

Supporting Information

Direct *Trans*-Selective Ruthenium-Catalyzed Reduction of Alkynes in Two-Chamber Reactors and Continuous Flow

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1. General Information:

Unless otherwise stated all reactions were carried out under Argon in flame dried glassware using standard Schlenk- and GloveBox- techniques. All hydrogenations were carried out in flame dried two-chamber systems (COware) with a total volume of 20 ml, capped with H-caps.

All commercially available reagents were purchased from either *Acros Organics*, *Alfa Aesar*, *Fluorochem*, *Sigma Aldrich*, *Strem Chemicals Inc.* or *TCI* and were used without further purification, unless otherwise stated. All solvents were purified according to standard procedures,¹ absolute solvents were stored over molecular sieves under an atmosphere of Argon. NMR solvents were purchased from *Deutero GmbH* or *euriso-top* and were used as purchased. Diaryl alkynes that were not commercially available were prepared according to literature procedures from the corresponding mono-aryl alkynes and aryl halides.²

Whenever possible, reactions were monitored by thin layer chromatography (TLC) using silica gel precoated aluminium sheets (0.2 mm, *Merck and co*). Purifications were performed by flash column chromatography over silica (60 Å pore size, 230 – 400 mesh, *Fluka Analytical*) using a specified solvent mixture and elevated pressure.

All NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer (¹H: 400 MHz, ¹³C: 101 MHz, ¹⁹F: 376 MHz, ³¹P: 161 MHz) at 298K. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (0 ppm) using the solvent as internal standard (Acetone-*d*₆: ¹H δ = 2.05 ppm, ¹³C δ = 29.92 ppm; CD₃CN: ¹H δ = 1.94 ppm, ¹³C δ = 1.32 ppm; CDCl₃: ¹H δ = 7.26 ppm, ¹³C δ = 77.16 ppm; C₆D₆: ¹H δ = 7.16 ppm, ¹³C δ = 128.06 ppm; DMSO-*d*₆: δ = 2.05 ppm, ¹³C δ = 39.52; THF-*d*₈: ¹H δ = 3.58 ppm, ¹³C δ = 25.31 ppm).¹ Coupling constants are quoted in Hz (*J*). Splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), septet (sep) or combinations thereof. Splitting patterns that could not be interpreted were designated as multiplet (m).

2. COware and the H-cap System:

H-caps:

PFTE caps sealed with two NBR70, 7.1 x 1.6 mm O-rings for tight fit to the vials of COware.

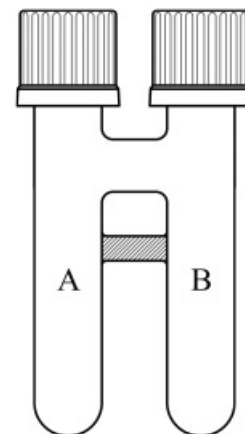
COware:

Two glass vials (Chamber A and B) connected with a glass tube to allow gas-transfer.

Total Volume = 20 mL.

Glassware under pressure - Warning!

- Glass equipment should always be examined for damages to its surface, which may weaken its strength.
- One must abide to all laboratory safety procedures and always work behind a shield when working with glass equipment under pressure.
- COware is pressure tested to 224 psi, but should under no circumstances be operated above 60 psi (5 bar).



3: Optimization of Reaction Parameters

Reaction progress was monitored by GC analysis, unless otherwise mentioned. All yields refer to GC yields, employing mesitylene as standard, using an Agilent HP-5 column, 30m, 0.32 mm diameter, 0.25µm film.

Table S1: Catalyst Screening for the Ru-Catalyzed Hydrogenation of Diphenylacetylene (**1a**).

$ \text{Ph}-\text{C}\equiv\text{C}-\text{Ph} \xrightarrow[\text{CHCl}_3, 45^\circ\text{C}, 18\text{ h}]{\begin{matrix} [\text{Ru}] (5\text{ mol \%}) \\ \text{H}_2 (10\text{ equiv.}) \end{matrix}} \text{Ph}-\text{CH}=\text{CH}-\text{Ph} + \text{Ph}-\text{CH}=\text{CH}-\text{Ph} + \text{Ph}-\text{CH}_2-\text{CH}_2-\text{Ph} $					
	1a		2a	3a	4a
Entry	Catalyst	1a [%]	2a [%]	3a [%]	4a [%]
1	Ru(Me-allyl) ₂ cod	55	12	33	0
2	[Cp*Ru(cod)Cl]	0	75	0	25
3	[(p-cymene)RuCl ₂] ₂	100	0	0	0
4	Ru(PPh ₃) ₃ Cl ₂	0	5	95	0
5	Ru(acac) ₃	100	0	0	0
6	[RuCp(CO) ₂] ₂	100	0	0	0
7 ^a	Ru(PPh ₃) ₃ Cl ₂	0	10	90	0
8	Milstein	100	0	0	0
9	Ru(PPh ₃) ₃ CO(Cl)H	0	100	0	0
10	Ru ₃ (CO) ₁₂	75	4	21	0
11	Ru(PPh ₃) ₄ H ₂	0	4	96	0
12	RuCl ₃	100	0	0	0
13	Ru(PPh ₃) ₃ CO(Cl)H	0	100 (98%)	0	0
14 ^b	Ru(PPh ₃) ₃ CO(Cl)H	0	100	0	0
15 ^c	Ru(PPh ₃) ₃ CO(Cl)H	11	86	3	0
16 ^d	[Cp*Ru(cod)Cl]	60	30	0	10
17 ^e	[Cp*Ru(cod)Cl]	25	50	0	25

^aUsing Cul (10 mol%) as additive. ^bUsing 2.5 mol% catalyst. ^cUsing 1 mol% catalyst. ^dReaction conducted at rt. ^eUsing 2.5 mol% catalyst.

Table S2: Solvent Screening for the Ru-Catalyzed Hydrogenation of Diphenylacetylene (**1a**).

Entry	Solvent	1a [%]	2a [%]	3a [%]	4a [%]
1 ^a	CHCl ₃	50	40	10	0
2 ^a	CH ₂ Cl ₂	40	45	15	0
3 ^a	DCE	55	25	20	0
4	DCE	0	100	0	0
5	THF	0	100	0	0
6	MeCN	90	3	7	0
7	MeOH	85	5	10	0
8	Toluene	0	100	0	0

^aConducted at room temperature.**Table S3:** The Effect of AgOTf to the Ru-Catalyzed Hydrogenation of Diphenylacetylene (**1a**).

Entry	Cat. (%)	AgOTf (%)	Temp. °C	1a [%]	2a [%]	3a [%]	4a [%]
1	5	6	45	0	100	0	0
2	2.5	3.5	45	2	98	0	0
3	5	6	rt	60	25	15	0
4	2.5	3.5	rt	95	2	3	0

Table S4: Screening of the Catalyst Loading for the Ru-Catalyzed Hydrogenation of Diphenylacetylene (**1a**).

$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph} \xrightarrow[\text{CHCl}_3, 45^\circ\text{C}, 18\text{ h}]{[\text{Ru}] (5\text{ mol \%}), \text{H}_2 (10\text{ equiv.})} \text{Ph}-\text{CH}=\text{CH}-\text{Ph} + \text{Ph}-\text{CH}=\text{CH}-\text{Ph} + \text{Ph}-\text{CH}_2-\text{CH}_2-\text{Ph}$					
		1a	2a	3a	4a
Entry	Catalyst (mol %)	1a [%]	2a [%]	3a [%]	4a [%]
1	1	25	5	70	0
2	2	5	90	5	0
3	2.5	0	100	0	0
4	3	0	100	0	0
5 ^a	3	15	75	5	0
6 ^a	5	0	100	0	0
7 ^b	2.5	50	40	10	0

^aReaction was set up outside the glovebox without dry solvents. ^bReaction was performed with a hydrogen balloon.

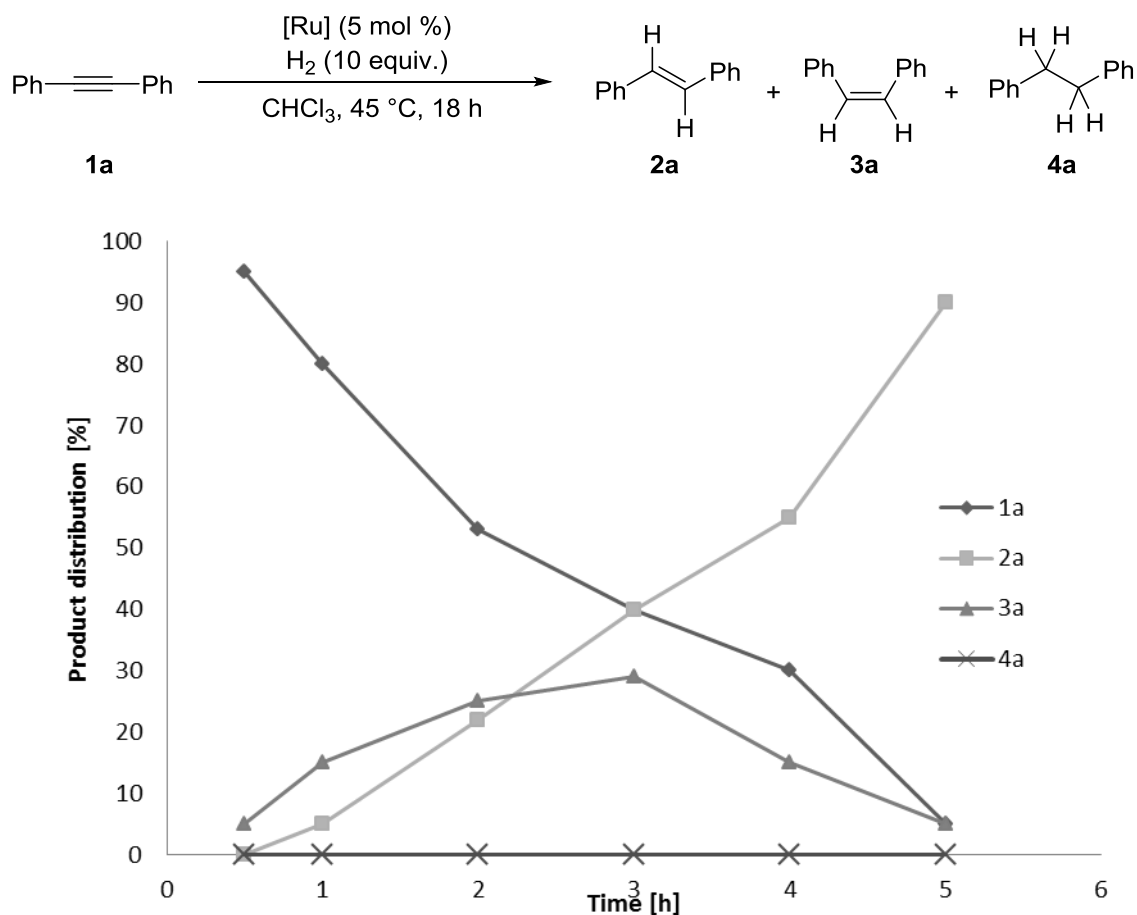


Figure S1: Product Distribution Over Time for the Ru-Catalyzed Hydrogenation of Diphenylacetylene (**1a**). The values for each measurement are from 5 independent experiments that were stopped after the corresponding reaction time and are an average over two independent experiments.

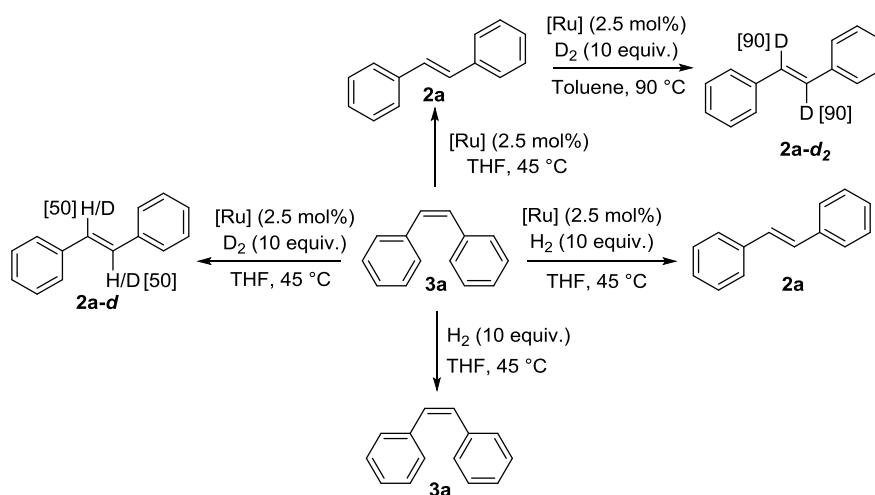


Figure S2: Reaction with *cis*-Stilbene. ^aProduct distribution is determined by GC and confirmed by H-NMR. [Ru]=Ru(PPh₃)₃CO(Cl)H. The number in squared brackets indicates the percentage of deuterium incorporation

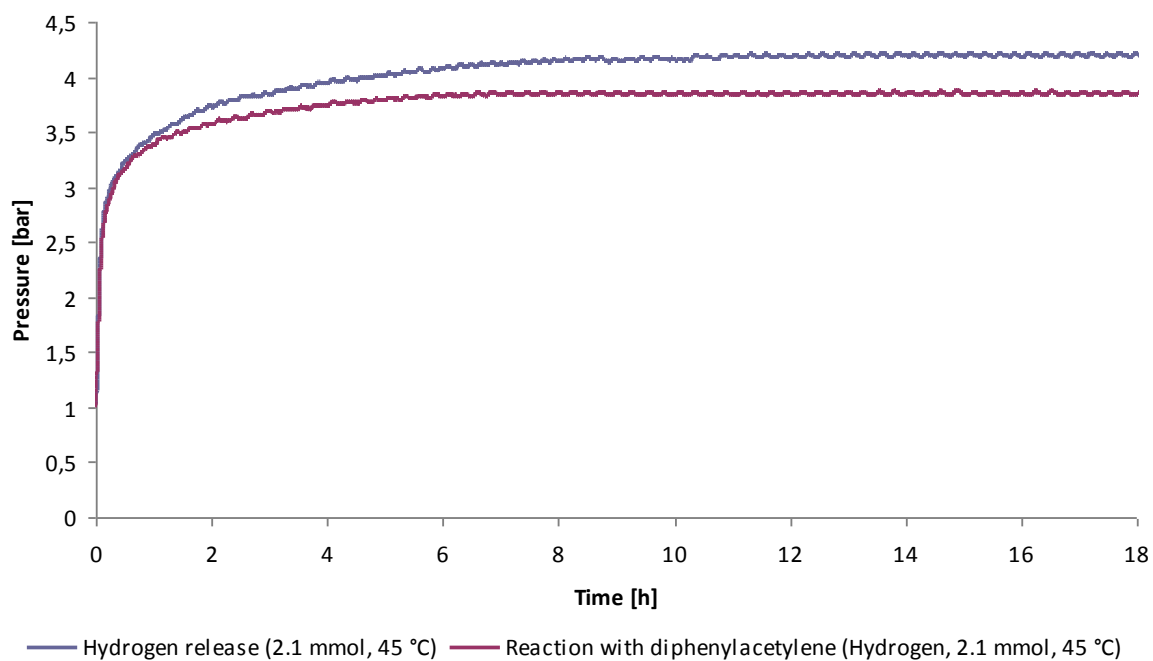


Figure S3: Pressure Measurements of the Ru-Catalyzed Hydrogenation of Diphenylacetylene (1a).

4. Mechanistic studies

4.1. H/D exchange experiments:

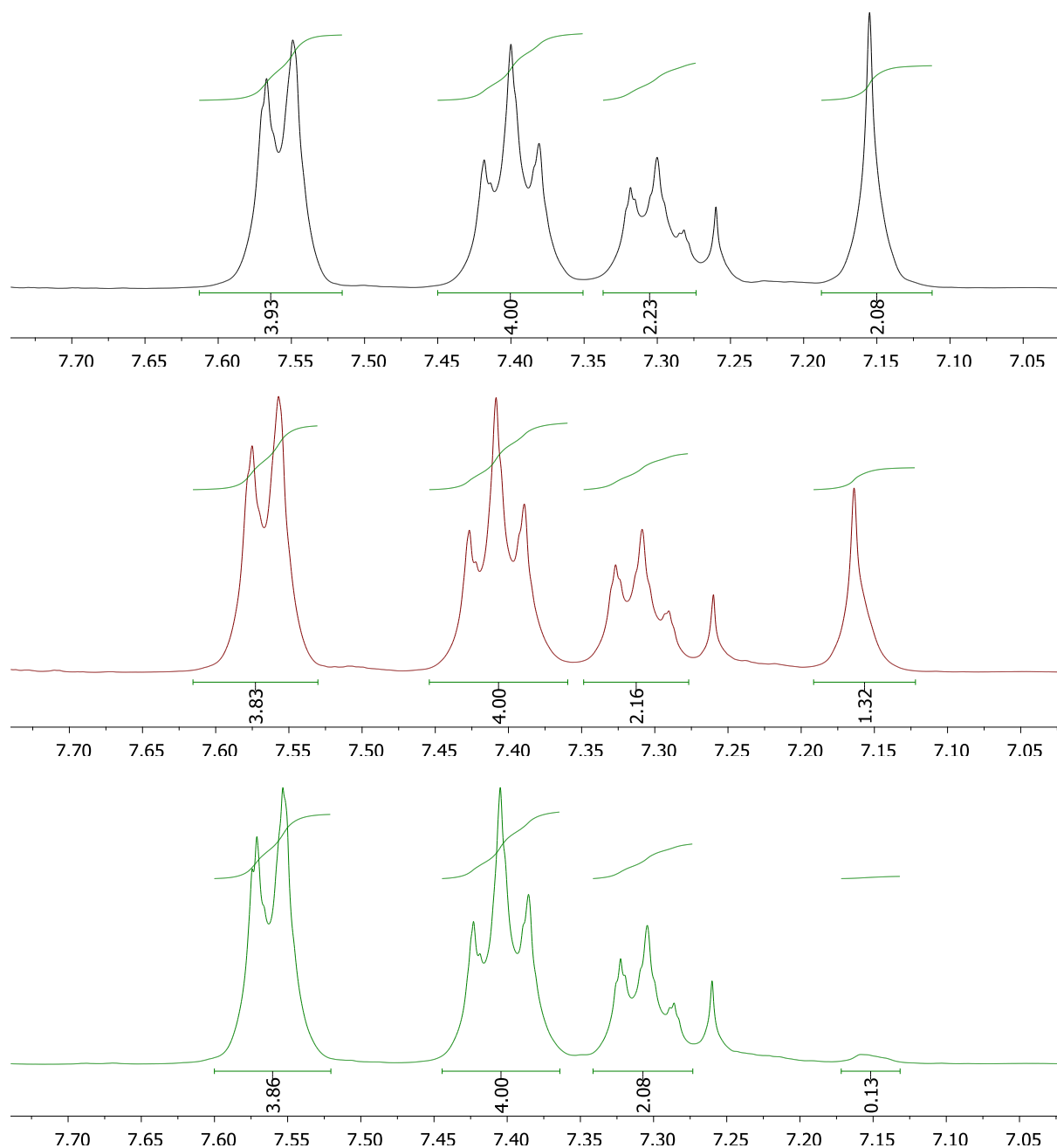


Figure S4: ^1H NMR (400 MHz, CDCl_3) spectra of *trans*-stilbene (**2a**) after treatment with $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{CO}$ and 10 equiv. of D_2 after 20 hours at 45 °C (black) 60 °C (red) and 90 °C (green). At 45 °C no H/D-exchange was observed, at 60 °C approximately 35% of deuterium incorporation can be observed, while the exchange at 90 °C was approximately 95%.

4.2. ^{31}P NMR studies:

All ^{31}P -NMR spectra were measured at 162 MHz in C_6D_6 on a Bruker Ascend 400 MHz NMR spectrometer. All measurements were conducted with 150 scans, employing triethylphosphate as internal standard ($\delta = 0.00$ ppm). To ensure reproducibility of all experiments a stock solution of triethylphosphate (38.23 μL) in C_6D_6 (15 mL) was used for all measurements.

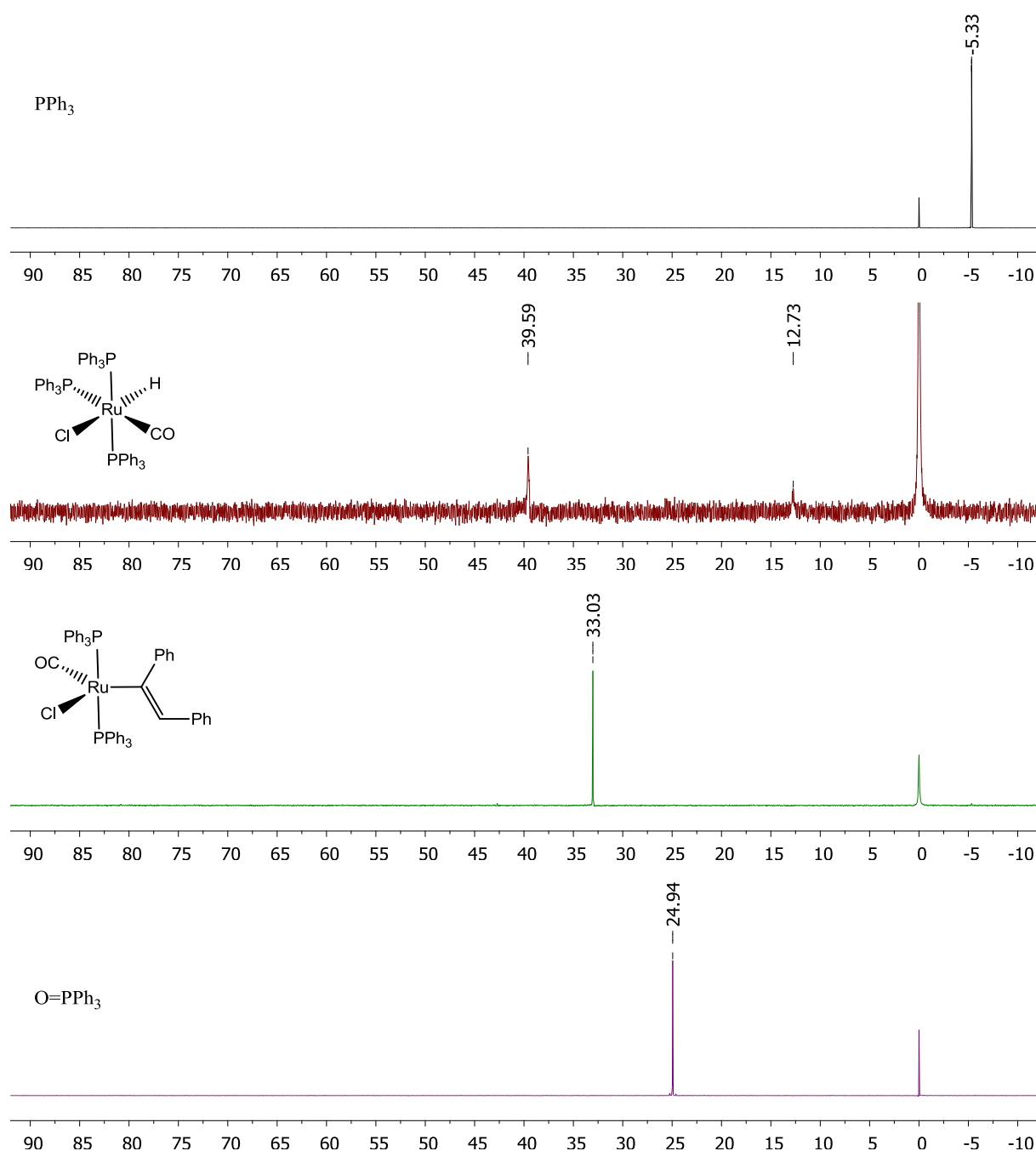


Figure S5: ^{31}P NMR Reference spectra of PPh_3 (black), $\text{Ru(PPh}_3)_3\text{H(Cl)CO}$ (red), $\text{Ru(PPh}_3)_2(\text{PhC=CHP(Cl)CO})$ (green) and OPPh_3 (purple).

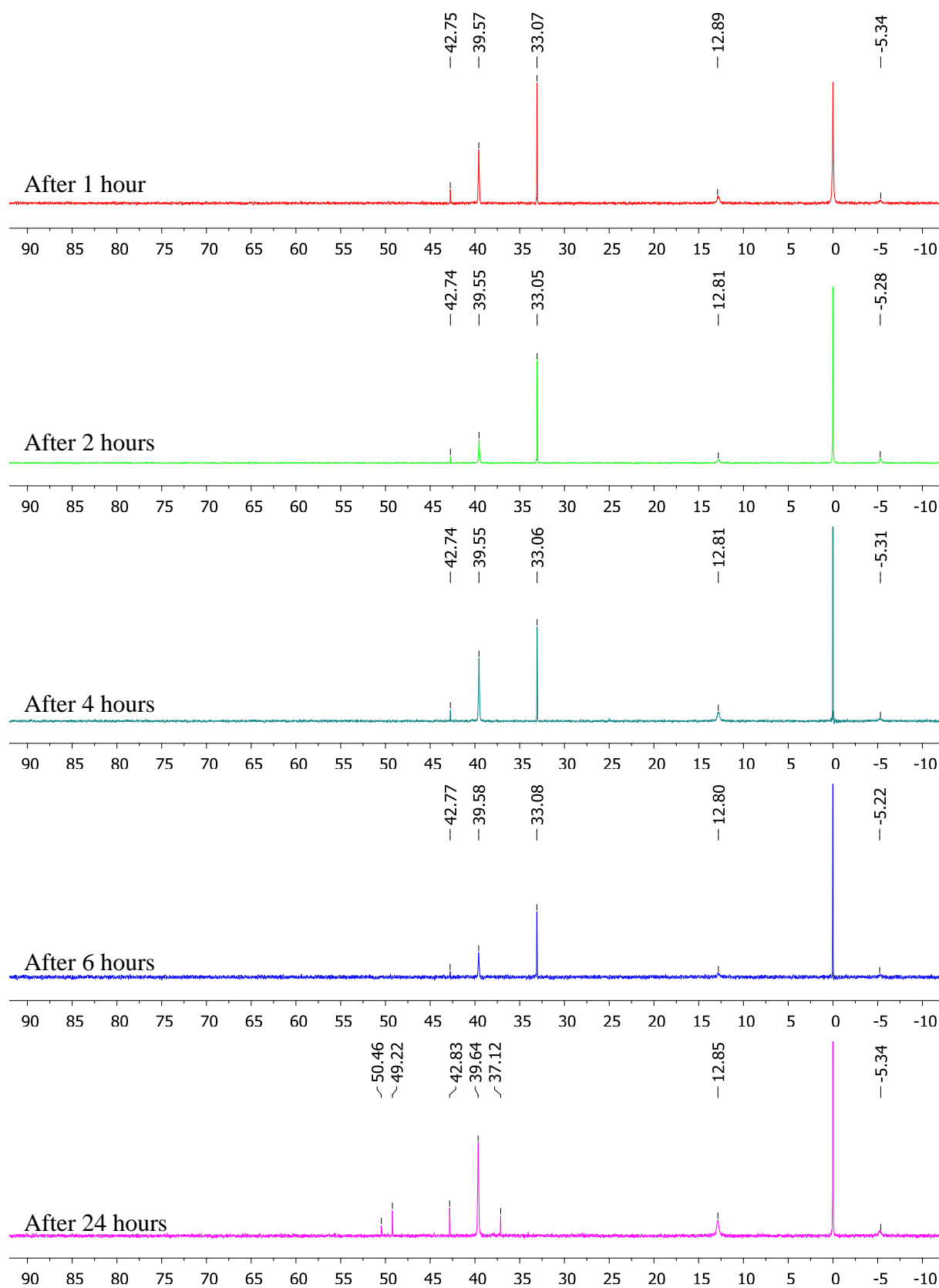


Figure S6: ^{31}P NMR spectra of the reaction mixture after 1- (red), 2- (green), 4- (cyan), 6- (blue) and 24 hours (magenta). Each spectrum was recorded from an independent reaction, which was stopped after the

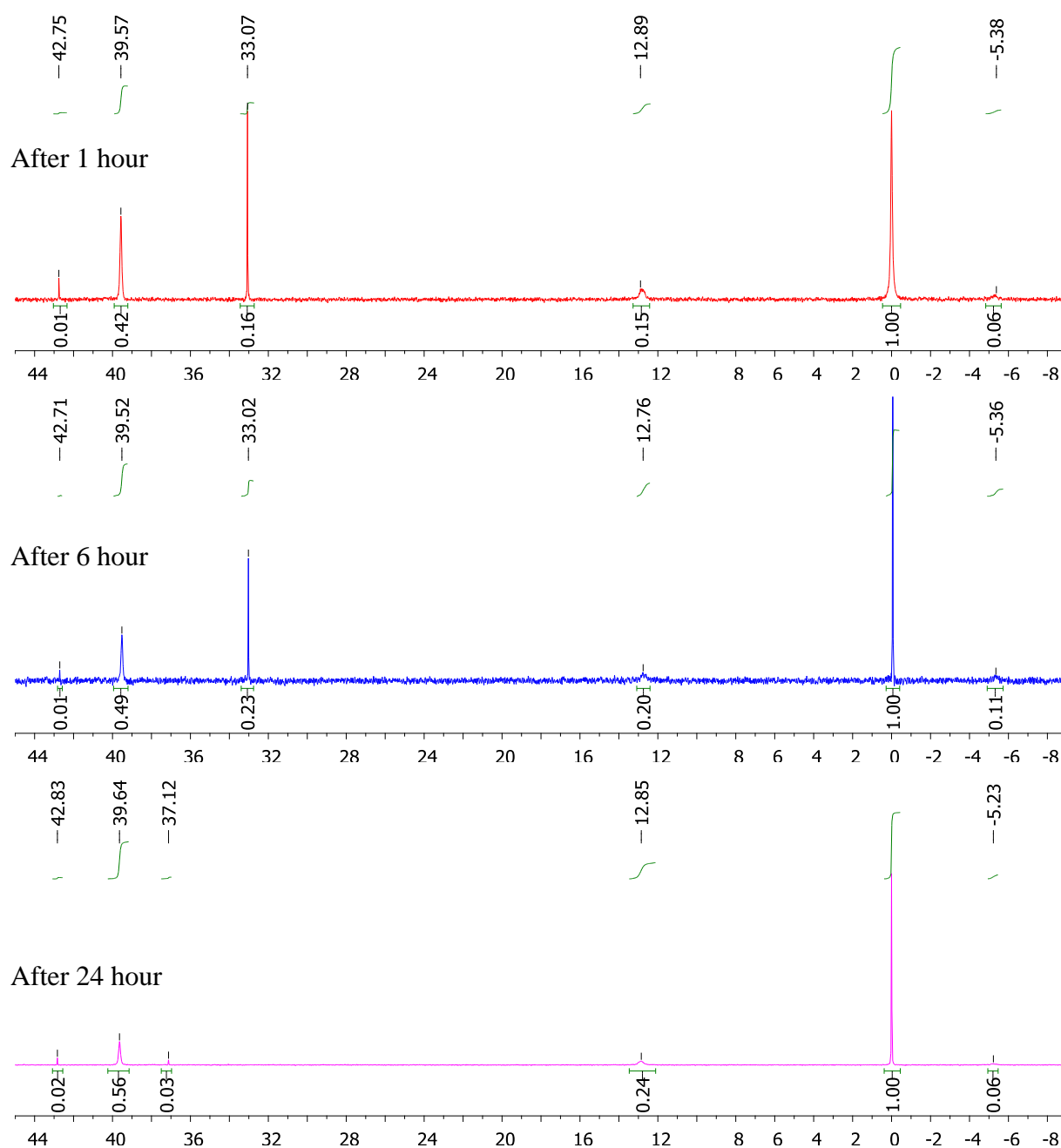
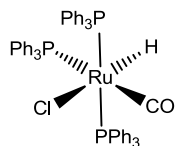


Figure S7: ^{31}P NMR spectra of the reaction mixture after 1-(red), 6-(blue) and 24 hours (magenta), with integration of the different phosphorous species, showing the high stability of the catalyst, which is reformed almost quantitatively.

5. Experimental Section

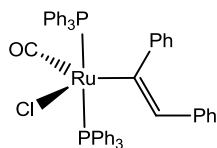
5.1. Preparation of Ru-complexes

$\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{CO}$



The compound was prepared following a procedure reported by Zeng *et al.*⁴ A solution of anhydrous RuCl_3 (207 mg, 1.0 mmol) in methoxyethanol (20 mL) and formaldehyde (37 – 40% in water, stabilised with 7 – 9% Methanol, 20 mL) was added to a refluxing solution of triphenylphosphine (1.58 g, 6.05 mmol) in methoxyethanol (60 mL) and the resulting mixture was refluxed for 2 h. After cooling to room temperature the precipitated off-white solid was collected, washed with ethanol, water, ethanol and *n*-pentane (50 mL each). Drying *in vacuo* afforded the title compound as an off-white microcrystalline solid (670 mg, 0.70 mmol, 70%). **^1H NMR (400 MHz, Acetonitrile- d_3):** δ = 7.77 – 7.26 (m, 45H), -13.00 (t, $J_{\text{P-H}}$ = 18.0 Hz, 1H) ppm. **^{31}P NMR (162 MHz, Acetonitrile- d_3):** δ = 50.31, -0.56 ppm. The spectral data corresponds to the one measured from a commercially available source.

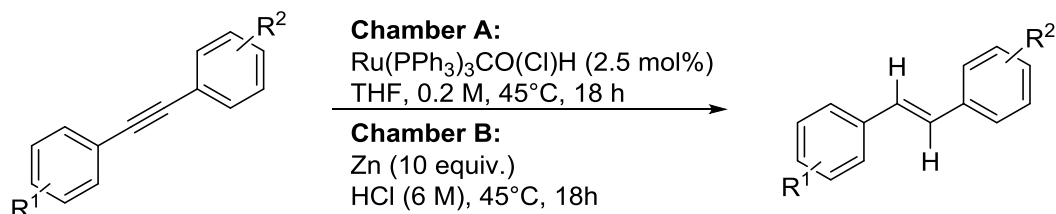
$\text{Ru}(\text{PPh}_3)_2(\text{PhC}=\text{CHPh})\text{CO}(\text{Cl})$



The compound was prepared following a procedure reported by Santos *et al.*⁵ To a solution of $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{CO}$ (193 mg, 0.2 mmol) in CH_2Cl_2 (7 mL) was added diphenylacetylene (135 mg, 0.76 mmol) and the resulting suspension was heated to reflux for 30 min. After cooling to room temperature all volatiles were removed *in vacuo*, and the resulting residue was purified by column chromatography over *Florisil*[®] (CH_2Cl_2). The red fractions were collected, and the solvent was evaporated to 1 mL and *n*-pentane (25 mL) was added and the resulting mixture was left to rest over night. Subsequent decantation of the solvent, from the formed orange-solid, and drying *in vacuo* resulted in the title compound (113 mg, 0.13 mmol, 65%). **^1H NMR (400 MHz, THF- d_8):** δ = 7.56 – 7.24 (m, 30H), 7.18 (t, J = 6.8 Hz, 1H), 6.87 – 6.73 (m, 5H), 6.57 (d, J = 7.2 Hz, 2H), 6.43 (d, J = 7.1 Hz, 2H), 5.36 (s, 1H) ppm. **^{31}P NMR (162 MHz, THF- d_8):** δ = 32.45 ppm. The spectral data corresponds to the one reported in literature.^{Fejl! Bogmærke er ikke defineret.}

5.2. *Trans*-Hydrogenation of Alkynes

General Procedure A (GPA):

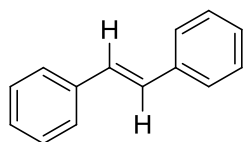


Chamber A: To chamber A of the two-chamber system was added alkyne (0.2 mmol) Ru(PPh₃)₃CO(Cl)H (4.8 mg, 0.005 mmol) and THF (1.0 mL) and the chamber was sealed using H-caps.

Chamber B: To chamber B of the two-chamber system was added Zn (137 mg, 2.0 mmol) and aqueous HCl (6M, 1 mL, 6.0 mmol) and the chamber was sealed using H-caps. (For deuterations the aqueous HCl solution was substituted for a 6M solution of DCl in D₂O.)

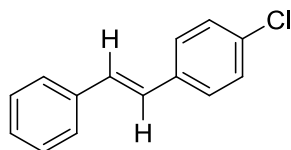
The loaded two-chamber system was heated to the required temperature (45-, 60- or 90 °C) for 18 hours and the crude reaction mixture was directly purified by flash column chromatography over silica.

(*E*)-1,2-Diphenylethene (2)



The compound was prepared following **GPA** at 45 °C, employing diphenylacetylene (36.5 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (36.0 mg, 199 μmol, 99%). ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (d, *J* = 7.2 Hz, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.33 – 7.25 (m, 2H), 7.15 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 137.5, 128.8, 128.8, 127.8, 126.7 ppm. Mp 125-126 °C. The spectral data correspond to the one reported in literature.¹⁸

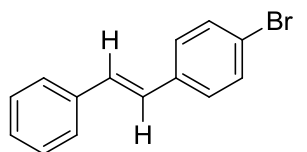
(*E*)-1-Chloro-4-styrylbenzene (5a)



The compound was prepared following **GPA** at 45 °C, employing 1-chloro-4-(phenylethynyl)benzene (42.5 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (41.2 mg, 192 μmol, 96%). ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.09 (d, *J* = 16.5 Hz, 1H), 7.05 (d, *J*

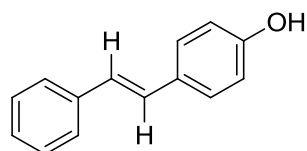
= 16.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 137.1, 136.0, 133.3, 129.5, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7 ppm. Mp 127-129 °C. The spectral data correspond to the one reported in literature.⁶

(E)-1-Bromo-4-styrylbenzene (5b)



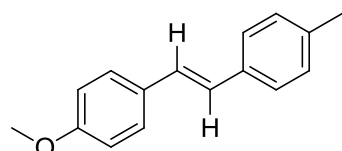
The compound was prepared following **GPA** at 45 °C, employing 1-bromo-4-(phenylethynyl)benzene (51.4 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (47.5 mg, 183 μmol , 92%). ^1H NMR (400 MHz, CDCl_3): δ = 7.55 – 7.46 (m, 4H), 7.44 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 7.11 (d, J = 16.3 Hz, 1H), 7.04 (d, J = 16.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 137.1, 136.4, 131.9, 129.6, 128.9, 128.1, 128.0, 127.5, 126.7, 121.4 ppm. Mp 139-140 °C. The spectral data correspond to the one reported in literature.⁷

(E)-4-Styrylphenol (5c)



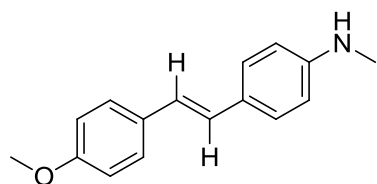
The compound was prepared following **GPA** at 45 °C, employing 4-(phenylethynyl)phenol (38.8 mg, 0.2 mmol). Purification by column chromatography over silica (CH_2Cl_2) afforded the title compound as yellow solid (37.3 mg, 190 μmol , 95%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 9.57 (s, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H), 7.01 (d, J = 16.5 Hz, 1H), 6.77 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$): δ = 157.3, 137.5, 128.6, 128.4, 128.1, 127.9, 126.9, 126.0, 125.1, 115.5 ppm. Mp 185-186 °C. The spectral data correspond to the one reported in literature.¹⁸

(E)-1-Methoxy-4-(4-methylstyryl)benzene (5d)



The compound was prepared following **GPA** at 45 °C, employing 1-methoxy-4-(*p*-tolylethynyl)benzene (44.5 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 7/3) afforded the title compound as light yellow solid (43.0 mg, 192 μmol , 96%). ^1H NMR (400 MHz, CDCl_3): δ = 7.45 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 16.4 Hz, 1H), 6.96 (d, J = 16.4 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 159.3, 137.2, 135.0, 130.5, 129.5, 127.7, 127.4, 126.7, 126.3, 114.3, 55.5, 21.4 ppm. Mp 167-168 °C. The spectral data correspond to the one reported in literature.⁸

(E)-4-(4-Methoxystyryl)-N-methylaniline (5e)

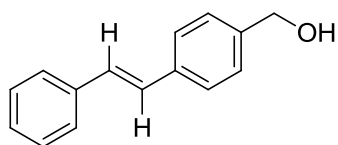


The compound was prepared following **GPA** at 45 °C, employing 4-((4-methoxyphenyl)ethynyl)-N-methylaniline (47.5 mg, 0.2 mmol).

Purification by column chromatography over silica (CH₂Cl₂) afforded the title compound as off-white solid (45.0 mg, 188 μmol, 94%).

¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.43 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.80 (m, 4H), 6.52 (d, *J* = 8.5 Hz, 2H), 5.81 (d, *J* = 4.6 Hz, 1H), 3.75 (s, 3H), 2.69 (d, *J* = 5.0 Hz, 3H) ppm. **¹³C NMR (101 MHz, DMSO-*d*₆)**: δ = 158.1, 149.4, 130.6, 127.3, 126.9, 126.8, 124.9, 122.5, 114.1, 111.7, 55.1, 29.6 ppm. **HRMS (ESIpos)**: C₁₆H₁₇NO [M+H⁺]; calculated 240.1383, found 240.1388. Mp 177-178 °C.

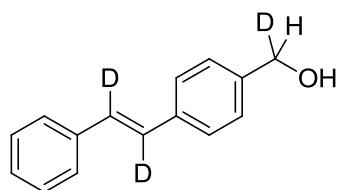
(E)-(4-Styrylphenyl)methanol (5f)



The compound was prepared following **GPA** at 45 °C, employing 4-(phenylethynyl)benzaldehyde (41.2 mg, 0.2 mmol). Purification by column chromatography over silica (CH₂Cl₂) afforded the title

compound as a colourless solid (37.1 mg, 176 μmol, 88%). **¹H NMR (400 MHz, DMSO-*d*₆)**: δ = 7.61 – 7.55 (m, 4H), 7.41 – 7.25 (m, 7H), 5.18 (t, *J* = 5.6 Hz, 1H), 4.50 (d, *J* = 5.6 Hz, 2H) ppm. **¹³C NMR (101 MHz, *d*₆-DMSO)** δ = 142.1, 137.1, 135.5, 128.7, 128.3, 127.8, 127.5, 126.8, 126.4, 126.2, 62.7 ppm. Mp 162-163 °C. The spectral data correspond to the one reported in literature.⁹

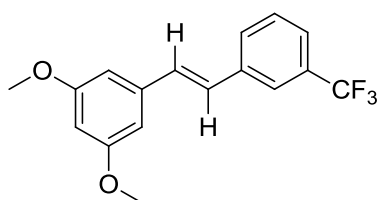
(E)-(4-(2-phenylvinyl-1,2-*d*₂)phenyl)methan-*d*₂-ol (5f-*d*₄)



The compound was prepared following the **GPA** at 45 °C, employing 4-(phenylethynyl)benzaldehyde (41.2 mg, 0.2 mmol). Purification by column chromatography over silica (CH₂Cl₂) afforded the title

compound as a colourless solid (39.0 mg, 180 μmol, 90%). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.64 – 7.52 (m, 4H), 7.43 – 7.21 (m, 5H), 5.20 – 5.11 (m, 1H), 4.48 (d, *J* = 5.4 Hz, 0.56H). **¹³C NMR (101 MHz, *d*₆-DMSO)**: δ = 142.6 (d, *J*_{D-C} = 5.1 Hz), 137.6, 136.0, 129.2, 128.0, 127.3 (d, *J*_{D-C} = 3.2 Hz), 126.8, 126.7, 62.4 (t, *J*_{D-C} = 21.4 Hz). **HRMS (ESIpos)**: C₁₅H₁₁D₃O [M+Na⁺]; calculated 237.1188, found 237.1182. Mp 165-166 °C.

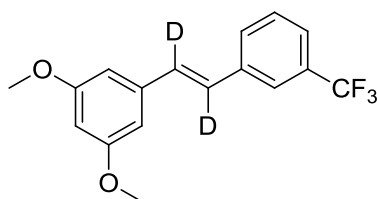
(E)-1,3-Dimethoxy-5-(3-(trifluoromethyl)styryl)benzene (5g)



The compound was prepared following the **GPA** at 45 °C, employing 1,3-dimethoxy-5-((3-(trifluoromethyl)phenyl)ethynyl)benzene (61.3 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/toluene 2/1) afforded the

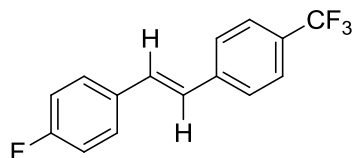
title compound as pale yellow oil (52.8 mg, 171 μ mol, 86%). **^1H NMR (400 MHz, CDCl_3):** δ = 7.75 (s, 1H), 7.67 (d, J = 6.9 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.10 (s, 2H), 6.69 (d, J = 2.1 Hz, 2H), 6.43 (s, 1H), 3.84 (s, 6H) ppm. **^{19}F NMR (376 MHz, CDCl_3):** δ = -62.73 ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 161.2, 138.8, 138.1, 131.2 (q, $J_{\text{F-C}}$ = 32.1 Hz), 130.7, 129.7, 129.3, 127.7, 124.3 (q, $J_{\text{F-C}}$ = 272.4 Hz), 124.3 (q, $J_{\text{F-C}}$ = 3.8 Hz), 123.3 (q, $J_{\text{F-C}}$ = 3.8 Hz), 104.9, 100.6, 55.5 ppm. **HRMS (ESIpos):** $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2$ [$\text{M}+\text{Na}^+$]; calculated 331.0916, found 331.1008. Mp 52-54 $^\circ\text{C}$.

***d*₂-(*E*)-1,3-Dimethoxy-5-(3-(trifluoromethyl)styryl)benzene (5g-*d*₂)**



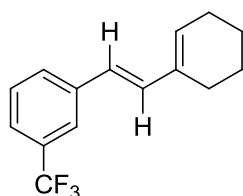
The compound was prepared following **GPA** at 45 $^\circ\text{C}$, employing 1,3-dimethoxy-5-((3-(trifluoromethyl)phenyl) ethynyl)benzene (64.5 mg, 0.211 mmol). Purification by column chromatography over silica (*n*-pentane/toluene 2/1) afforded the title compound as colorless oil (65.3 mg, 210 μ mol, 99%). **^1H NMR (400 MHz, CDCl_3):** δ = 7.75 (s, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.54 – 7.42 (m, 2H), 6.69 (d, J = 2.2 Hz, 2H), 6.46 – 6.38 (m, 1H), 3.84 (s, 6H) ppm. **^{19}F NMR (376 MHz, CDCl_3):** δ = -62.76 ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 161.2, 138.7, 138.0, 131.23 (q, $J_{\text{F-C}}$ = 32.1 Hz), 130.6 (t, $J_{\text{F-C}}$ = 23.0 Hz), 129.7, 129.2, 127.6 (t, $J_{\text{F-C}}$ = 23.0 Hz), 124.3 (q, $J_{\text{F-C}}$ = 272.4 Hz), 124.2 (q, $J_{\text{F-C}}$ = 3.7 Hz), 123.2 (q, $J_{\text{F-C}}$ = 3.8 Hz), 104.87, 100.61, 55.48 ppm. **HRMS (ESIpos):** $\text{C}_{17}\text{H}_{14}\text{D}_2\text{F}_3\text{O}_2$ [$\text{M}+\text{H}^+$]; calculated 311.1222, found 311.1204. Mp 52-53 $^\circ\text{C}$.

(*E*)-1-Fluoro-4-(4-(trifluoromethyl)styryl)benzene (5h)



The compound was prepared following **GPA** at 45 $^\circ\text{C}$, employing 1-fluoro-4-((4-(trifluoromethyl)phenyl)ethynyl) benzene (52.8 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (41.0 mg, 154 μ mol, 77%). **^1H NMR (400 MHz, CDCl_3):** δ = 7.52 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.07 (d, J = 16.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.95 (d, J = 16.7 Hz, 1H) ppm. **^{19}F NMR (376 MHz, CDCl_3):** δ = -62.47, -113.06 ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 162.7 (d, $J_{\text{F-C}}$ = 248.4 Hz), 140.7, 132.9 (d, $J_{\text{F-C}}$ = 3.4 Hz), 130.0, 129.3 (q, $J_{\text{F-C}}$ = 32.5 Hz), 128.3 (d, $J_{\text{F-C}}$ = 8.1 Hz), 126.9 (d, $J_{\text{F-C}}$ = 2.1 Hz), 126.5, 125.7 (q, $J_{\text{F-C}}$ = 3.8 Hz), 124.2 (d, $J_{\text{F-C}}$ = 271.7 Hz), 115.8 (d, $J_{\text{F-C}}$ = 21.7 Hz). **HRMS (ESIpos):** $\text{C}_{15}\text{H}_{11}\text{F}_4$ [$\text{M}+\text{H}^+$]; calculated 267.0791, found 267.0819. Mp 87-89 $^\circ\text{C}$.

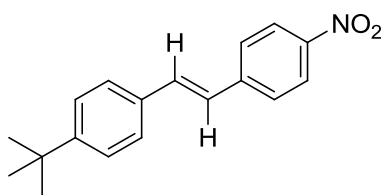
(*E*)-1-(2-(Cyclohex-1-en-1-yl)vinyl)-3-(trifluoromethyl)benzene (5i)



The compound was prepared following the **GPA** at 45 $^\circ\text{C}$, employing 1-(cyclohex-1-en-1-ylethynyl)-3-(trifluoromethyl)benzene (50.1 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the

title compound as colorless oil (40.1 mg, 160 μ mol, 80%). **^1H NMR (400 MHz, Acetone):** δ = 7.79 - 7.71 (m, 2H), 7.56 - 7.48 (m, 2H), 7.01 (d, J = 16.3 Hz, 1H), 6.58 (d, J = 16.3 Hz, 1H), 6.01 (s, 1H), 2.28 (s, 2H), 2.19 (s, 3H), 1.72 (dd, J = 7.4, 3.5 Hz, 3H), 1.63 (dd, J = 7.3, 3.5 Hz, 2H) ppm. **^{19}F NMR (376 MHz, Acetone):** δ = -63.24 ppm. **^{13}C NMR (101 MHz, Acetone):** 140.3, 136.7, 135.5, 133.0, 131.4 (q, $J_{\text{F-C}}$ = 31.7 Hz), 130.5, 130.5, 130.4, 125.5 (q, $J_{\text{F-C}}$ = 271.5 Hz), 124.1 (q, $J_{\text{F-C}}$ = 3.9 Hz), 124.1, 123.5 (q, $J_{\text{F-C}}$ = 3.9 Hz), 26.8, 25.2, 23.3 ppm. **HRMS (ESIpos):** $\text{C}_{15}\text{H}_{15}\text{F}_3$ [$\text{M}+\text{H}^+$]; calculated 253.1199, found 253.1198.

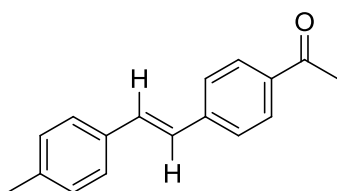
(*E*)-1-(*tert*-Butyl)-4-(4-nitrostyryl)benzene (5j)



The compound was prepared following **GPA** at 45 $^{\circ}\text{C}$, employing 1-(*tert*-butyl)-4-((4-nitrophenyl)ethynyl)benzene (55.9 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 1/1) afforded the title compound as yellow solid (55.0 mg, 199 μ mol, 99%). **^1H NMR (400 MHz, CDCl_3):** δ = 8.21 (d, J

= 8.8 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 16.3 Hz, 1H), 7.11 (d, J = 16.3 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 152.4, 146.8, 144.3, 133.6, 133.3, 127.0, 126.9, 126.0, 125.6, 124.38, 34.9, 31.4 ppm. Mp 159-160 $^{\circ}\text{C}$. The spectral data correspond to the one reported in literature.¹⁰

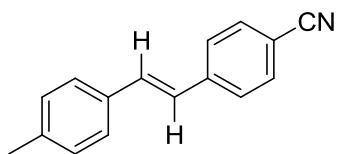
(*E*)-1-(4-(4-Methylstyryl)phenyl)ethanone (5k)



The compound was prepared following **GPA** at 45 $^{\circ}\text{C}$, employing 1-(4-(*p*-tolylethynyl)phenyl)ethanone (46.9 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 1/1) afforded the title compound as yellow solid (34.9 mg, 148 μ mol, 74%). **^1H NMR**

(400 MHz, CDCl_3): δ = 7.85 (d, J = 6.3 Hz, 2H), 7.47 (d, J = 6.3 Hz, 2H), 7.34 (d, J = 5.7 Hz, 2H), 7.19 - 7.05 (m, 3H), 6.98 (d, J = 16.1 Hz, 1H), 2.50 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 197.6, 142.3, 138.5, 135.9, 134.0, 131.5, 129.6, 129.0, 126.9, 126.5, 126.5, 26.7, 21.4 ppm. Mp 170-172 $^{\circ}\text{C}$. The spectral data correspond to the one reported in literature.¹¹

(*E*)-4-(4-Methylstyryl)benzonitrile (5l)

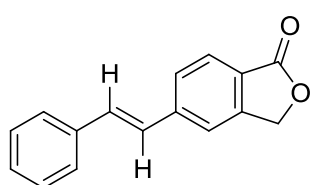


The compound was prepared following **GPA** at 60 $^{\circ}\text{C}$, employing 4-(*p*-tolylethynyl)benzonitrile (43.5 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 100/0 to 1/1) afforded the title compound as off-white solid (39.0 mg, 178 μ mol, 89%). **^1H**

NMR (400 MHz, CDCl_3): δ = 7.62 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H),

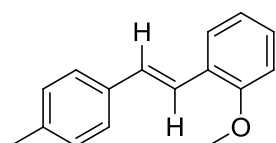
7.24 – 7.14 (m, 3H), 7.04 (d, J = 16.4 Hz, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 142.2, 138.9, 133.7, 132.6, 132.5, 129.7, 127.0, 126.9, 125.8, 119.2, 110.4, 21.5 ppm. Mp 172-173 °C. The spectral data correspond to the one reported in literature.¹²

(*E*)-5-Styrylisobenzofuran-1(3*H*)-one (5m)



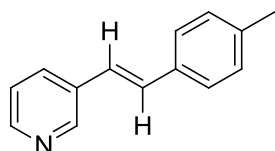
The compound was prepared following **GPA** at 45 °C, employing 5-(phenylethynyl)isobenzofuran-1(3*H*)-one (46.9 mg, 0.2 mmol). Purification by column chromatography over silica ($\text{CH}_2\text{Cl}_2/n$ -pentane 2/1) afforded the title compound as off-white solid (41.8 mg, 177 μmol , 88%). ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 7.61 – 7.50 (m, 3H), 7.40 (t, J = 7.3 Hz, 2H), 7.36 – 7.13 (m, 3H), 5.32 (s, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 171.0, 147.5, 143.6, 136.5, 132.7, 129.0, 128.8, 127.6, 127.2, 127.1, 126.2, 124.7, 119.6, 69.6 ppm. Mp 166-167 °C. The spectral data correspond to the one reported in literature.¹³

(*E*)-1-Methoxy-2-(4-methylstyryl)benzene (5n)



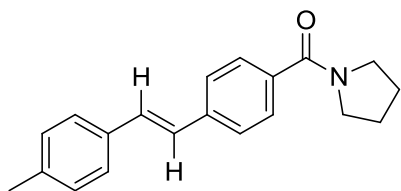
The compound was prepared following **GPA** at 90 °C, employing 1-methoxy-2-(*p*-tolylethynyl)benzene (48.5 mg, 0.218 mmol). Purification by column chromatography over silica (n -pentane/ CH_2Cl_2 10/1) afforded the title compound as off-white solid (48.9 mg, 218 μmol , 99%). ^1H NMR (400 MHz, CDCl_3): δ = 7.53 – 7.46 (m, 1H), 7.39 – 7.31 (m, 3H), 7.17 – 7.10 (m, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 16.5 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 3.78 (s, 3H), 2.26 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 157.0, 137.3, 135.3, 129.4, 129.2, 128.6, 126.8, 126.6, 126.4, 122.6, 120.9, 111.1, 55.6, 21.4 ppm. Mp 68-70 °C. The spectral data correspond to the one reported in literature.¹⁴

(*E*)-3-(4-Methylstyryl)pyridine (5o)



The compound was prepared following **GPA** at 60 °C, employing 3-(*p*-tolylethynyl)pyridine (38.6 mg, 0.20 mmol). Purification by column chromatography over silica (n -pentane/ethyl acetate 2/1) afforded the title compound as yellow solid (23.8 mg, 122 μmol , 61%). The product still contained 4% of the *cis*-isomer. ^1H NMR (400 MHz, CDCl_3): δ = 8.71 (s, 1H), 8.47 (d, J = 3.0 Hz, 1H), 7.81 (d, J = 6.9 Hz, 1H), 7.42 (d, J = 7.3 Hz, 2H), 7.23 – 6.97 (m, 5H), 2.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 148.6, 148.5, 138.3, 134.0, 133.3, 132.6, 130.9, 129.6, 126.7, 124.0, 123.6, 21.4 ppm. The spectral data correspond to the one reported in literature.¹⁵

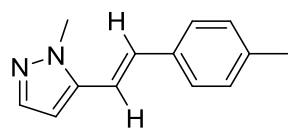
(E)-(4-(4-Methylstyryl)phenyl)(pyrrolidin-1-yl)methanone (5p)



The compound was prepared following **GPA** at 45 °C, employing pyrrolidin-1-yl(4-(*p*-tolylethynyl)phenyl)methanone (57.8 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane/ethyl acetate 1/2) afforded the title compound as off-

white solid (46.0 mg, 158 μ mol, 79%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.51 (s, 4H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.11 d, *J* = 16.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 3.68 - 3.60 (m, 2H), 3.50 - 3.40 (m, 2H), 2.36 (s, 3H), 2.00 - 1.91 (m, 2H), 1.91 - 1.82 (m, 2H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 169.6, 139.2, 138.1, 136.0, 134.3, 130.1, 129.6, 127.8, 127.0, 126.7, 126.2, 49.8, 46.4, 26.6, 24.6, 21.4 ppm. **HRMS (ESIpos):** C₂₀H₂₂NO [M+H⁺]; calculated 292.1696, found 292.1679.

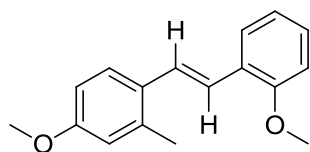
(E)-1-methyl-5-(4-methylstyryl)-1H-pyrazole (5q)



The compound was prepared following **GPA** at 60 °C, employing 1-methyl-5-(*p*-tolylethynyl)-1H-pyrazole (39.3 mg, 0.2 mmol). Purification by column chromatography over silica (CH₂Cl₂/ethyl acetate 98/2 to 9/1) afforded the

title compound as light yellow solid (30.9 mg, 156 μ mol, 78%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.44 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.46 (s, 1H), 3.93 (s, 3H), 2.37 (s, 3H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 141.1, 138.6, 138.4, 133.8, 132.1, 129.6, 126.6, 113.7, 102.8, 36.7, 21.4 ppm. **HRMS (ESIpos):** C₁₃H₁₂N₂ [M+H⁺]; calculated 199.1230, found 199.1238. Mp 88-89 °C.

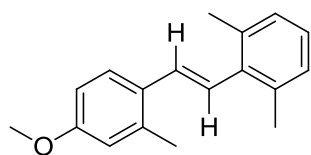
(E)-4-methoxy-1-(2-methoxystyryl)-2-methylbenzene (5r)



The compound was prepared following **GPA** at 90 °C, employing 4-methoxy-1-((2-methoxyphenyl)ethynyl)-2-methylbenzene (50.5 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/CH₂Cl₂ 5/1) afforded the title compound as colorless solid (46.4

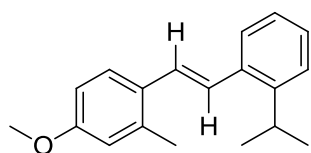
mg, 182 μ mol, 91%). **¹H NMR (400 MHz, Acetone-*d*₆):** δ = 7.64 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 16.3 Hz, 1H), 7.27 (d, *J* = 16.3 Hz, 1H), 7.24 - 7.20 (m, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.82 - 6.75 (m, 2H), 3.89 (s, 3H), 3.79 (s, 3H), 2.40 (s, 3H) ppm. **¹³C NMR (101 MHz, Acetone-*d*₆):** δ = 160.2, 157.9, 138.1, 130.5, 129.3, 127.8, 127.3, 127.2, 127.1, 123.5, 121.6, 116.4, 112.8, 112.0, 56.0, 55.5, 20.2 ppm. **HRMS (ESIpos):** C₁₇H₁₈O₂ [M+H⁺]; calculated 255.1380, found 255.1373. Mp 53-55 °C.

(E)-2-(4-Methoxy-2-methylstyryl)-1,3-dimethylbenzene (5s)



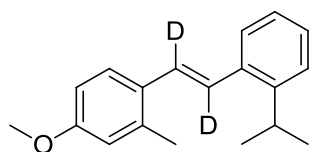
The compound was prepared following **GPA** at 90 °C, employing 2-((4-methoxy-2-methylphenyl)ethynyl)-1,3-dimethylbenzene (50.0 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane/CH₂Cl₂ 5/1) afforded the title compound as colorless solid (44.5 mg, 176 μmol, 88%). ¹H NMR (400 MHz, C₆D₆): δ = 7.04 (d, *J* = 6.7 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 1.9 Hz, 1H), 6.65 (d, *J* = 12.1 Hz, 1H), 6.39 (d, *J* = 12.1 Hz, 1H), 6.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.18 (s, 3H), 2.15 (s, 9H) ppm. ¹³C NMR (101 MHz, C₆D₆): δ = 159.7, 137.8, 136.3, 129.8, 129.8, 129.7, 128.3, 127.8, 127.4, 116.7, 111.3, 54.8, 20.8, 20.5 ppm. The spectral data correspond to the one reported in literature.¹⁶

(E)-1-(2-Isopropylstyryl)-4-methoxy-2-methylbenzene (5t)



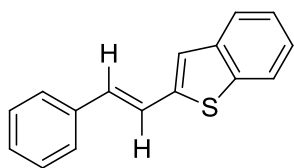
The compound was prepared following **GPA** at 90 °C, employing 1-((2-isopropylphenyl)ethynyl)-4-methoxy-2-methylbenzene (57.6 mg, 0.218 mmol). Purification by column chromatography over silica (*n*-pentane/CH₂Cl₂ 10/1) afforded the title compound as colorless solid (57.9 mg, 218 μmol, 99%). ¹H NMR (400 MHz, CDCl₃): δ = 7.48 – 7.42 (m, 2H), 7.24 – 7.08 (m, 4H), 7.00 (d, *J* = 15.8 Hz, 1H), 6.72 – 6.67 (m, 1H), 6.66 – 6.64 (m, 1H), 3.72 (s, 3H), 3.26 (sep, *J* = 6.7 Hz, 1H), 2.31 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 159.2, 146.2, 137.5, 136.4, 129.9, 128.3, 127.8, 126.9, 126.4, 126.3, 126.0, 125.1, 115.8, 111.9, 55.4, 29.4, 23.6, 20.3 ppm. HRMS (ESIpos): C₁₉H₂₃O [M+H⁺]; calculated 267.1743, found 267.1745.

*d*₂-(E)-1-(2-Isopropylstyryl)-4-methoxy-2-methylbenzene (5t-*d*₂)



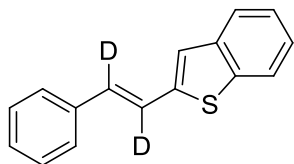
The compound was prepared following the **GPA** at 90 °C, employing 1-((2-isopropylphenyl)ethynyl)-4-methoxy-2-methylbenzene (57.6 mg, 0.218 mmol) and a 6M solution of DCl in D₂O (1 mL). Purification by column chromatography over silica (*n*-pentane/CH₂Cl₂ 10/1) afforded the title compound as colorless solid (57.9 mg, 218 μmol, 99%). ¹H NMR (400 MHz, CDCl₃): δ = 7.64 – 7.57 (m, 2H), 7.38 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 6.84 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 3.86 (s, 3H), 3.41 (sep, *J* = 6.8 Hz, 1H), 2.46 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 159.2, 146.1, 137.5, 136.3, 129.8, 127.7, 126.8, 126.3, 126.0, 125.1, 115.8, 111.9, 55.4, 29.4, 23.6, 20.3 ppm. HRMS (ESIpos): C₁₉H₂₁D₂O [M+H⁺]; calculated 269.1869, found 269.1870.

(E)-2-Styrylbenzo[*b*]thiophene (5u)



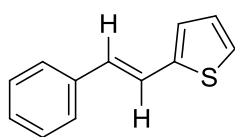
The compound was prepared following **GPA** at 45 °C, employing 2-(phenylethynyl)benzo[*b*]thiophene (46.9 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (33.4 mg, 141 μ mol, 71%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.79 (d, *J* = 6.5 Hz, 1H), 7.71 (d, *J* = 6.4 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.27 (m, 7H), 7.01 (d, *J* = 16.0 Hz, 1H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 143.1, 140.4, 139.0, 136.8, 131.0, 128.9, 128.2, 126.7, 124.9, 124.6, 123.6, 123.4, 122.5, 122.4 ppm. Mp 190-192 °C. The spectral data correspond to the one reported in literature.¹⁷

*d*₂-(E)-2-Styrylbenzo[*b*]thiophene (5u-*d*₂)



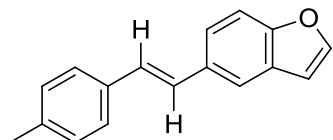
The compound was prepared following **GPA** at 45 °C, employing 2-(phenylethynyl)benzo[*b*]thiophene (46.9 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (43.7 mg, 183 μ mol, 92%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.69 (d, *J* = 6.2 Hz, 1H), 7.61 (d, *J* = 6.2 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.16 (s, 2H). ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 143.0, 140.4, 139.1, 136.7, 128.9, 128.2, 126.7, 124.9, 124.6, 123.5, 123.4, 122.4 ppm. **HRMS (ESIpos):** C₁₆H₁₁D₂S [M+H⁺]; calculated 239.0858, found 239.0869. Mp 191-193 °C.

(E)-2-Styrylthiophene (5v)



The compound was prepared following **GPA** at 45 °C, employing 2-(phenylethynyl)thiophene (16.9 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless solid (32.2 mg, 173 μ mol, 86%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.47 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.17 (m, 3H), 7.07 (d, *J* = 2.9 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.93 (d, *J* = 16.1 Hz, 1H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 143.0, 137.1, 128.83, 128.5, 127.7, 126.4, 126.2, 124.5, 121.9 ppm. Mp 108-110 °C. The spectral data correlates to those reported in literature.¹⁸

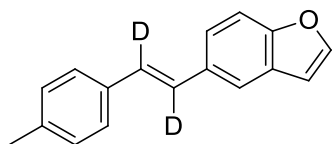
(E)-5-(4-Methylstyryl)benzofuran (5w)



The compound was prepared following **GPA** at 45 °C, employing 5-(*p*-tolylethynyl)benzofuran (46.5 mg, 0.2 mmol). Purification by column chromatography over silica (toluene) afforded the title compound as

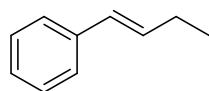
colorless solid (46.3 mg, 198 μ mol, 99%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.71 (s, 1H), 7.62 (s, 1H), 7.49 (s, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.07 (d, J = 16.3 Hz, 1H), 6.77 (s, 1H), 2.37 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 154.7, 145.6, 137.4, 134.9, 132.8, 129.5, 128.1, 128.0, 127.8, 126.4, 123.1, 119.2, 111.6, 106.8, 21.4 ppm. **HRMS (ESIpos)**: $\text{C}_{17}\text{H}_{14}\text{O}$ [$\text{M}+\text{H}^+$]; calculated 235.1117, found 235.1113. Mp 138-140 $^\circ\text{C}$.

d_2 -(*E*)-5-(4-Methylstyryl)benzofuran (5w- d_2)



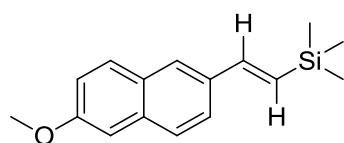
The compound was prepared following **GPA** at 45 $^\circ\text{C}$, employing 5-(*p*-tolylethynyl)benzofuran (46.5 mg, 0.2 mmol) and a 6M solution of DCl in D_2O (1 mL). Purification by column chromatography over silica (toluene) afforded the title compound as colorless solid (47.1 mg, 199 μ mol, 99%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.71 (s, 1H), 7.62 (d, J = 1.8 Hz, 1H), 7.49 (s, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 1.5 Hz, 1H), 2.37 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 154.7, 145.6, 137.3, 134.8, 132.7, 129.5, 128.0, 126.4, 123.1, 119.2, 111.6, 106.8, 21.4 ppm. The deuterated carbons could not be observed. **HRMS (ESIpos)**: $\text{C}_{17}\text{H}_{13}\text{D}_2\text{O}$ [$\text{M}+\text{H}^+$]; calculated 237.1243, found 237.1245. Mp 138-139 $^\circ\text{C}$.

(*E*)-But-1-en-1-ylbenzene (5x)



The compound was prepared following **GPA** at 45 $^\circ\text{C}$, employing but-1-yn-1-ylbenzene (26.0 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colorless oil (23.5 mg, 178 μ mol, 89%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.38 – 7.25 (m, 4H), 7.19 (t, J = 7.2 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.27 (dt, J = 15.8, 6.3 Hz, 1H), 2.29 – 2.17 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl_3)**: δ = 138.1, 132.8, 128.9, 128.6, 126.9, 126.1, 26.2, 13.8 ppm. The spectral data correspond to the one reported in literature.¹⁹

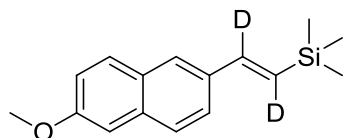
(*E*)-(2-(6-Methoxynaphthalen-2-yl)vinyl)trimethylsilane (5y)



The compound was prepared following **GPA** at 45 $^\circ\text{C}$, employing ((6-methoxynaphthalen-2-yl)ethynyl)trimethylsilane (50.8 mg, 0.2 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 10/1) afforded the title compound as colorless solid (48.0 mg, 187 μ mol, 94%). **^1H NMR (400 MHz, Acetone- d_6)**: δ = 7.83 – 7.74 (m, 3H), 7.73 – 7.68 (m, 1H), 7.27 (d, J = 1.7 Hz, 1H), 7.14 (dd, J = 8.9, 2.4 Hz, 1H), 7.09 (d, J = 19.3 Hz, 1H), 6.61 (d, J = 19.2 Hz, 1H), 3.91 (s, 3H), 0.18 (s, 9H) ppm. **^{13}C NMR (101 MHz, Acetone- d_6)**: δ = 159.1, 145.0, 135.7, 134.8, 130.6, 130.0, 128.9, 128.0, 127.4, 124.7, 119.9,

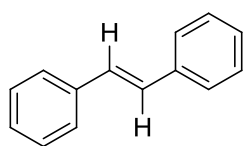
106.9, 55.7, -1.0 ppm. **HRMS (ESIpos):** C₁₆H₂₁OSi [M+H⁺]; calculated 257.1356, found 257.1357. Mp 110-112 °C.

***d*₂-(E)-(2-(6-Methoxynaphthalen-2-yl)vinyl)trimethylsilane (5y-*d*₂)**



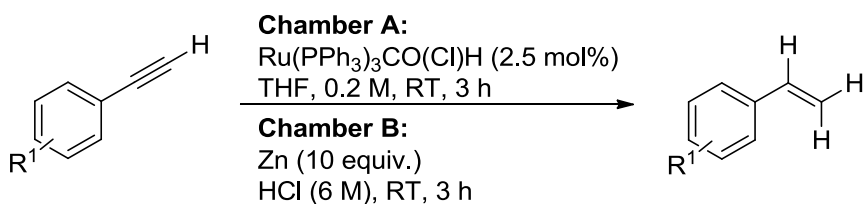
The compound was prepared following the **GPA** at 45 °C, employing ((6-methoxynaphthalen-2-yl)ethynyl)trimethylsilane (50.8 mg, 0.2 mmol) and a 6M solution of DCl in D₂O (1 mL). Purification by column chromatography over silica (*n*-pentane/CH₂Cl₂ 10/1) afforded the title compound as colourless solid (48.0 mg, 187 μmol, 94%). **¹H NMR (400 MHz, Acetone-*d*₆):** δ 7.85 – 7.74 (m, 3H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.27 (s, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 3.91 (s, 3H), 0.19 (s, 9H) ppm. **¹³C NMR (101 MHz, Acetone-*d*₆):** δ = 159.1, 135.7, 134.7, 130.6, 130.0, 128.0, 127.4, 124.7, 119.9, 106.8, 55.7, - 1.0 ppm. **HRMS (ESIpos):** C₁₆H₁₉D₂OSi [M+H⁺]; calculated 259.1482, found 259.1481. Mp 109-112 °C.

Scale-up Preparation of (E)-1,2-diphenylethene (2)



To chamber A of a 2-chamber system (total volume = 100 mL) was added diphenylacetylene (1.78 g, 10.0 mmol), Ru(PPh₃)₃CO(Cl)H (9.6 mg, 0.01 mmol) and toluene (5 mL) and the chamber was sealed with a H-cap. To chamber B was added zinc-powder (785 mg, 12.0 mmol) and a 6M aqueous HCl solution (6 mL) and the chamber was sealed with a H-cap. After heating to 90 °C for 18 h. the mixture was allowed to cool to room temperature, and the suspension in chamber A was diluted with CH₂Cl₂ (10 mL) and filtered through a silica plug. All volatiles were removed *in vacuo* to afford the title compound as a colourless solid (1.80 g, 10 mmol, >99%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.55 (d, *J* = 7.2 Hz, 4H), 7.39 (dd, *J* = 10.3, 4.7 Hz, 4H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.14 (s, 2H) ppm. The data corresponds to the one reported for the 0.2 mmol scale reaction. No *cis*-isomer or overreduction could be observed by ¹H NMR or GC analysis.

General Procedure B (GPB):

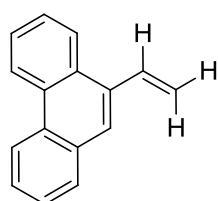


Chamber A: To chamber A of the two-chamber system was added alkyne (0.2 mmol) Ru(PPh₃)₃CO(Cl)H (4.8 mg, 0.005 mmol) and THF (1.0 mL) and the chamber was sealed using H-caps.

Chamber B: To chamber B of the two-chamber system was added Zn (137 mg, 2.0 mmol) and aqueous HCl (6M, 1 mL, 6.0 mmol) and the chamber was sealed using H-caps. (For deuterations the aqueous HCl solution was substituted for a 6M solution of DCl in D₂O.)

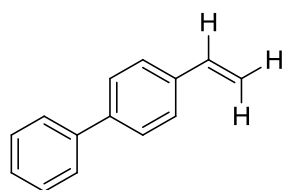
The loaded two-chamber system was stirred for 3 hours at room temperature, and the crude reaction mixture was directly purified by flash column chromatography over silica.

9-Vinylphenanthrene (6a)



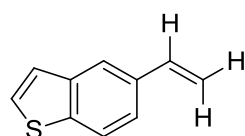
The compound was prepared following **GPB** employing 9-ethynylphenanthrene (40.5 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as colourless solid (37.6 mg, 184 μ mol, 92%). **¹H NMR (400 MHz, CDCl₃):** δ = 8.75 (d, *J* = 7.3 Hz, 1H), 8.69 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 6.8 Hz, 1H), 7.98 – 7.84 (m, 2H), 7.78 – 7.58 (m, 4H), 7.51 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.91 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.57 (dd, *J* = 10.8, 1.2 Hz, 1H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 135.2, 134.8, 131.9, 130.7, 130.5, 130.9, 128.8, 126.9, 126.8, 126.6, 126.6, 124.8, 123.2, 122.6, 117.7 ppm. **HRMS (ESIpos):** C₁₆H₁₃ [M+H⁺]; calculated 205.1013, found 205.1003. Mp 87-88 °C.

4-Vinyl-1,1'-biphenyl (6b)



The compound was prepared following **GPB** employing 4-ethynyl-1,1'-biphenyl (36.5 mg, 0.2 mmol). Purification by column chromatography (*n*-pentane) afforded the title compound as colorless solid (32.2 mg, 178 μ mol, 89%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.62 (dd, *J* = 12.4, 7.9 Hz, 4H), 7.57 – 7.43 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.84 (d, *J* = 17.6 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 140.9, 140.7, 136.7, 136.6, 128.9, 127.5, 127.4, 127.1, 126.8, 114.0 ppm. Mp 119-120 °C. The spectral data corresponds to the one reported in literature.²⁰

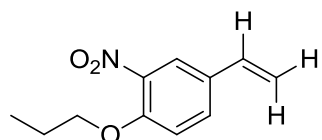
5-Vinylbenzo[*b*]thiophene (6c)



The compound was prepared following **GPB** employing 5-ethynylbenzo[*b*]thiophene (40.5 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane) afforded the title compound as off-white solid (22.0 mg, 137 μ mol, 69%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.89 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.32 (d, *J* = 5.3 Hz, 1H), 6.84 (dd, *J* = 17.5,

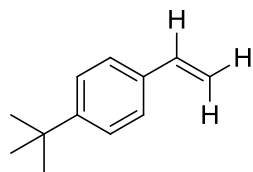
10.9 Hz, 1H), 5.84 (d, J = 17.5 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 140.4, 139.4, 136.9, 134.2, 126.9, 123.8, 123.6, 122.5, 120.6, 113.9 ppm. **HRMS (ESIpos)**: $\text{C}_{10}\text{H}_9\text{S}$ [$\text{M}+\text{H}^+$]; calculated 161.0419, found 161.0417.

2-Nitro-1-propoxy-4-vinylbenzene (6d)



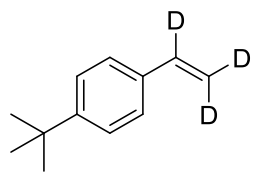
The compound was prepared following **GPB** employing 4-ethynyl-2-nitro-1-propoxybenzene (41.0 mg, 0.20 mmol). Purification by column chromatography over silica (*n*-pentane/ CH_2Cl_2 5/1) afforded the title compound as bright yellow solid (37.5 mg, 181 μmol , 91%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.87 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 8.6, 2.0 Hz, 1H), 7.04 (d, J = 8.7 Hz, 1H), 6.66 (dd, J = 17.5, 10.9 Hz, 1H), 5.72 (d, J = 17.5 Hz, 1H), 5.30 (d, J = 10.9 Hz, 1H), 4.09 (t, J = 6.4 Hz, 2H), 1.93 – 1.79 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 152.0, 134.4, 131.6, 130.4, 123.1, 114.6, 114.6, 71.4, 22.5, 10.5 ppm. **HRMS (ESIpos)**: $\text{C}_{11}\text{H}_{14}\text{NO}_3$ [$\text{M}+\text{H}^+$]; calculated 208.0968, found 208.0964.

1-(*tert*-Butyl)-4-vinylbenzene (6e)



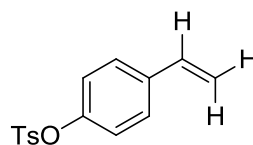
The compound was prepared following **GPB** employing 1-(*tert*-butyl)-4-ethynylbenzene (31.6 mg, 0.2 mmol). Purification by column chromatography (*n*-pentane) afforded the title compound as colorless oil (28.3 mg, 177 μmol , 88%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.39 (s, 4H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.74 (dd, J = 17.6, 0.7 Hz, 1H), 5.23 (dd, J = 10.9, 0.7 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 151.0, 136.7, 134.9, 126.1, 125.5, 113.1, 34.7, 31.4 ppm. The spectral data corresponds to the one reported in literature.²¹

1-(*tert*-Butyl)-4-(vinyl- d_3)benzene (6e- d_3)



The compound was prepared following the **GPB** employing 1-(*tert*-butyl)-4-ethynylbenzene (31.6 mg, 0.2 mmol). Purification by column chromatography (*n*-pentane) afforded the title compound as colorless oil (26.8 mg, 164 μmol , 82%). **^1H NMR (400 MHz, CDCl_3)**: δ = 7.39 (s, 4H), 6.73 (s, 0.08H), 5.73 (s, 0.14H), 5.22 (s, 0.14H), 1.36 (s, 9H) ppm. **^{13}C NMR (101 MHz, CDCl_3)**: δ = 151.0, 134.9, 126.1, 125.6, 34.7, 31.4 ppm. **HRMS (ESIpos)**: $\text{C}_{12}\text{H}_{14}\text{D}_3$ [$\text{M}+\text{H}^+$]; calculated 164.1513, found 164.1187.

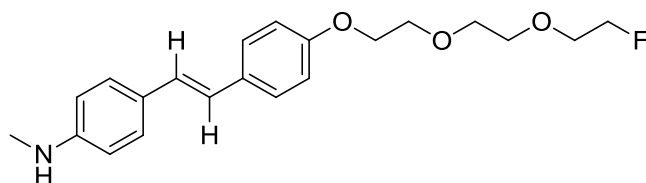
4-Vinylphenyl 4-methylbenzenesulfonate (6f)



The compound was prepared following the **GPB** employing 4-ethynylphenyl 4-methylbenzenesulfonate (54.5 mg, 0.2 mmol). Purification by column

chromatography (1:1 *n*-pentane/CH₂Cl₂) afforded the title compound as colorless solid (44.7 mg, 163 μmol, 82%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.48 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 4H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.42 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.46 (d, *J* = 17.6 Hz, 1H), 5.03 (d, *J* = 10.9 Hz, 1H), 2.22 (s, 3H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 149.2, 145.5, 136.6, 135.6, 132.5, 129.9, 128.6, 127.4, 122.6, 115.0, 21.8. ppm. Mp 65-67 °C. The spectral data corresponds to the one reported in literature.²⁰

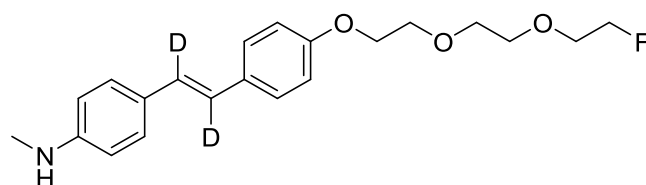
(*E*)-4-(4-(2-(2-(2-Fluoroethoxy)ethoxy)ethoxy)styryl)-*N*-methylaniline (7a)



The compound was prepared following GPA at 45 °C, employing 4-((4-(2-(2-(2-fluoroethoxy)ethoxy)ethoxy)phenyl)ethynyl)-*N*-methylaniline (71.5 mg, 0.2 mmol).

Purification by column chromatography over silica (CH₂Cl₂/EtOAc 100/0 to 95/5) afforded the title compound as colorless solid (54.7 mg, 152 μmol, 76%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.39 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.84 (m, 4H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.63 (t, *J* = 4.05 Hz, 1H), 4.51 (t, *J* = 4.05 Hz, 1H), 4.19 – 4.12 (t, *J* = 4.95 Hz, 2H), 3.87 (t, *J* = 4.95 Hz, 2H), 3.83 – 3.78 (t, *J* = 4.05 Hz, 1H), 3.77 – 3.68 (m, 5H), 2.86 (s, 3H) ppm. **¹⁹F NMR (376 MHz, CDCl₃)** δ = -222.91 ppm. **¹³C NMR (100 MHz, CDCl₃):** δ = 158.0, 148.6, 131.3, 127.6, 127.5, 127.3, 127.1, 124.3, 114.9, 112.9, 83.3 (d, *J*_{F-C} = 168.9 Hz), 71.0 (d, *J*_{F-C} = 1.5 Hz), 70.6 (d, *J*_{F-C} = 19.7 Hz), 70.0, 67.6, 31.0 ppm. **HRMS (ESIpos):** C₂₁H₂₇FNO₃ [M+H⁺]; calculated 360.1969, found 360.1979. Mp 125-127 °C.

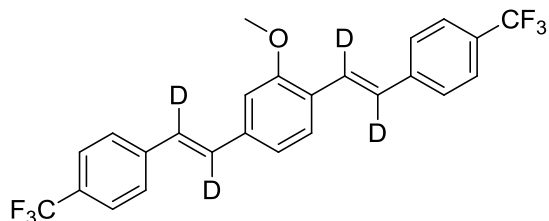
(*E*)-4-(2-(4-(2-(2-(2-Fluoroethoxy)ethoxy)ethoxy)phenyl)vinyl-1,2-*d*₂)-*N*-methylaniline (7a-*d*₂)



The compound was prepared following GPA at 45 °C, employing 4-((4-(2-(2-(2-fluoroethoxy)ethoxy)ethoxy)phenyl)ethynyl)-*N*-methylaniline (71.5 mg, 0.2 mmol).

Purification by column chromatography over silica (CH₂Cl₂/EtOAc 100:0 to 95:5) afforded the title compound as colorless solid (52.8 mg, 146 μmol, 73%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.39 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 4.63 (t, *J* = 4.09 Hz, 1H), 4.51 (t, *J* = 4.09 Hz, 1H), 4.15 (t, *J* = 4.68 Hz, 2H), 3.87 (t, *J* = 4.68 Hz, 1H), 3.80 (t, *J* = 4.09 Hz, 1H), 3.78 - 3.68 (m, 5H), 2.88 (s, 3H) ppm. **¹⁹F NMR (376 MHz, CDCl₃):** δ = -222.88 ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 158.0, 132.8, 130.9, 127.4, 127.2, 114.8, 113.6, 83.2 (d, *J*_{F-C} = 169.0 Hz), 70.9 (d, *J*_{F-C} = 1.7 Hz), 70.5 (d, *J*_{F-C} = 19.7 Hz), 69.9, 67.5, 31.5 ppm. **HRMS (ESIpos):** C₂₁H₂₅D₂FNO₃ [M+H⁺]; calculated 362.2095, found 362.2100. Mp 124-126 °C.

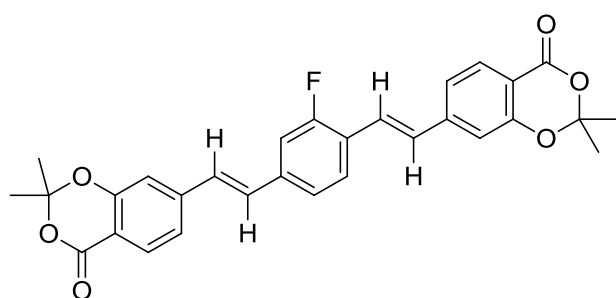
4,4'-((1*E*,1'*E*)-(2-methoxy-1,4-phenylene)bis(ethene-2,1-diyl))bis((trifluoromethyl) benzene) (7b-*d*₂)



The compound was prepared following **GPA** at 90 °C, employing 4,4'-((2-methoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis((trifluoro methyl) benzene) (437 mg, 0.98 mmol). Purification by column chromatography over silica (*n*-pentan/CH₂Cl₂

1/1), followed by recrystallisation by slow diffusion *n*-pentane into a saturated CH₂Cl₂-solution afforded the title compound as yellow solid (286 mg, 632 μmol, 64%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.62 (s, 8H), 7.26 (s, 1H, overlapping with the solvent signal), 7.17 (d, *J* = 6.6 Hz, 1H), 7.06 (s, 1H), 3.98 (s, 3H) ppm. **¹⁹F NMR (376 MHz, CDCl₃):** δ = -62.37, -62.44 ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 157.5, 141.4, 140.7, 137.9, 129.5 (q, *J*_{F-C} = 32.5 Hz), 129.2 (q, *J*_{F-C} = 32.0 Hz), 127.1, 126.7, 125.8 (q, *J*_{F-C} = 3.8 Hz), 125.7 (q, *J*_{F-C} = 3.9 Hz), 124.4 (q, *J*_{F-C} = 271.4 Hz), 124.3 (q, *J*_{F-C} = 271.4 Hz), 119.8, 109.1, 55.7 ppm. **HRMS (ESIpos):** C₂₅H₁₄D₄F₆O [M+H⁺]; calculated 453.1586, found 453.1620.

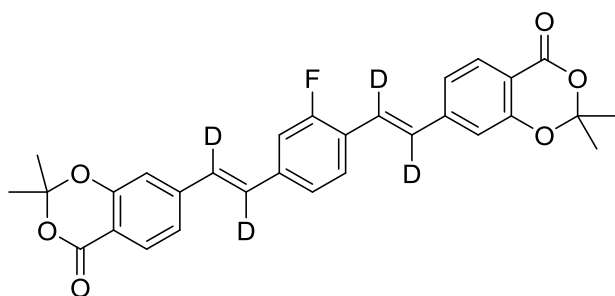
7,7'-((1*E*,1'*E*)-(2-Fluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(2,2-dimethyl-4*H*-benzo[1,3]dioxin-4-one) (7c)



The compound was prepared following **GPA** at 90 °C, employing 7,7'-((2-fluoro-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2,2-dimethyl-4*H*-benzo[1,3]dioxin-4-one) (99.3 mg, 0.2 mmol). Purification by column chromatography over silica (CH₂Cl₂) afforded

the title compound as a colorless solid (74.1 mg, 148 μmol, 74%). **¹H NMR (400 MHz, CDCl₃):** δ = 8.12 (s, 2H), 7.73 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.69 (dd, *J* = 8.5, 2.0 Hz, 1H) 7.56 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.18 (d, *J* = 13.9 Hz, 2H), 7.04 (d, *J* = 4.2 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 1.76 (s, 12H) ppm. **¹⁹F NMR (376 MHz, CDCl₃):** δ = -117.61 ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 162.1, 161.2, 161.2, 159.6, 155.7, 155.7, 138.4, 138.3, 134.5 (d, *J*_{F-C} = 11.9 Hz), 132.3 (d, *J*_{F-C} = 42.6 Hz), 128.9 (d, *J*_{F-C} = 5.4 Hz), 127.9, 127.8 (d, *J*_{F-C} = 2.5 Hz), 127.6, 127.5, 127.5, 127.4, 124.3 (d, *J*_{F-C} = 12.5 Hz), 122.95, 122.8, 121.4, 121.3, 117.8, 117.8, 113.9 (d, *J*_{F-C} = 4.0 Hz), 113.4 (d, *J*_{F-C} = 23.0 Hz), 106.8, 106.8, 26.0 ppm. **HRMS (ESIpos):** C₃₀H₂₆FO₆ [M+H⁺]; calculated 501.1708, found 501.1714. Mp 282-283 °C.

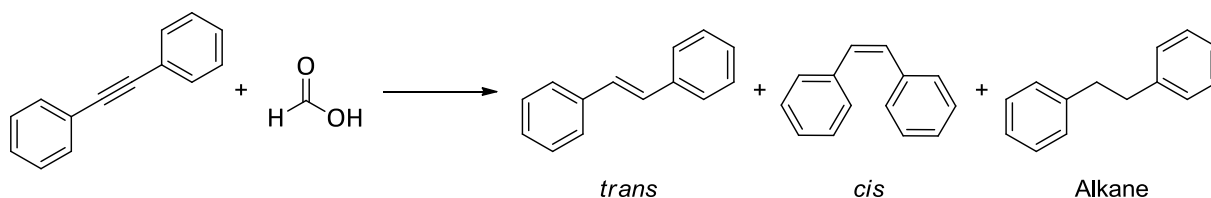
7,7'-((1*E*,1'*E*)-(2-fluoro-1,4-phenylene)bis(ethene-2,1-diyl-1,2-*d*₂))bis(2,2-dimethyl-4*H*-benz[1,3]dioxin-4-one) (7c-*d*₄)



The compound was prepared following **GPA** at 90 °C, employing 7,7'-((2-fluoro-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2,2-dimethyl-4*H*-benz[1,3]dioxin-4-one) (99.3 mg, 0.2 mmol). Purification by column chromatography over silica (CH₂Cl₂) afforded

the title compound as a colorless solid (76.7 mg, 152 μmol, 76%). **¹H NMR (400 MHz, CDCl₃)** δ = 8.16 – 8.07 (m, 2H), 7.73 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.69 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.18 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 1.76 (s, 12H). **¹⁹F NMR (376 MHz, CDCl₃)** δ = -118.37 ppm. **¹³C NMR (101 MHz, CDCl₃)** δ = 162.1, 161.2, 161.2, 159.6, 155.7, 138.3, 134.6, 134.4, 132.4, 132.0, 127.5, 127.5 (d, *J*_{F-C} = 15.0 Hz), 127.5, 122.8, 117.8 (d, *J*_{F-C} = 2.8 Hz), 113.9 (d, *J* = 4.0 Hz), 113.4 (d, *J* = 23.1 Hz), 106.8 (d, *J* = 2.8 Hz), 26.0 ppm. **HRMS (ESIpos):** C₃₀H₂₂D₄FO₆ [M+H⁺]; calculated 505.1959, found 505.1964. Mp 284-286 °C.

6. Optimization of Reaction Parameters in Flow:



All reactions for the optimisation were carried out employing a stainless steel tube, filled with the immobilized Ru catalyst. The Reactor was heated to the appropriate temperature and the pre-heated solution containing diphenylacetylene and formic acid was pumped over the catalyst with the appropriate flow rate. Diphenylacetylene was dissolved in the appropriate solvent and formic acid was added. Before submitting the reactant solution to the catalyst it was degassed for 5 minutes in an argon-stream and was subsequently loaded into the sample loop. The product distribution was measured by means of GC.

Table S6: Optimisation of reaction conditions for the *trans*-selective hydrogenation of alkynes.

	T[°C]	Solvent	RT [min]	Starting Material [%]	<i>trans</i> [%]	<i>cis</i> [%]	Alkane [%]
1	110	toluene	5.75	3.3	94.8	1.9	0.0
2	110	toluene ¹	5.75	4.5	91.6	3.9	0.0
3	110	toluene ²	5.75	5.5	89.9	4.6	0.0
4	110	1,4-dioxane ²	5.75	7,7	87.5	4.8	0.0
5	110	benzene	5.75	7.5	86.1	6.4	0.0
6	110	fluorobenzene	5.75	5.3	90.9	3.8	0.0
7	110	trifluorotoluene	5.75	7.1	88.5	4.3	0.0
8 ³	110	acetonitrile	5.75	55.7	22.7	21.6	0.0
9 ⁴	110	toluene	5.75	16.1	74.8	9.1	0.0
10 ⁴	110	toluene ⁵	5.75	15.9	74.3	9.8	0.0
11 ⁴	115	toluene	5.75	10.2	83.5	6.3	0.0
12 ⁴	120	toluene	5.75	8.0	86.9	5.2	0.0
13 ⁶	110	toluene	5.75	18.2	71.4	10.4	0.0
14 ^{6,7}	110	toluene	5.75	6.3	90.1	3.5	0.0
15 ^{6,7}	90	toluene	10	23.3	68.8	7.9	0.0
16 ^{6,7}	95	toluene	10	15.7	77.7	6.6	0.0
17 ^{6,7}	100	toluene	10	9.0	86.7	4.3	0.0
18 ^{6,7}	105	toluene	10	2.1	96.1	1.2	0.6
19 ^{6,7,8}	110	toluene	10	0.7	98.1	0.8	0.6

¹- The reaction mixture was degassed for 15 min. prior to the reaction. ²- The reaction was set up inside the GloveBox with *anhydrous* and degassed solvent. ³- Partial degradation of the column was observed. ⁴- The reactions were carried on the degraded column. ⁵- The toluene was saturated with water prior to the reaction. ⁶- The column was placed vertically instead of horizontally. ⁷- A newly packed column was used. ⁸- 99 % isolated yield.

7. EXPERIMENTAL SECTION FLOW:

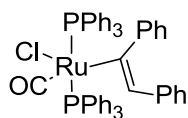
7.1 Synthesis of Ruthenium Catalysts:

Ru(PPh₃)₃H(Cl)CO²²

$$\begin{array}{c}
 \text{PPh}_3 \\
 | \\
 \text{Ph}_3\text{P}-\text{Ru}-\text{H} \\
 | \quad | \\
 \text{OC} \quad \text{Cl} \\
 | \\
 \text{PPh}_3
 \end{array}$$
 To a refluxing solution of triphenylphosphine (11.9 g, 45.4 mmol) in 2-methoxyethanol (550 ml) was added a suspension of RuCl₃ (1.55 g, 7.50 mmol) in an aqueous formaldehyde solution (37 – 40%; 150 ml) and 2-methoxyethanol (50 ml). The resulting suspension was kept at this temperature for 2 hours, upon which a micro-crystalline grey

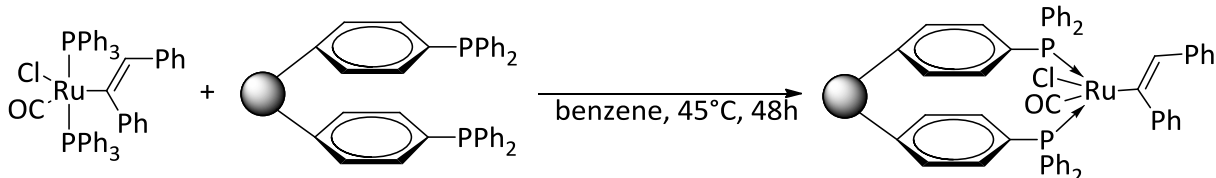
precipitate forms. After cooling to room temperature the formed precipitate is filtered off and washed with ethanol, water, ethanol and *n*-pentan (150 ml each) in this order. The resulting grey solid was dried *in vacuo* over night, delivering the title compound as grey fine powder (5.35 g, 5.56 mmol, 74%).

$\text{Ru}(\text{PPh}_3)_2(\text{PhCCHPh})(\text{Cl})\text{CO}^{23}$



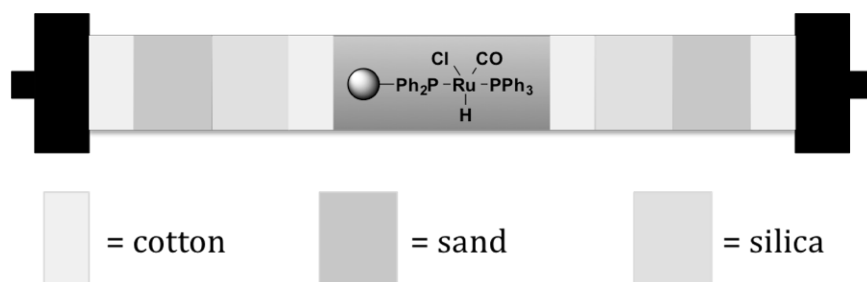
A suspension of $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{CO}$ (5.35 g, 5.56 mmol) and diphenylacetylene (9.91 g, 55.6 mmol) in CH_2Cl_2 (170 ml) was heated to reflux for 2 hours. The resulting dark red solution was evaporated, and the residue was purified by chromatography over Florisile (CH_2Cl_2). The red fractions were evaporated to dryness, and the resulting dark red oil was recrystallised by slow diffusion *n*-heptane (450 ml) into a saturated CH_2Cl_2 solution (20 ml). The formed orange microcrystalline material was filtered off and washed with *n*-pentane (3 x 150 ml). Drying *in vacuo* afforded the title complex as orange micro-crystalline solid (4.21 g, 4.85 mmol, 87%). **^1H NMR (400 MHz, CDCl_3):** δ = 7.51 (dd, J = 17.4, 3.5 Hz, 12H), 7.41 – 7.32 (m, 7H), 7.33 – 7.25 (m, 10H), 7.20 (t, J = 7.3 Hz, 1H), 6.92 (t, J = 7.3 Hz, 2H), 6.85 (t, J = 7.5 Hz, 3H), 6.56 (d, J = 7.0 Hz, 2H), 6.43 (d, J = 7.3 Hz, 2H), 5.35 (s, 1H) ppm. **^{31}P NMR (162 MHz, CDCl_3):** δ = 32.22 ppm. **^{13}C NMR (101 MHz, CDCl_3):** δ = 138.6 (d, J = 6.6 Hz), 134.7 (t, J = 5.6 Hz), 131.8, 131.6, 130.1, 129.1, 128.4, 128.2 (d, J = 6.5 Hz), 128.0 (t, J = 4.8 Hz), 127.7, 127.3 (d, J = 6.0 Hz), 124.0, 123.3, 89.4 ppm. The spectroscopic data corresponds to one reported in literature.^{Fejl! Bogmærke er ikke defineret.}

Immobilization of the catalyst



A mixture of polystyrene supported triphenylphosphine (3 mmol/g, 4.0 g, 12.0 mmol) and $\text{Ru}(\text{PPh}_3)_2(\text{PhCCHPh})(\text{Cl})\text{CO}$ (3.13 g, 3.6 mmol) were suspended in dry, degassed benzene and the resulting suspension was heated to 45 °C for 48 hours. After cooling to room temperature the now pale red solution was filtered over glass-sinter filter, and the resulting ruby-red solid was washed with CH_2Cl_2 (4 x 60 ml) until the solvent remained colourless. Subsequently it was washed with *n*-pentane (4 x 60 ml), and dried *in vacuo* to afford the title compound as ruby-red solid (4.66 g). The combined washing fluids were collected and evaporated to dryness and the amount of remaining $\text{Ru}(\text{PPh}_3)_2(\text{PhCCHPh})(\text{Cl})\text{CO}$ was determined by ^{31}P NMR spectroscopy employing triethylphosphate (611 μl , 3.6 mmol) as internal standard. 27.5 % of starting material was recovered, giving a 0.65 mmol/g loading of catalyst onto the modified styrene beads.

Packing and catalyst activation of packed bed reactor.

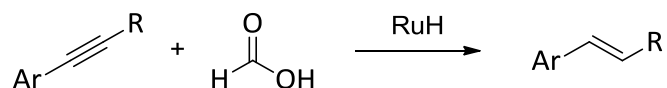


An HPLC column (ID = 4.6 mm, L = 125 mm) was loaded with styrene supported immobilized catalyst (1,12 grams). The column was packed according to the graphic above with both ends capped of with layers of cotton, sand, silica and cotton. The remaining reactor volume (dead-volume) was determined by weighing of the dry column and then reweighing after loading it with toluene under pressure. The reactor volume was determined to 1.05 mL.

The catalyst was activated by flushing the packed bed reactor with a 2 % formic acid in toluene at 110°C for 1 hour at a flowrate of 1 ml/min. After 1 hour a small aliquot was collected and analyzed to determine that no more stilbene was coming of the reactor indication catalyst activation was complete.

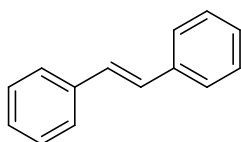
7.2 General Procedure for the *trans*-selective reduction of Alkynes in continuous flow

(GPC):



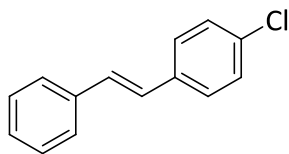
9 ml of a degassed toluene-solution of Alkyne (1.8 mmol) and formic acid (5eqare loaded into a 9 ml sample loop, and are submitted to the reaction conditions (T = 110 °C; RetentionTime = 10 min). After collection the appropriate amount of reaction mixture, all volatiles were evaporated *in vacuo* to give the desired products in purities >95/5

(E)-1,2-Diphenylethene (2):



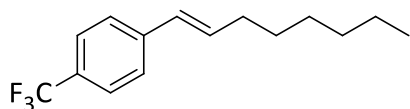
The compound was prepared following **GPC**, employing diphenylacetylene (321 mg, 1.8 mmol). Removing all volatiles *in vacuo* afforded the title compound as colorless solid (322 mg, 1.79 mmol, 99%). **¹H NMR (400 MHz, Acetone):** δ = 7.61 (d, J = 7.3 Hz, 4H), 7.37 (t, J = 7.5 Hz, 4H), 7.30 – 7.21 (m, 4H) ppm. **¹³C NMR (101 MHz, Acetone):** δ = 138.5, 129.6, 129.5, 128.5, 127.5 ppm.

(E)-1-Chloro-4-styrylbenzene (5a):



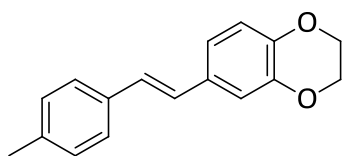
The compound was prepared following **GPC**, employing 1-chloro-4-(phenylethynyl)benzene (383 mg, 1.8 mmol). Removing all volatiles *in vacuo* afforded the title compound as colorless solid (376 mg, 1.75 mg, 97%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.51 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 - 7.34 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.30 - 7.24 (m, 1H), 7.09 (d, *J* = 16.5 Hz, 1H), 7.05 (d, *J* = 16.6 Hz, 1H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 137.1, 136.0, 133.3, 129.5, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7 ppm.

(E)-1-(Oct-1-en-1-yl)-4-(trifluoromethyl)benzene (8a):



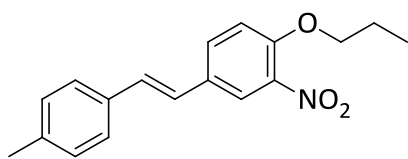
The compound was prepared following **GPC**, employing 1-(oct-1-yn-1-yl)-4-(trifluoromethyl)benzene (483 mg, 1.9 mmol). The reaction was carried out at 115 °C with a retention time of 15 minutes. Removing all volatiles *in vacuo* afforded the title compound as orange oil (457 mg, 1.78 mmol, 99%). The compound still contained 10% of the *cis*-isomer. **¹H NMR (400 MHz, CDCl₃):** δ = 7.53 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.8, 6.3 Hz, 1H), 2.23 (dd, *J* = 14.0, 6.9 Hz, 2H), 1.53 - 1.44 (m, 2H), 1.40 - 1.24 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm. **¹⁹F NMR (376 MHz, CDCl₃):** δ = -62.39 ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 141.6, 134.3, 129.1, 128.7, 128.6, 126.2, 125.6 (q, *J* = 3.9 Hz), 33.2, 31.8, 29.2, 29.0, 22.7, 14.2 ppm. **HRMS (ESIpos):** calculated for (M+Na⁺) = C₁₅H₁₉F₃Na⁺: 279.1331; found: 279.1318.

(E)-6-(4-Methylstyryl)-2,3-dihydrobenzo[*b*][1,4]dioxine (8b):



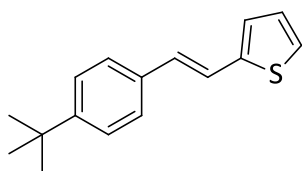
The compound was prepared following **GPC**, employing 6-(*p*-tolylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (450 mg, 1.8 mmol). Removing all volatiles *in vacuo* afforded the title compound as off-white solid (452 mg, 1.79 mg, 99%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.38 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.96 (d, *J* = 16.6 Hz, 1H), 6.92 (d, *J* = 16.6 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.27 (s, 4H), 2.35 (s, 3H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 143.8, 143.4, 137.3, 134.9, 131.6, 129.5, 127.3, 127.3, 126.4, 120.1, 117.5, 115.0, 64.6, 64.5, 21.4 ppm. **HRMS(ESIpos):** calculated for (M+H⁺) = C₁₇H₁₇O₂⁺: 253.1223; found: 253.1222. Mp 133-134 °C.

(E)-4-(4-Methylstyryl)-2-nitro-1-propoxybenzene (8c):



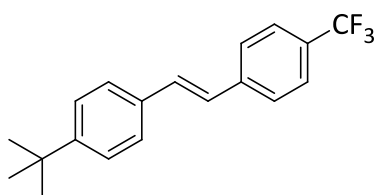
The compound was prepared following **GPC**, employing 2-nitro-1-propoxy-4-(*p*-tolylethynyl)benzene (531 mg, 1.8 mmol). Removing all volatiles *in vacuo* afforded the title compound as orange solid (528 mg, 1.78 mg, 99%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.96 (d, *J* = 2.2 Hz, 1H), 7.61 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 16.3 Hz, 2H), 6.96 (d, *J* = 16.3 Hz, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 2.00 – 1.75 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 151.7, 140.3, 138.1, 134.1, 131.7, 130.5, 129.6, 129.5, 126.6, 125.0, 123.1, 114.8, 71.4, 22.6, 21.4, 10.6 ppm. **HRMS(ESIpos):** calculated for (M+H⁺) = C₁₈H₂₀NO₃⁺: 298.1438; found: 298.1441. Mp 81-83 °C.

(E)-2-(4-(*tert*-Butyl)styryl)thiophene (8d):



The compound was prepared following **GPC**, employing 2-((4-(*tert*-Butyl)phenyl)ethynyl)thiophene (284 mg, 1.25 mmol). Removing all volatiles *in vacuo* afforded the title compound as colorless solid (275 mg, 1.14 mmol, 96%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.06 (d, *J* = 3.4 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.92 (d, *J* = 16.1 Hz, 1H), 1.34 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 150.9, 143.3, 134.3, 128.4, 127.7, 126.2, 125.9, 125.8, 124.2, 121.2, 34.8, 31.4 ppm. **HRMS(ESIpos):** calculated for (M+H⁺) = C₁₆H₁₉S⁺: 243.1202; found: 243.1203. Mp 89-92 °C.

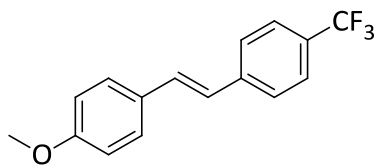
(E)-1-(*tert*-Butyl)-4-(4-(trifluoromethyl)styryl)benzene (8e):



The compound was prepared following **GPC**, employing 1-(*tert*-butyl)-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene (544 mg, 1.8 mmol). The reaction was carried out at 115 °C with a retention time of 15 minutes. Removing all volatiles *in vacuo* afforded the

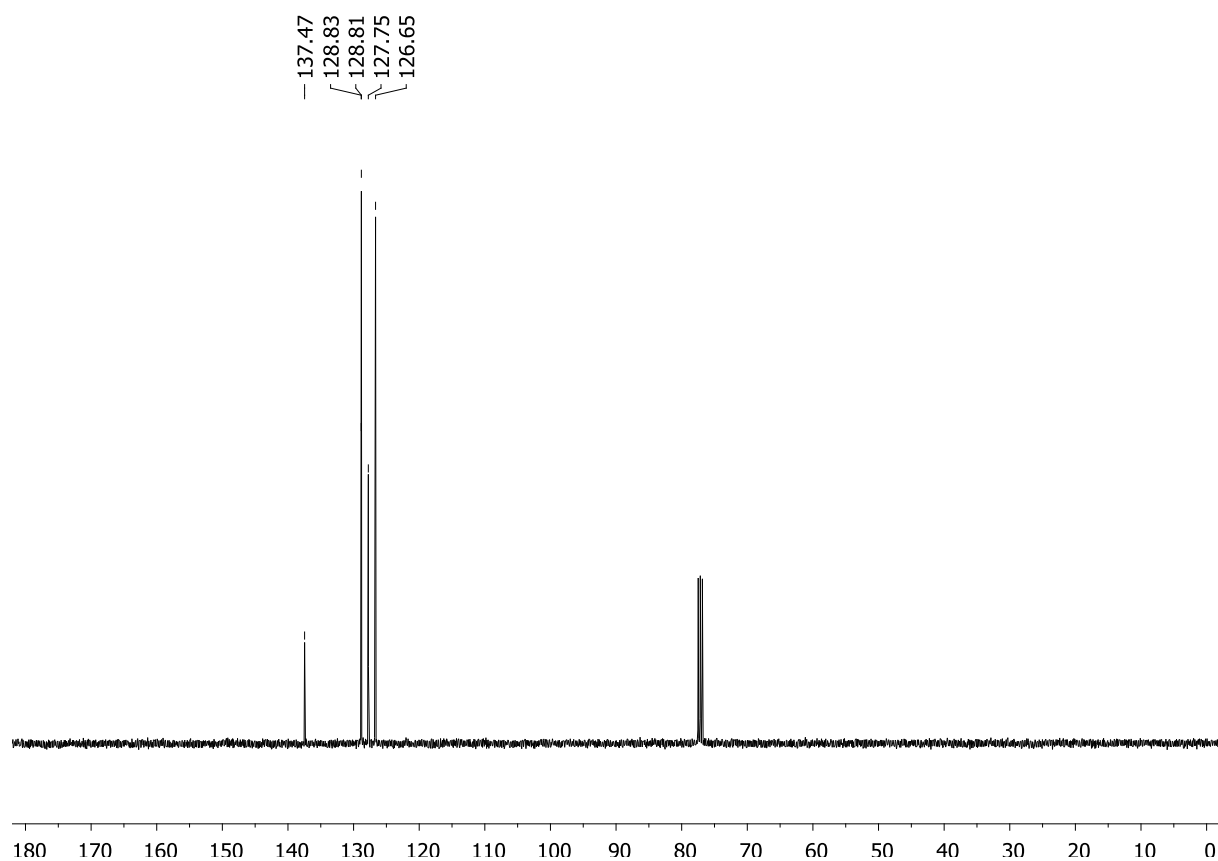
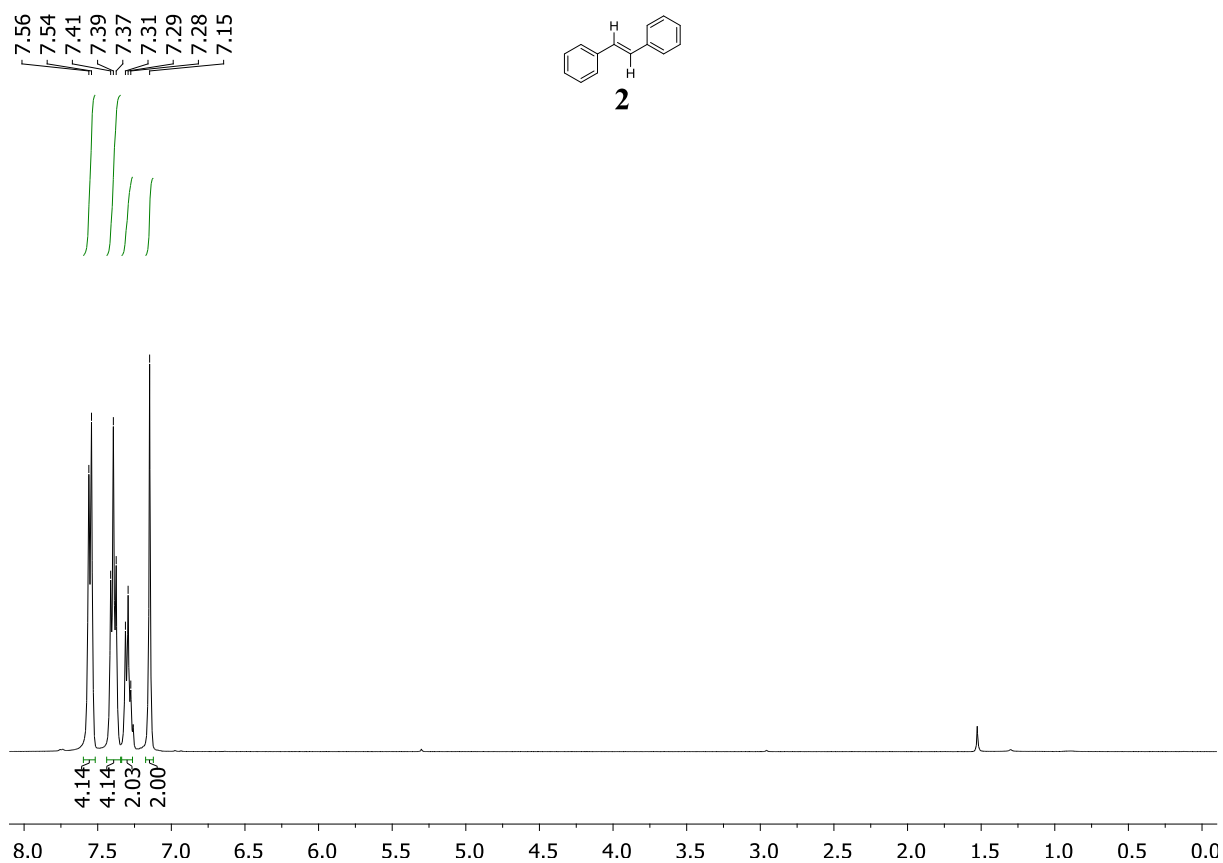
title compound as colorless solid (542 mg, 1.78 mmol, 99%). **¹H NMR (400 MHz, CDCl₃):** δ = 7.60 (s, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 16.3 Hz, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 1.35 (s, 9H) ppm. **¹⁹F NMR (376 MHz, CDCl₃):** δ = -62.41 ppm. **¹³C NMR (101 MHz, CDCl₃):** δ = 151.7, 141.2, 134.0, 131.2, 129.2 (q, *J* = 32.5 Hz), 126.7, 126.6, 126.5, 125.9, 125.7 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.4 Hz), 34.9, 31.4 ppm. **HRMS(ESIpos):** calculated for (M+H⁺) = C₁₉H₂₀F₃⁺: 305.1512; found: 105.1526. Mp 125-128 °C.

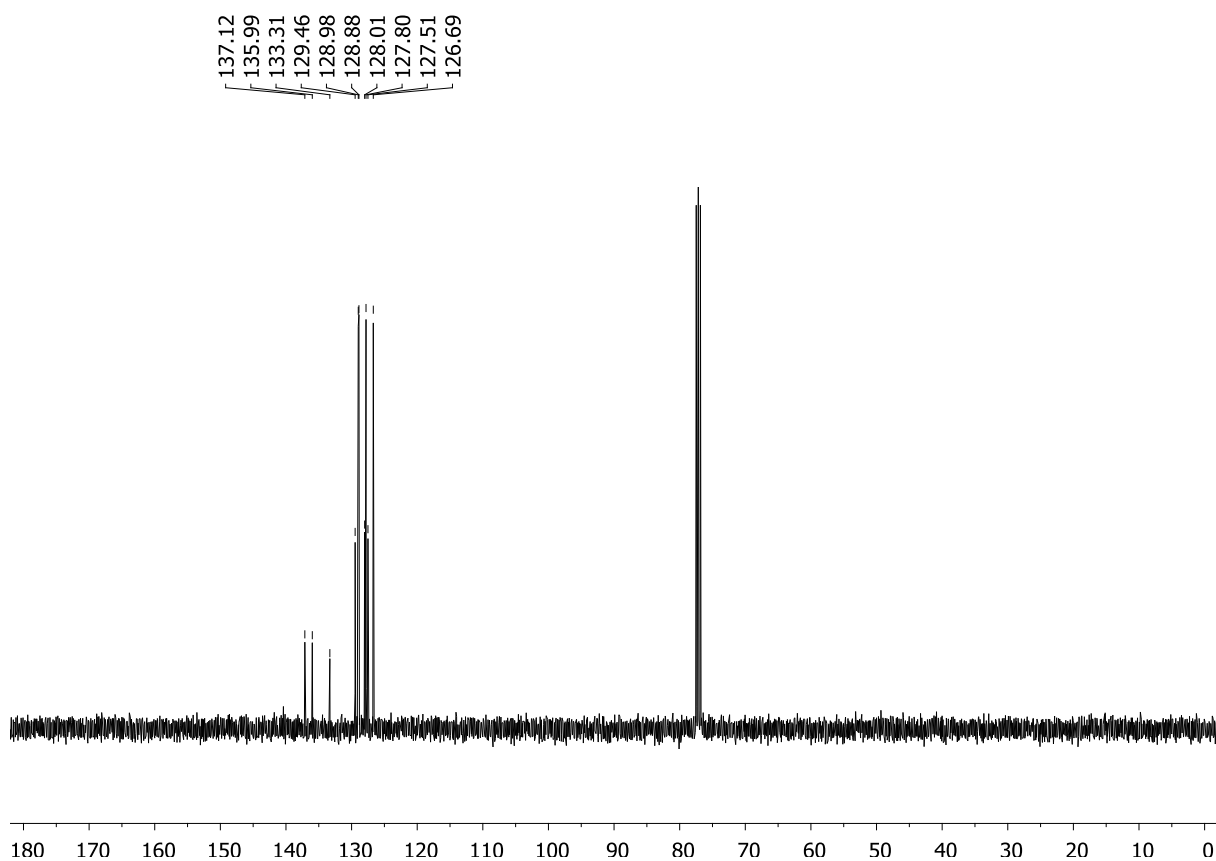
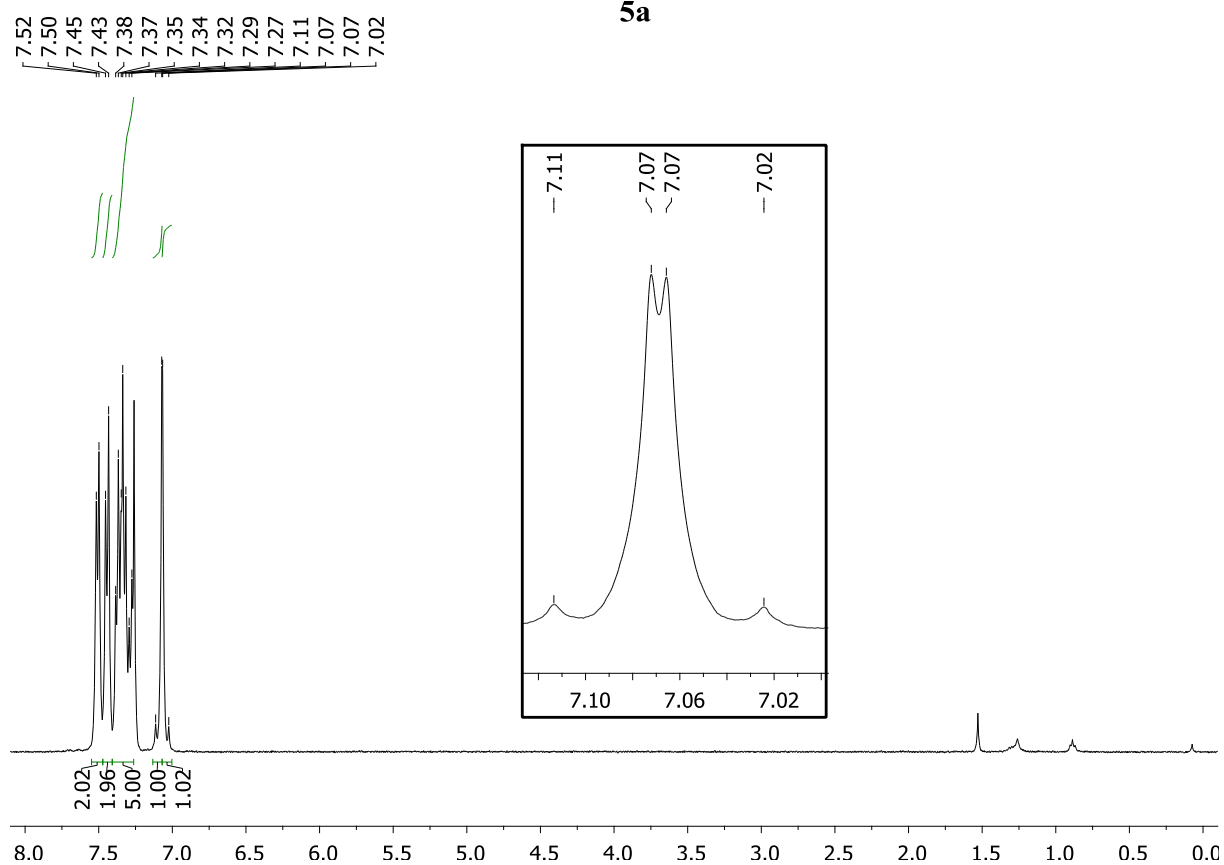
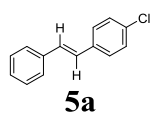
(E)-1-Methoxy-4-(4-(trifluoromethyl)styryl)benzene (8f):

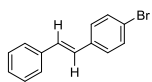


The compound was prepared following **GPC**, employing 1-methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene (497 mg, 1.8 mmol). The reaction was carried out at 115 °C with a retention time of 15 minutes. Removing all volatiles *in vacuo* afforded the title compound as colorless solid (493 mg, 1.77 mg, 98%). **¹H NMR (400 MHz, CDCl₃)**: δ = 7.61 – 7.58 (m, 2H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H) ppm. **¹⁹F NMR (376 MHz, CDCl₃)**: δ = -62.38 ppm. **¹³C NMR (101 MHz, CDCl₃)**: δ = 159.8, 141.2 (d, *J* = 1.3 Hz), 130.7, 129.4, 128.8 (q, *J* = 32.3 Hz), 128.1, 126.3, 125.6 (q, *J* = 3.7 Hz), 125.0, 123.0 (q, *J* = 272.6 Hz), 114.3, 55.3 ppm. **HRMS(ESIpos)**: calculated for (M+H⁺) = C₁₆H₁₄F₃O⁺: 279.0991; found: 279.0985. Mp 168-169 °C.

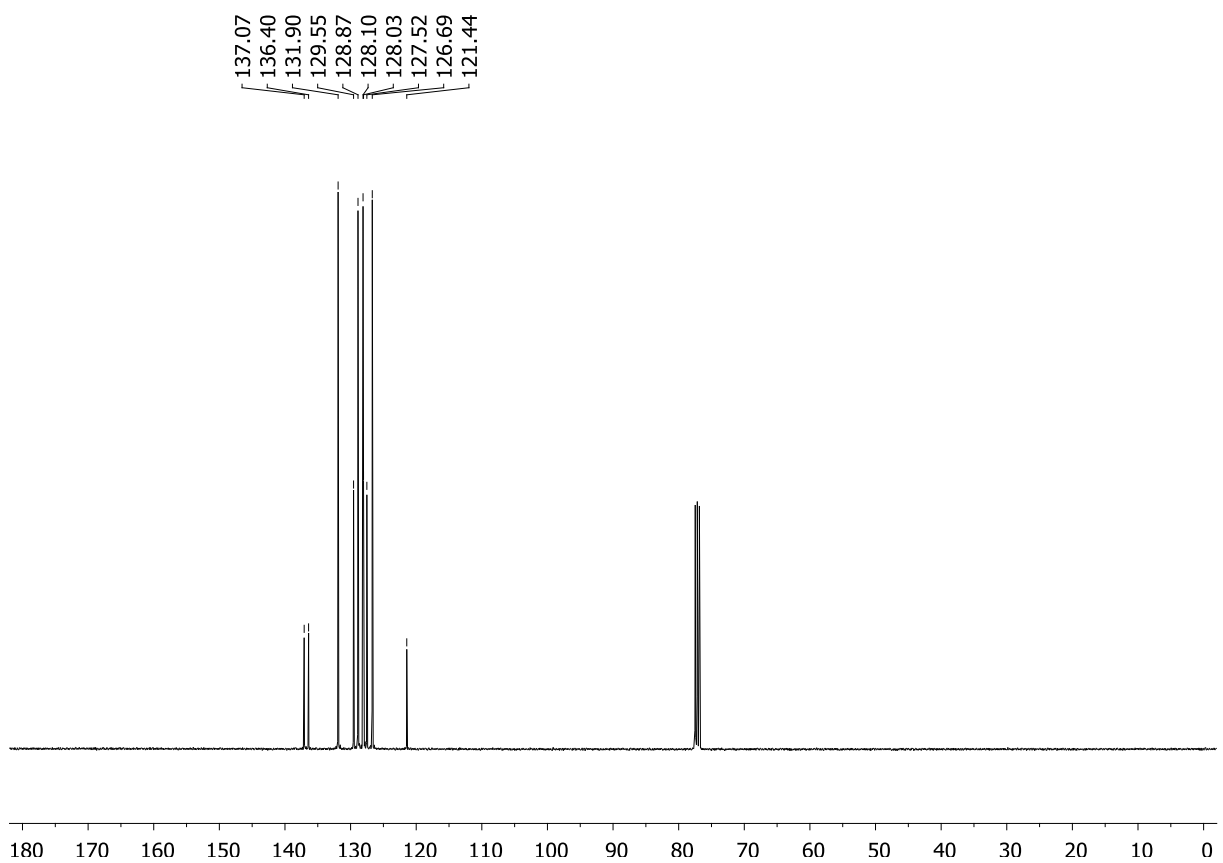
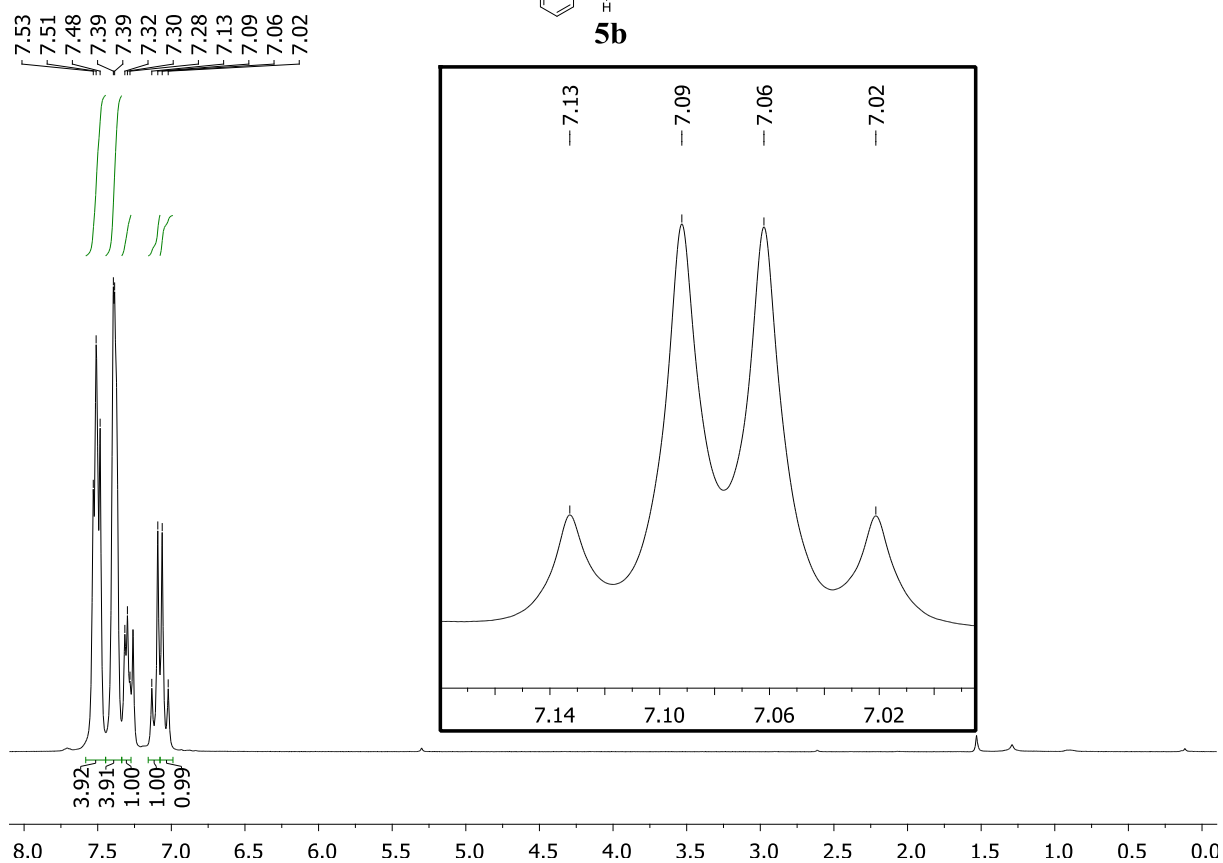
8. Spectral Data for *trans*-Stilbenes and Styrenes

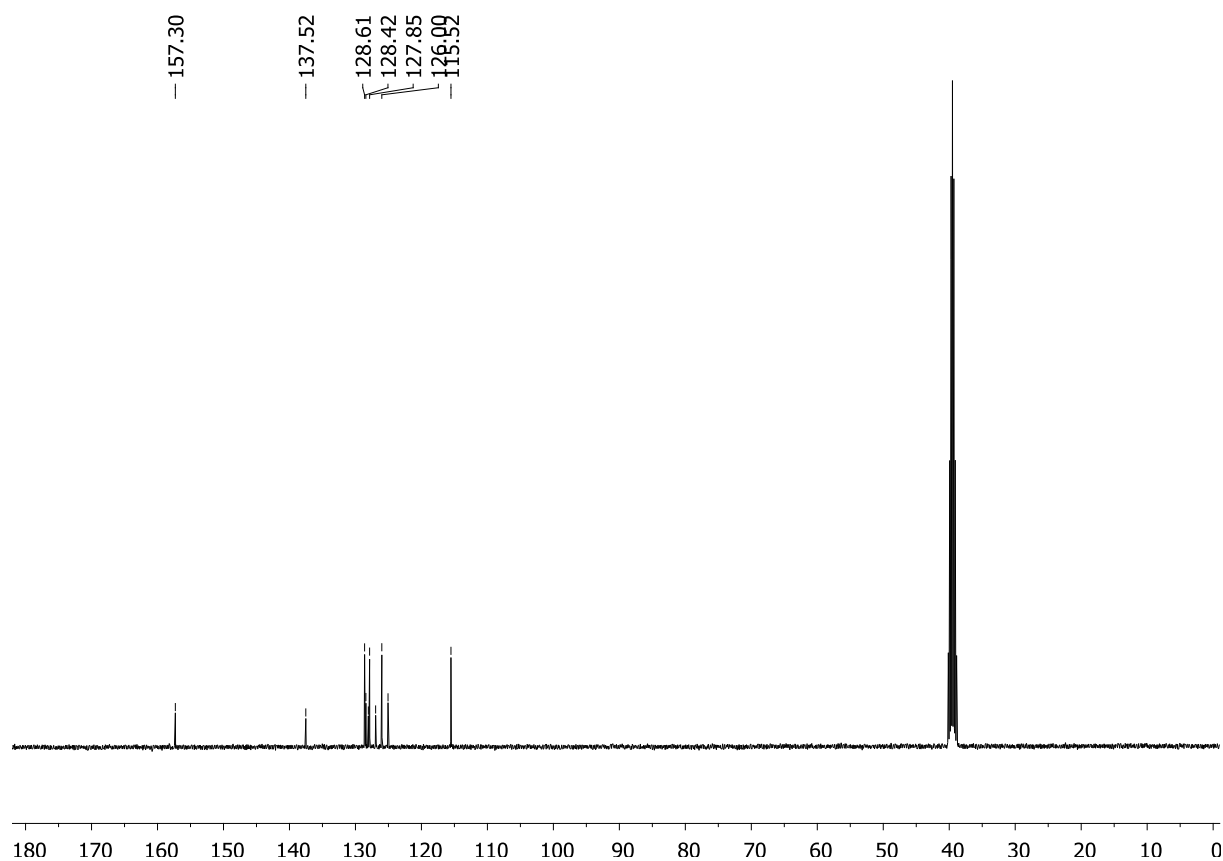
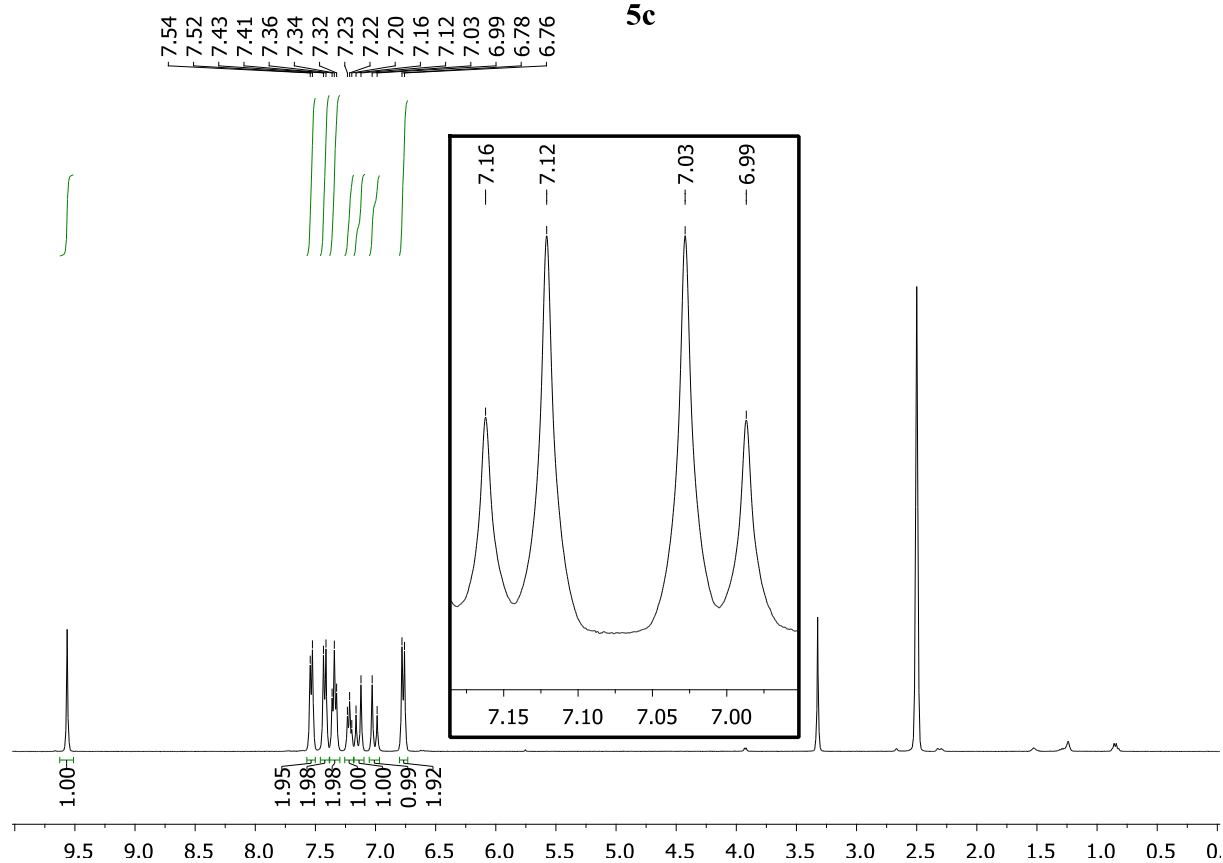
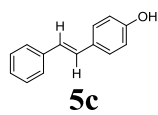


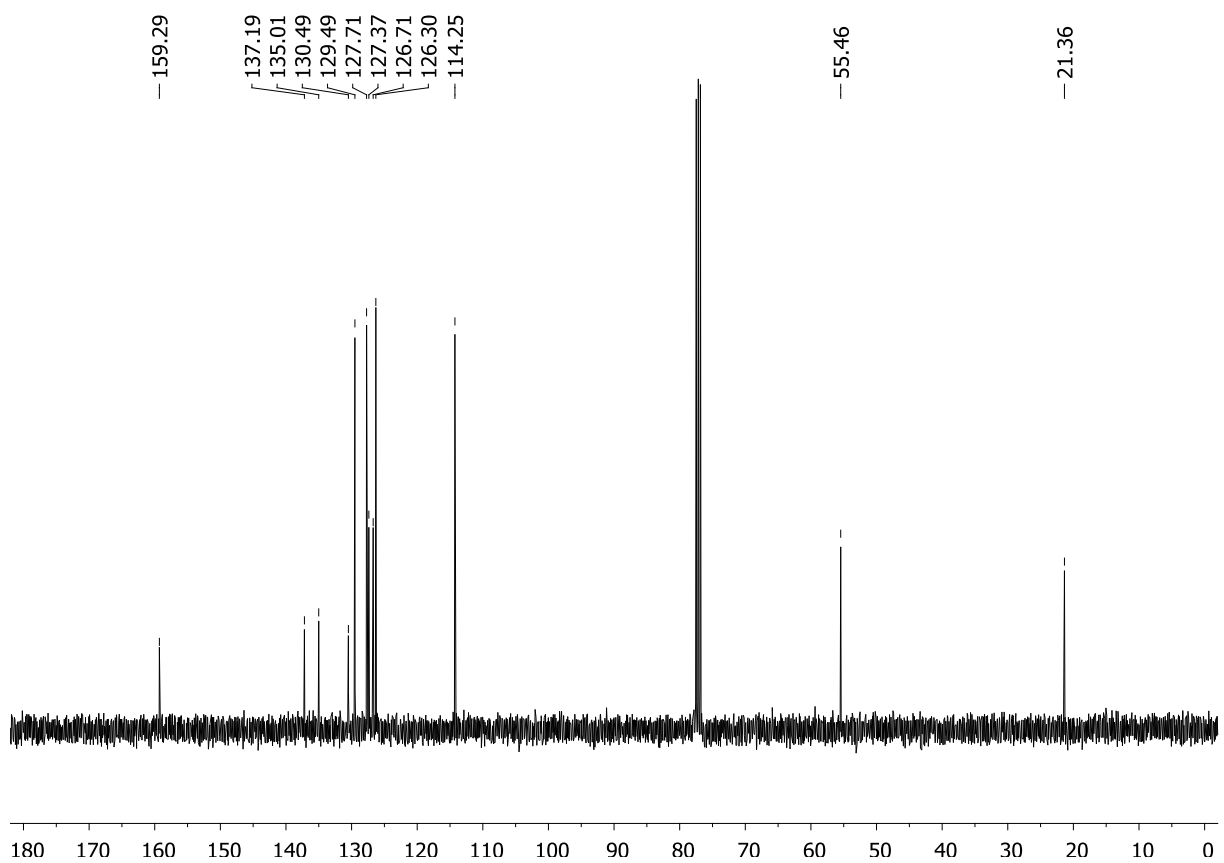
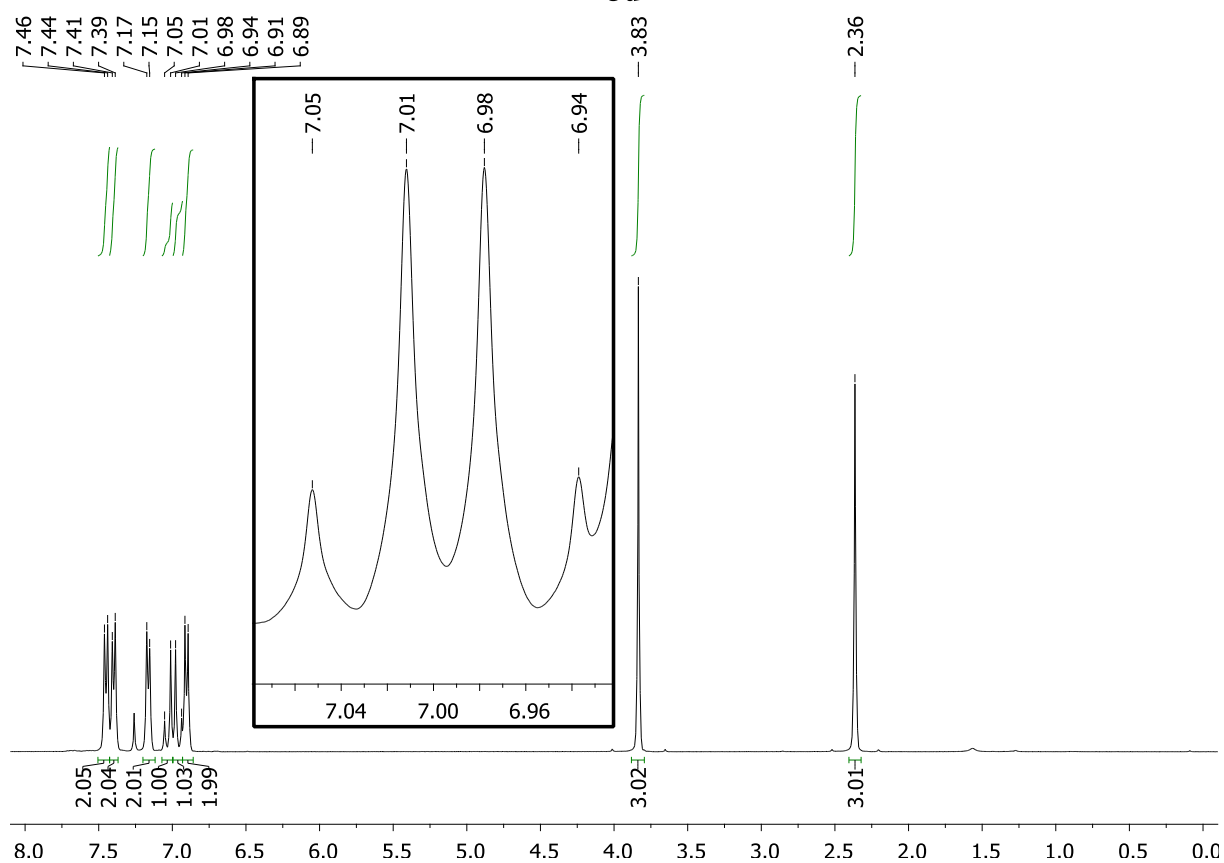
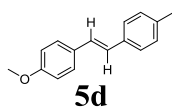


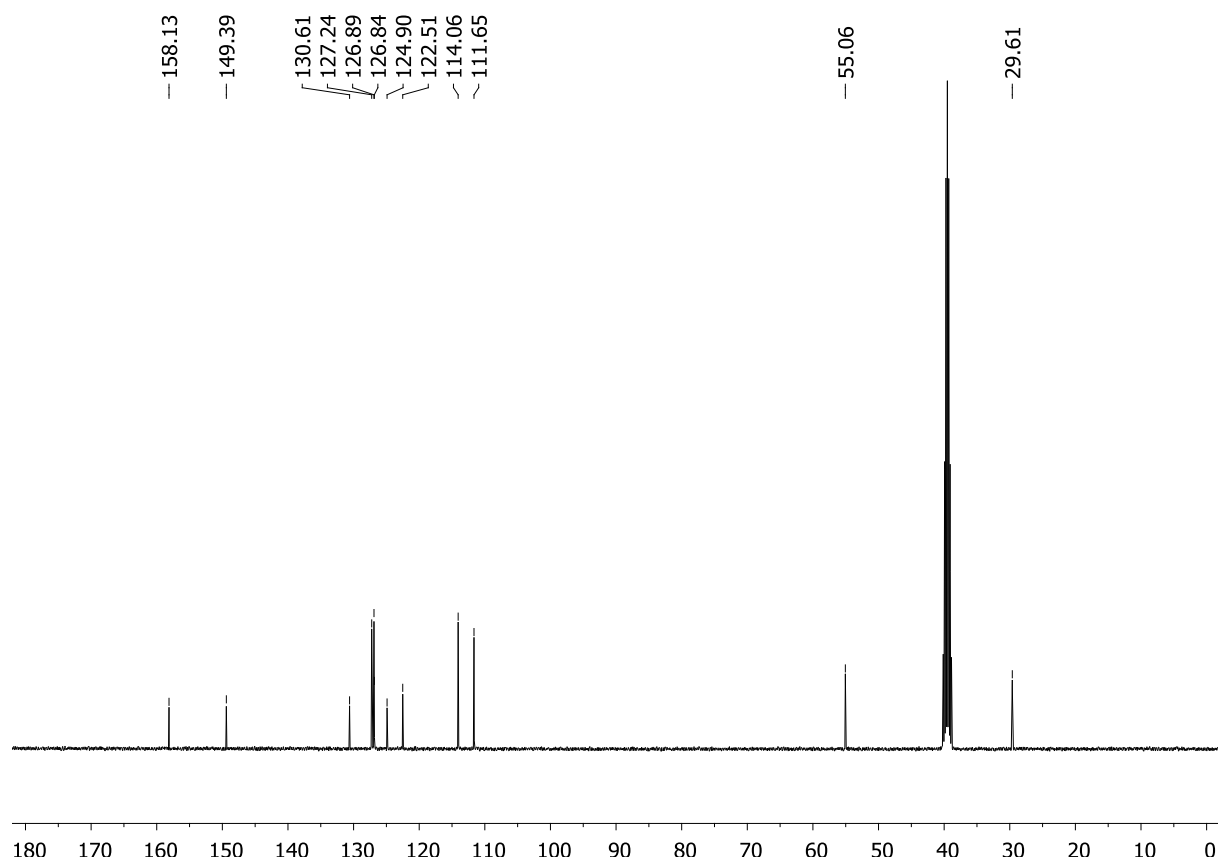
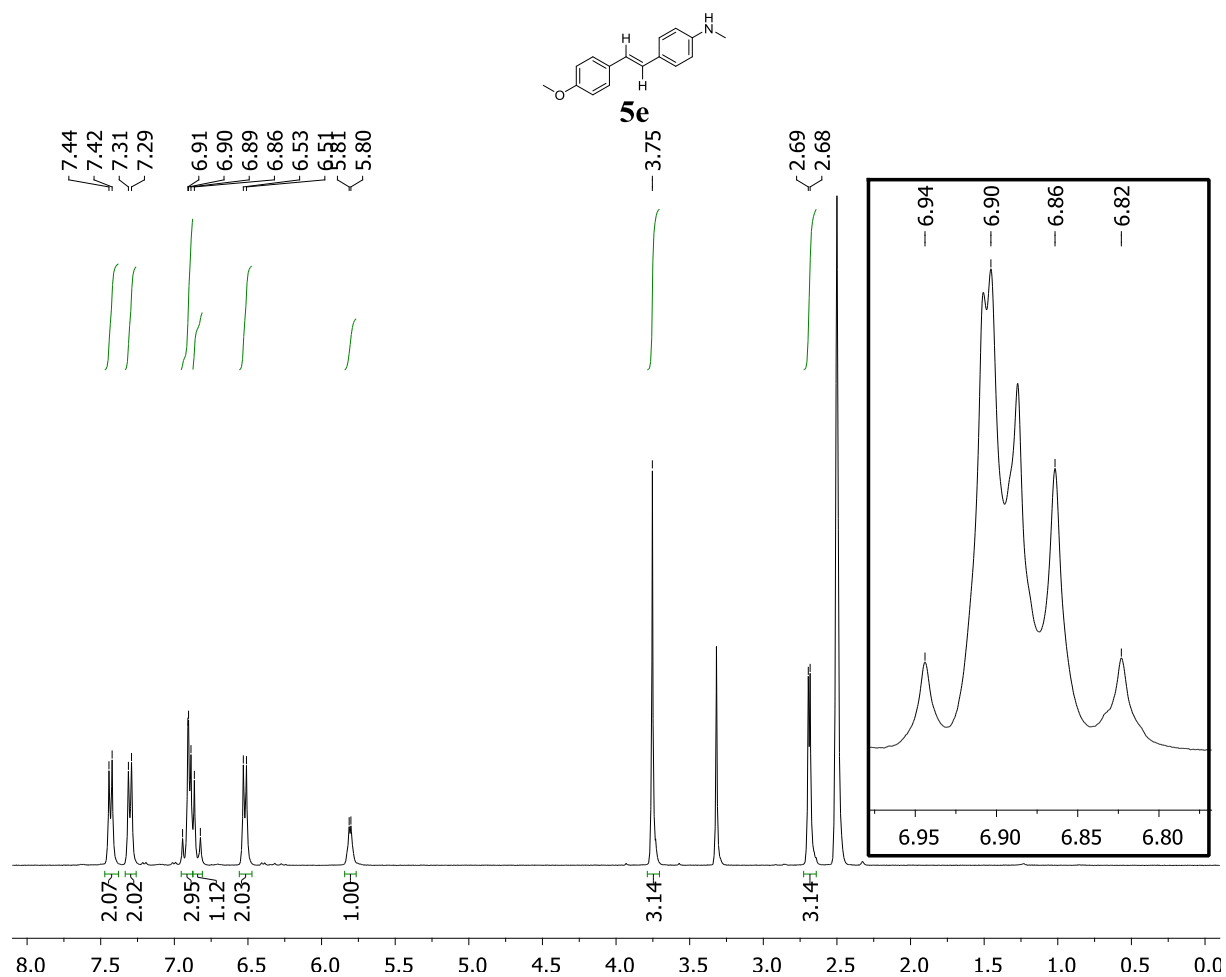


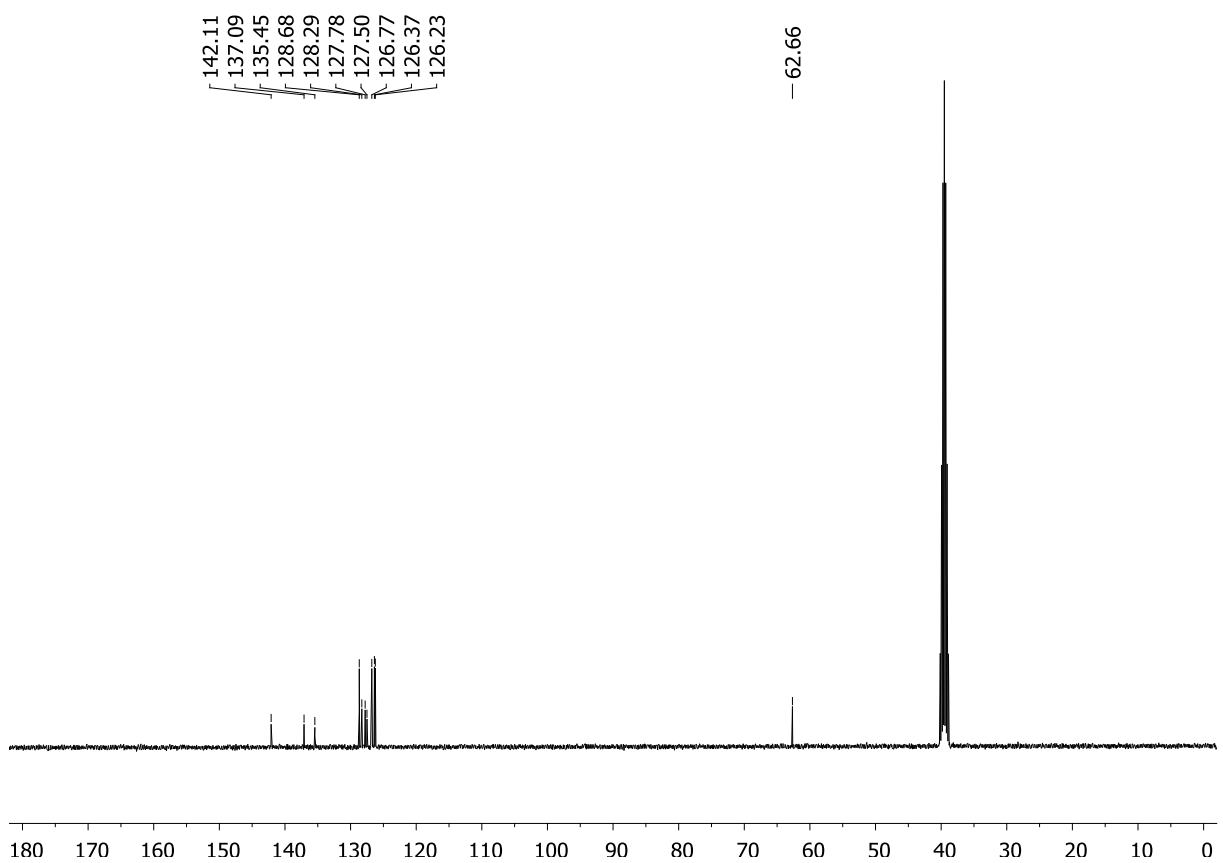
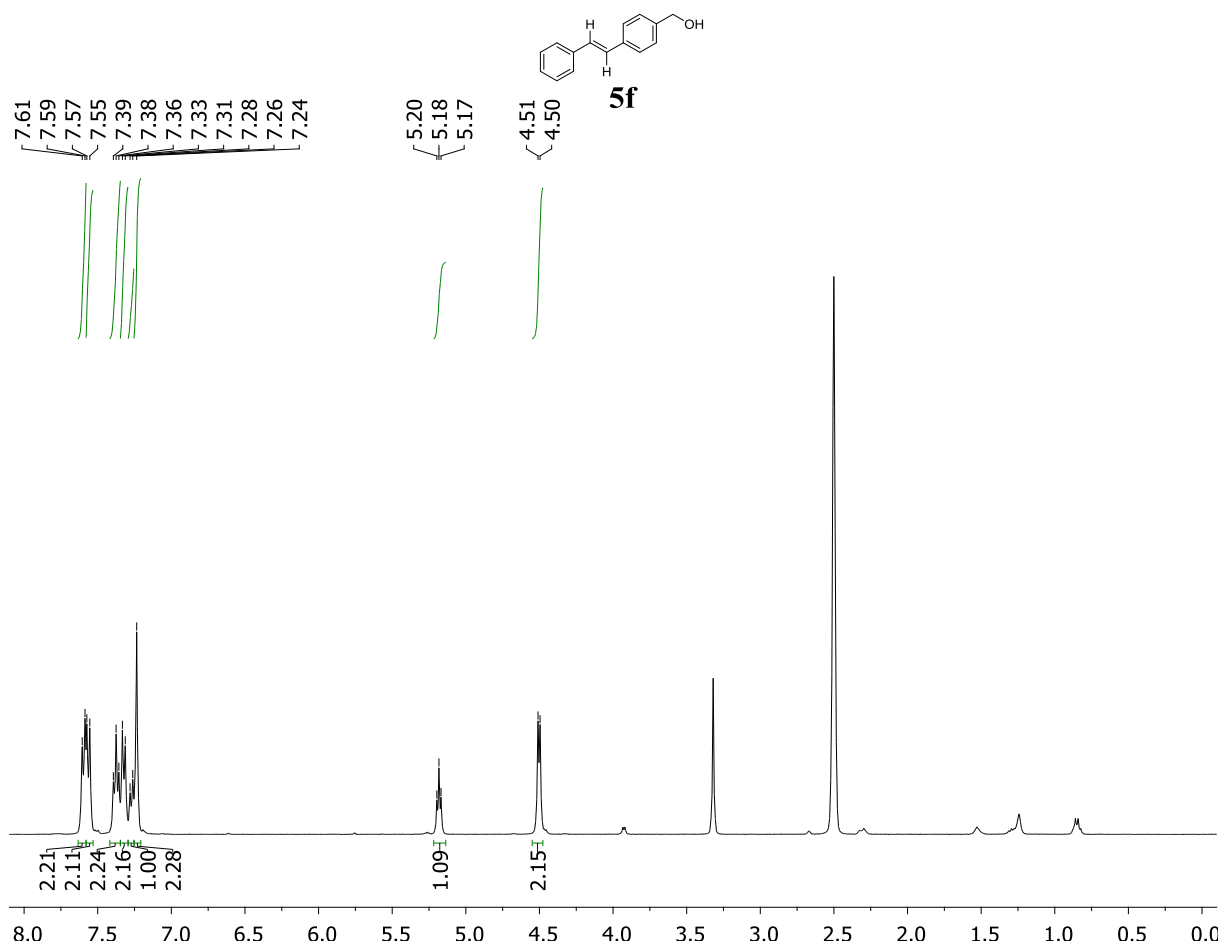
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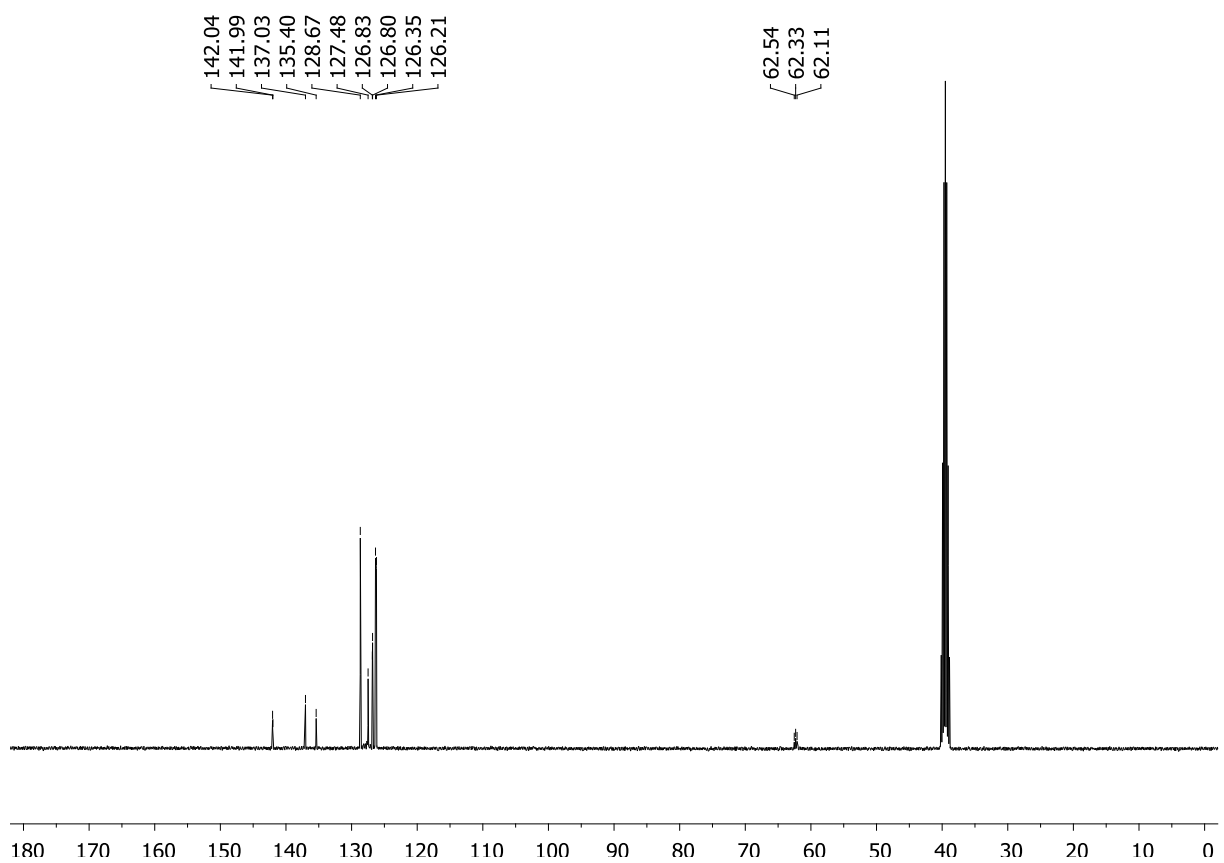
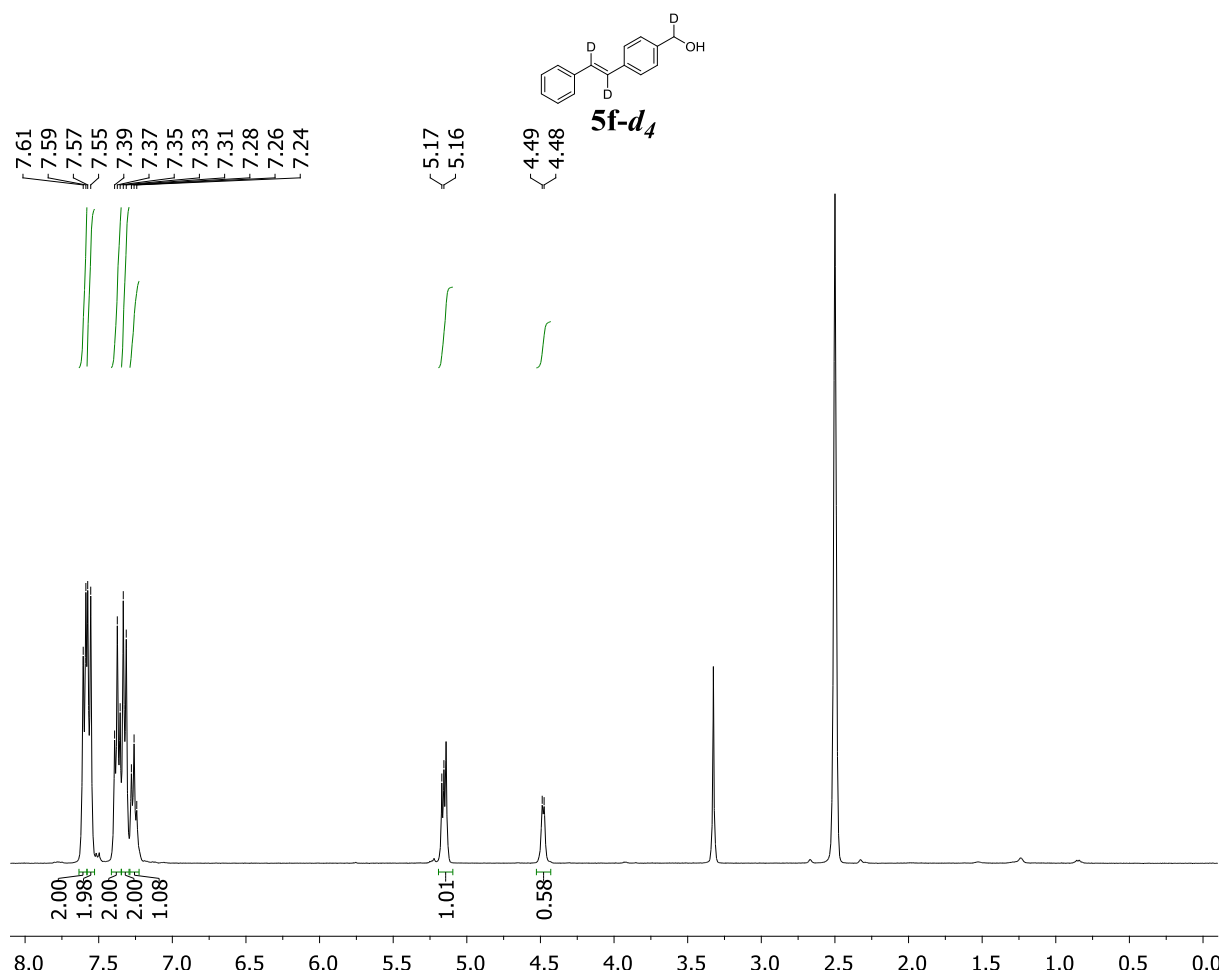


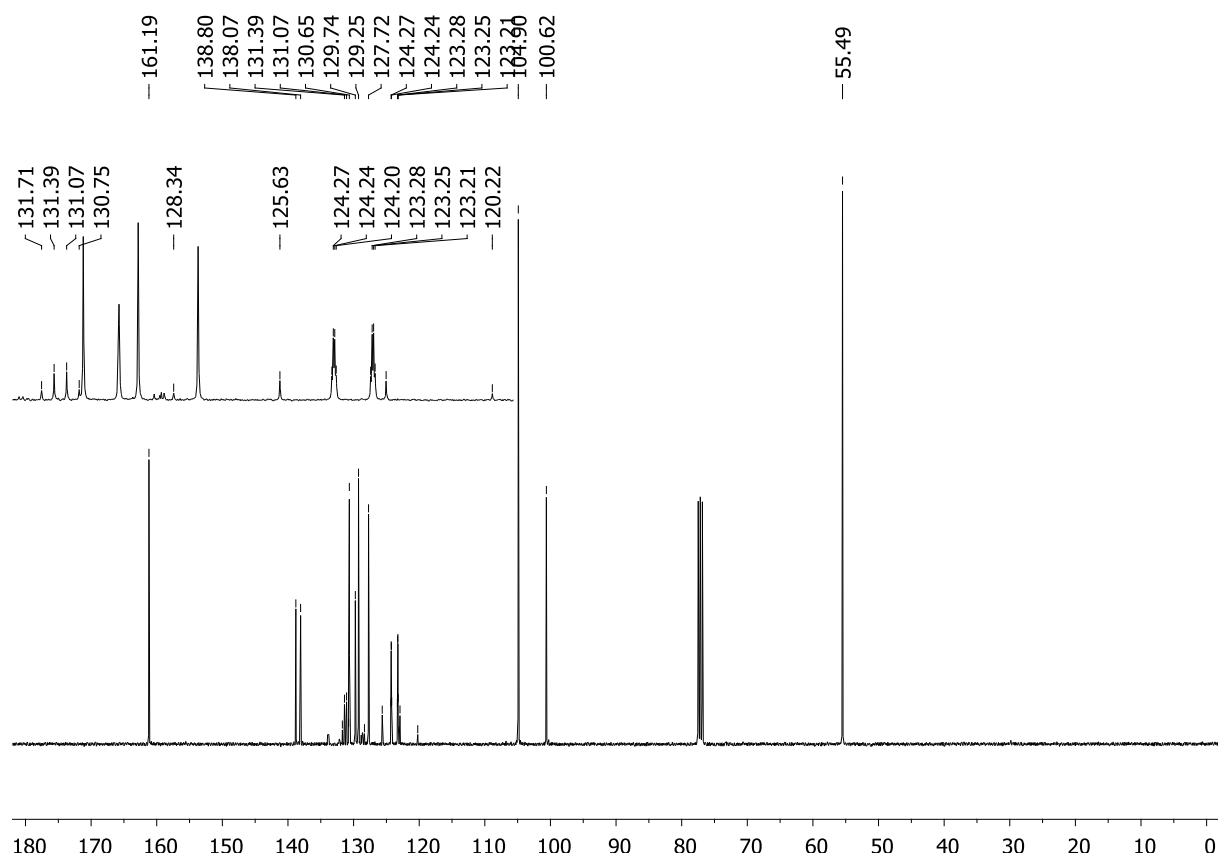
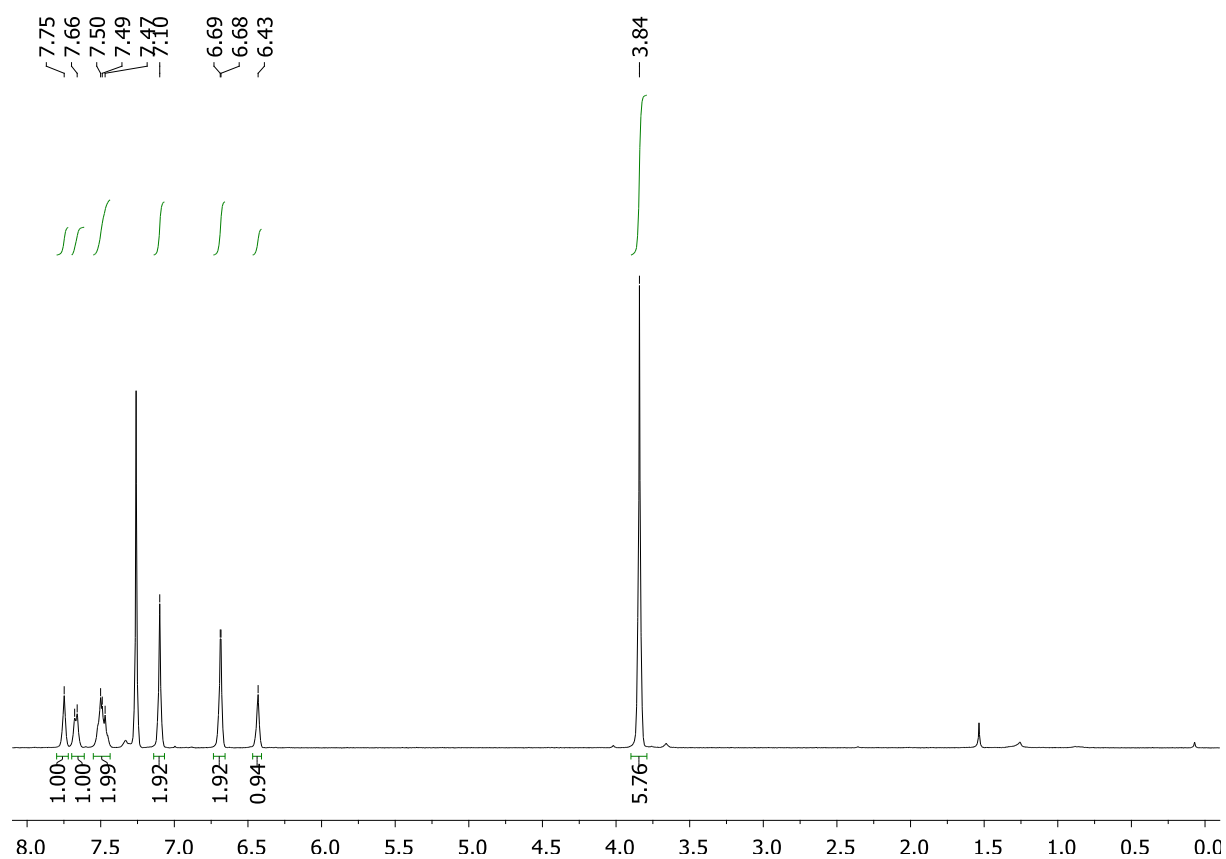
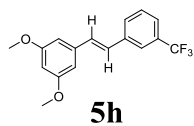


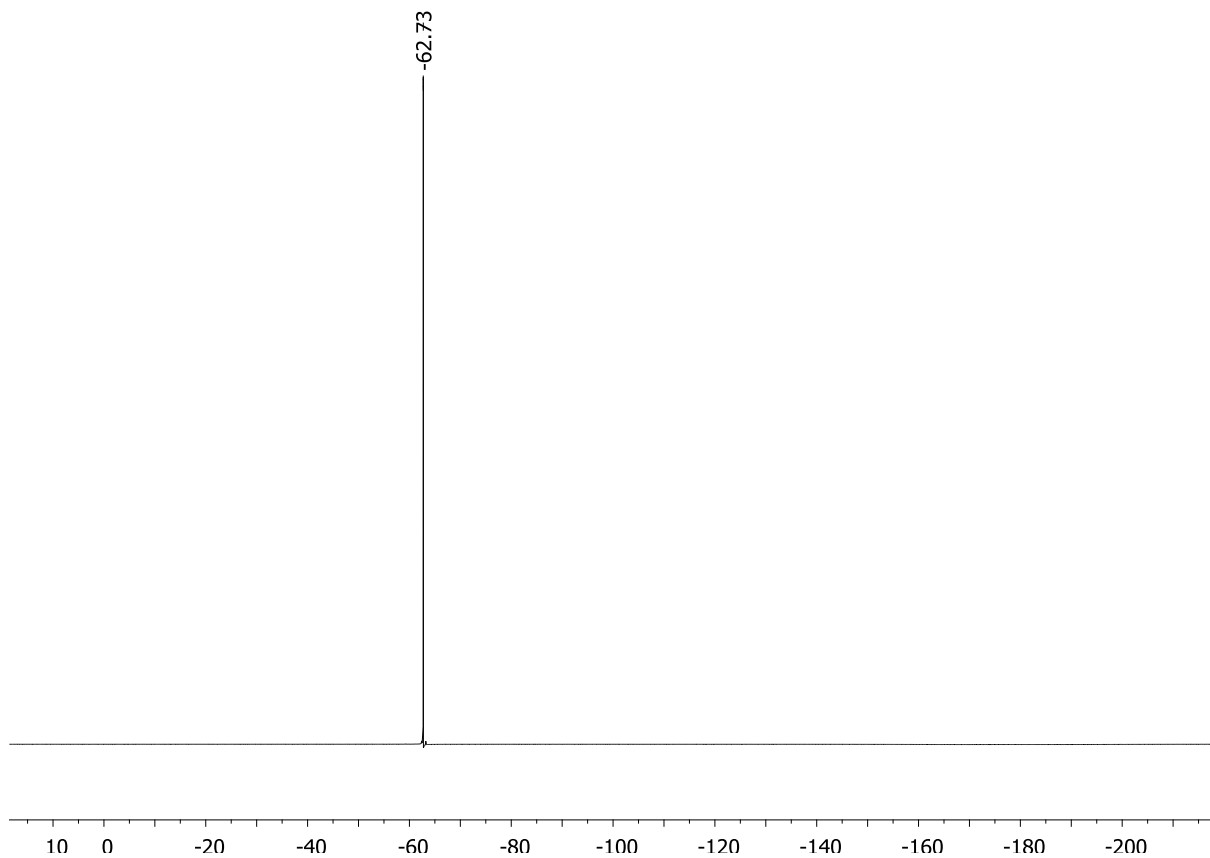


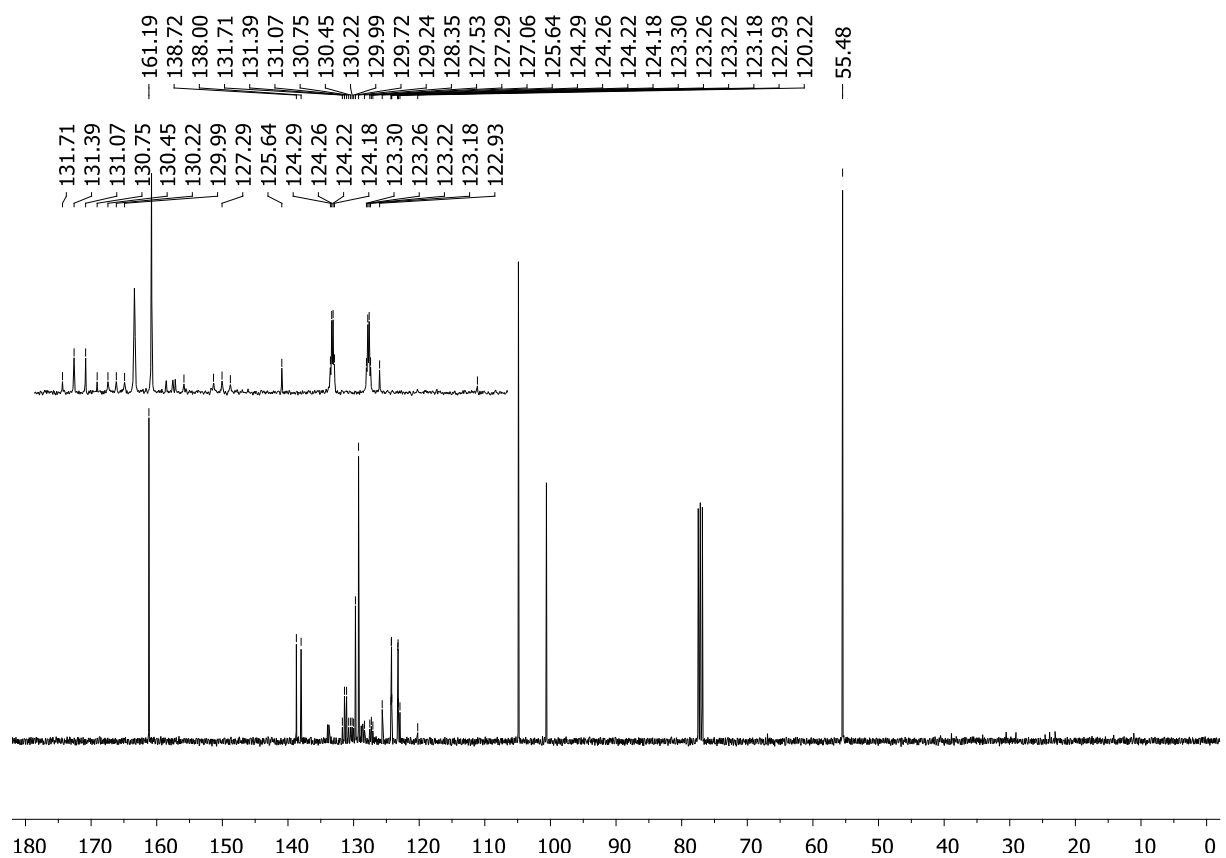
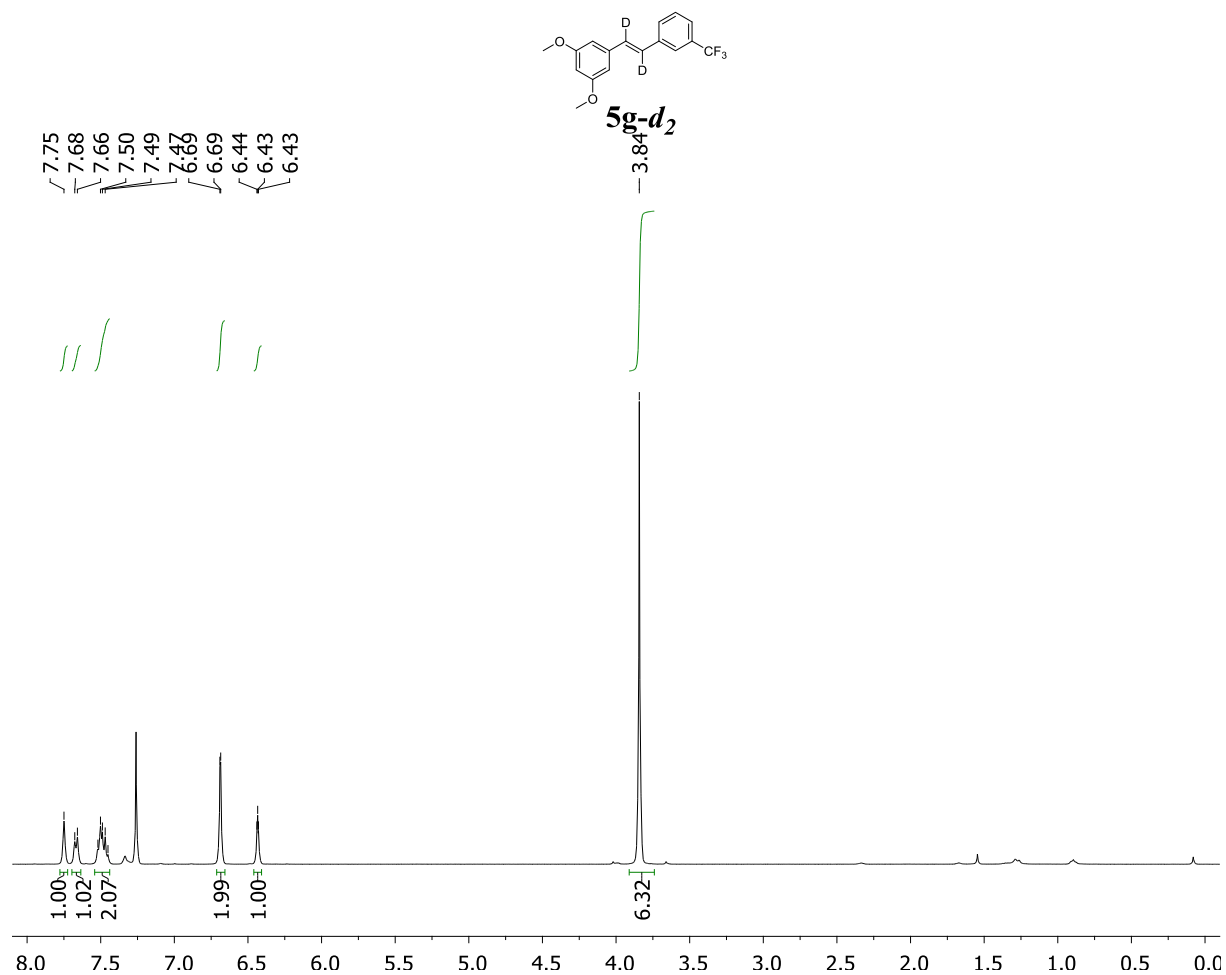


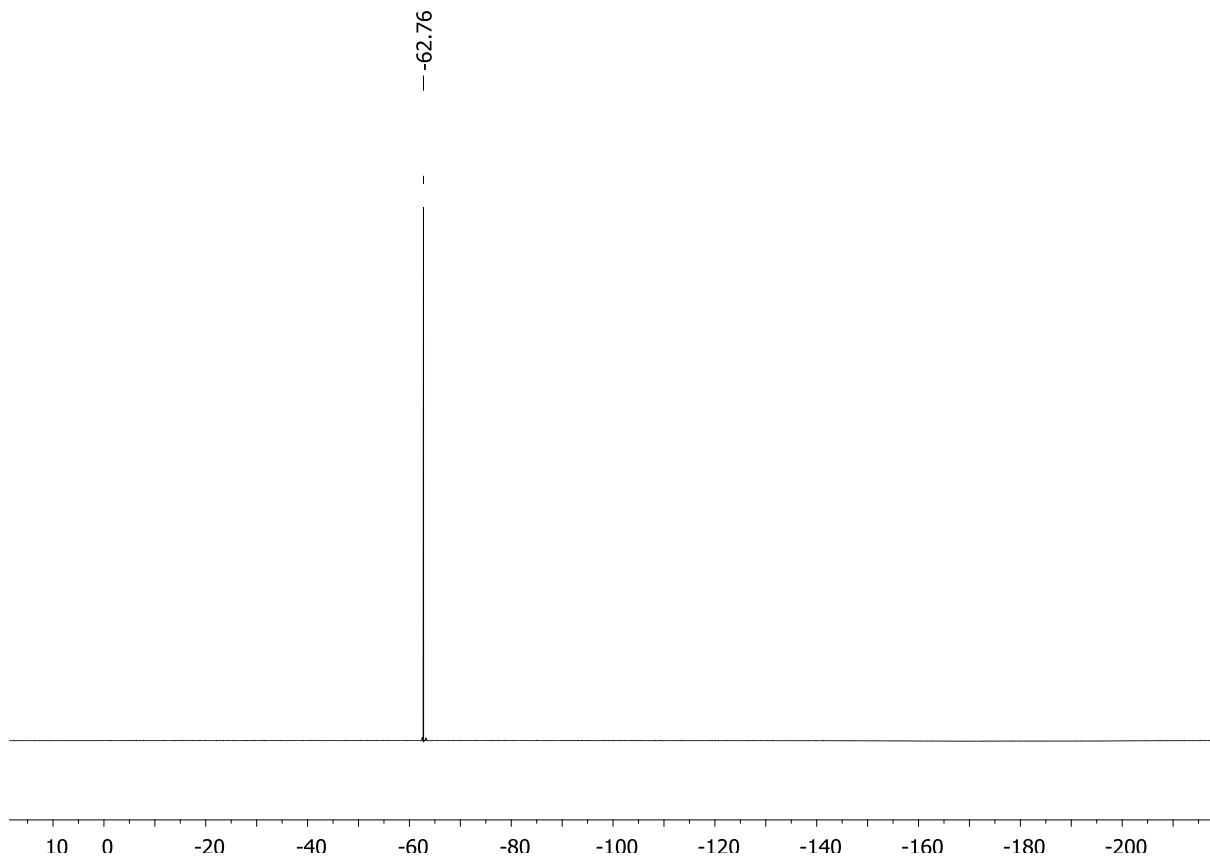


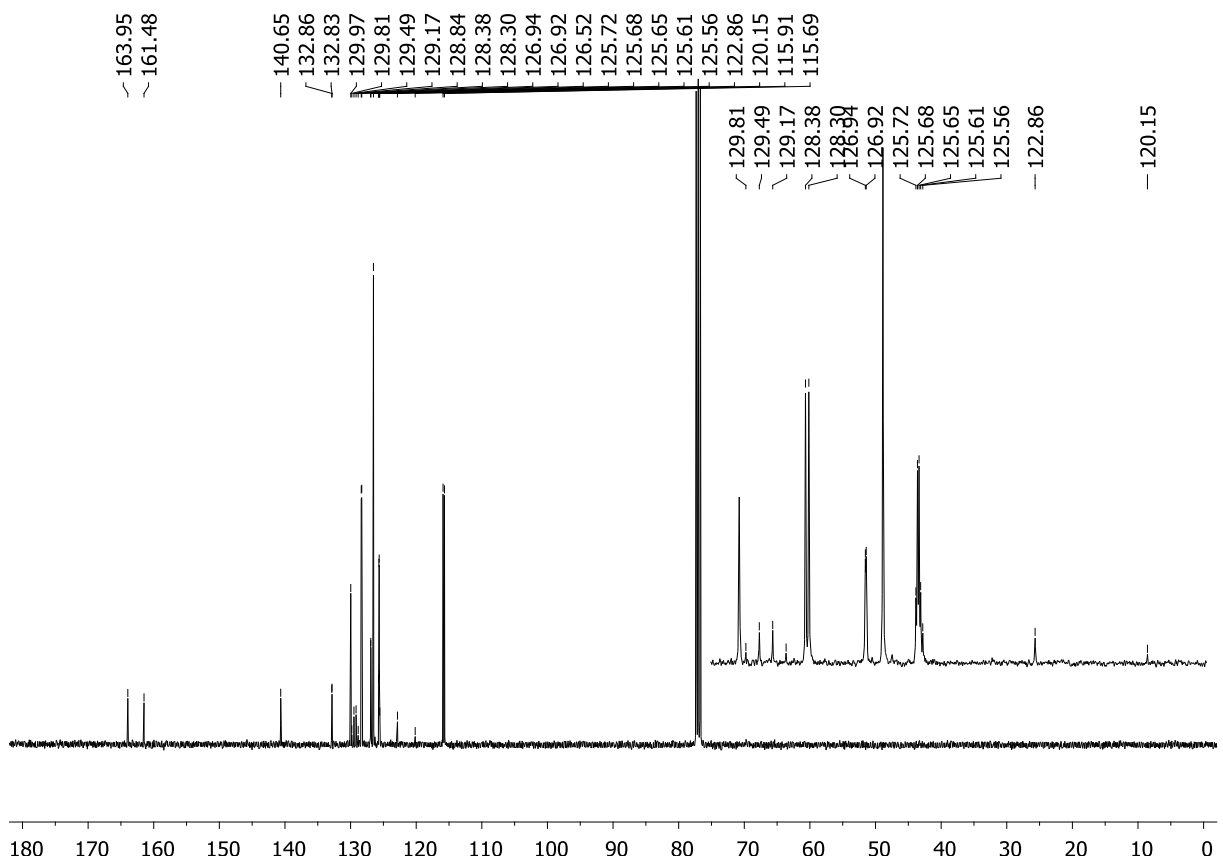
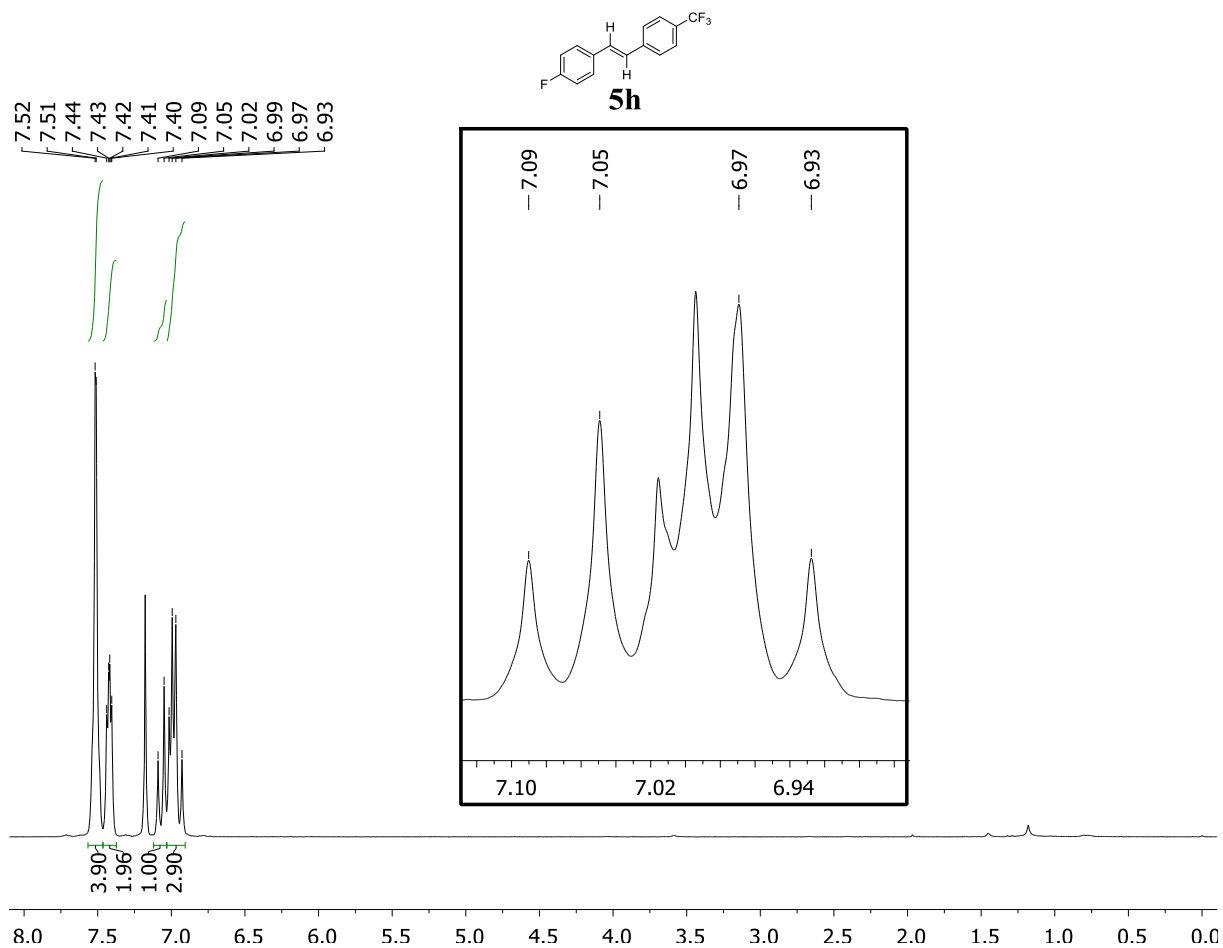


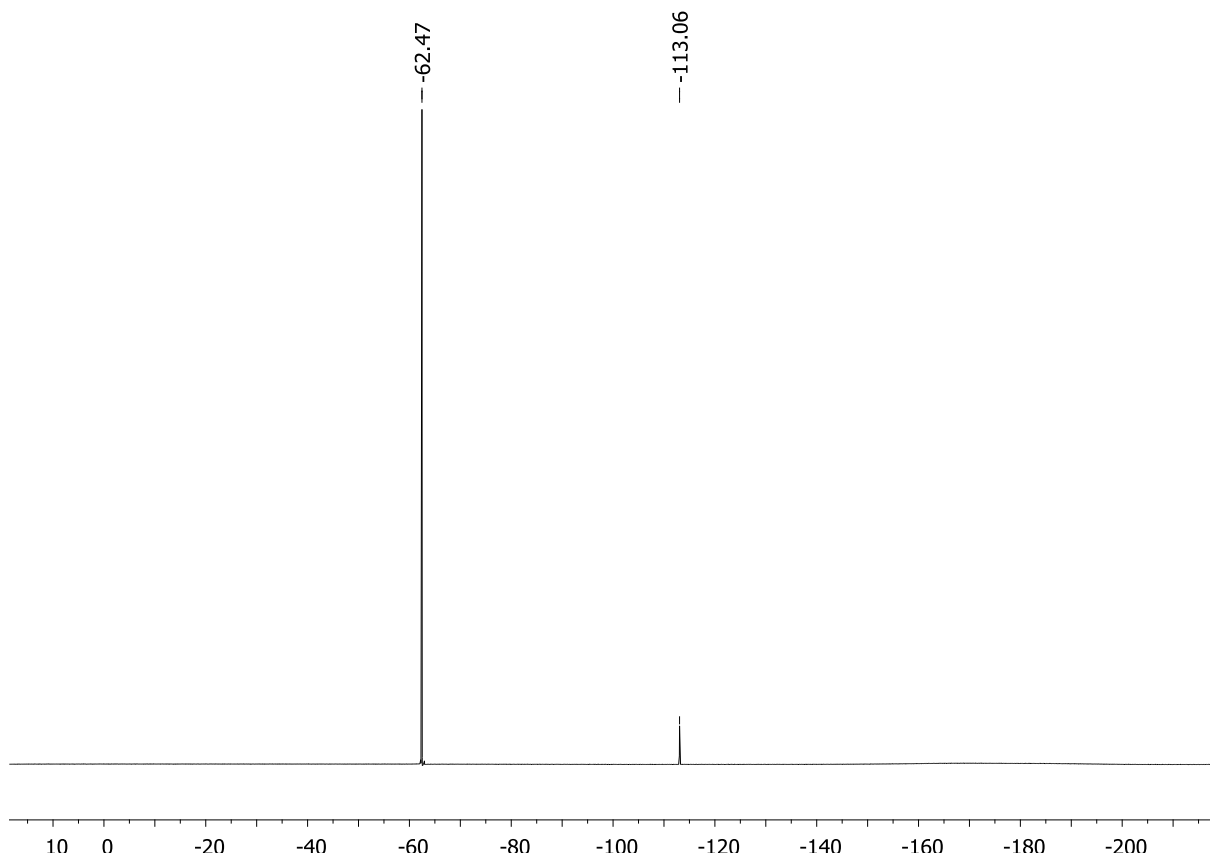


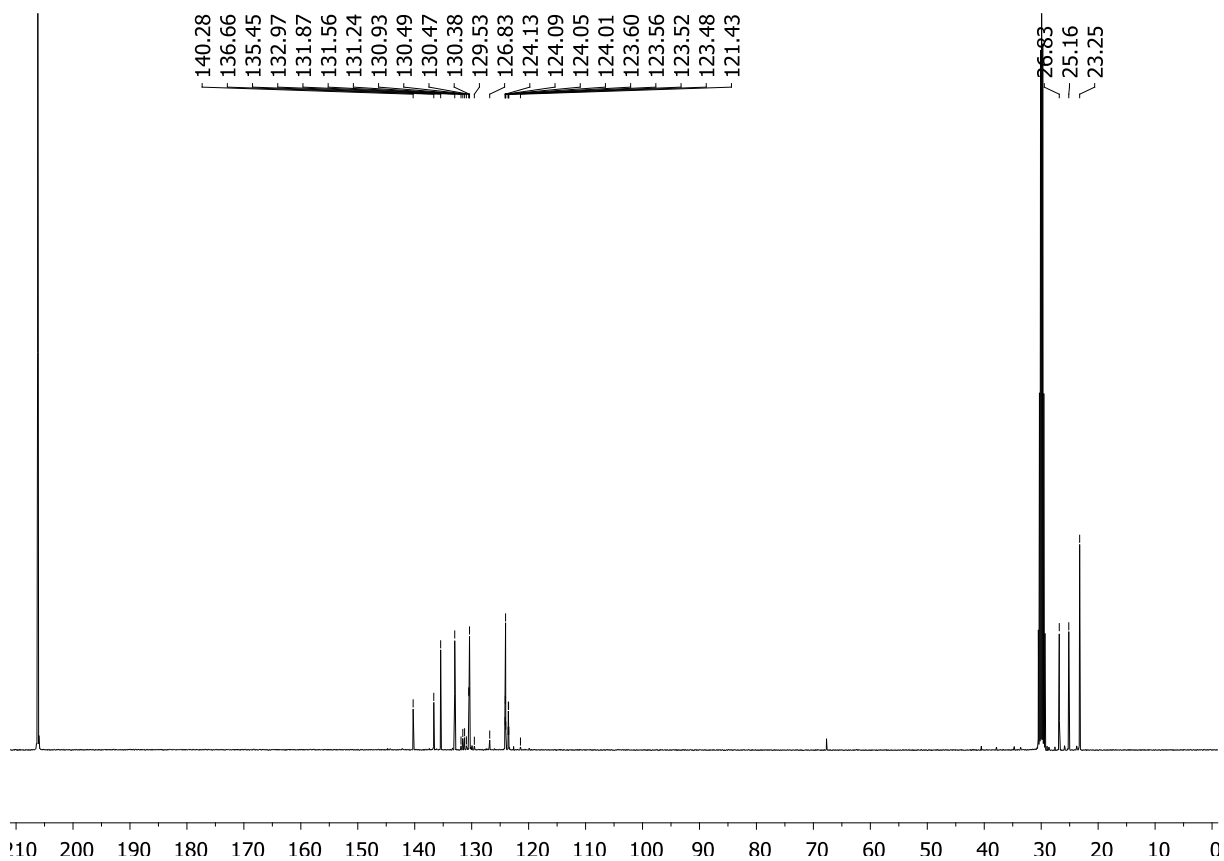
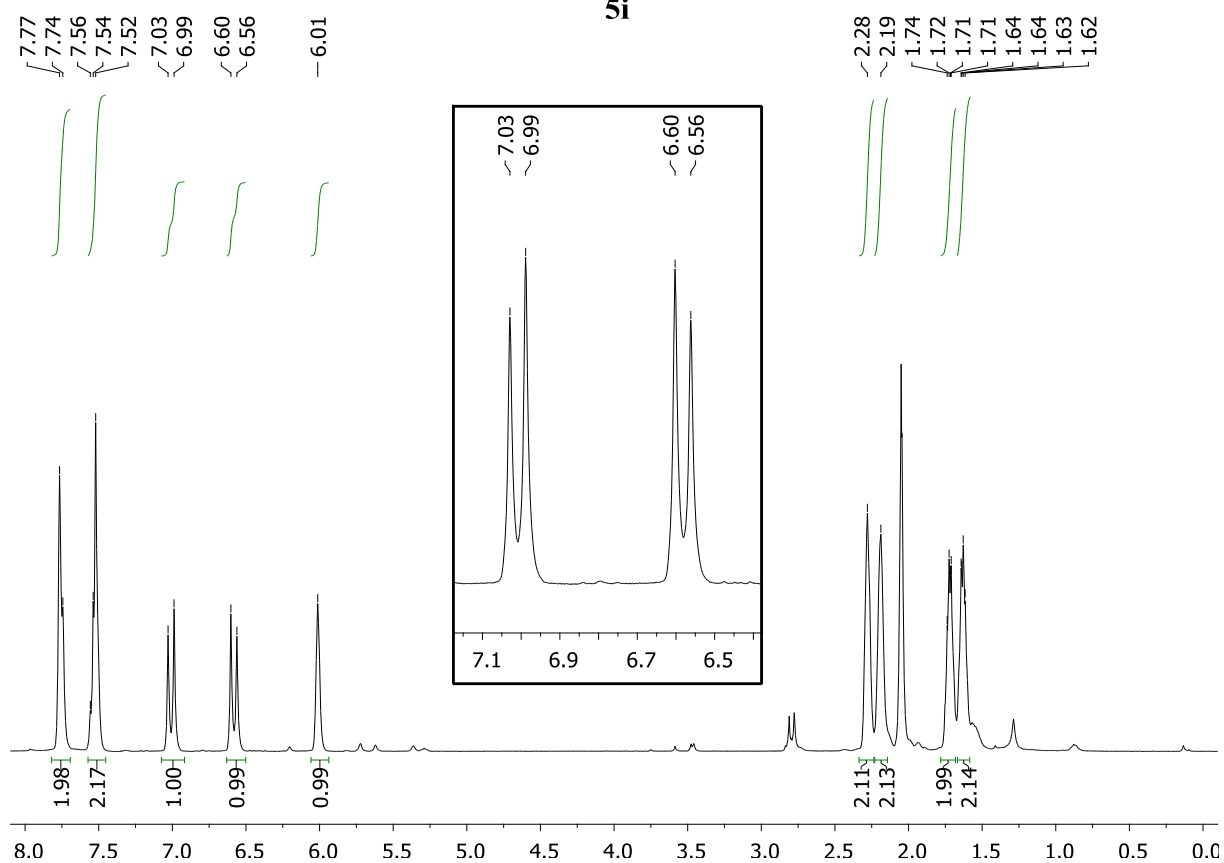
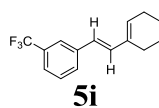


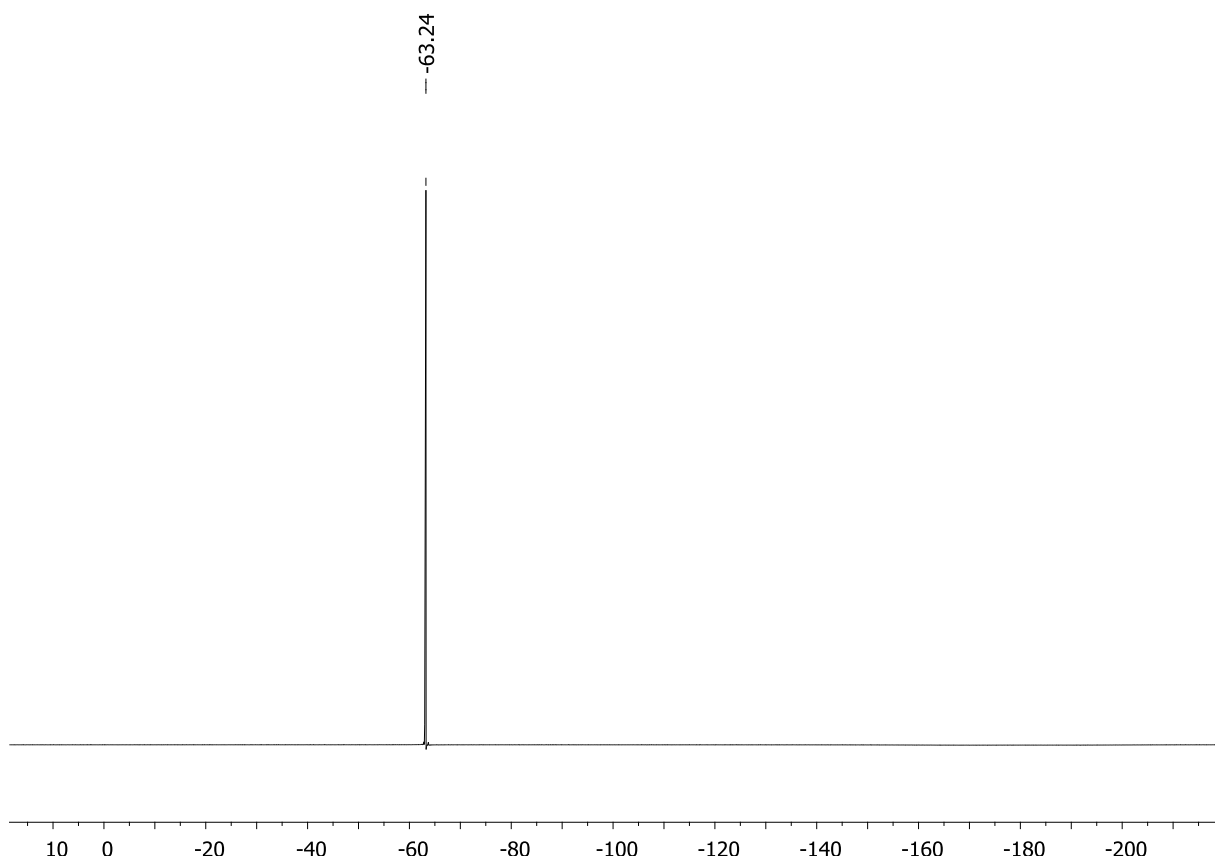


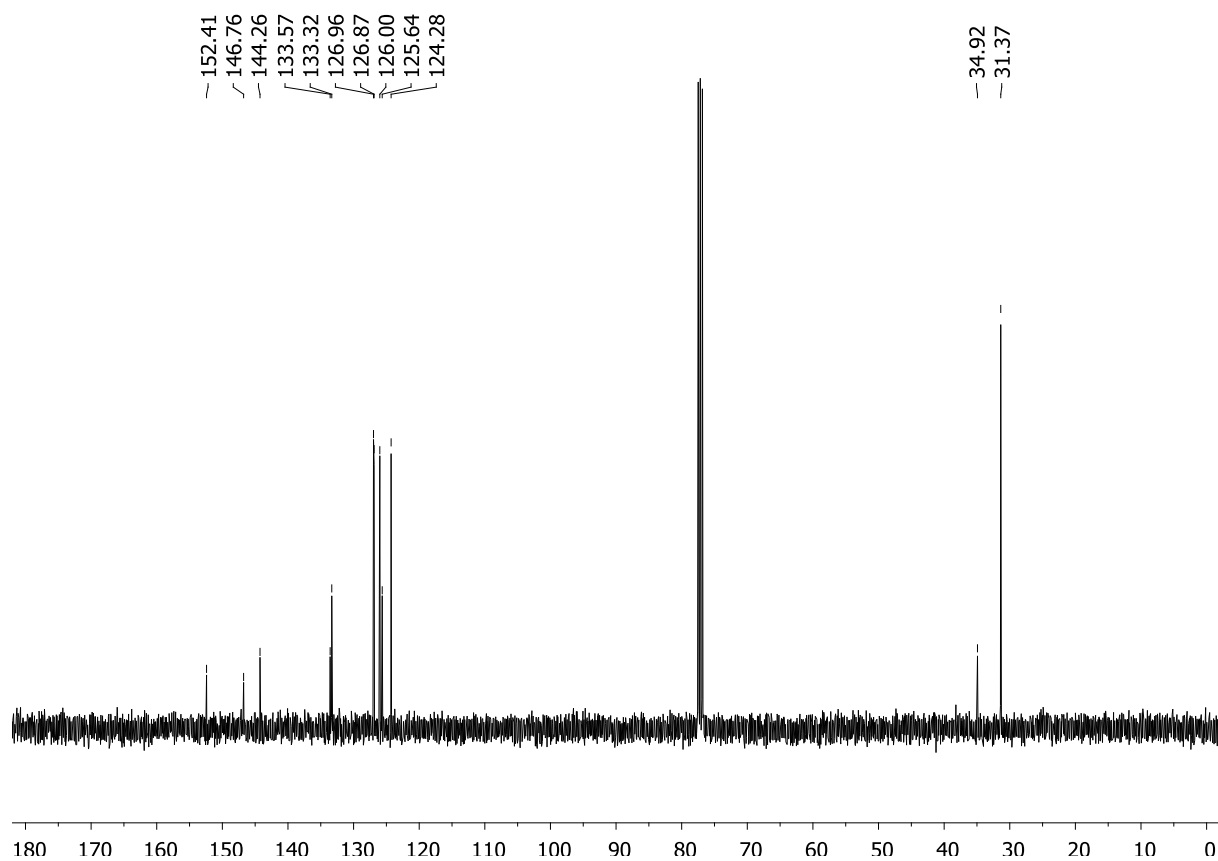
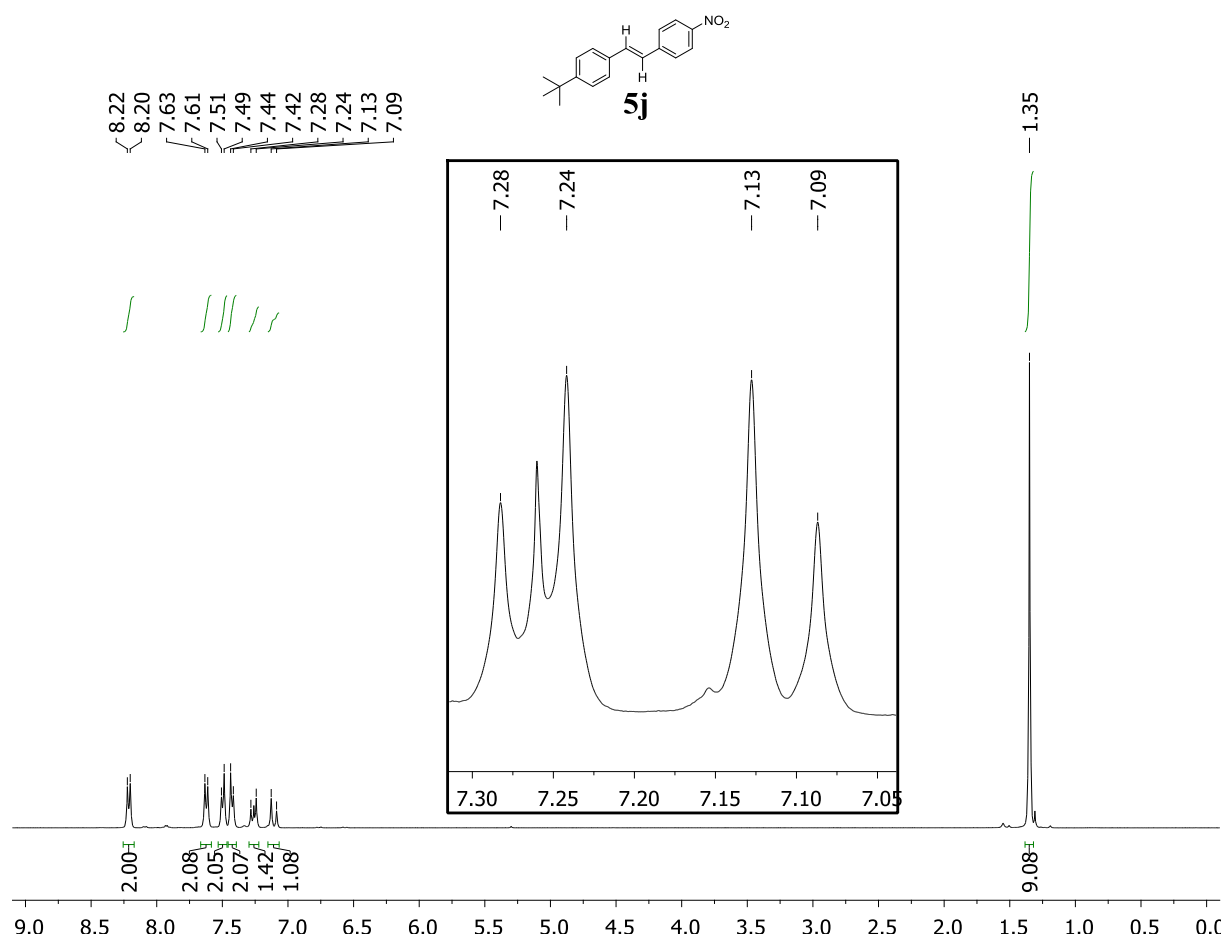


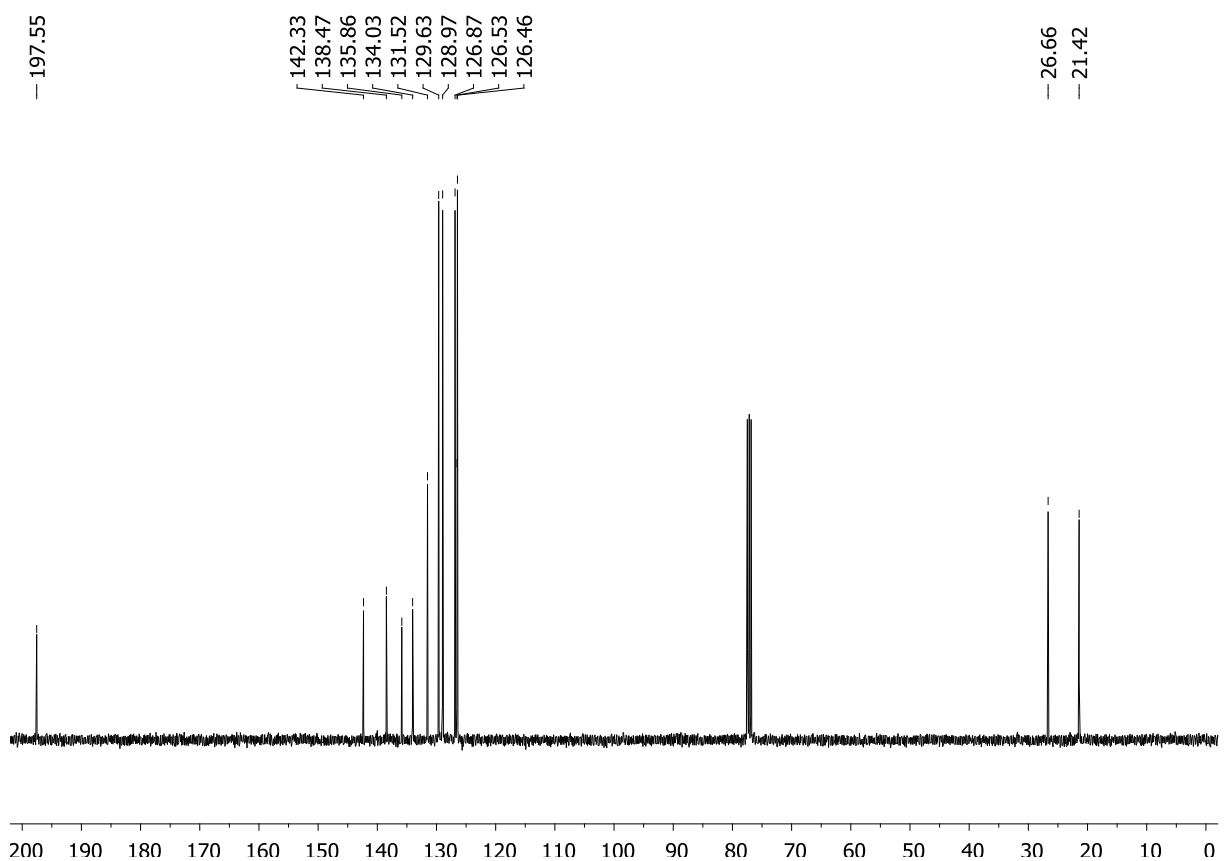
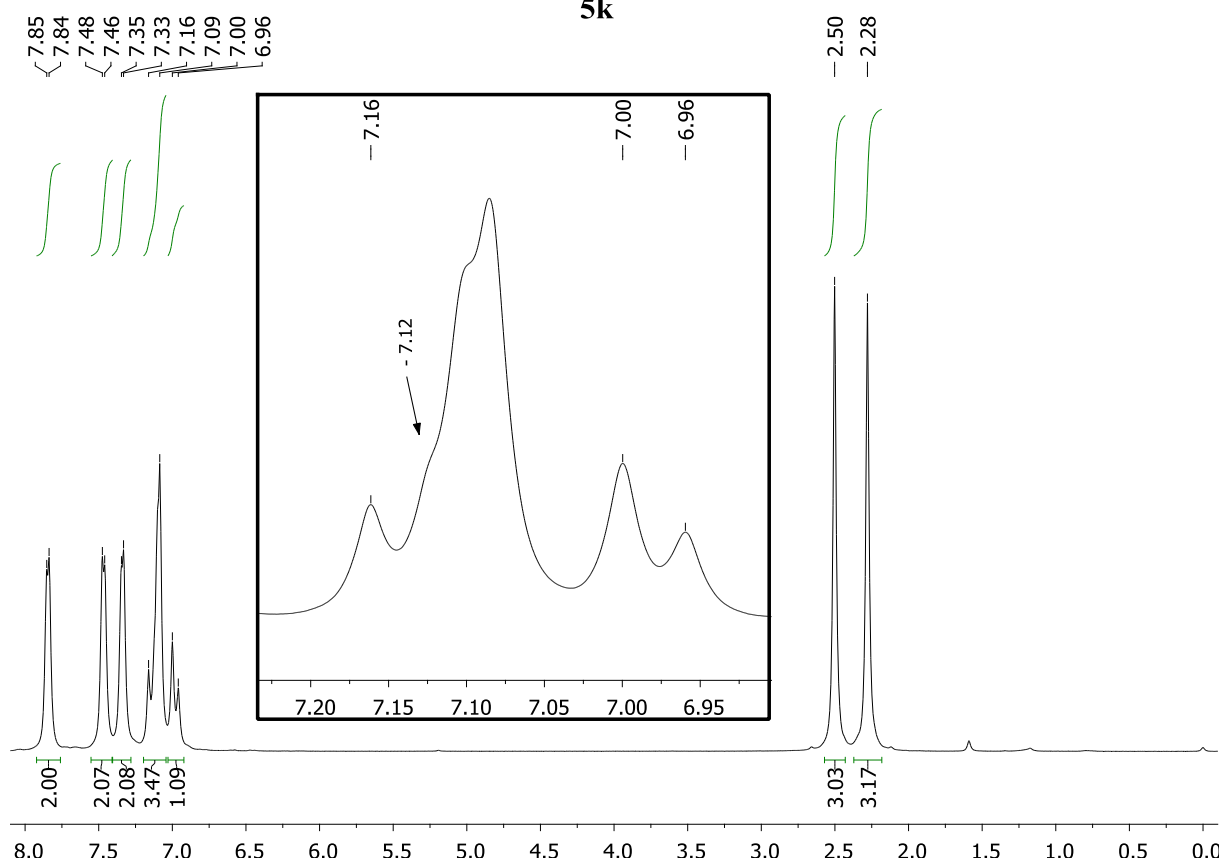
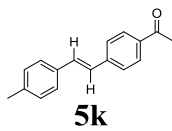


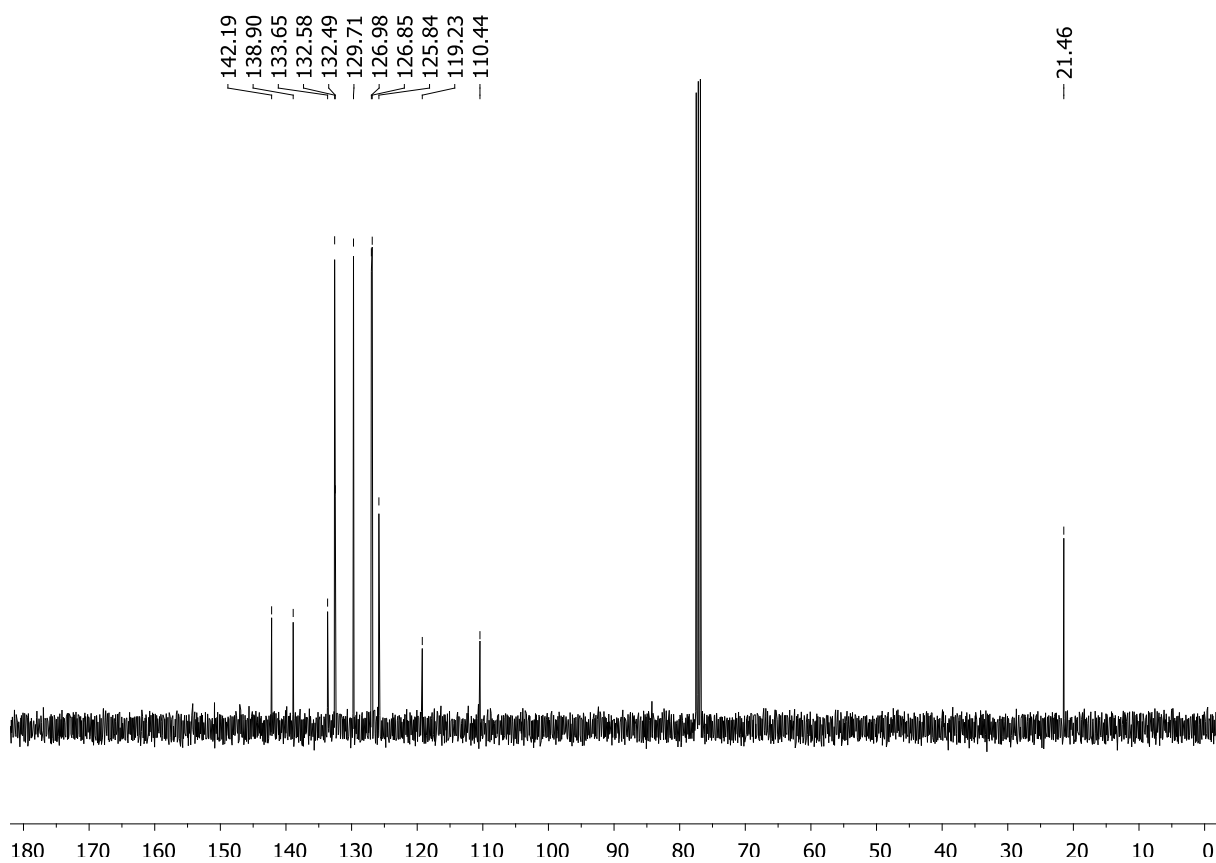
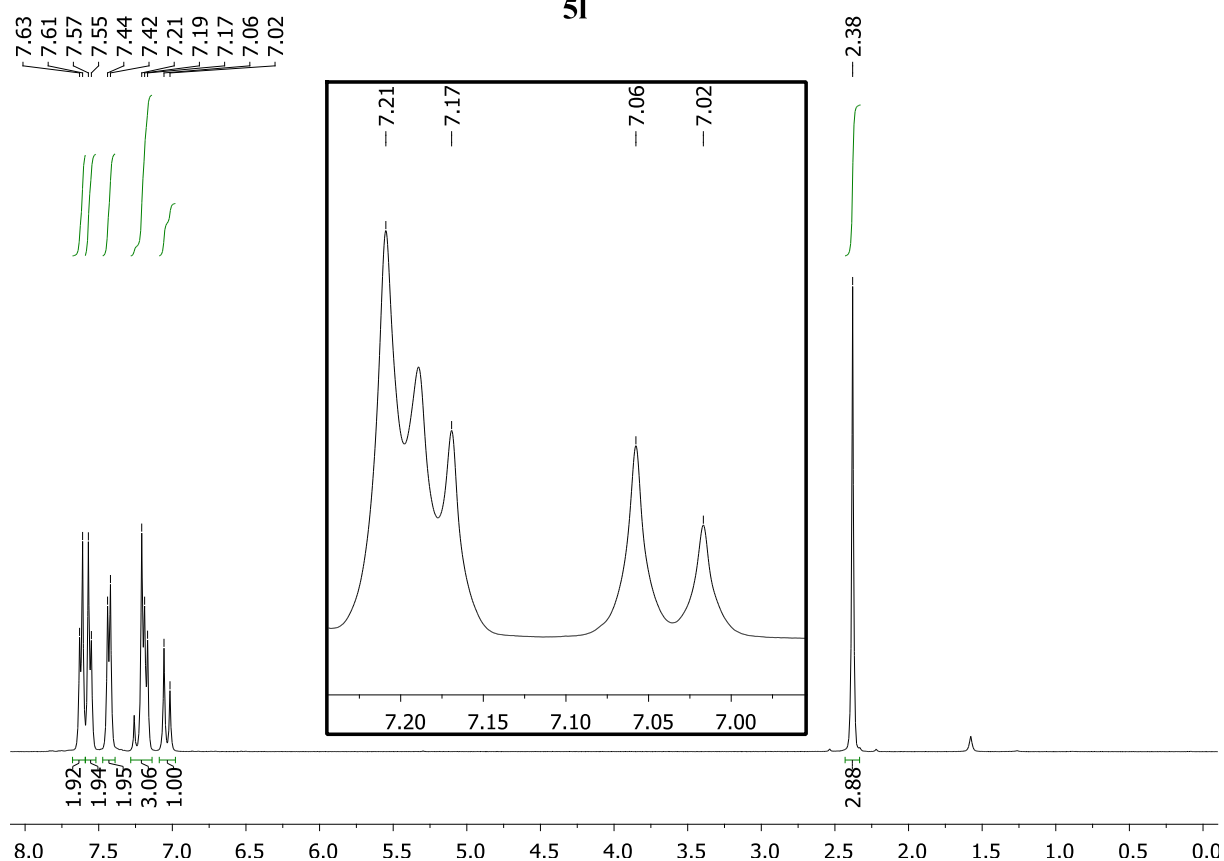
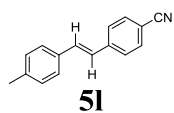


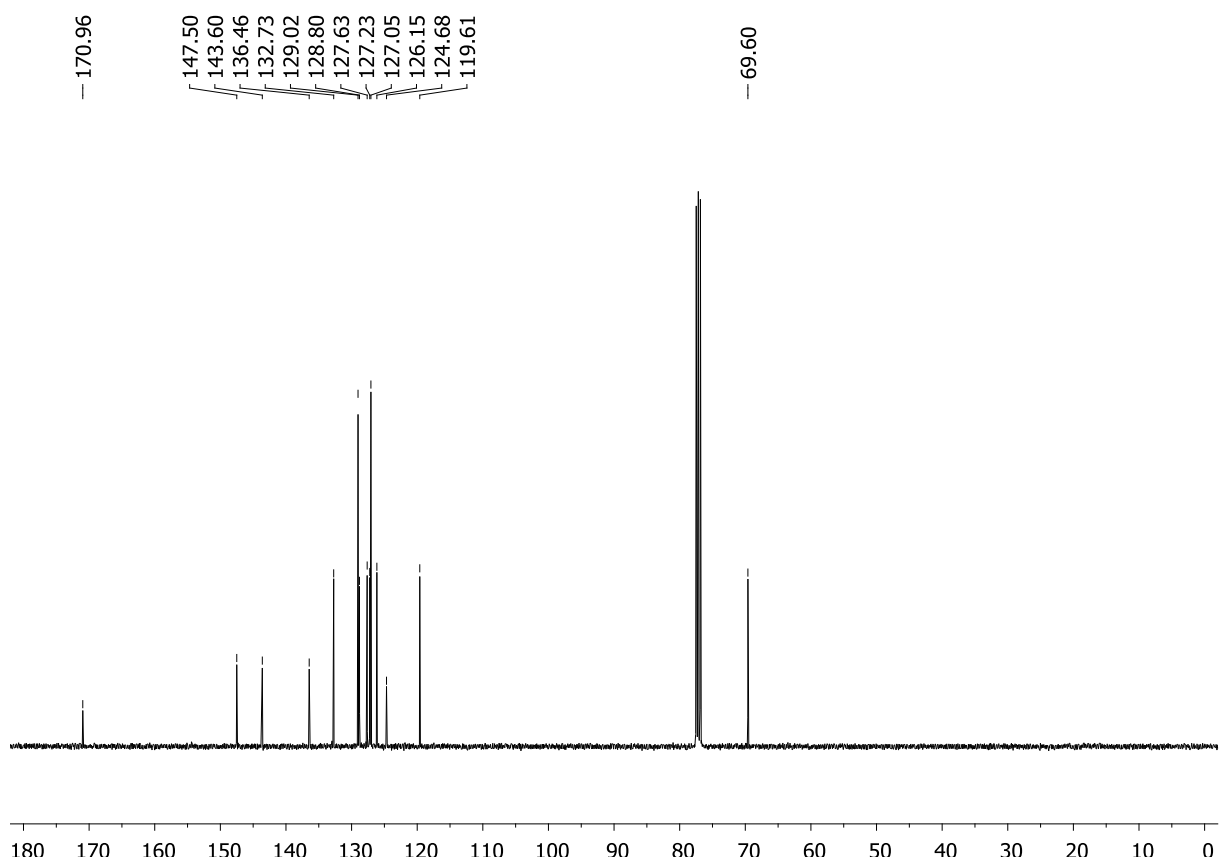
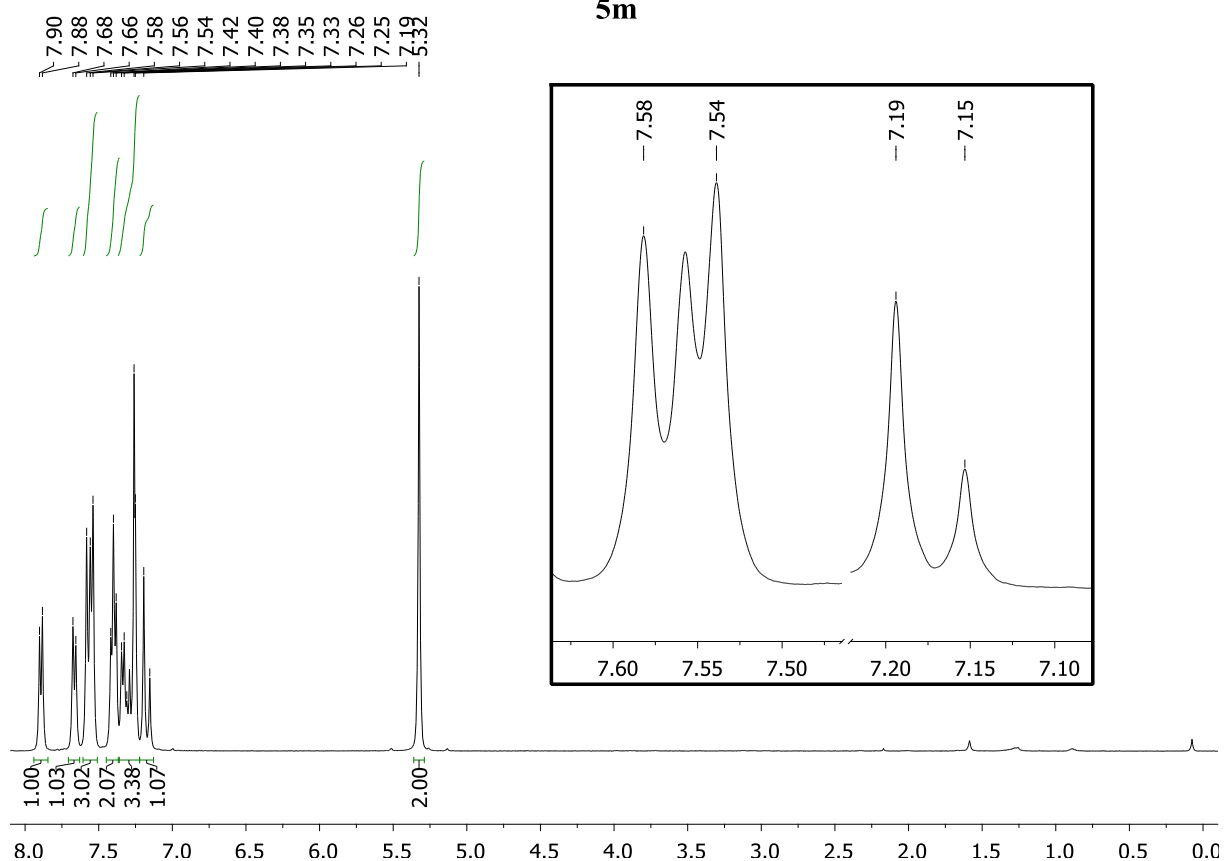
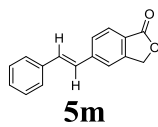


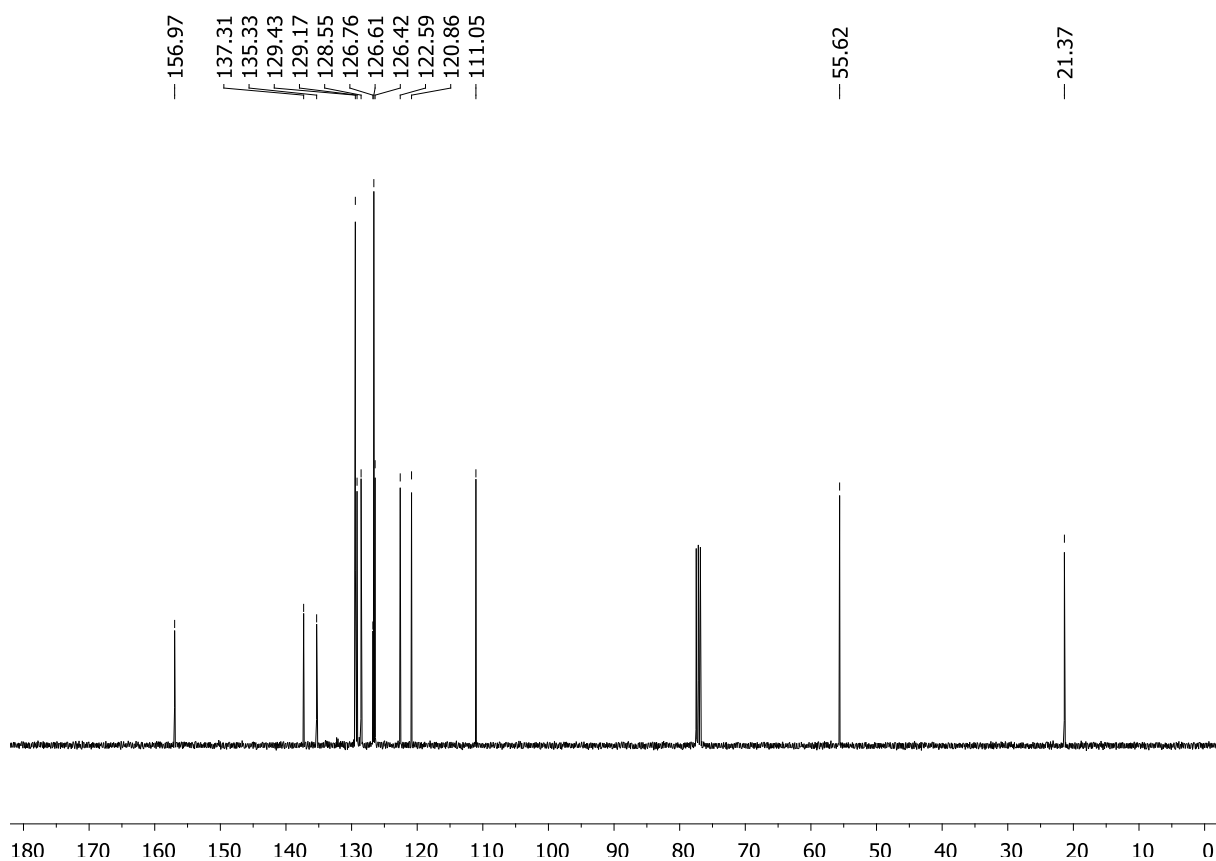
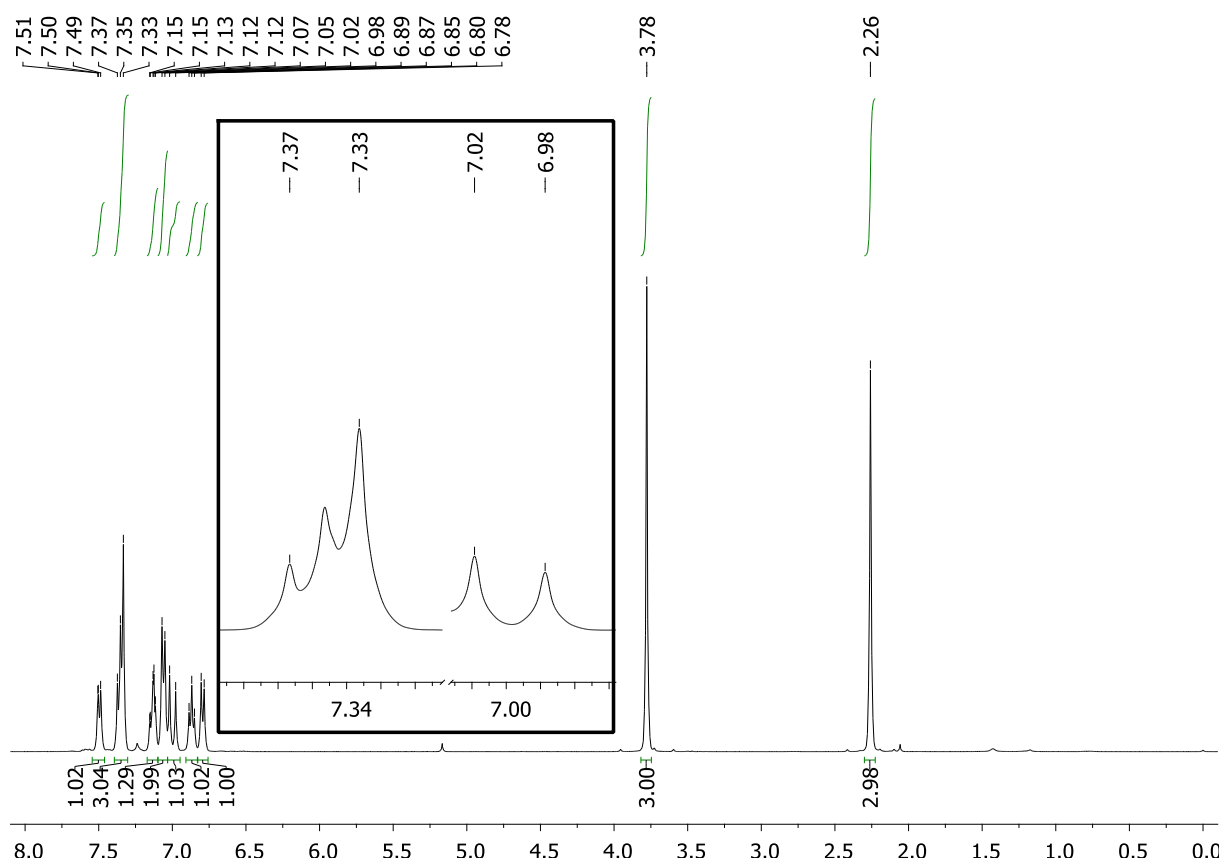
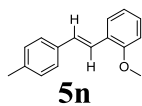


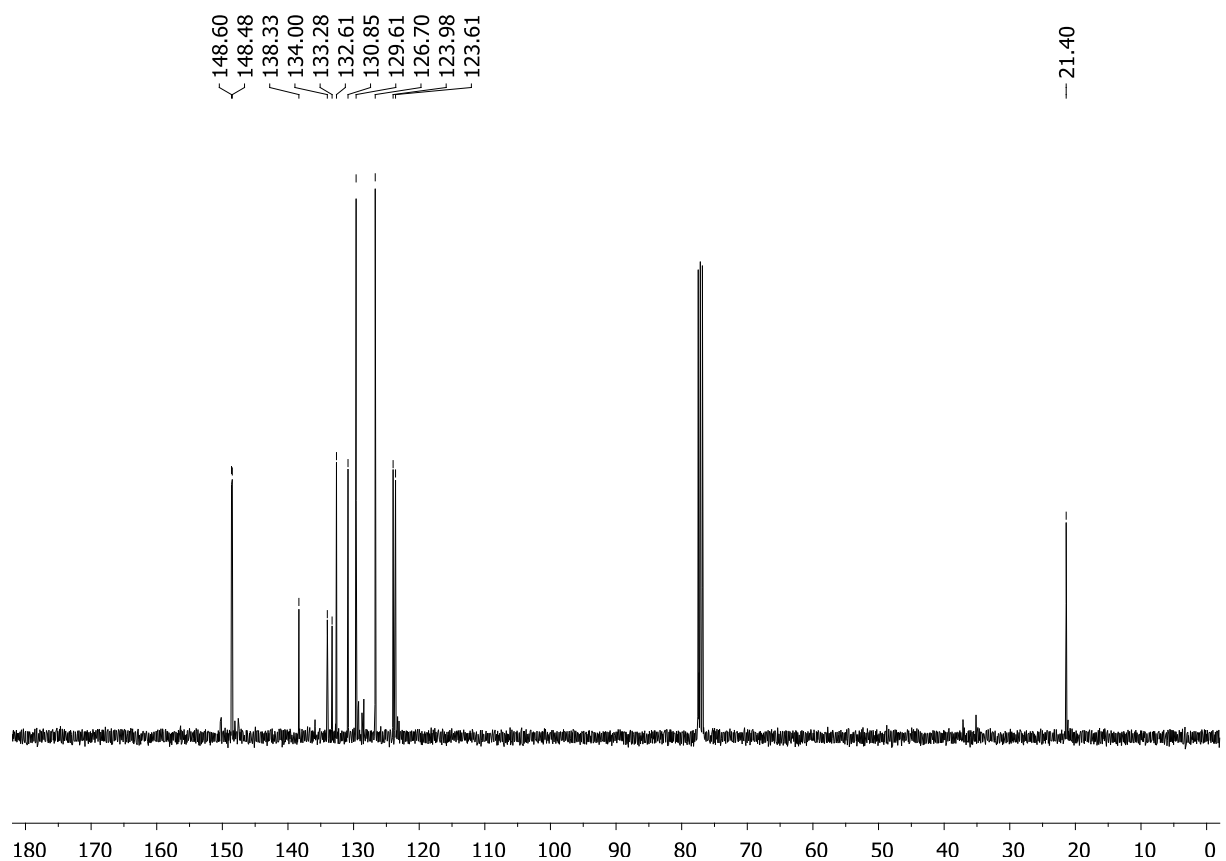
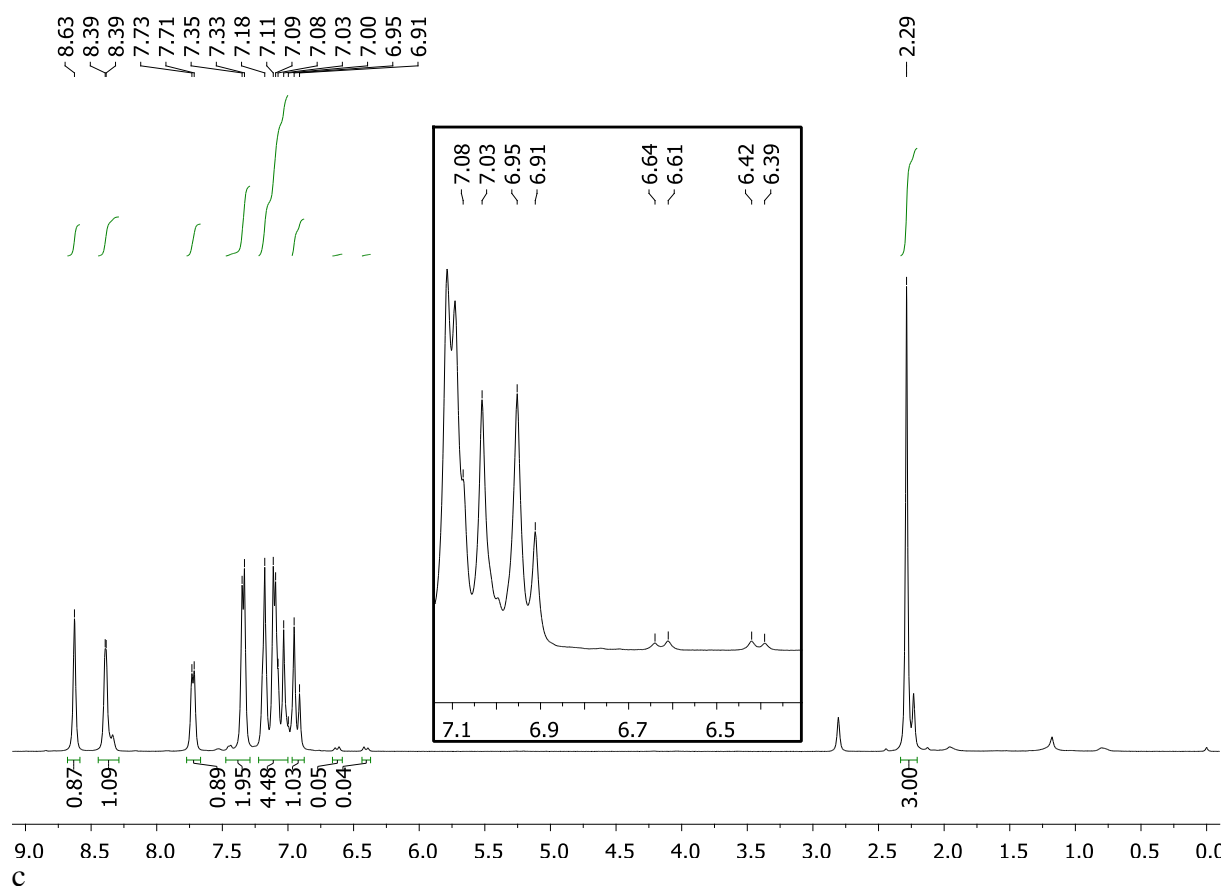
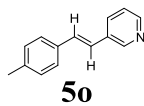


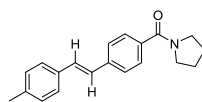




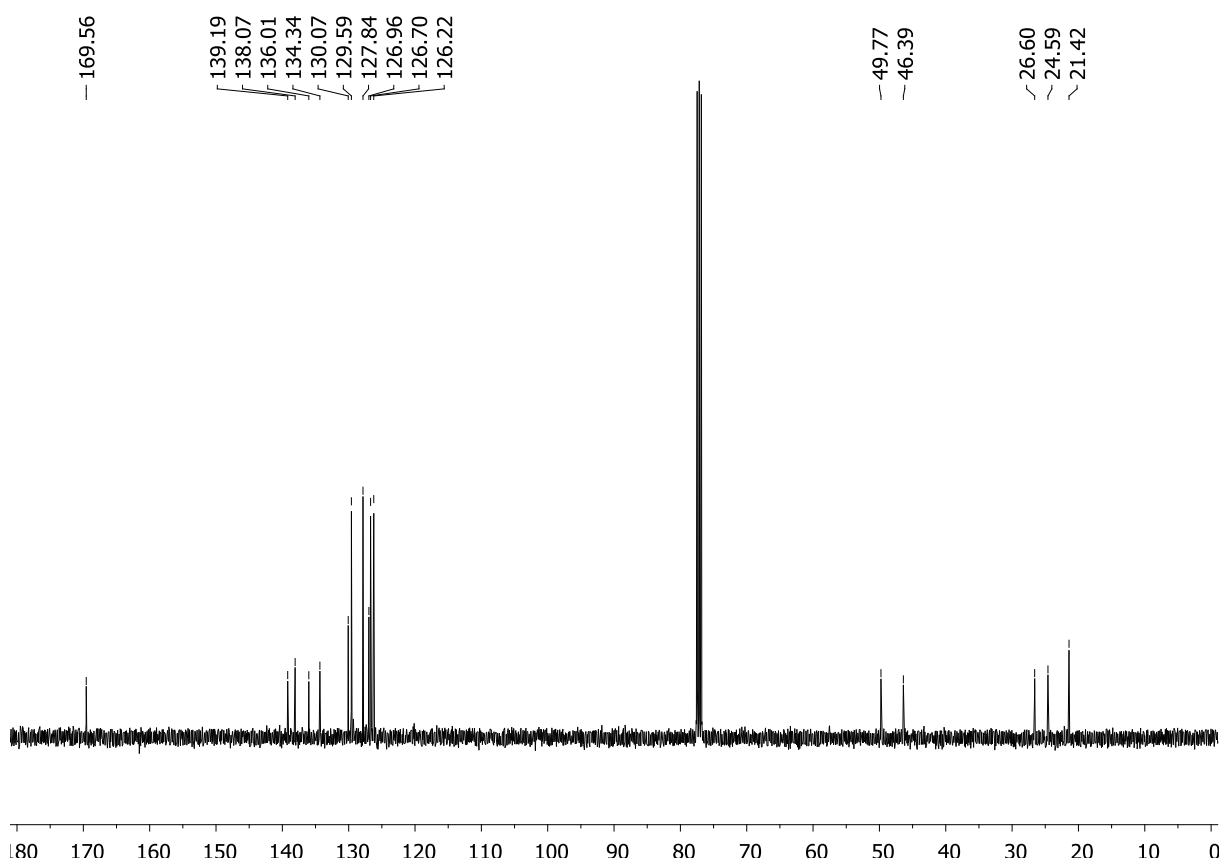
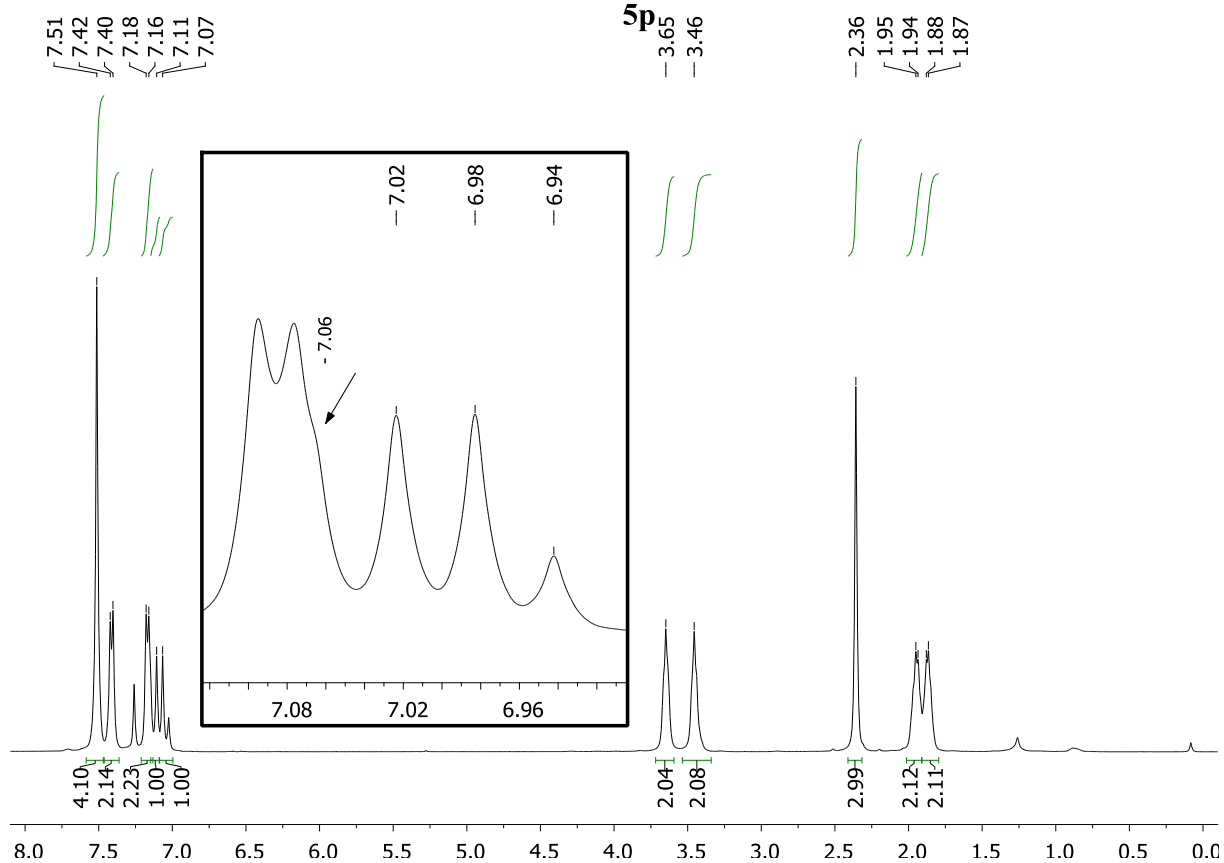


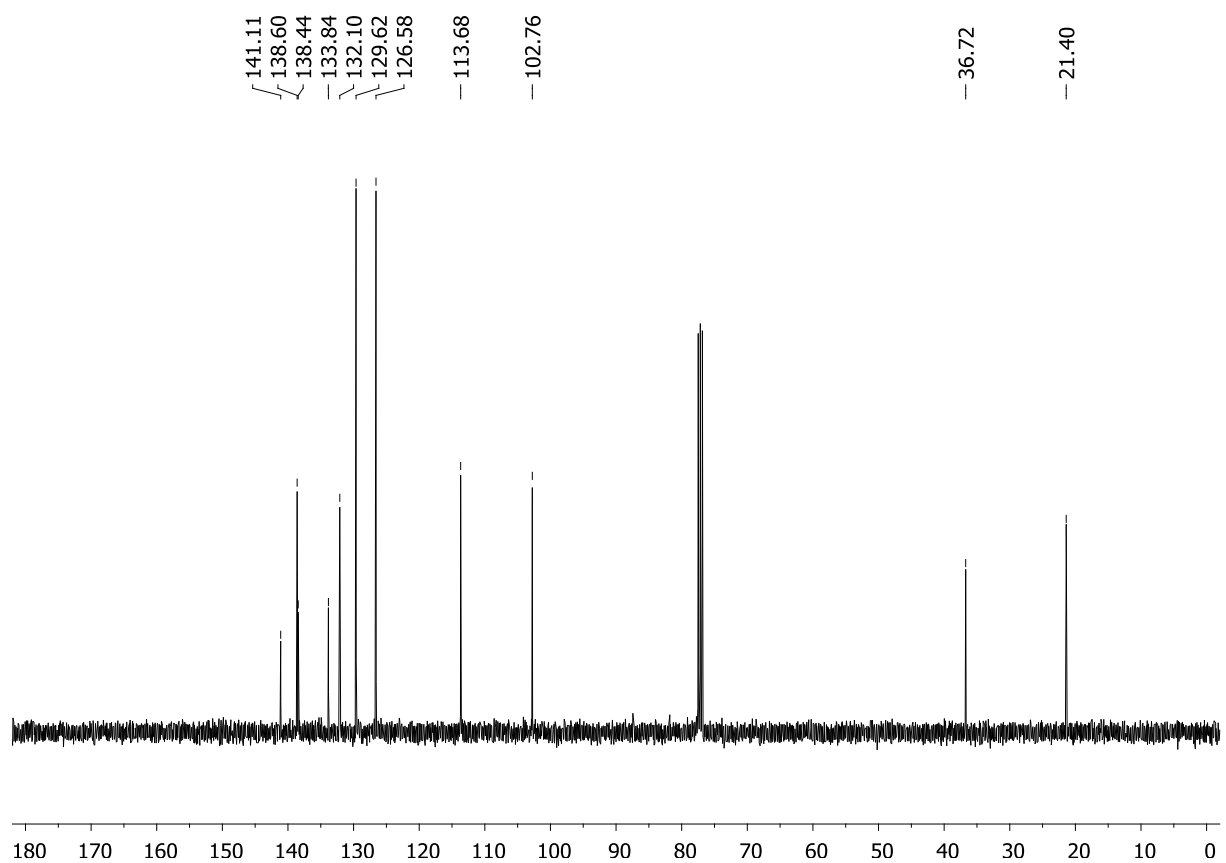
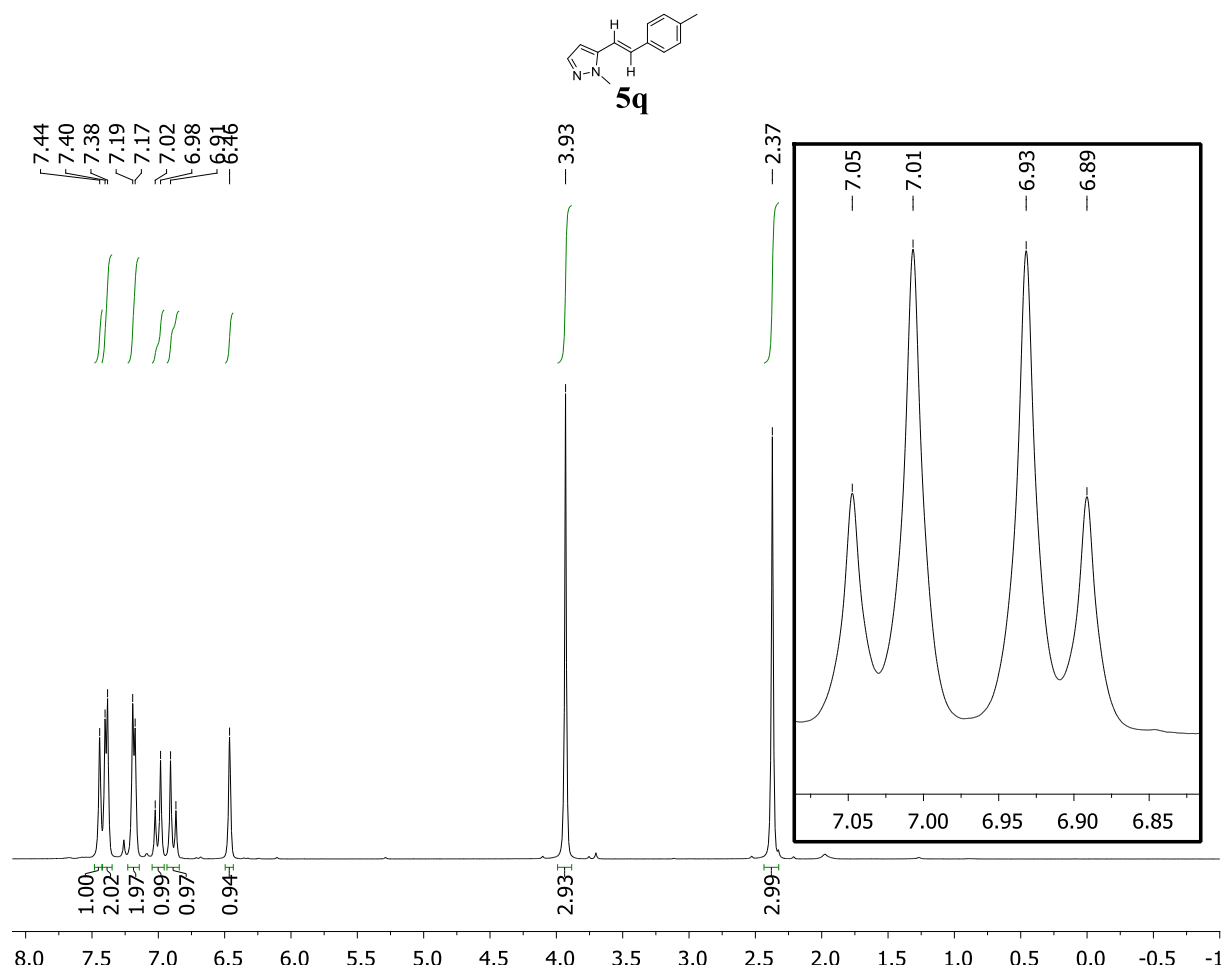


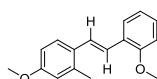




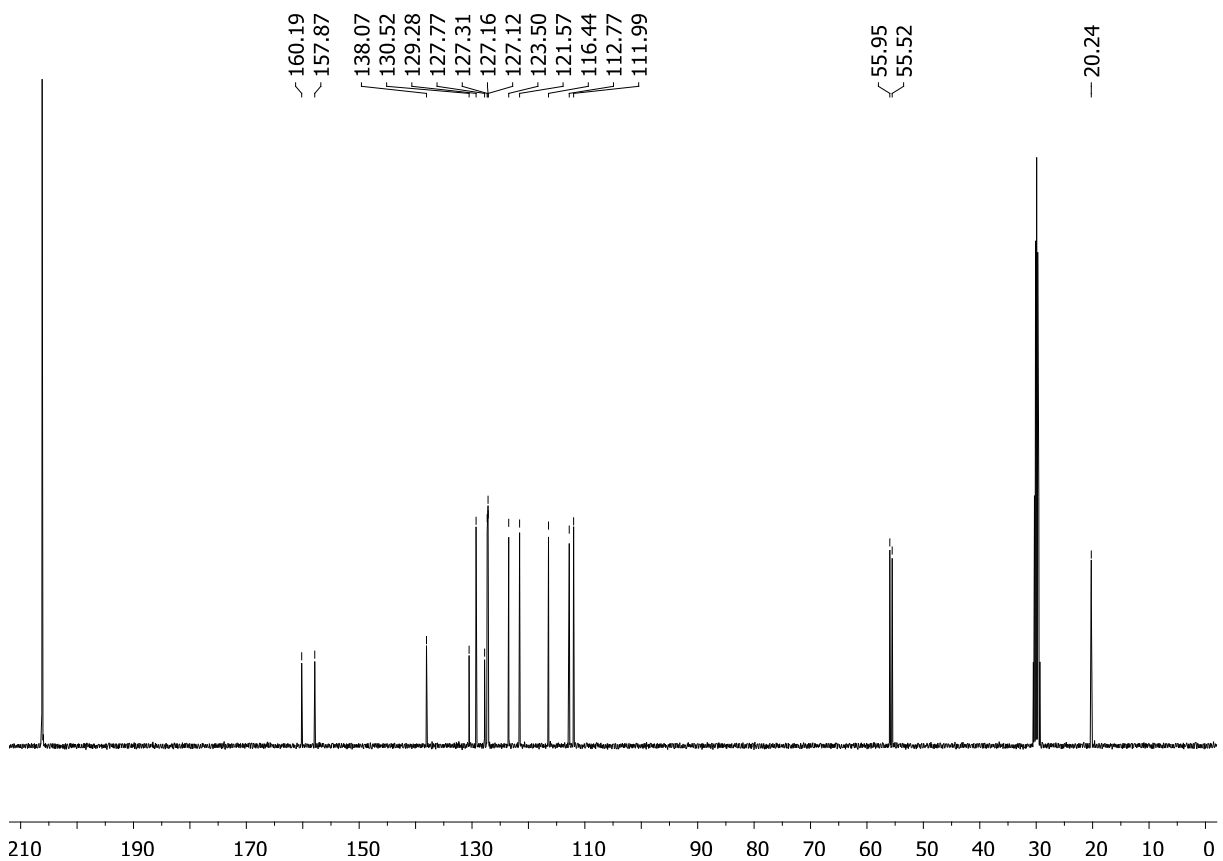
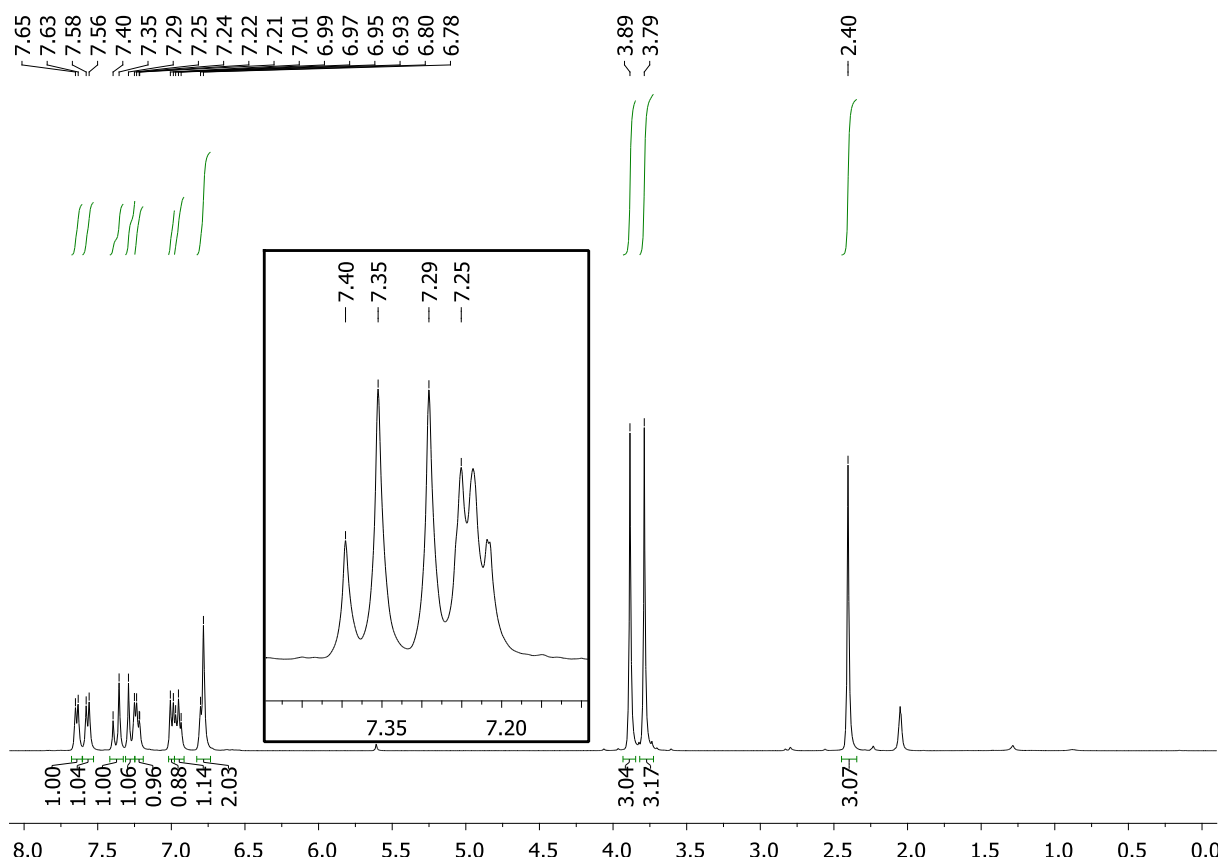
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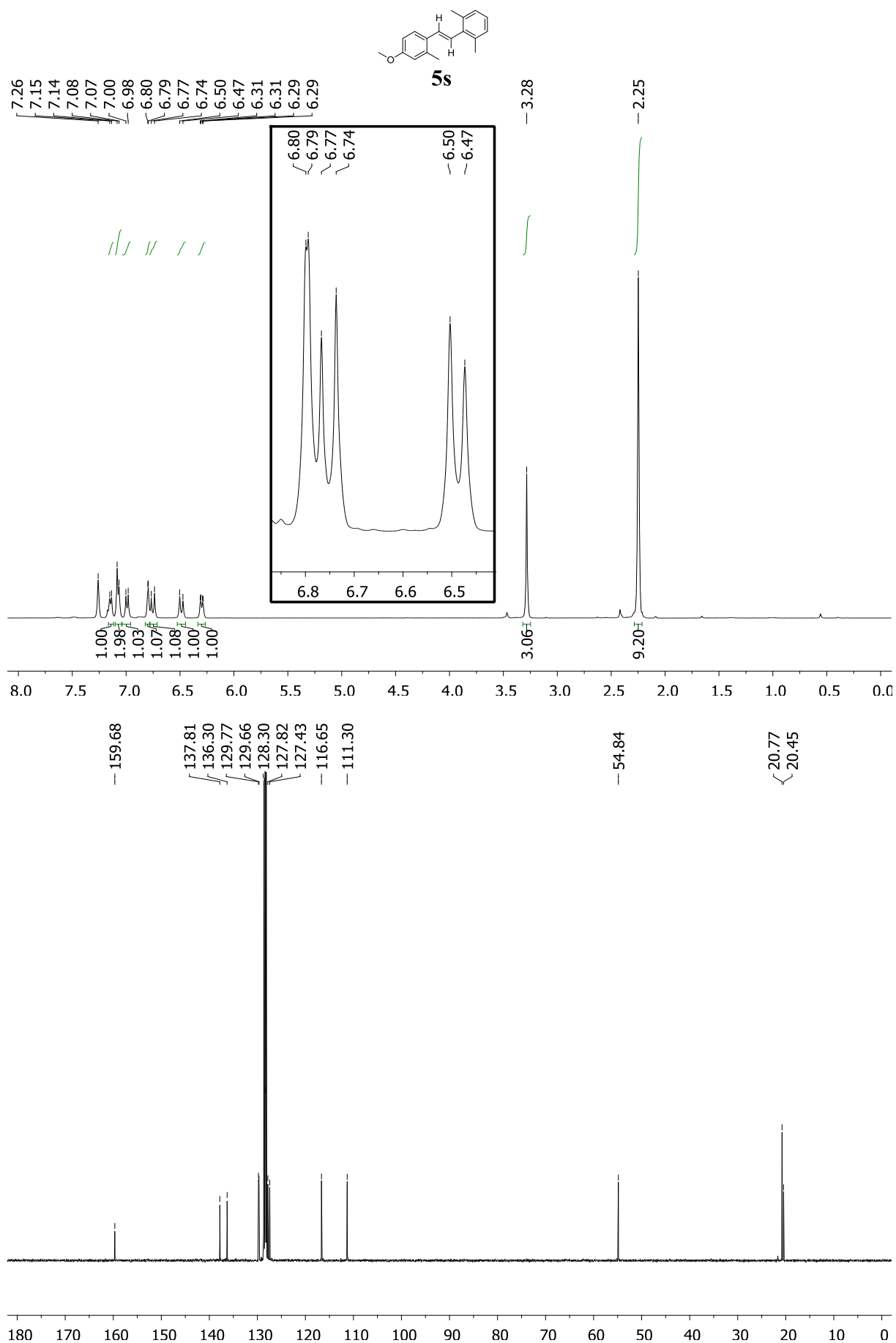


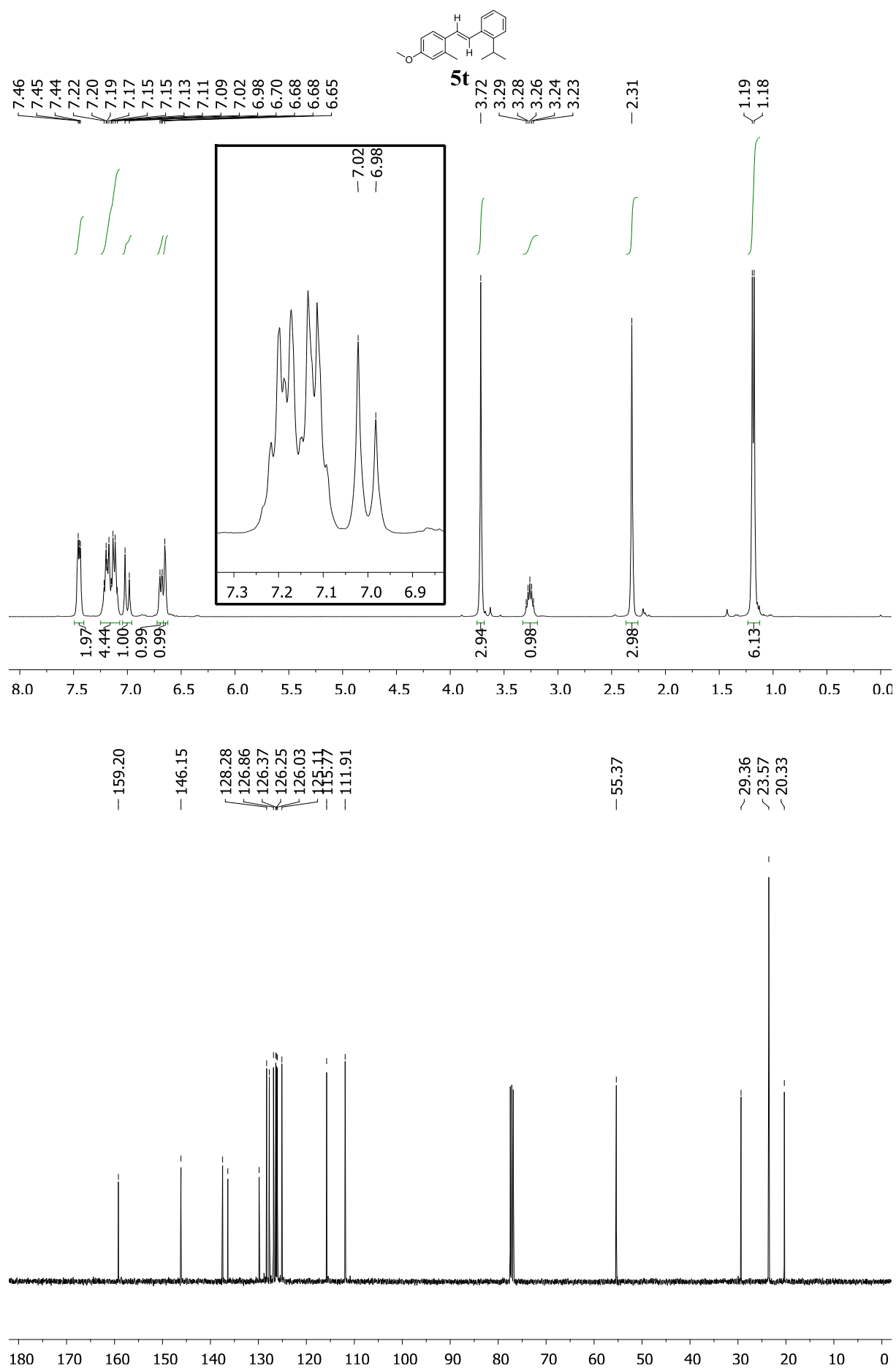


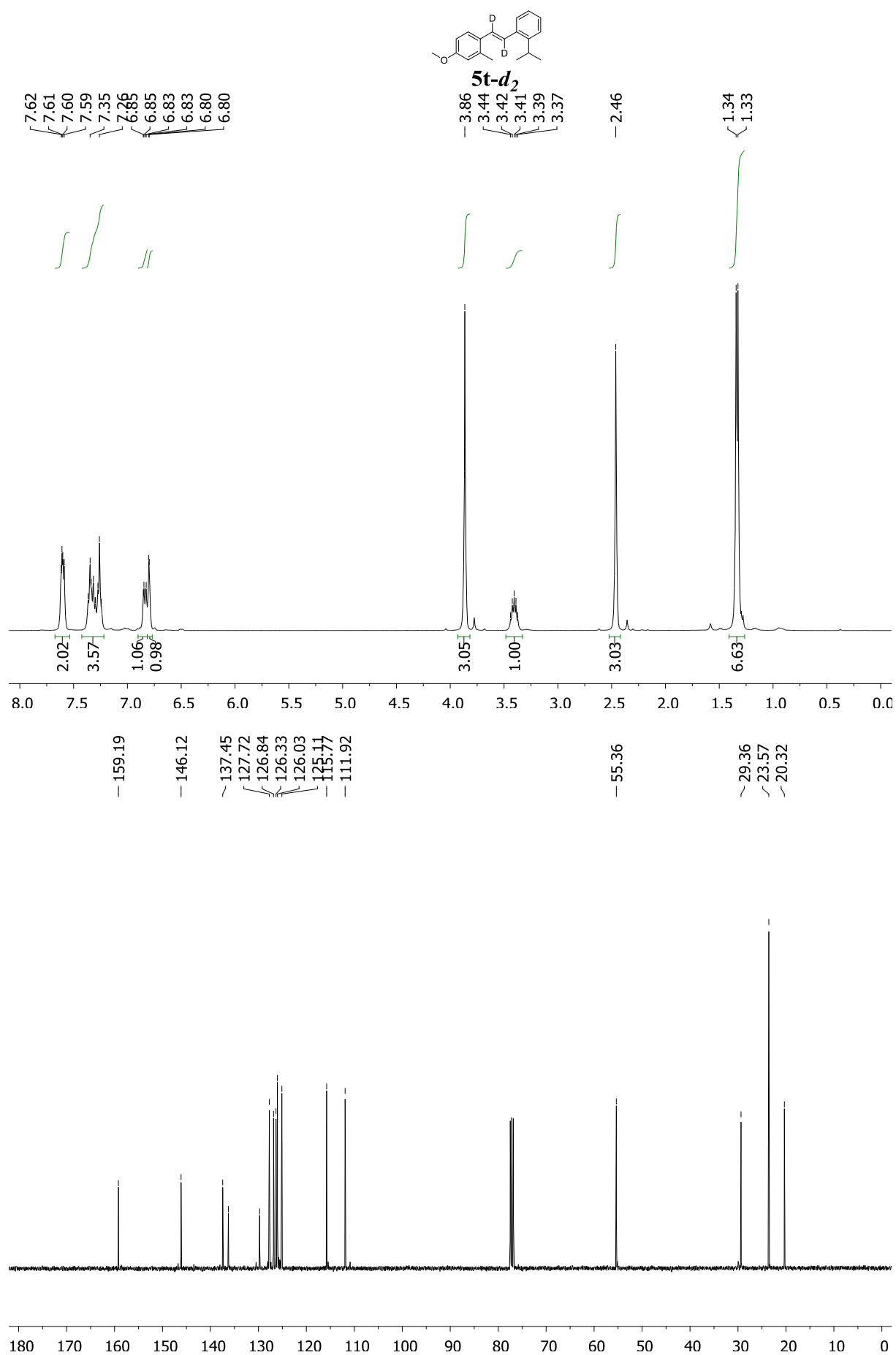


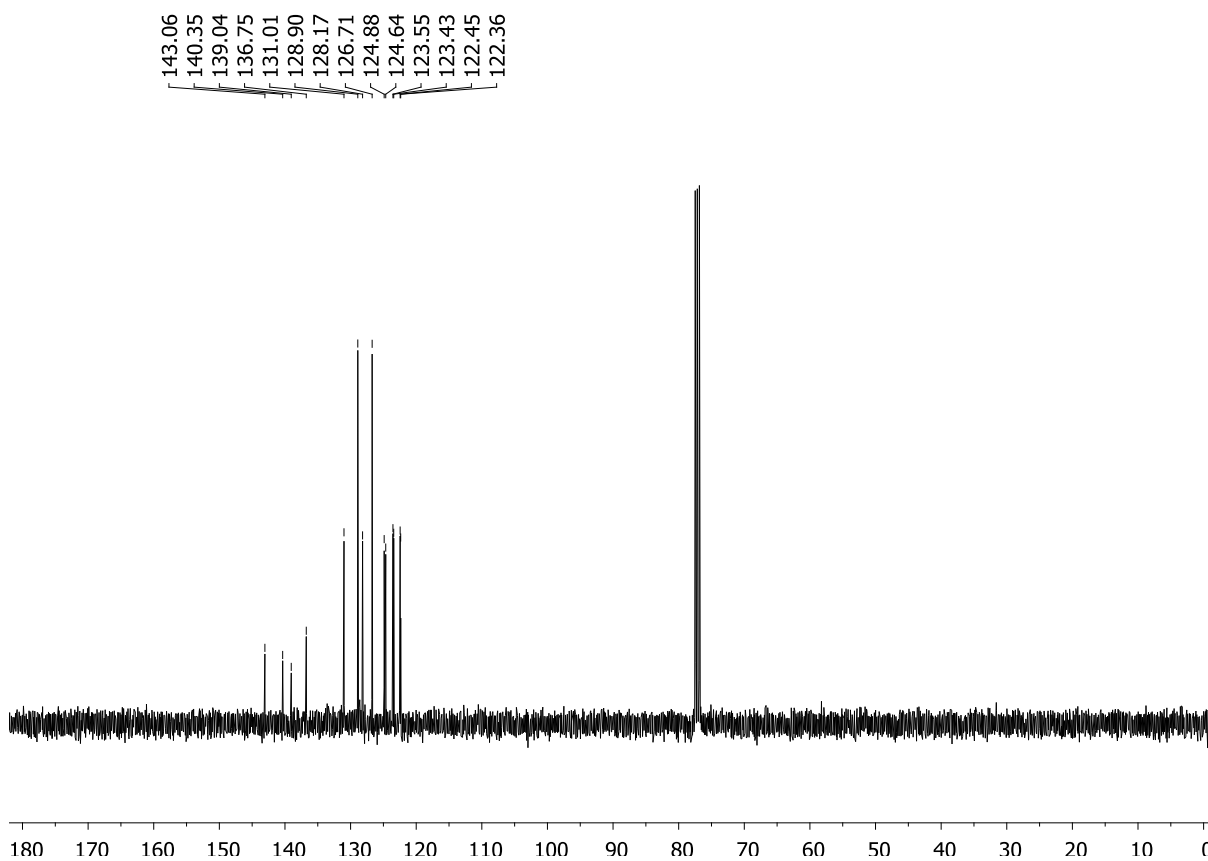
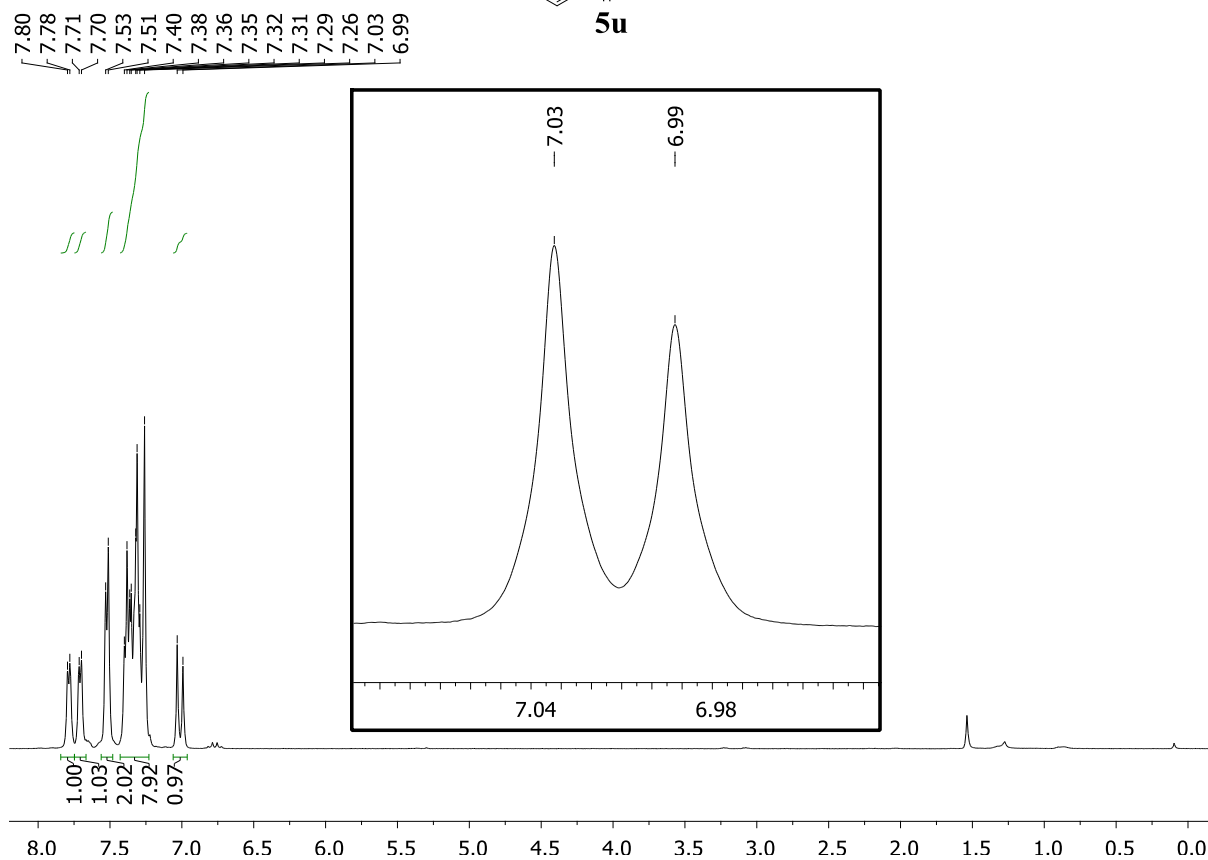
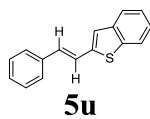
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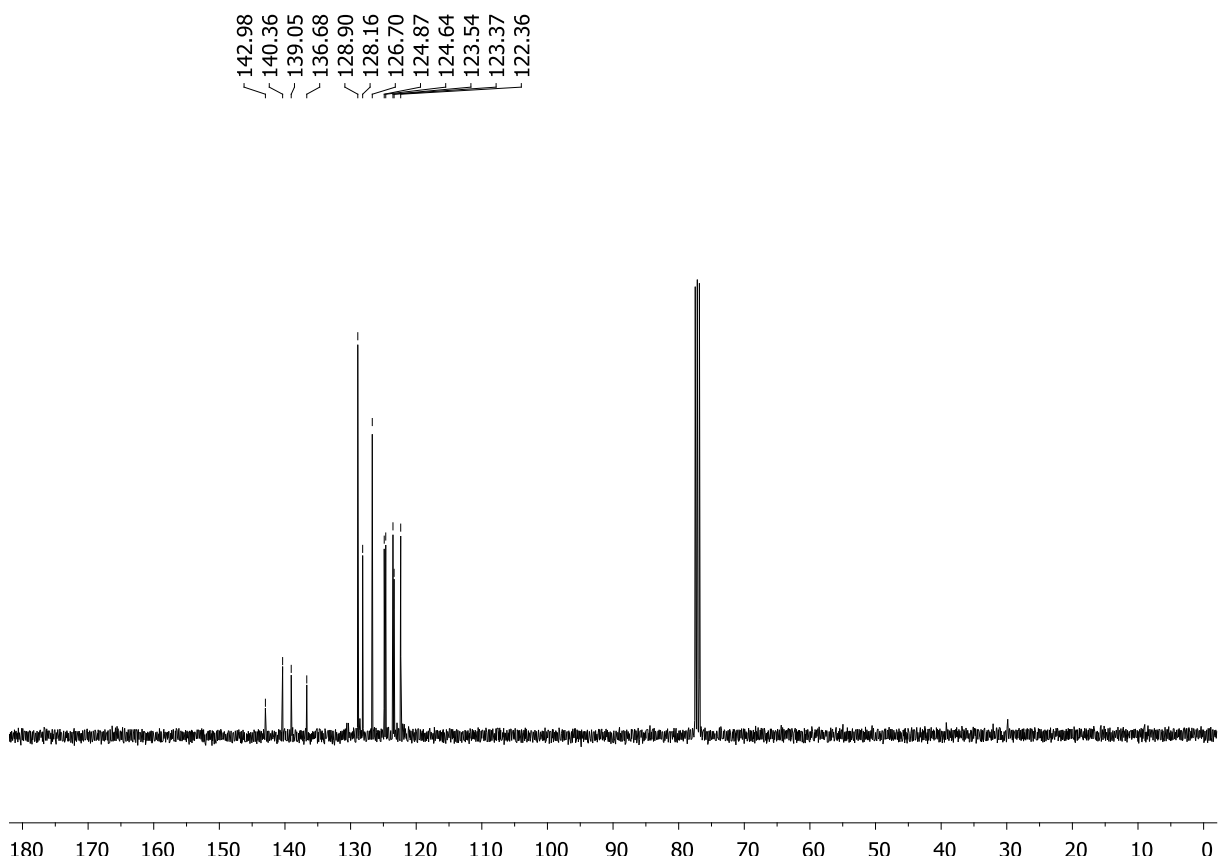
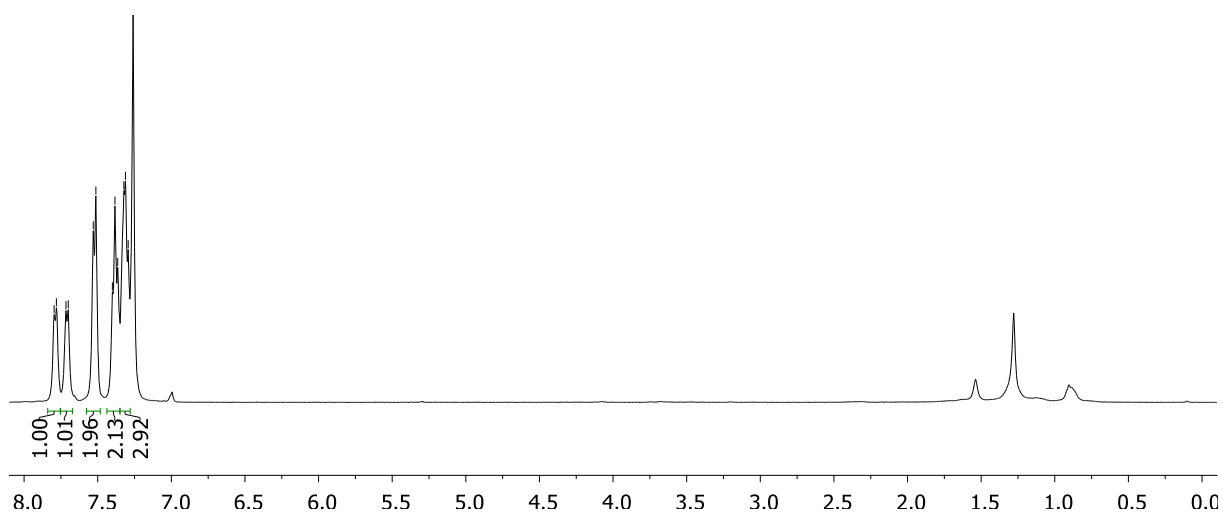
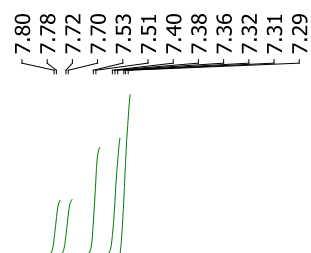
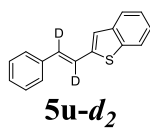


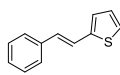




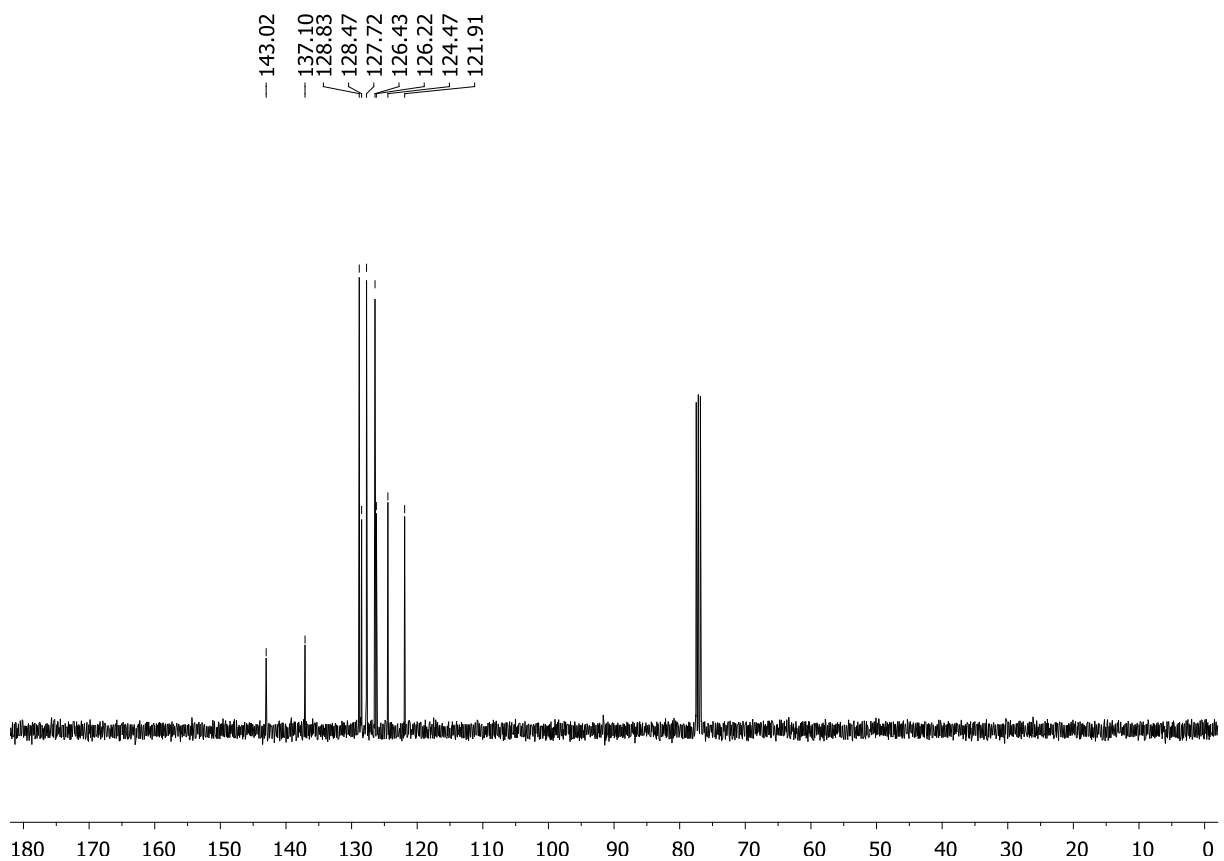
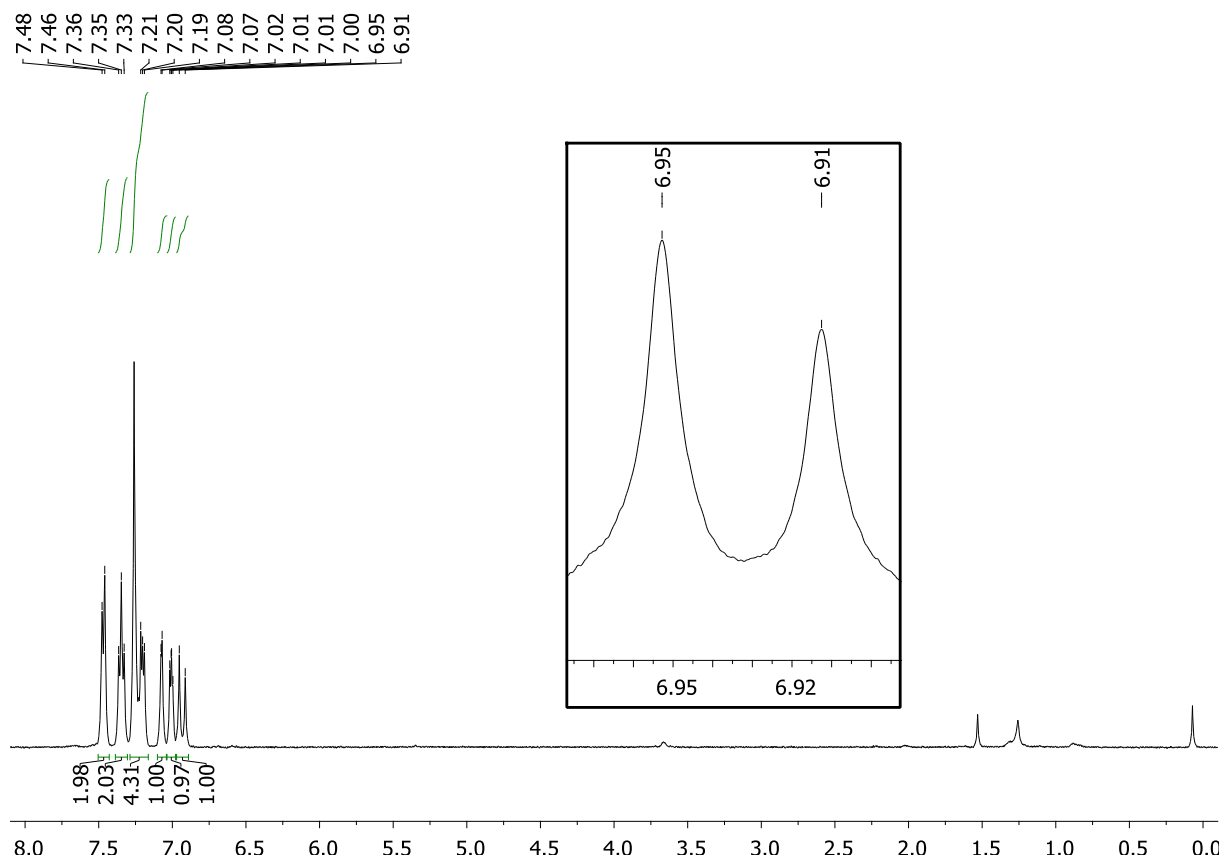


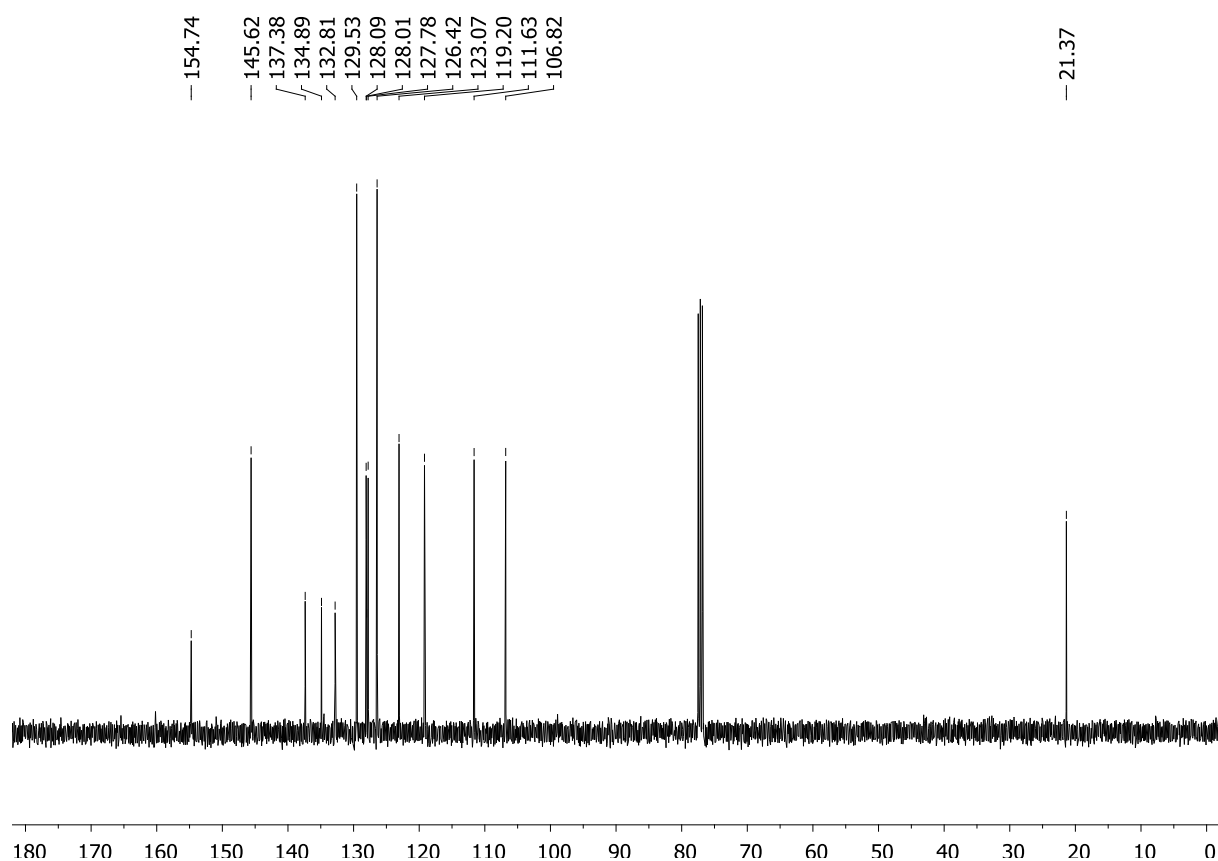
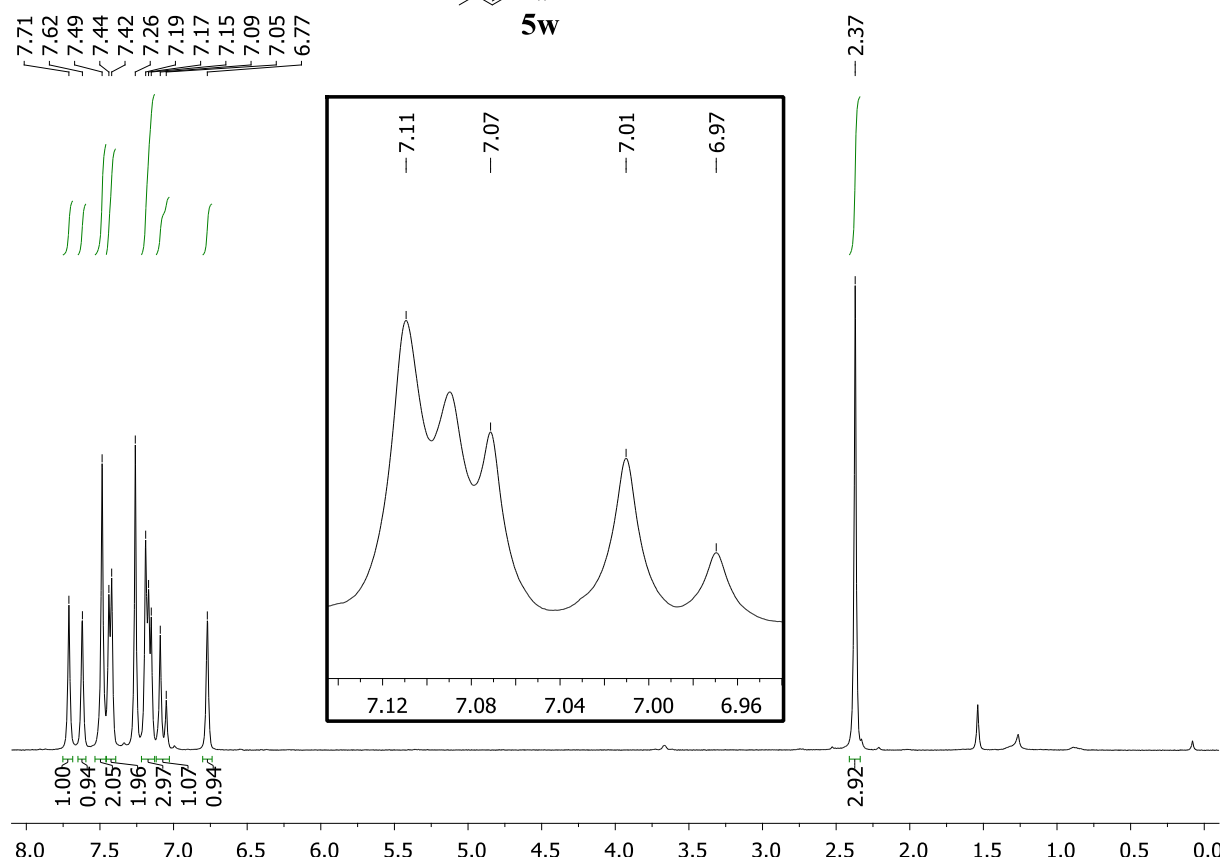
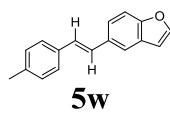


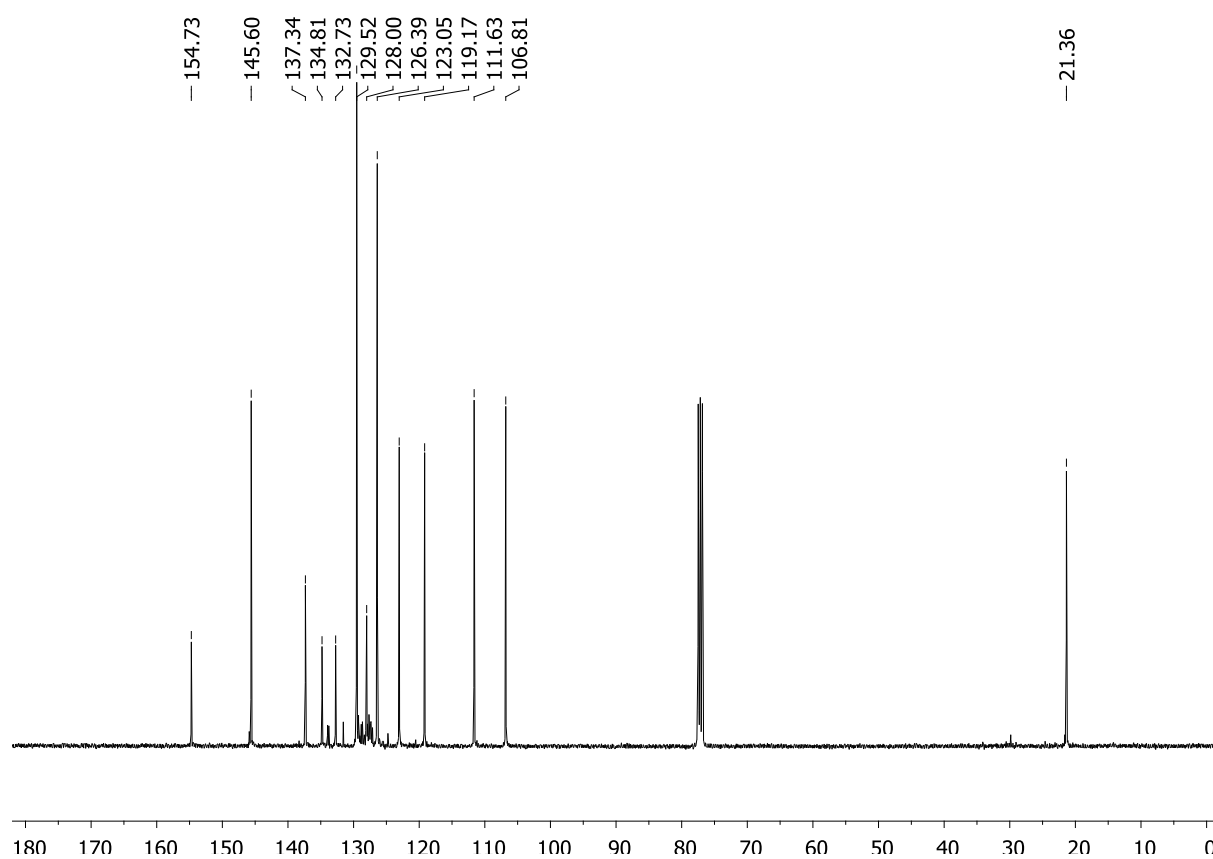
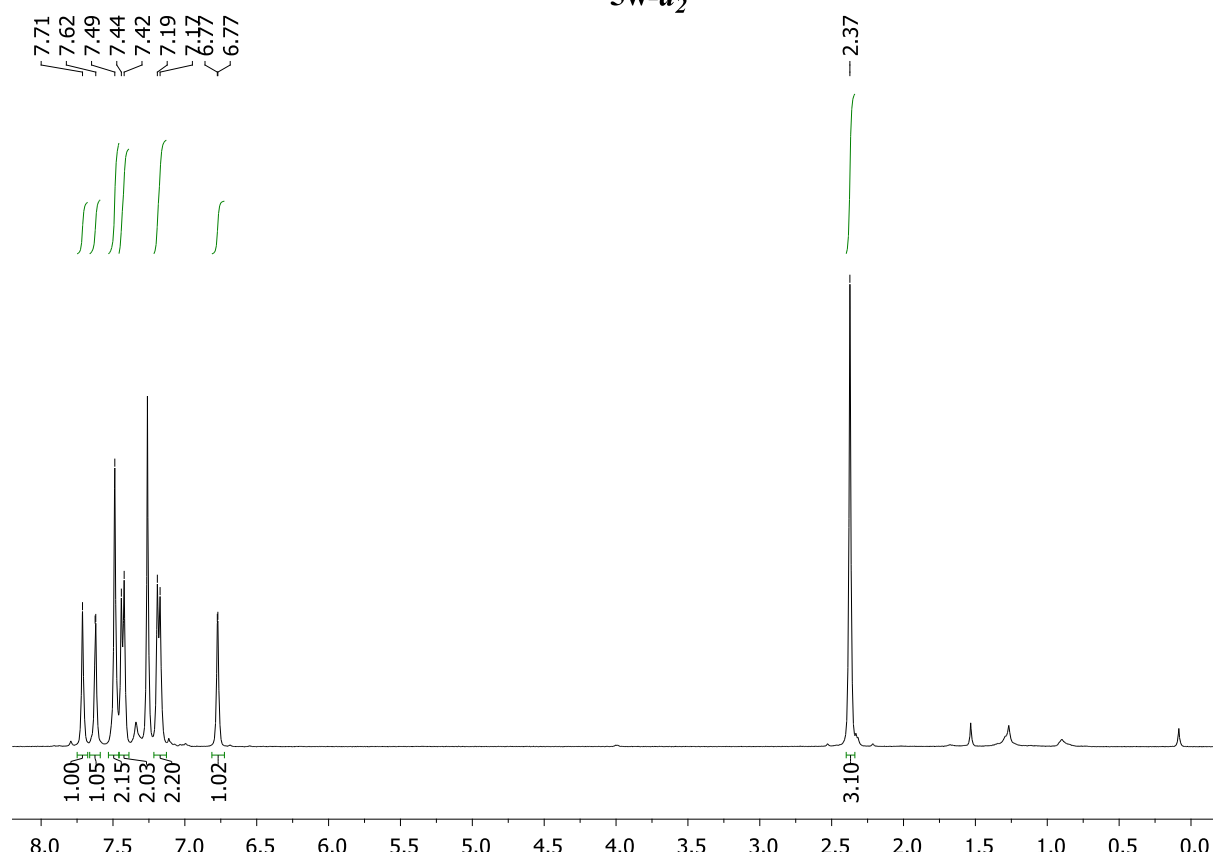
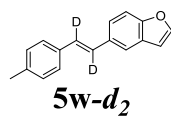


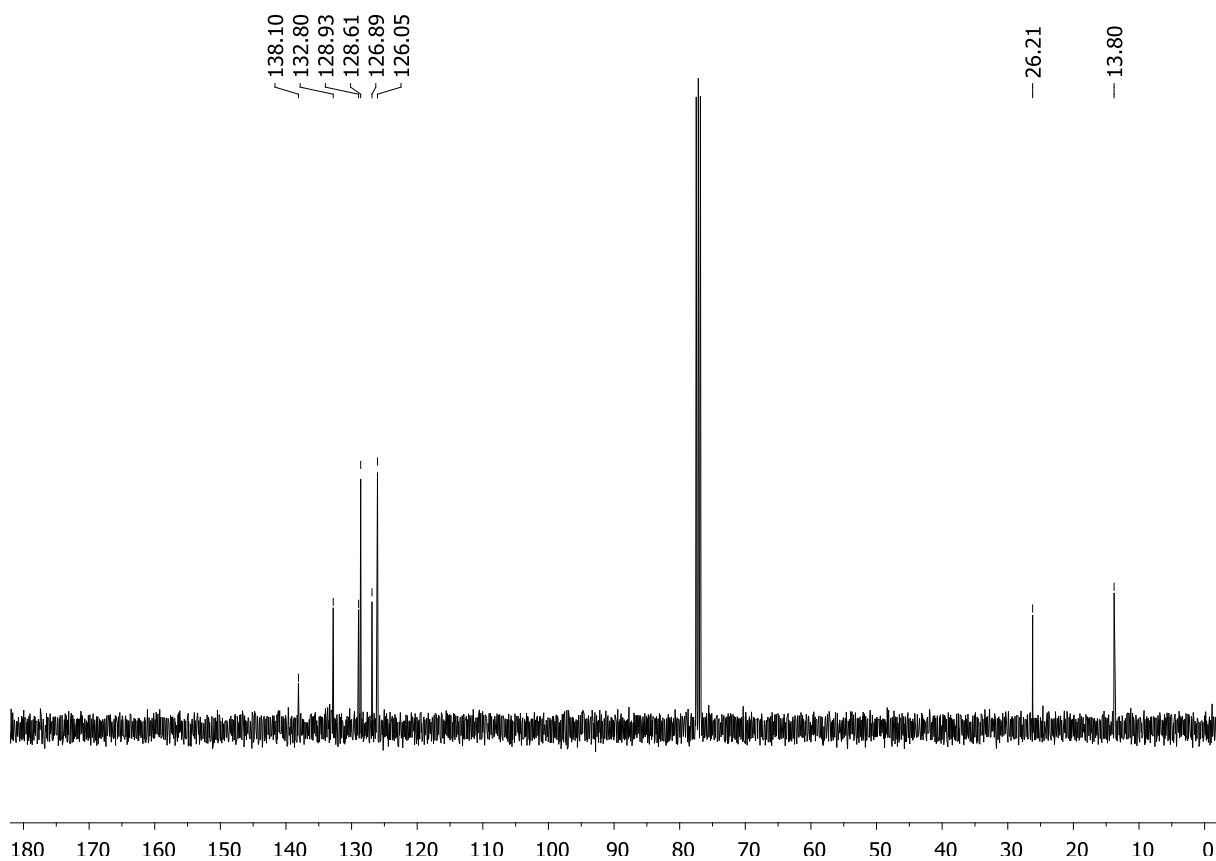
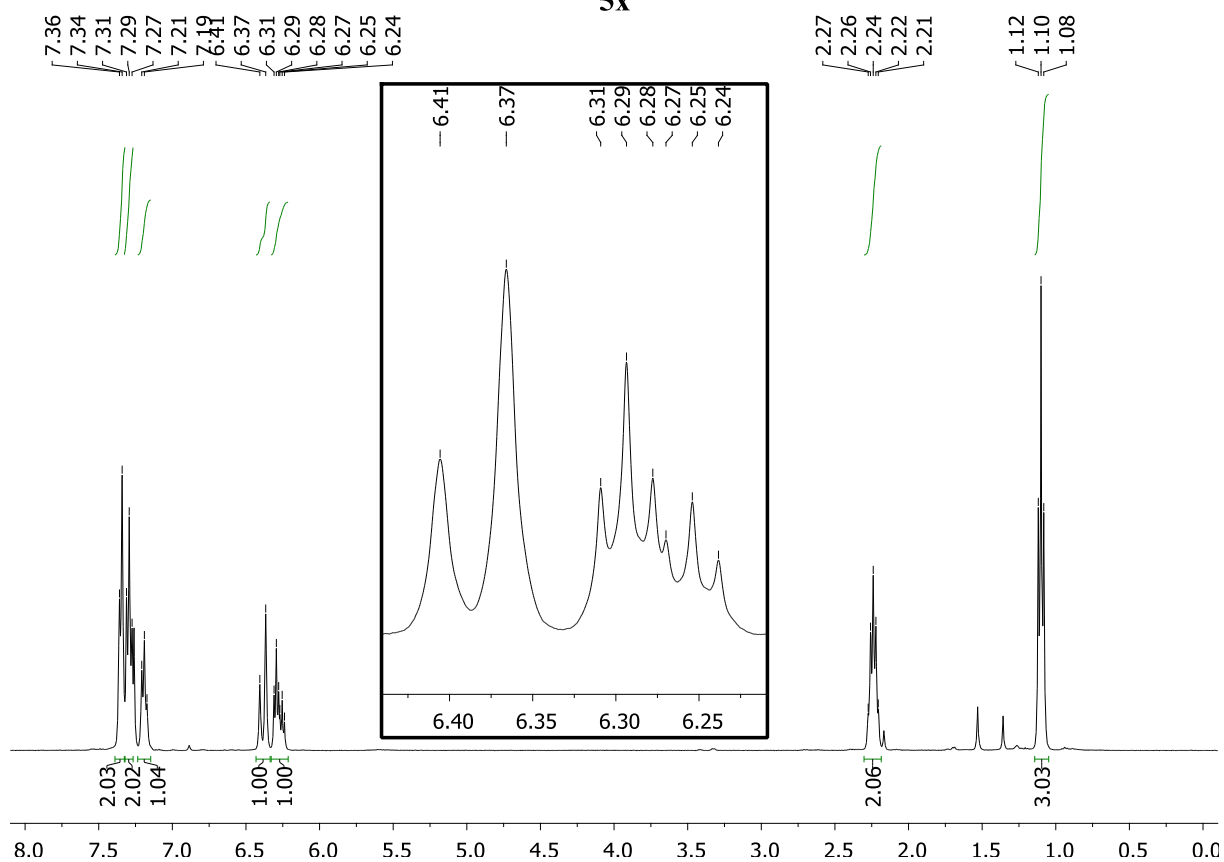
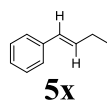


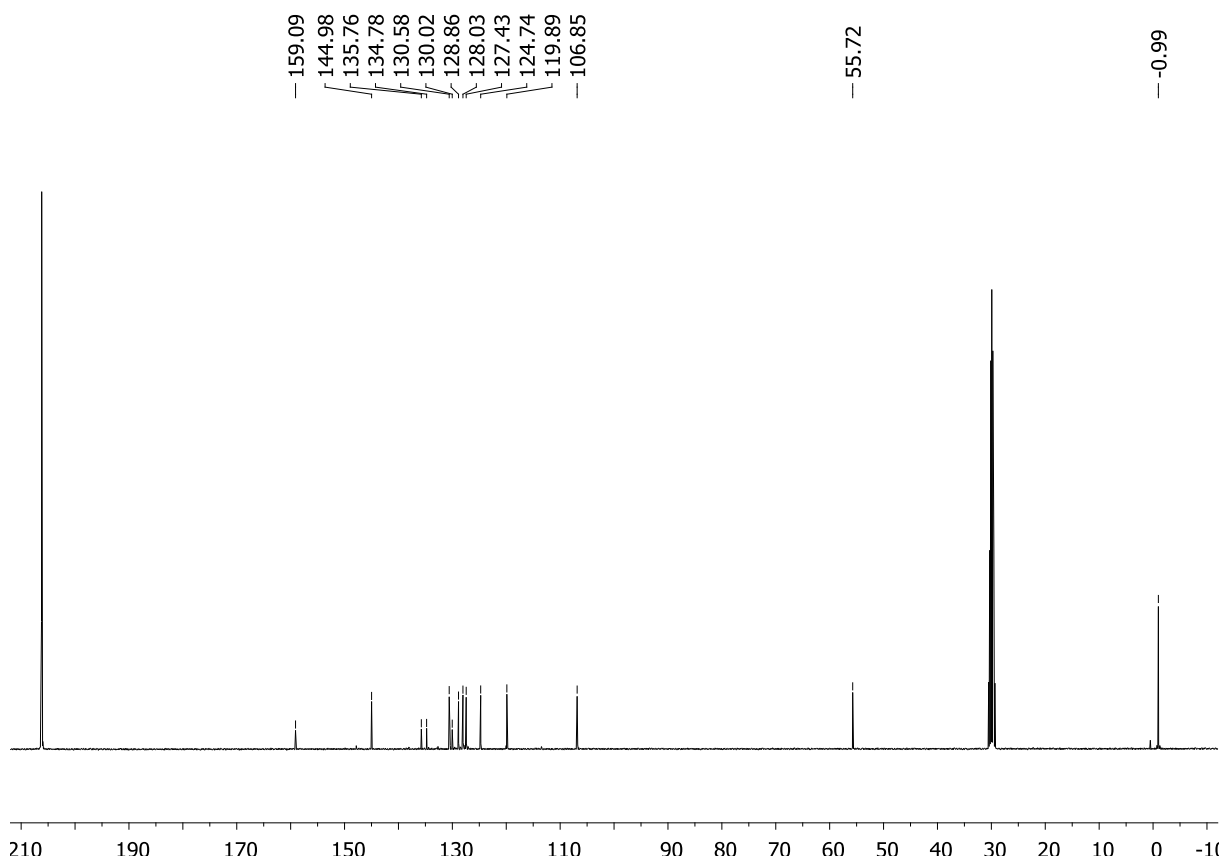
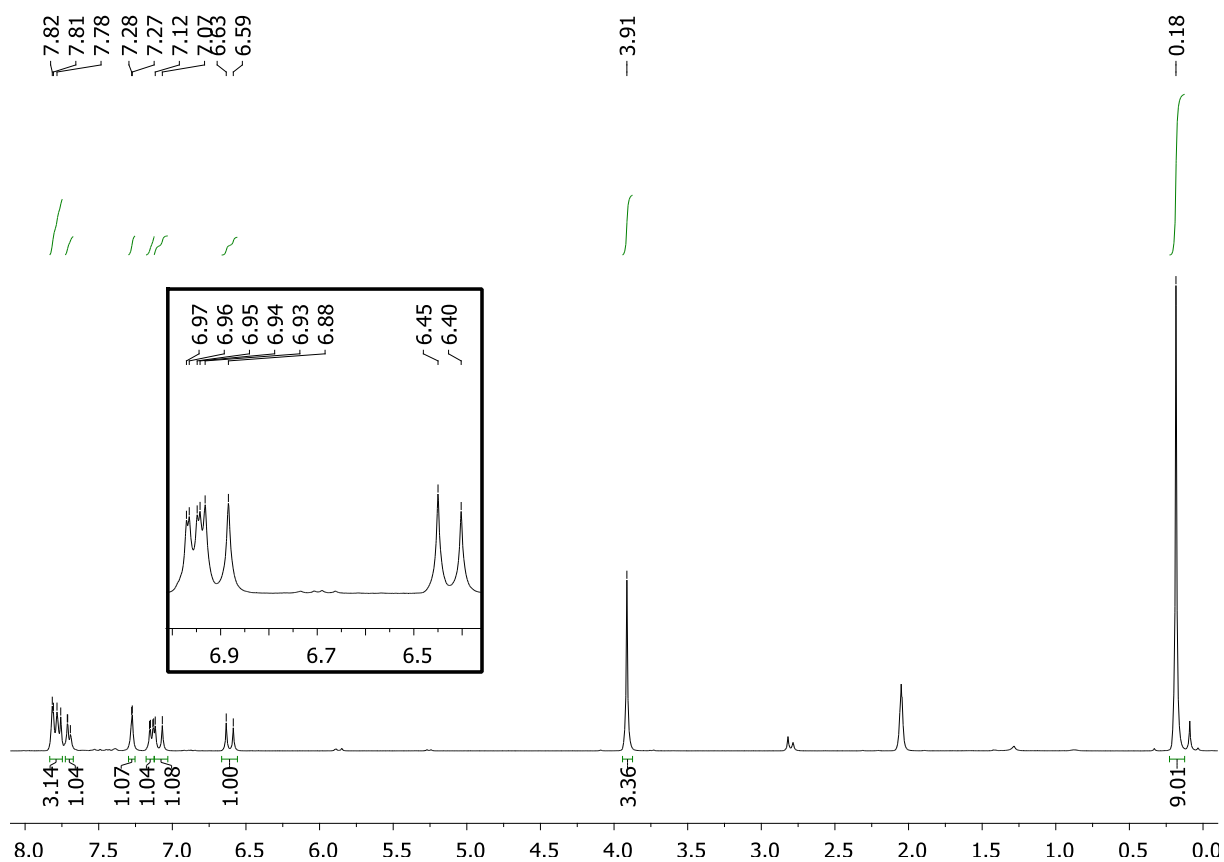
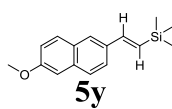
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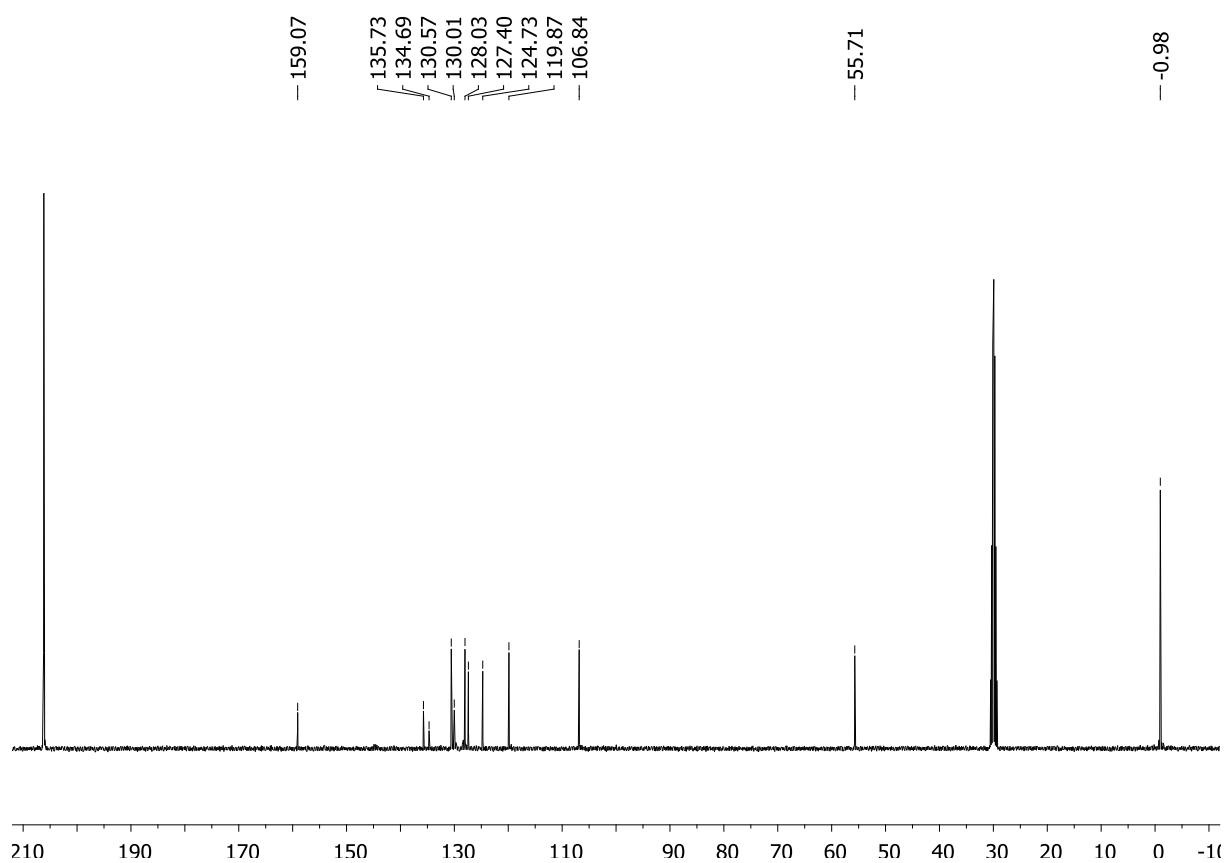
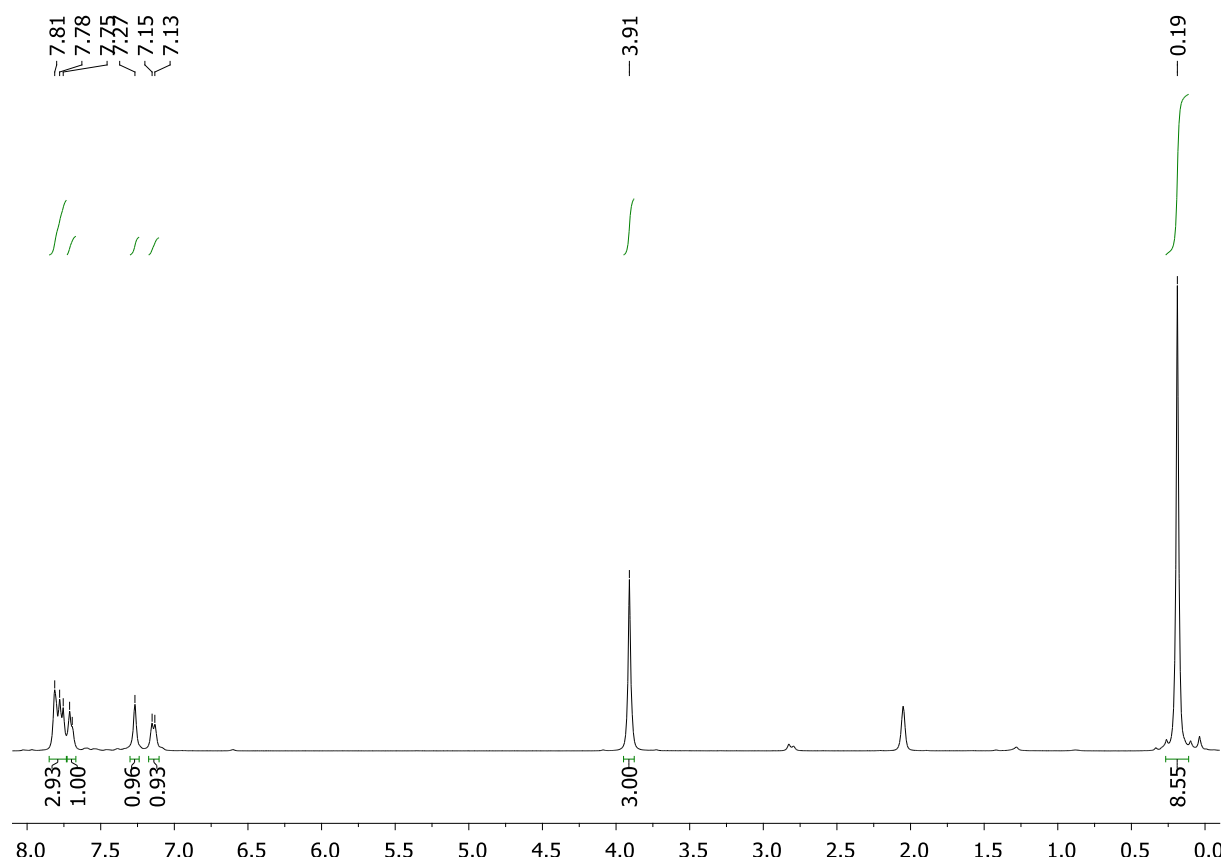
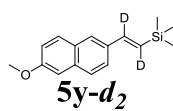


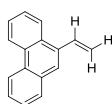




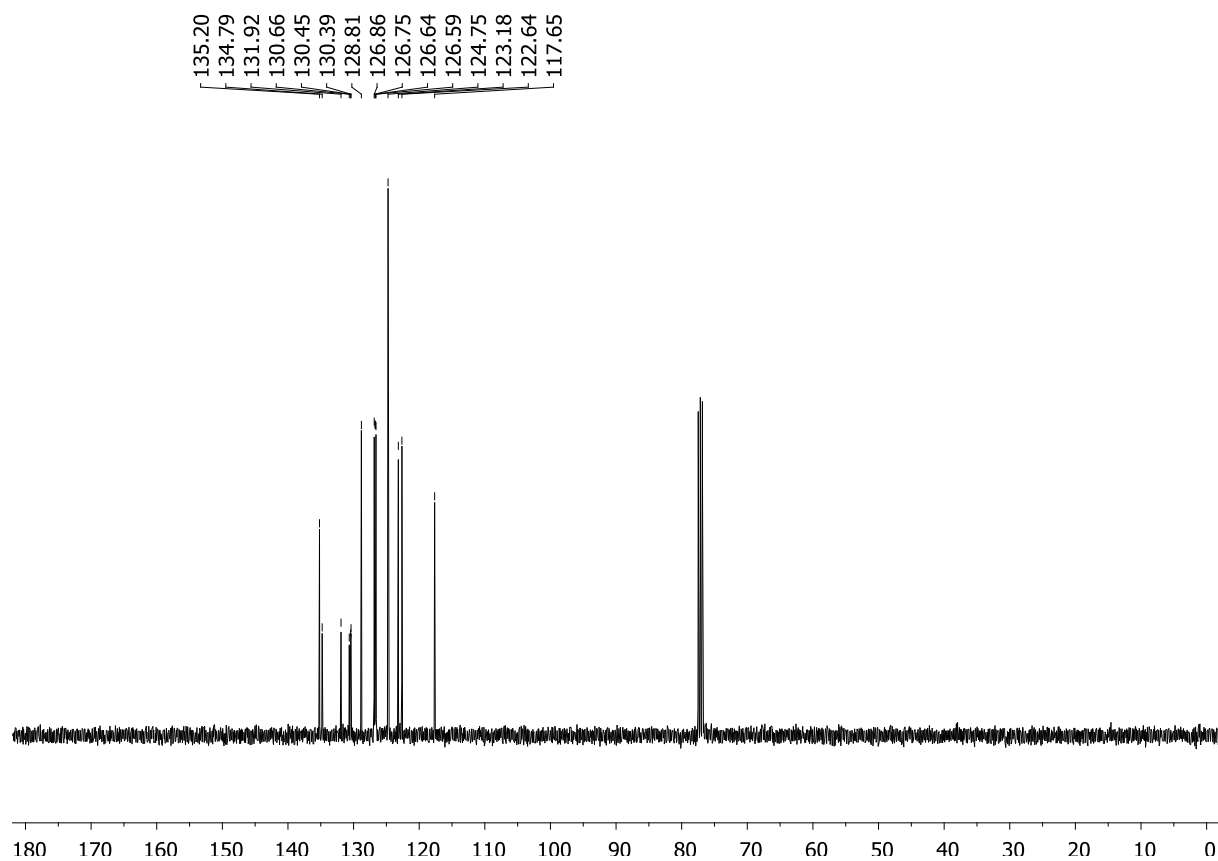
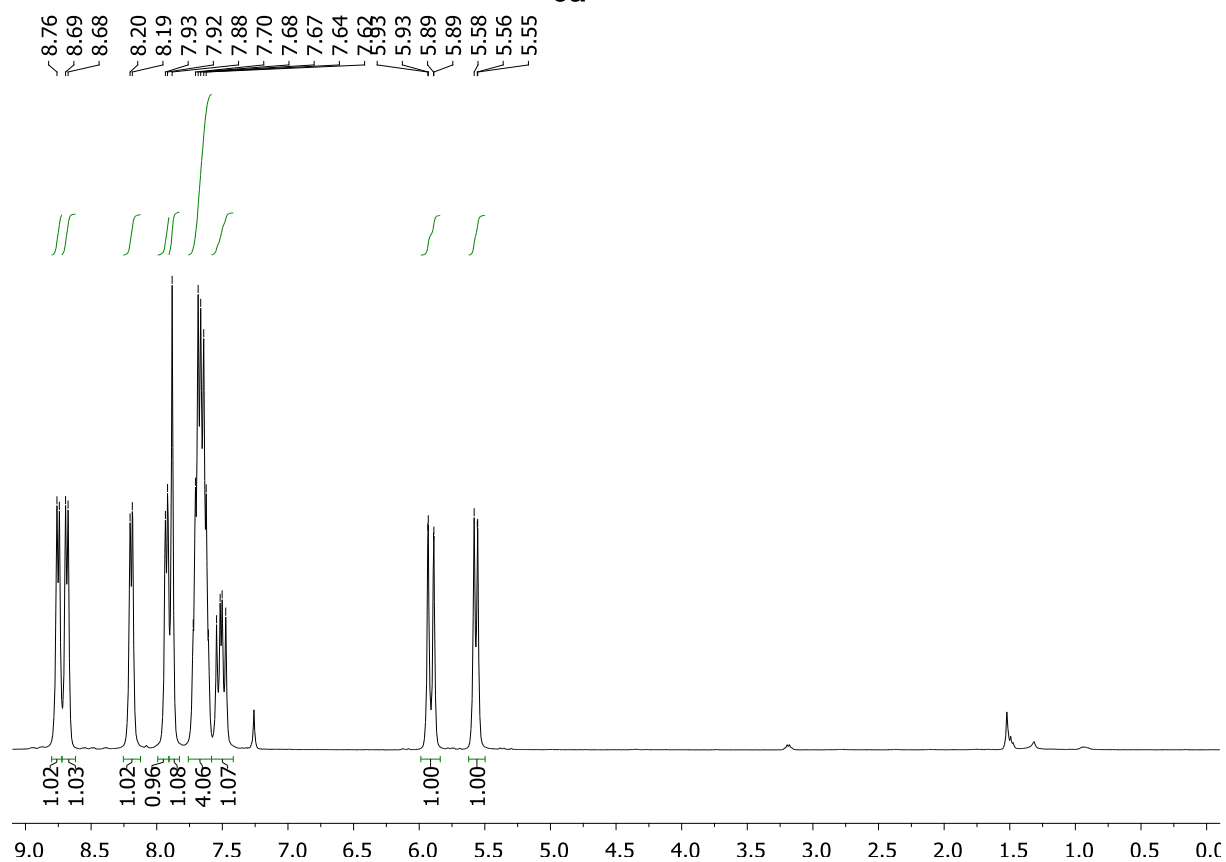


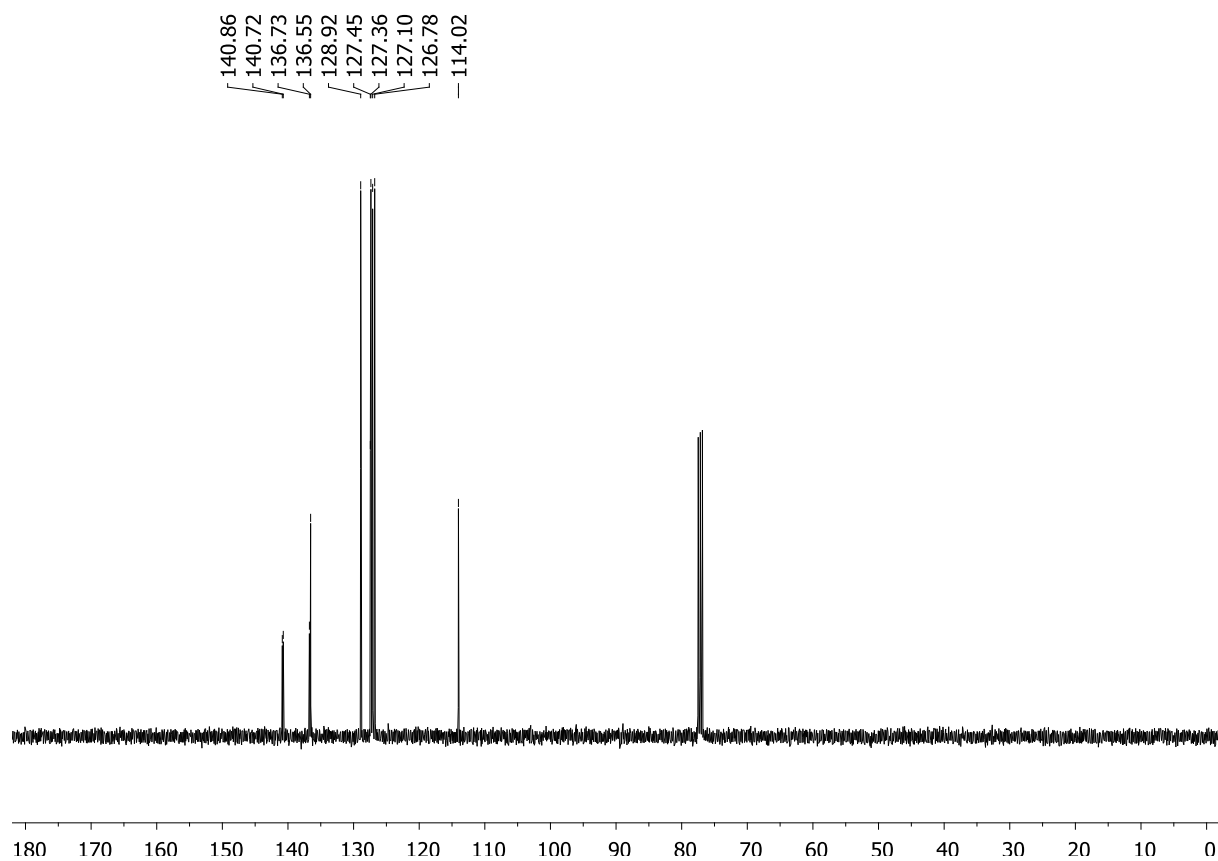
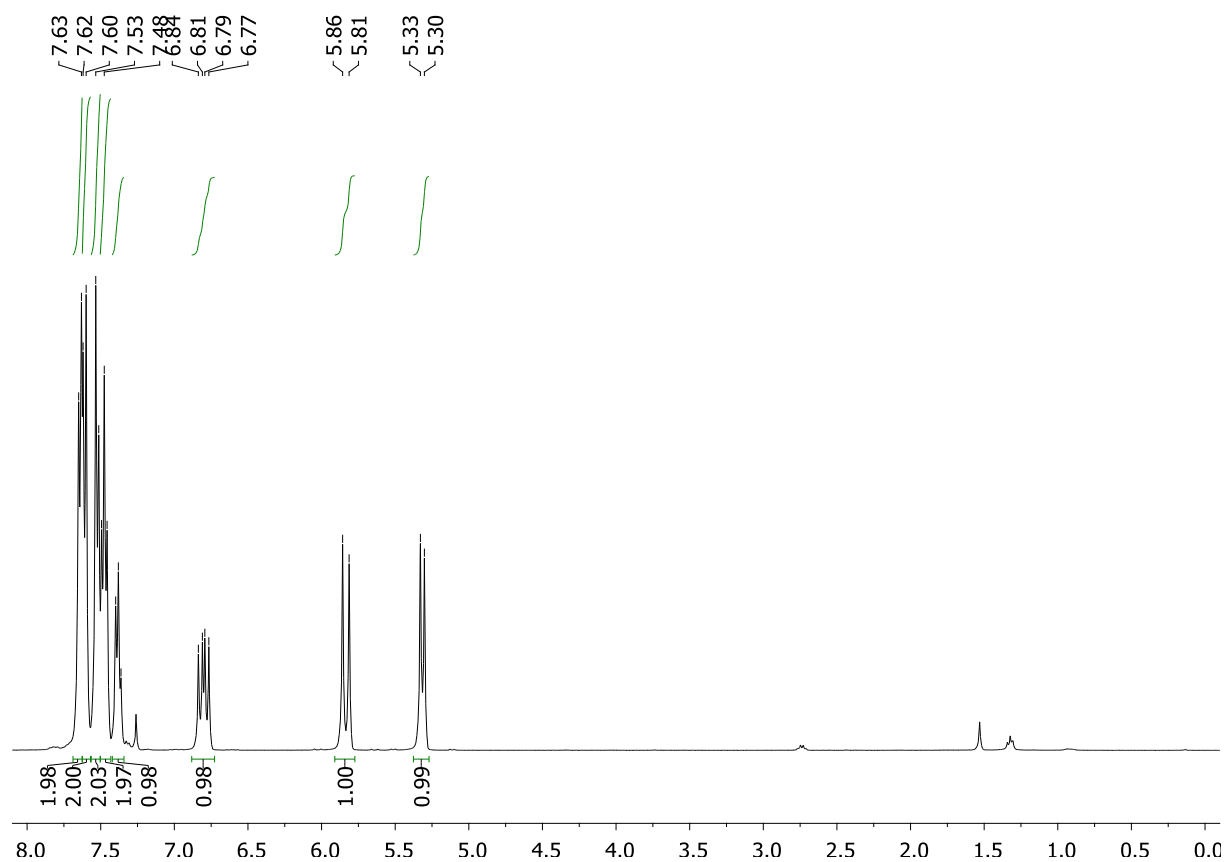
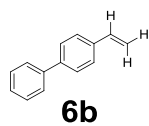


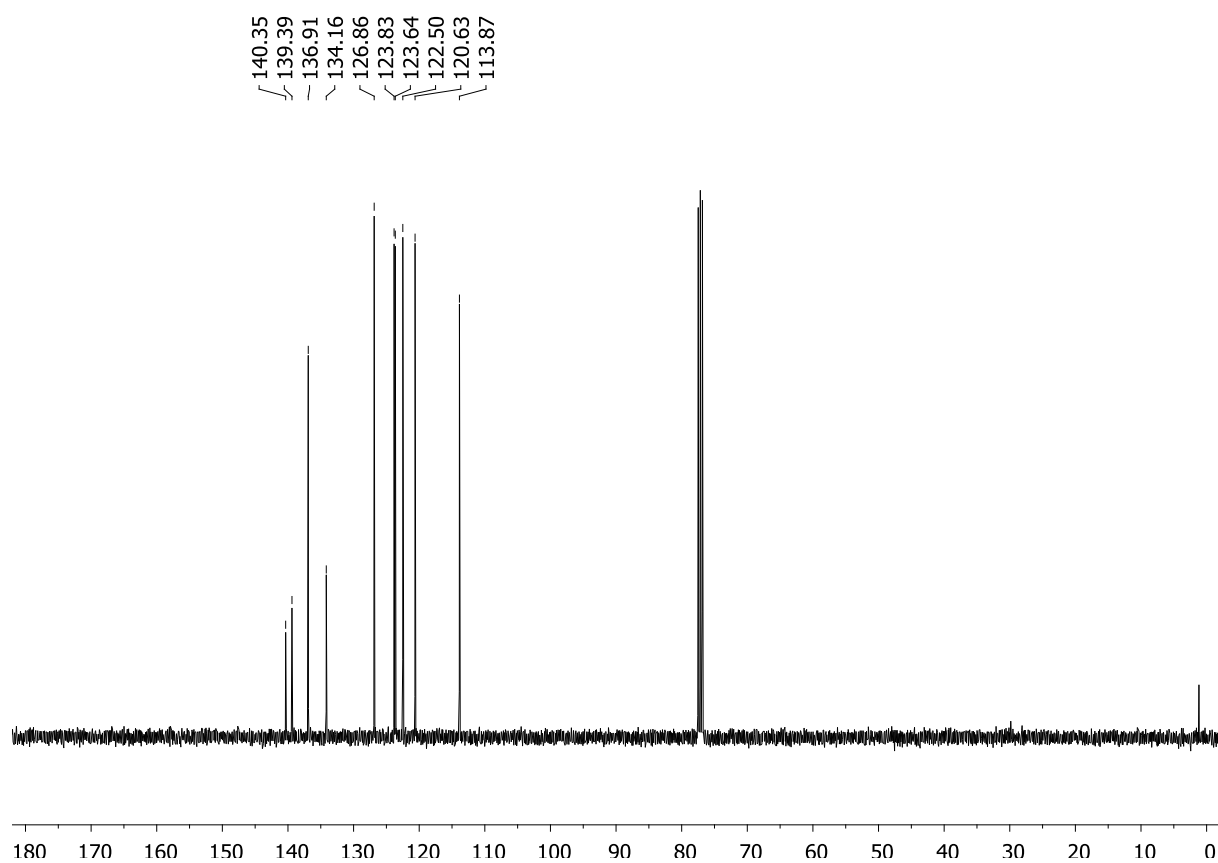
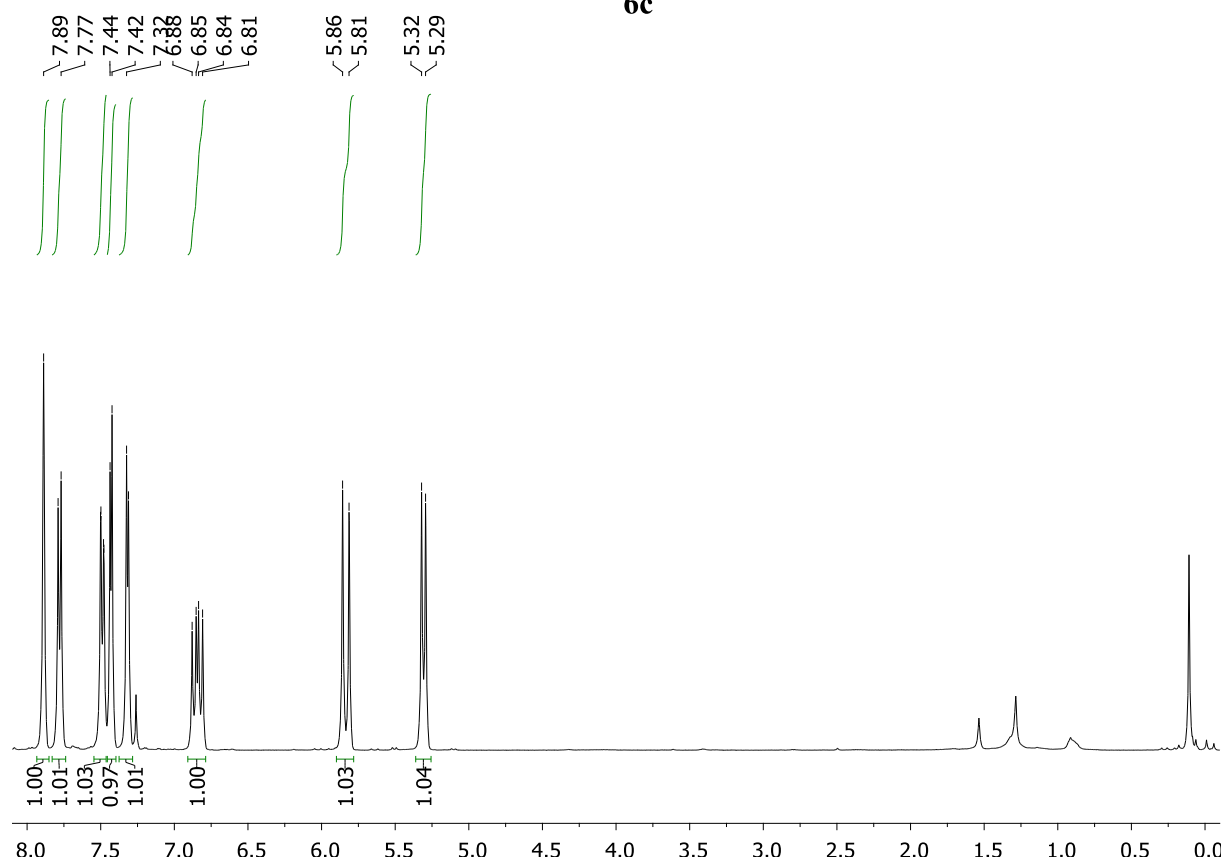
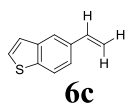


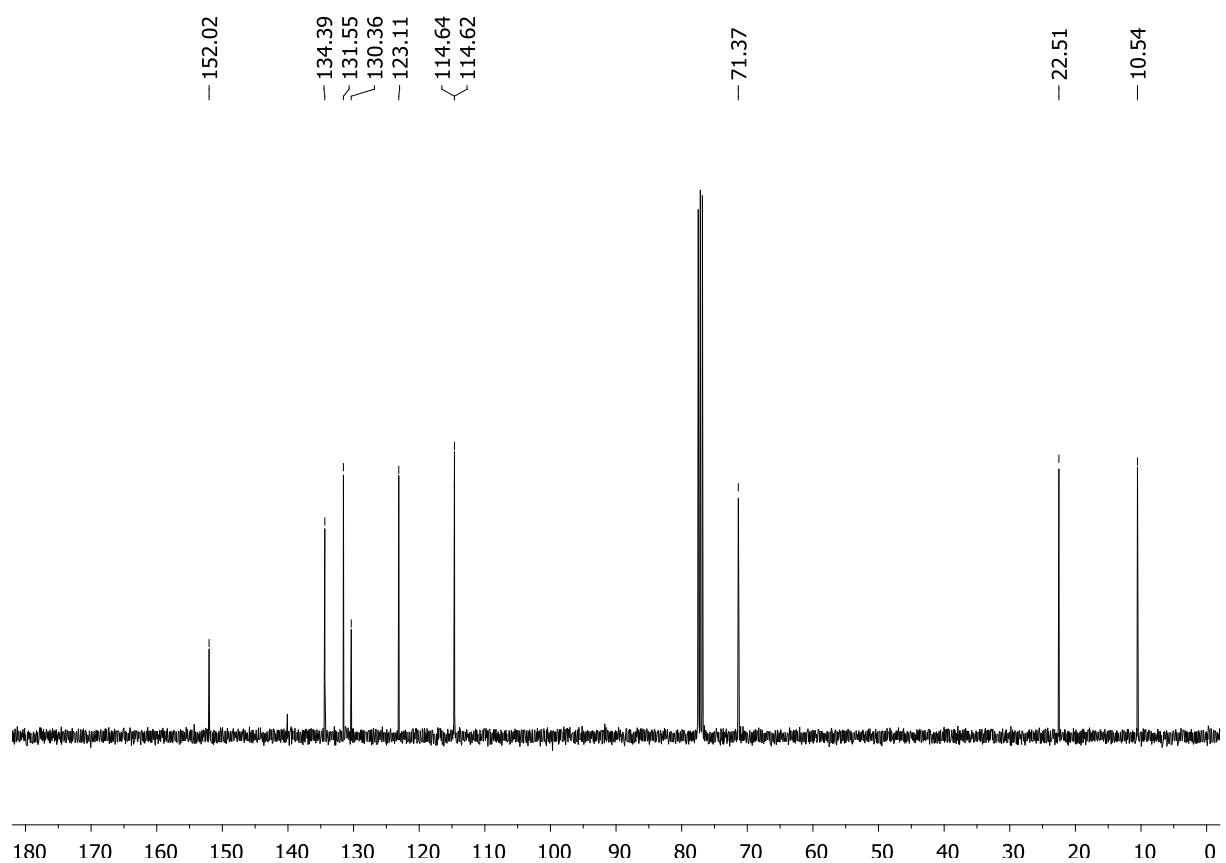
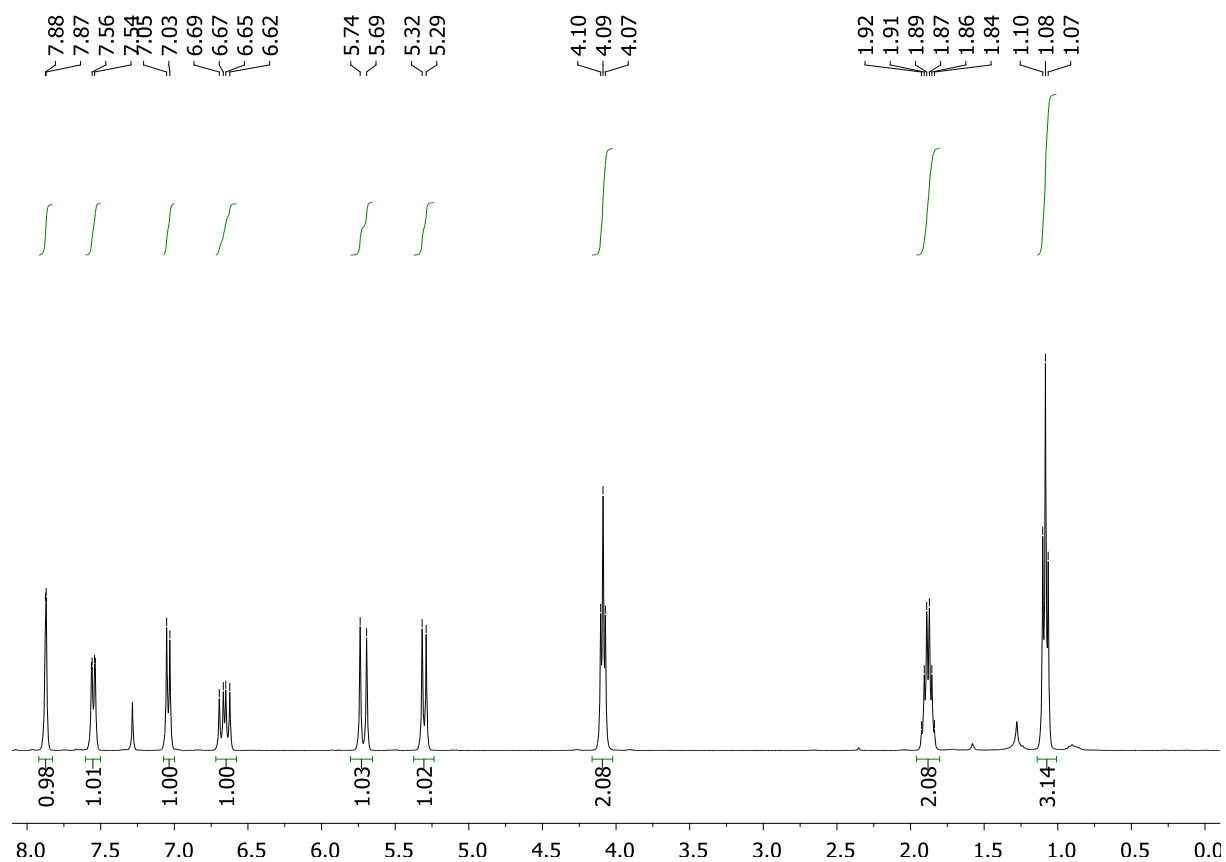
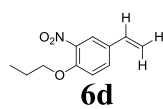


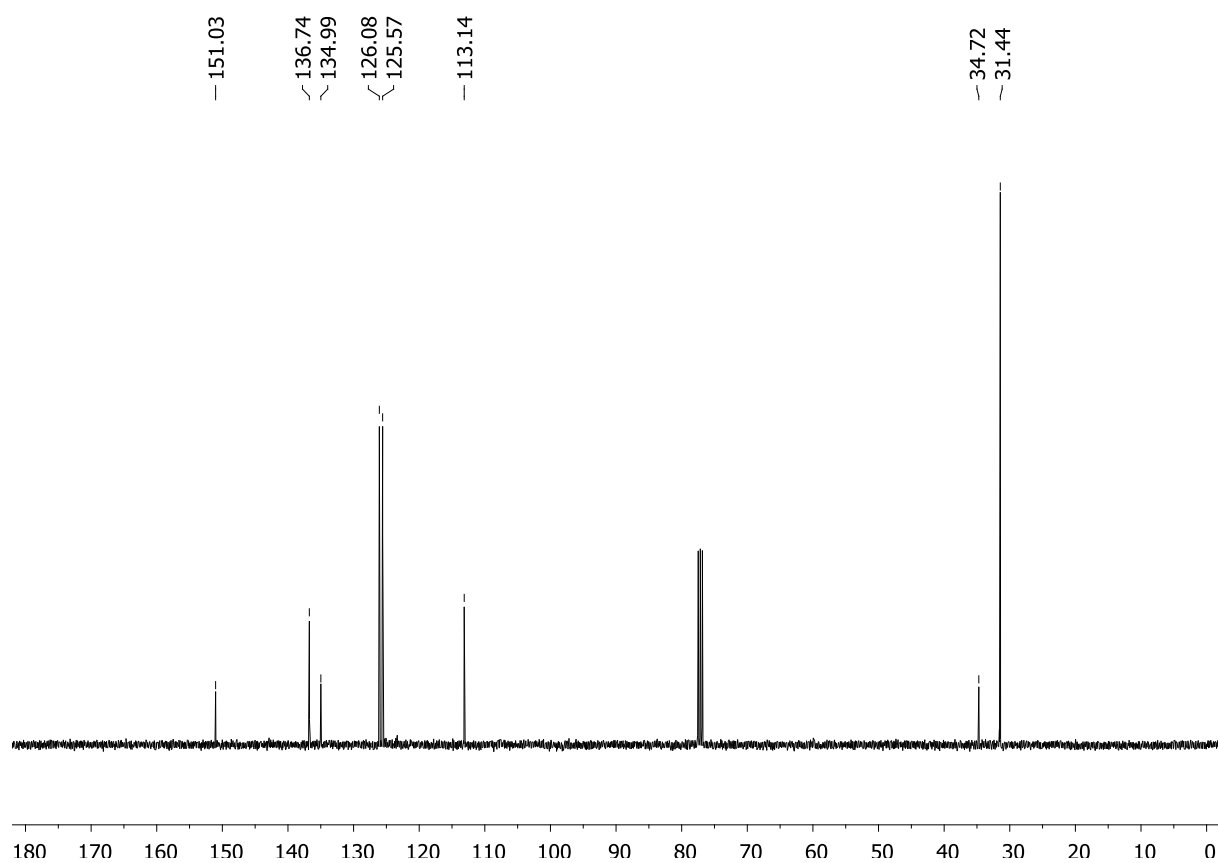
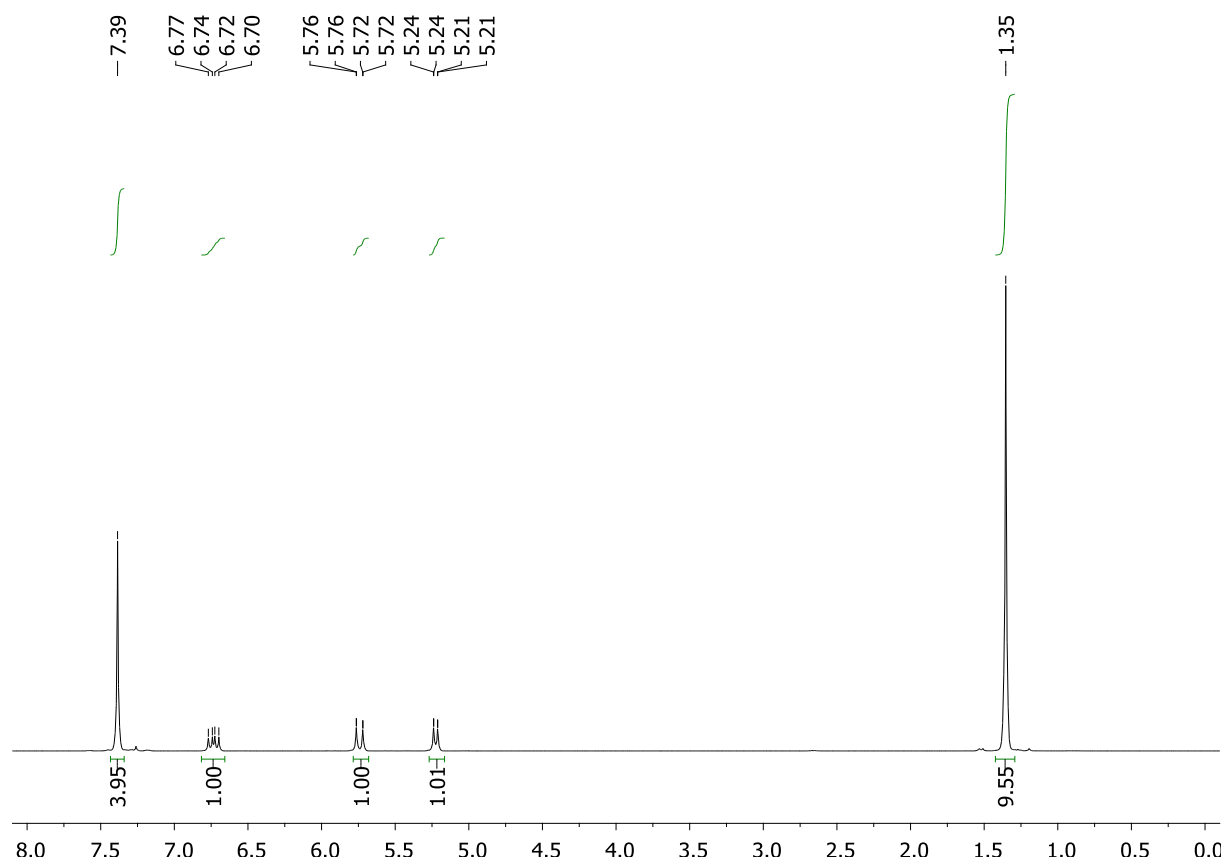
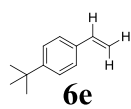
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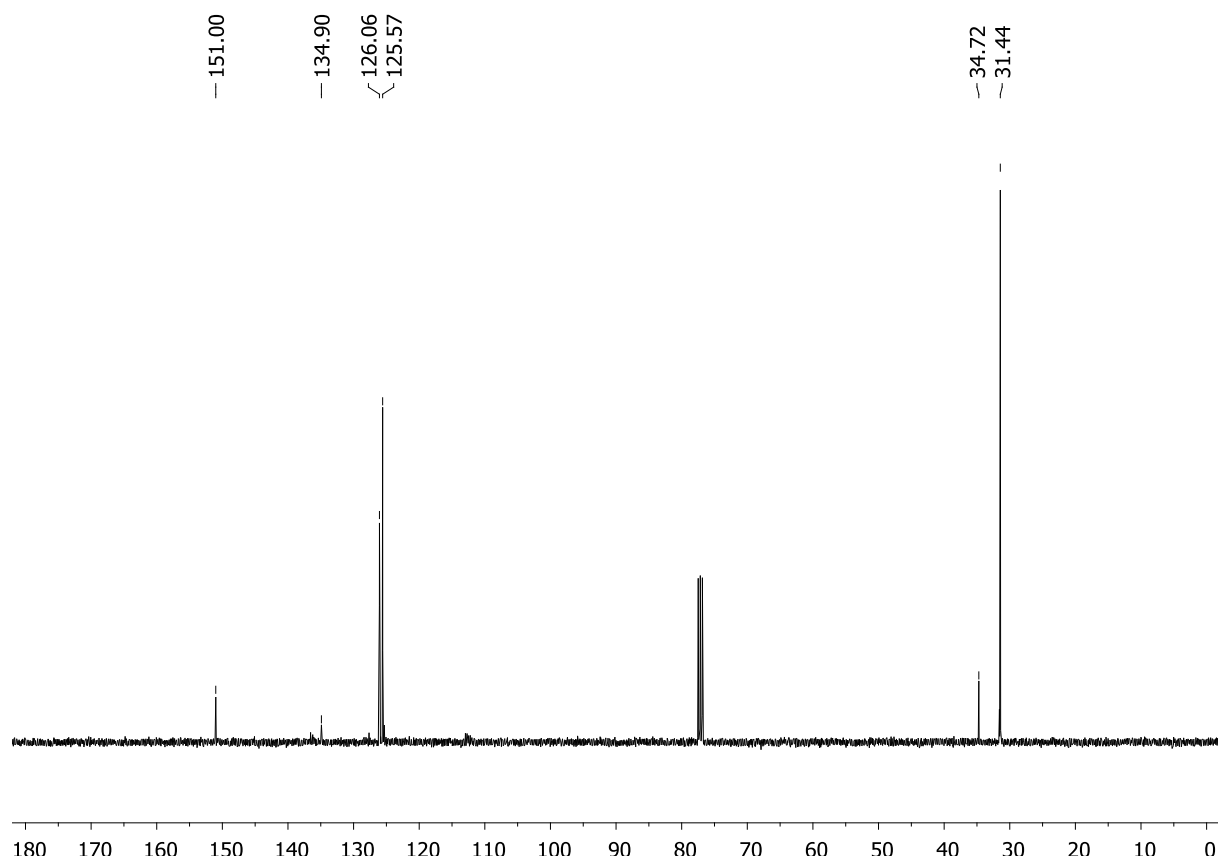
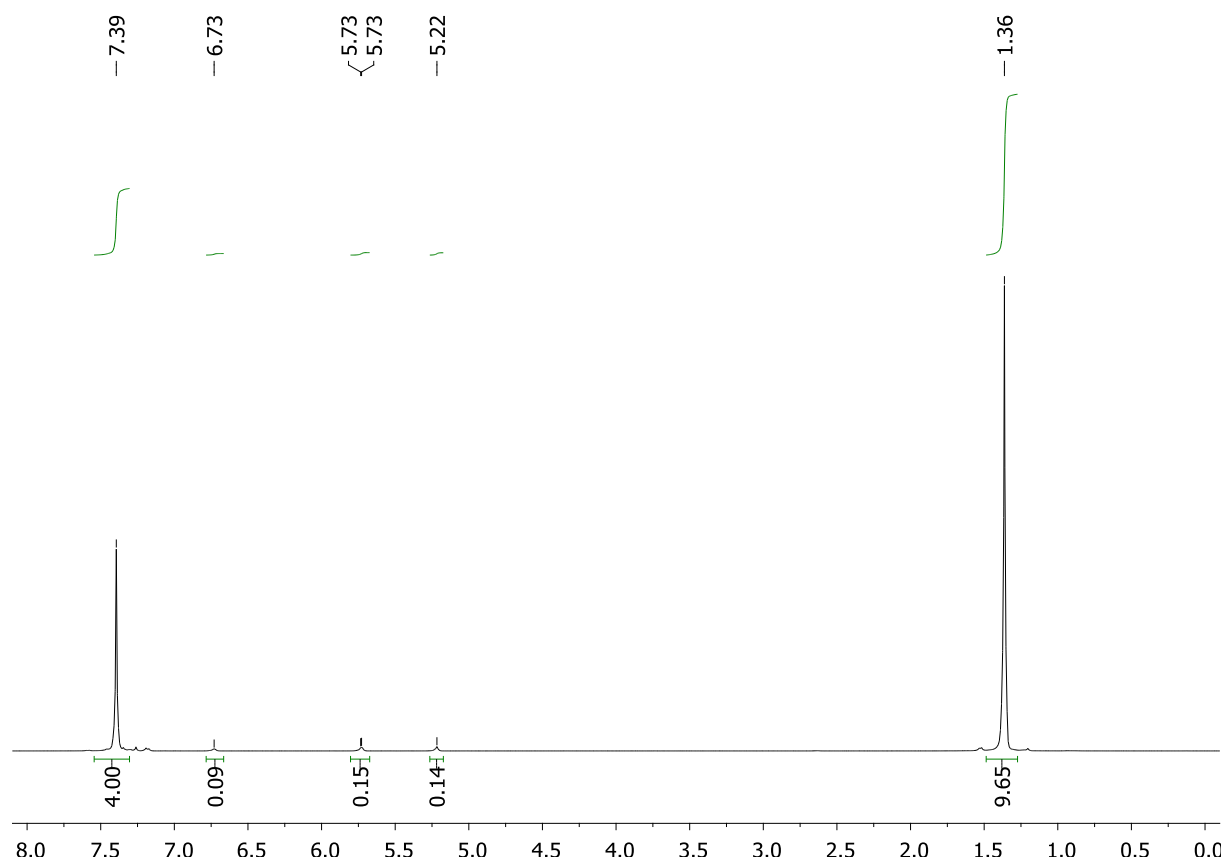
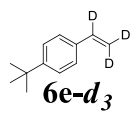


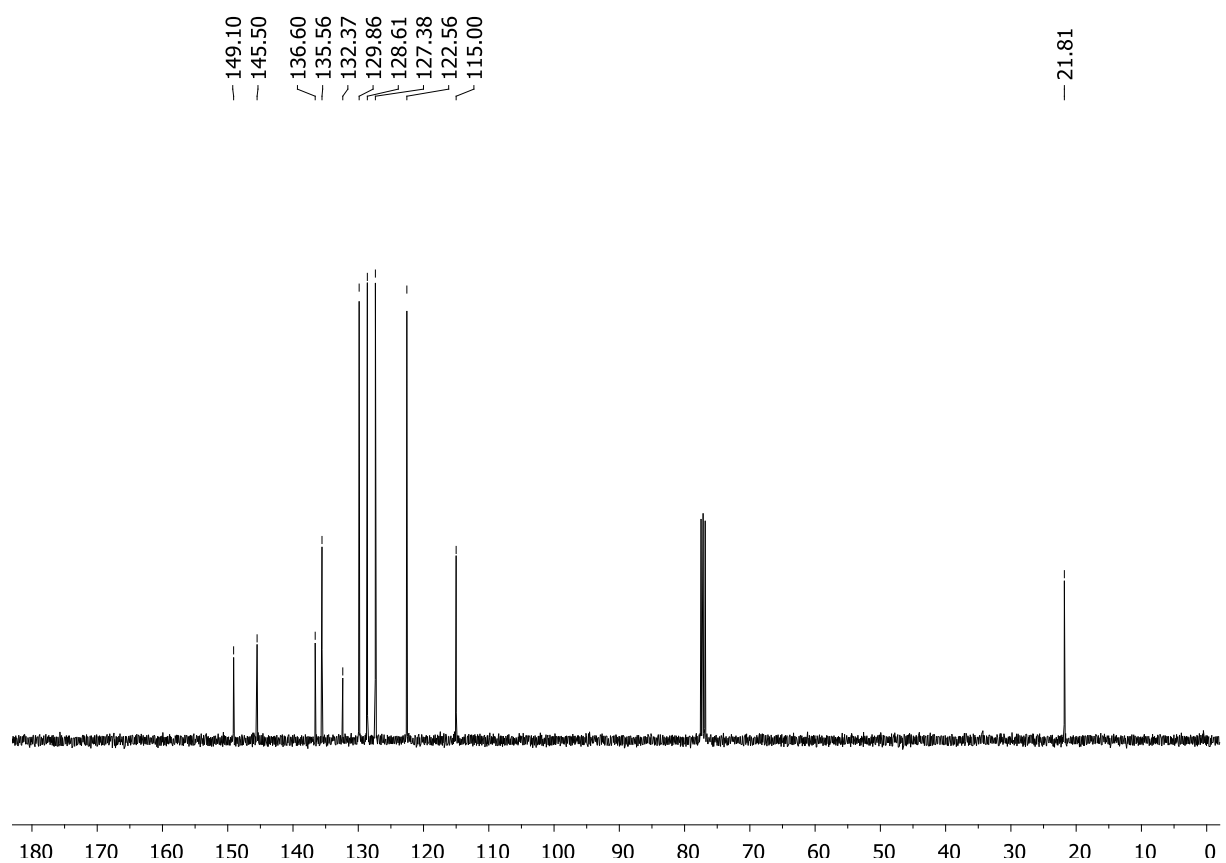
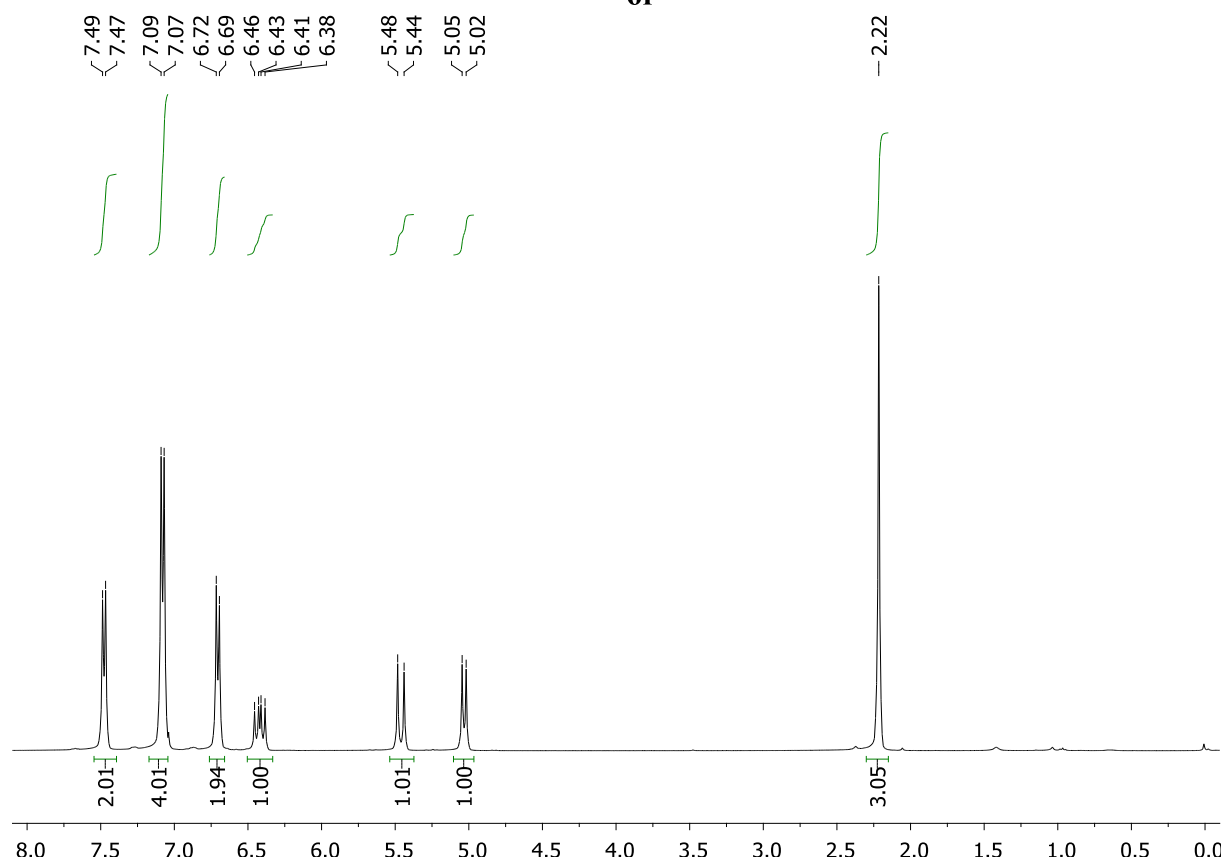
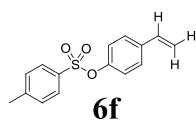


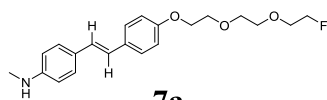




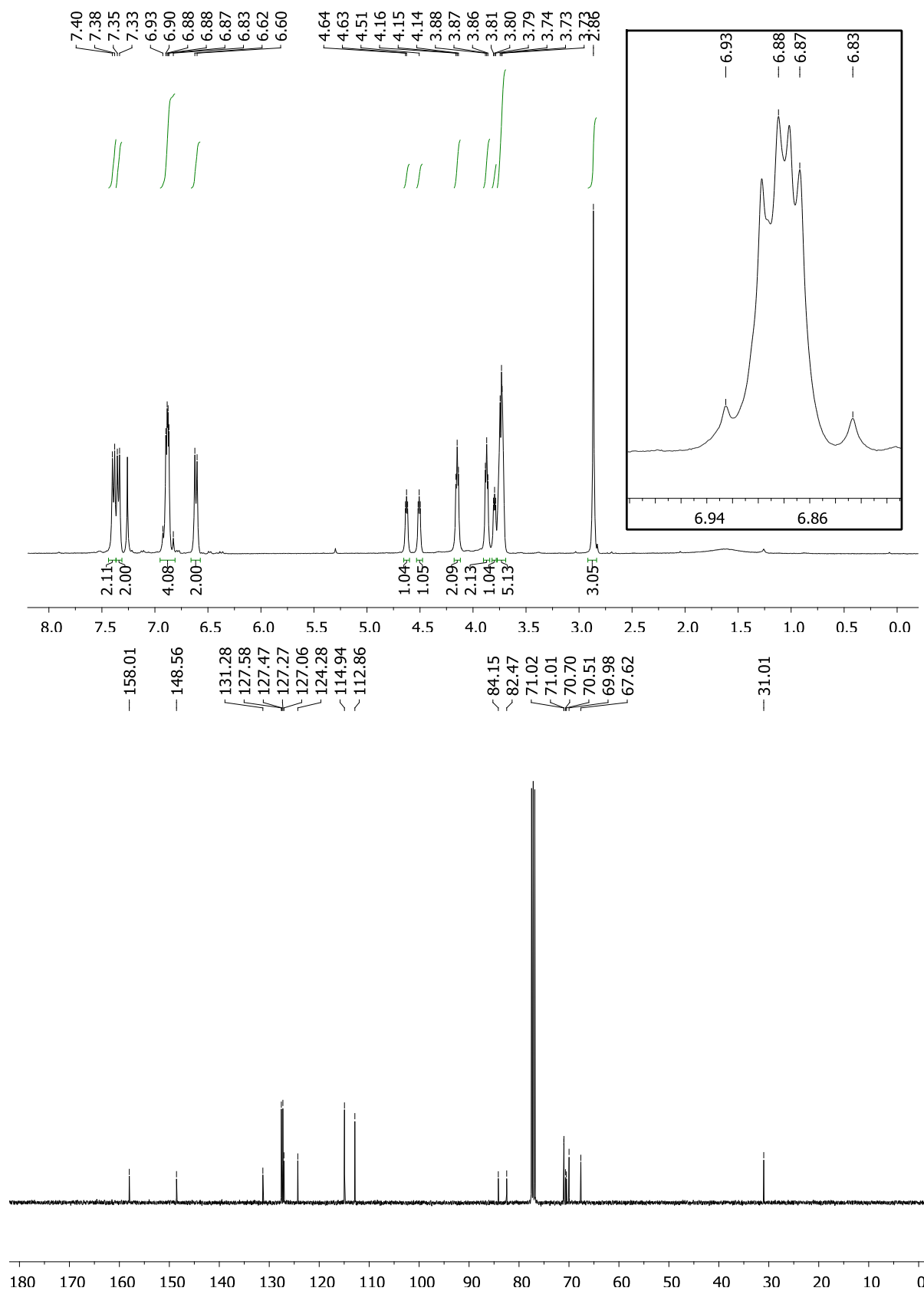


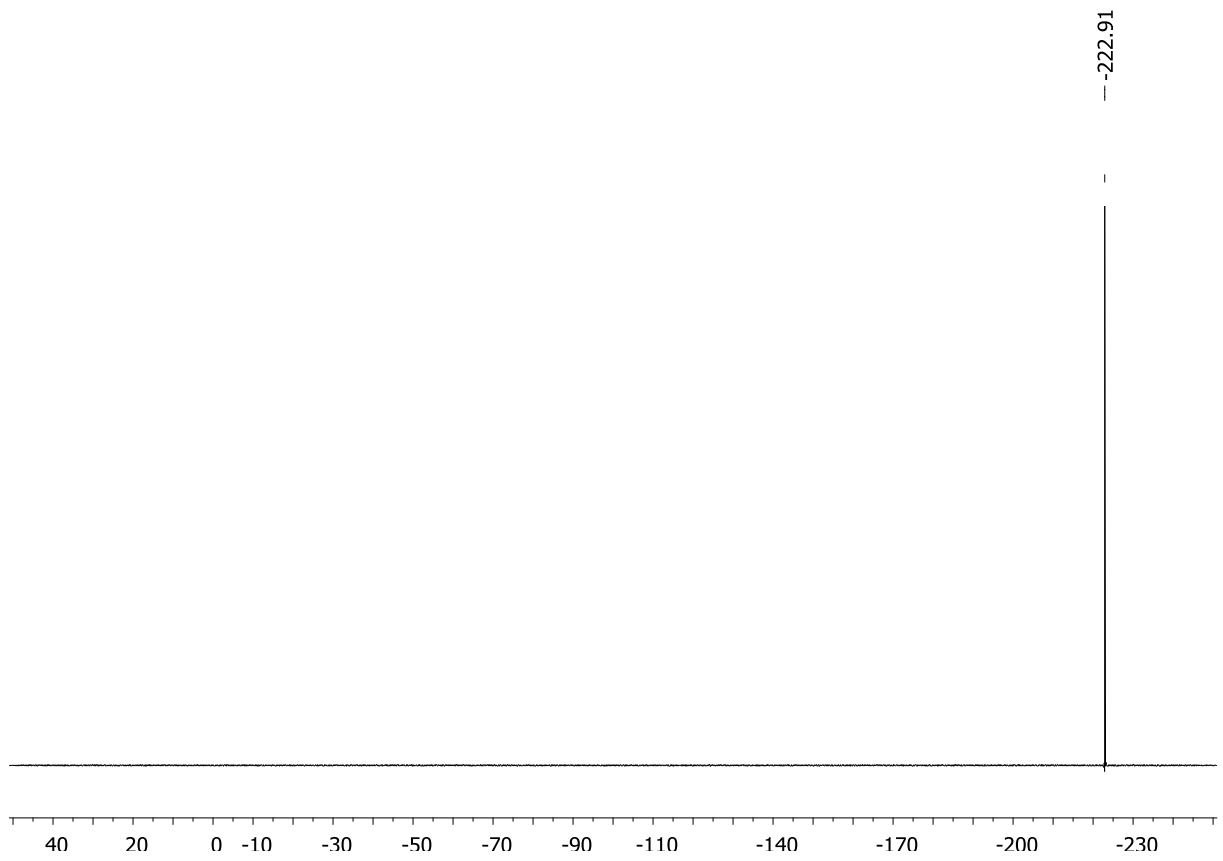


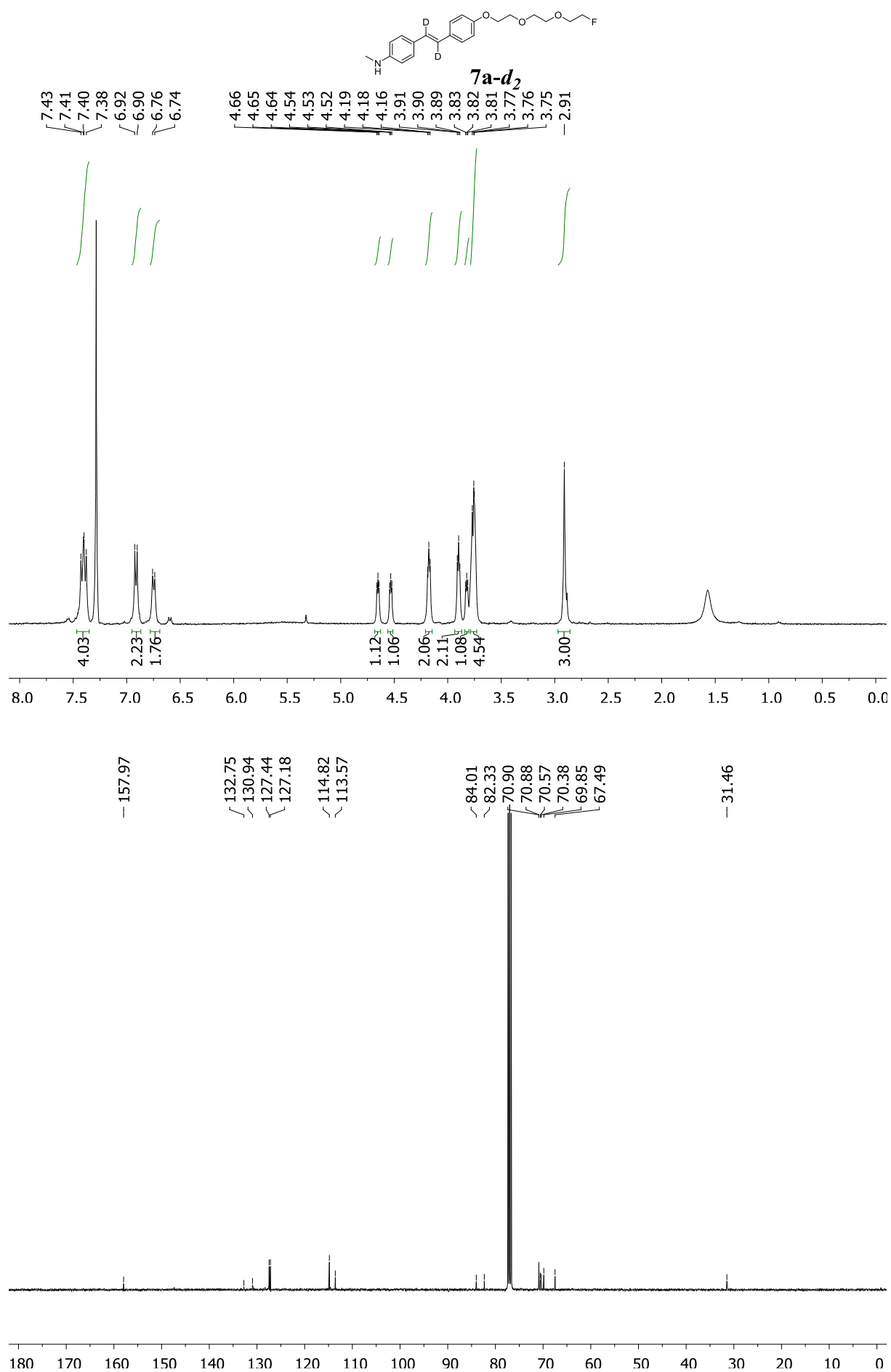


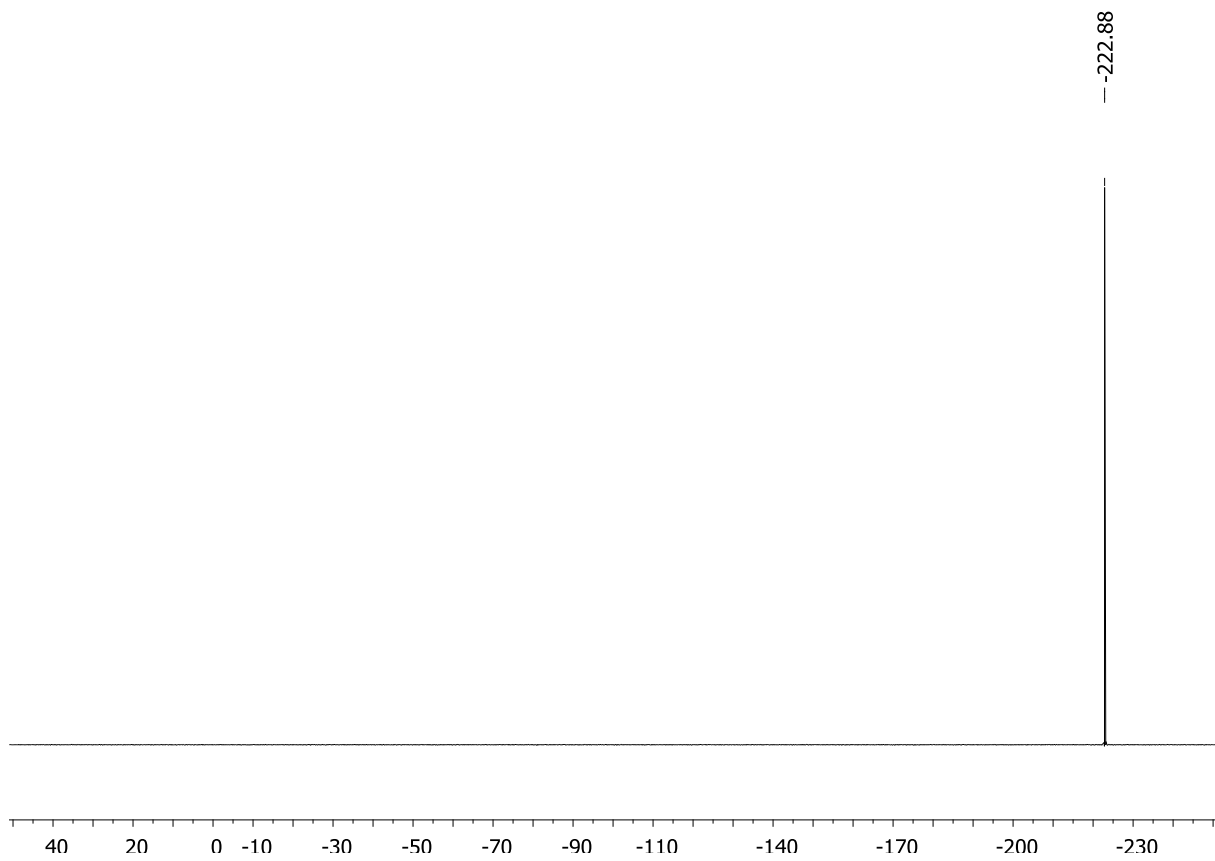


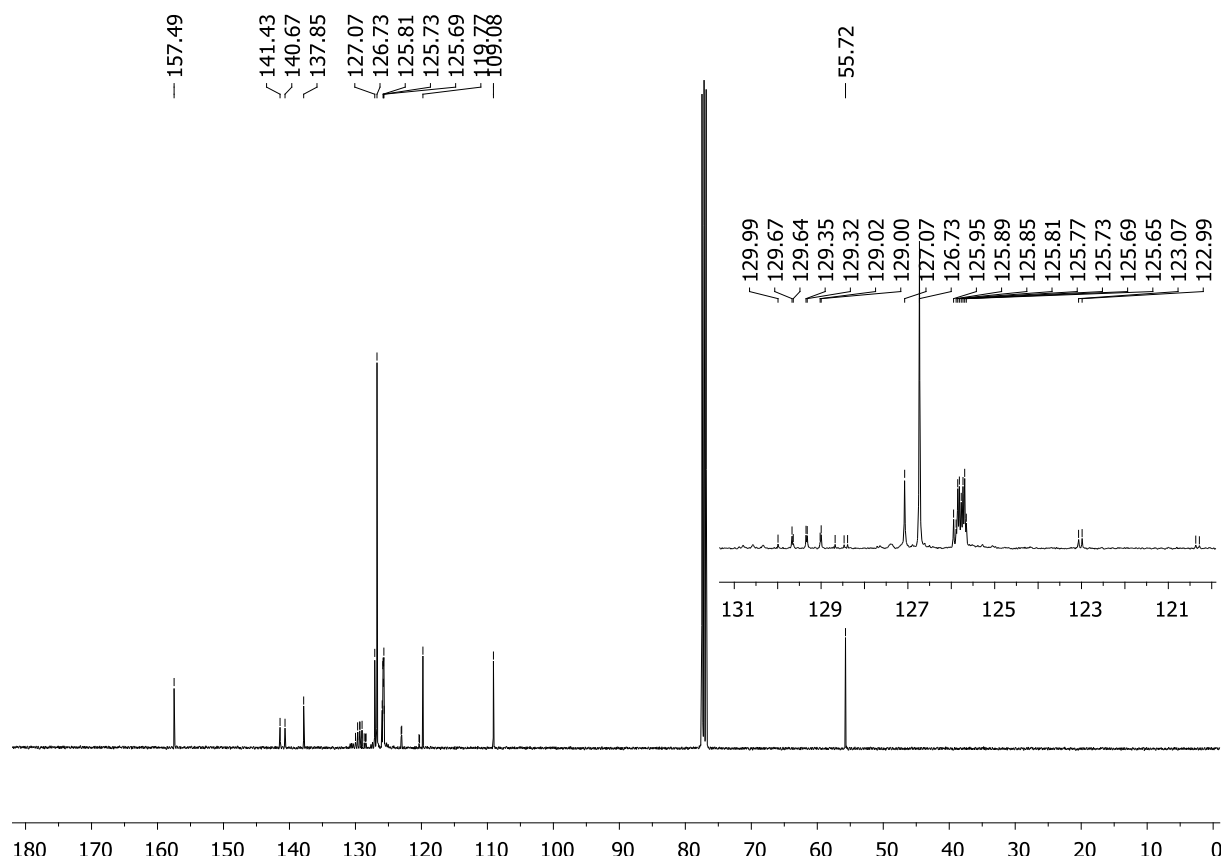
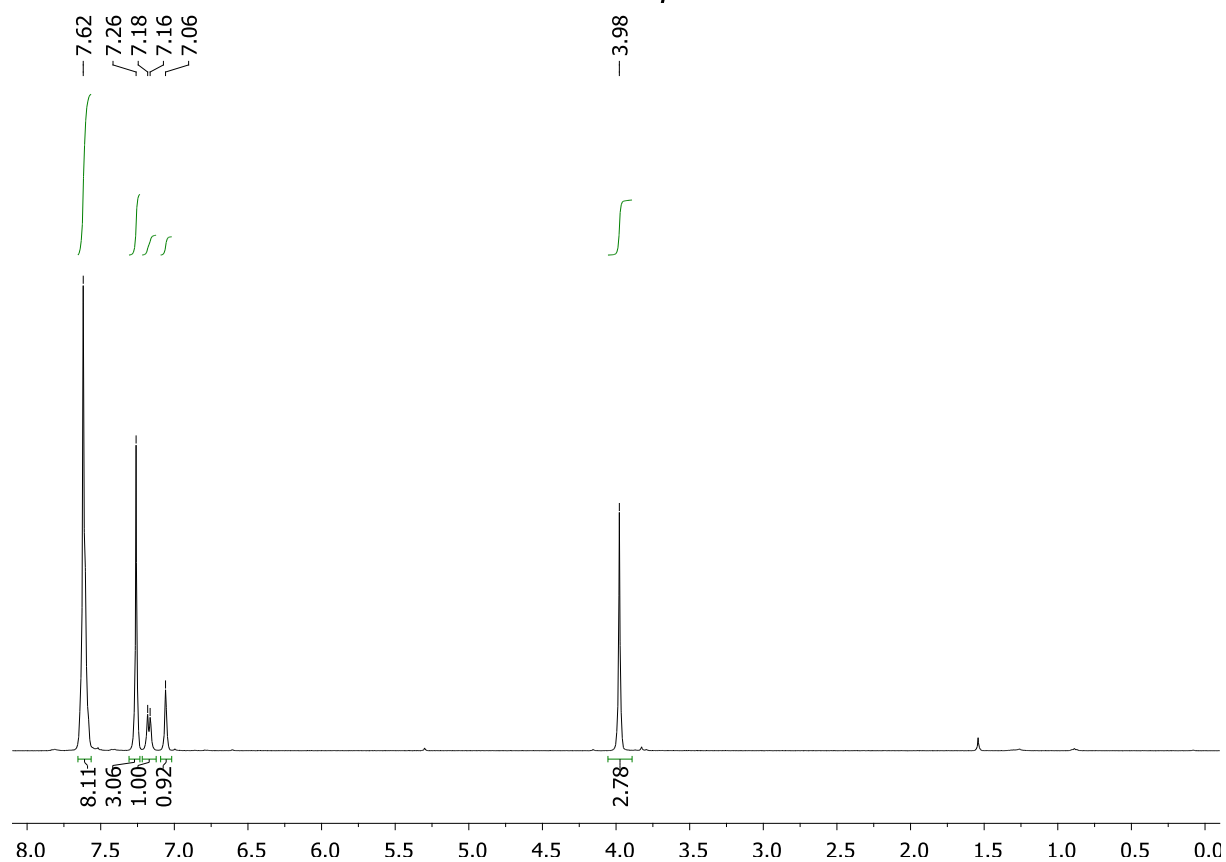
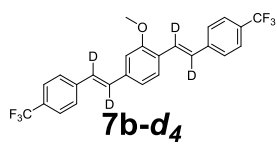
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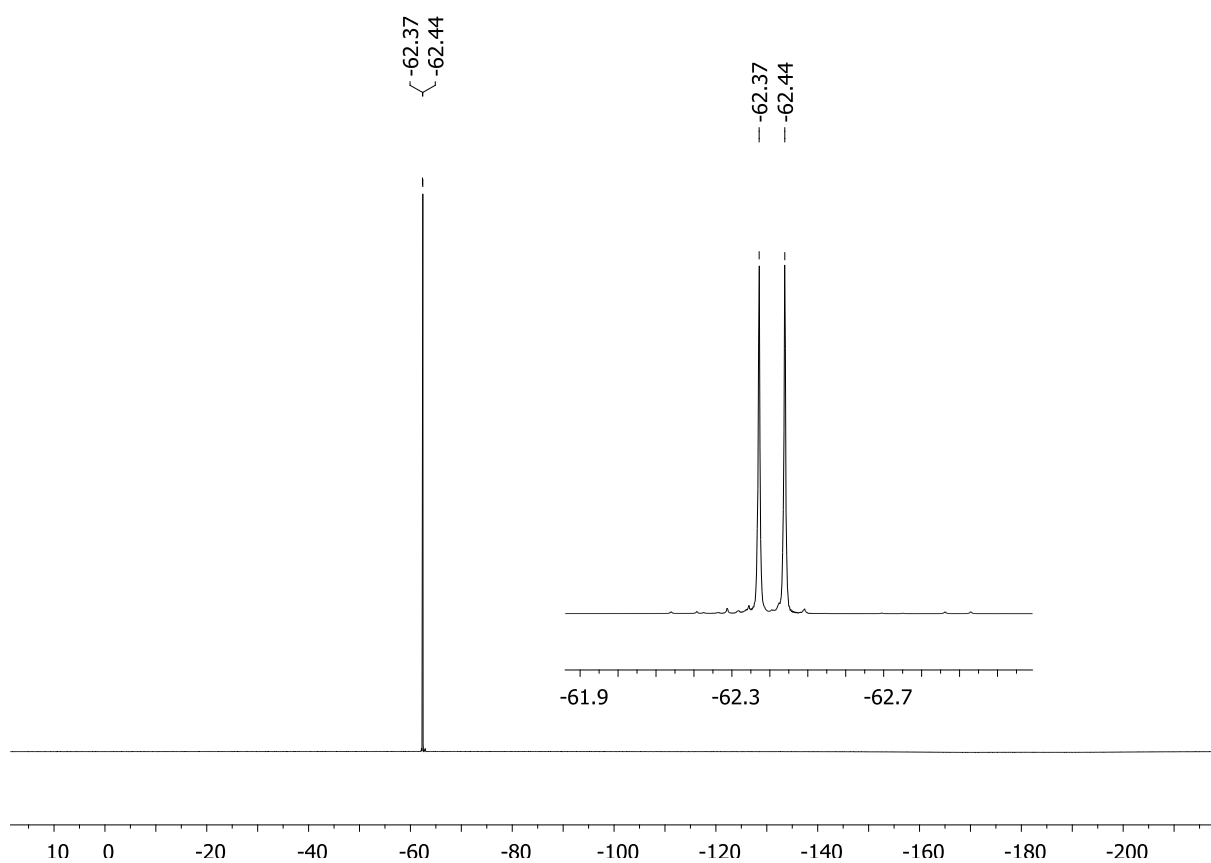


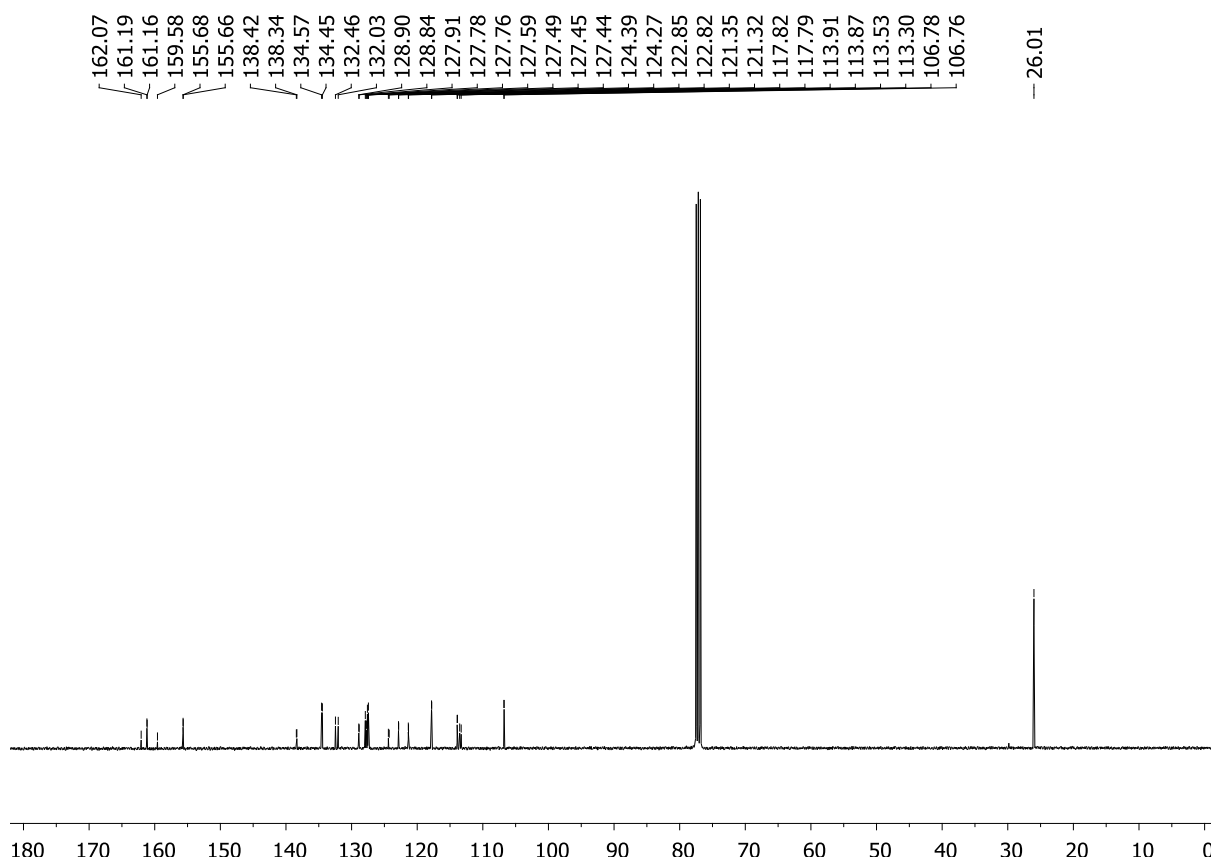
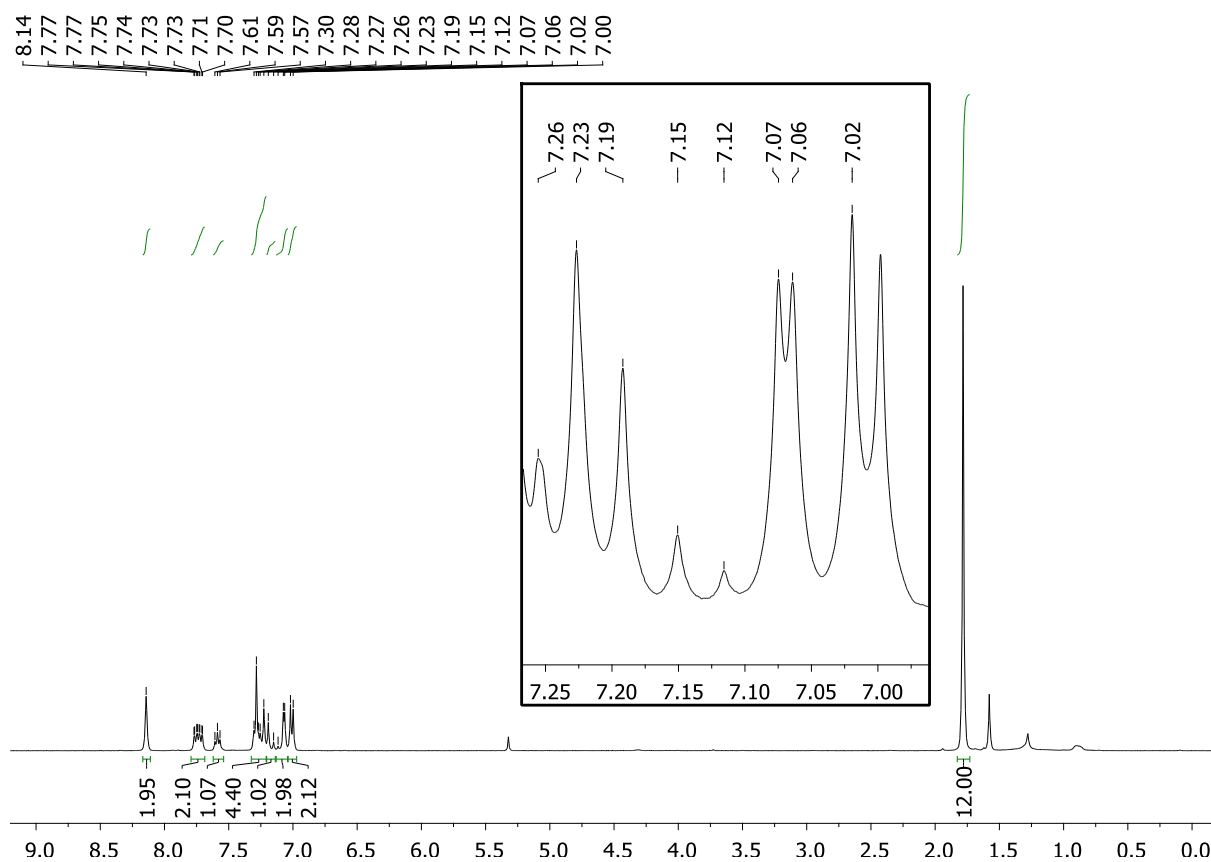
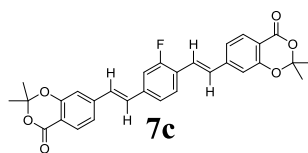


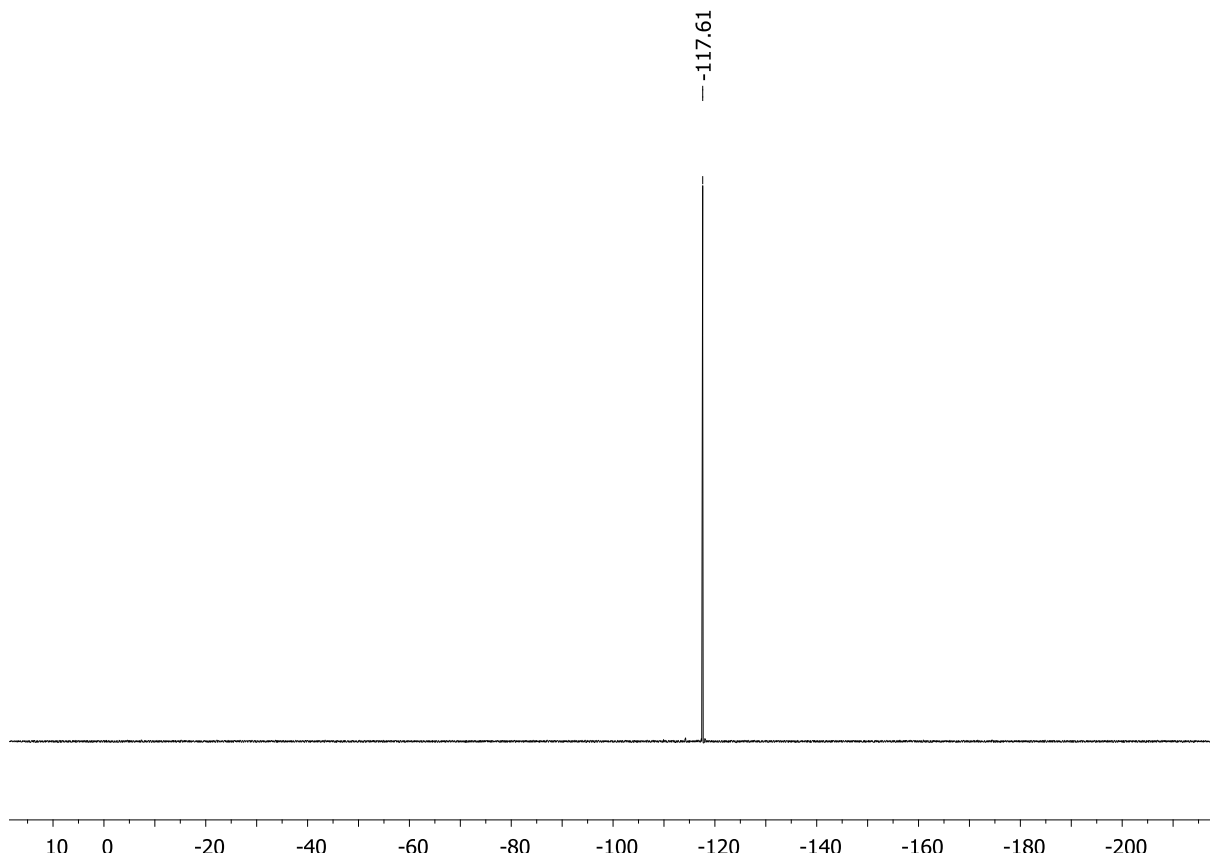


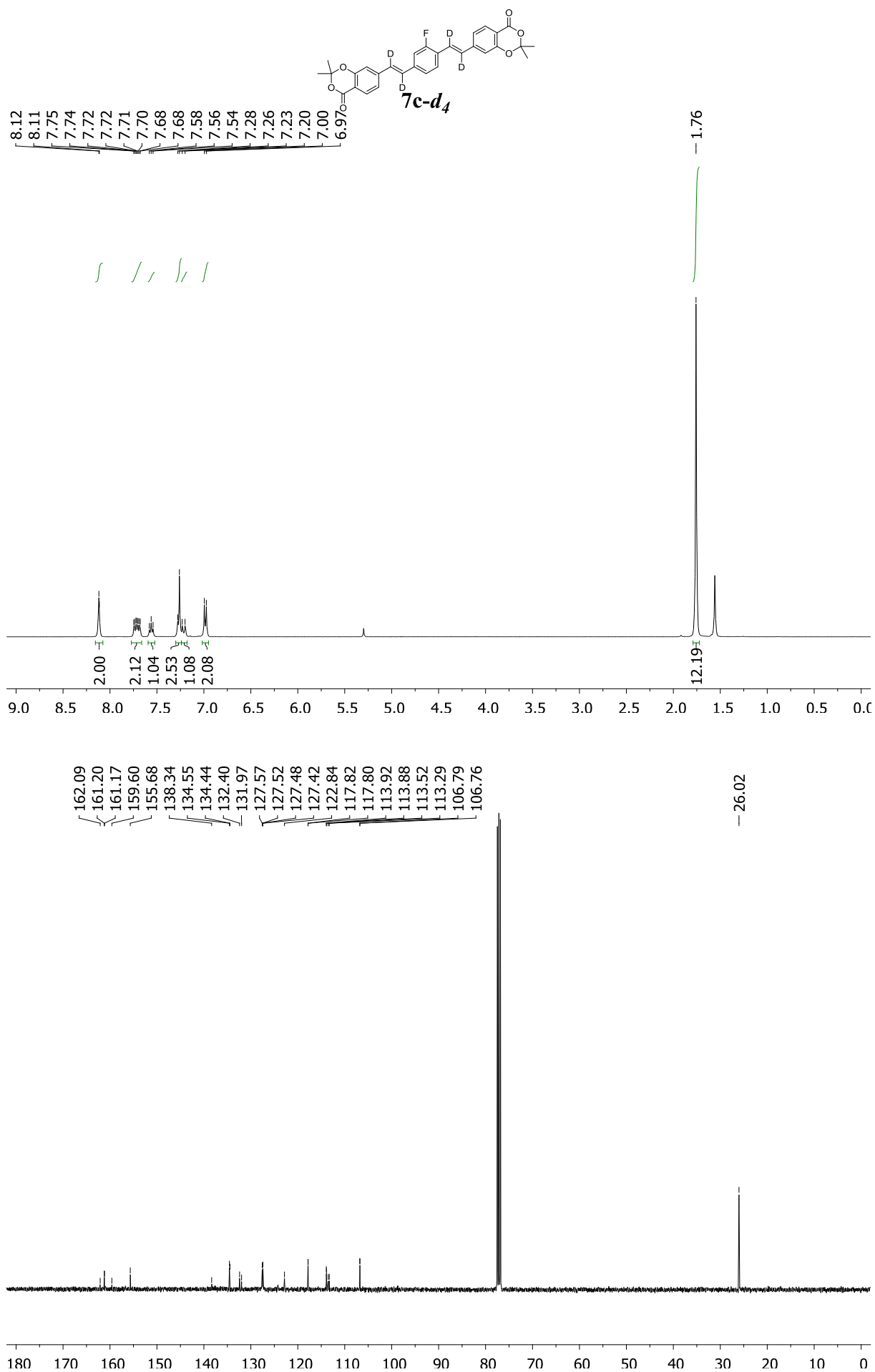


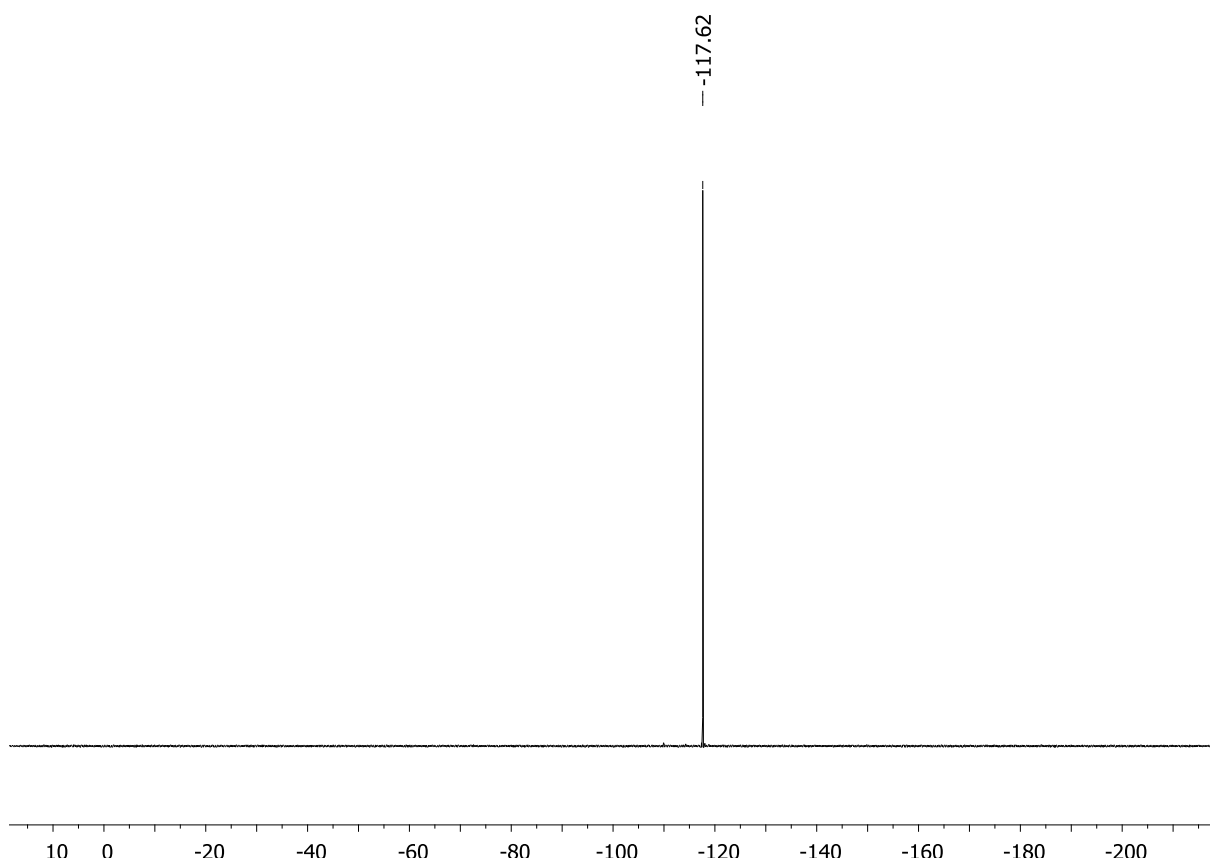


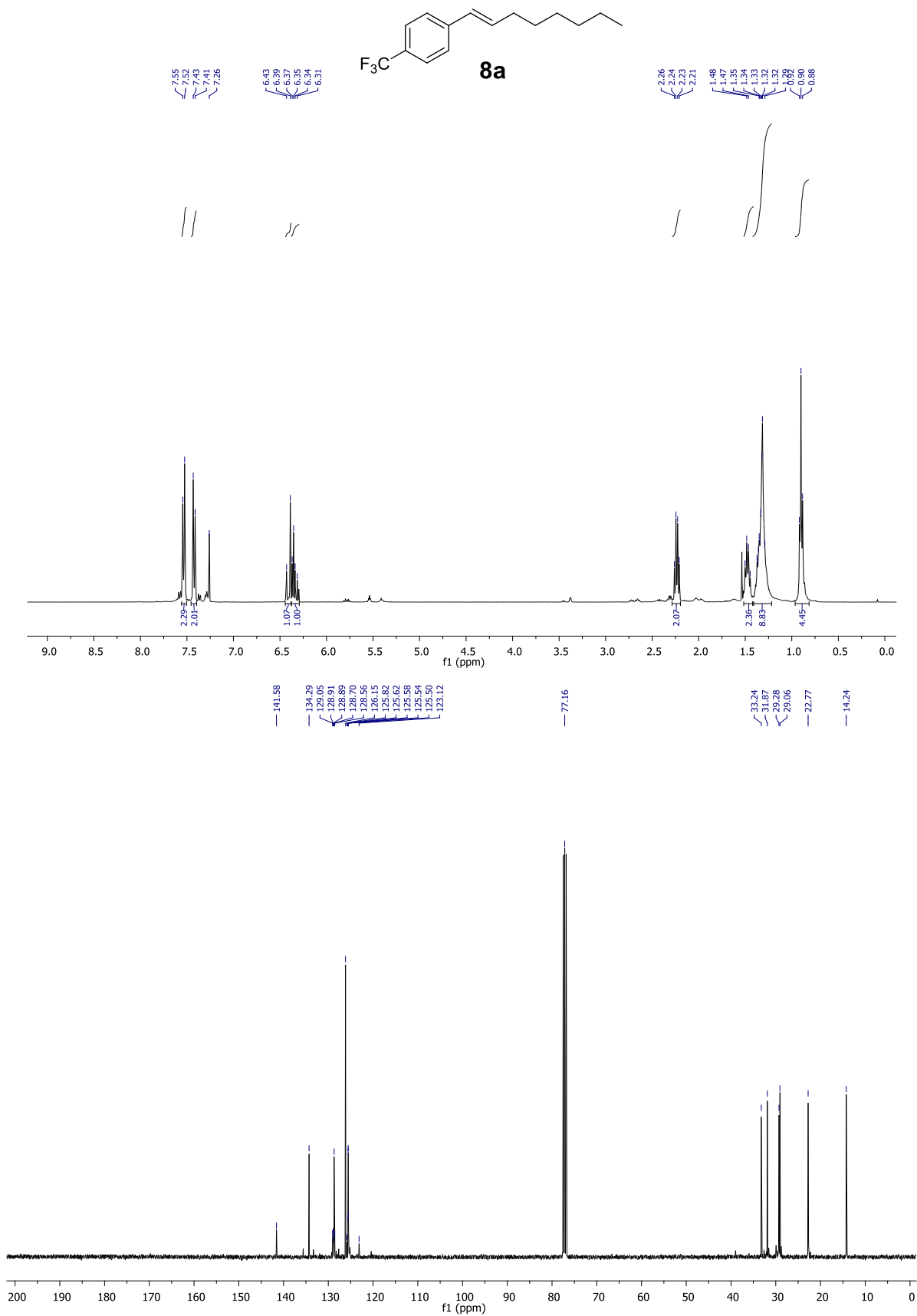


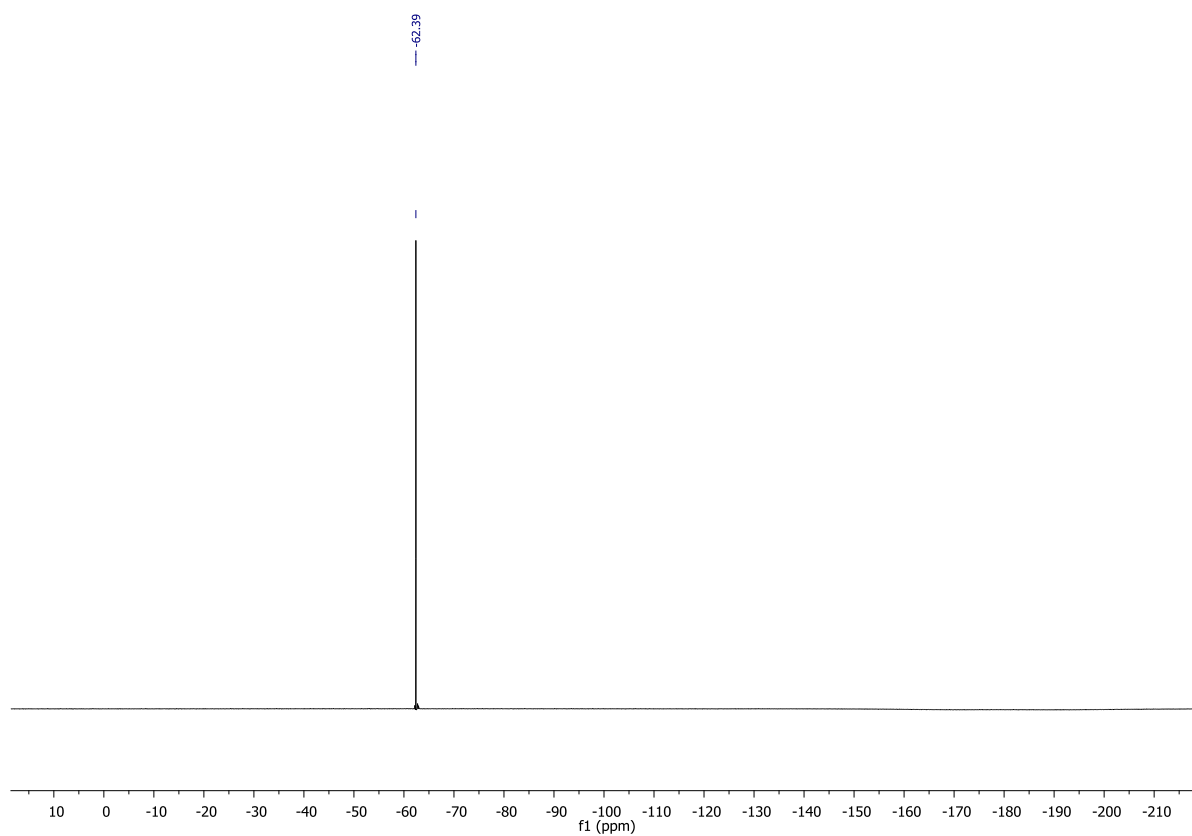


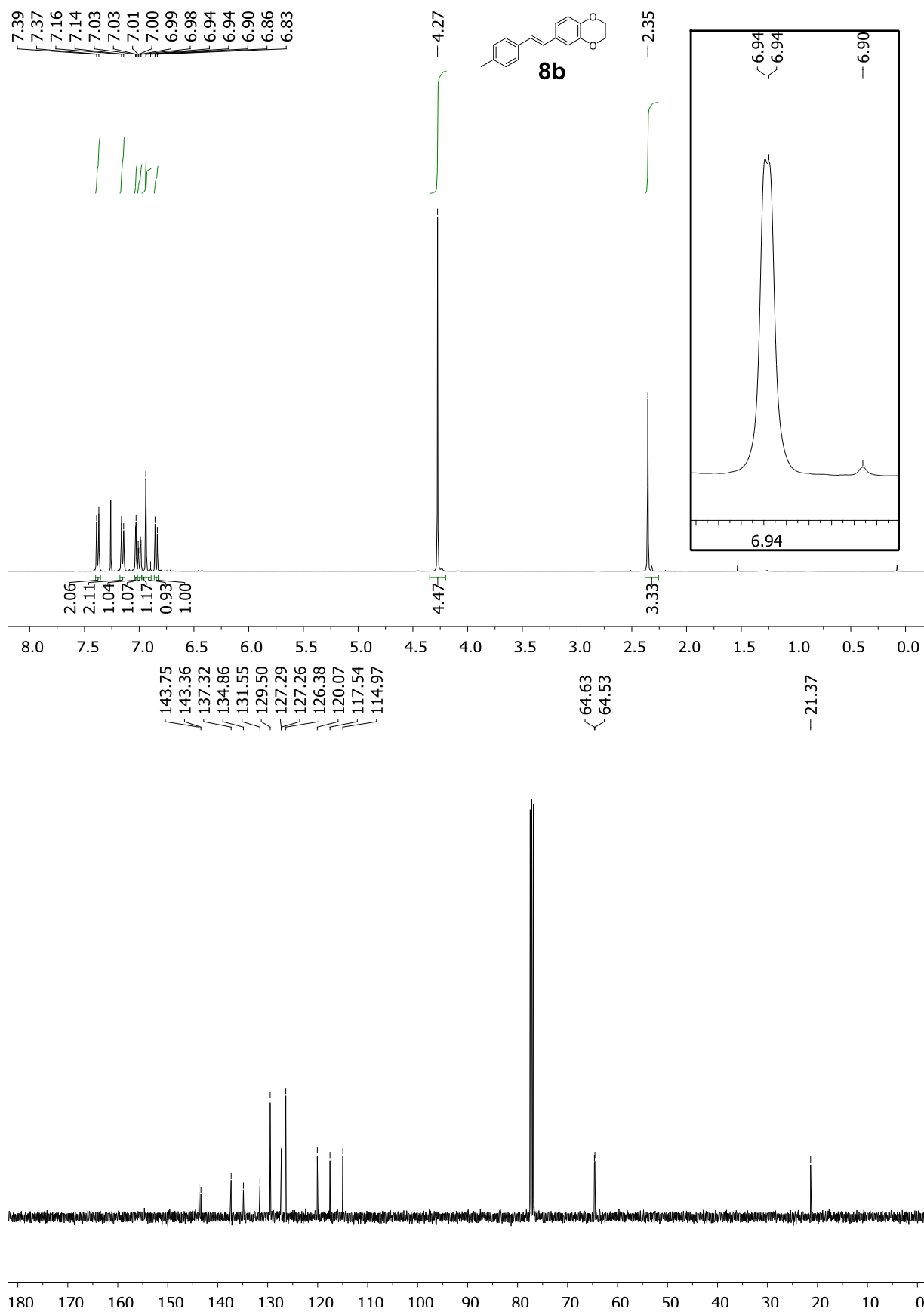


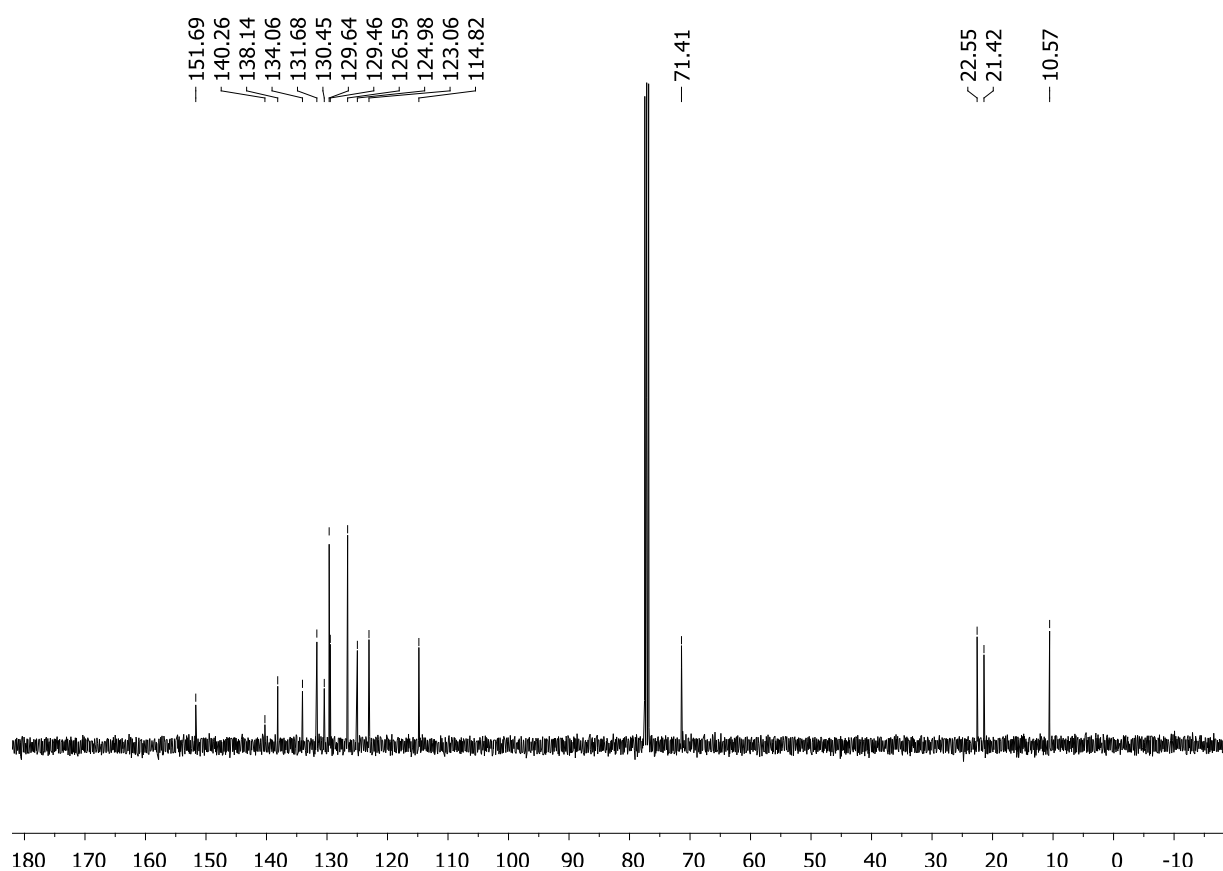
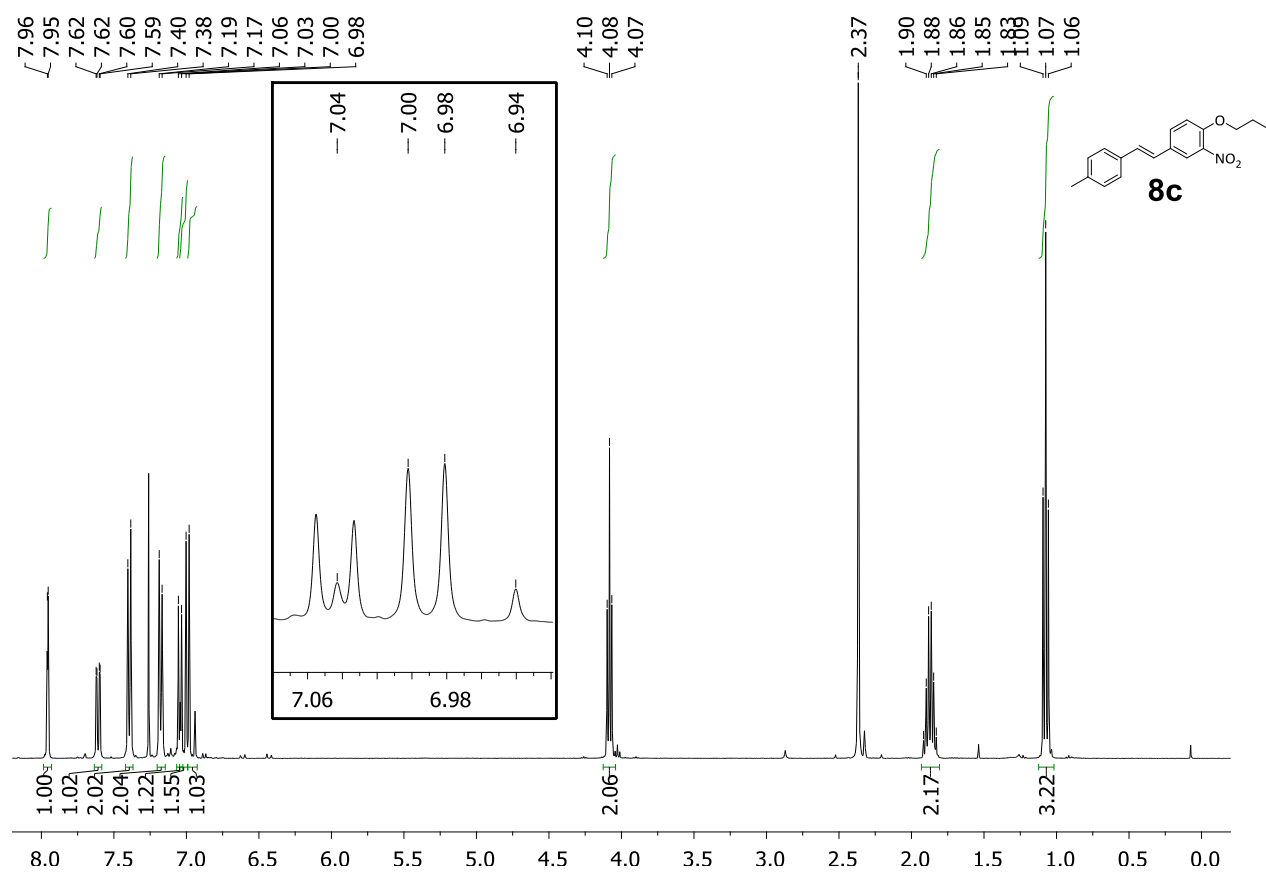


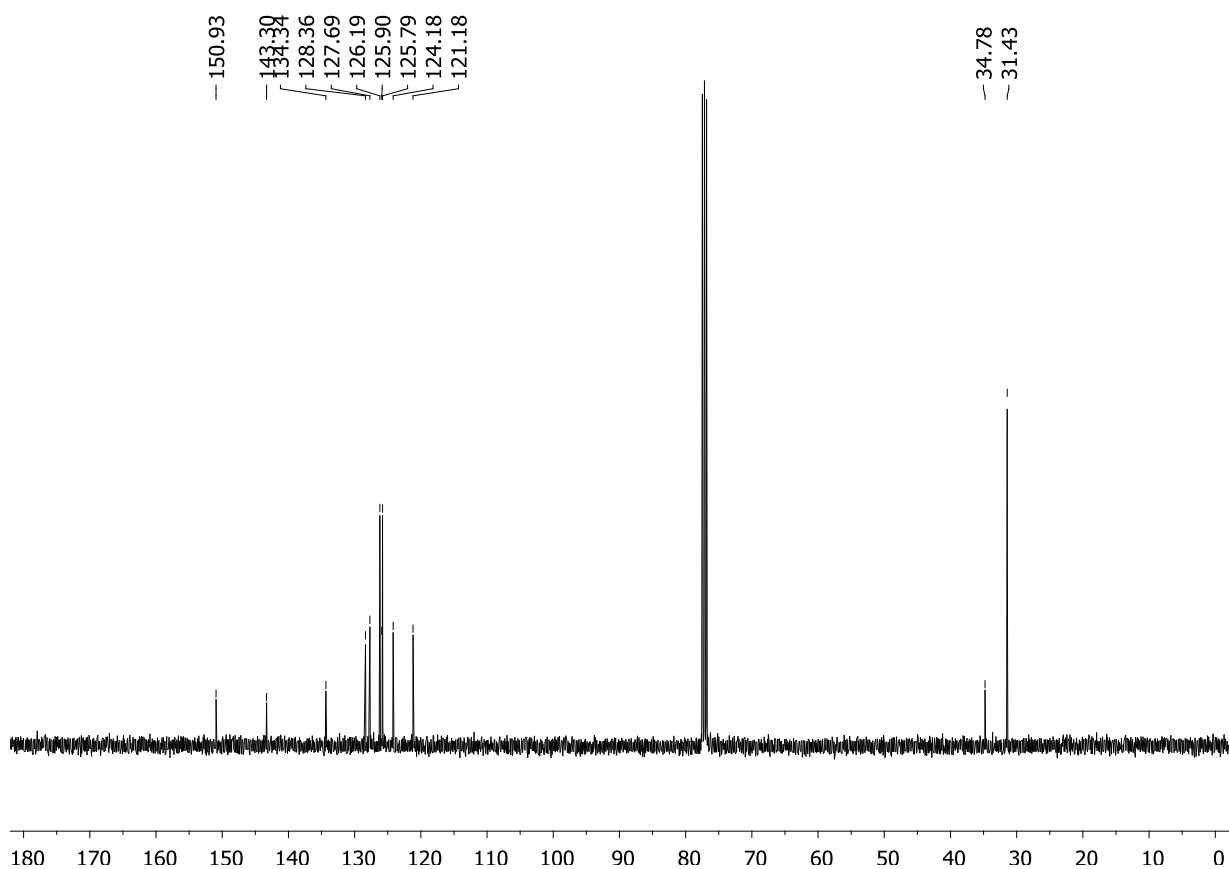
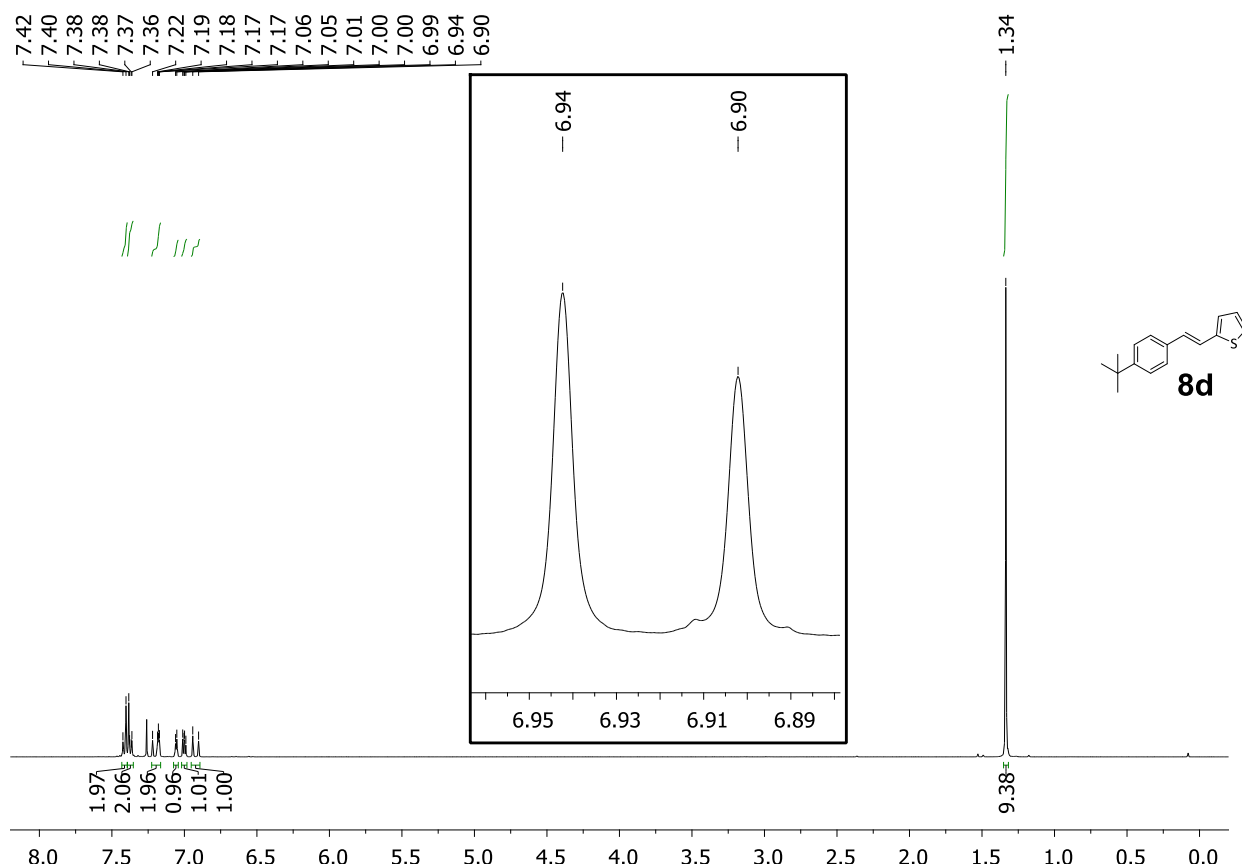


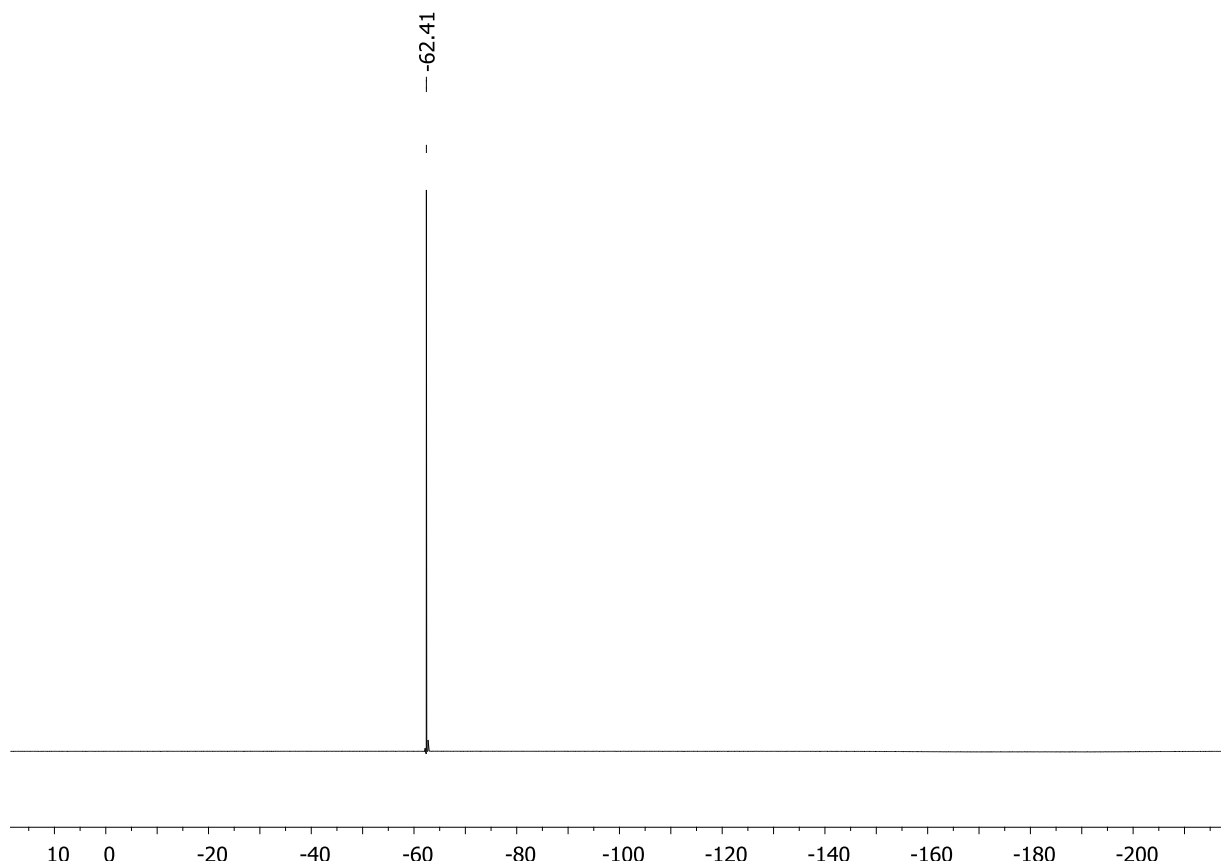
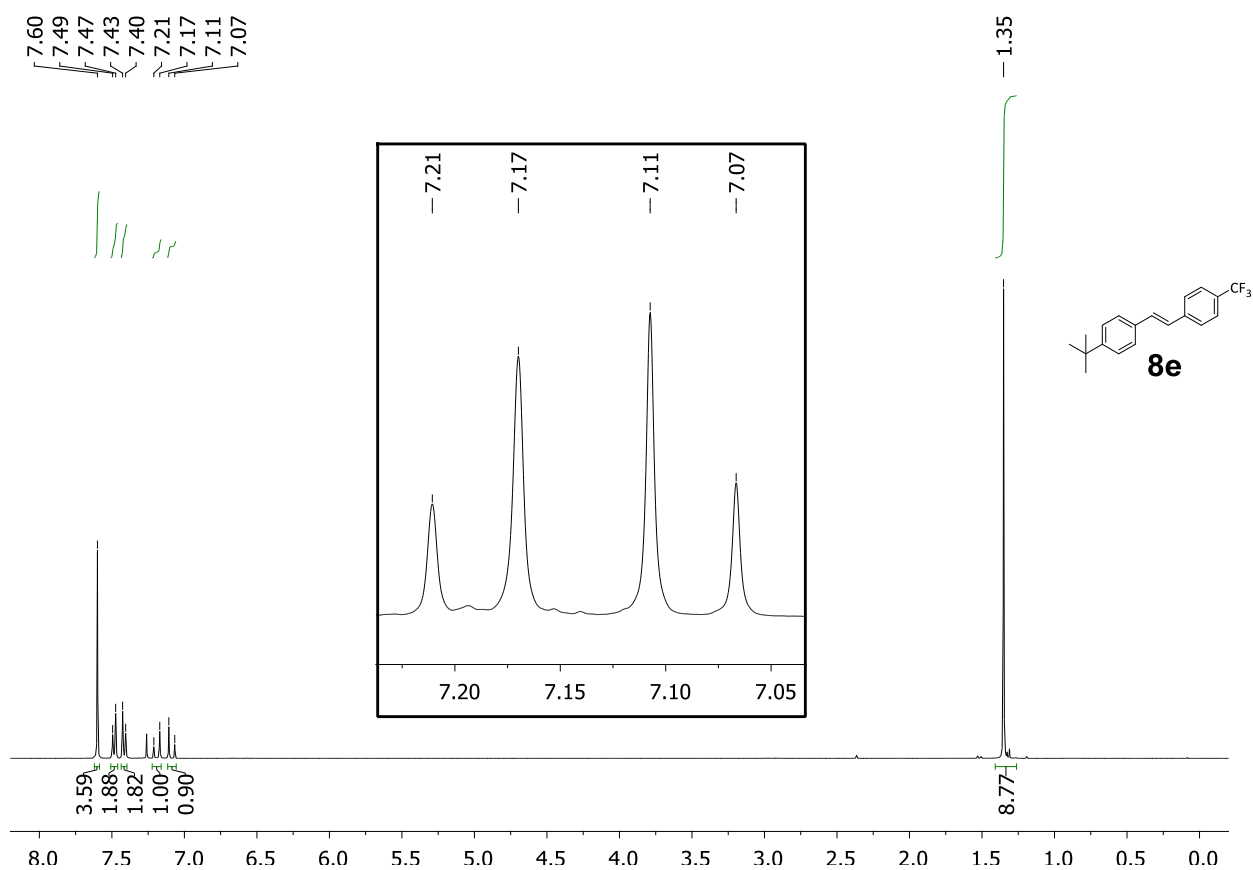


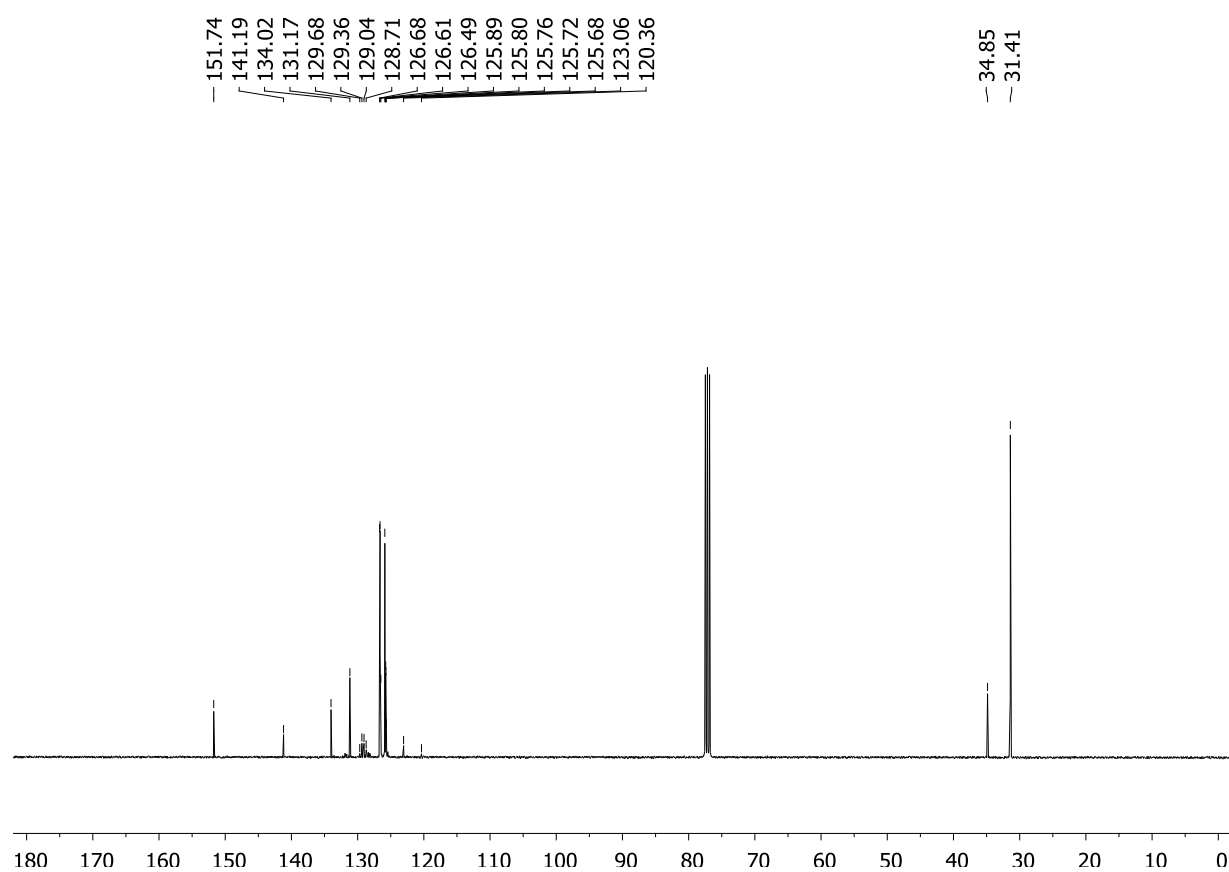


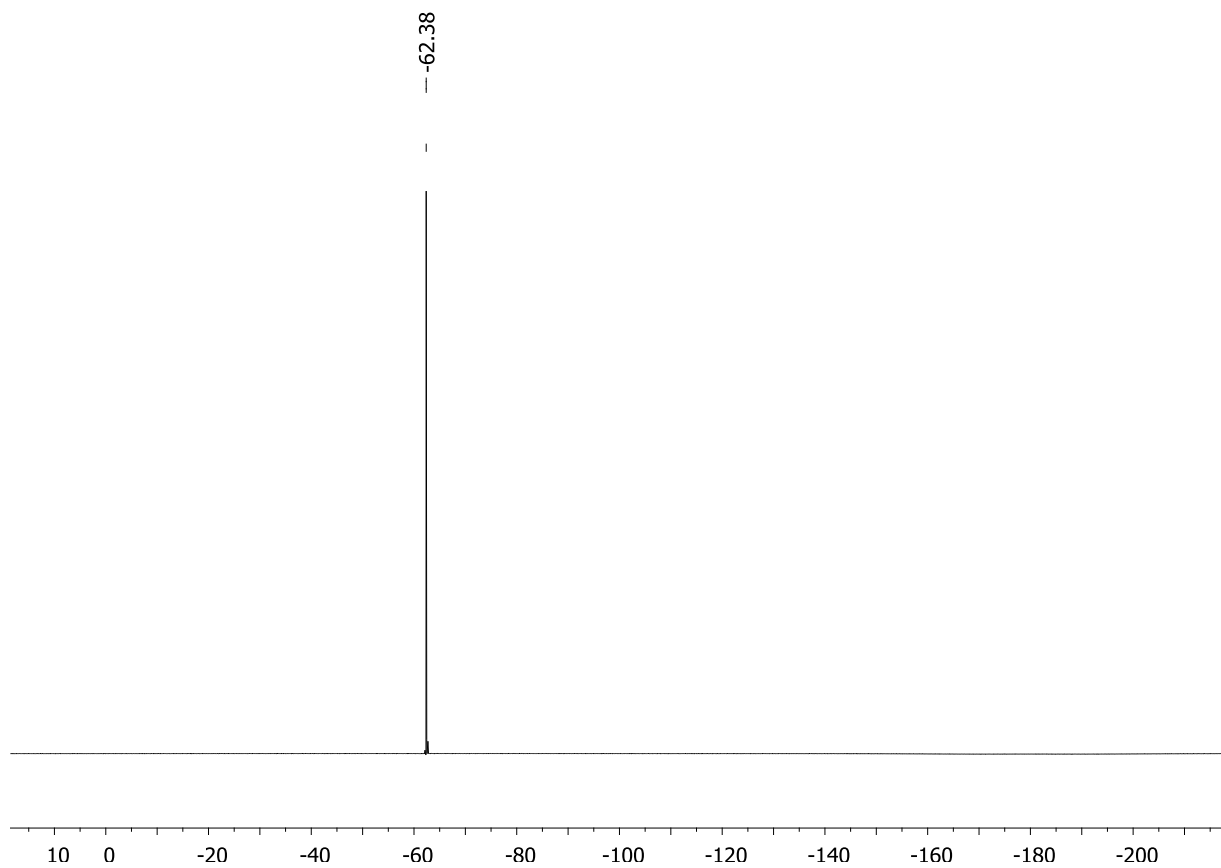
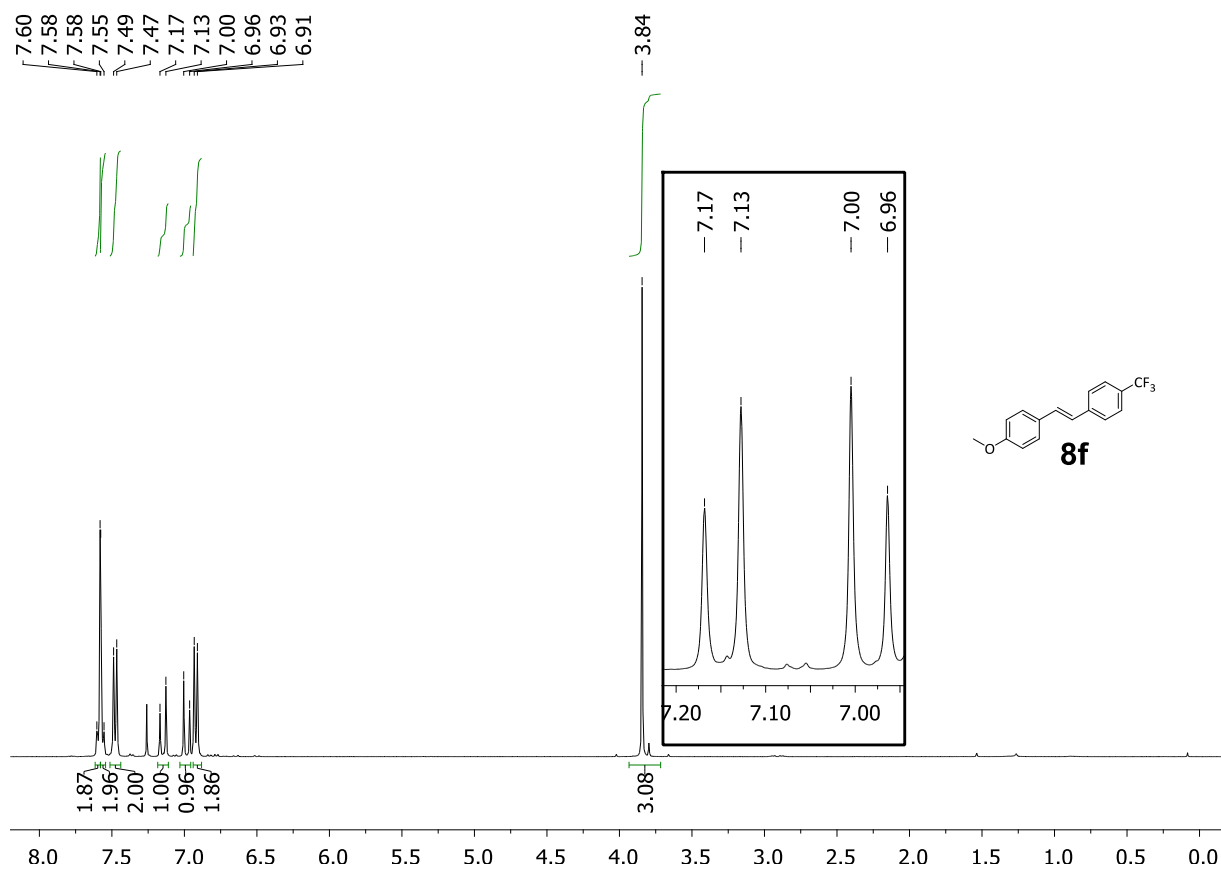


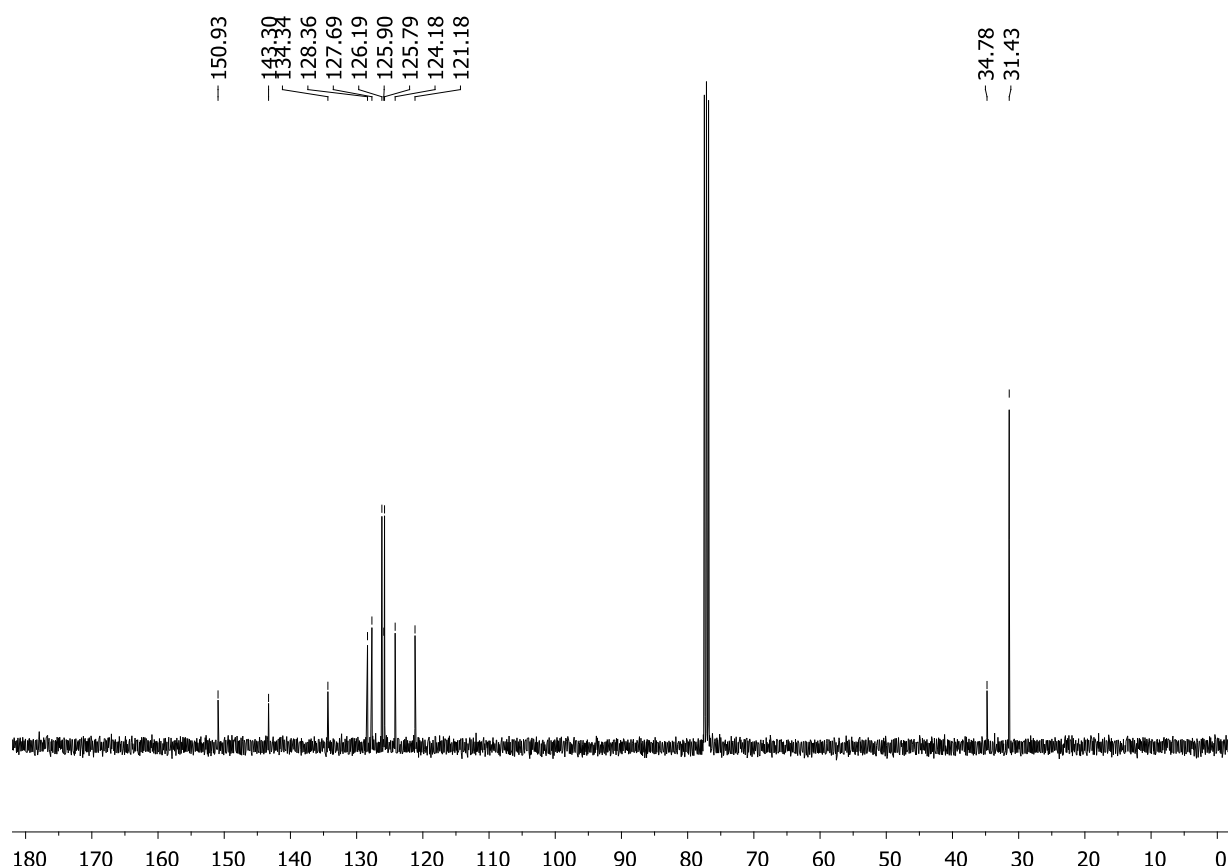












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