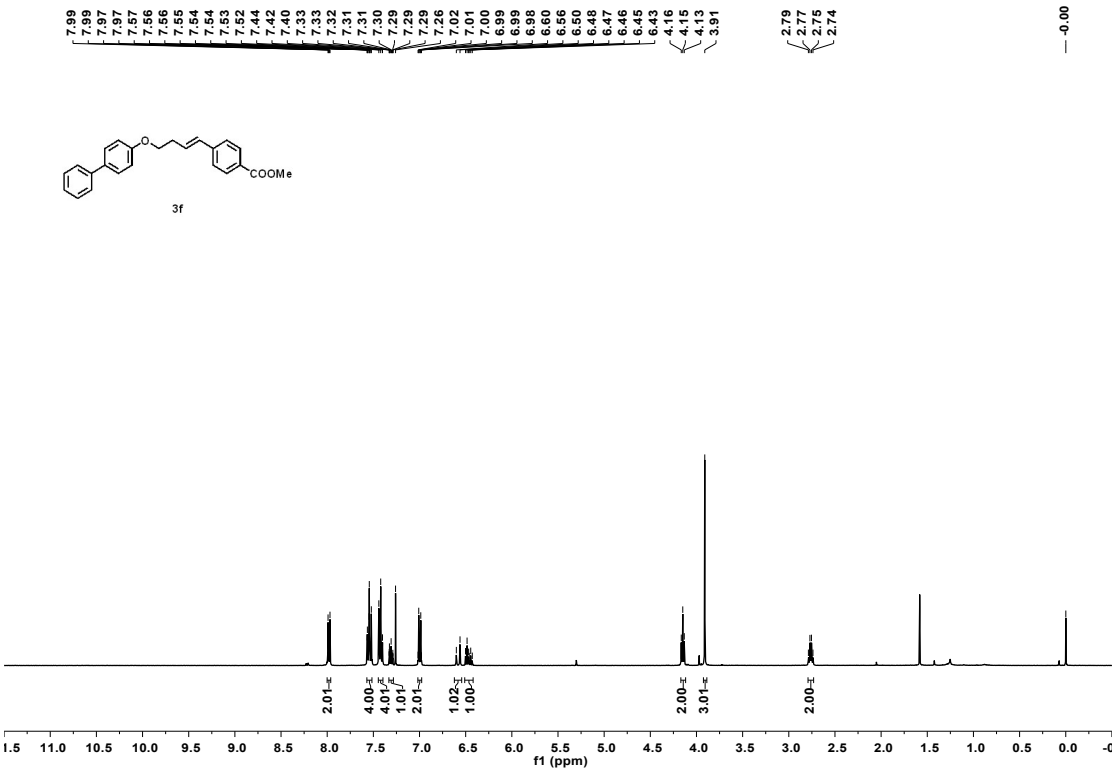
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3e**



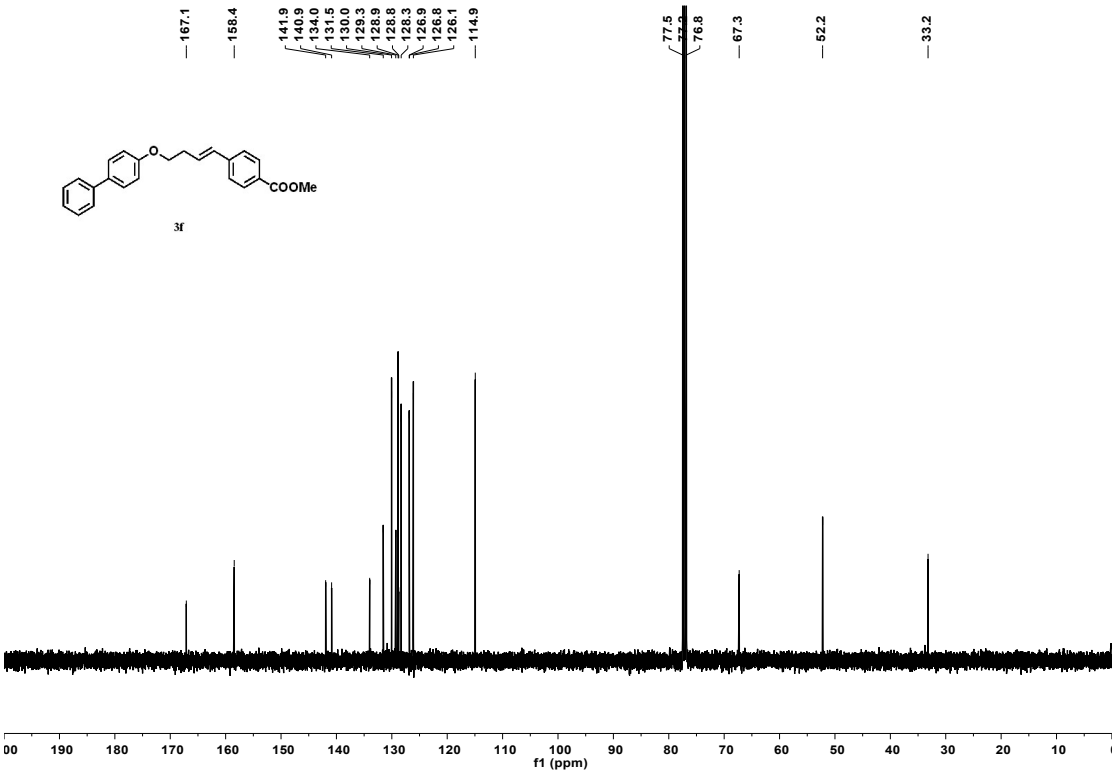
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3e**



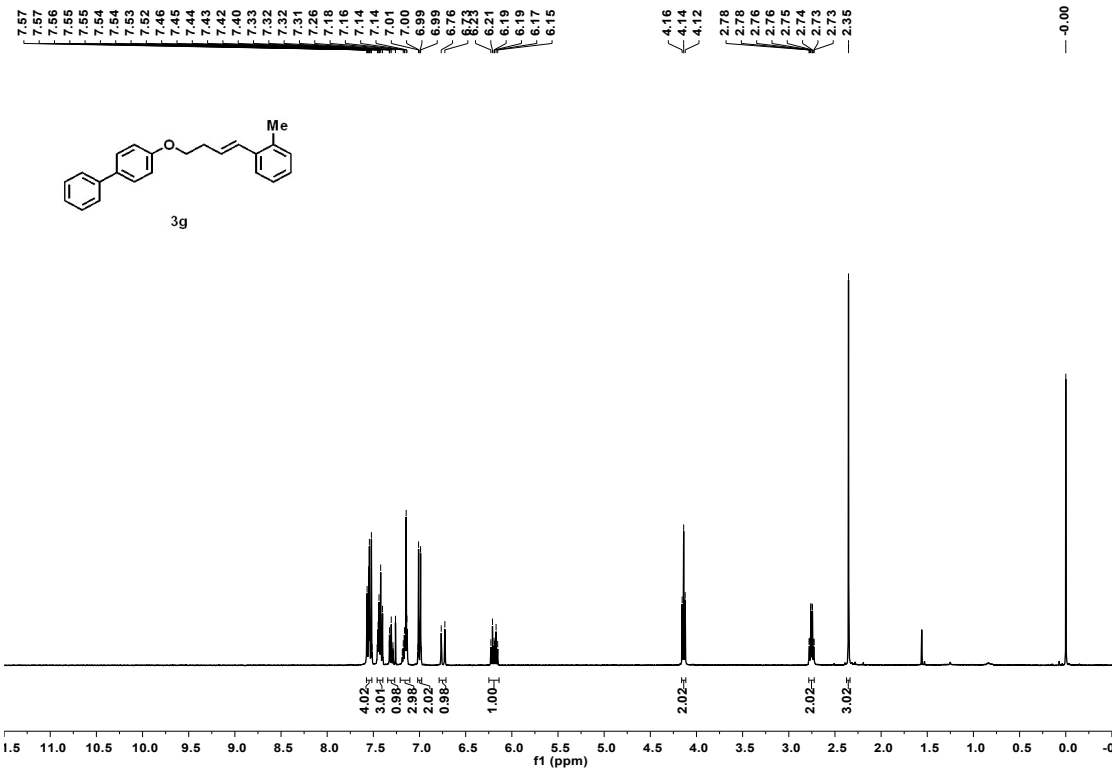
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**



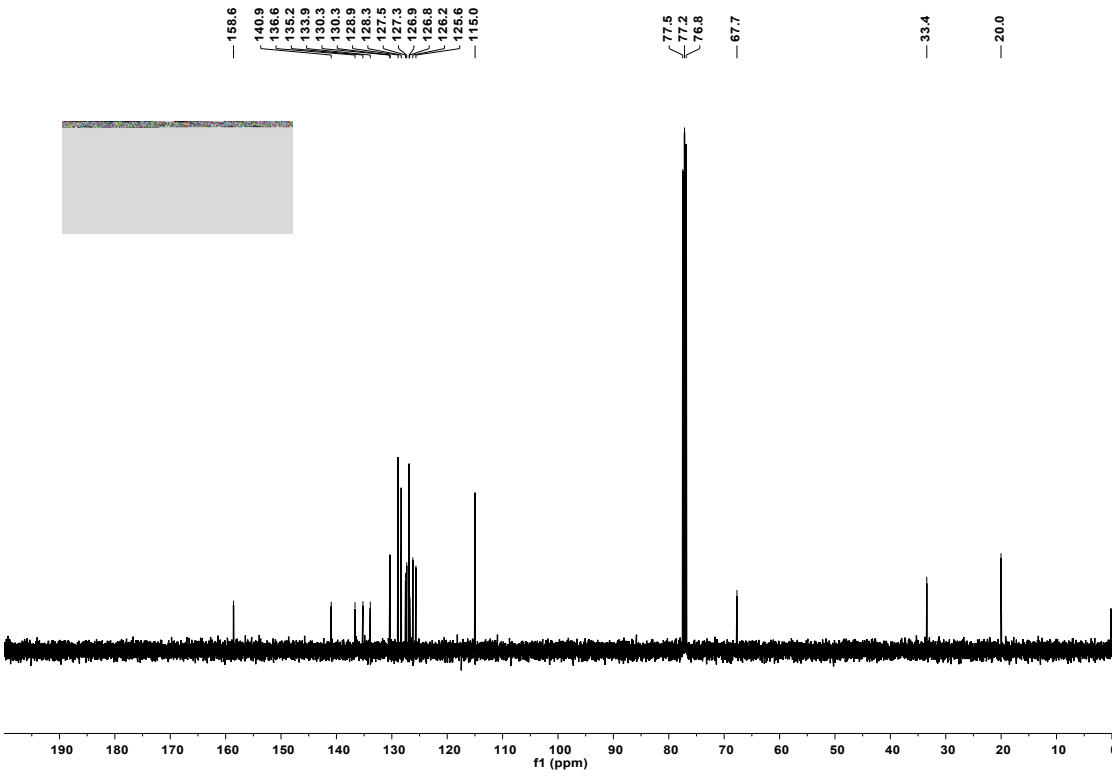
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3f**



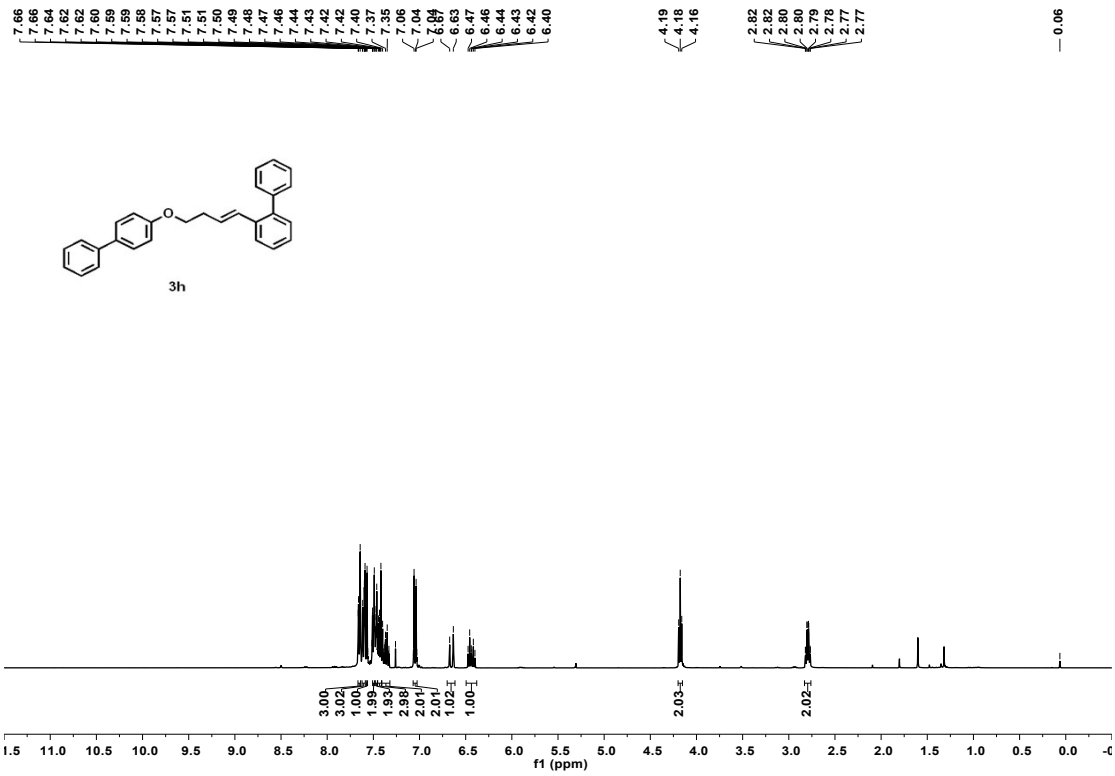
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3g**



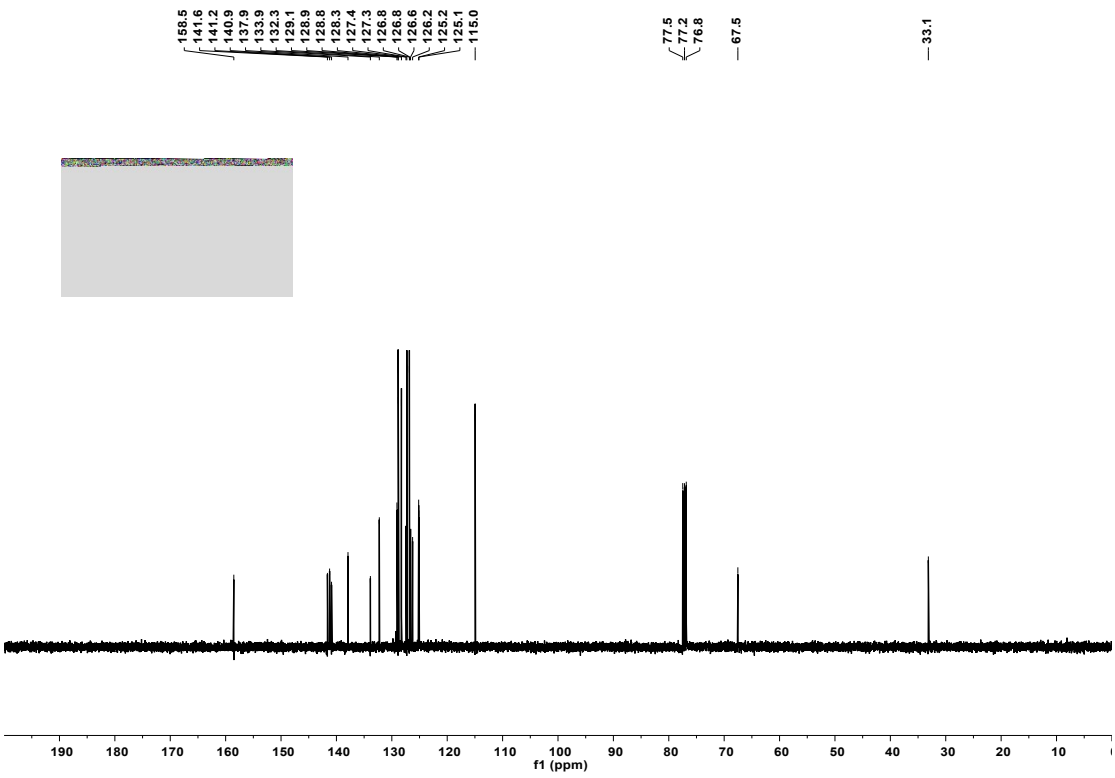
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3g**



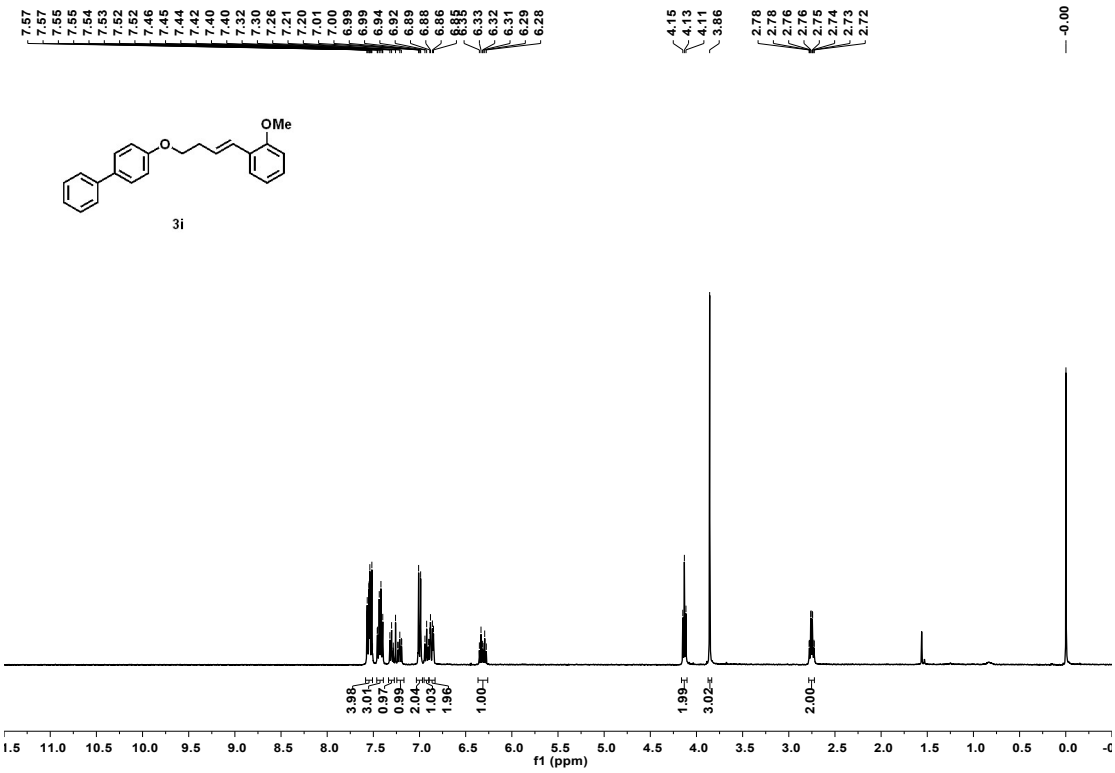
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



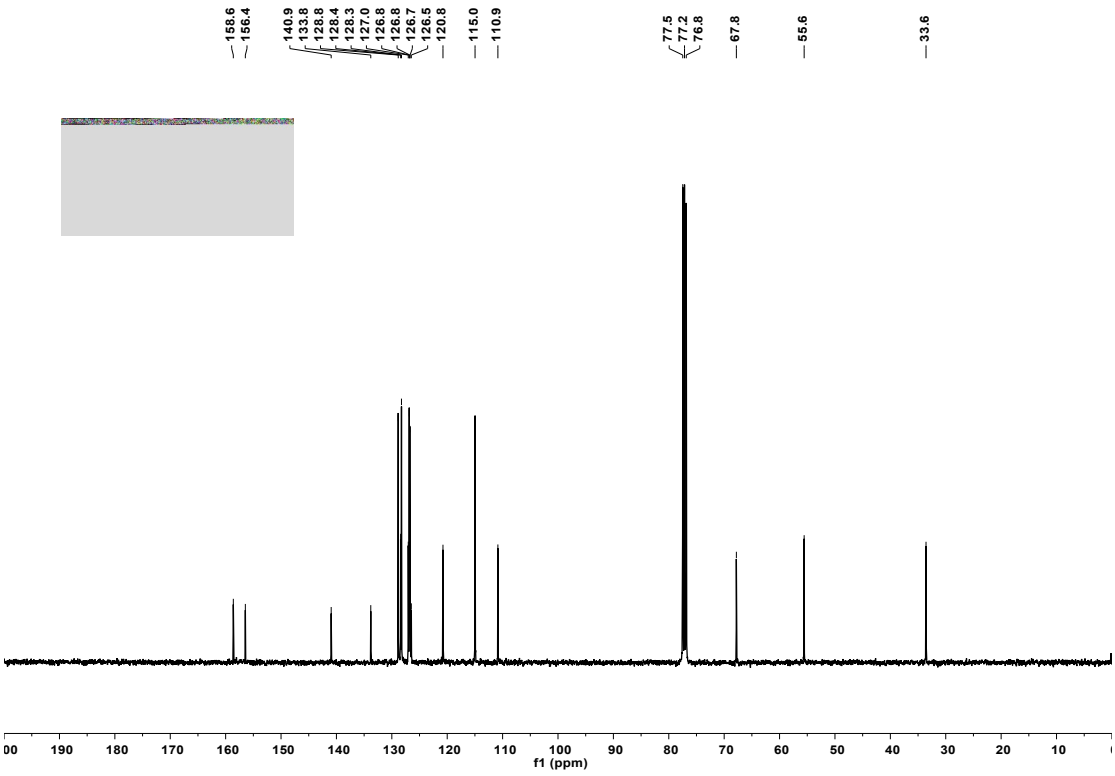
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3h**



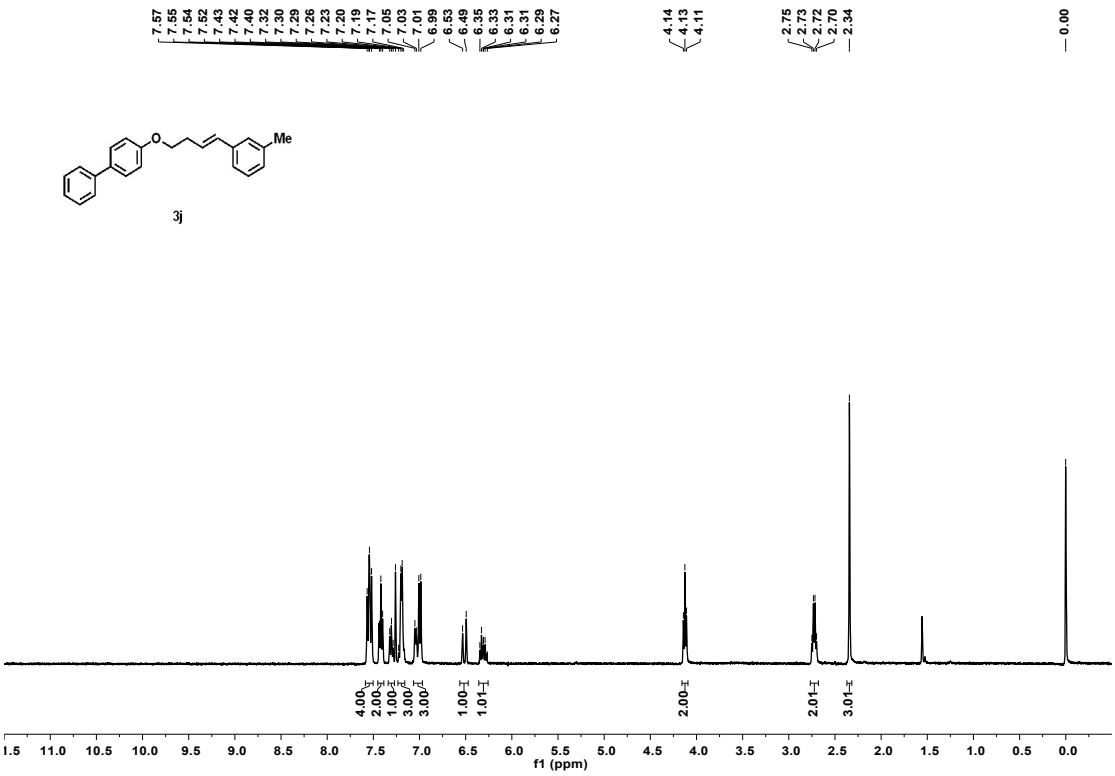
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3i**



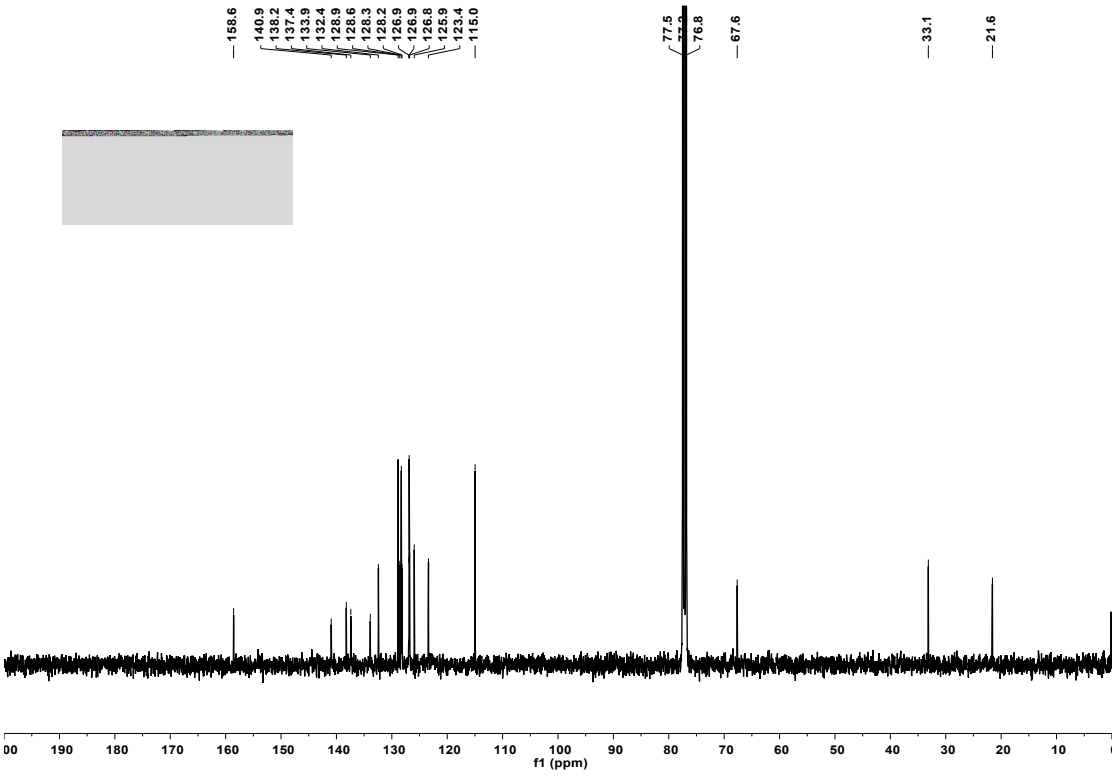
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3i**



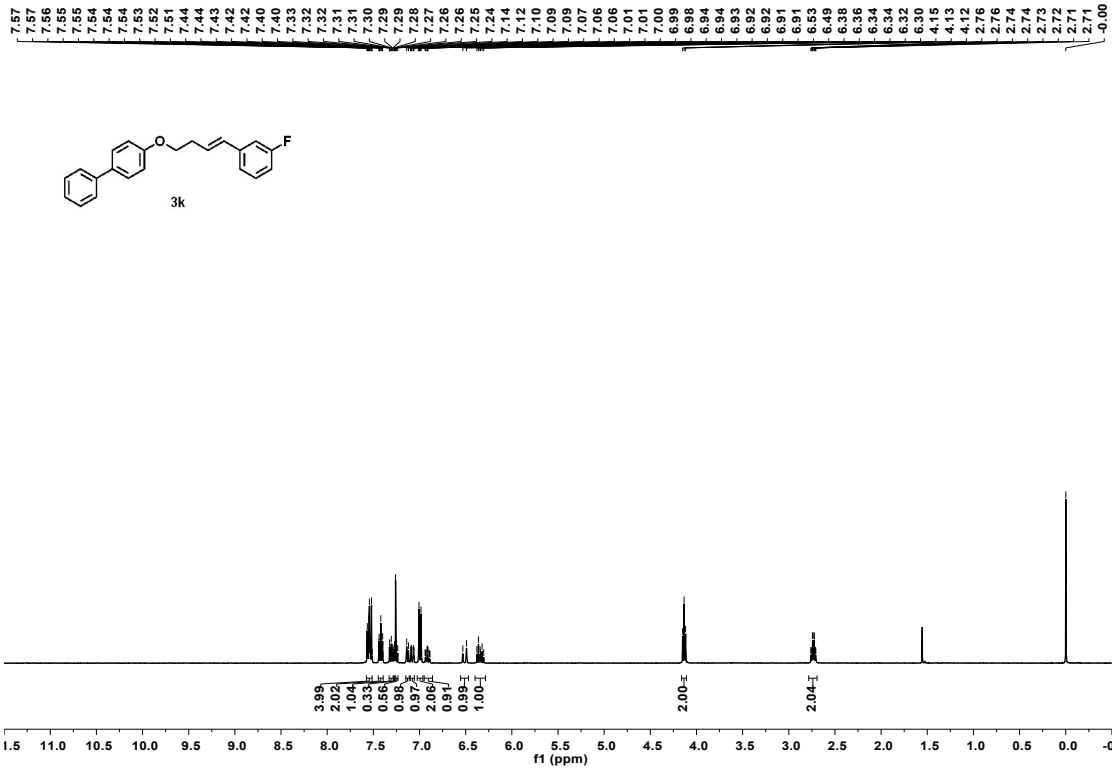
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3j**



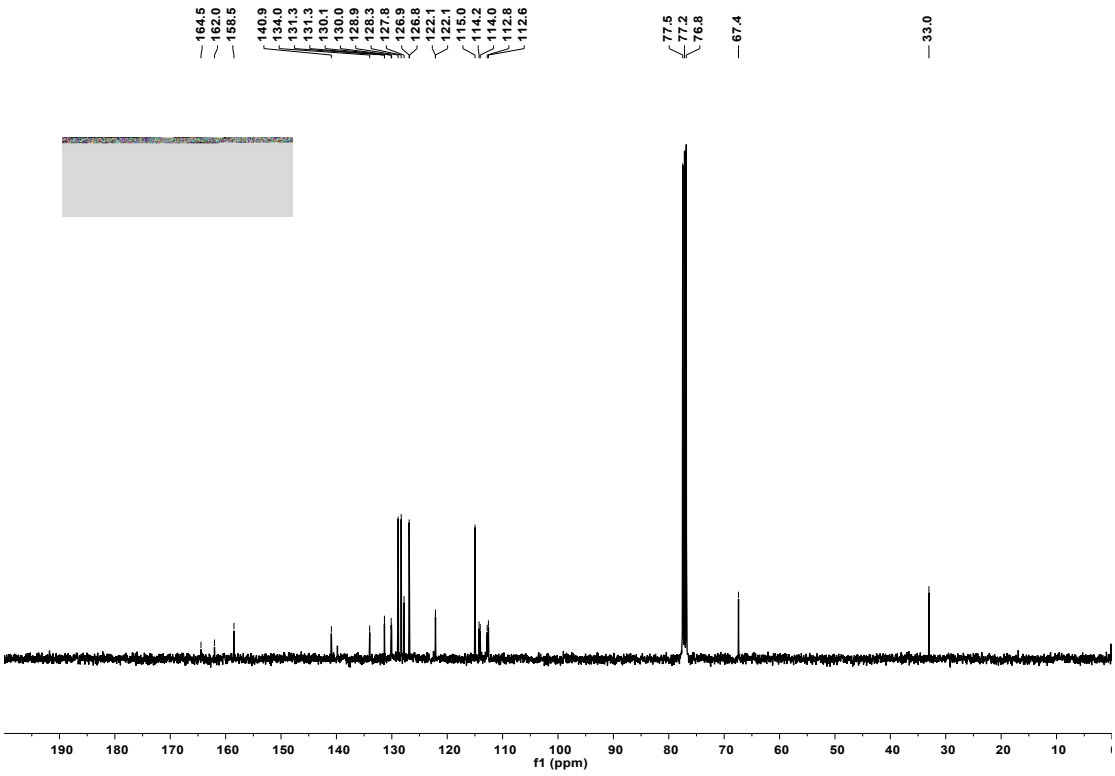
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3j**



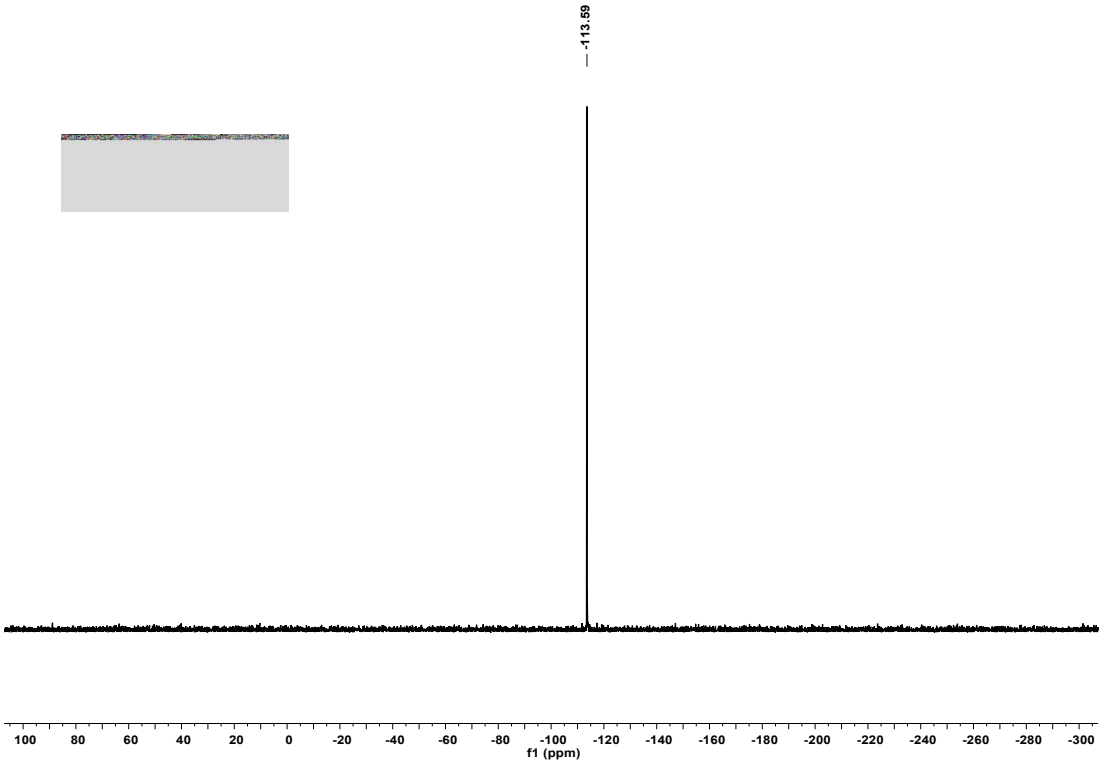
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3k**



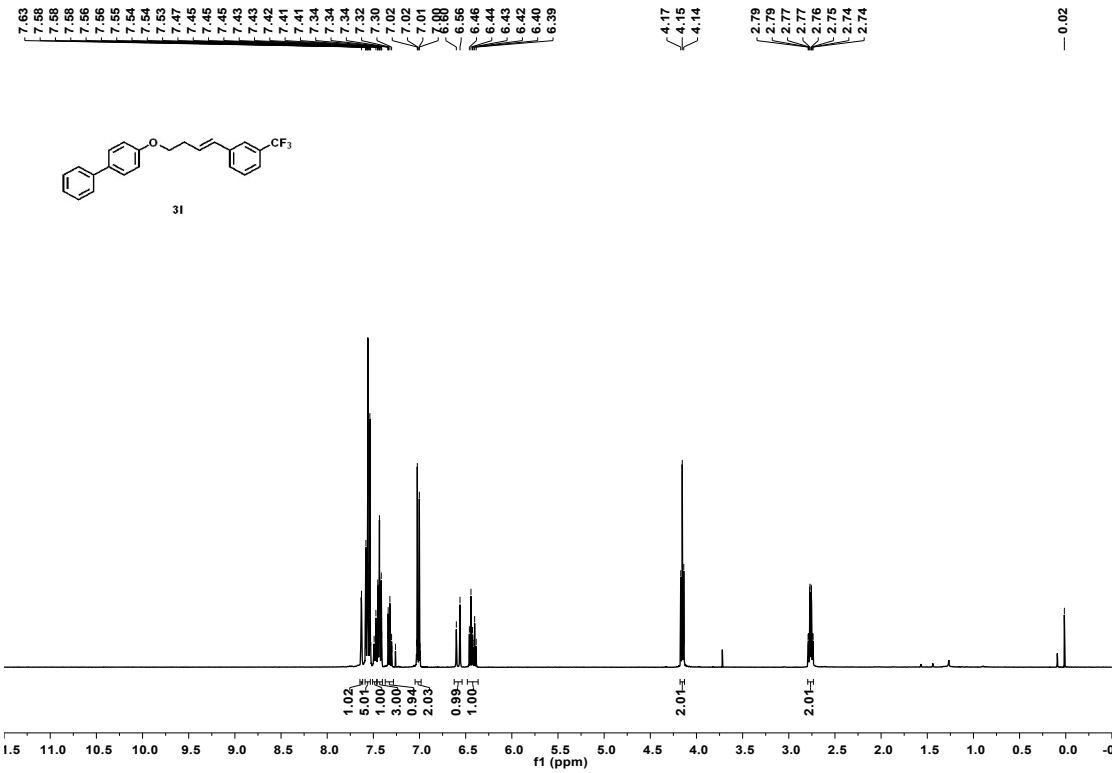
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3k**



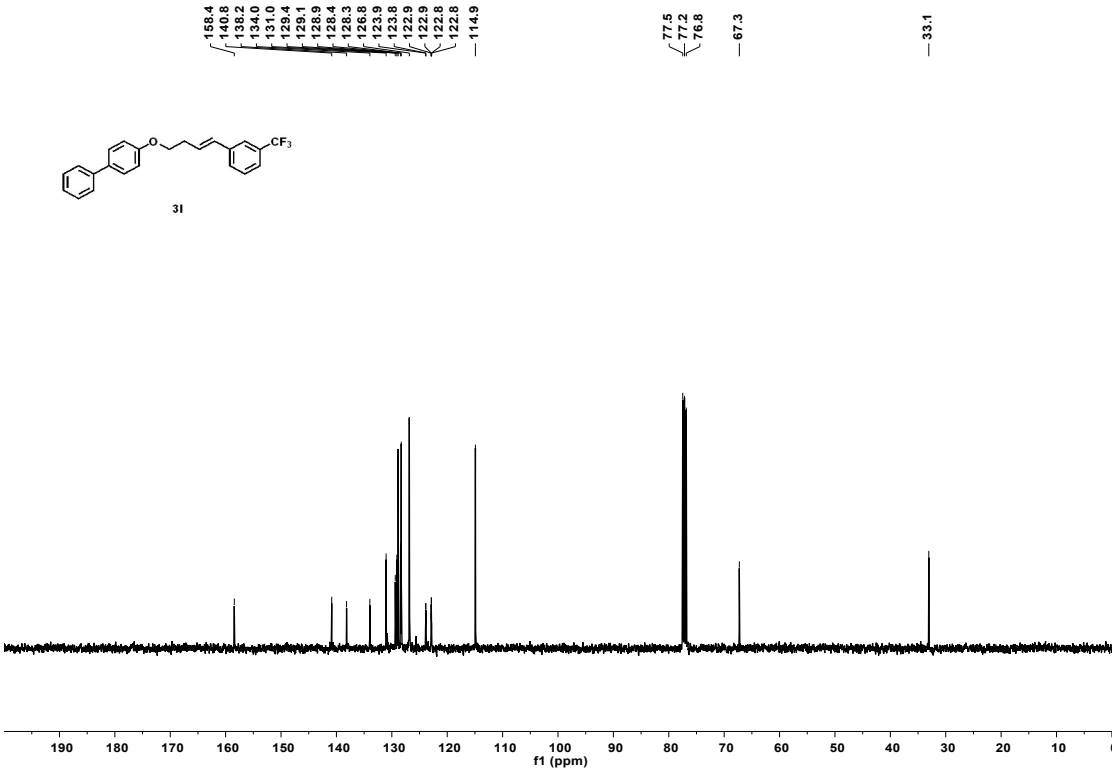
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3k**



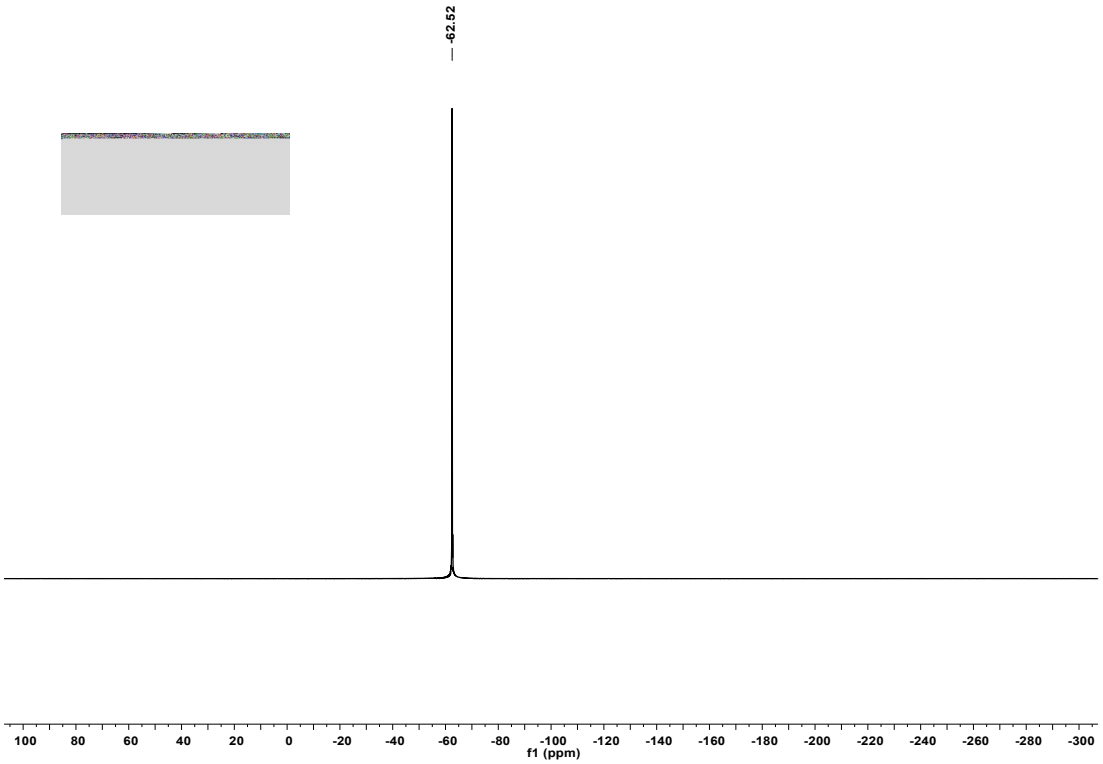
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3l**



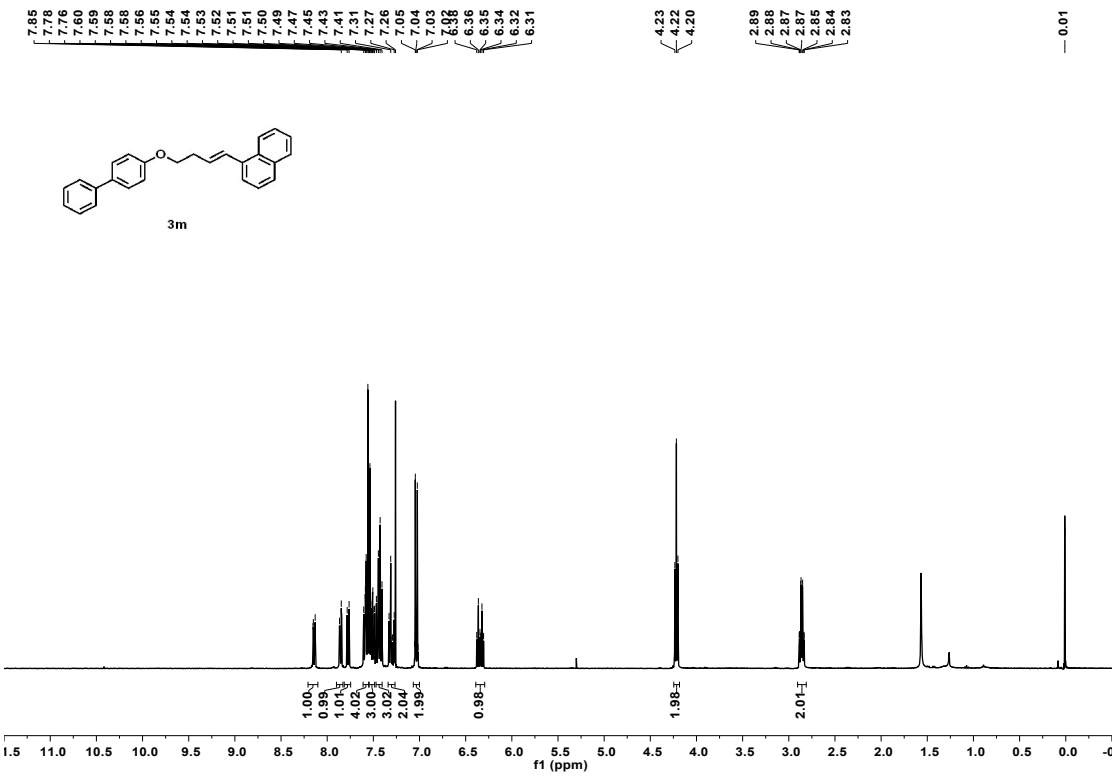
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3l**



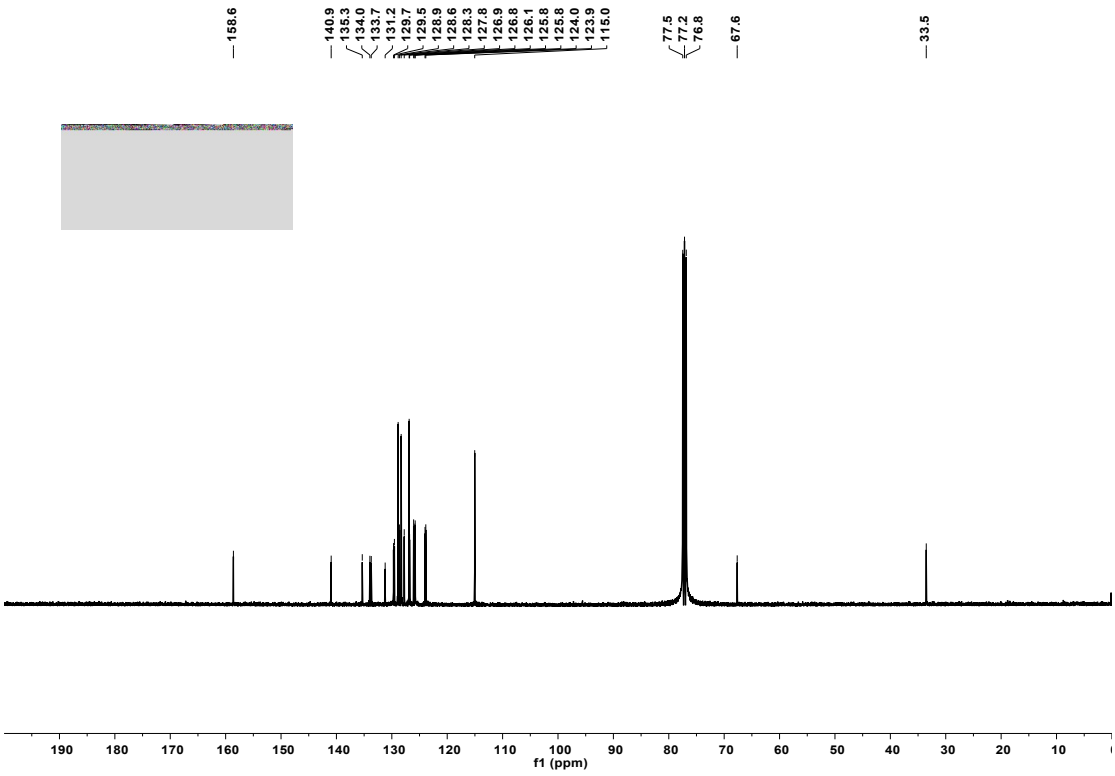
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3l**



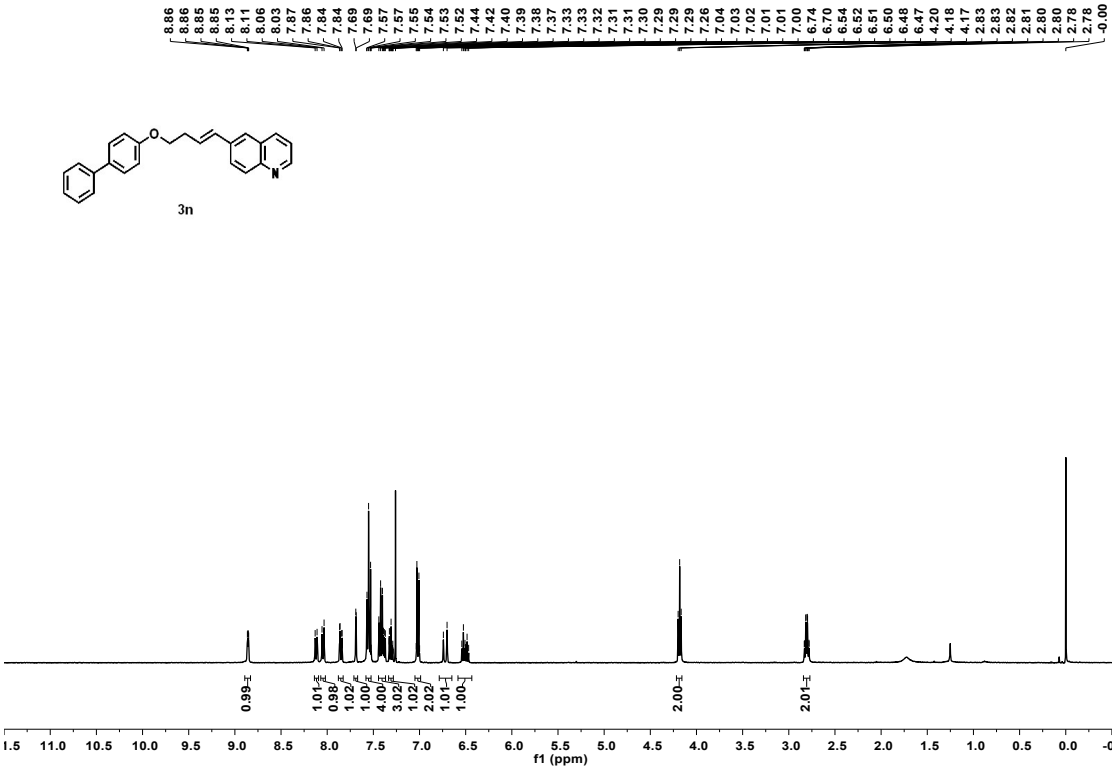
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3m**



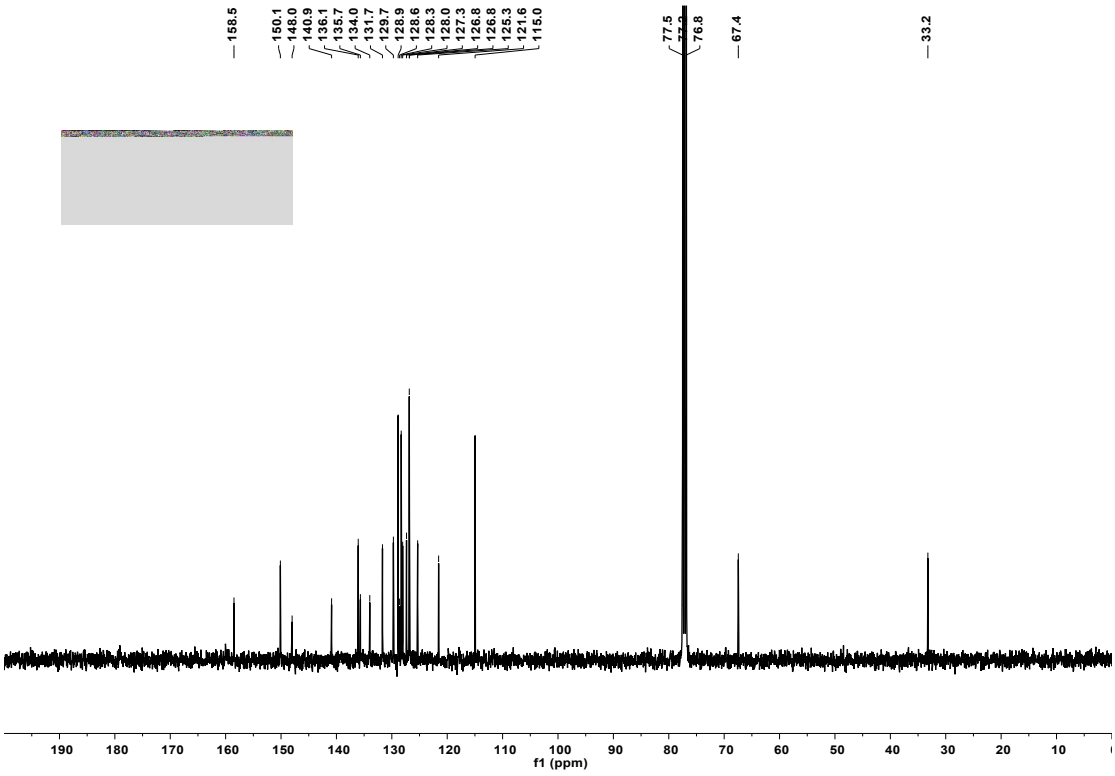
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3m**



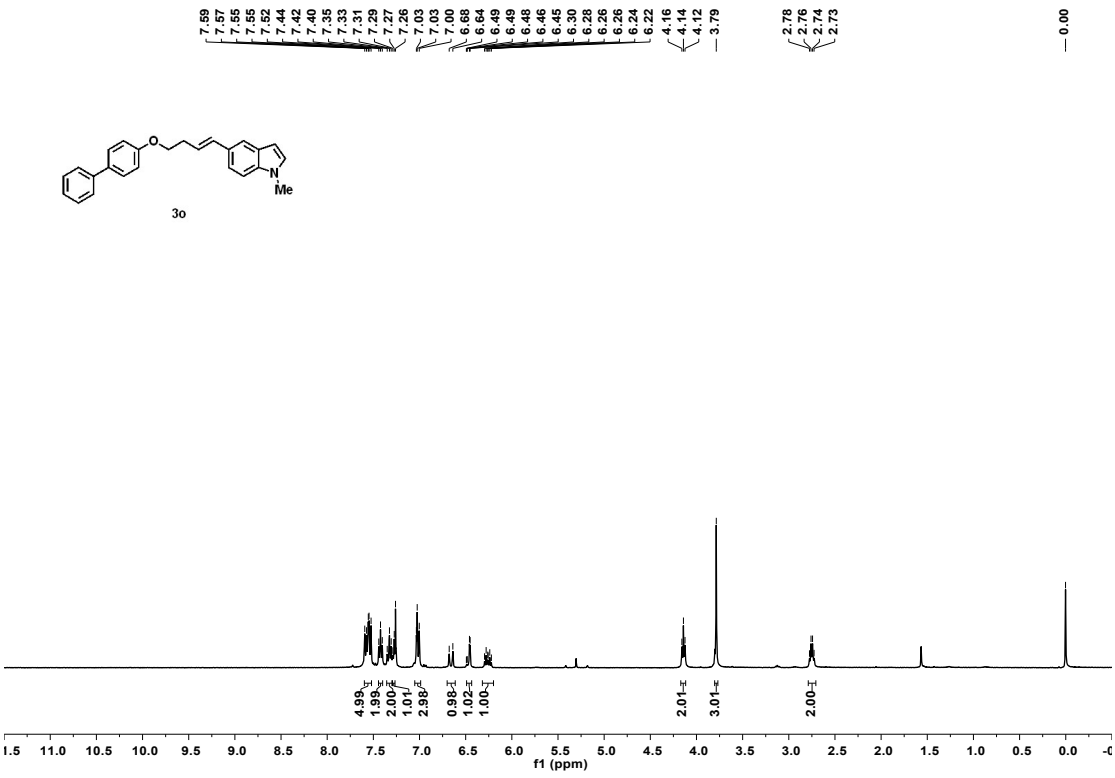
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3n**



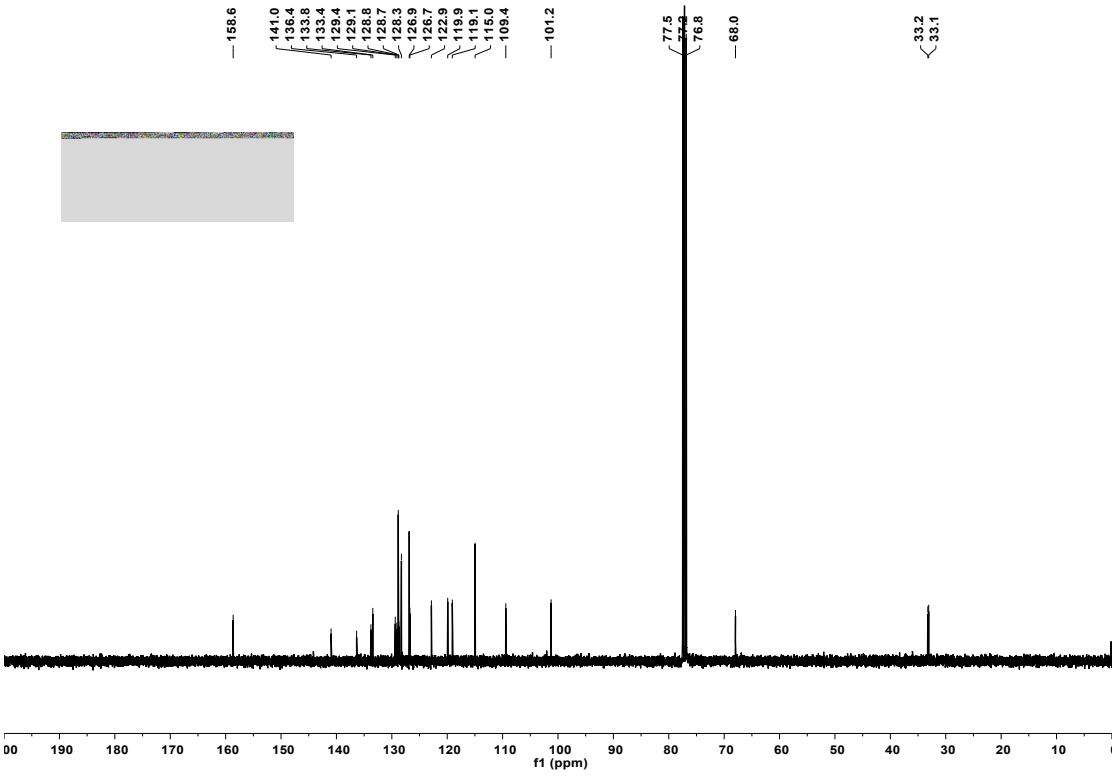
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3n**



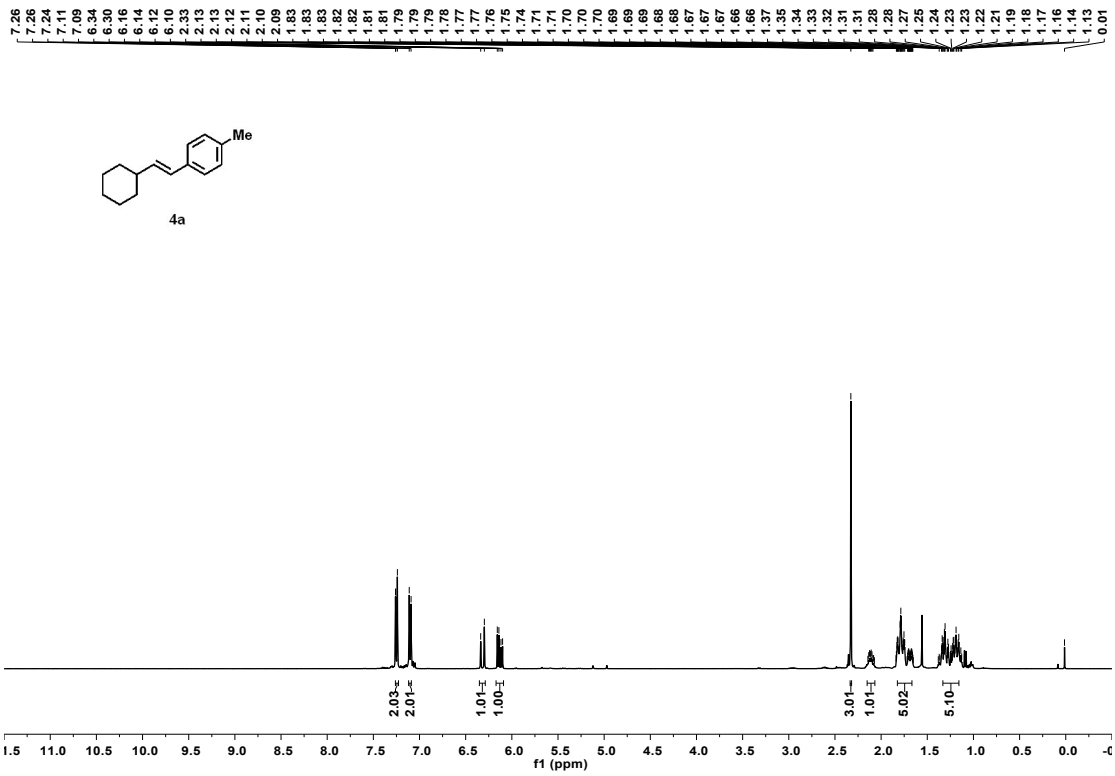
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3o**



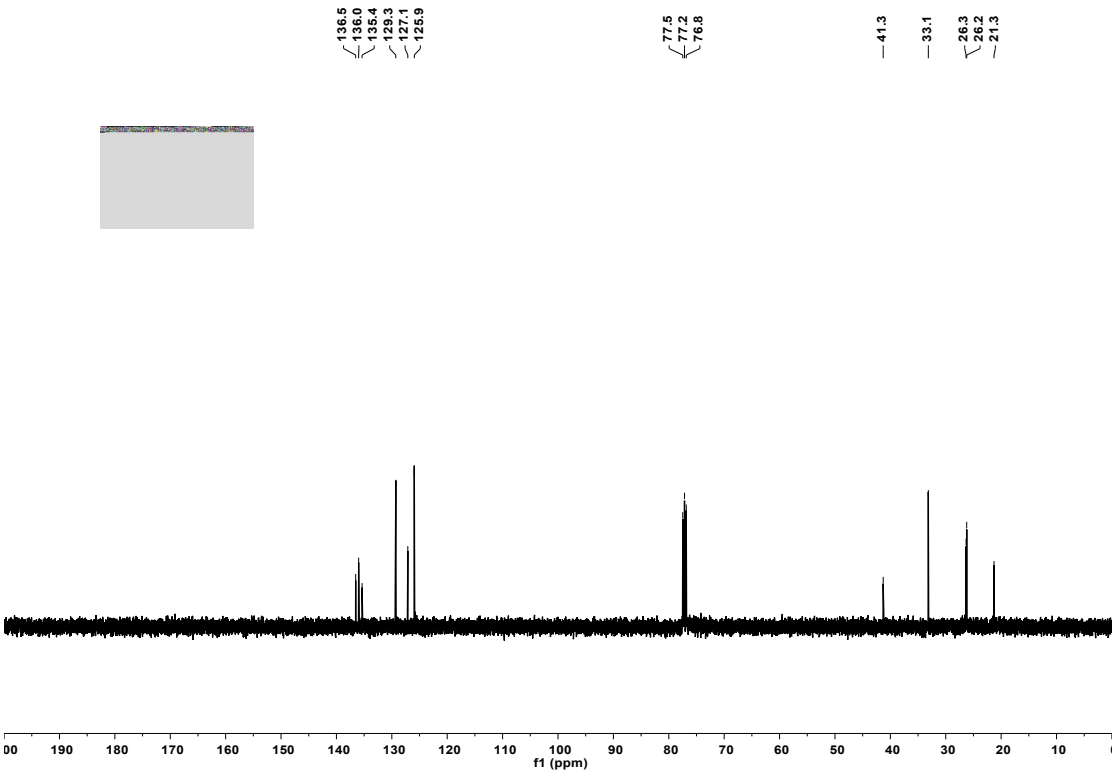
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3o**



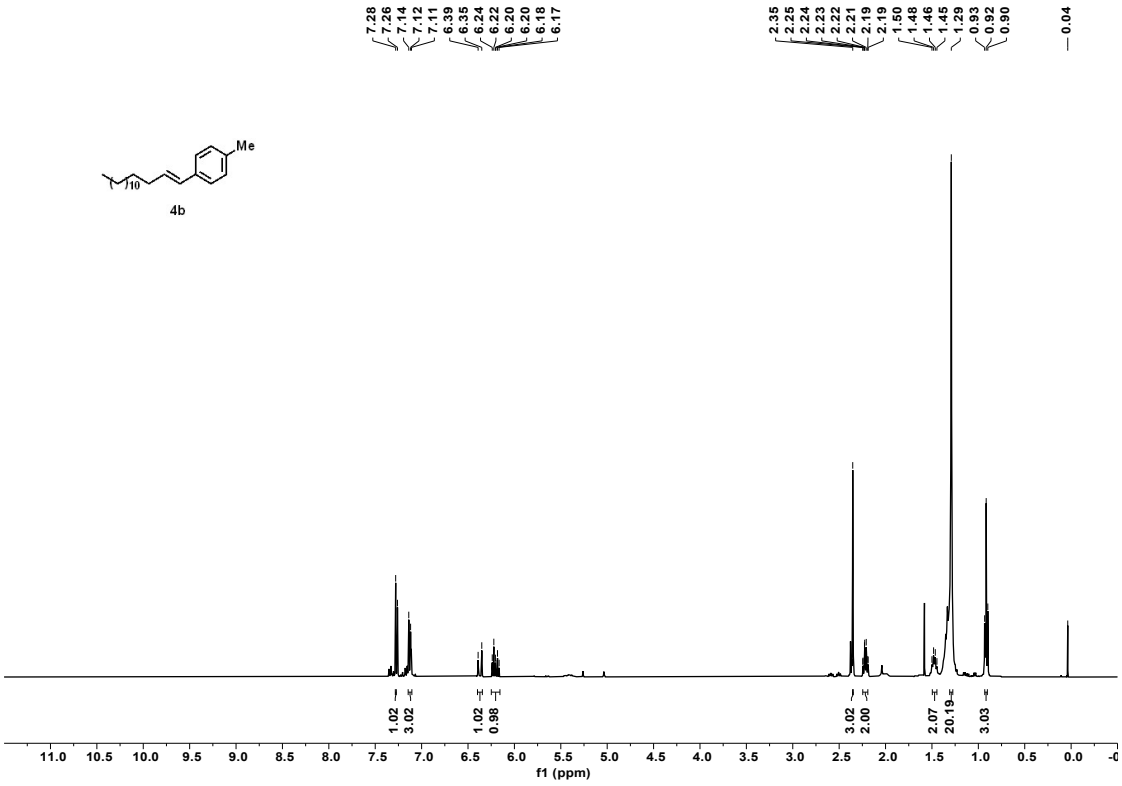
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4a**



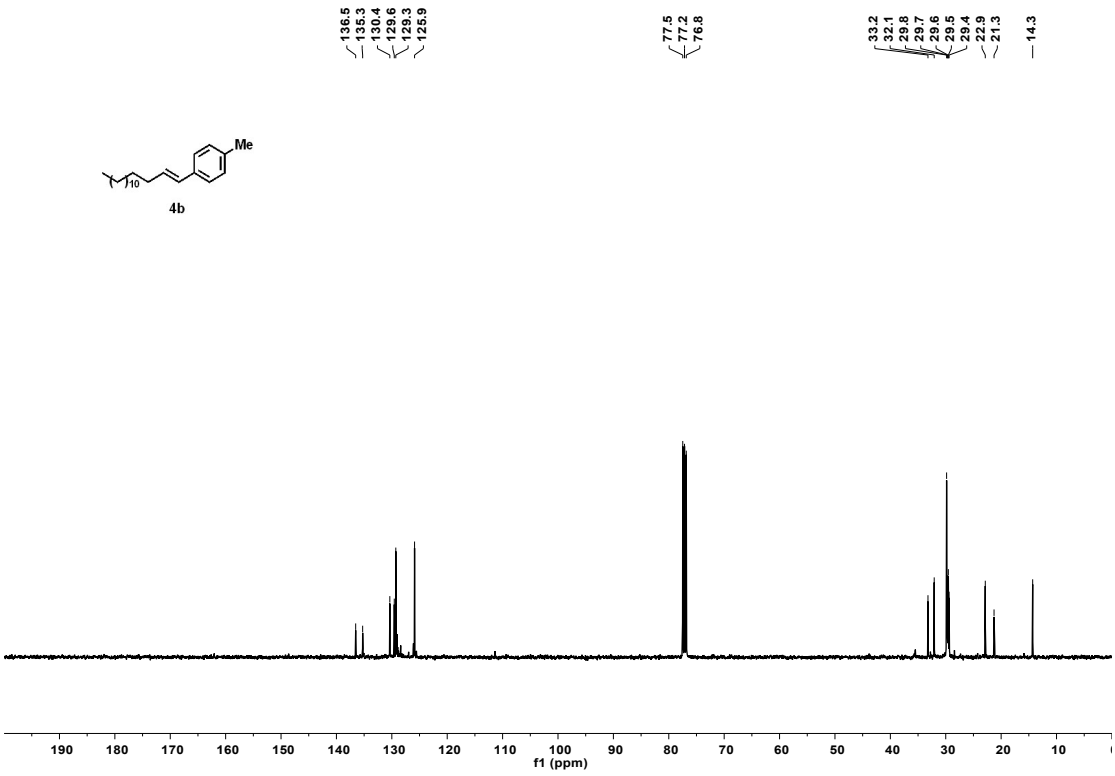
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4a**



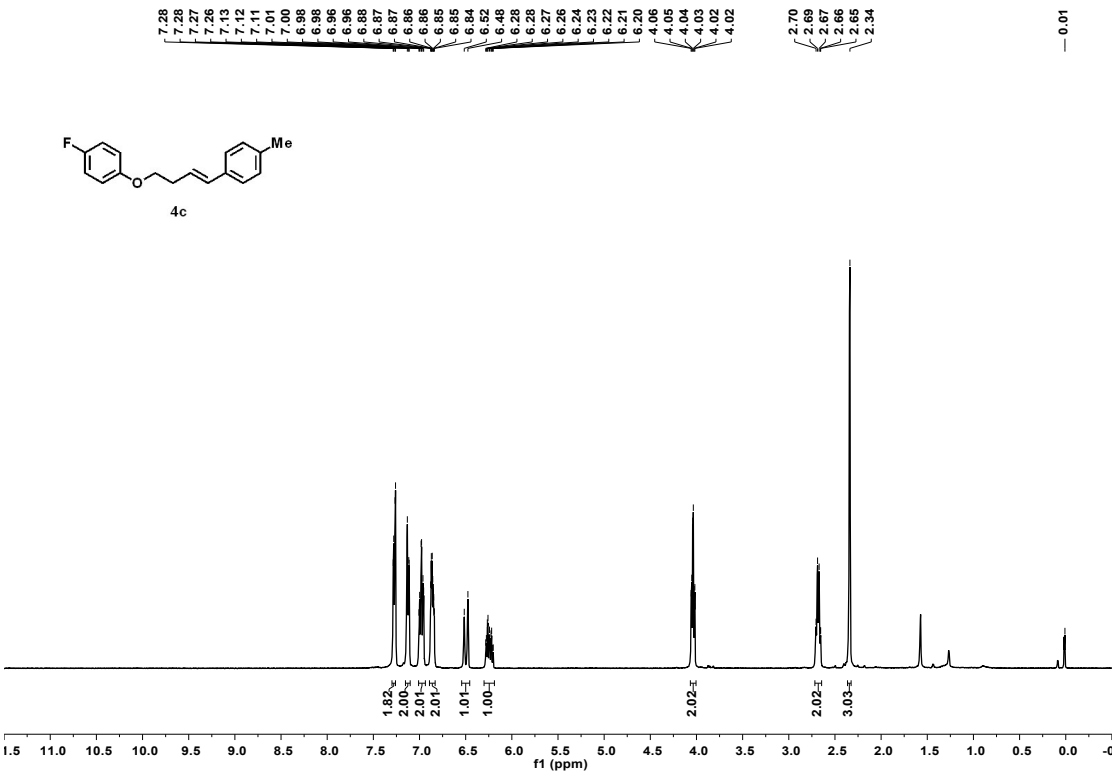
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4b**



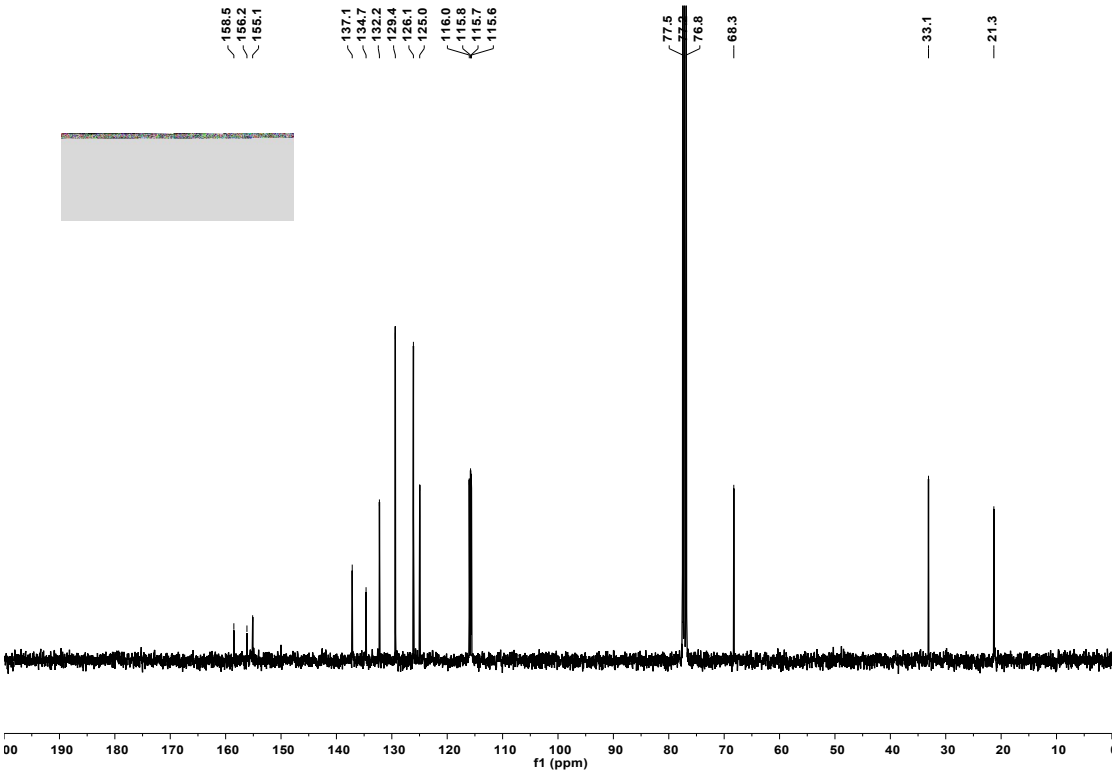
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4b**



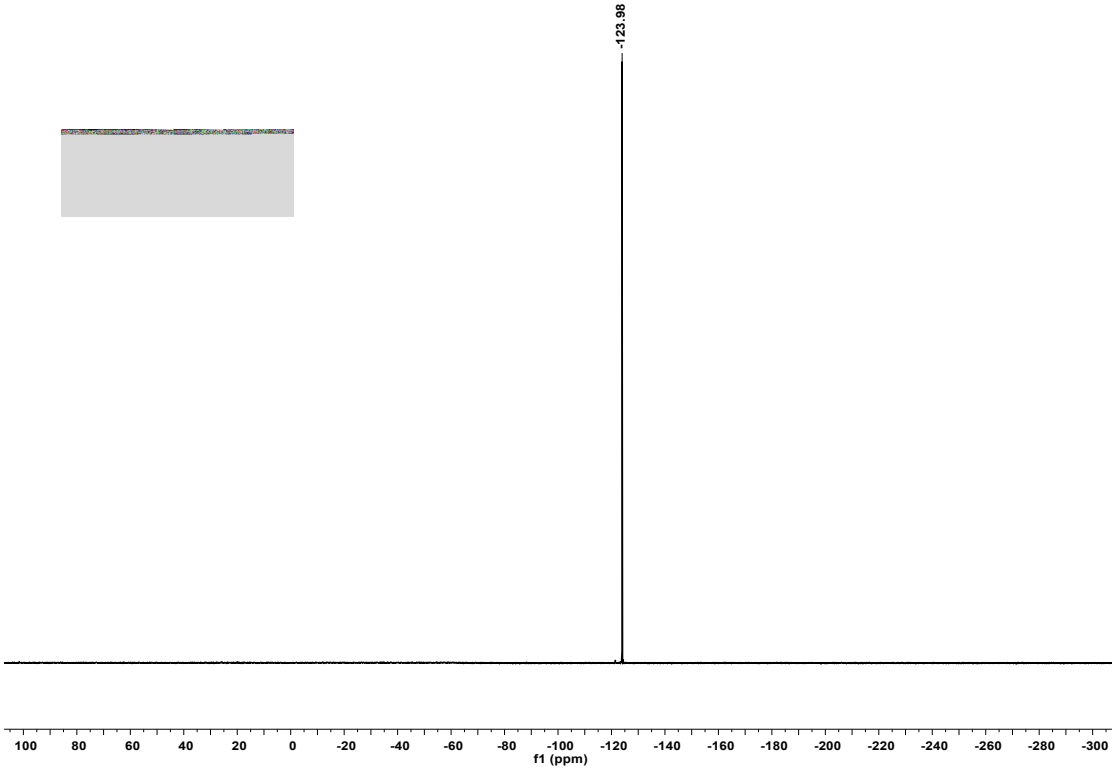
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4c**



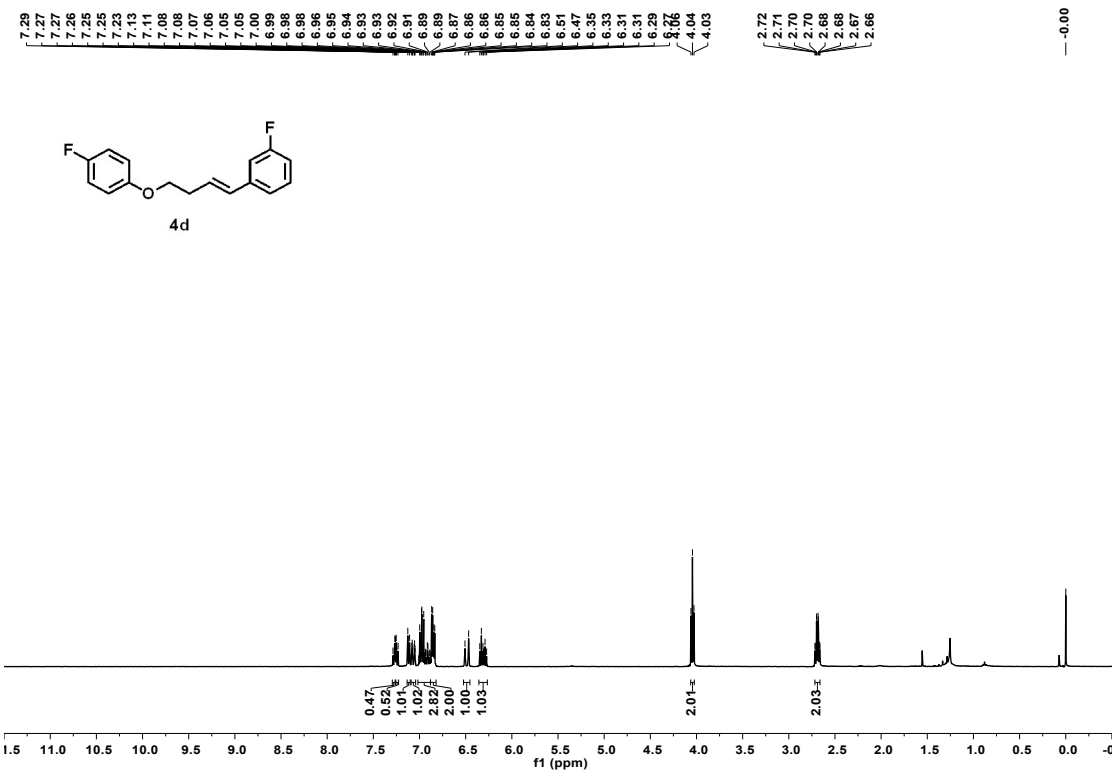
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4c**



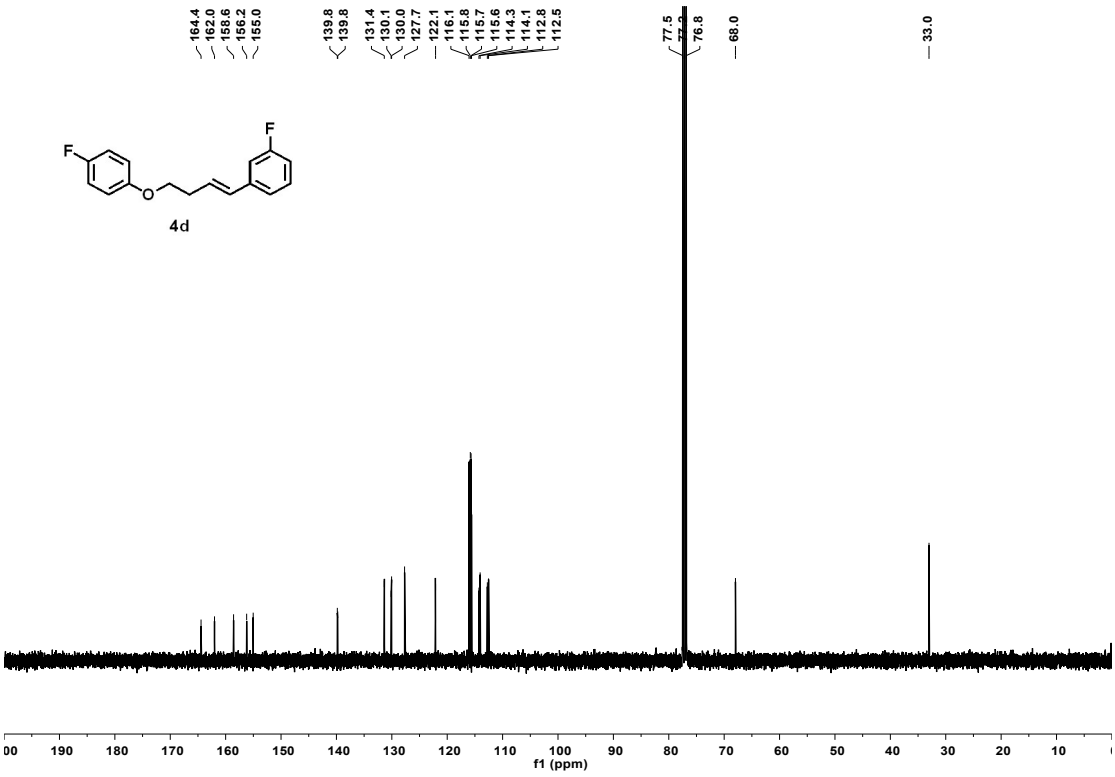
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4c**



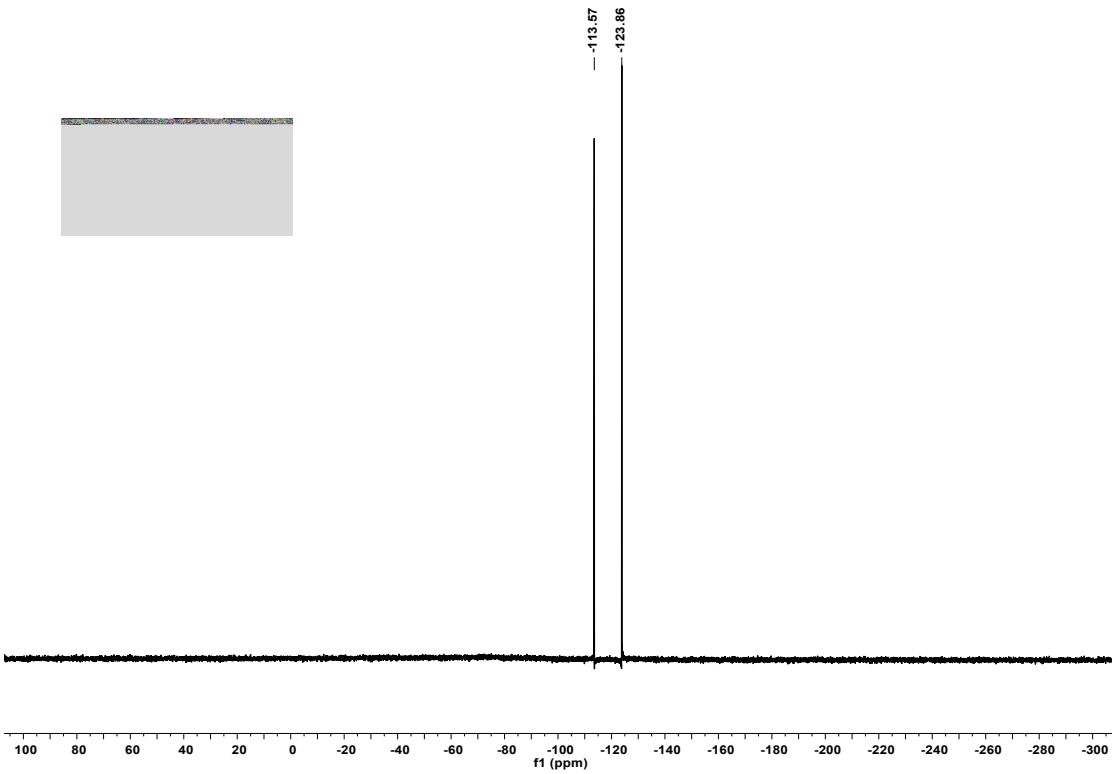
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4d**



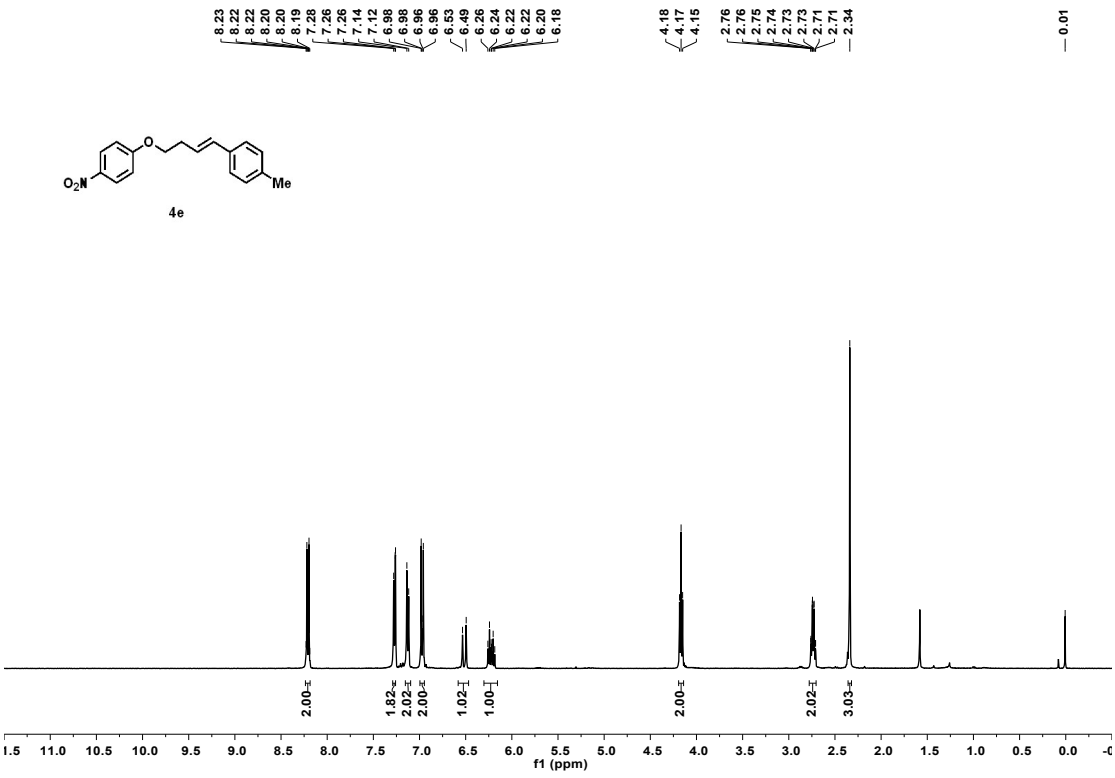
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4d**



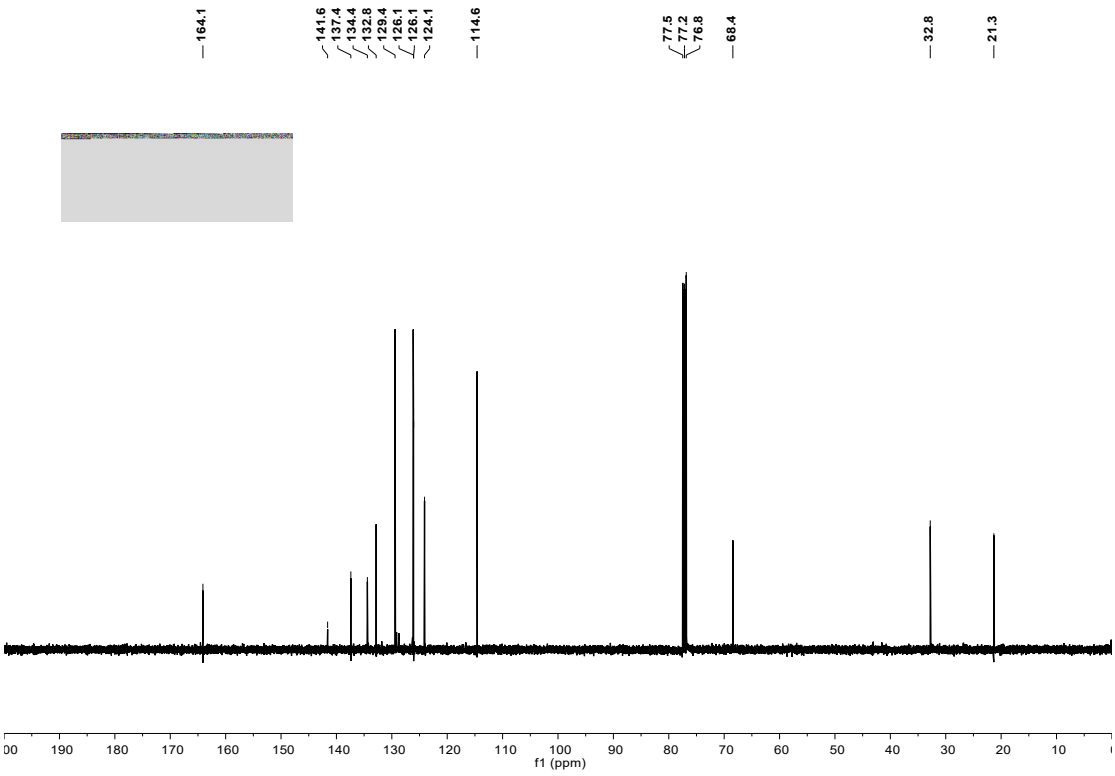
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4d**



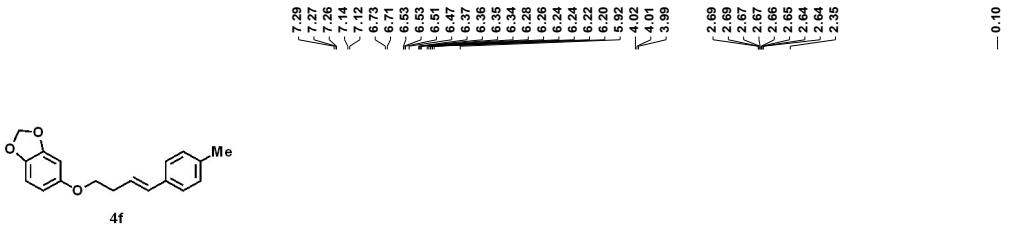
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4e**



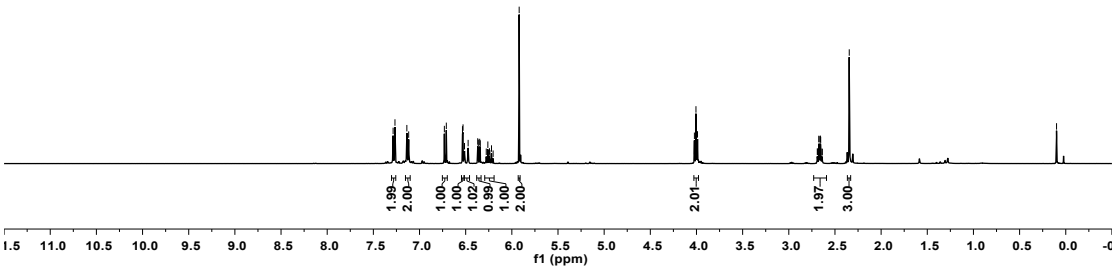
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4e**



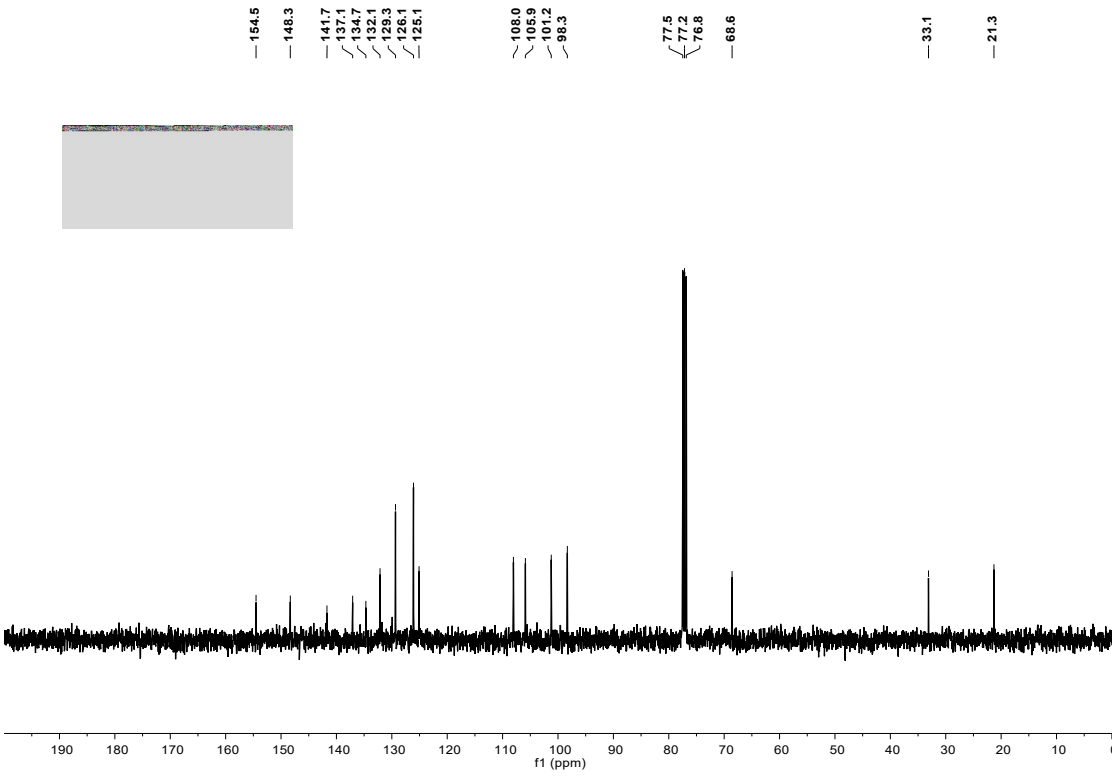
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4f**



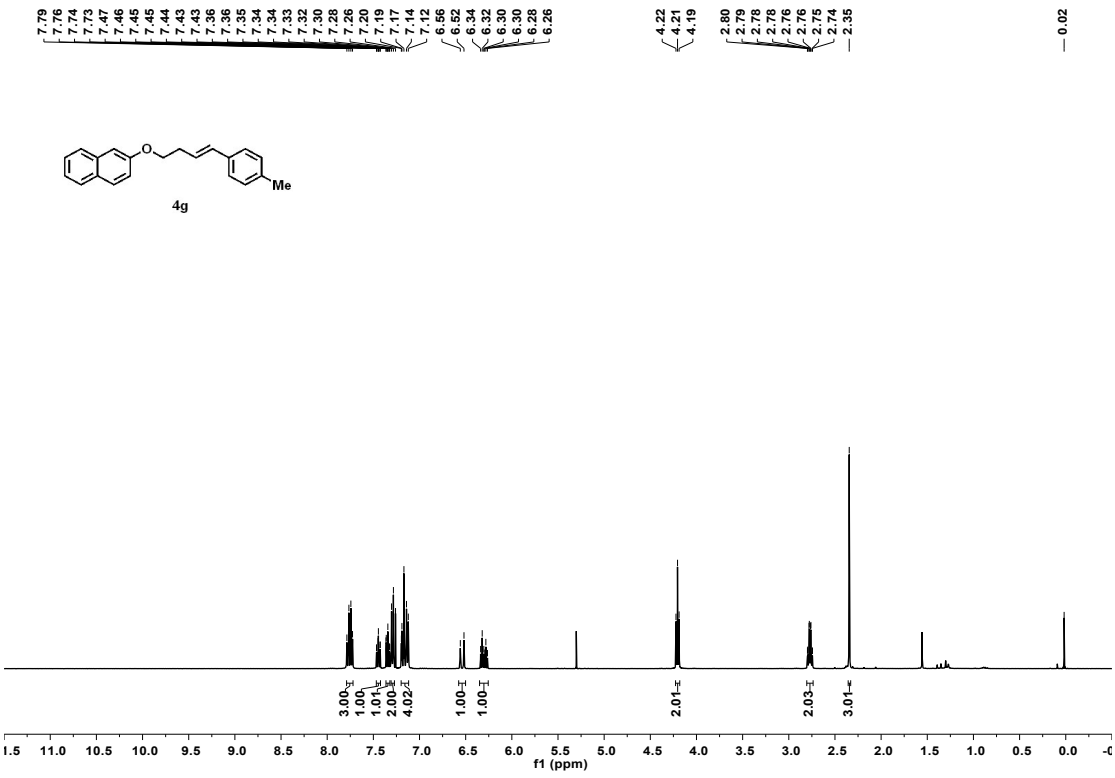
4f



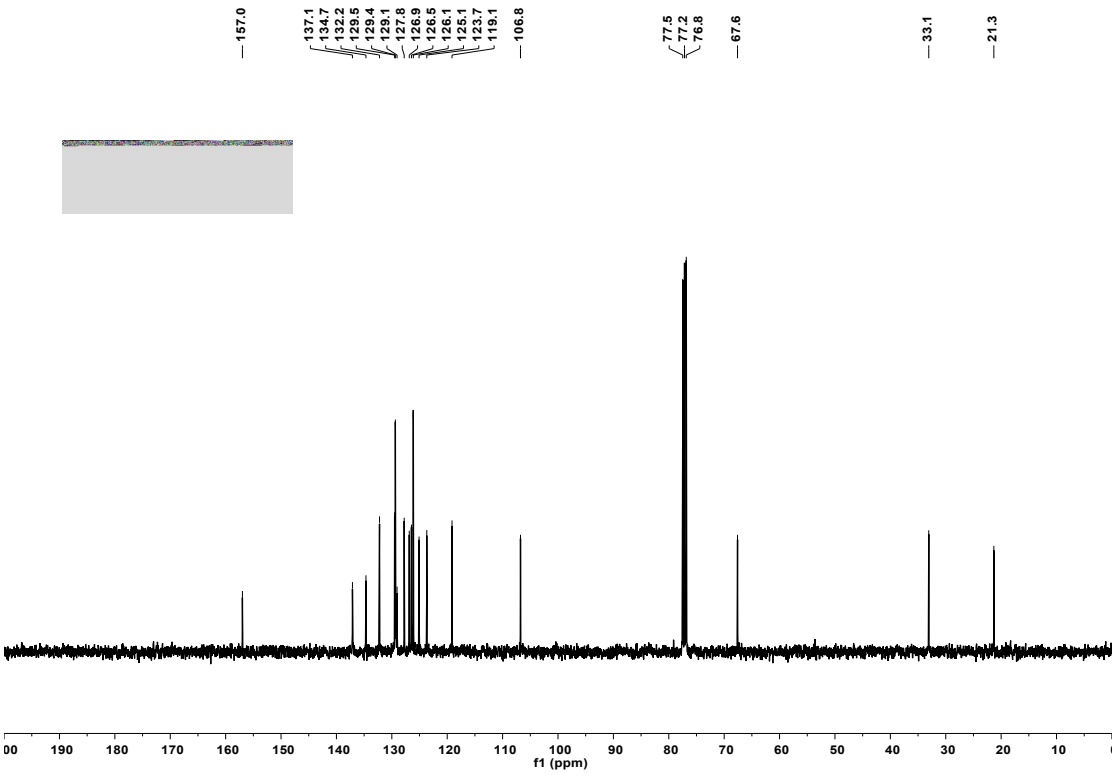
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4f**



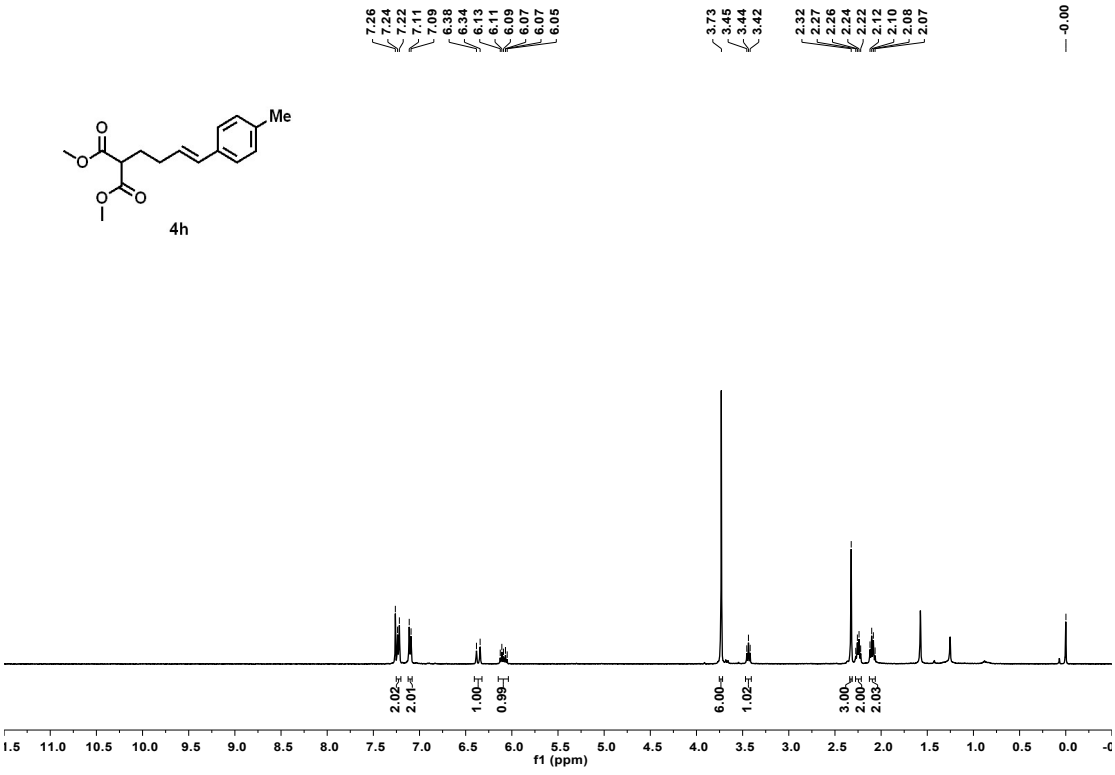
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4g**



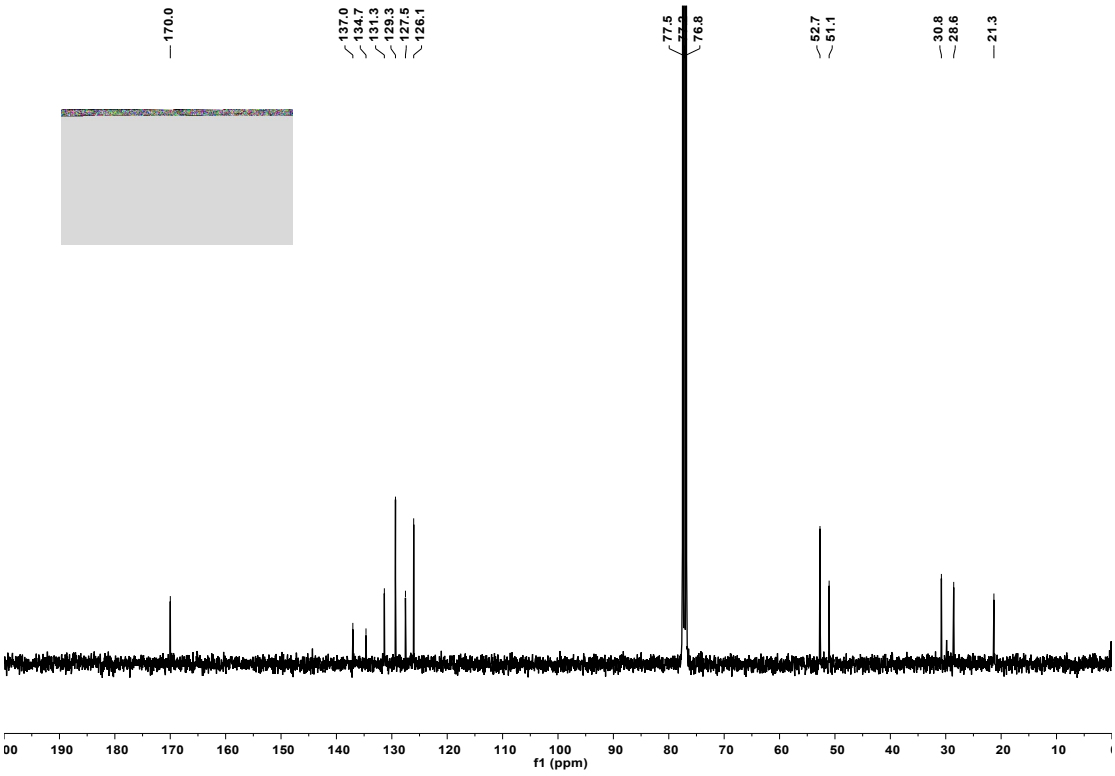
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4g**



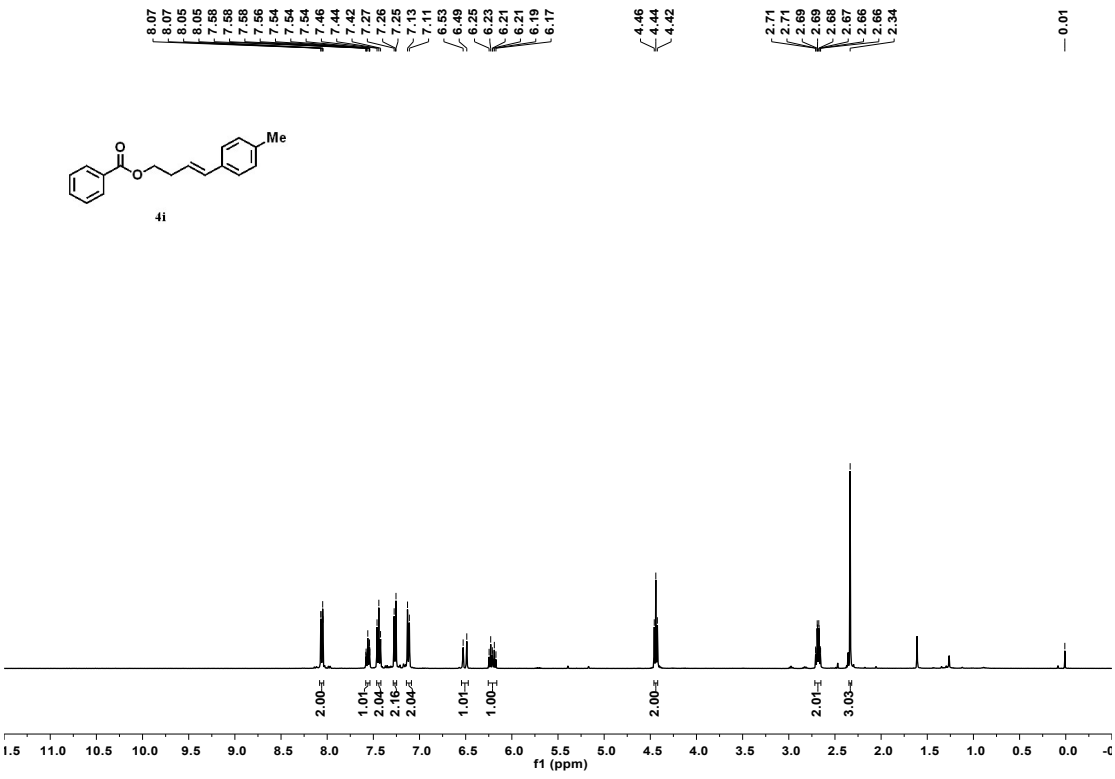
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4h**



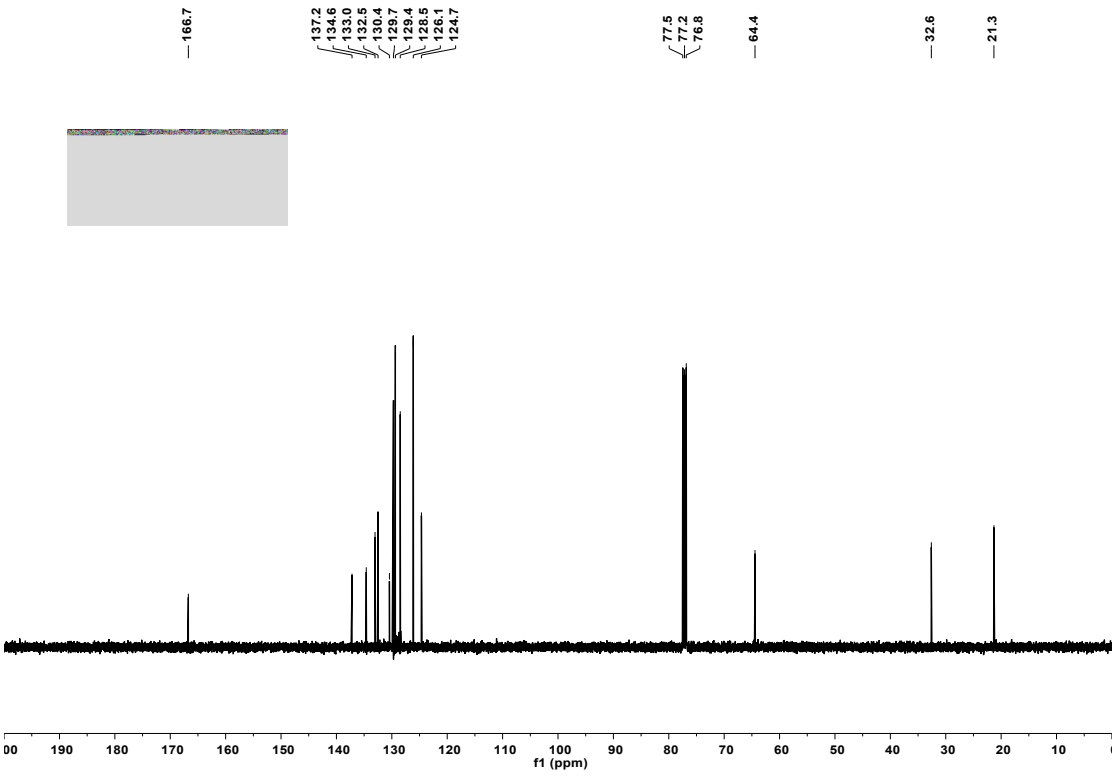
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4h**



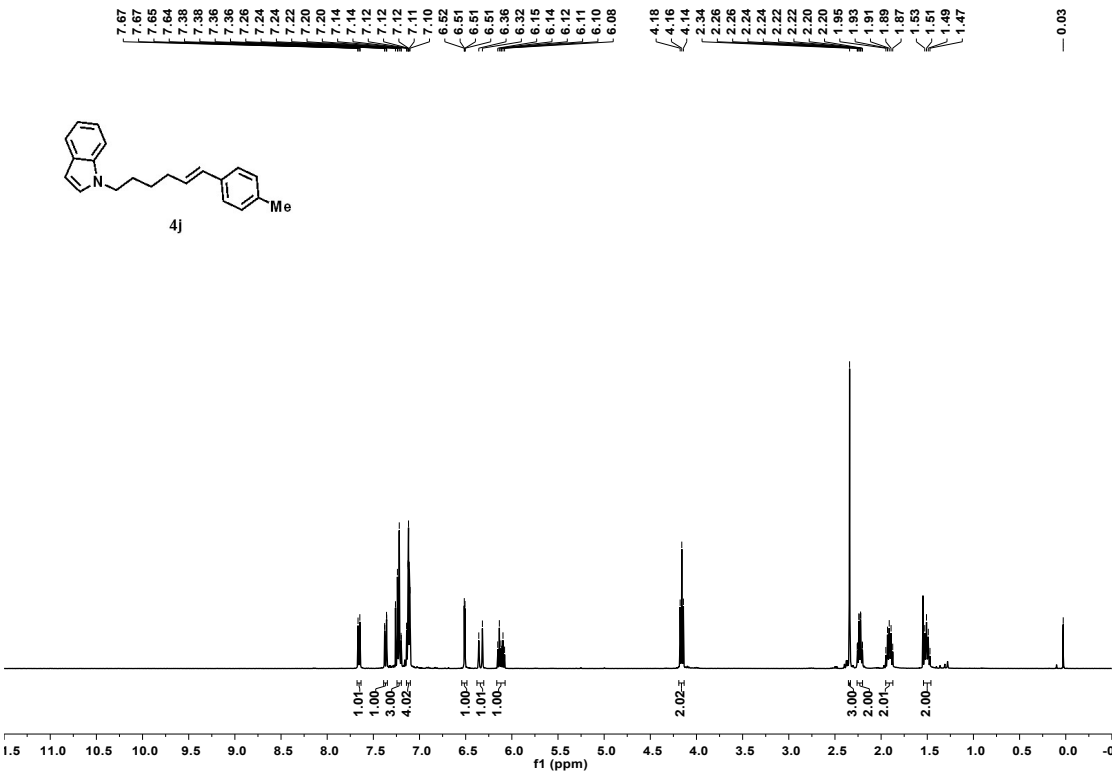
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4i**



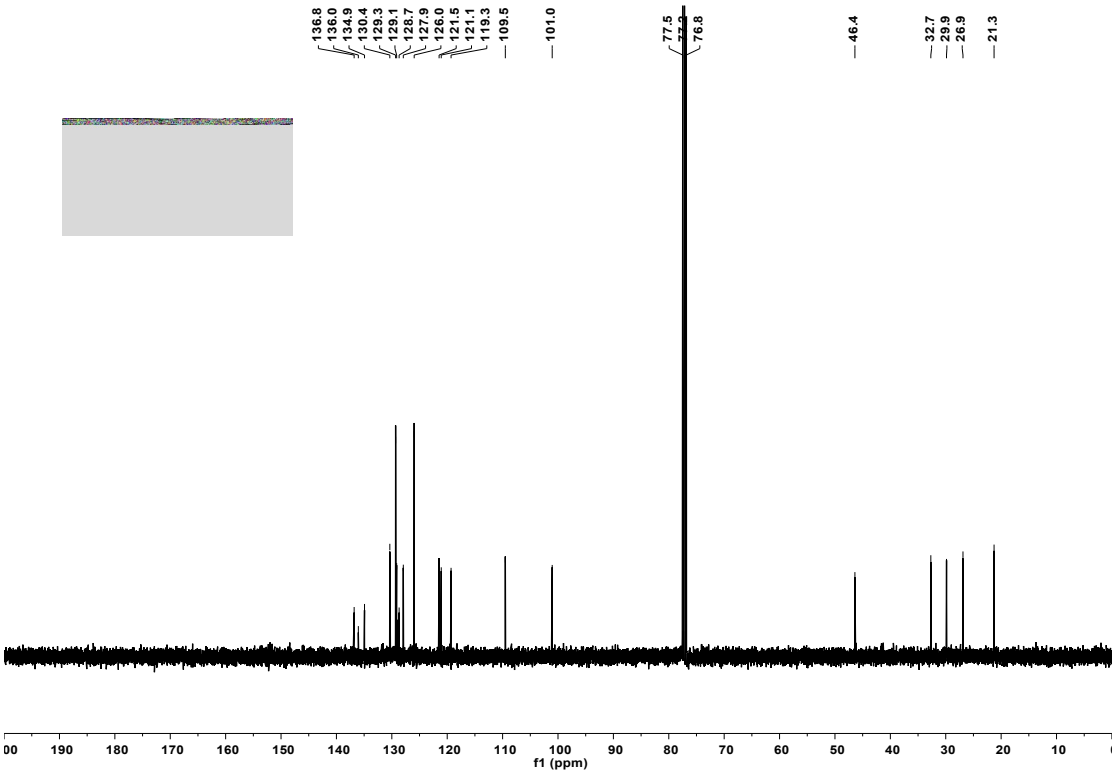
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4i**



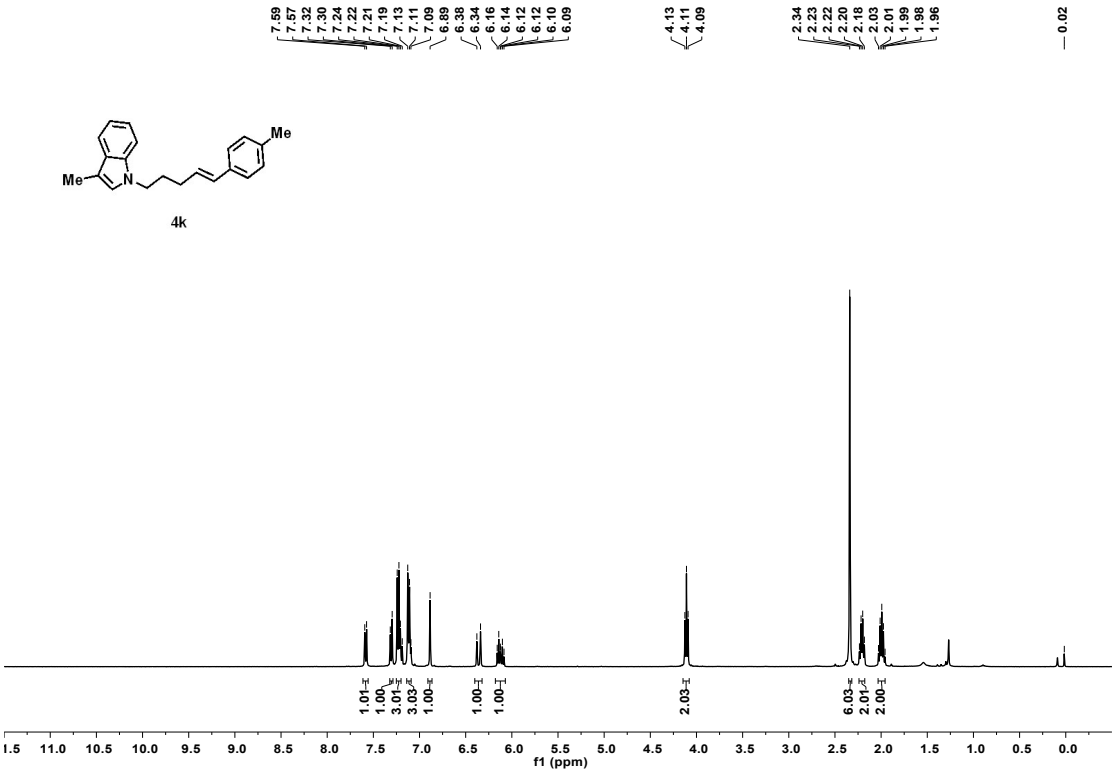
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4j**



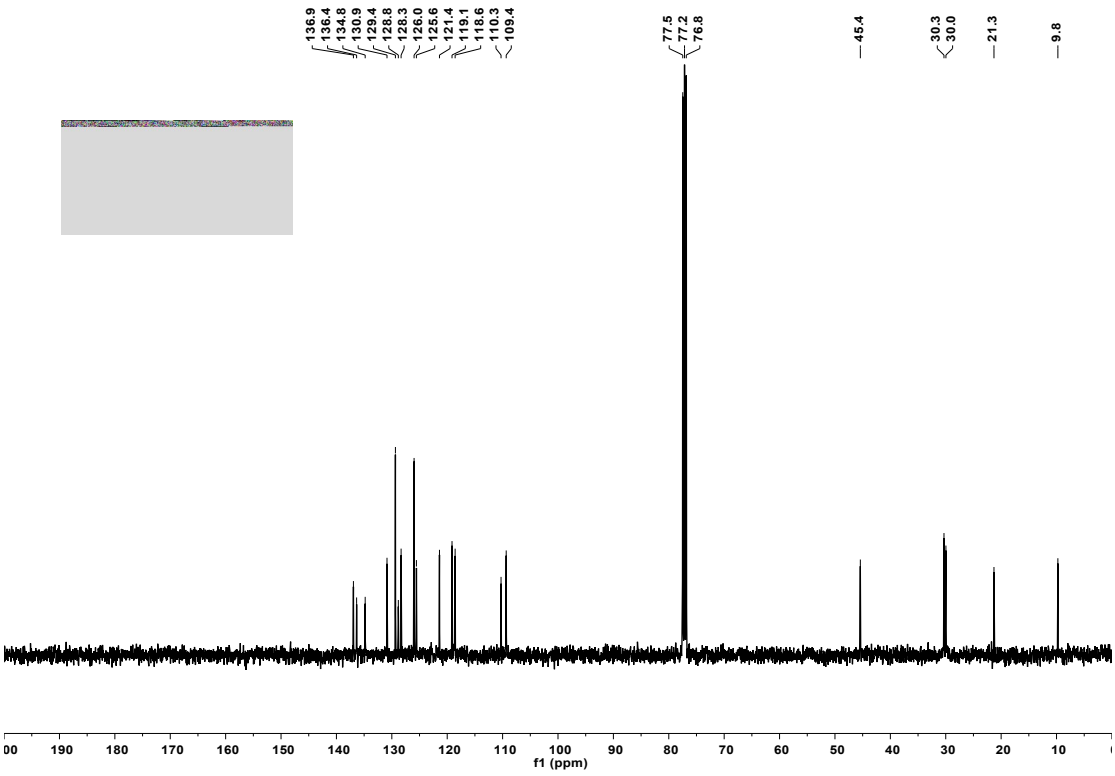
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4j**



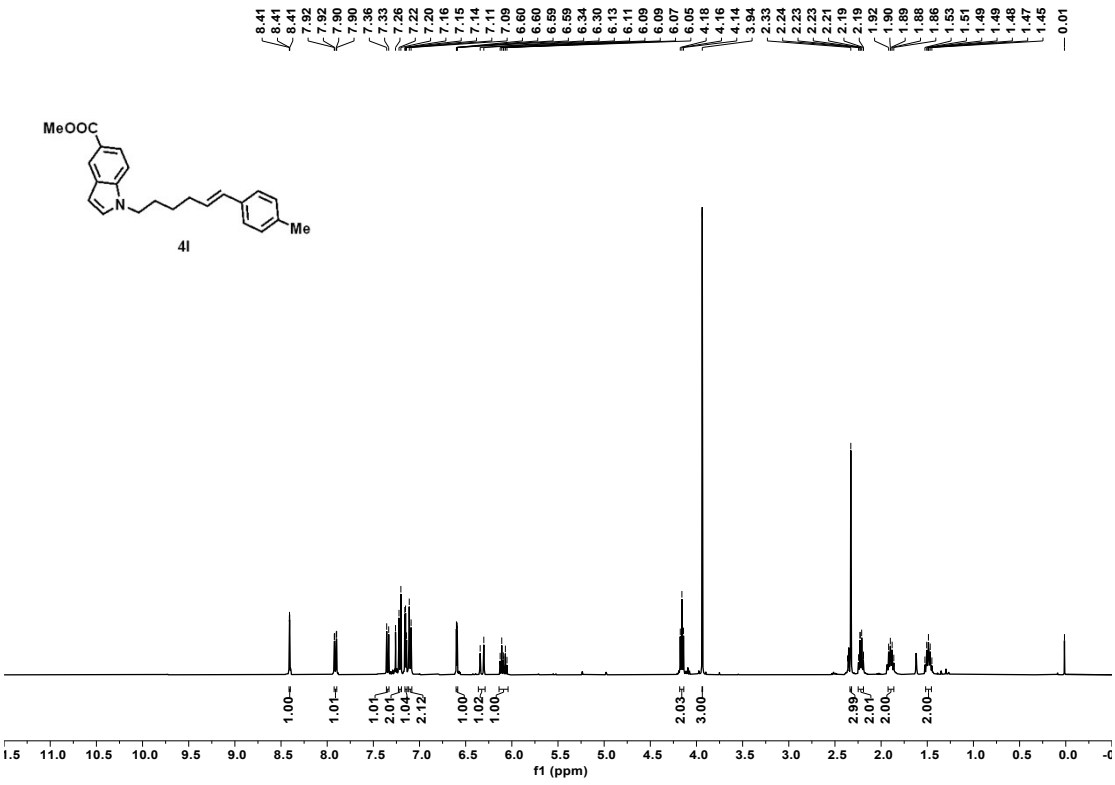
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4k**



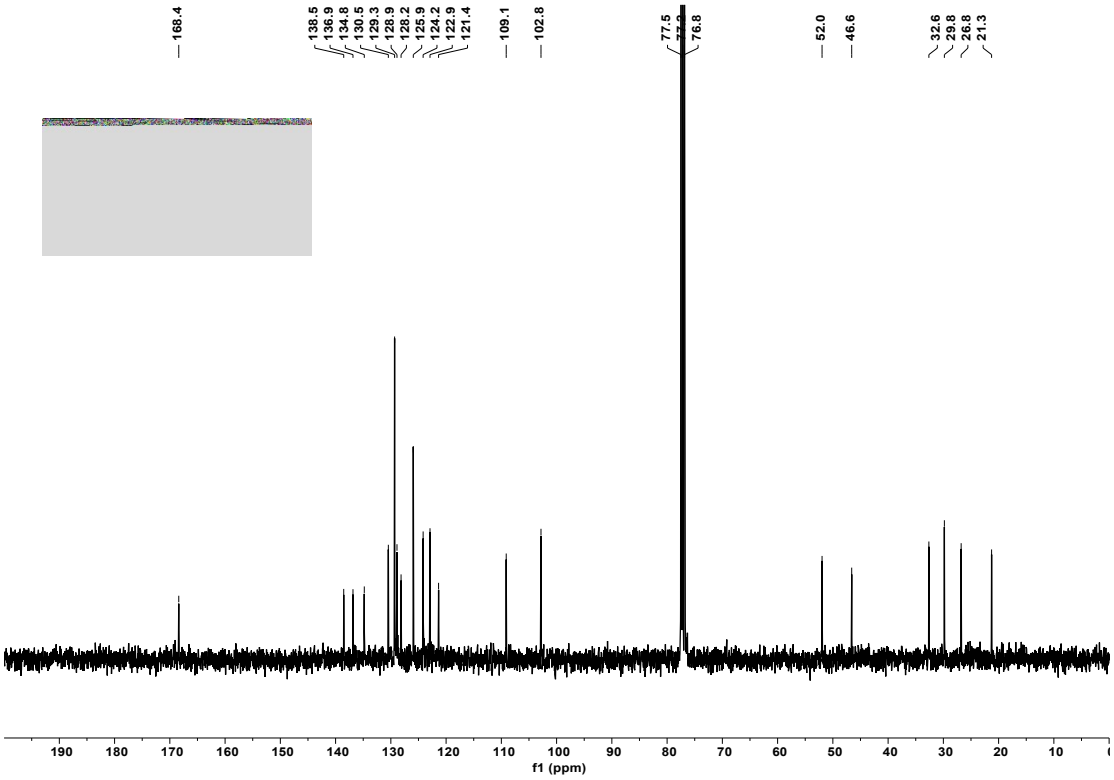
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4k**



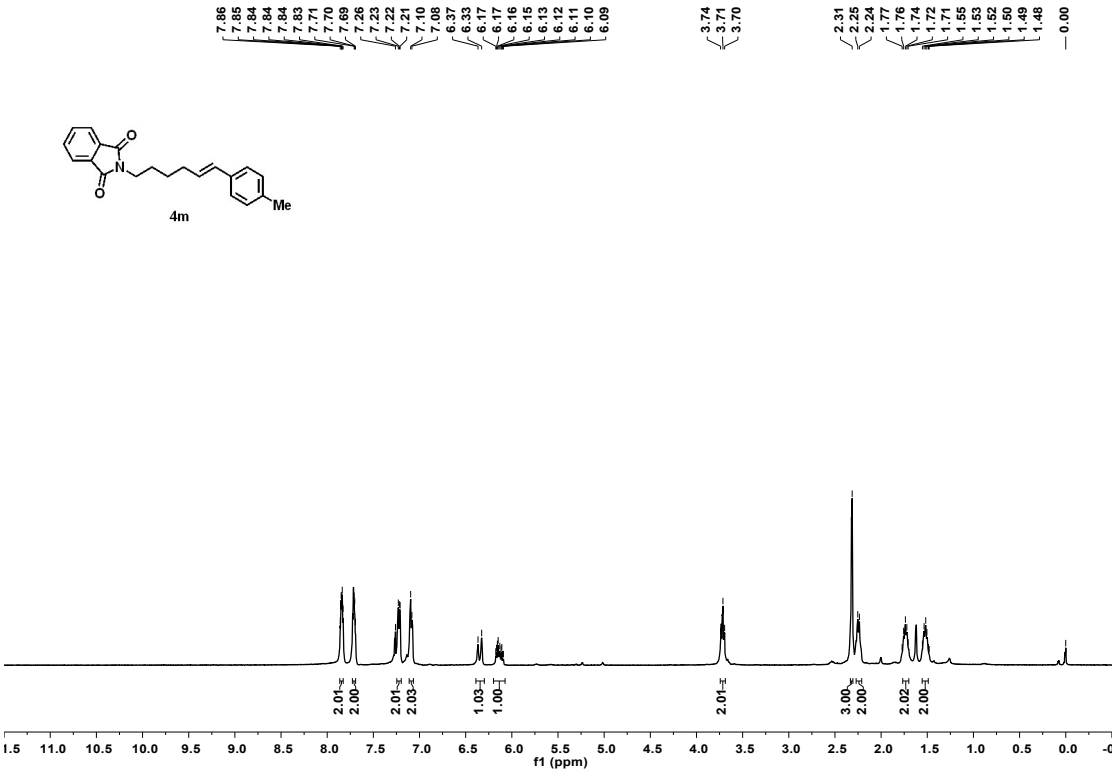
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4l**



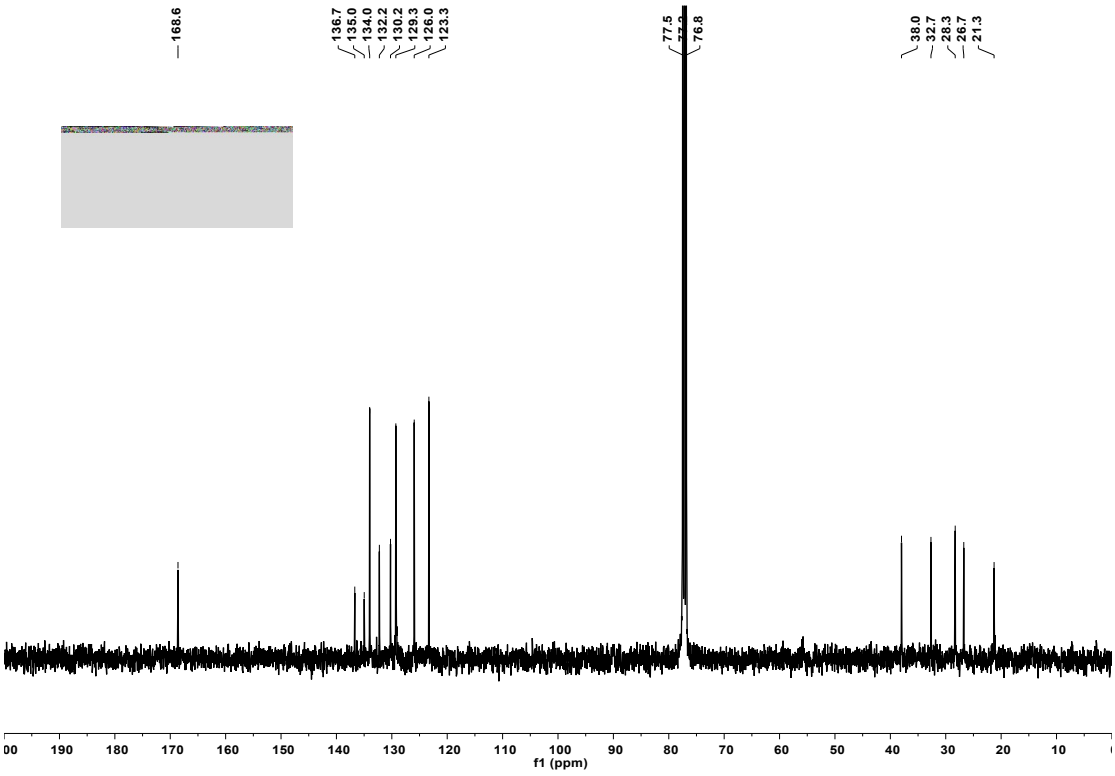
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4l**



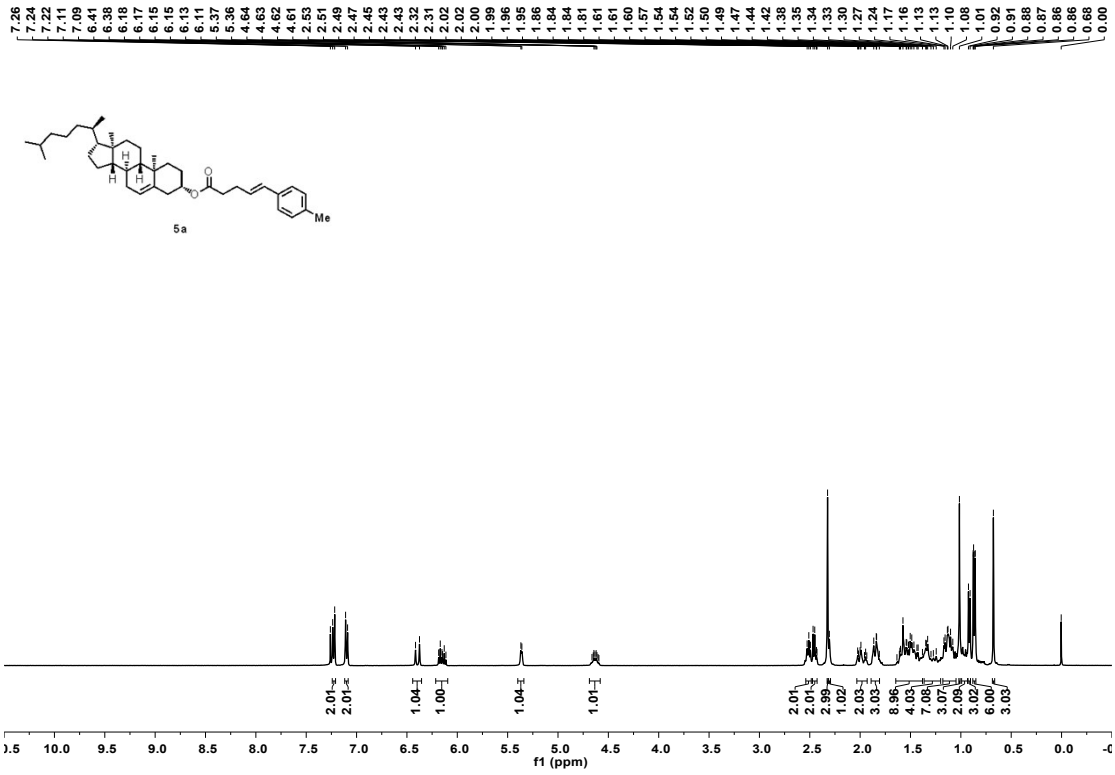
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4m**



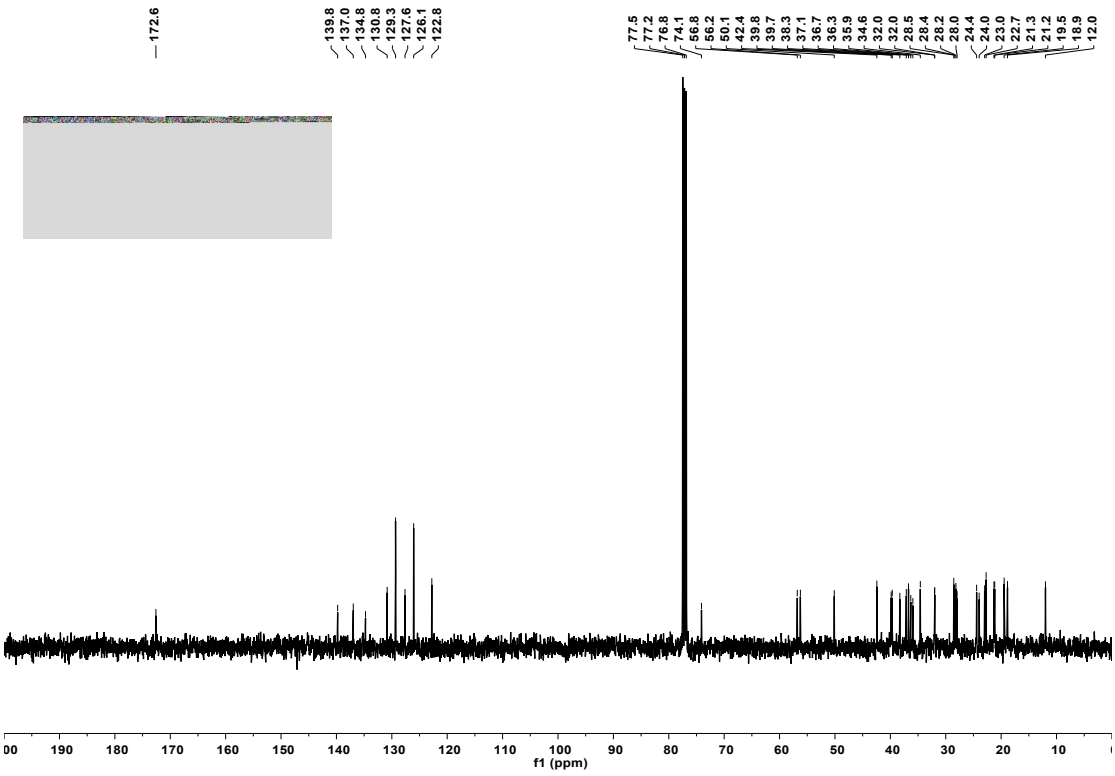
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4m**



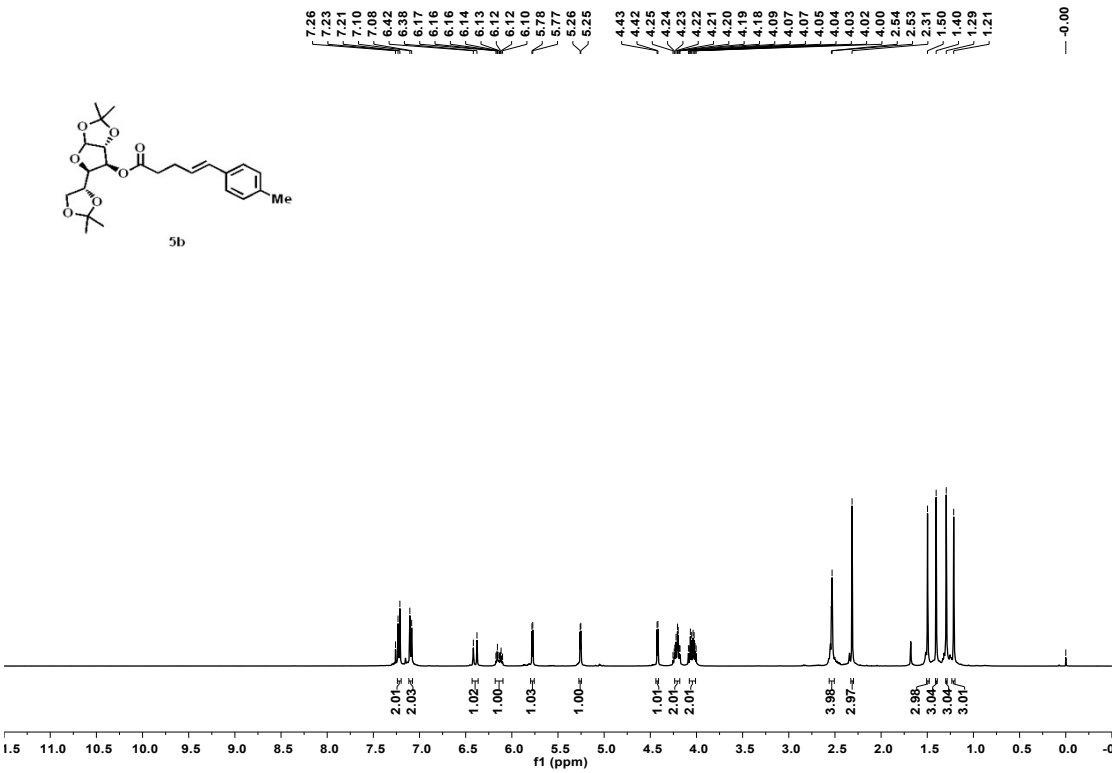
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5a**



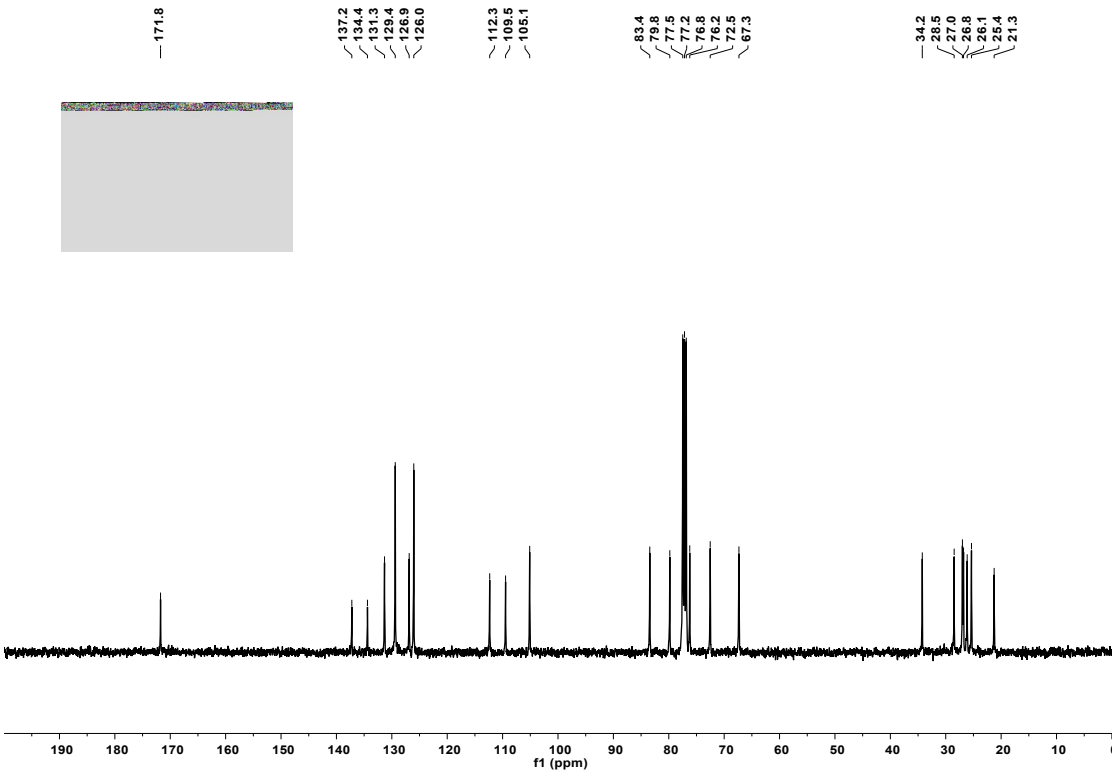
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **5a**



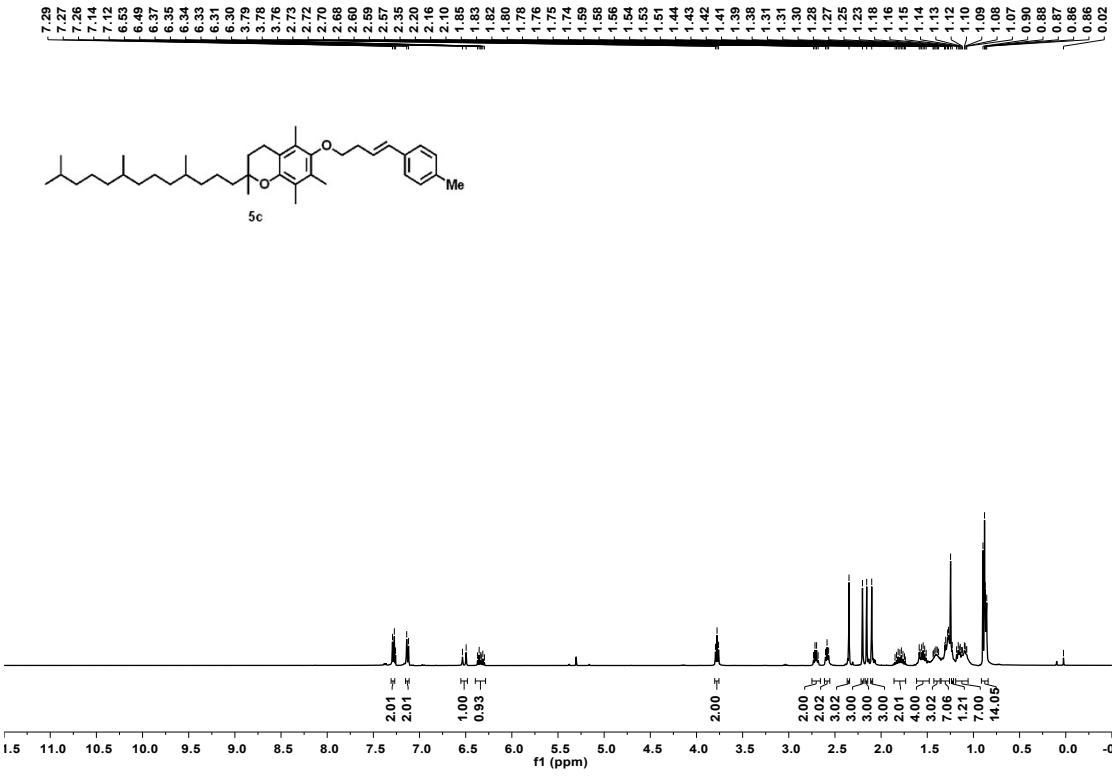
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5b**



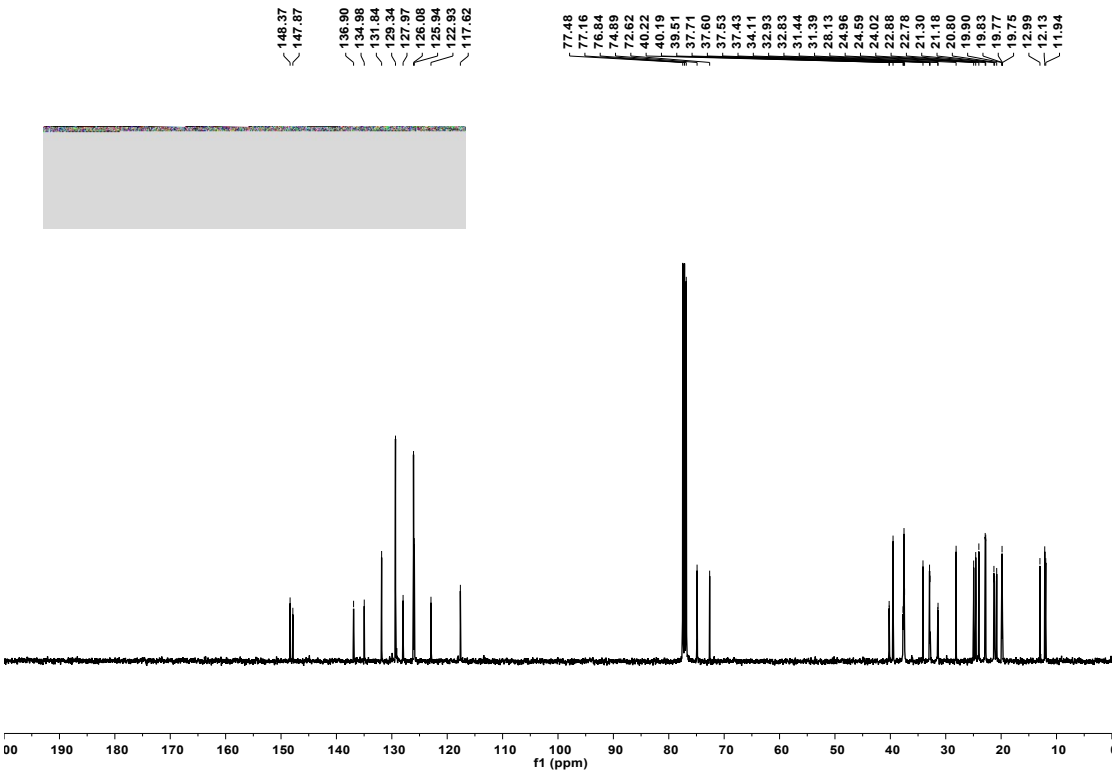
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **5b**



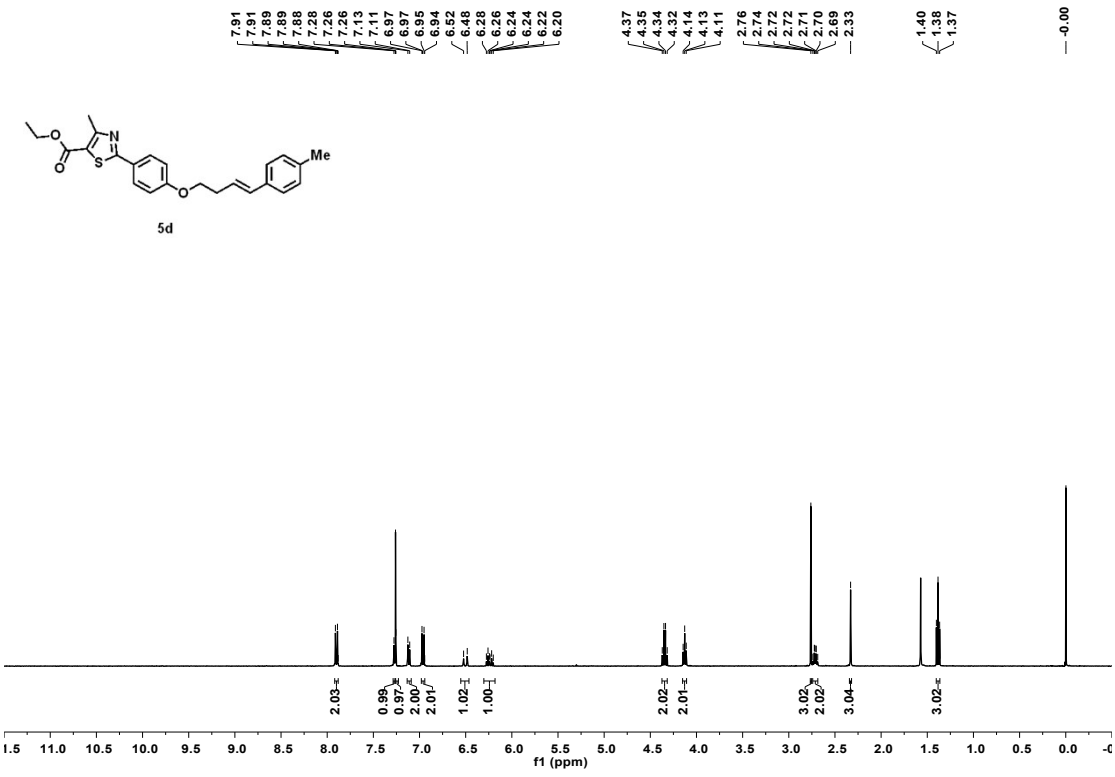
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5c**



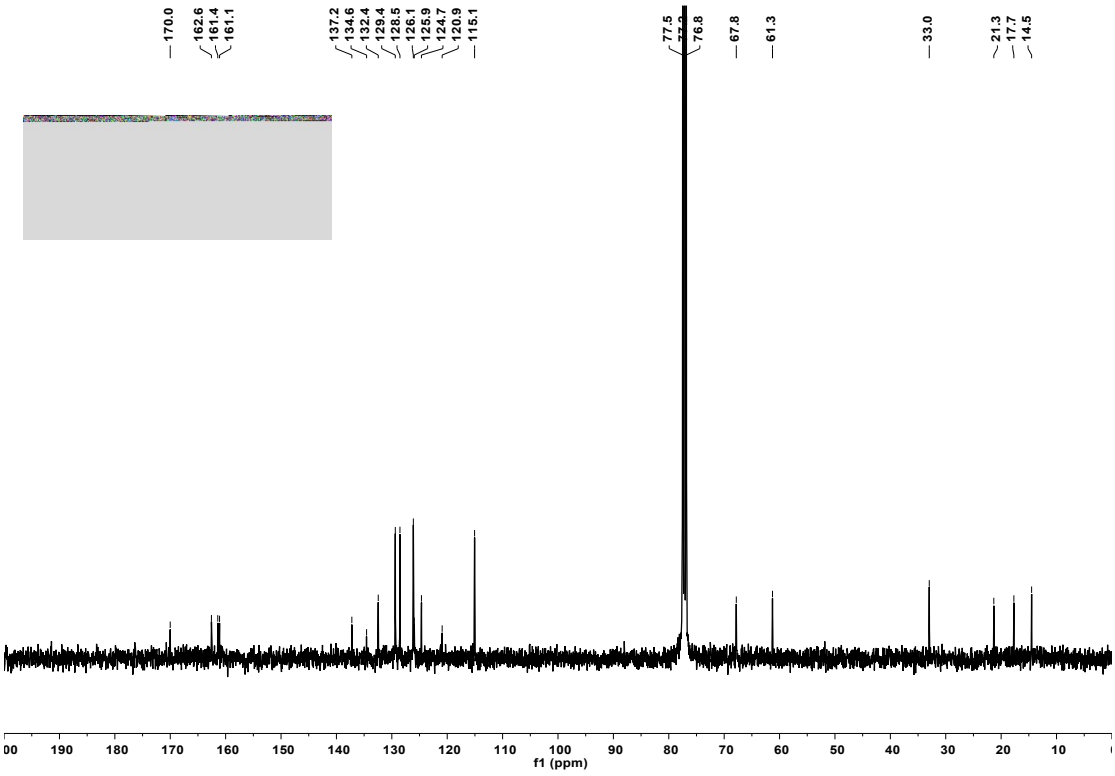
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **5c**



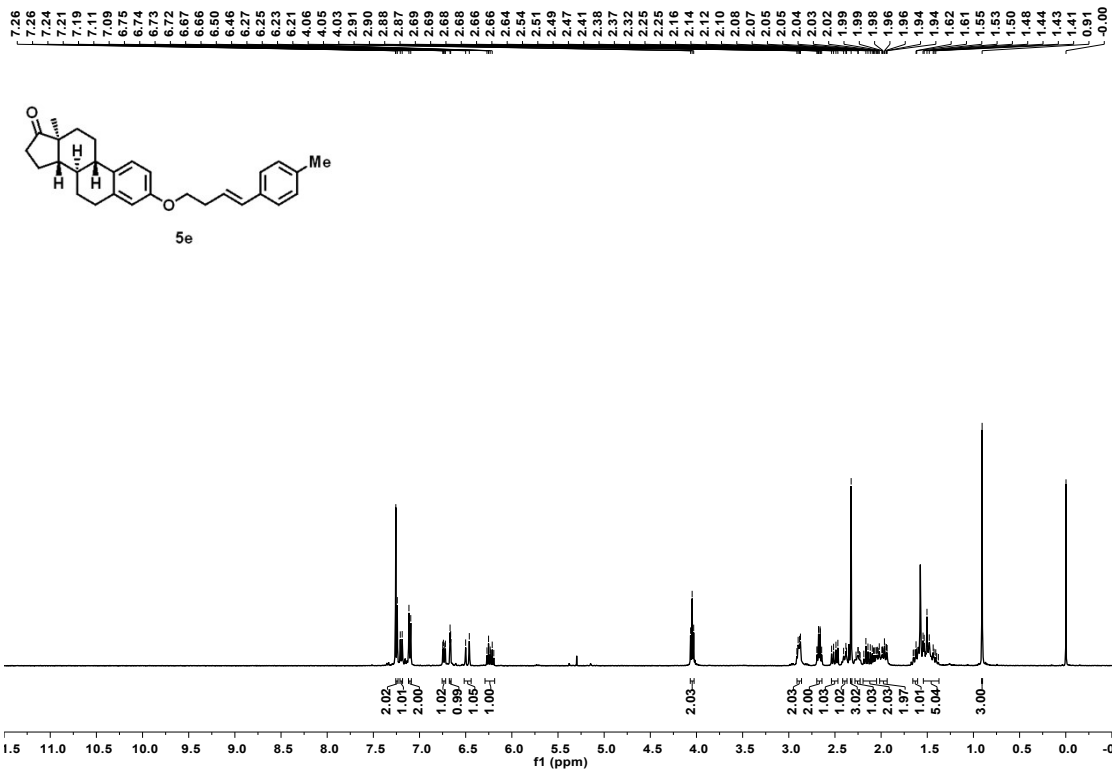
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5d**



^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **5d**



^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5e**



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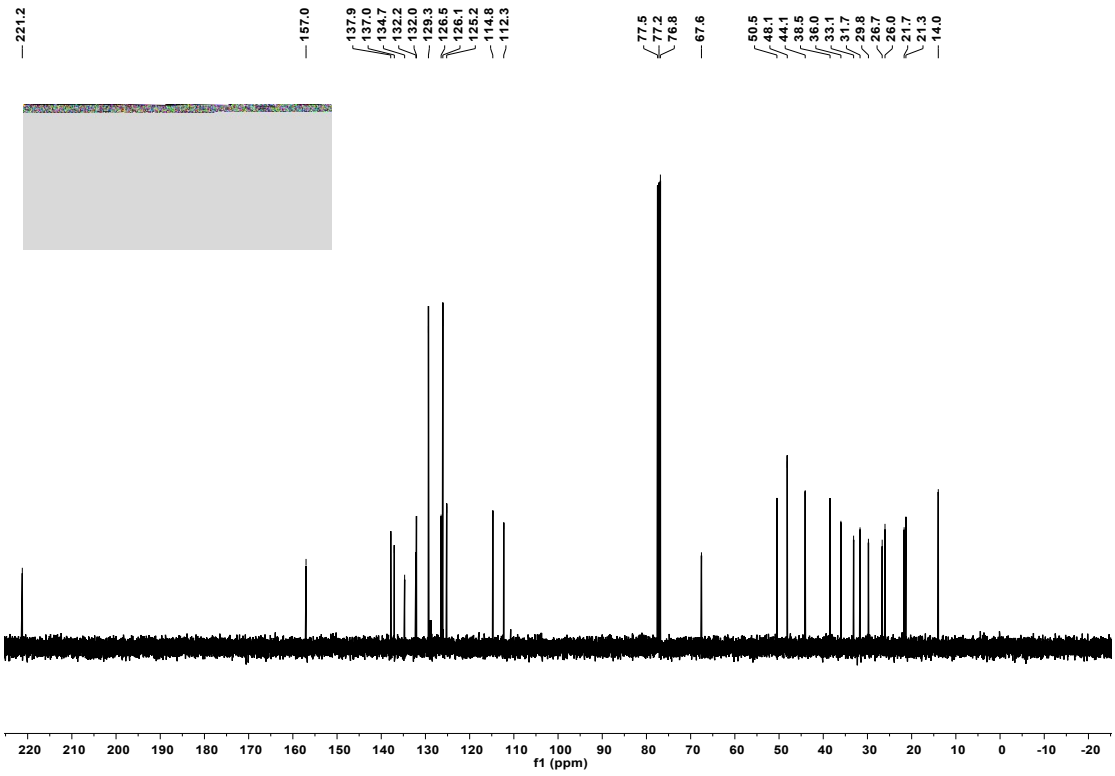
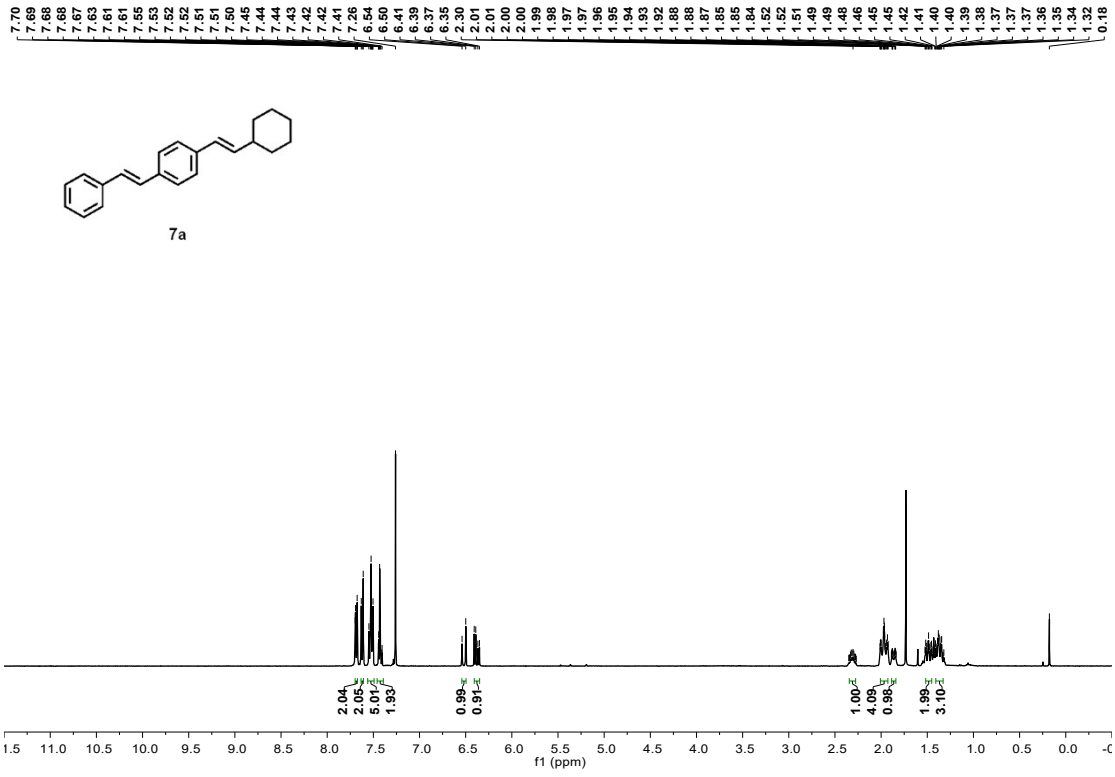
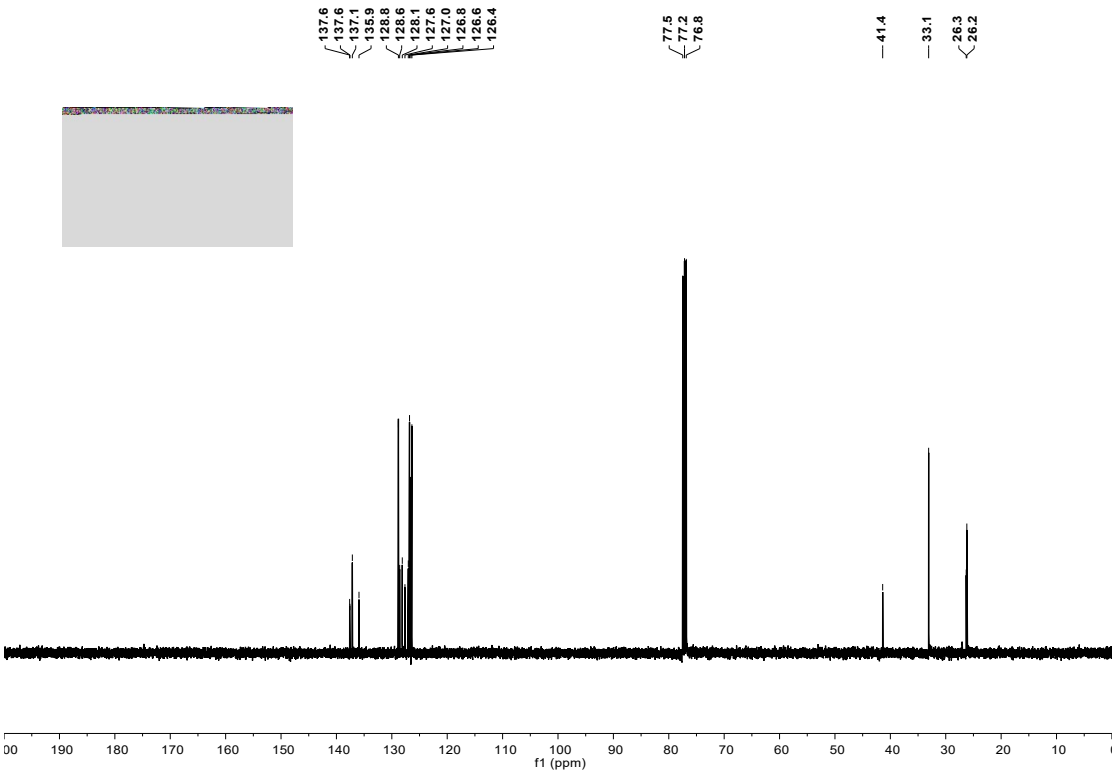


^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7a**



^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **7a**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77.2
76.8
41.4
33.1
26.3
26.2
f1 (ppm)