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Supporting Information

Investigations on Gold-Catalyzed Thioalkyne Activation Toward Facile Synthesis of Ketene Dithioacetals

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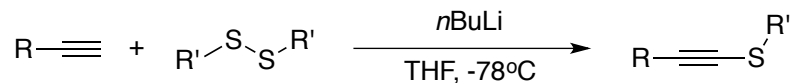
I. General Methods and Materials	S2
II. Screen Table	S5
II. ORTEP Drawing of the Crystal Structures	S7
III. NMR analysis	S13
V. Compounds Characterization	S18
VI. NMR Spectra Data	S32

I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 400 MHz spectrometers/ Varian 500 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.00 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on Agilent 6540 LC/QTOF spectrometer.

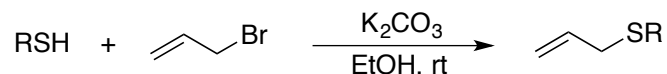
ESI-MS spectra were collected using a Thermo Scientific Orbitrap Q Extractive Plus (Bremen, Germany) in the positive ion mode. The samples were infused with a flow rate of 10 $\mu\text{L}/\text{min}$ and sprayed at a high voltage of 5 kV.

1.1 General procedure to synthesize thioalkyne



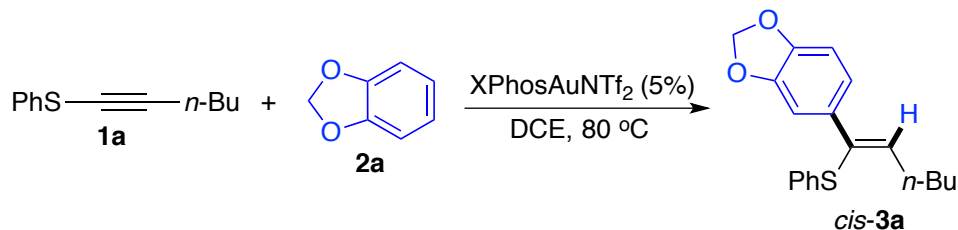
Thioalkynes were prepared according to known literatures. To a THF solution (50 mL) of alkyne (22 mmol, 1.1 eq) was added 9.6 mL *n*-BuLi (2.5 M in hexane, 24 mmol, 1.2 eq) dropwise at -78°C . The reaction mixture was allowed to react at -78°C for 1 h, then disulfide (20 mmol, 1 eq) in THF (10 mL) was added. The reaction mixture was brought up to RT and stirred for overnight (14 h). The reaction was quenched using sat. K_2CO_3 solution, and organic layers was extracted three time with DCM. The combined organic solution was dried over Na_2SO_4 and concentrated. Crude product was further purified by flash chromatography using pure hexane as elute.

1.2 General procedure to synthesize Allyl phenyl sulfide



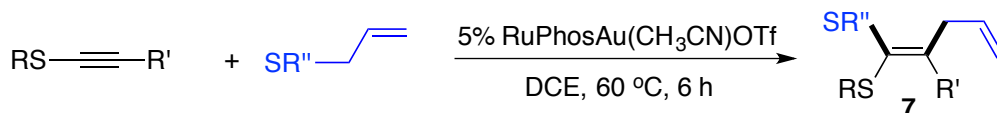
To a EtOH solution (10 mL) of thiol (5 mmol, 1 eq) and allyl bromide (6 mmol, 1.2 eq) was added K_2CO_3 in one portion. The reaction mixture was allowed to react overnight (14 h). The reaction solution was diluted with water and extracted with DCM three times. The combined organic solution was dried over Na_2SO_4 and concentrated. Crude product was further purified by flash chromatography using 100:1 hexane/ethyl acetate as elute.

1.3 General procedure for gold catalyzed C-nucleophile addition to thioalkyne



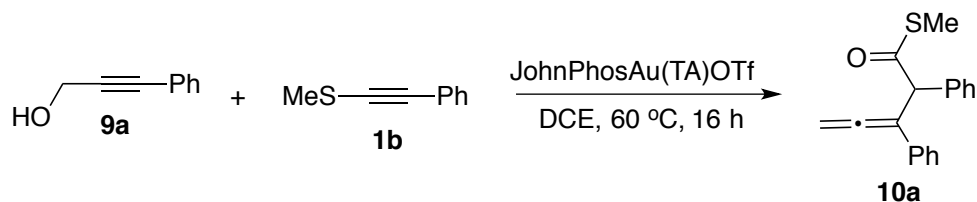
To a DCE solution (1.2 mL) of thioalkyne (0.2 mmol, 1 eq) and benzodioxole (0.6 mmol, 3 eq) was added Au catalyst (0.01 mmol, 0.05 eq) in one portion. The reaction vial was flushed with Argon, and the reaction mixture was allowed to react at 80 °C for 10 h. The reaction solution was filtered through a short pad of silica gel, and concentrated. Crude product was further purified by Flash Chromatography, preparative TLC or HPLC.

1.4 General procedure for gold catalyzed thioether addition to thioalkyne



To a DCE solution (1.2 mL) of alkyne (0.2 mmol, 1 eq) was added thiophenol (0.2 mmol, 1 eq). Catalyst (0.01 mmol, 0.05 eq) was added in one portion if needed. The reaction vial was flushed with Argon, and the reaction mixture was allowed to react at designated temperature for 10 h. The reaction solution was filtered through a short pad of silica gel, and concentrated. Crude product was further purified by Flash Chromatography, preparative TLC or HPLC.

1.5 General procedure for gold catalyzed propargyl alcohol addition to thioalkyne



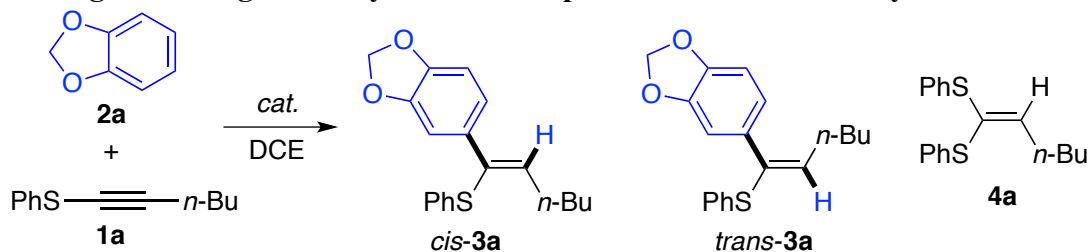
To a DCE solution (1.2 mL) of thioalkyne (0.2 mmol, 1 eq) and thioether (0.24 mmol, 1.2 eq) was added Au catalyst (0.01 mmol, 0.05 eq) in one portion. The reaction vial was flushed with Argon, and the reaction mixture was allowed to react at 60 °C for 6 h. The reaction solution was filtered through a short pad of silica gel, and concentrated. Crude product was further purified by preparative TLC.

1.6 General procedure for competing reaction between alkyne and thioalkyne

To a DCE solution (1.2 mL) of thioalkyne (0.2 mmol, 1 eq), phenylacetylene (0.2 mmol, 1 eq) and propargyl alcohol (0.2 mmol, 1 eq) was added Au catalyst (0.01 mmol, 0.05 eq) in one portion. The reaction vial was flushed with Argon, and the reaction mixture was allowed to react at 80 °C for 16 h. The reaction solution was filtered through a short pad of silica gel, and concentrated. Crude product was further purified by preparative TLC.

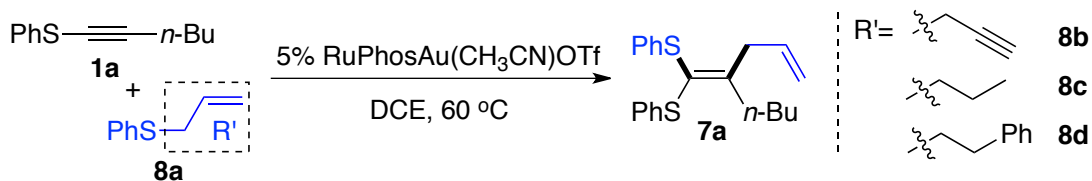
II. Screening Table

2.1 Screening table for gold catalyzed C-nucleophile addition to thioalkyne



Cat. and loading	Temp (°C)	Reaction time	Conv	Yield	cis/trans by dioxole peak
AgOTf+XPhosAuCl (0.05)	60	10 h	59%	31%	3.1:1
AgNTf ₂ (0.05) + XPhosAuCl(0.05)	80	10 h	84%	59%	4.2:1
PPh ₃ AuNTf ₂ (0.05)	80	16 h	80%	52%	6.8:1
JohnPhosAuNTf ₂ (0.05)	80 °C	10 h	84%	59%	6.0:1
XPhosAuNTf ₂ (0.05)	80 °C	16 h	70%	64%	7.3:1
XPhosAuNTf ₂ (0.05), degas	80 °C	10 h	87%	51%	4.7:1
RuPhosAuNTf ₂ (0.05)	80 °C	6 h	77%	45%	6.7:1
IPrAuNTf ₂ (0.05)	80 °C	16 h	80%	59%	6.1:1
(ArO) ₃ PAu(TA-Ph)OTf (0.05)	80 °C	16 h	<5%	<5%	NA
XPhosAuNTf ₂ (0.05)	70 °C	10 h	84%	51%	4.4:1
XPhosAuNTf ₂ (0.05)	60 °C	16 h	75%	51%	8.3:1
JohnPhosAu(CH ₃ CN)OTf (0.05)	60 °C	16 h	100%	36%	4.4:1
JohnPhosAu(TA-Me)OTf (0.05)	80 °C	16 h	<5%	<5%	NA
JohnPhosAu(TA-Me)OTf + Cu(OTf) ₂ (0.05+ 0.01)	60 °C then 80 °C	16 h, 10 h	38%	22%	NA
JohnPhosAu(TA-Me)OTf + Ga(OTf) ₃ (0.05+ 0.01)	60 °C then 80 °C	16 h, 10h	<5%	<5%	NA
HOTf (0.05)	80 °C	16 h	<5%	<5%	NA
Cu(OTf) ₂ (0.05)	80 °C	16 h	100%	0%	NA
AgOTf(0.05)	60	6 h	93%	47%	3.3:1
AgNTf ₂ (0.05)	80	6 h	92%	59%	4.8:1

2.2 General procedure for gold catalyzed thioether addition to thioalkyne



Alternation from above conditions	1a convn	yield 7a
none	>95%	75%
5% Cu(OTf) ₂ instead of [Au]	>95%	39%
5% AgOTf instead of [Au]	>95%	49%
[Au] = IPrAuNTf ₂	>95%	60%
R' = <i>n</i> -Pr, CH ₂ CCH, Bn	<5%	<5%
Other catalysts: Pd, Ir, Ru, Rh, Pt, HOTf	<20%	<5%
CyJohnPhosAu(CH ₃ CN)OTf	>95%	65%
JohnPhosAu(CH ₃ CN)OTf	>95%	64%
XJohnPhosAu(CH ₃ CN)OTf	>95%	61%
PPh ₃ Au(CH ₃ CN)OTf	>95%	67%
CyJohnPhosAuNTf ₂	46%	29%
CyJohnPhosAu(TA-H)OTf	62%	31%
IPrAu(TA-H)OTf	59%	36%

III. ORTEP Drawing of the Crystal Structures

The X-ray diffraction data for **3d**, **6b** and **7p** were measured on Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K α INCOATEC ImuS micro-focus source ($\lambda = 1.54178$ Å). The diffraction data for **6a** was measured on Bruker Smart diffractometer with Apex2 detector and CuK α radiation. Indexing was performed using *APEX3* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX3 [1]. Structures were solved using SHELXT and refined using SHELXL-2016 [4-7] (full-matrix least-squares on F²) through OLEX2 interface program [8]. All non-hydrogen atoms (except some of disordered) were refined anisotropically. Hydrogen atoms of -CH,-CH₂ and -CH₃ groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2(1.5)Ueq(-CH,-CH₂, (-CH₃)). Crystal data and refinement conditions are shown in Tables 1-4.

Notes: 3d: The structure was refined as inversion twin, which improved weighting scheme parameters and R value. **6a and 6b:** Disordered anions were refined with restraints.

[1] Bruker (2016). *APEX3* (Version 2015.9). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2016) SAINT V8.35A. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany.

[4] G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", *Acta Cryst.*, C71, 3-8

[5] Sheldrick, G.M. (1990) *Acta Cryst.* A46, 467-473

[6] Sheldrick, G. M. (2008) *Acta Cryst.* A64, 112-122.

[7] Sheldrick, G. M. (2015) *Acta Cryst.* A71, 3-8

[8] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). *J. Appl. Cryst.*, 42, 339-341.

Table 1 Crystal data and structure refinement for 7p.

Identification code	7p
Empirical formula	C ₂₁ H ₂₂ Cl ₂ S ₂
Formula weight	409.40
Temperature/K	100.05
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	6.3457(2)
b/Å	22.0777(6)
c/Å	14.2069(4)
α/°	90
β/°	95.9762(16)
γ/°	90
Volume/Å ³	1979.55(10)
Z	4
ρ _{calc} /cm ³	1.374
μ/mm ⁻¹	4.915
F(000)	856.0
Crystal size/mm ³	0.183 × 0.029 × 0.021
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.428 to 155.294
Index ranges	-8 ≤ h ≤ 7, -27 ≤ k ≤ 27, -17 ≤ l ≤ 17
Reflections collected	30613
Independent reflections	4109 [R _{int} = 0.1149, R _{sigma} = 0.0565]
Data/restraints/parameters	4109/0/229
Goodness-of-fit on F ²	1.035
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0443, wR ₂ = 0.0826
Final R indexes [all data]	R ₁ = 0.0698, wR ₂ = 0.0913
Largest diff. peak/hole / e Å ⁻³	0.32/-0.29

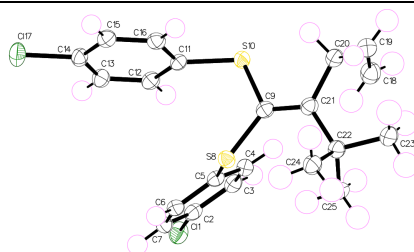


Fig. 1. Conformation and numbering scheme of molecule in asymmetric unit of **7p**. Thermal ellipsoids were drawn at 50% probability. CCDC# 1547919

Table 2 Crystal data and structure refinement for 3d.

Identification code	3d
Empirical formula	C ₁₉ H ₂₀ O ₂ S
Formula weight	312.41
Temperature/K	100(2)
Crystal system	monoclinic
Space group	Cc
a/Å	15.0719(4)
b/Å	9.4326(2)
c/Å	11.4784(3)
α/°	90
β/°	92.5702(12)
γ/°	90
Volume/Å ³	1630.21(7)
Z	4
ρ _{calc} /g/cm ³	1.273
μ/mm ⁻¹	1.791
F(000)	664.0
Crystal size/mm ³	0.305 × 0.097 × 0.09
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	11.068 to 154.112
Index ranges	-16 ≤ h ≤ 18, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	11967
Independent reflections	3082 [R _{int} = 0.0363, R _{sigma} = 0.0347]
Data/restraints/parameters	3082/2/203
Goodness-of-fit on F ²	1.099
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0283, wR ₂ = 0.0660
Final R indexes [all data]	R ₁ = 0.0300, wR ₂ = 0.0671

Largest diff. peak/hole / e Å⁻³ 0.17/-0.23

Flack parameter 0.288(19)

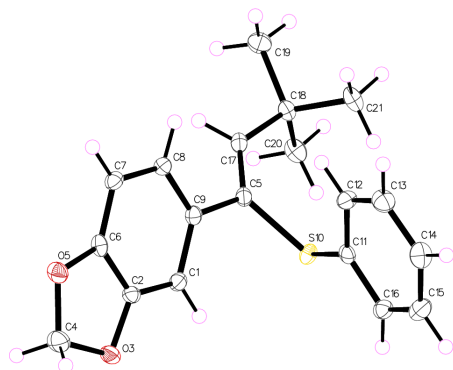


Fig.2. Conformation and numbering scheme of molecule in asymmetric unit of **3d**. Thermal ellipsoids were drawn at 50% probability. CCDC# 1547926

Table 3 Crystal data and structure refinement for 6b.

Identification code	6b
Empirical formula	$C_{43.5}H_{57}Au_2F_{7.5}N_{1.25}O_5P_2S_{3.5}$
Moiety formula	$C_{41}H_{57}Au_2P_2S, 1.25(C_2F_6NO_4S_2)$
Formula weight	1387.98
Temperature/K	100.03
Crystal system	triclinic
Space group	P-1
a/Å	12.4159(6)
b/Å	14.0289(7)
c/Å	17.6541(8)
$\alpha/^\circ$	108.043(2)
$\beta/^\circ$	93.939(2)
$\gamma/^\circ$	115.751(2)
Volume/Å ³	2558.2(2)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.802
μ/mm^{-1}	13.164
F(000)	1356.0
Crystal size/mm ³	0.21 × 0.15 × 0.03
Radiation	CuK α ($\lambda = 1.54178$)
2 θ range for data collection/ $^\circ$	5.42 to 154.864
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	28501
Independent reflections	10365 [$R_{\text{int}} = 0.0621$, $R_{\text{sigma}} = 0.0632$]
Data/restraints/parameters	10365/832/833
Goodness-of-fit on F ²	1.038
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0509$, $wR_2 = 0.1348$
Final R indexes [all data]	$R_1 = 0.0616$, $wR_2 = 0.1418$
Largest diff. peak/hole / e Å ⁻³	2.78/-2.64

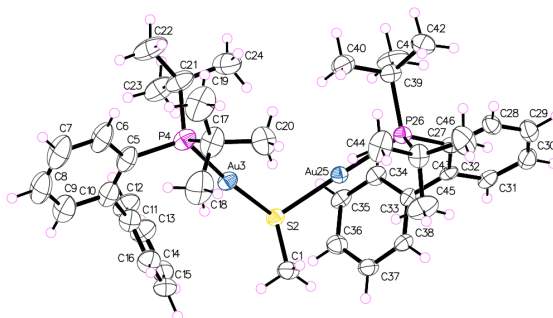


Fig.3. Conformation and numbering scheme of cation in 6b. Disordered anions were omitted for clarity. Thermal ellipsoids were drawn at 50% probability.

CCDC#1547929

Table 4 Crystal data and structure refinement for 6a.

Identification code	6a
Empirical formula	C _{47.5} H _{59.5} Au ₂ Cl _{1.5} F ₃ O ₃ P ₂ S ₂
Moiety formula	C ₄₆ H ₅₉ Au ₂ P ₂ S, CF ₃ O ₃ S, 0.5(CHCl ₃)
Formula weight	1308.62
Temperature/K	298.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	24.5358(7)
b/Å	13.8415(4)
c/Å	30.5610(9)
α/°	90
β/°	100.8595(17)
γ/°	90
Volume/Å ³	10193.0(5)
Z	8
ρ _{calc} /cm ³	1.705
μ/mm ⁻¹	13.152
F(000)	5128.0
Crystal size/mm ³	0.167 × 0.098 × 0.096
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.248 to 142.782
Index ranges	-29 ≤ h ≤ 29, -16 ≤ k ≤ 15, -36 ≤ l ≤ 36
Reflections collected	131865
Independent reflections	19385 [R _{int} = 0.0987, R _{sigma} = 0.0565]
Data/restraints/parameters	19385/321/1185
Goodness-of-fit on F ²	1.006
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0384, wR ₂ = 0.0784
Final R indexes [all data]	R ₁ = 0.0705, wR ₂ = 0.0910
Largest diff. peak/hole / e Å ⁻³	0.61/-0.79

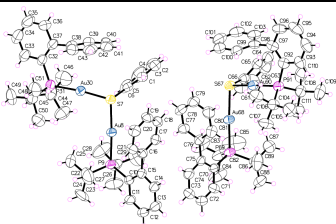
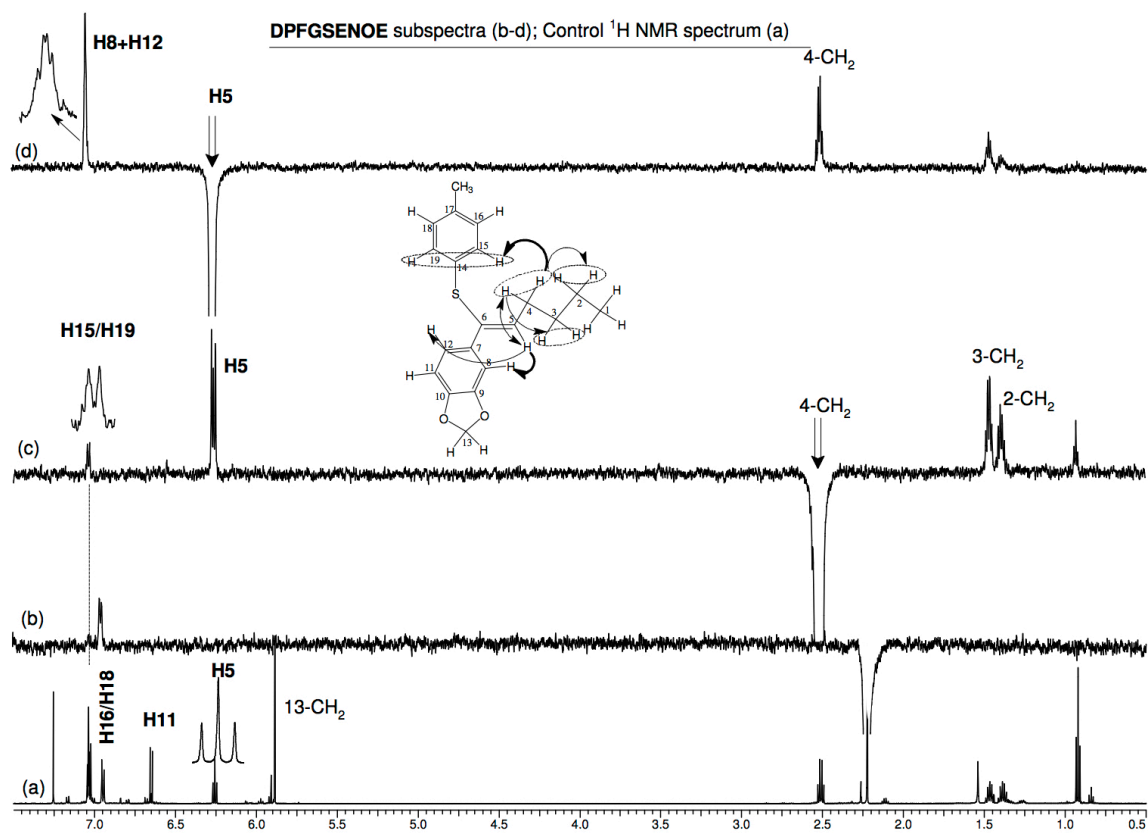


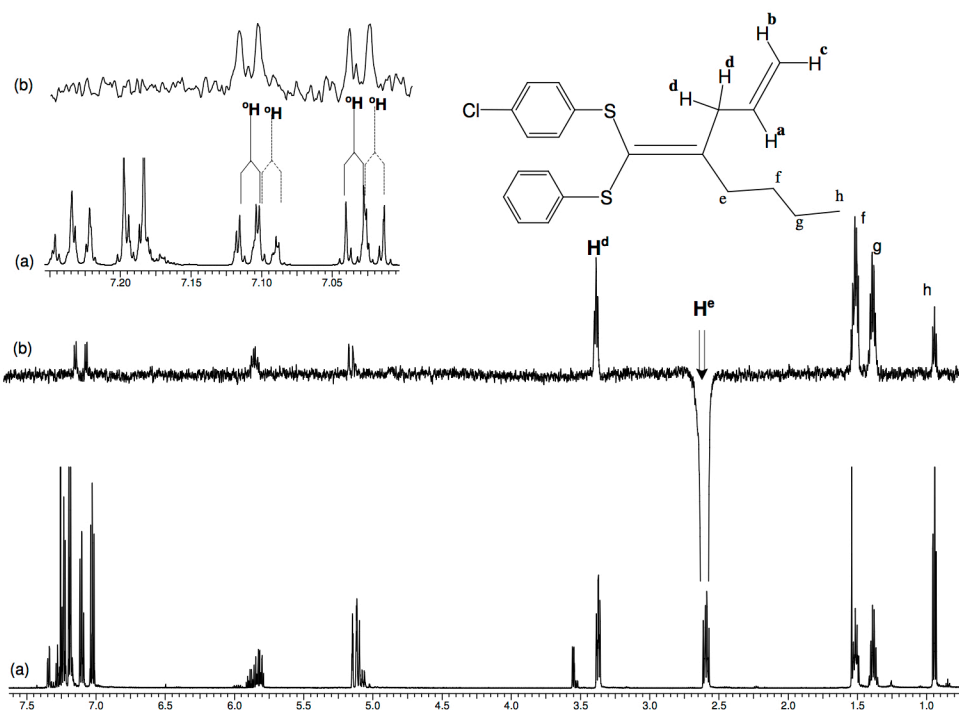
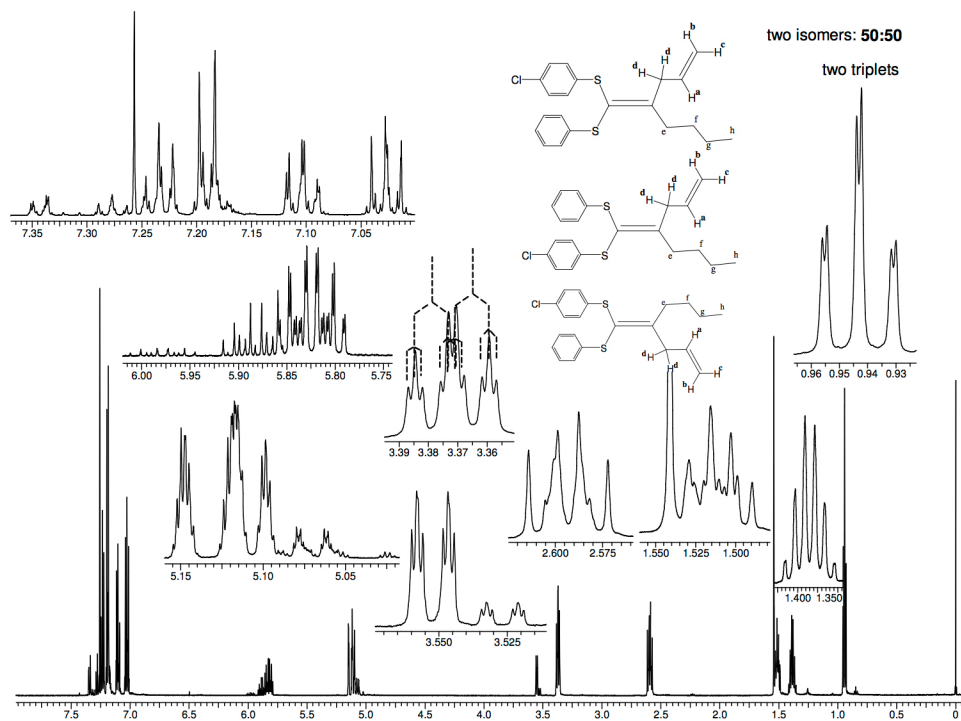
Fig.4. Conformation and numbering scheme of two symmetrically independent cations in 6a. Disordered anions were omitted for clarity. Thermal ellipsoids were drawn at 50% probability. CCDC#1547928

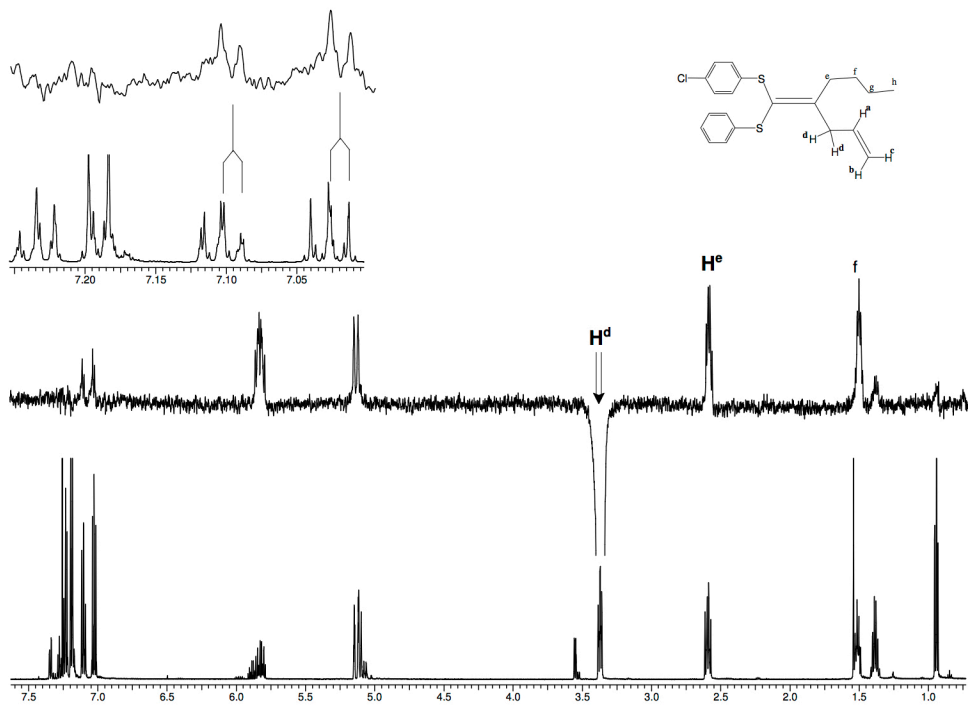
IV. NMR experiment

3.1 NOE Study for the conformation analysis of cis-addition product 3c

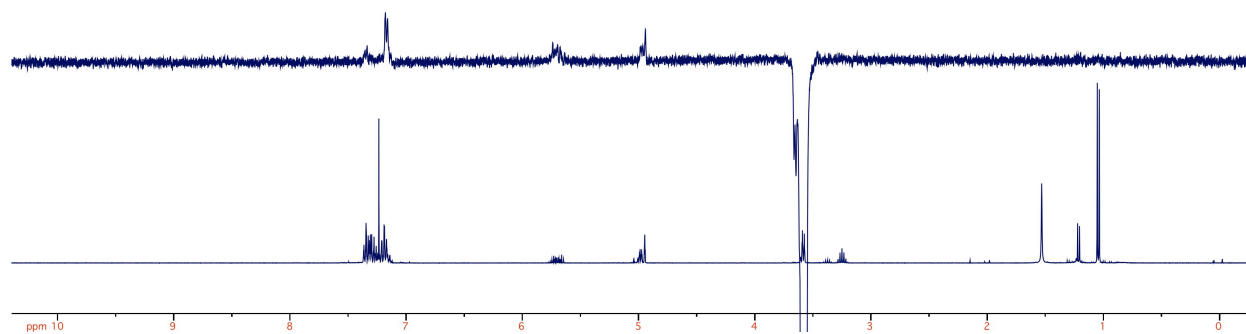
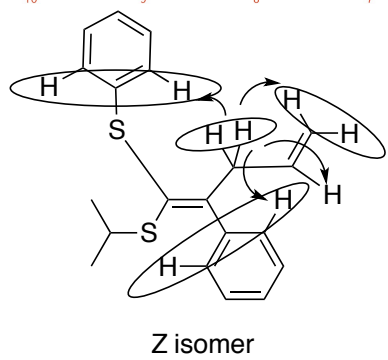
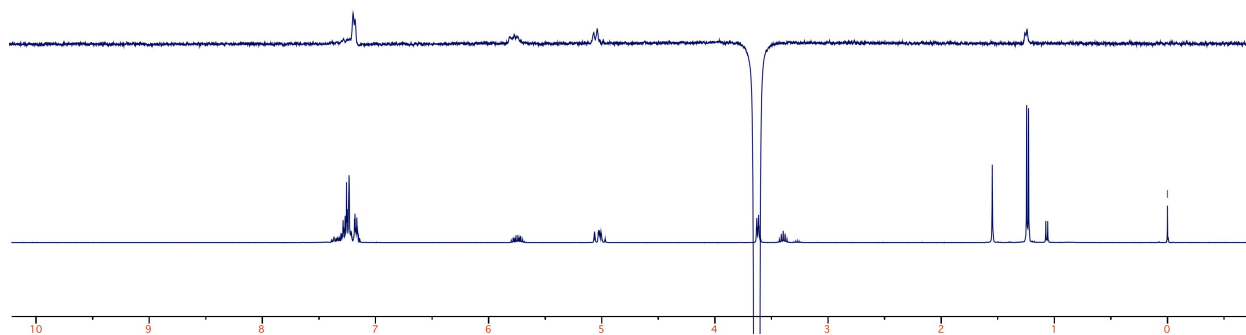
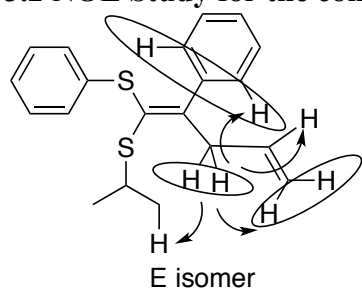


3.2 NOE Study for the conformation analysis of Z/E product 7d

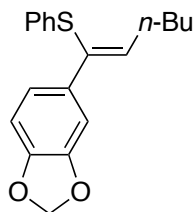




3.2 NOE Study for the conformation analysis of Z/E product 7j



V. Compound Characterization



3a

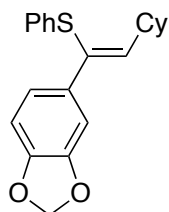
(Z)-5-(1-(phenylthio)hex-1-en-1-yl)benzo[d][1,3]dioxole

3a was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as pale yellow oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.14-7.13 (m, 4H), 7.06-7.02 (m, 3H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.31 (t, *J* = 7.2 Hz, 1H), 5.88 (s, 2H), 2.51 (q, *J* = 7.3 Hz, 2H), 1.49-1.43 (m, 2H), 1.38 (dd, *J* = 15.0, 7.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 147.5, 147.0, 139.1, 136.1, 134.9, 132.7, 128.6, 128.0, 125.3, 121.2, 107.9, 101.0, 36.6, 31.5, 30.7, 22.4, 14.0

HRMS *m/z* (ESI) calcd. for C₁₉H₂₁O₂S⁺ (M+K)⁺ 351.0821, found 351.0826.



3b

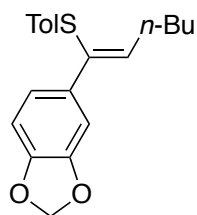
(Z)-5-(2-cyclohexyl-1-(phenylthio)vinyl)benzo[d][1,3]dioxole

3b was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as pale yellow oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.14-7.13 (m, 4H), 7.07-7.02 (m, 3H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.14 (d, *J* = 9.1 Hz, 1H), 5.88 (s, 2H), 2.86 (dt, *J* = 8.6, 3.1 Hz, 1H), 1.75-1.65 (m, 5H), 1.37-1.29 (m, 2H), 1.25-1.16 (m, *J* = 3.8 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 147.4, 147.0, 144.7, 136.1, 134.7, 130.7, 128.6, 128.1, 125.3, 121.3, 107.92, 107.80, 101.0, 39.9, 32.8, 25.9, 25.7

HRMS *m/z* (ESI) calcd. for C₂₁H₂₃O₂S⁺ (M+H)⁺ 339.1413, found 339.1423.



3c

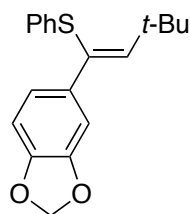
(Z)-5-(1-(*p*-tolylthio)hex-1-en-1-yl)benzo[*d*][1,3]dioxole

3c was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as pale yellow oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.05-7.02 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.26 (t, *J* = 7.2 Hz, 1H), 5.88 (s, 2H), 2.51 (q, *J* = 7.2 Hz, 2H), 2.22 (s, 3H), 1.51-1.43 (m, 2H), 1.41-1.34 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 147.4, 146.9, 138.57, 138.55, 135.17, 135.07, 133.3, 132.3, 129.4, 128.4, 121.3, 107.97, 107.78, 101.0, 31.6, 30.7, 22.4, 20.9, 14.0

HRMS *m/z* (ESI) calcd. for C₂₁H₂₃O₂S⁺ (M+H)⁺ 327.1413, found 327.1417.



3d

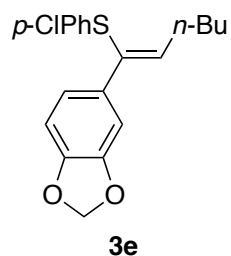
(Z)-5-(3,3-dimethyl-1-(phenylthio)but-1-en-1-yl)benzo[*d*][1,3]dioxole

3b was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as white solid.

¹H-NMR (400 MHz; CDCl₃): δ 7.12-7.11 (m, 4H), 7.04-6.99 (m, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 5.85 (s, 2H), 1.35 (s, 9H).

¹³C-NMR (101 MHz; CDCl₃): δ 148.6, 147.3, 146.9, 136.04, 135.85, 132.2, 128.66, 128.52, 125.4, 121.5, 108.3, 107.6, 100.9, 33.9, 30.6

HRMS *m/z* (ESI) calcd. for C₁₉H₂₁O₂S⁺ (M+H)⁺ 313.1257, found 313.1267.



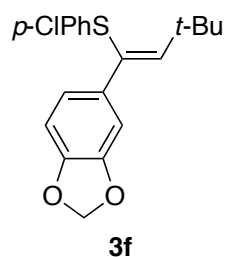
(Z)-5-(1-((4-chlorophenyl)thio)hex-1-en-1-yl)benzo[d][1,3]dioxole

3e was prepared following the to the General Procedure and purified by flash Chromatography (Hexane: Ether= 100:1) as colorless oil, which contained *E/Z* isomer (6:1) as unrepeatably mixture

¹H-NMR (400 MHz; CDCl₃): *Z* isomer δ 7.15-7.10 (m, 3H), 7.06-7.02 (m, 3H), 6.67 (d, *J* = 8.7 Hz, 1H), 6.30 (t, *J* = 7.3 Hz, 1H), 5.91 (s, 2H), 2.50 (q, *J* = 7.3 Hz, 2H), 1.48-1.44 (m, 2H), 1.40-1.36 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). *E* isomer: δ 7.15-7.09 (m, 3H), 7.06-7.02 (m, 3H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.12 (t, *J* = 7.5 Hz, 1H), 5.92 (s, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.38-1.35 (m, 2H), 1.29-1.26 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 1H).

¹³C-NMR (101 MHz; CDCl₃): *Z* isomer was detected as major peak δ 147.6, 147.1, 139.3, 134.61, 134.47, 132.5, 131.2, 129.4, 128.8, 121.2, 107.89, 107.81, 101.1, 31.5, 30.7, 22.4, 14.0

HRMS *m/z* (ESI) calcd. for C₁₉H₂₀ClO₂S⁺ (M+H)⁺ 347.0867, found 347.0933.



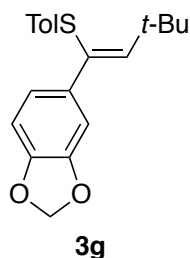
(Z)-5-(1-((4-chlorophenyl)thio)-3,3-dimethylbut-1-en-1-yl)benzo[d][1,3]dioxole

3f was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as pale white solid, which contained *E/Z* isomer (5:1) as unrepeatably mixture.

¹H-NMR (500 MHz; CDCl₃): *Z* isomer: δ 7.09-7.07 (m, 2H), 7.04-7.01 (m, 2H), 6.98-6.95 (m, 2H), 6.66-6.55 (m, 1H), 6.28 (s, 1H), 5.91 (s, 1H), 5.89 (s, 2H), 1.32 (s, 9H). *E* isomer: **¹H-NMR** (500 MHz; CDCl₃): δ 7.21-7.16 (m, 4H), 6.98-6.95 (m, 2H), 6.66-6.55 (m, 1H), 6.11 (s, 1H), 5.91 (s, 2H), 0.94 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): Z isomer was detected as major peak δ 149.0, 147.4, 147.0, 135.6, 134.4, 133.1, 131.8, 131.3, 129.9, 128.7, 121.5, 108.2, 107.7, 101.0, 33.9, 30.9, 30.6

HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{20}\text{ClO}_2\text{S}^+$ ($\text{M}+\text{K}$) $^+$ 385.0431, found 385.0435.

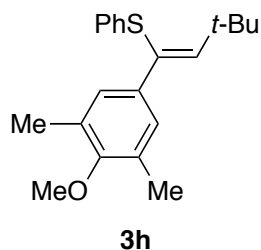


3g was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as colorless oil.

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 6.99-6.89 (m, 6H), 6.58 (d, $J = 8.2$ Hz, 1H), 6.20 (s, 1H), 5.84 (s, 2H), 2.18 (s, 3H), 1.30 (d, $J = 12.1$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): δ 149.0, 147.4, 147.0, 135.6, 134.4, 133.1, 131.8, 131.3, 129.9, 128.7, 121.5, 108.2, 107.7, 101.0, 33.9, 30.9, 30.6

HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{20}\text{ClO}_2\text{S}^+$ ($\text{M}+\text{K}$) $^+$ 365.0977, found 365.0973.



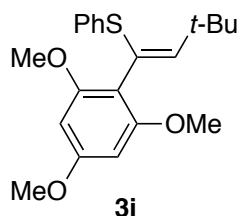
(Z)-1-(4-methoxy-3,5-dimethylphenyl)-3,3-dimethylbut-1-en-1-yl(phenyl)sulfane

3g was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as colorless oil.

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 7.14-7.11 (m, 6H), 7.02-6.99 (m, 1H), 6.30 (s, 1H), 3.63 (s, 3H), 2.18 (s, 6H), 1.33 (s, 9H)

$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): δ 156.4, 149.1, 137.0, 136.2, 131.9, 130.1, 128.46, 128.42, 128.1, 125.2, 59.6, 34.0, 30.6, 16.1

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{27}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 327.1777, found 327.1770.



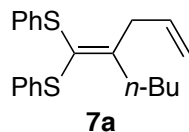
(Z)-(3,3-dimethyl-1-(2,4,6-trimethoxyphenyl)but-1-en-1-yl)(phenyl)sulfane

3i was prepared following the General Procedure **1.3** and purified by flash Chromatography (Hexane: Ether= 100:1) as colorless oil.

¹H-NMR (500 MHz; CDCl₃): δ 7.40-7.39 (m, 2H), 7.17-7.12 (m, 3H), 6.05 (s, 1H), 5.97 (s, 2H), 3.75 (s, 3H), 3.66 (s, 6H), 0.88 (s, 9H).

¹³C-NMR (101 MHz; CDCl₃): δ 160.8, 157.9, 144.8, 135.4, 133.0, 127.9, 126.7, 124.9, 109.6, 90.0, 55.27, 55.15, 34.8, 29.5

HRMS *m/z* (ESI) calcd. for C₂₁H₂₇O₃S⁺ (M+H)⁺ 359.1675, found 359.1683.



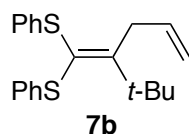
(2-allylhex-1-ene-1,1-diyl)bis(phenylsulfane)

7a was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.24-7.10 (m, 10H), 5.83 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.16-5.08 (m, 2H), 3.38 (d, *J* = 6.6 Hz, 2H), 2.60 (t, *J* = 7.9 Hz, 2H), 1.56-1.48 (m, 2H), 1.38 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 157.5, 135.64, 135.64, 135.0, 129.6, 129.4, 128.57, 128.55, 126.20, 126.13, 123.2, 116.6, 40.0, 35.1, 31.0, 22.8, 13.9

HRMS *m/z* (ESI) calcd. for C₂₁H₂₅S₂⁺ (M+H)⁺ 341.1392, found 341.1367.



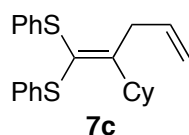
(2-(tert-butyl)penta-1,4-diene-1,1-diyl)bis(phenylsulfane)

7b was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.32-7.16 (m, 7H), 7.13-7.07 (m, 3H), 5.99-5.89 (m, 1H), 5.18-5.12 (m, 2H), 3.59 (dt, *J* = 5.6, 1.8 Hz, 2H), 1.49 (s, 9H).

¹³C-NMR (101 MHz; CDCl₃): δ 162.4, 136.6, 136.4, 135.8, 129.7, 129.3, 128.49, 128.47, 126.11, 125.97, 125.1, 115.9, 39.8, 38.6, 30.8

HRMS *m/z* (ESI) calcd. for C₂₁H₂₅S₂⁺ (M+H)⁺ 341.1392, found 341.1399.



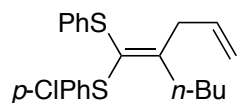
(2-cyclohexylpenta-1,4-diene-1,1-diyl)bis(phenylsulfane)

7c was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (500 MHz; CDCl₃): δ 7.25-7.20 (m, 4H), 7.18-7.15 (m, 2H), 7.13-7.12 (m, 2H), 7.09-7.08 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.14-5.07 (m, 2H), 3.40-3.34 (m, 3H), 1.78-1.76 (m, 2H), 1.70-1.64 (m, 3H), 1.45 (qd, *J* = 12.4, 3.0 Hz, 2H), 1.33 (qt, *J* = 12.8, 3.1 Hz, 2H), 1.19 (tt, *J* = 12.8, 3.3 Hz, 1H).

¹³C-NMR (101 MHz; CDCl₃): δ 160.8, 136.3, 135.9, 135.6, 129.60, 129.53, 128.57, 128.54, 126.2, 123.4, 116.2, 45.4, 36.5, 31.6, 26.3, 26.0

HRMS *m/z* (ESI) calcd. for C₂₃H₂₇S₂⁺ (M+H)⁺ 367.1549, found 367.1545.



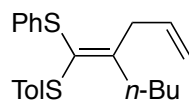
(Z/E)-(2-allyl-1-((4-chlorophenyl)thio)hex-1-en-1-yl)(phenyl)sulfane

7d was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

¹H-NMR (400 MHz; CDCl₃): δ 7.24-7.16 (m, 5H), 7.12-7.08 (m, *J* = 1.2 Hz, 2H), 7.04-7.00 (m, 2H), 5.87-5.77 (m, 1H), 5.15-5.08 (m, 2H), 3.38-3.35 (m, 2H), 2.62-2.56 (m, 2H), 1.55-1.47 (m, 2H), 1.38 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 157.43, 157.38, 135.3, 134.90, 134.85, 134.1, 132.28, 132.21, 131.0, 130.8, 129.7, 129.5, 128.69, 128.68, 128.63, 128.61, 126.38, 126.32, 123.02, 122.96, 116.7, 40.03, 39.99, 35.19, 35.14, 31.0, 22.8, 13.9.

HRMS *m/z* (ESI) calcd. for C₂₁H₂₄ClS₂⁺ (M+H)⁺ 375.1002, found 374.0995.



7e Z/E= 1:1

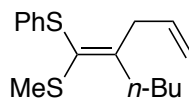
(Z/E)-(2-allyl-1-(p-tolylthio)hex-1-en-1-yl)(phenyl)sulfane

7e was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

¹H-NMR (400 MHz; CDCl₃): δ 7.24-7.21 (m, 2H), 7.17-7.10 (m, 3H), 7.05-7.00 (m, 4H), 5.89-5.77 (m, 1H), 5.16-5.07 (m, 2H), 3.38 (dd, *J* = 13.4, 6.5 Hz, 2H), 2.63-2.57 (m, 2H), 2.30 (s, 3H), 1.55-1.49 (m, 2H), 1.42-1.34 (m, 2H), 0.94 (q, *J* = 7.4 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 156.6, 136.41, 136.33, 135.9, 135.1, 131.9, 130.4, 130.1, 129.39, 129.38, 129.1, 128.6, 126.05, 125.99, 123.8, 116.5, 40.04, 39.95, 35.15, 35.06, 31.0, 22.9, 21.1, 14.0

HRMS *m/z* (ESI) calcd. for C₂₂H₂₇S₂⁺ (M+H)⁺ 355.1549, found 355.1540.



7f Z/E= 1:1

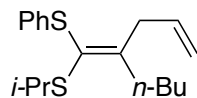
(Z/E)-(2-allyl-1-(methylthio)hex-1-en-1-yl)(phenyl)sulfane

7f was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

¹H-NMR (400 MHz; CDCl₃): δ 7.29-7.21 (m, 8H), 7.18-7.14 (m, 2H), 5.87-5.80 (m, 1H), 5.78-5.69 (m, 1H), 5.15-5.00 (m, 4H), 3.31-3.26 (m, *J* = 1.4 Hz, 4H), 2.53-2.48 (m, 4H), 2.20 (s, 3H), 2.19 (s, 3H), 1.51-1.28 (m, 9H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (101 MHz; CDCl₃): δ 152.94, 152.83, 136.3, 135.4, 135.0, 128.76, 128.74, 127.8, 127.6, 125.68, 125.64, 124.53, 124.33, 116.19, 116.18, 40.2, 39.5, 35.4, 34.6, 30.9, 30.5, 22.87, 22.73, 17.10, 17.05, 13.98, 13.93

HRMS m/z (ESI) calcd. for $C_{18}H_{25}S_2^+$ (M+H) $^+$ 305.1392, found 305.1400.



7g Z/E= 1:1

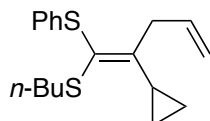
(Z/E)-(2-allyl-1-(isopropylthio)hex-1-en-1-yl)(phenyl)sulfane

7g was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

1H -NMR (400 MHz; $CDCl_3$): δ 7.29-7.21 (m, 8H), 7.20-7.14 (m, 2H), 5.86-5.72 (m, 2H), 5.13-5.02 (m, 4H), 3.37-3.28 (m, 7H), 2.53 (q, $J = 7.7$ Hz, 5H), 1.47-1.31 (m, 8H), 1.18 (d, $J = 4.5$ Hz, 6H), 1.16 (d, $J = 4.4$ Hz, 6H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H).

^{13}C -NMR (101 MHz; $CDCl_3$): δ 155.61, 155.56, 136.28, 136.26, 135.5, 135.3, 128.67, 128.65, 128.4, 128.2, 125.70, 125.64, 123.83, 123.70, 116.13, 116.03, 39.9, 39.7, 37.19, 37.14, 35.00, 34.85, 31.1, 30.9, 22.89, 22.76, 22.67, 14.03, 13.97

HRMS m/z (ESI) calcd. for $C_{18}H_{25}S_2^+$ (M+H) $^+$ 305.1392, found 305.1400.



7h Z/E= 1:1

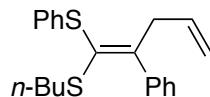
(Z/E)-butyl(2-cyclopropyl-1-(phenylthio)penta-1,4-dien-1-yl)sulfane

7h was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

1H -NMR (400 MHz; $CDCl_3$): δ 7.28-7.21 (m, 4H), 7.17-7.13 (m, 1H), 5.83-5.72 (m, 1H), 5.10-4.97 (m, 2H), 2.90 (ddt, $J = 9.6, 5.8, 1.8$ Hz, 2H), 2.71 (dd, $J = 7.3$ Hz, 2H), 2.56-2.47 (m, 1H), 1.52-1.41 (m, 2H), 1.34 (ddt, $J = 14.9, 10.0, 7.4$ Hz, 2H), 0.88-0.81 (m, 4H), 0.74-0.64 (m, 3H).

^{13}C -NMR (101 MHz; $CDCl_3$): δ 153.25, 153.21, 136.7, 136.3, 136.1, 135.6, 128.69, 128.65, 128.2, 127.7, 125.7, 125.5, 123.6, 123.2, 115.8, 115.6, 34.4, 34.0, 33.4, 33.1, 31.82, 31.72, 21.89, 21.79, 16.5, 16.3, 13.67, 13.63, 6.7, 6.5

HRMS m/z (ESI) calcd. for $C_{18}H_{25}S_2^+$ (M+H) $^+$ 305.1392, found 305.1400.



7i, Z/E= 2:1

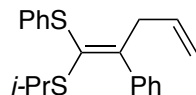
(Z/E)-butyl(2-phenyl-1-(phenylthio)penta-1,4-dien-1-yl)sulfane

7i was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil

¹H-NMR (500 MHz; CDCl₃): Major Z isomer: δ 7.38-7.28 (m, 7H), 7.26-7.20 (m, 3H), 5.75-5.67 (m, 1H), 5.00-4.97 (m, 2H), 3.60 (d, *J* = 6.6 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.37 (quintet, *J* = 7.4 Hz, 2H), 1.20 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): Major Z isomer: δ 151.0, 141.9, 135.7, 134.7, 128.9, 128.6, 128.4, 128.0, 127.2, 126.1, 116.5, 42.9, 33.2, 31.6, 21.7, 13.6

HRMS *m/z* (ESI) calcd. for C₂₁H₂₅S₂⁺ (M+K)⁺ 379.0956, found 370.0953.



7j, Z/E= 1.5:1

7j was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

(Z)-isopropyl(2-phenyl-1-(phenylthio)penta-1,4-dien-1-yl)sulfane

¹H-NMR (500 MHz; CDCl₃): δ 7.39-7.28 (m, 7H), 7.23-7.20 (m, 3H), 5.75-5.69 (m, 1H), 5.01-4.97 (m, 2H), 3.61 (t, *J* = 7.6 Hz, 2H), 3.27 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 6H).

¹³C-NMR (126 MHz; CDCl₃): δ 151.6, 141.9, 135.6, 134.7, 128.90, 128.80, 128.4, 127.9, 127.1, 126.1, 116.5, 42.8, 37.3, 22.7

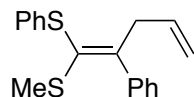
HRMS *m/z* (ESI) calcd. for C₂₀H₂₃S₂⁺ (M+H)⁺ 327.1236, found 327.1235.

(E)-isopropyl(2-phenyl-1-(phenylthio)penta-1,4-dien-1-yl)sulfane

¹H-NMR (500 MHz; CDCl₃): δ 7.29-7.23 (m, 7H), 7.17 (dt, *J* = 8.2, 1.9 Hz, 3H), 5.78-5.71 (m, 1H), 5.06-5.01 (m, 2H), 3.62 (d, *J* = 6.6 Hz, 2H), 3.40 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.24 (d, *J* = 6.7 Hz, 6H).

¹³C-NMR (126 MHz; CDCl₃): δ 152.3, 142.3, 136.1, 134.4, 129.3, 128.5, 128.02, 127.86, 127.67, 127.1, 126.0, 116.5, 77.3, 77.0, 76.7, 42.6, 37.3, 22.9

HRMS *m/z* (ESI) calcd. for C₂₀H₂₃S₂⁺ (M+H)⁺ 327.1236, found 127.1230.



7k, Z/E= 1.5:1

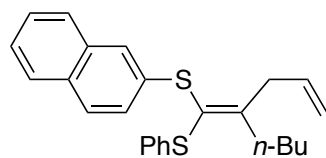
(Z/E)-methyl(2-phenyl-1-(phenylthio)penta-1,4-dien-1-yl)sulfane

7k was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1.5:1) as an inseparable mixture.

¹H-NMR (500 MHz; CDCl₃): δ 7.40-7.17 (m, 10H), 5.80-5.67 (m, 1H), 5.07-4.96 (m, 2H), 3.59 (d, *J* = 6.6 Hz, 2H), 2.25 (s, 1H), 2.09 (s, 2H).

¹³C-NMR (126 MHz; CDCl₃): δ 149.7, 141.5, 135.78, 135.77, 134.6, 130.8, 128.9, 128.68, 128.58, 128.33, 128.25, 128.23, 128.22, 128.09, 128.03, 128.02, 128.01, 128.00, 127.94, 127.93, 127.86, 127.78, 127.4, 127.12, 127.11, 126.06, 125.89, 116.54, 116.53, 42.88, 42.87, 42.86, 42.4, 17.3, 16.8

HRMS *m/z* (ESI) calcd. for C₁₈H₁₉S₂⁺ (M+H)⁺ 299.0923, found 299.0917.



7l, Z/E= 1:1

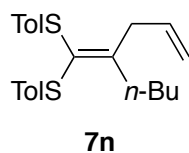
(Z/E)-(2-allyl-1-(naphthalen-2-ylthio)hex-1-en-1-yl)(phenyl)sulfane

7l was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained Z/E isomer (1:1) as an inseparable mixture.

¹H-NMR (400 MHz; CDCl₃): δ 7.77-7.64 (m, 3H), 7.51 (d, *J* = 6.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.26-7.16 (m, 4H), 7.12-7.09 (m, 2H), 5.92-5.82 (m, 1H), 5.20-5.10 (m, 2H), 3.42 (dd, *J* = 6.5, 1.3 Hz, 2H), 2.65 (t, *J* = 7.9 Hz, 2H), 1.59-1.52 (m, 2H), 1.41 (dt, *J* = 14.6, 7.3 Hz, 2H), 0.95 (q, *J* = 7.8 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): δ 157.63, 157.61, 135.62, 135.60, 135.09, 135.05, 133.56, 133.56, 133.07, 133.05, 131.93, 131.90, 129.7, 129.4, 128.59, 128.57, 128.11, 128.10, 128.06, 127.79, 127.67, 127.66, 127.53, 127.34, 127.25, 127.22, 126.29, 126.28, 126.27, 126.20, 125.66, 125.63, 123.12, 123.10, 116.69, 116.67, 40.1, 35.2, 31.1, 22.9, 13.99, 13.97

HRMS *m/z* (ESI) calcd. for C₁₈H₁₉S₂⁺ (M+H)⁺ 391.1549, found 391.1542.



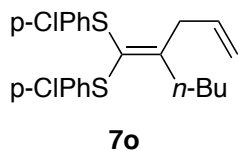
(2-allylhex-1-ene-1,1-diyl)bis(*p*-tolylsulfane)

7n was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.03 (q, *J* = 7.1 Hz, 8H), 5.86-5.79 (m, 1H), 5.10 (t, *J* = 13.9 Hz, 2H), 3.38 (d, *J* = 6.5 Hz, 2H), 2.59 (t, *J* = 7.9 Hz, 2H), 2.31 (s, 6H), 1.53-1.47 (m, 2H), 1.38 (q, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): δ 156.0, 136.25, 136.18, 135.3, 132.1, 130.1, 129.9, 129.39, 129.38, 124.4, 116.4, 40.0, 35.1, 31.0, 22.9, 21.1, 14.0

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+H)⁺ 369.1705, found 369.1710.



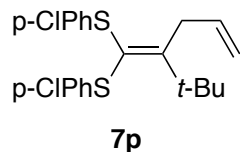
(2-allylhex-1-ene-1,1-diyl)bis((4-chlorophenyl)sulfane)

7o was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained trace inseparable Allyl 4-chlorophenyl sulfide starting material.

¹H-NMR (500 MHz; CDCl₃): δ 7.21-7.19 (m, 4H), 7.03-7.00 (m, 4H), 5.87-5.77 (m, *J* = 4.6 Hz, 1H), 5.15-5.06 (m, 2H), 3.36 (d, *J* = 6.6 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.49 (ddd, *J* = 5.6, 4.5, 4.4 Hz, 2H), 1.38 (q, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): δ 157.6, 134.7, 133.7, 132.48, 132.42, 131.10, 130.90, 128.8, 122.7, 116.9, 40.0, 35.2, 31.0, 22.8, 13.9

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+H)⁺ 409.0613, found 409.0610.



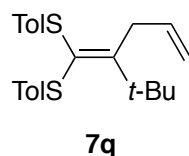
(2-(*tert*-butyl)penta-1,4-diene-1,1-diyl)bis((4-chlorophenyl)sulfane)

7p was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as white solid.

¹H-NMR (500 MHz; CDCl₃): δ 7.26-7.18 (m, 5H), 6.98 (dd, *J* = 21.6, 8.5 Hz, 4H), 5.89 (td, *J* = 11.1, 5.9 Hz, 1H), 5.15-5.08 (m, 2H), 3.54 (d, *J* = 5.7 Hz, 2H), 1.44 (s, 10H).

¹³C-NMR (126 MHz; CDCl₃): δ 162.8, 136.3, 134.5, 133.9, 132.4, 132.2, 131.3, 130.6, 128.75, 128.71, 124.5, 116.1, 39.8, 38.6, 30.7

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+K)⁺ 409.0618, found 409.0617.



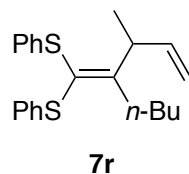
(2-(*tert*-butyl)penta-1,4-diene-1,1-diyl)bis(*p*-tolylsulfane)

7q was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as white solid.

¹H-NMR (500 MHz; CDCl₃): δ 7.04 (dt, *J* = 24.0, 8.1 Hz, 6H), 6.95 (d, *J* = 8.1 Hz, 2H), 5.91 (ddd, *J* = 12.0, 9.7, 5.8 Hz, 1H), 5.13-5.09 (m, 2H), 3.57 (dd, *J* = 4.0, 1.7 Hz, 2H), 2.32 (d, *J* = 4.9 Hz, 6H), 1.45 (s, 9H).

¹³C-NMR (126 MHz; CDCl₃): δ 161.2, 136.8, 136.2, 135.9, 133.0, 132.3, 130.2, 129.48, 129.33, 129.31, 126.2, 115.7, 39.7, 38.5, 30.8, 21.12, 21.11

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+H)⁺ 369.1705, found 369.1710.



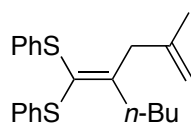
(2-(but-3-en-2-yl)hex-1-ene-1,1-diyl)bis(phenylsulfane)

7r was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil, which contained trace inseparable **4a** byproduct.

¹H-NMR (500 MHz; CDCl₃): δ 7.26-7.22 (m, 5H), 7.19-7.16 (m, 2H), 7.12-7.10 (m, 3H), 5.94-5.87 (m, 1H), 5.11-5.07 (m, 2H), 4.28 (quintet, *J* = 6.6 Hz, 1H), 2.44 (dd, *J* = 9.0, 6.2 Hz, 2H), 1.58-1.51 (m, 2H), 1.43-1.35 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): δ 162.6, 140.6, 136.0, 135.7, 131.2, 130.2, 129.7, 128.9, 128.63, 128.59, 126.2, 126.0, 114.5, 43.3, 33.1, 32.2, 23.3, 18.1, 13.8

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+H)⁺ 355.1549, found 355.1540.



7s

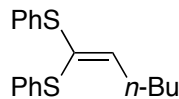
(2-(2-methylallyl)hex-1-ene-1,1-diyl)bis(phenylsulfane)

7s was prepared following the General Procedure **1.4** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (500 MHz; CDCl₃): δ 7.26-7.22 (m, 5H), 7.19-7.16 (m, 2H), 7.14-7.09 (m, 3H), 4.87 (s, 1H), 4.76 (s, 1H), 3.37 (s, 2H), 2.60-2.57 (m, 2H), 1.78 (s, 3H), 1.55-1.50 (m, 2H), 1.39 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (126 MHz; CDCl₃): δ 157.2, 143.1, 135.70, 135.69, 129.9, 129.5, 128.6, 126.27, 126.17, 124.1, 112.1, 43.5, 34.9, 31.3, 22.92, 22.80, 14.0

HRMS *m/z* (ESI) calcd. for C₂₃H₂₉S₂⁺ (M+H)⁺ 355.1549, found 355.1544.



4a

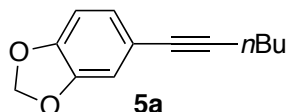
Hex-1-ene-1,1-diylbis(phenylsulfane)

4a was separated as byproduct following the General Procedure **1.3** and purified by flash Chromatography (Hexane) as colorless oil.

¹H-NMR (400 MHz; CDCl₃): δ 7.27-7.19 (m, 10H), 6.39 (t, *J* = 7.4 Hz, 1H), 2.44 (q, *J* = 7.3 Hz, 2H), 1.45-1.33 (m, 5H), 0.91 (t, *J* = 7.2 Hz, 3H).

$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): δ 145.0, 134.47, 134.43, 131.2, 130.2, 128.78, 128.64, 128.51, 127.2, 126.6, 31.20, 31.03, 22.4, 13.9

HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 301.1085, found 355.1088.



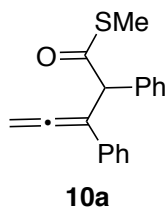
5-(hex-1-yn-1-yl)benzo[d][1,3]dioxole

5a was separated as byproduct following the General Procedure **1.3** and purified by flash Chromatography (Hexane) as colorless oil.

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 7.56 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.44 (d, $J = 1.6$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.03 (s, 2H), 2.87 (t, $J = 7.5$ Hz, 2H), 1.73-1.70 (m, 2H), 1.35 (dt, $J = 6.7, 3.6$ Hz, 4H), 0.91 (dd, $J = 8.9, 4.7$ Hz, 3H).

$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): δ 198.6, 151.5, 148.1, 132.0, 124.2, 107.89, 107.77, 101.7, 38.3, 31.5, 24.3, 22.5, 13.9.

HRMS m/z (ESI) calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 203.1067, found 203.1001.



S-methyl 2,3-diphenylpenta-3,4-dienethioate

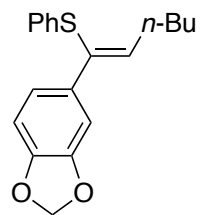
10a was separated following the General Procedure **1.5** and purified by flash Chromatography (Hexane) as colorless oil.

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 7.40-7.23 (m, 10H), 7.19-7.16 (m, 1H), 5.22-5.10 (m, 2H), 5.02 (t, $J = 2.5$ Hz, 1H), 2.28 (s, 3H).

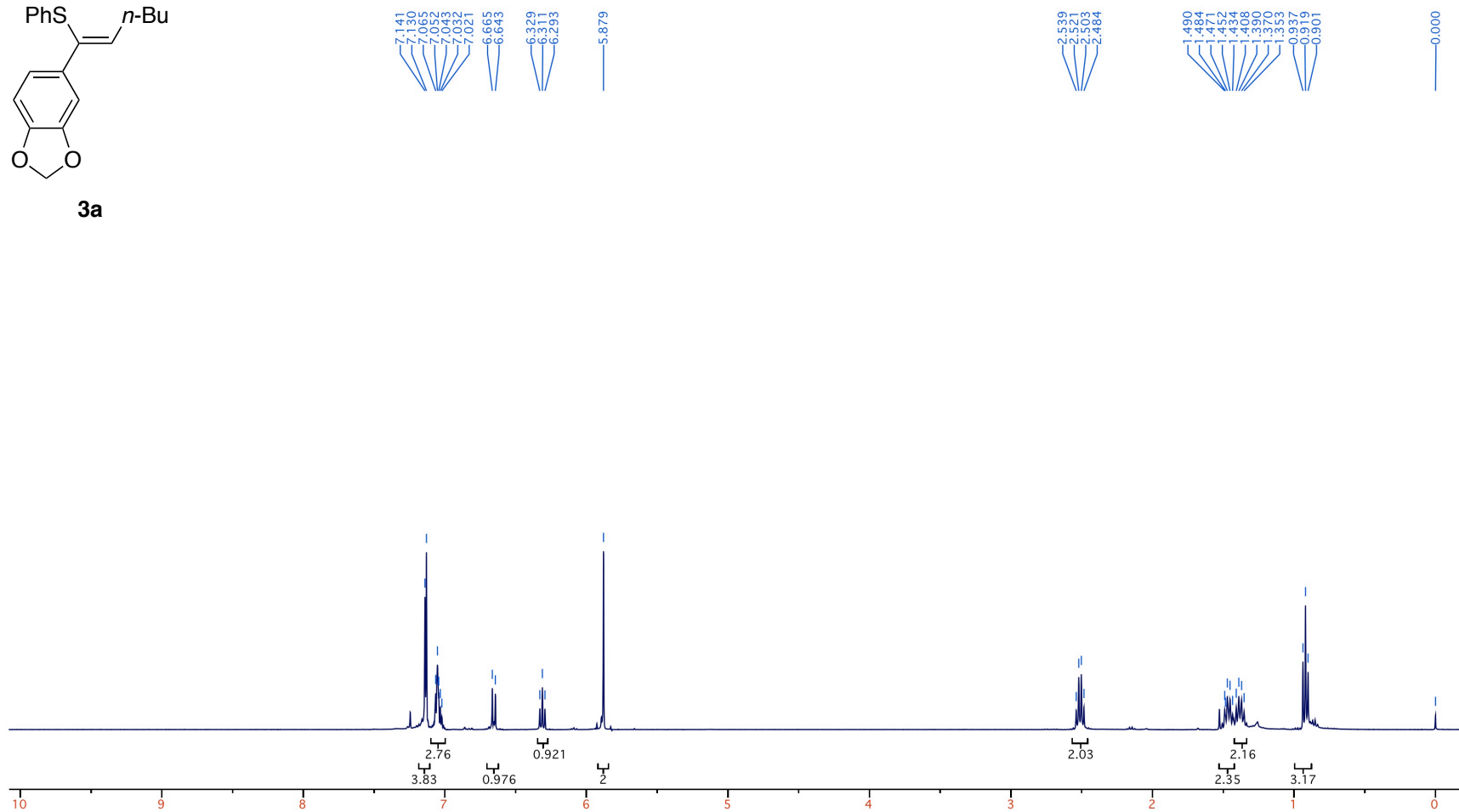
$^{13}\text{C-NMR}$ (101 MHz; CDCl_3): δ 209.8, 198.2, 136.5, 135.1, 129.10, 129.10, 128.47, 128.46, 128.44, 127.8, 127.0, 126.22, 126.22, 104.6, 80.7, 60.5, 12.1

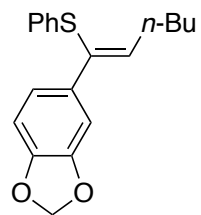
HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{17}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 281.0995, found 280.0862.

VI. NMR Spectra Data

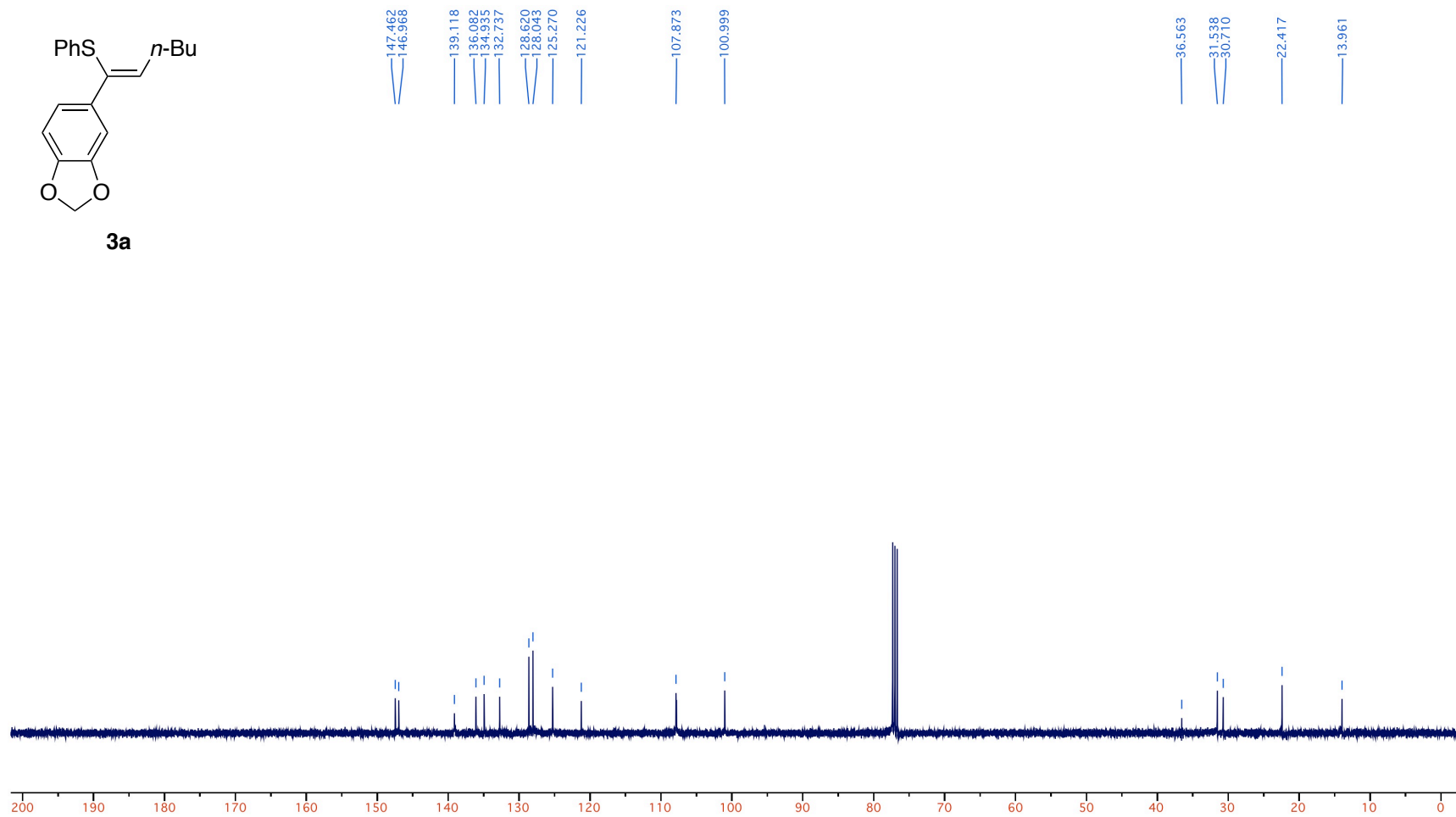


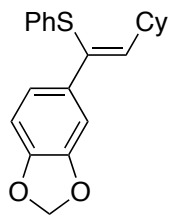
3a



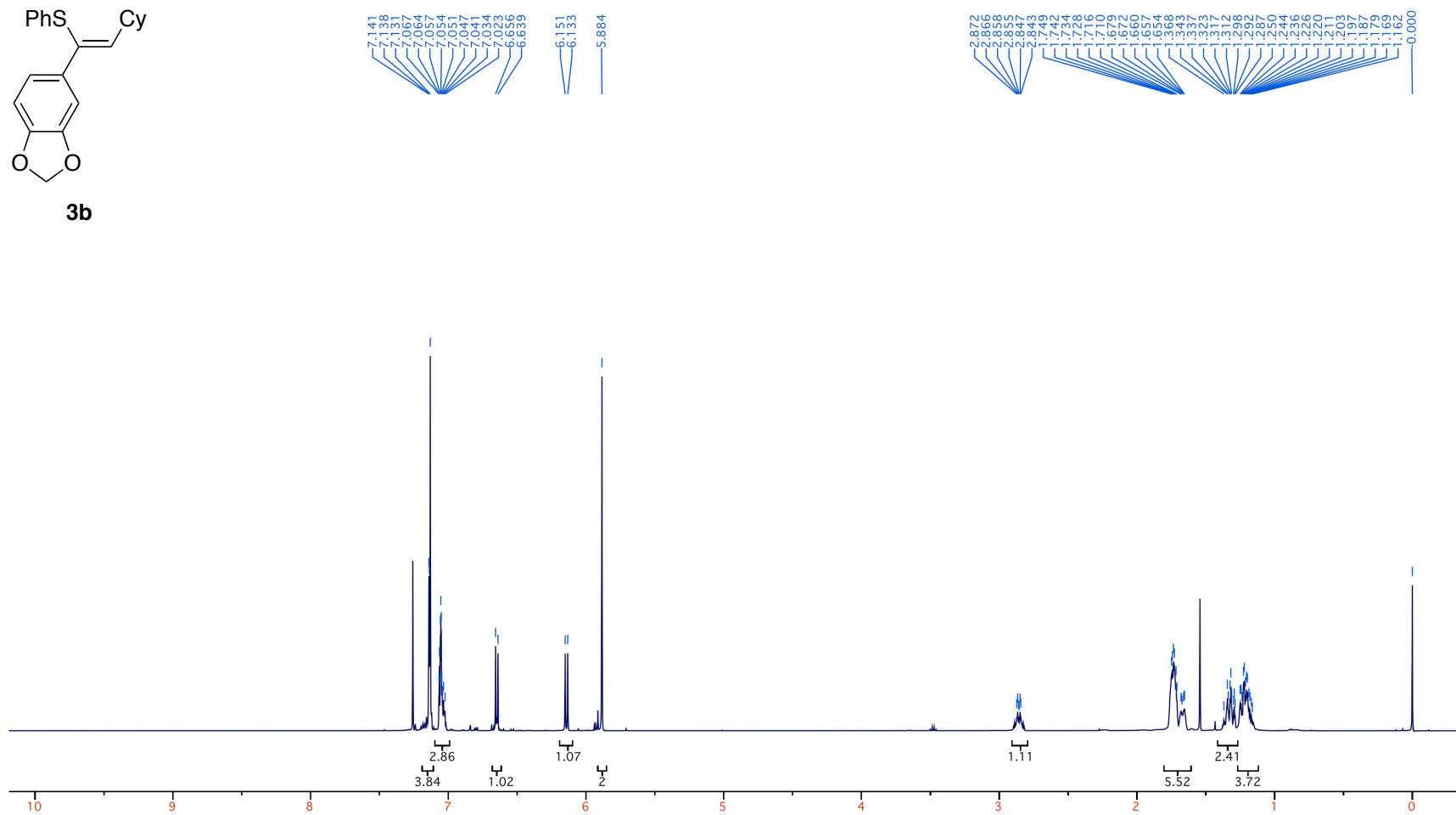


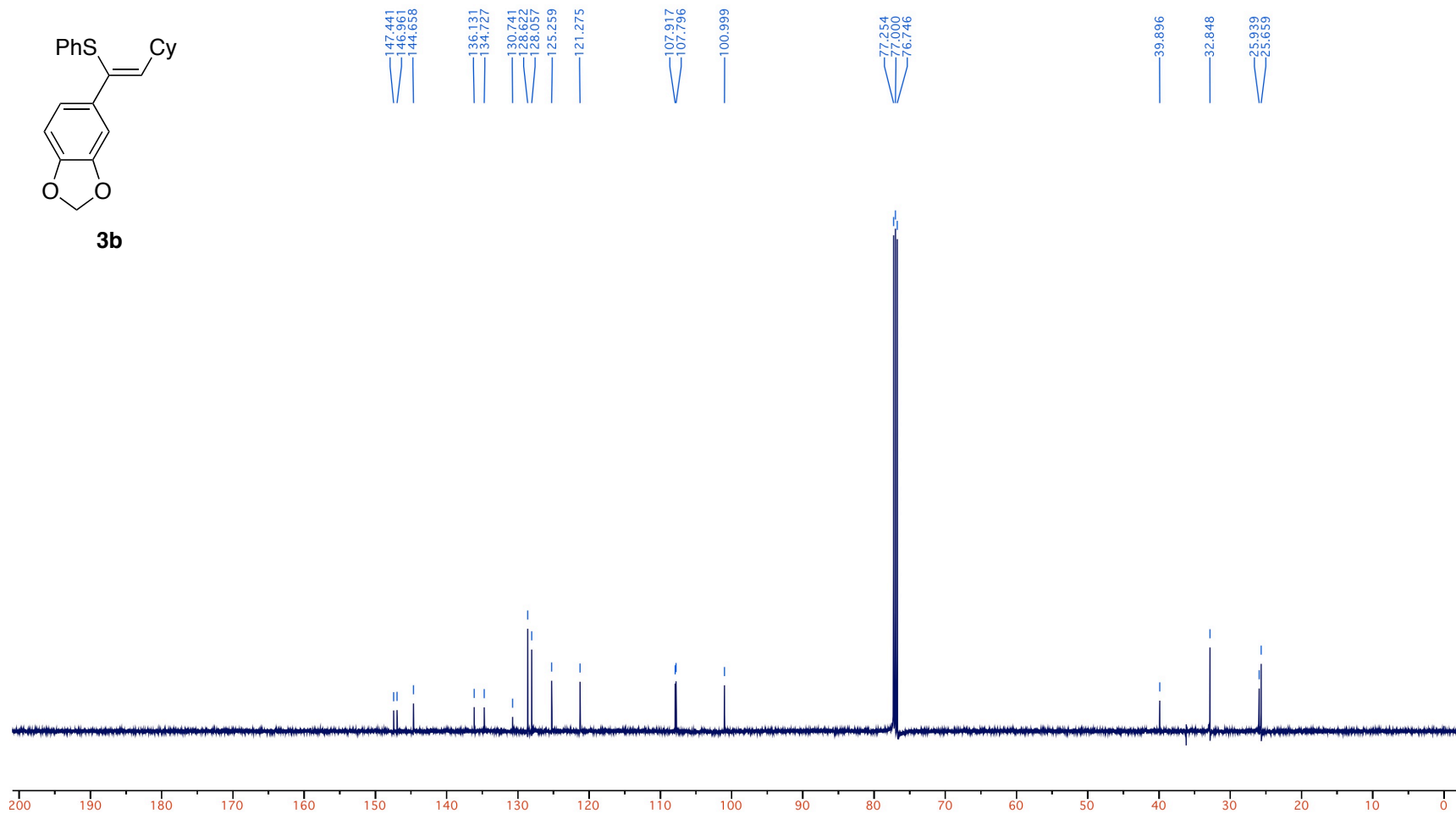
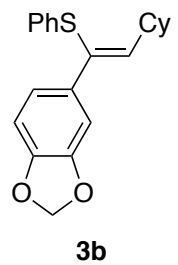
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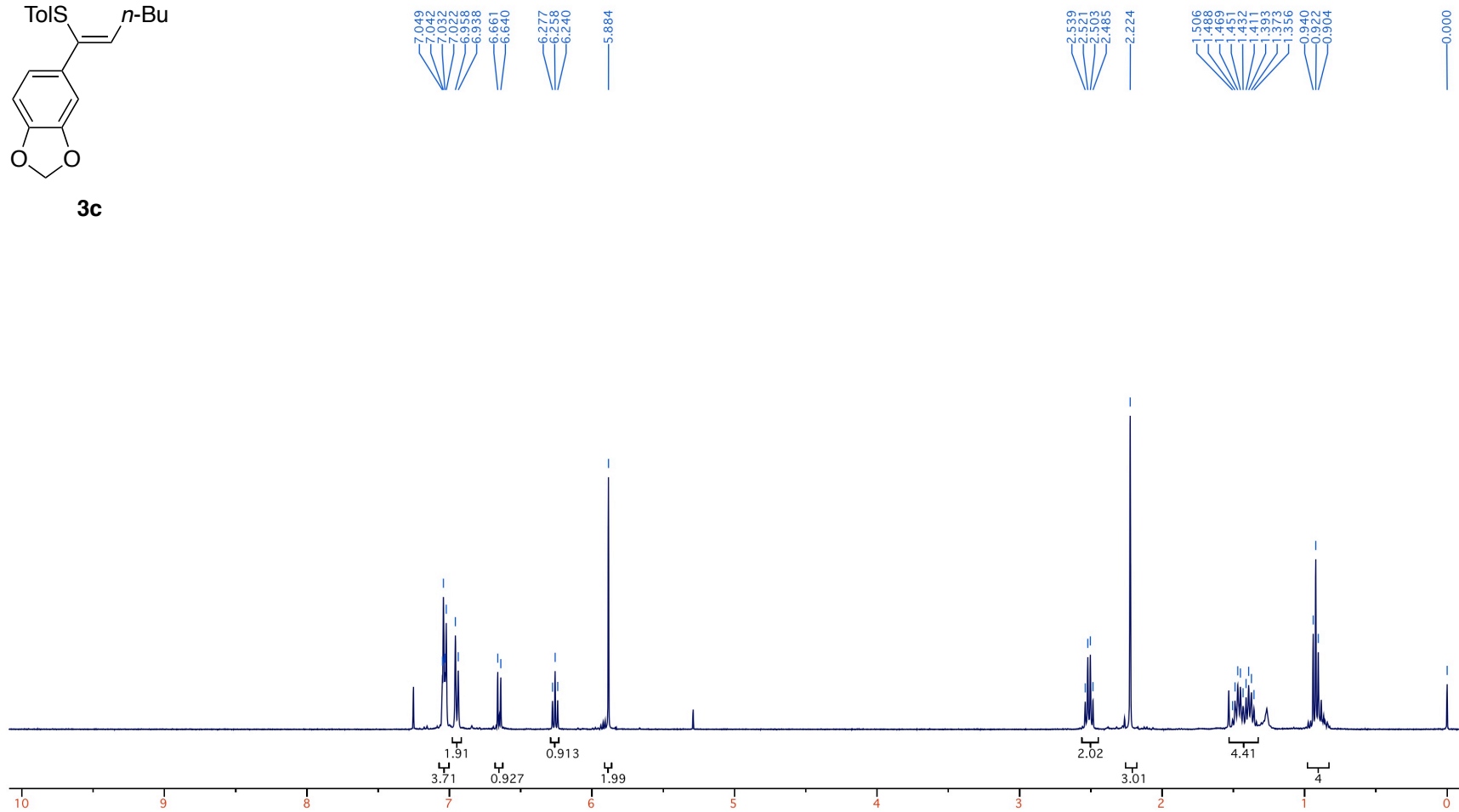
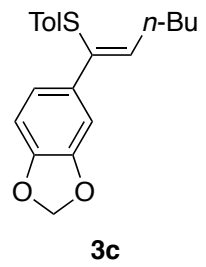


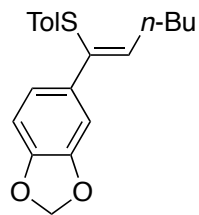


3b

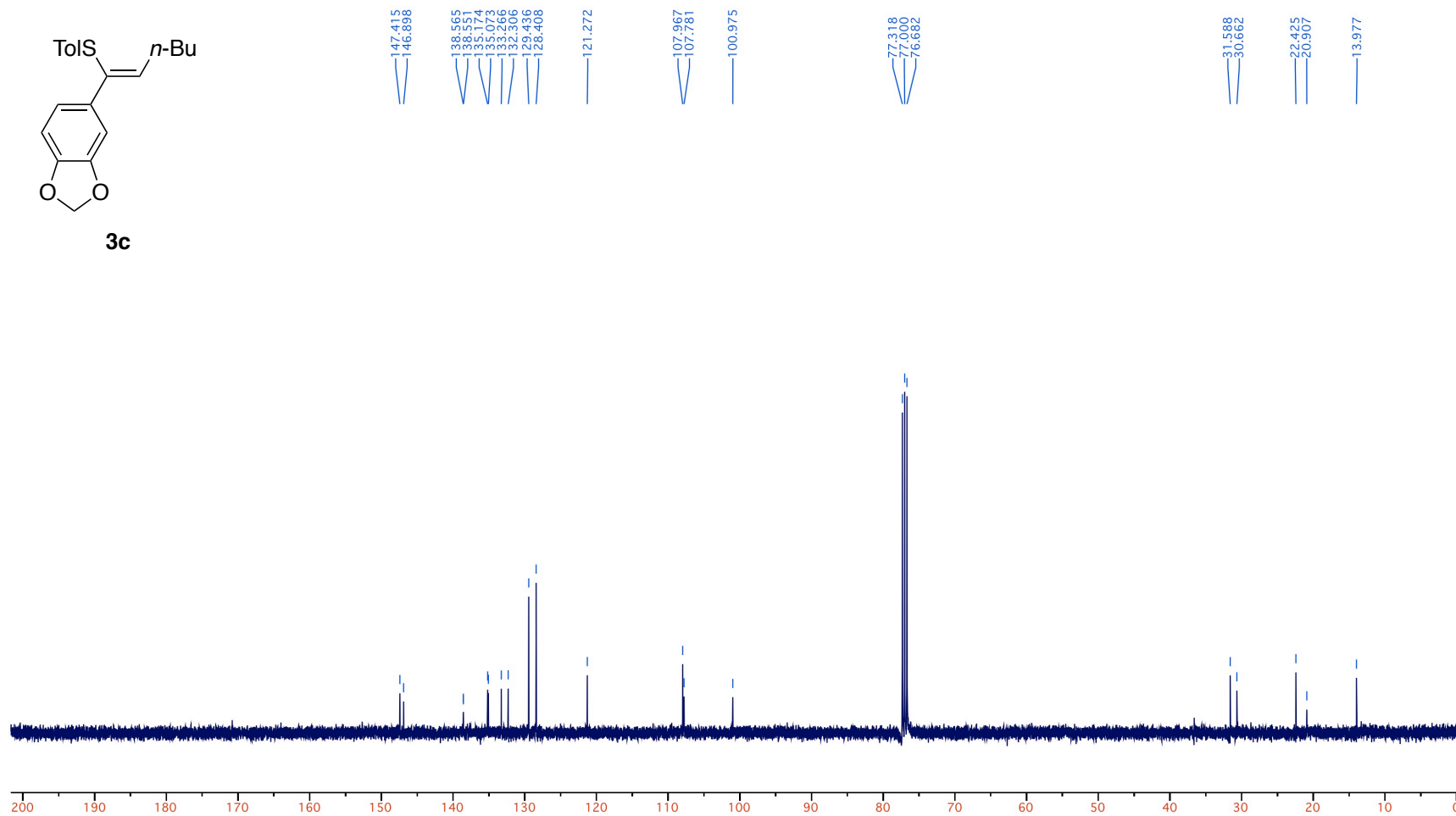


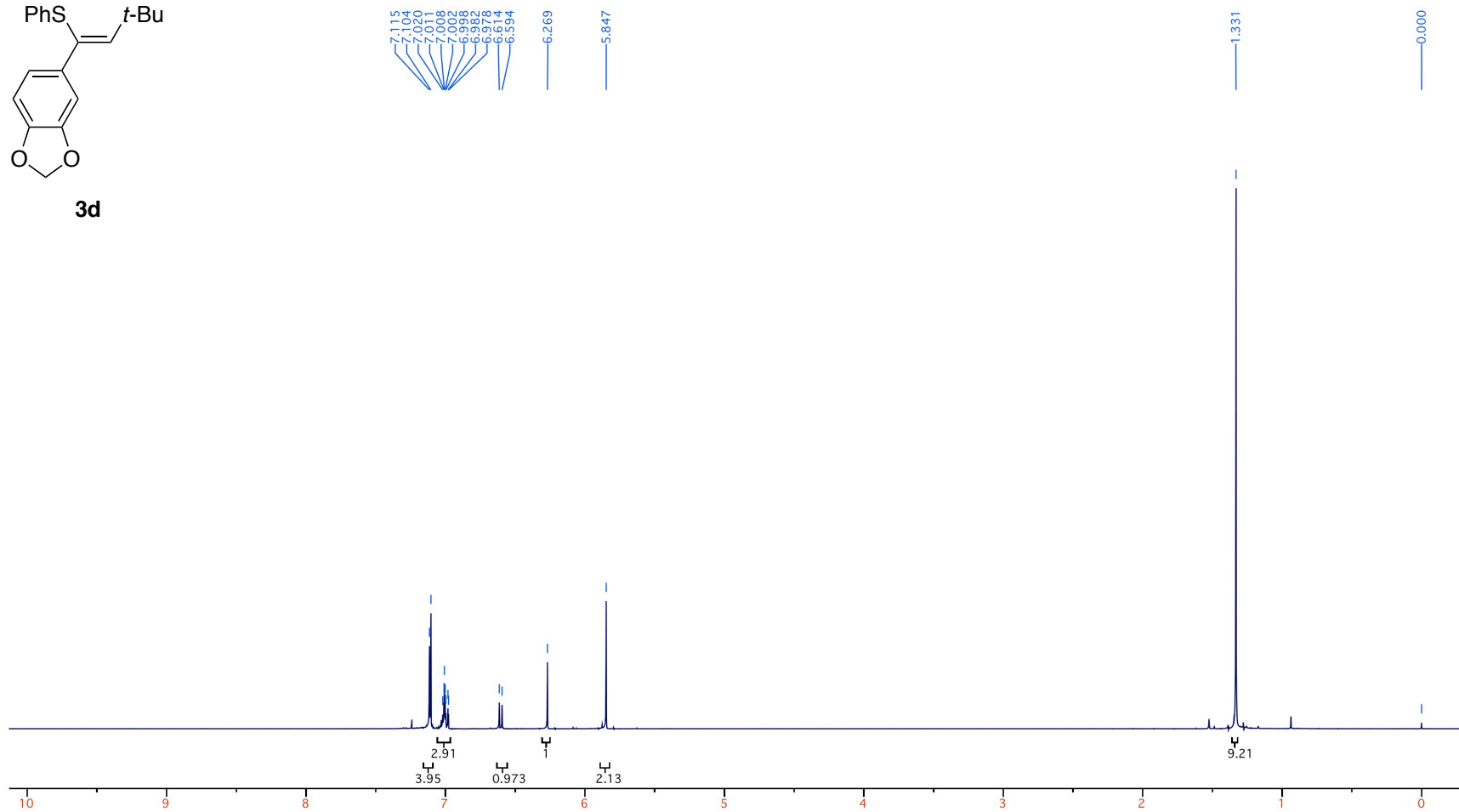
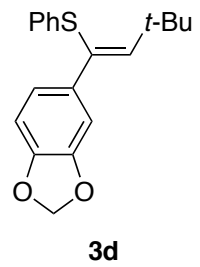


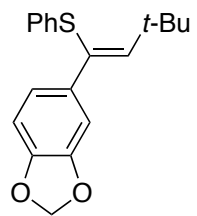




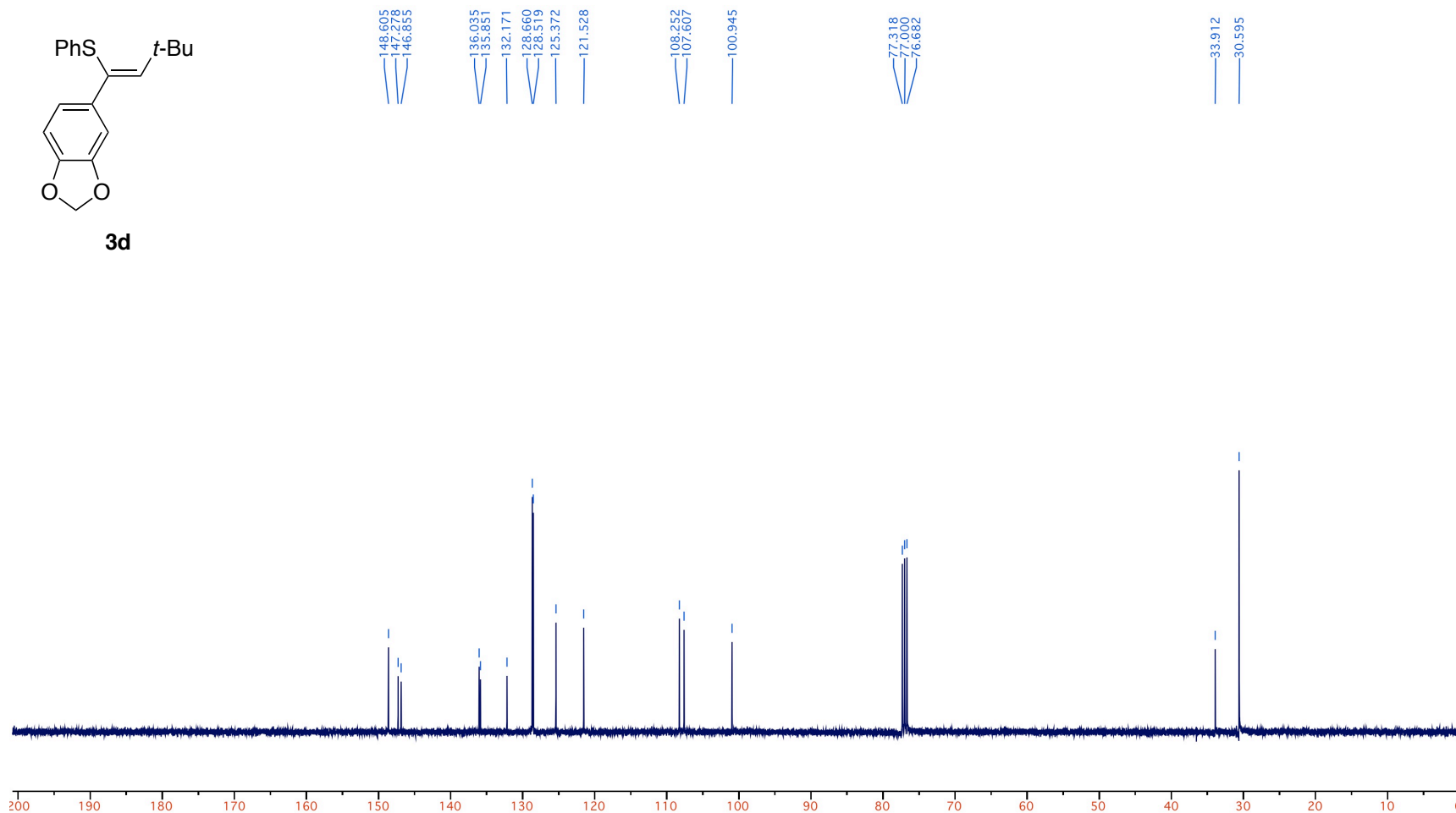
3c

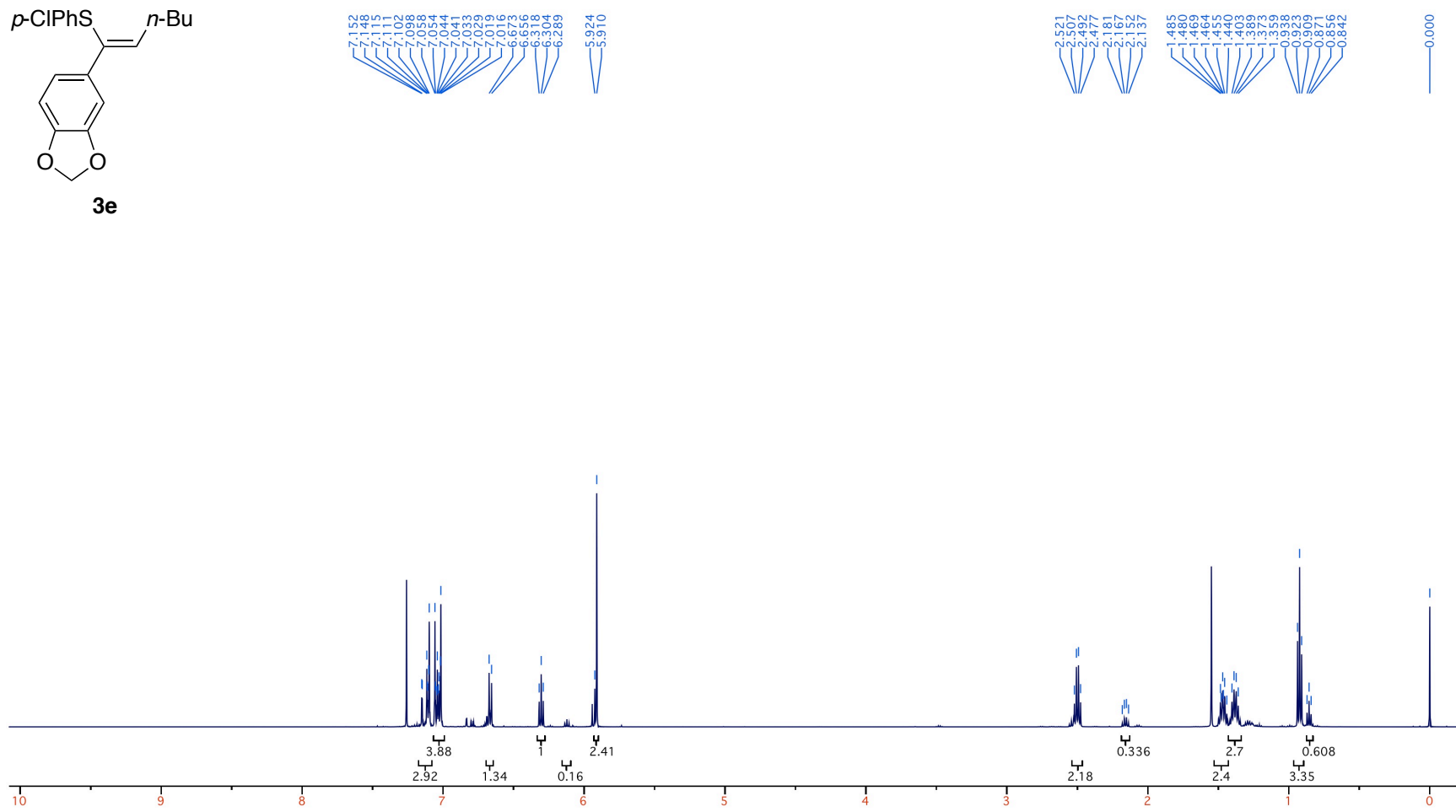
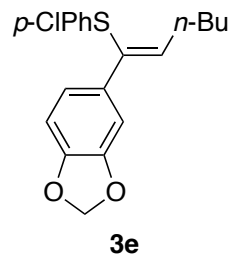


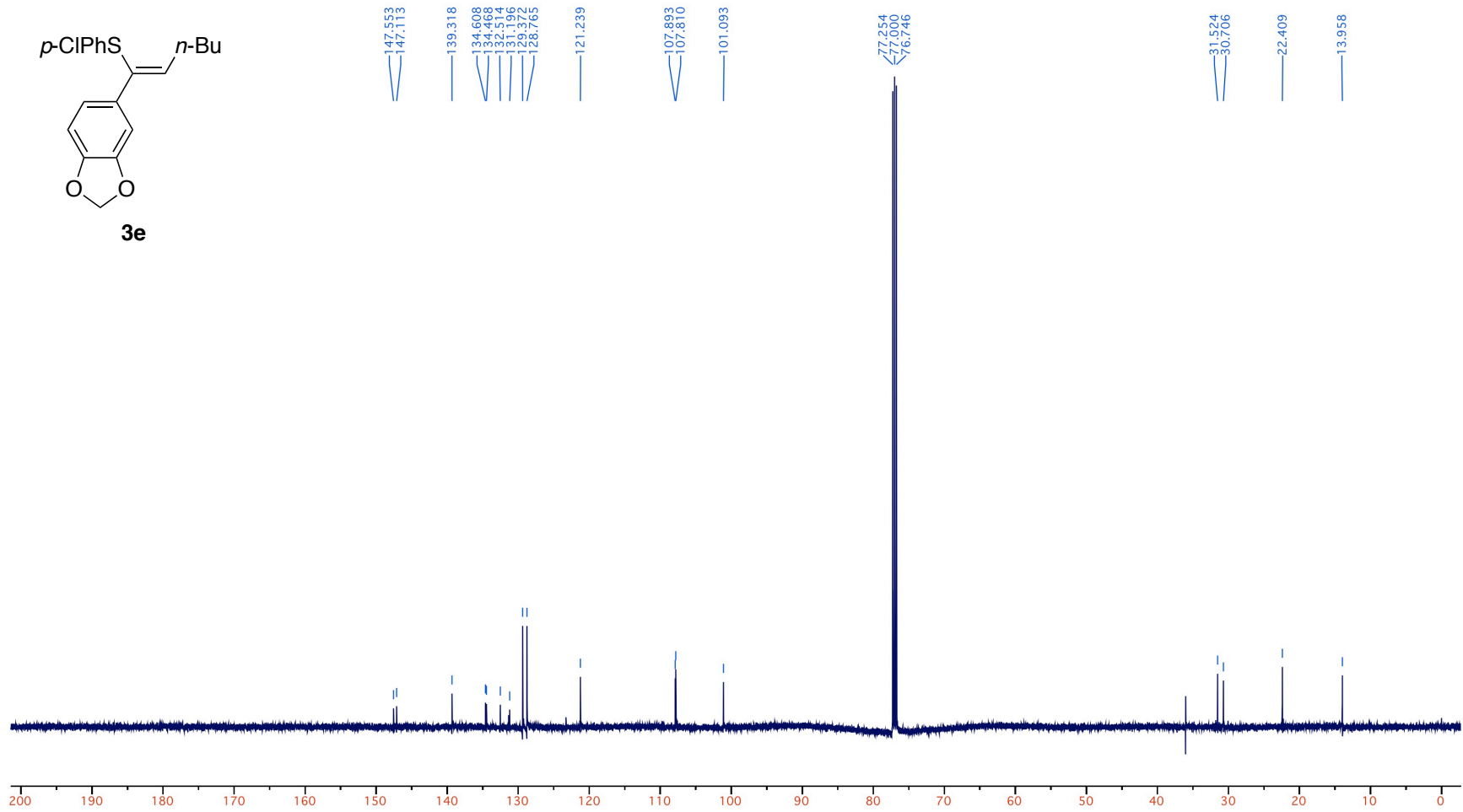
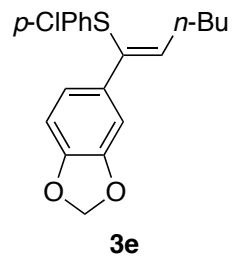


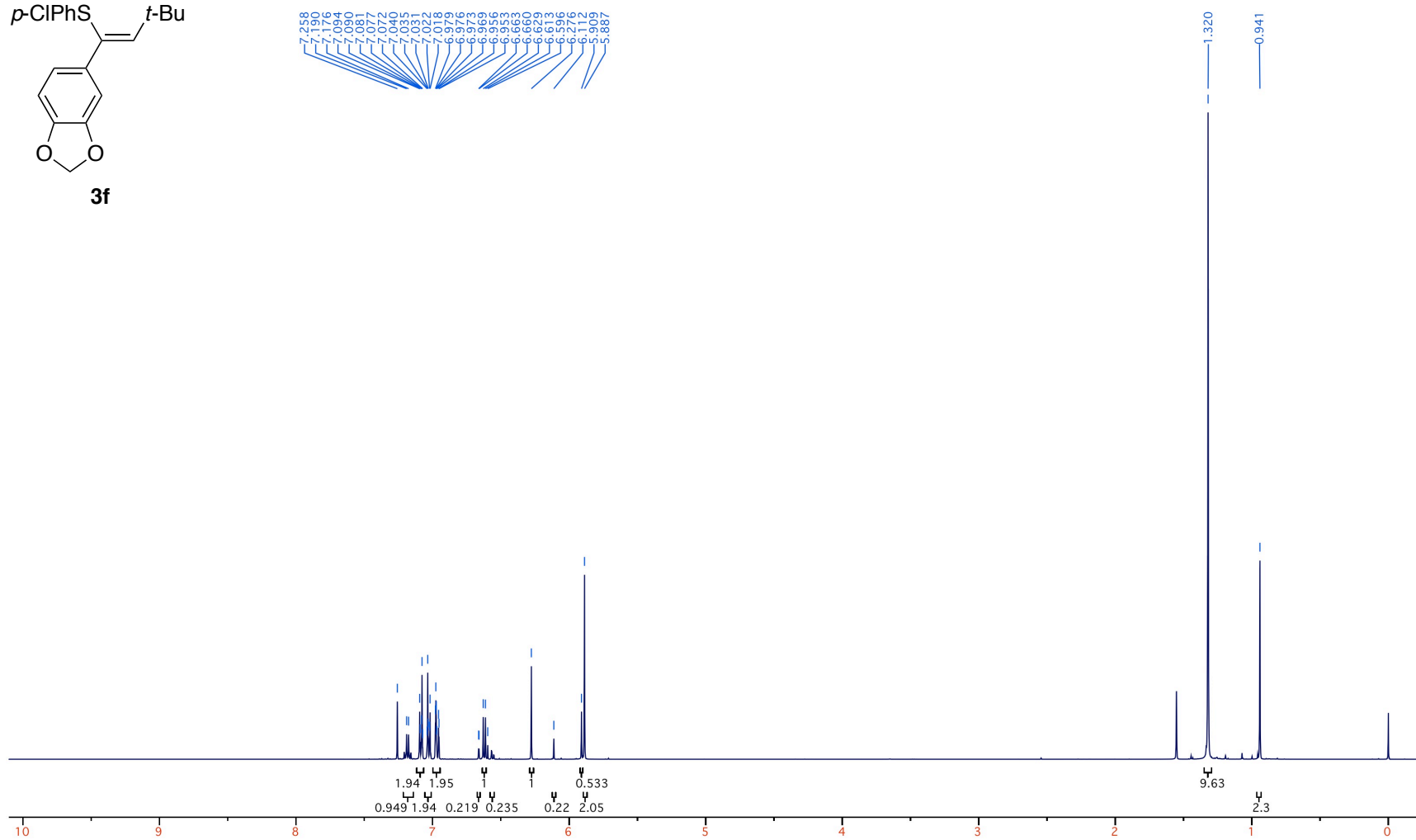
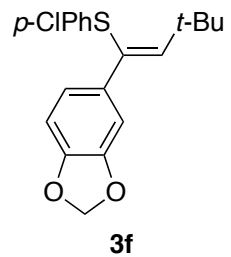


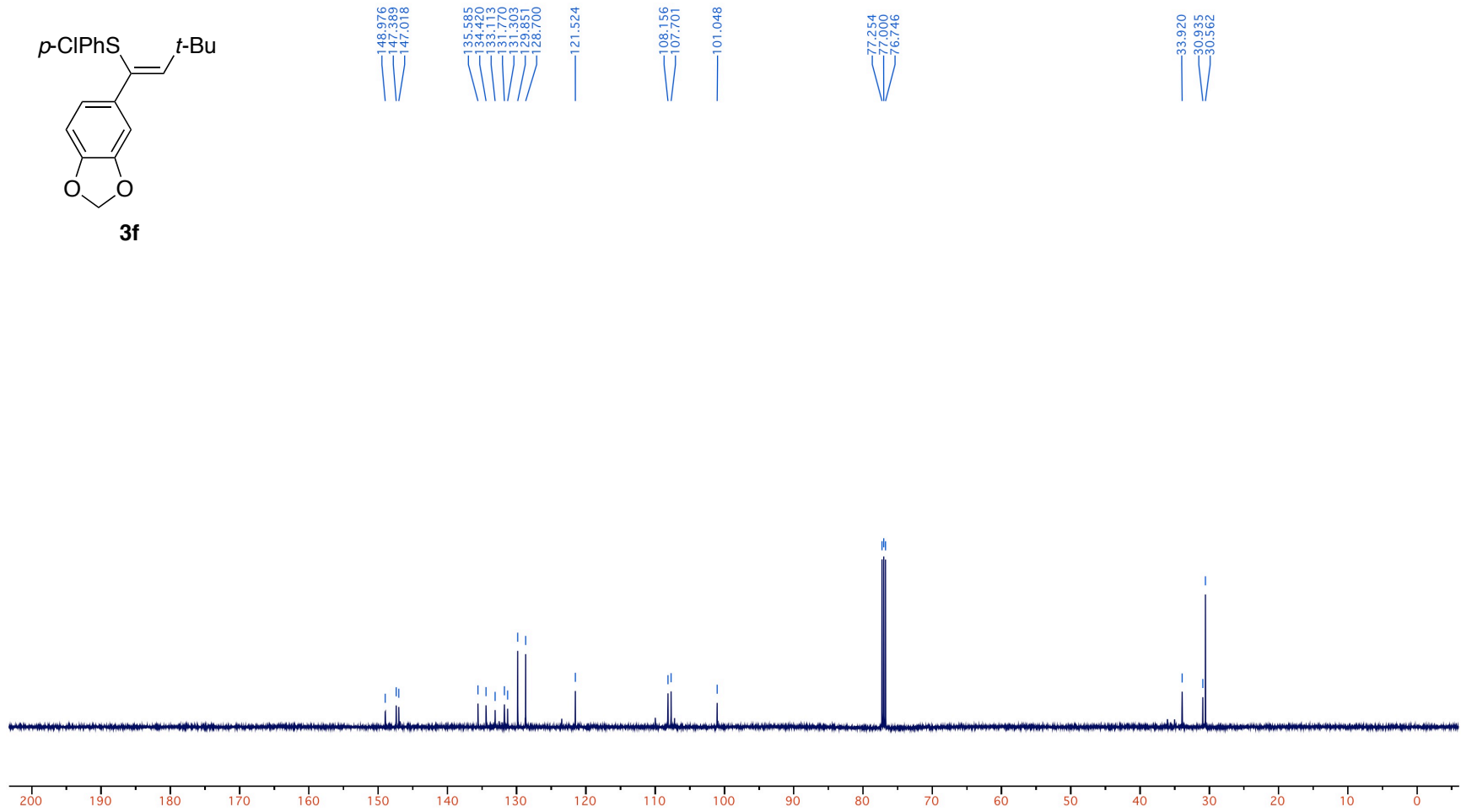
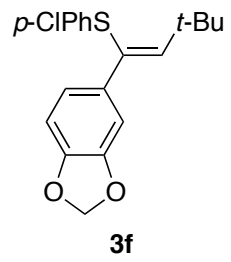
3d

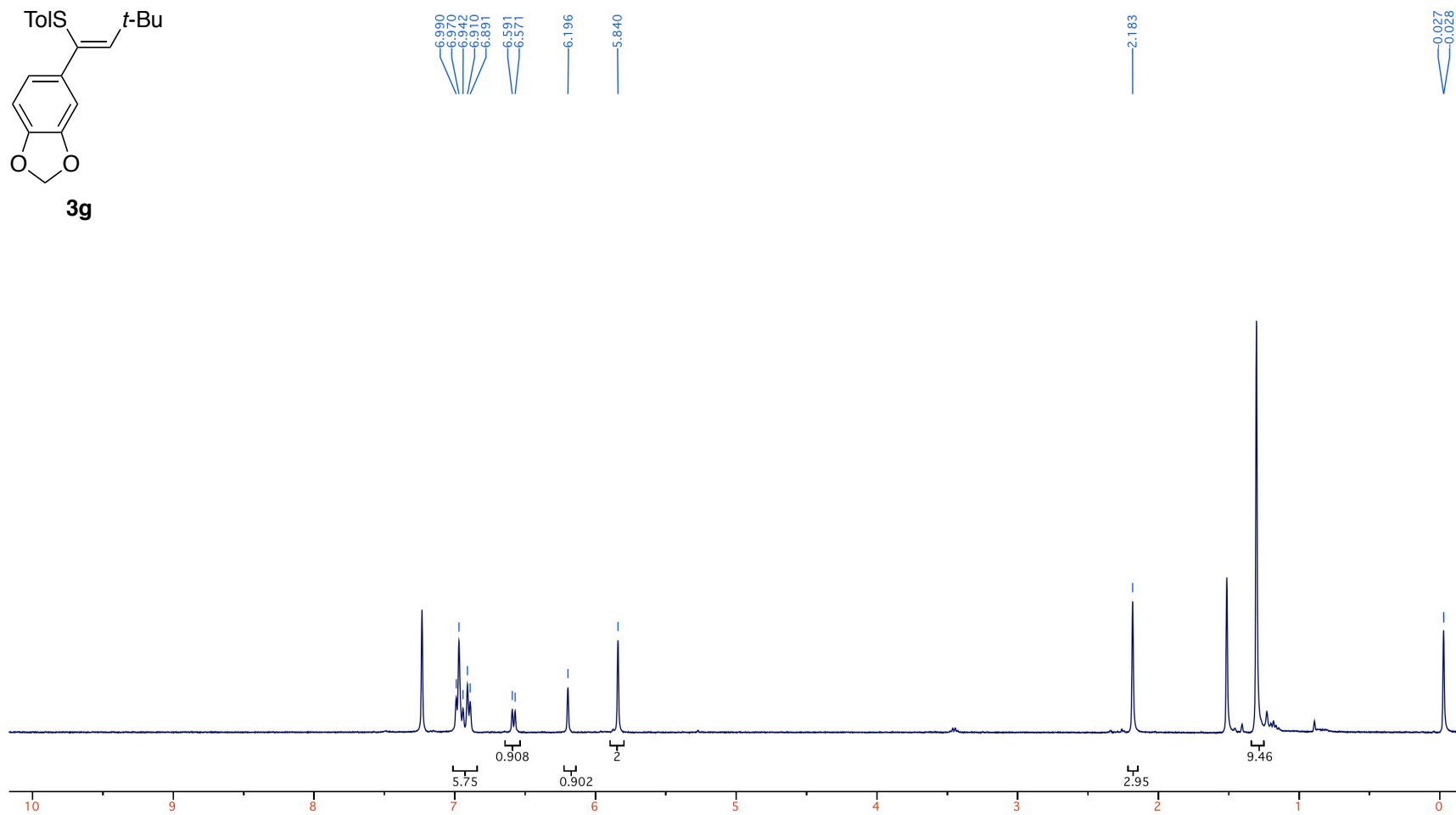
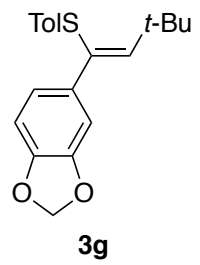


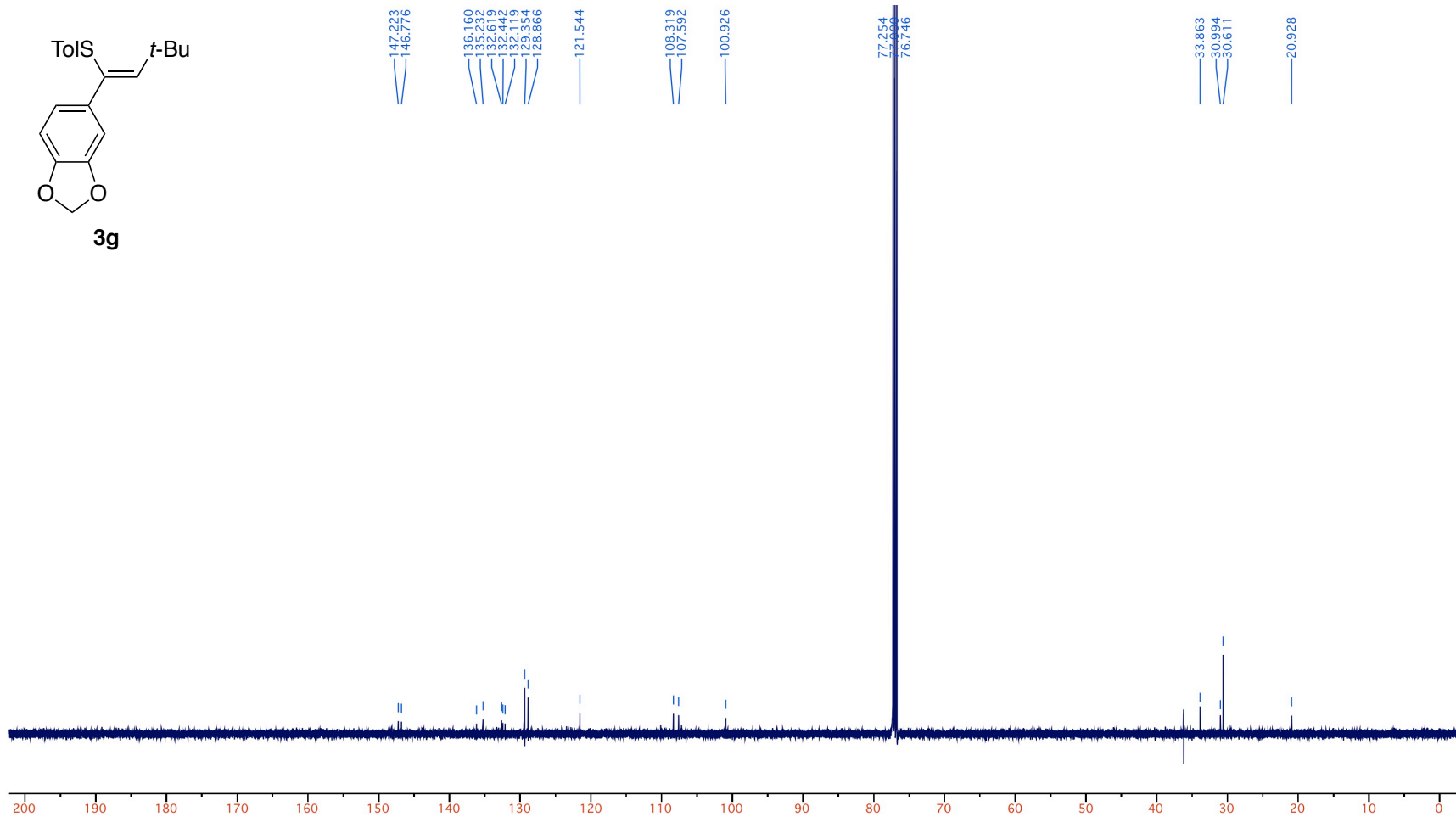
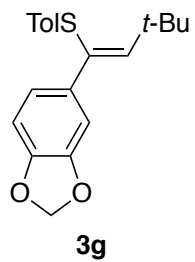


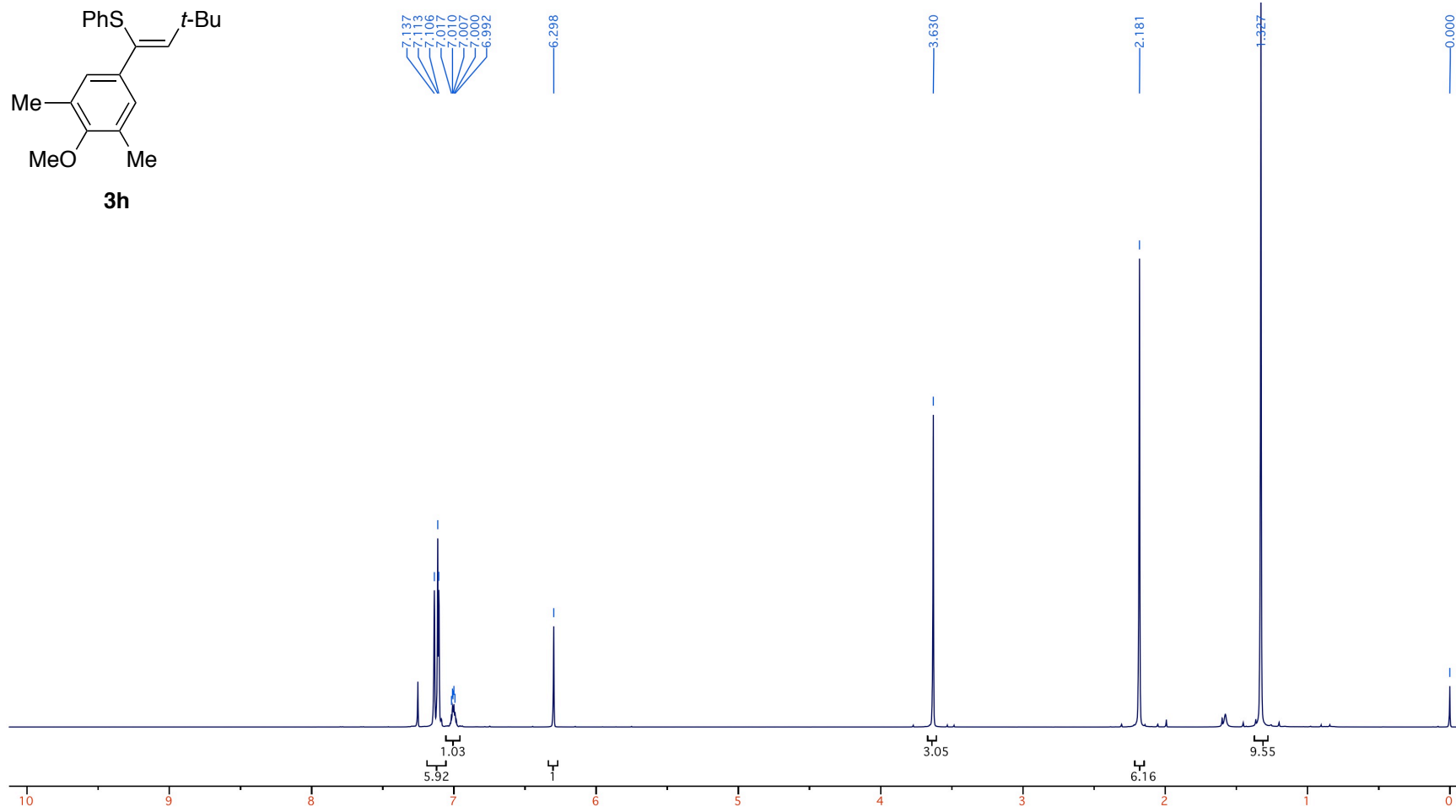
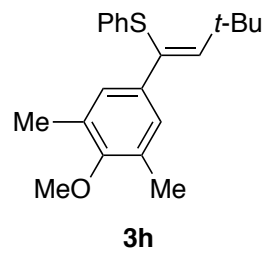


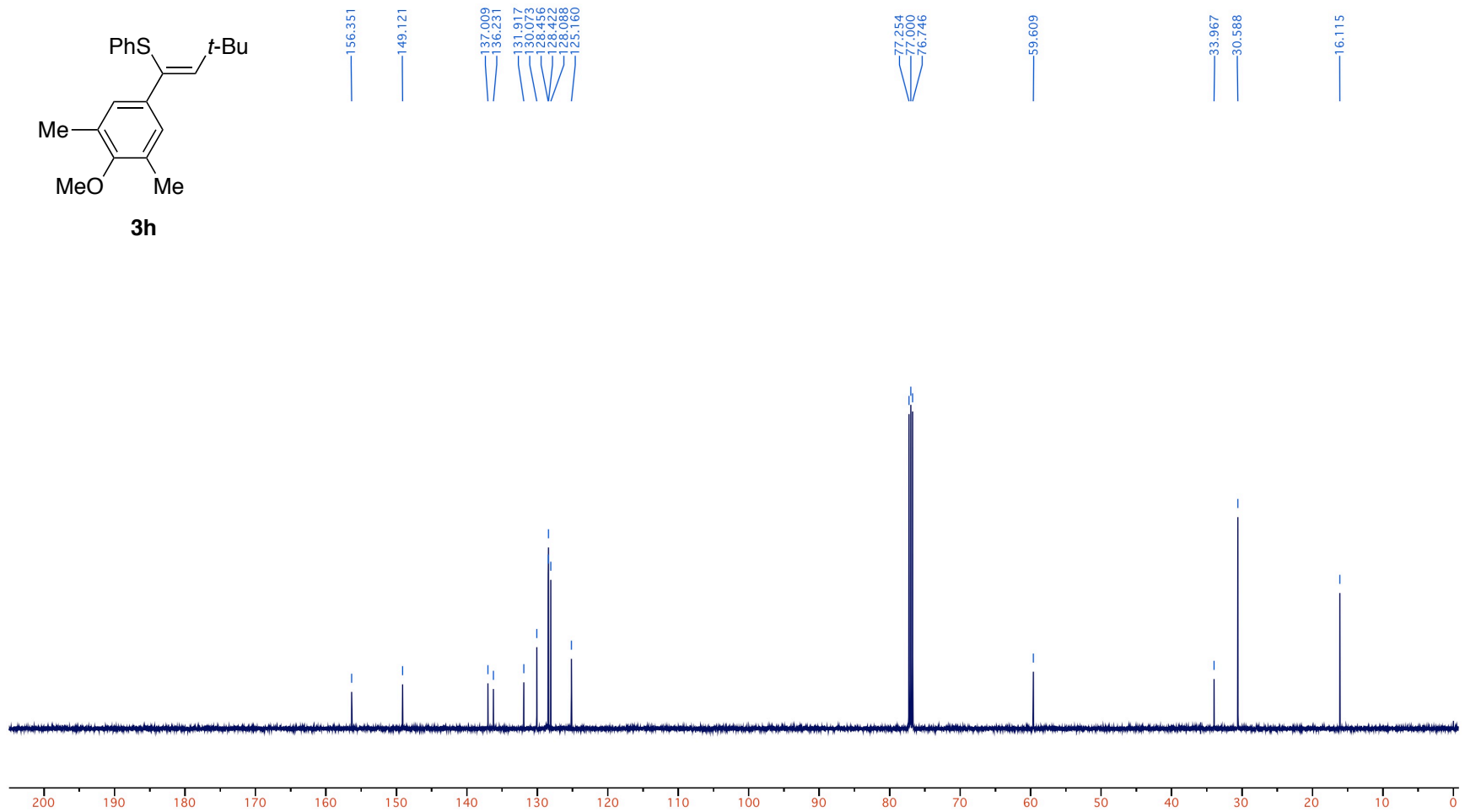
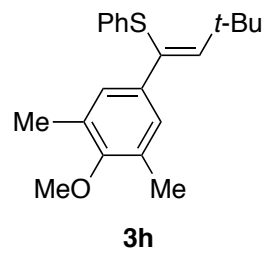


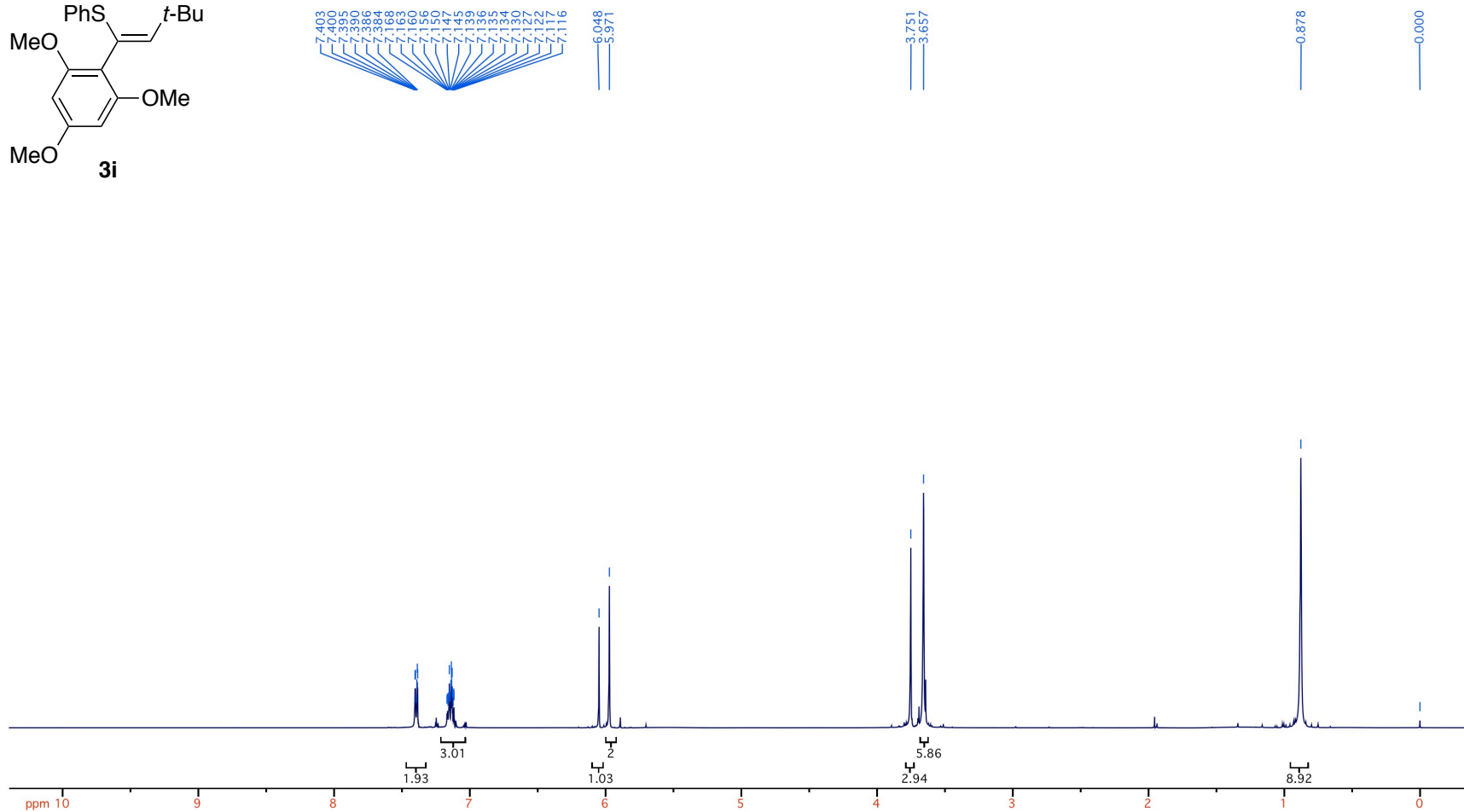
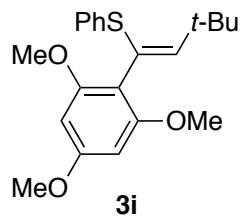


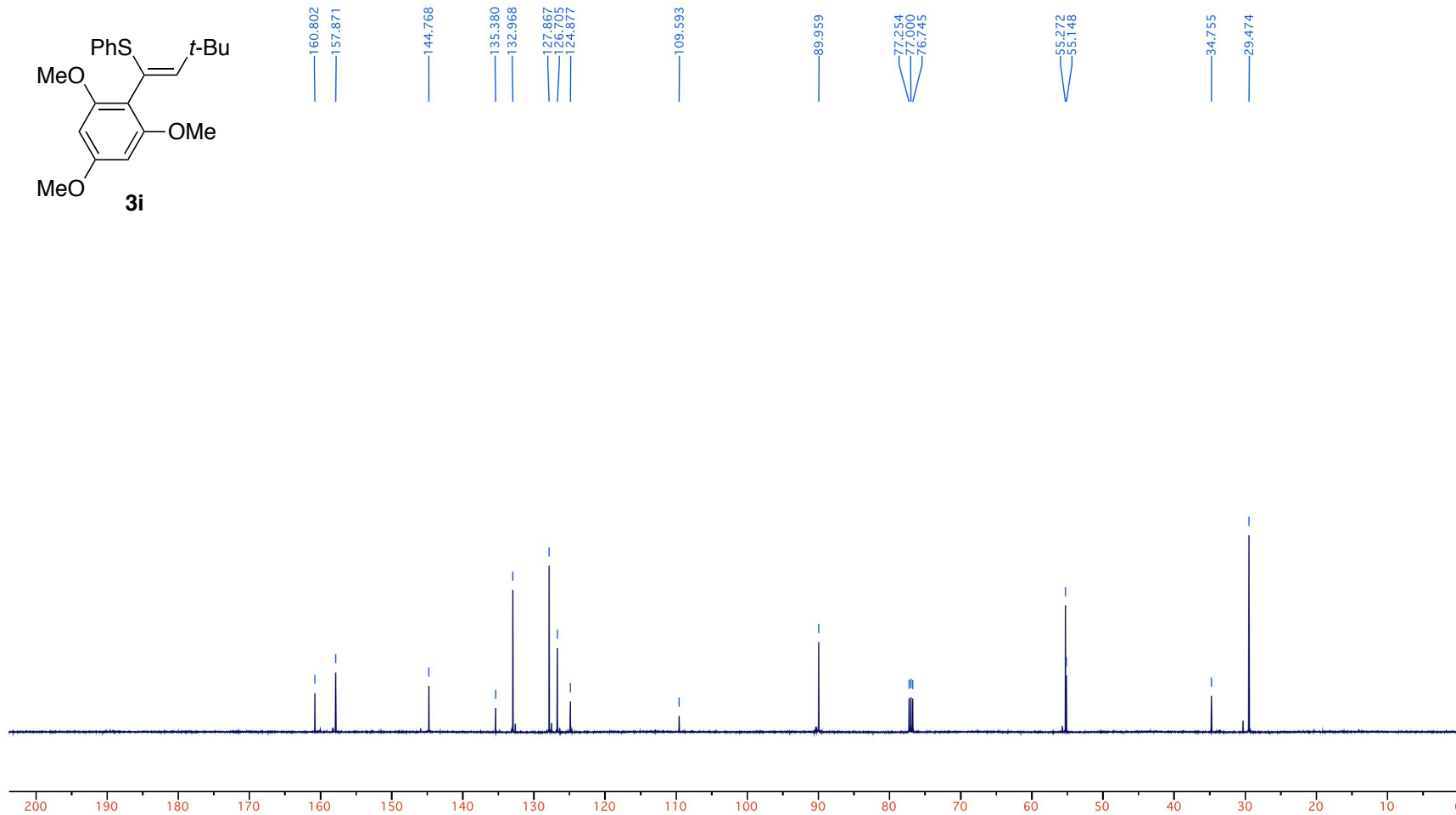
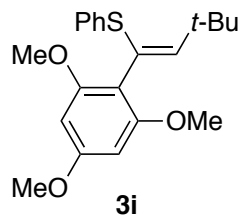


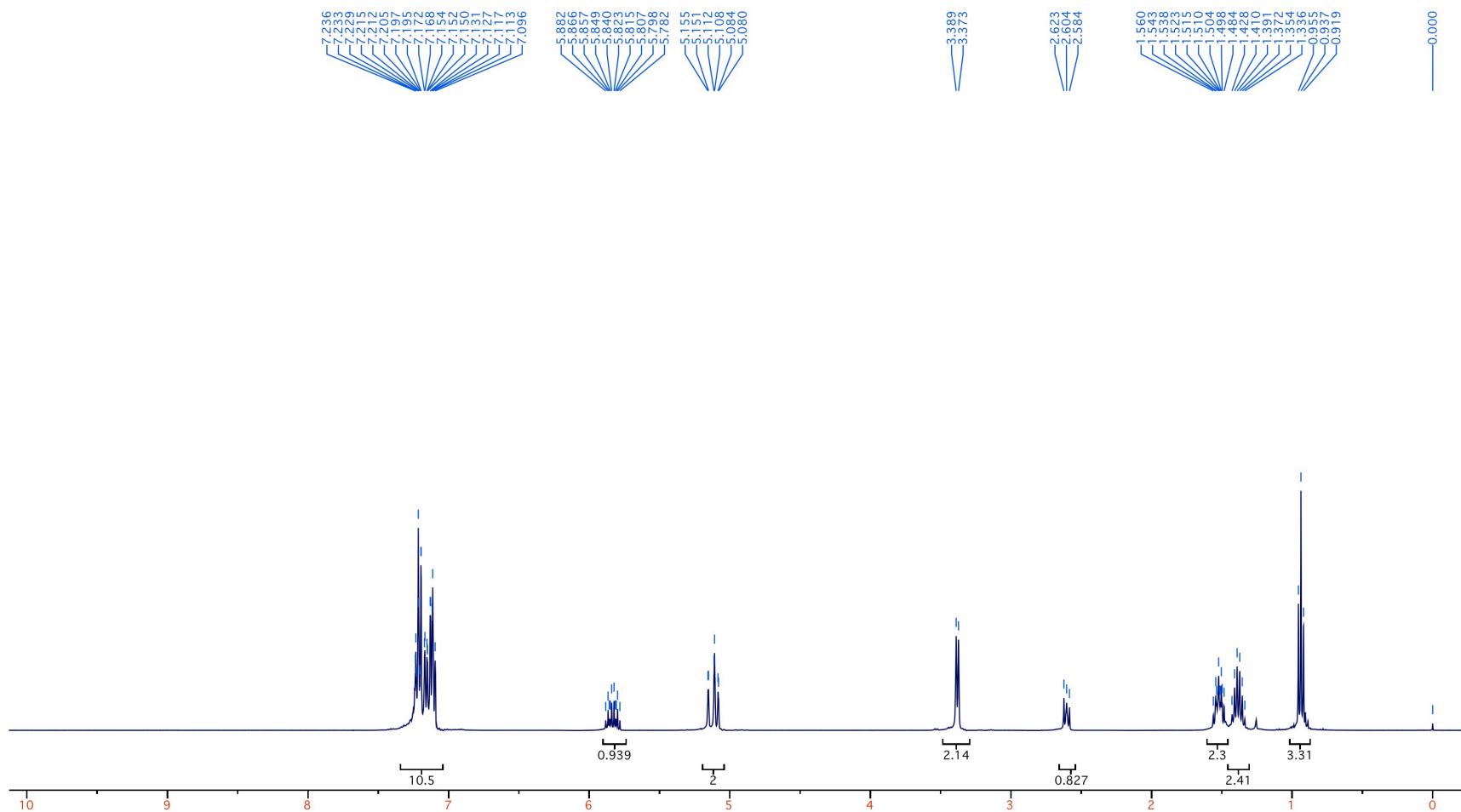
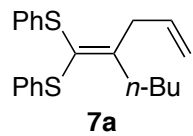


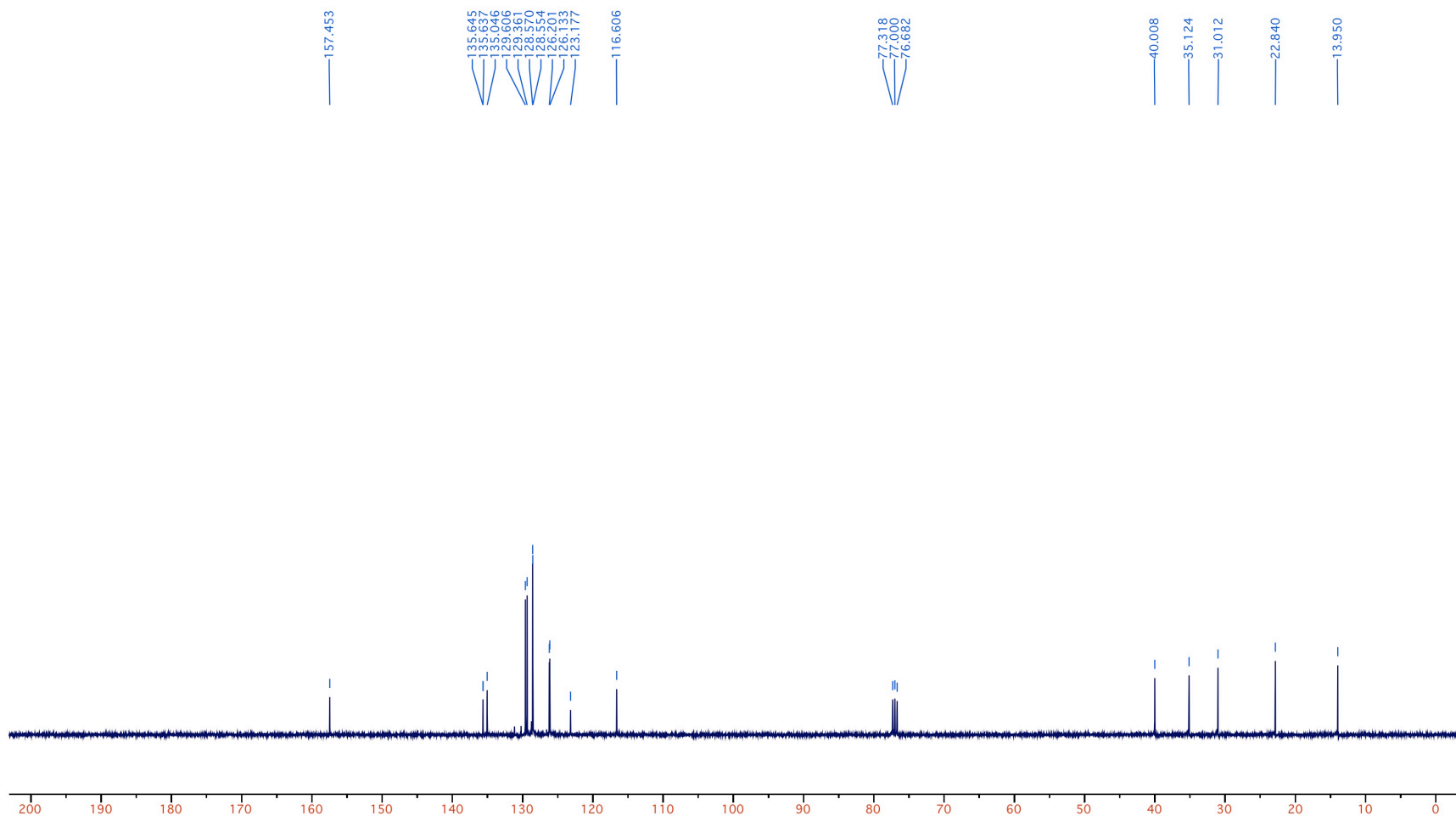
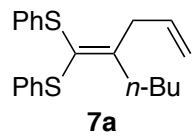


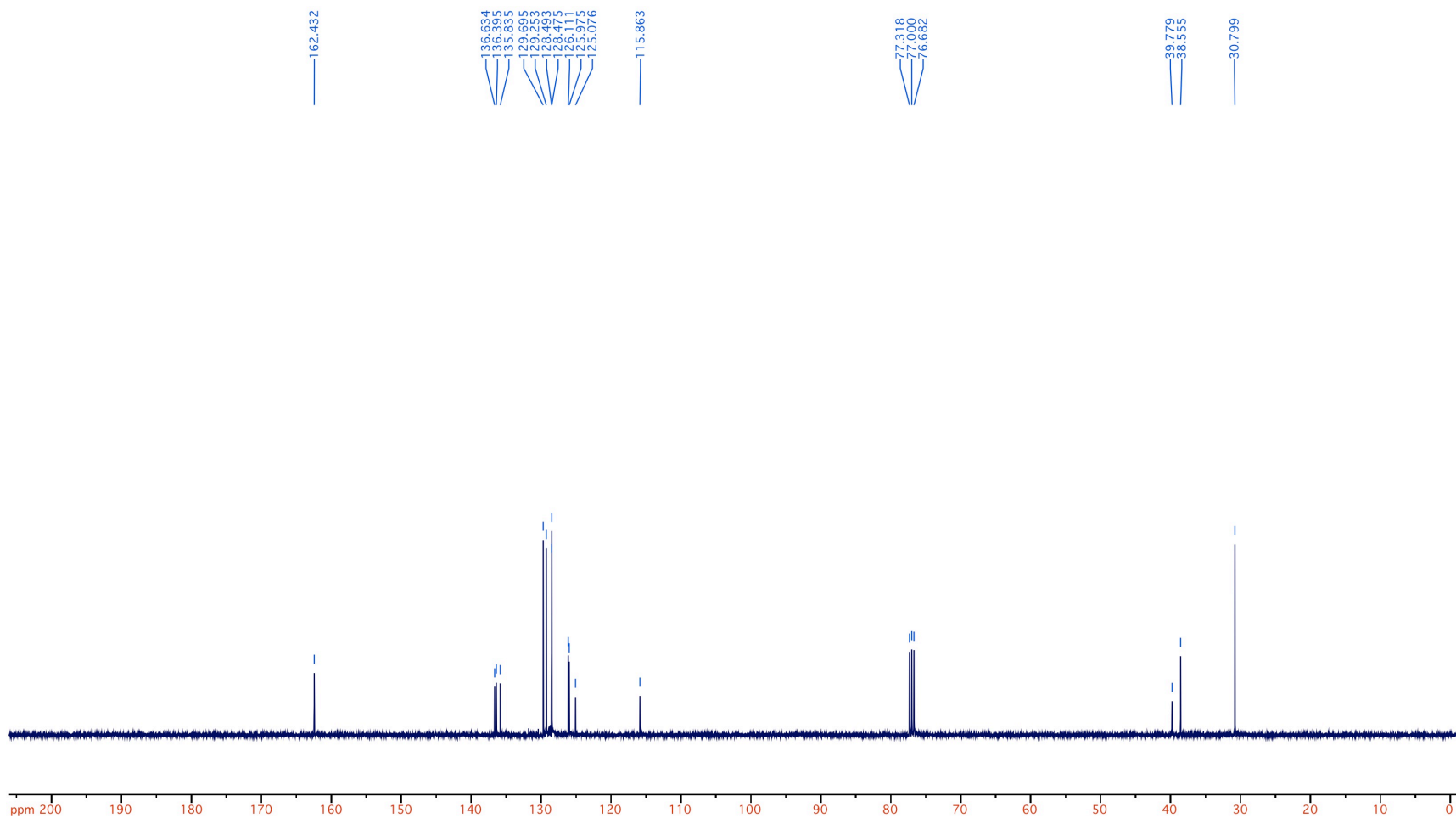
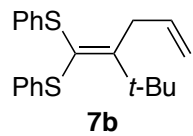


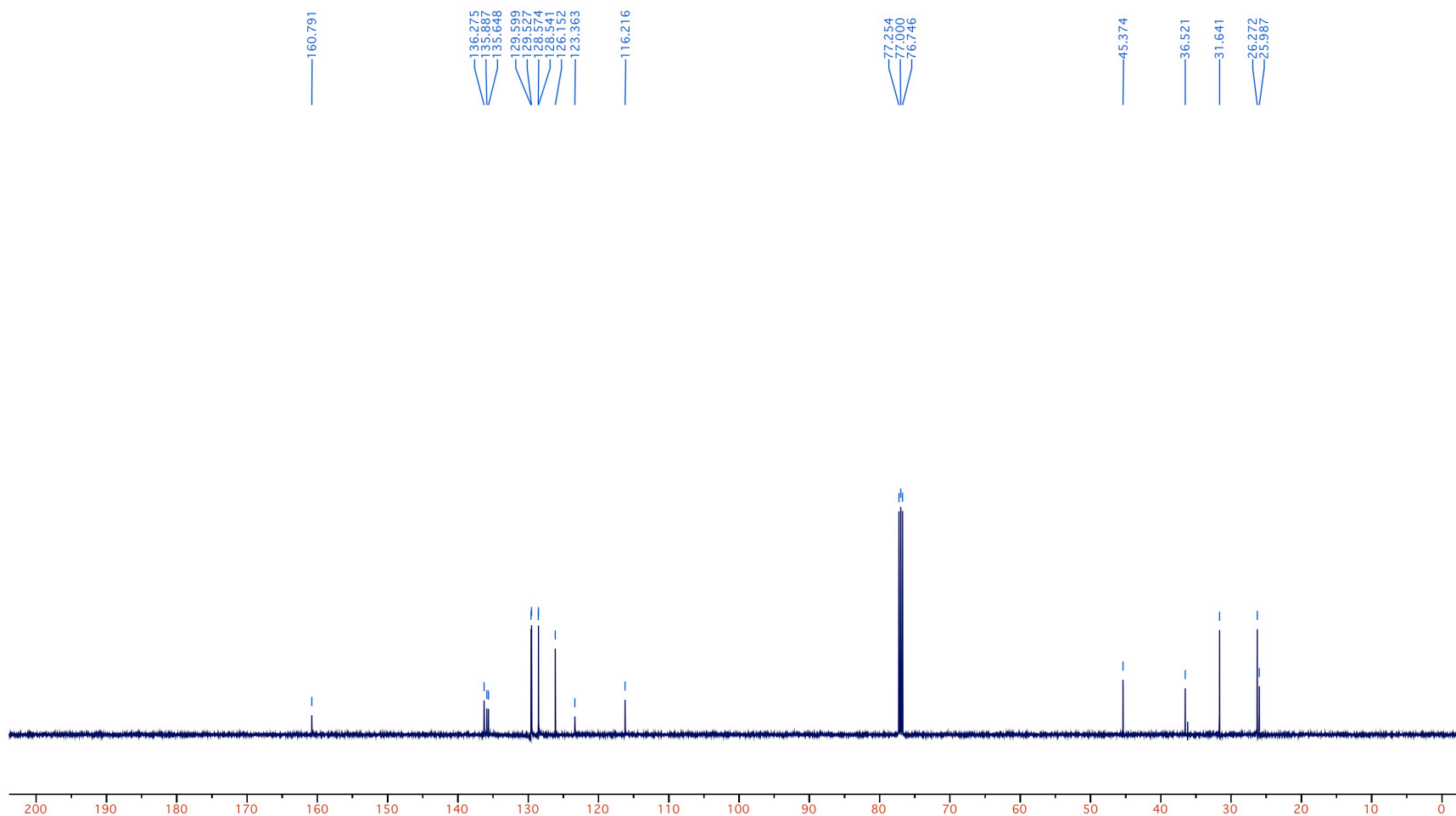
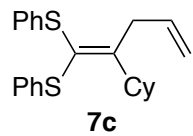


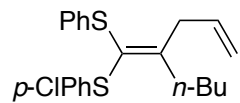




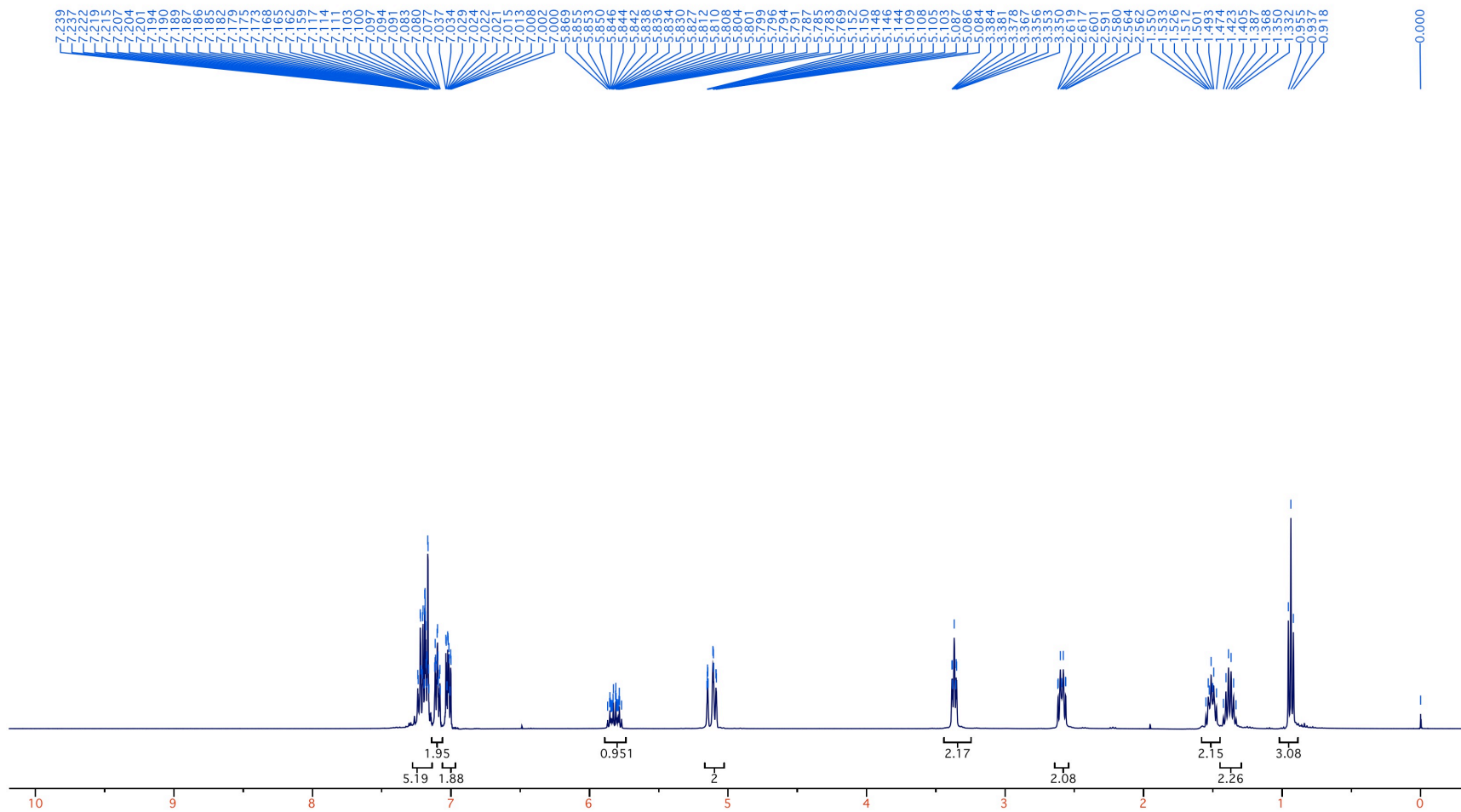


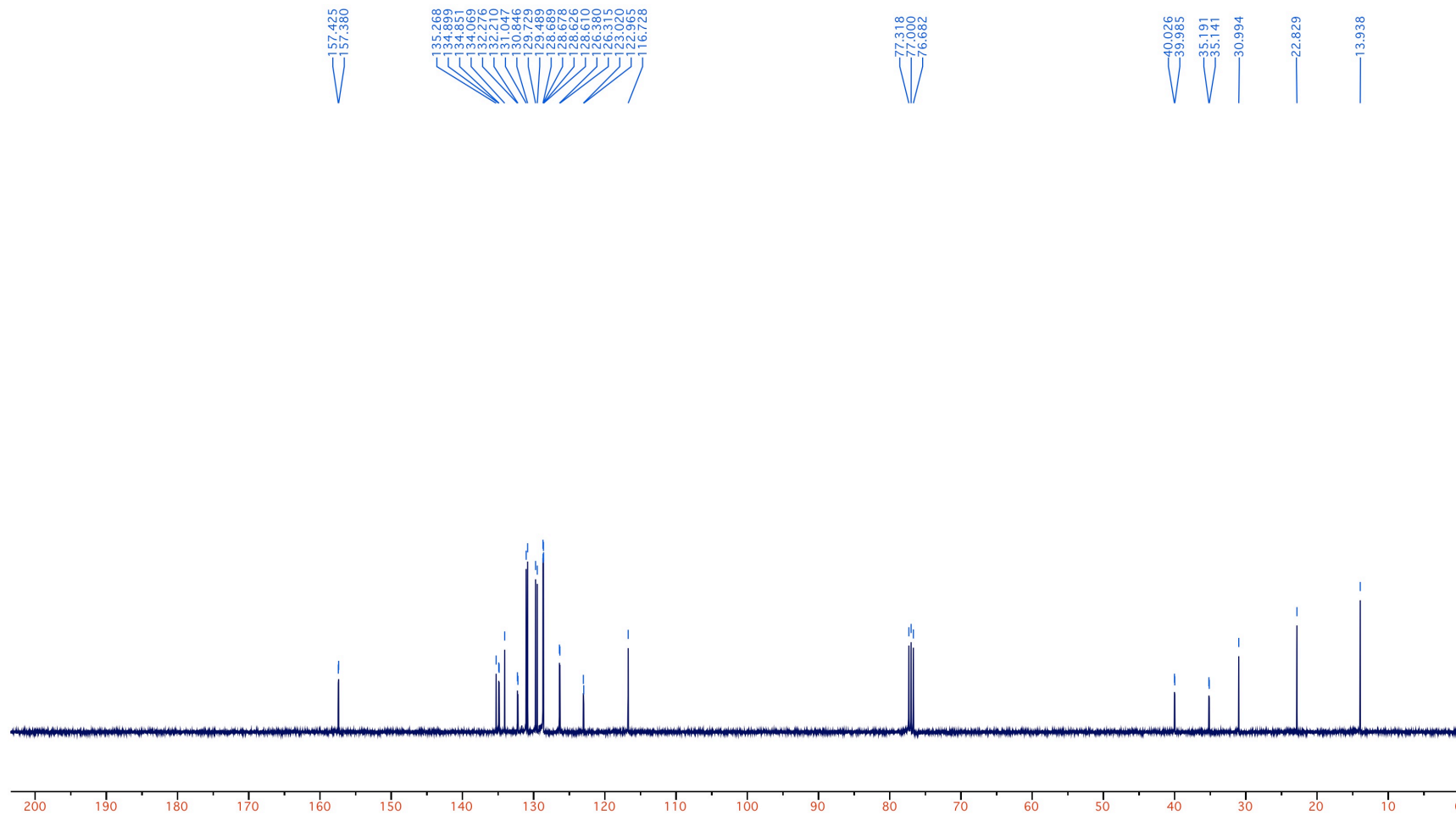
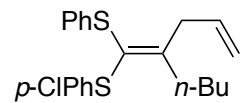


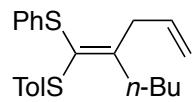




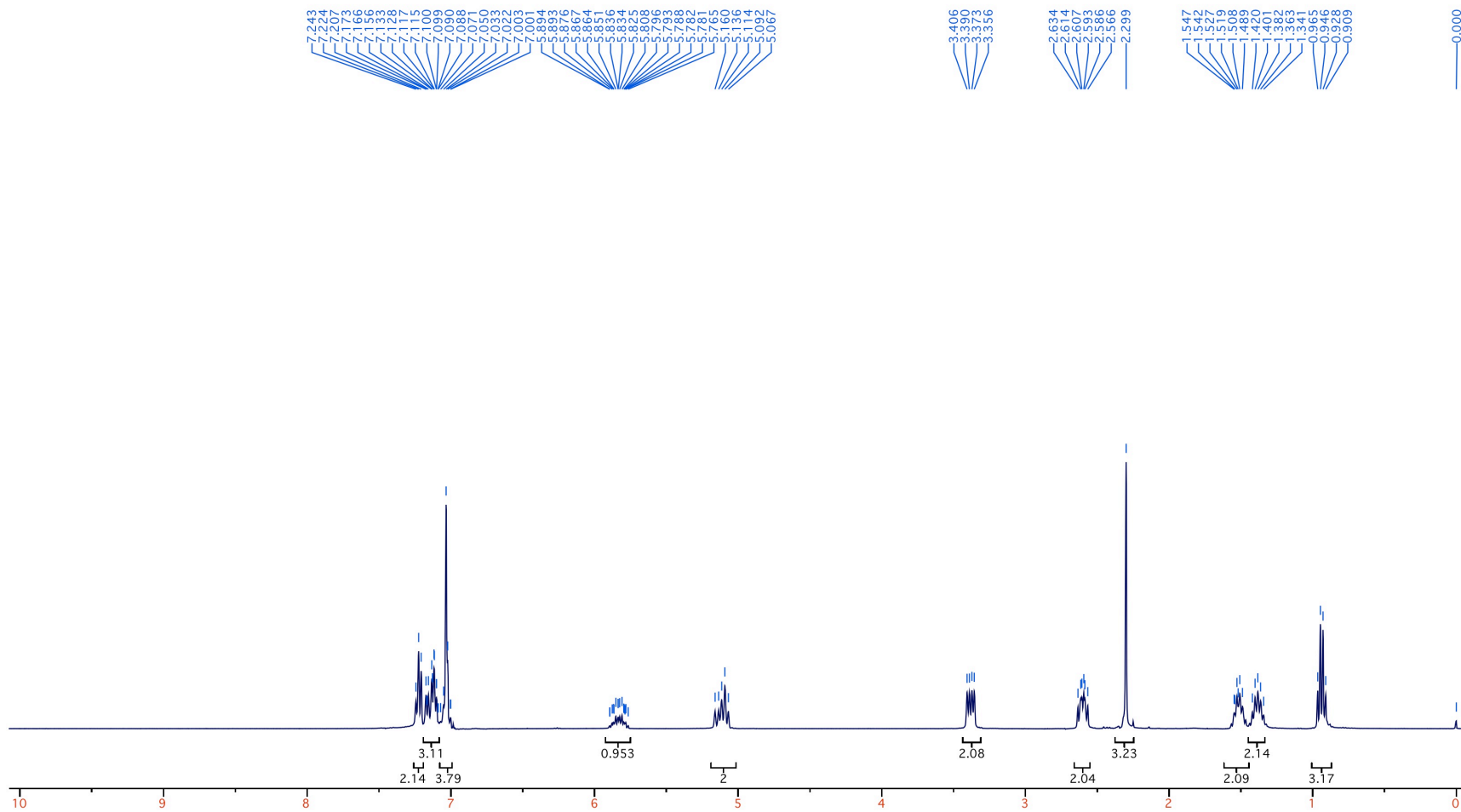
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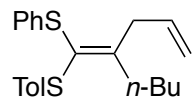




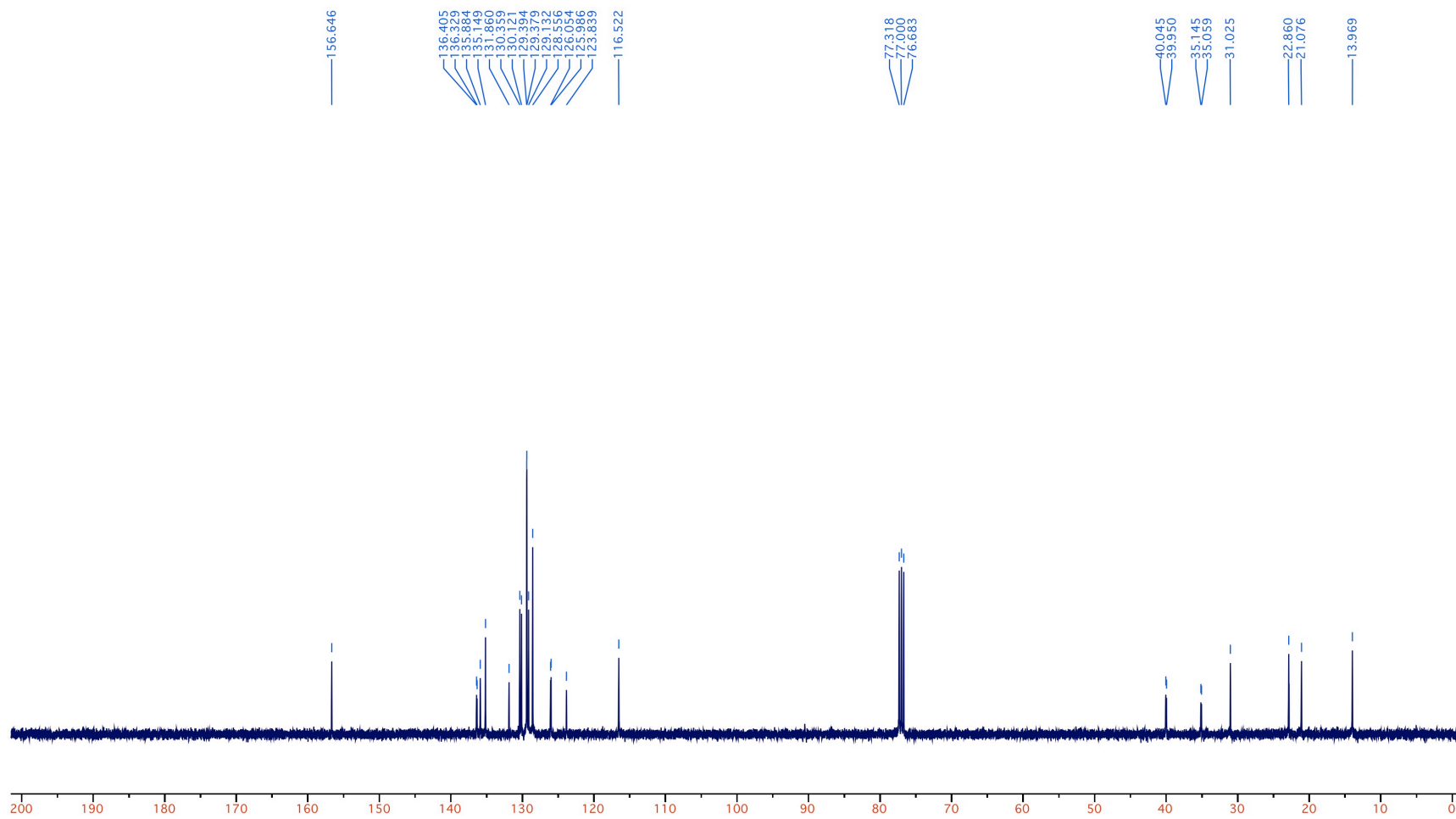


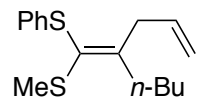
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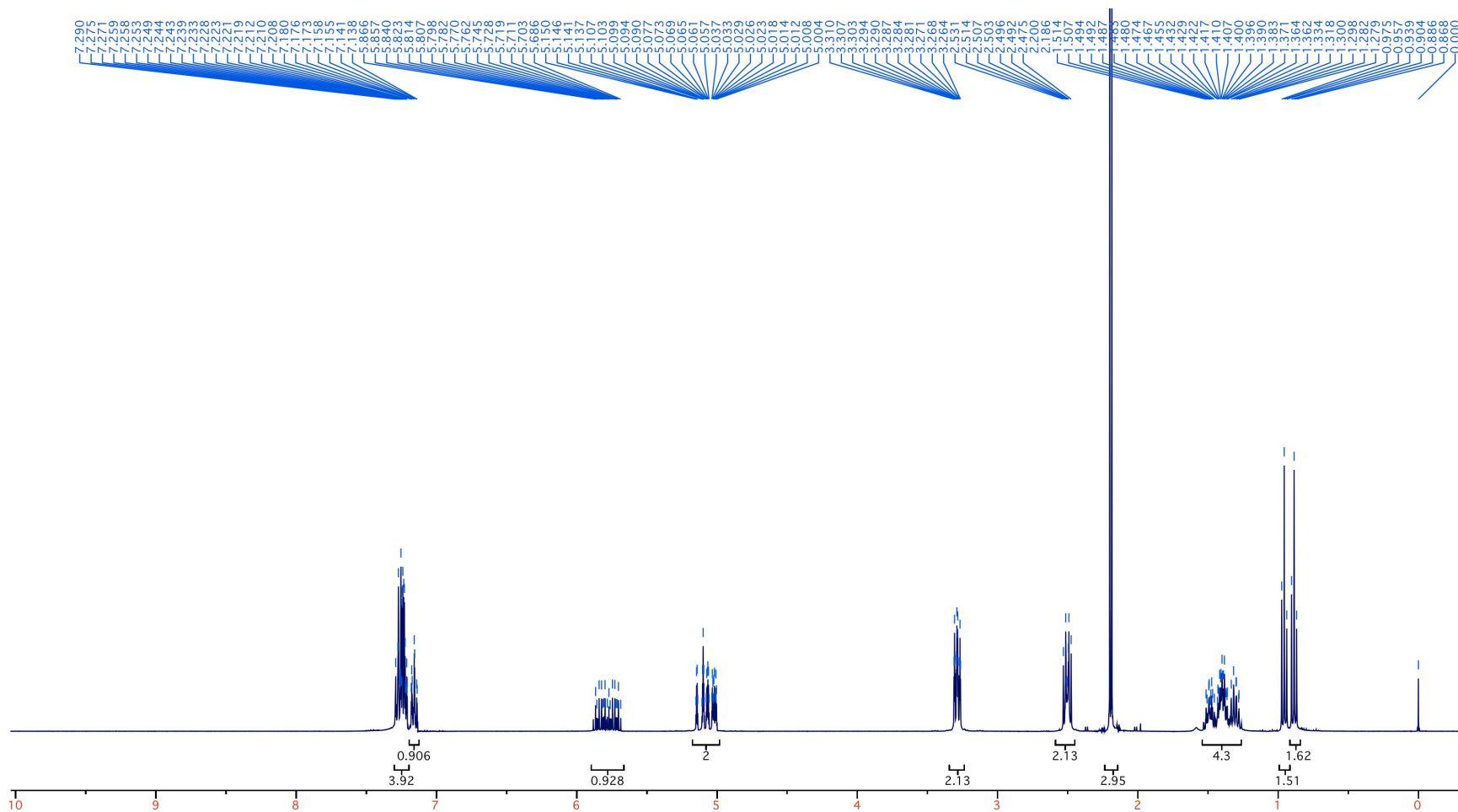


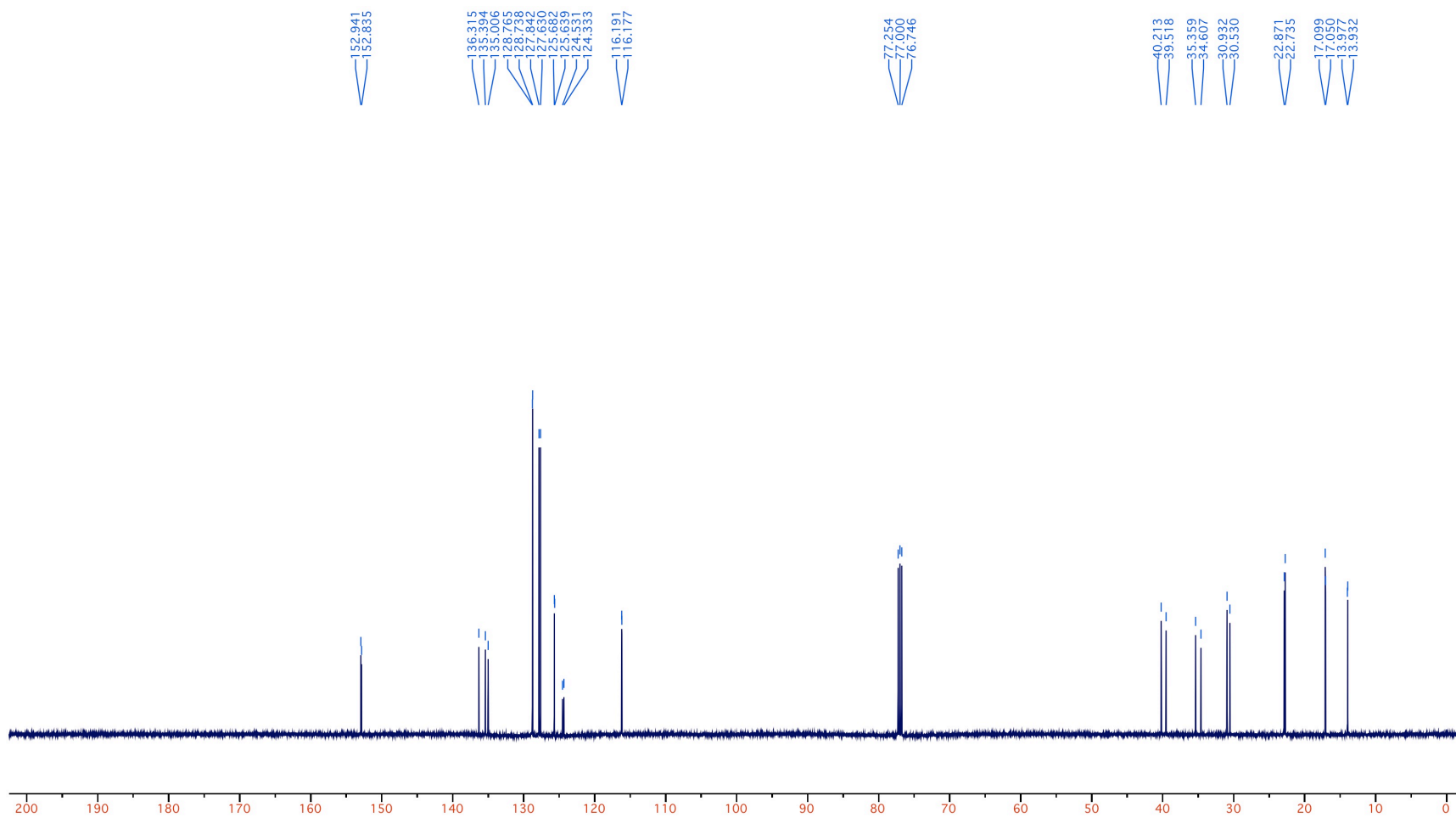
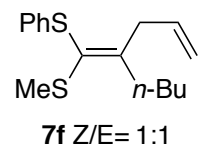
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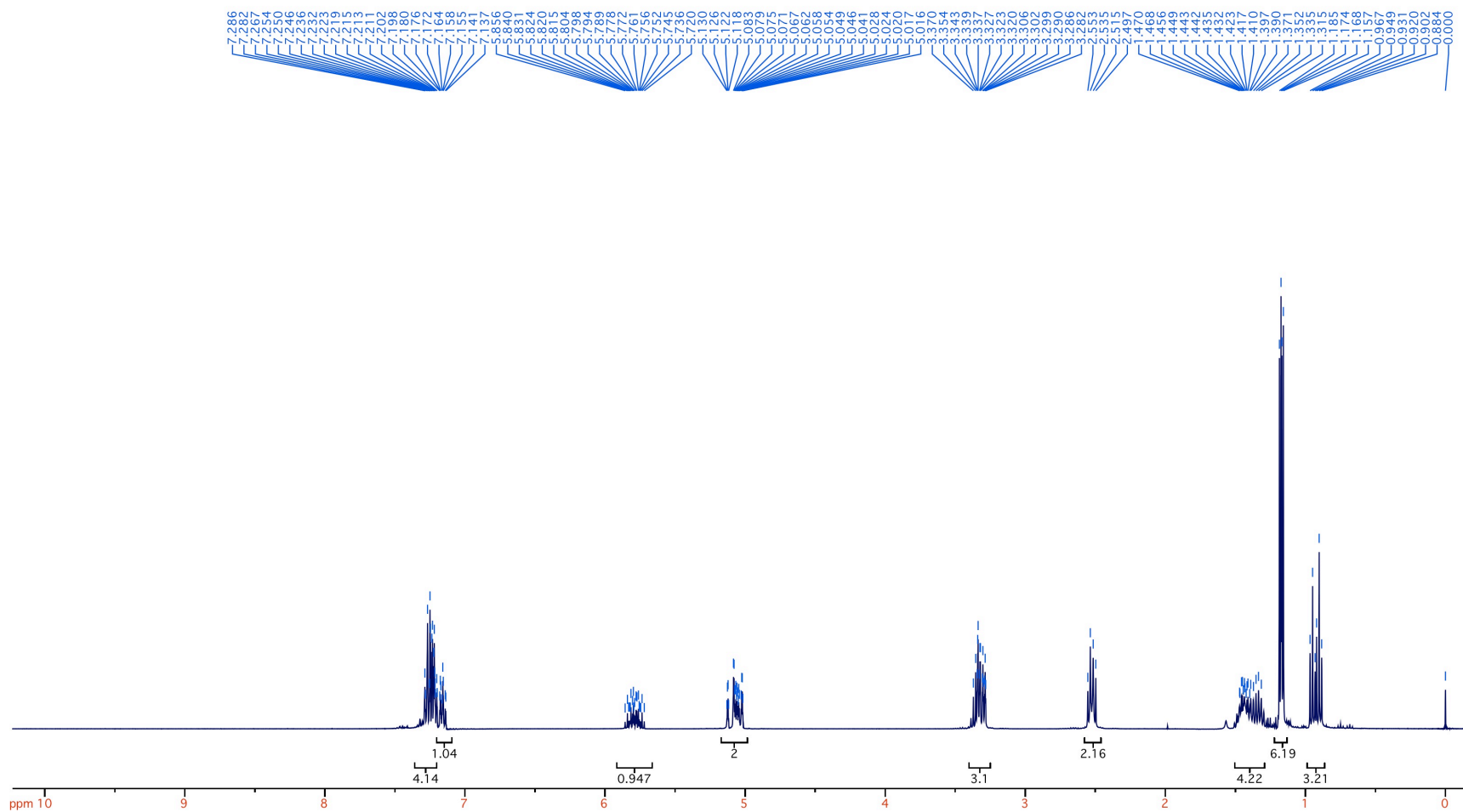
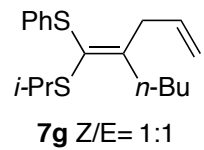


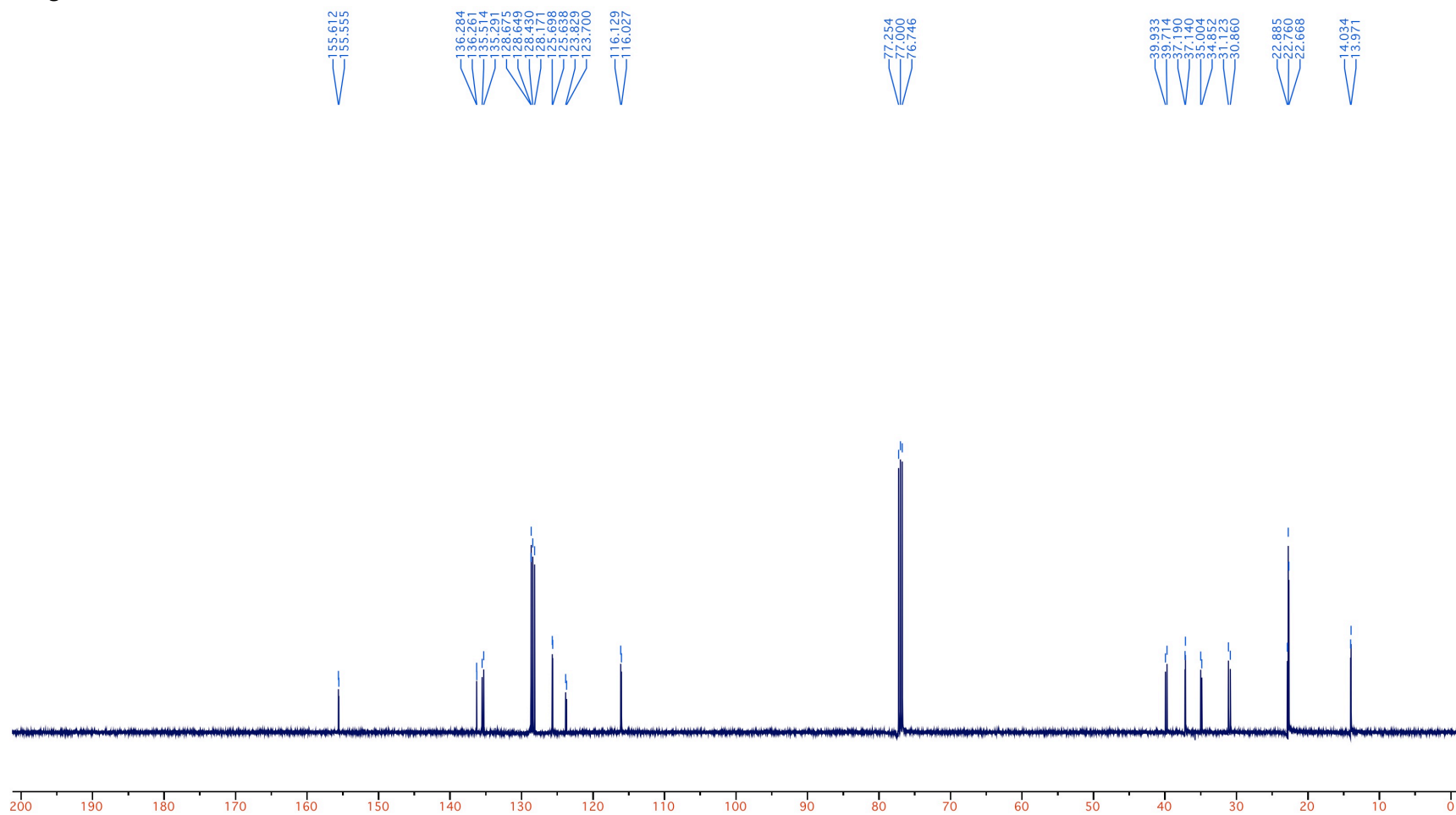
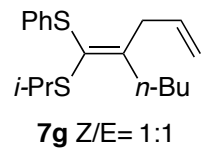


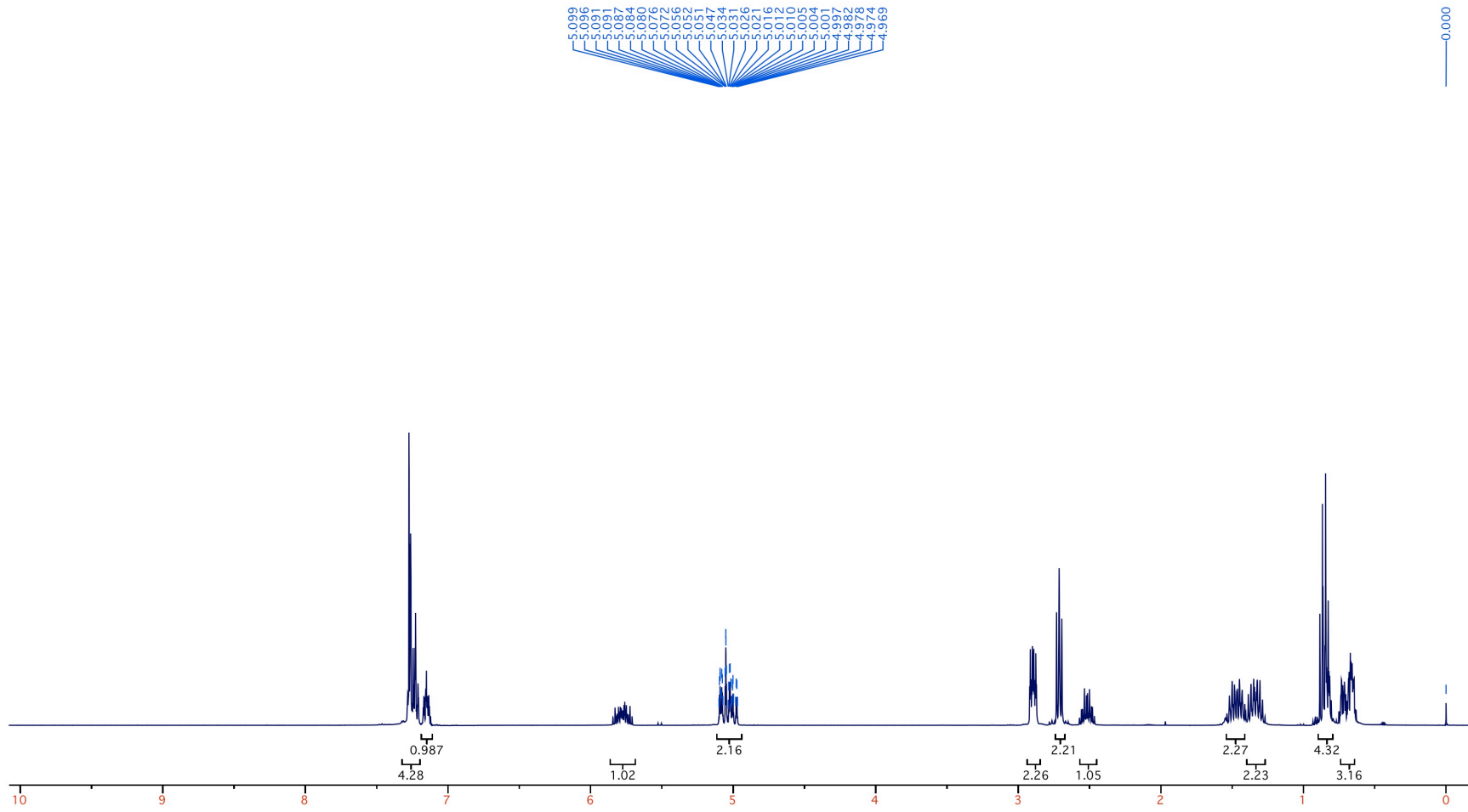
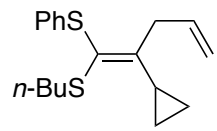
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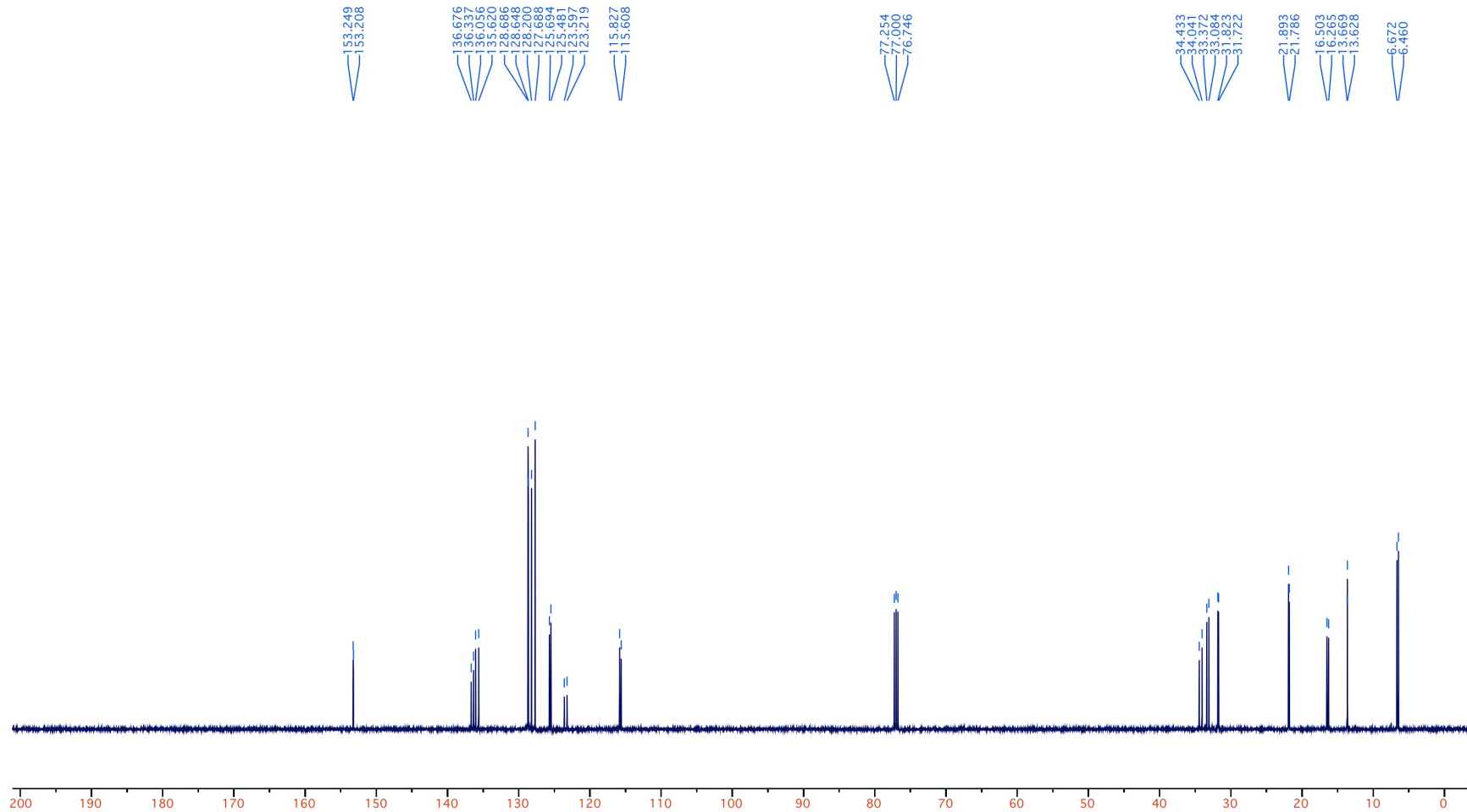
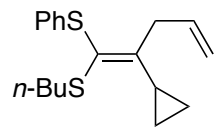


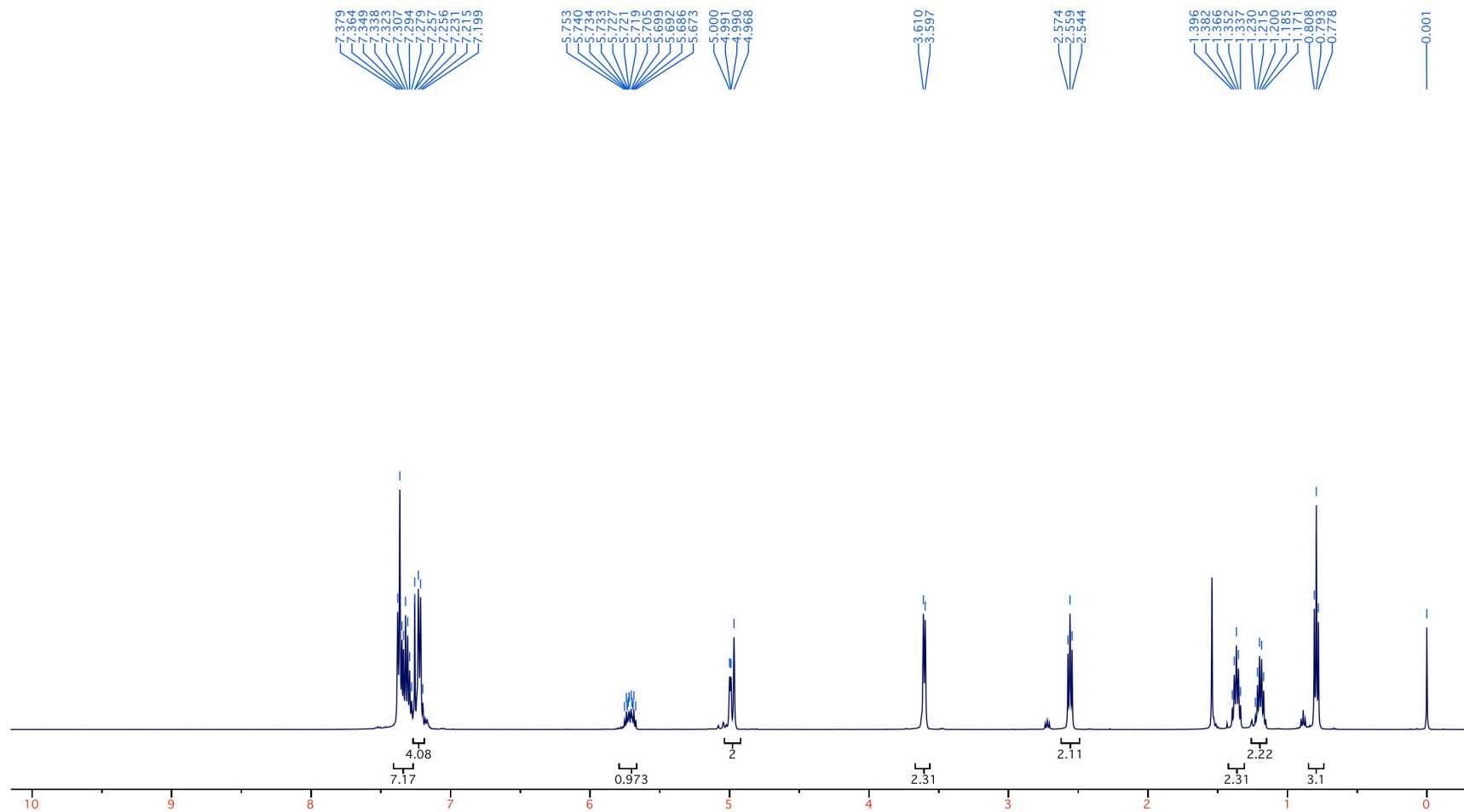
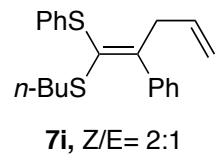


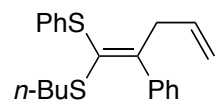




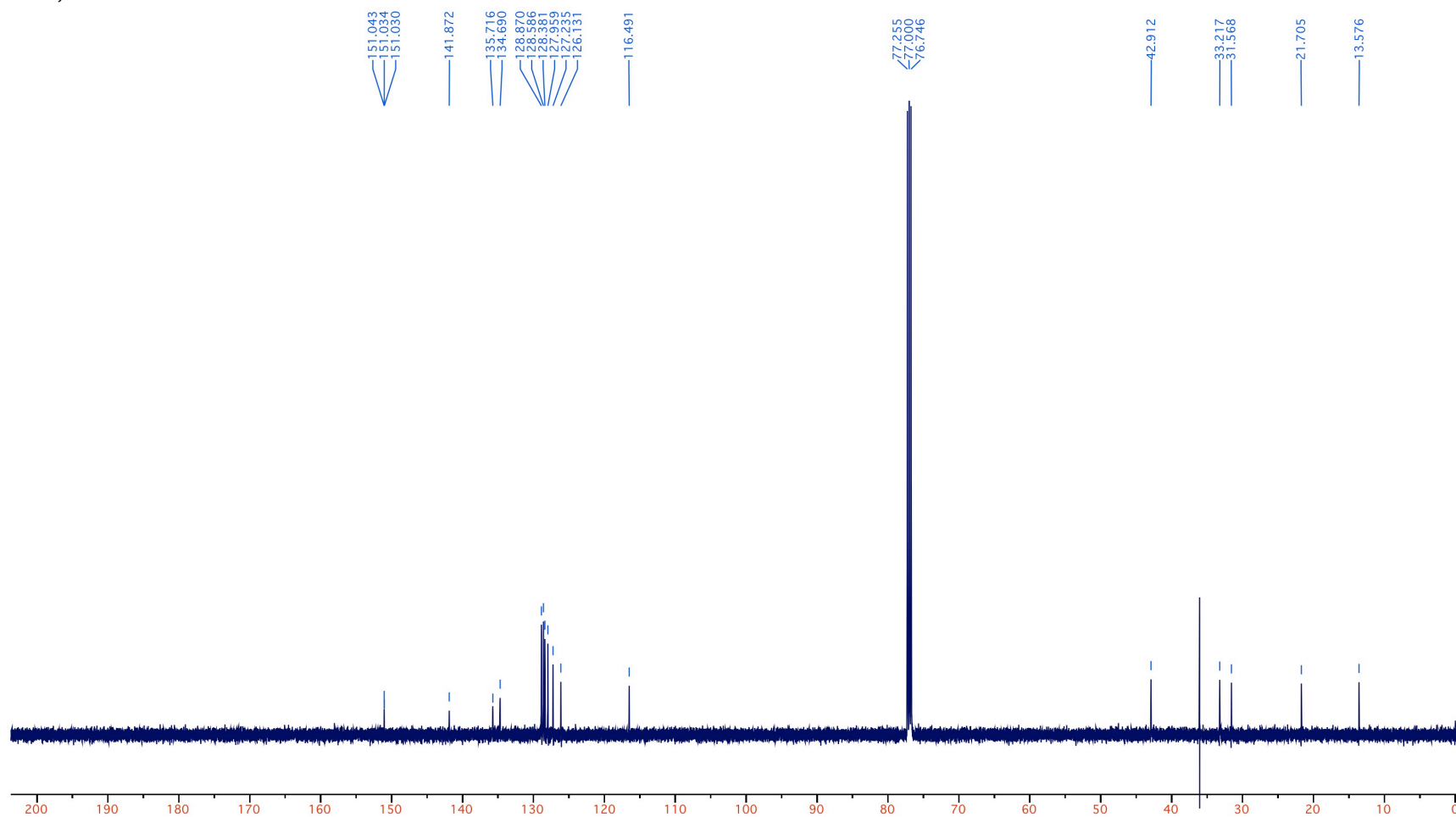


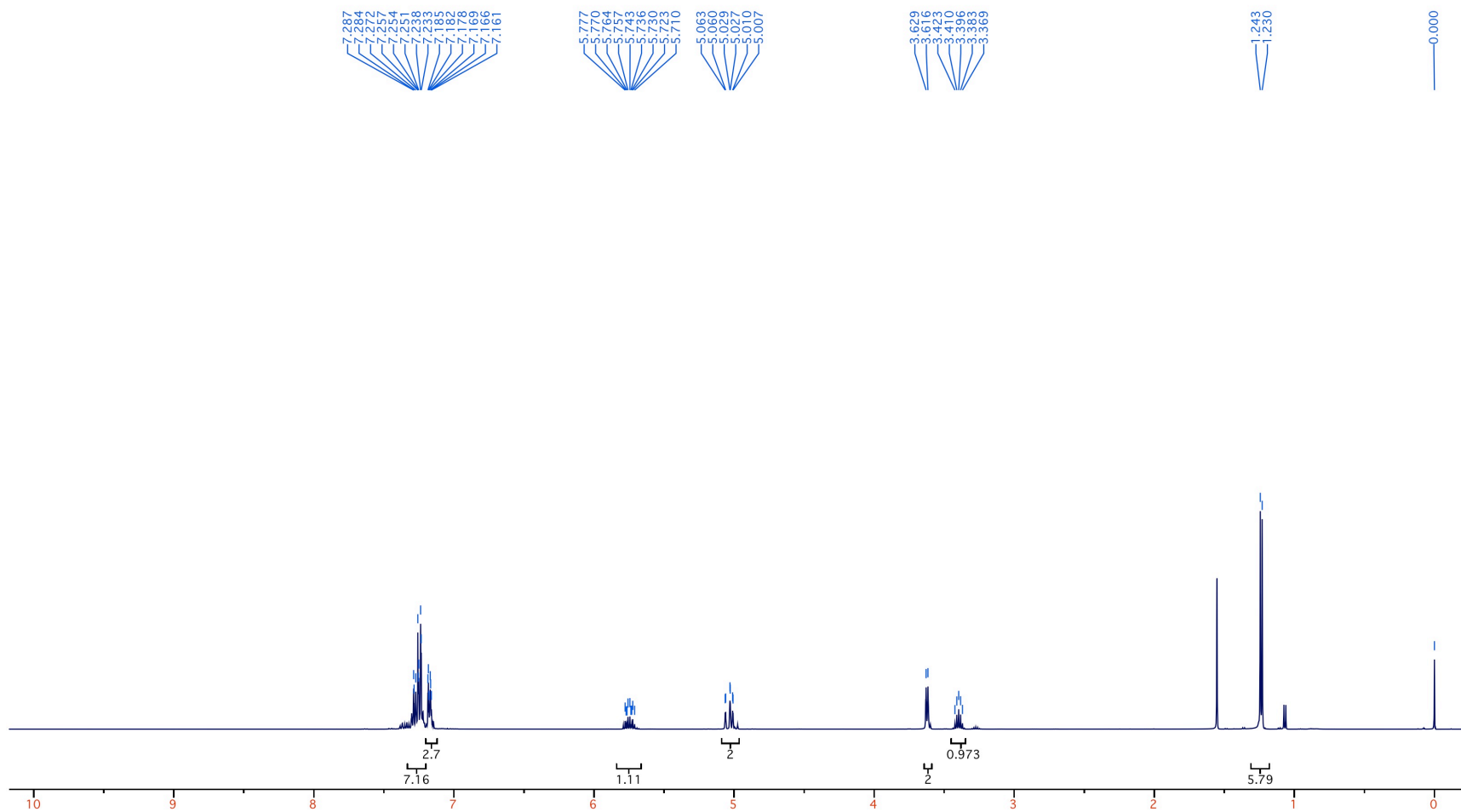
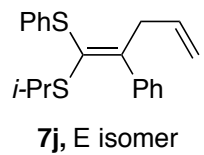


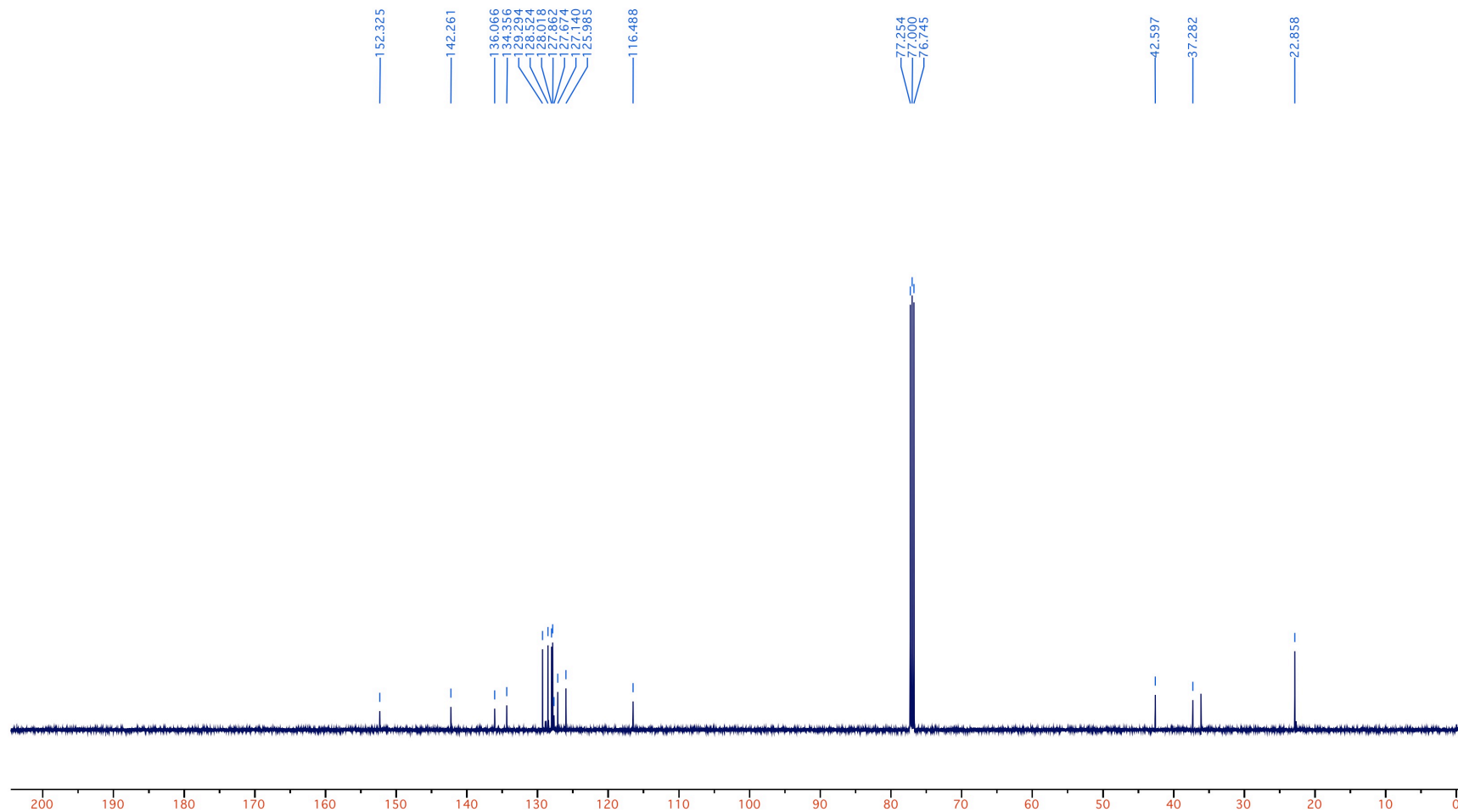
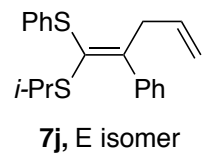


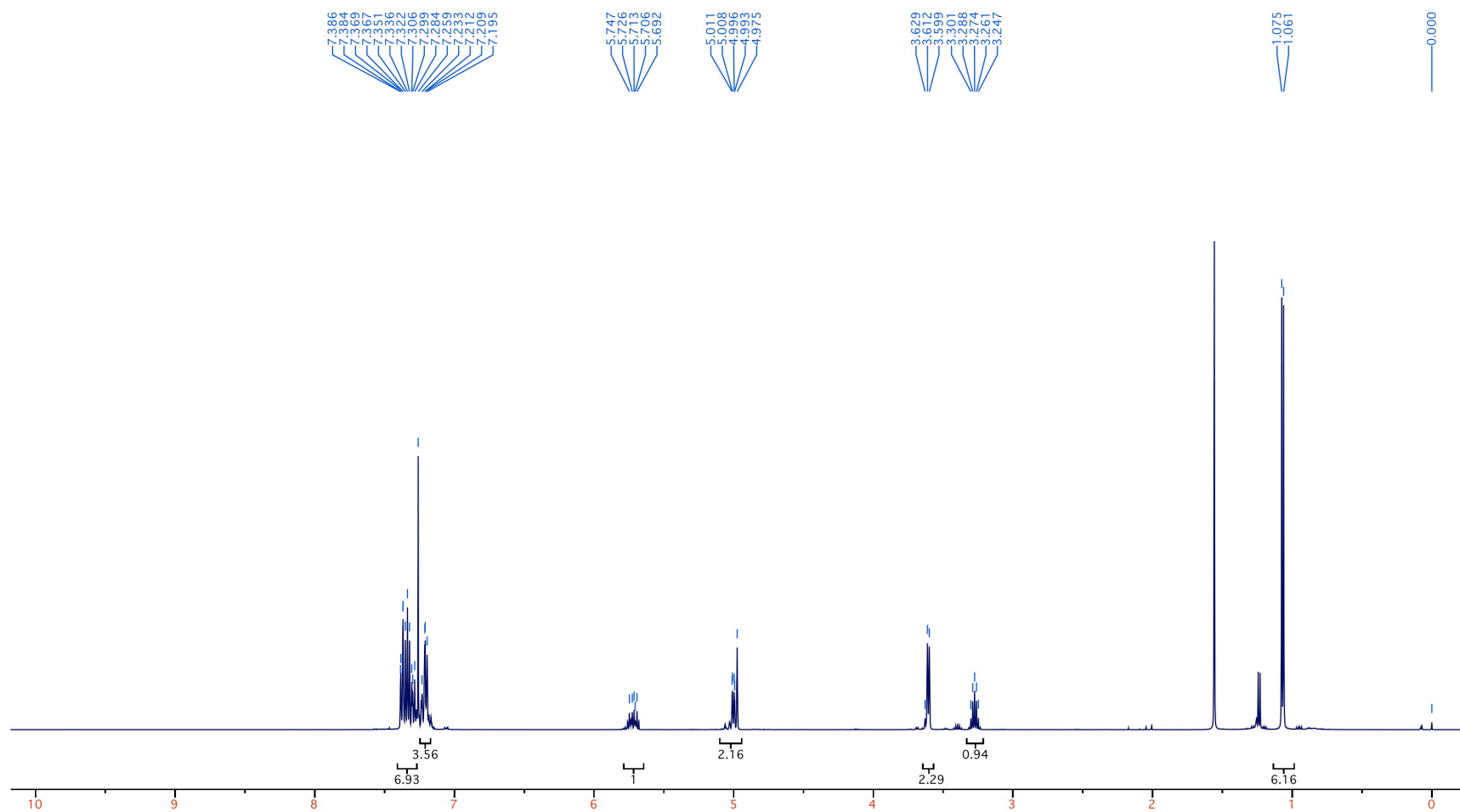
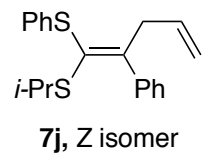


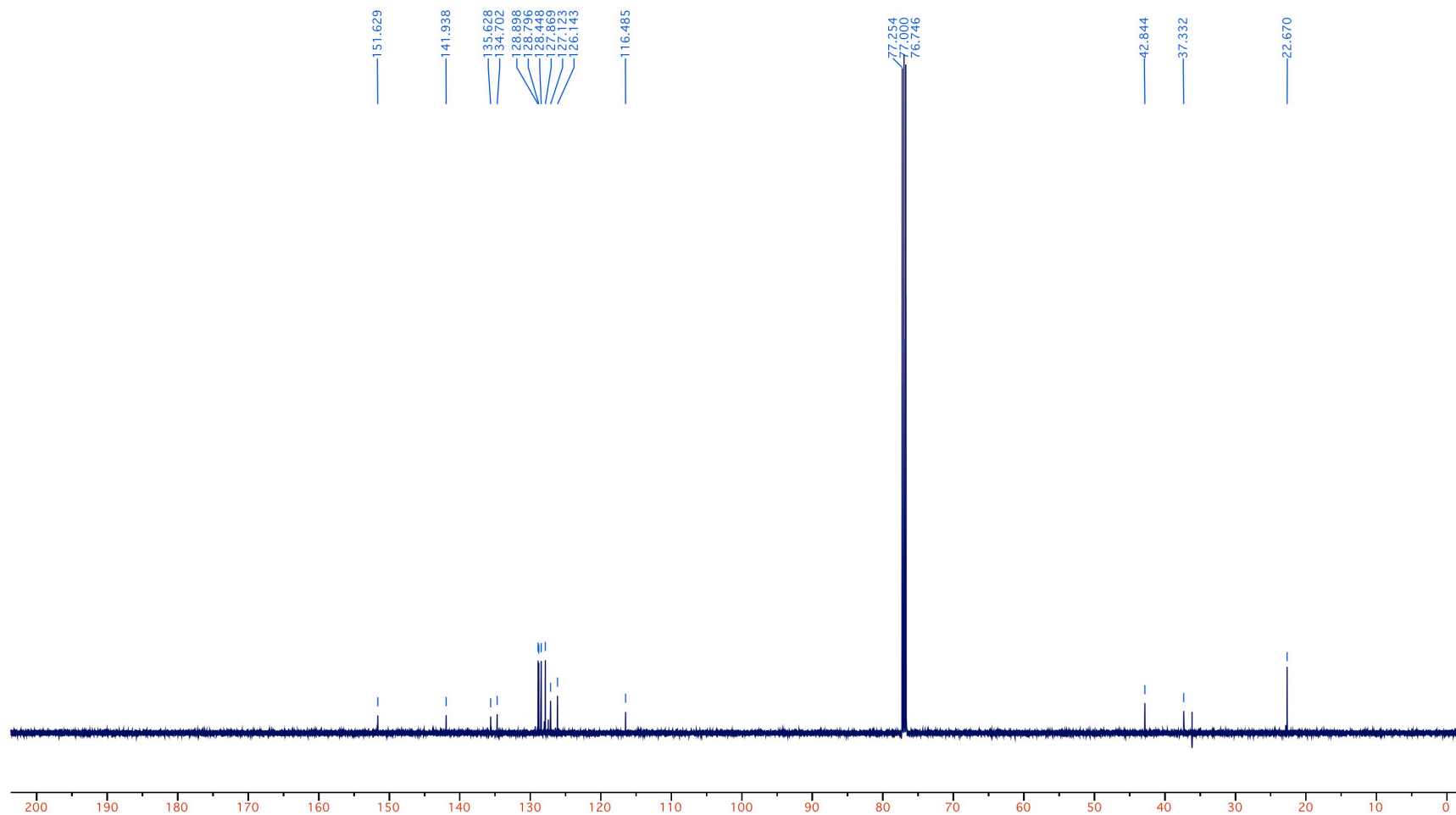
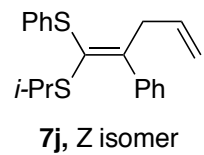
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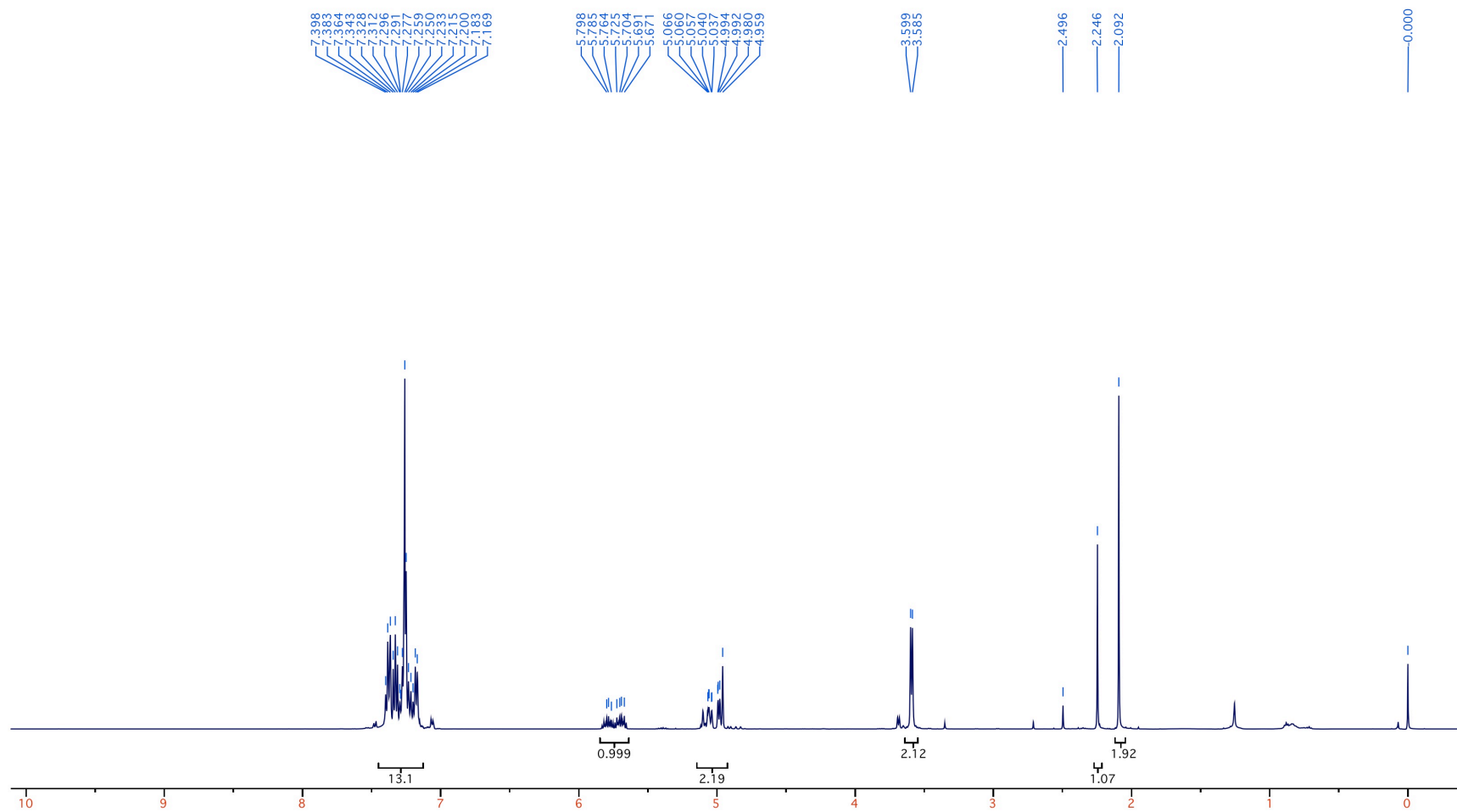
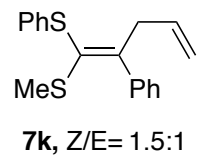


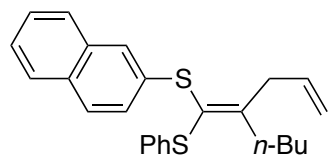




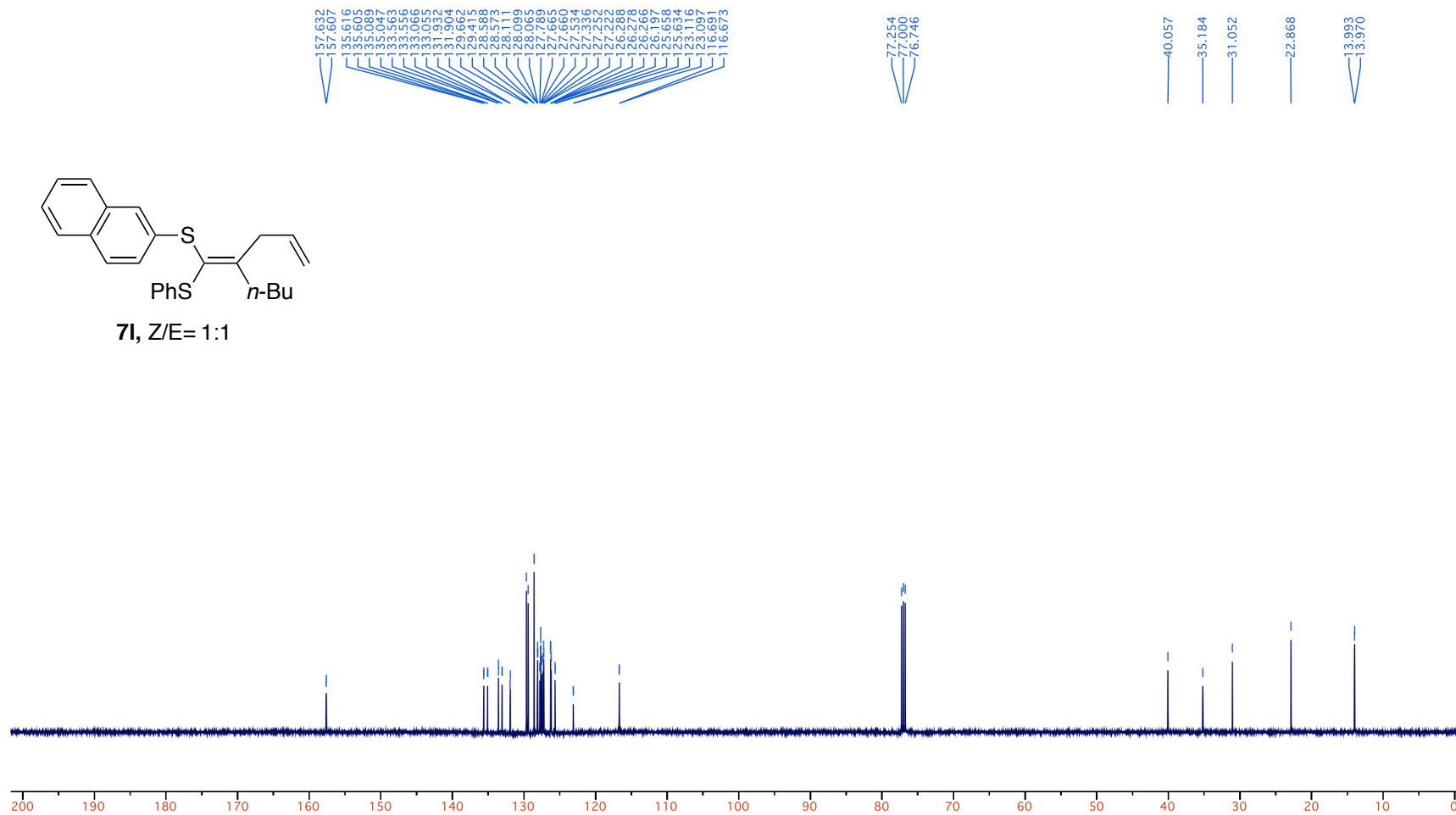


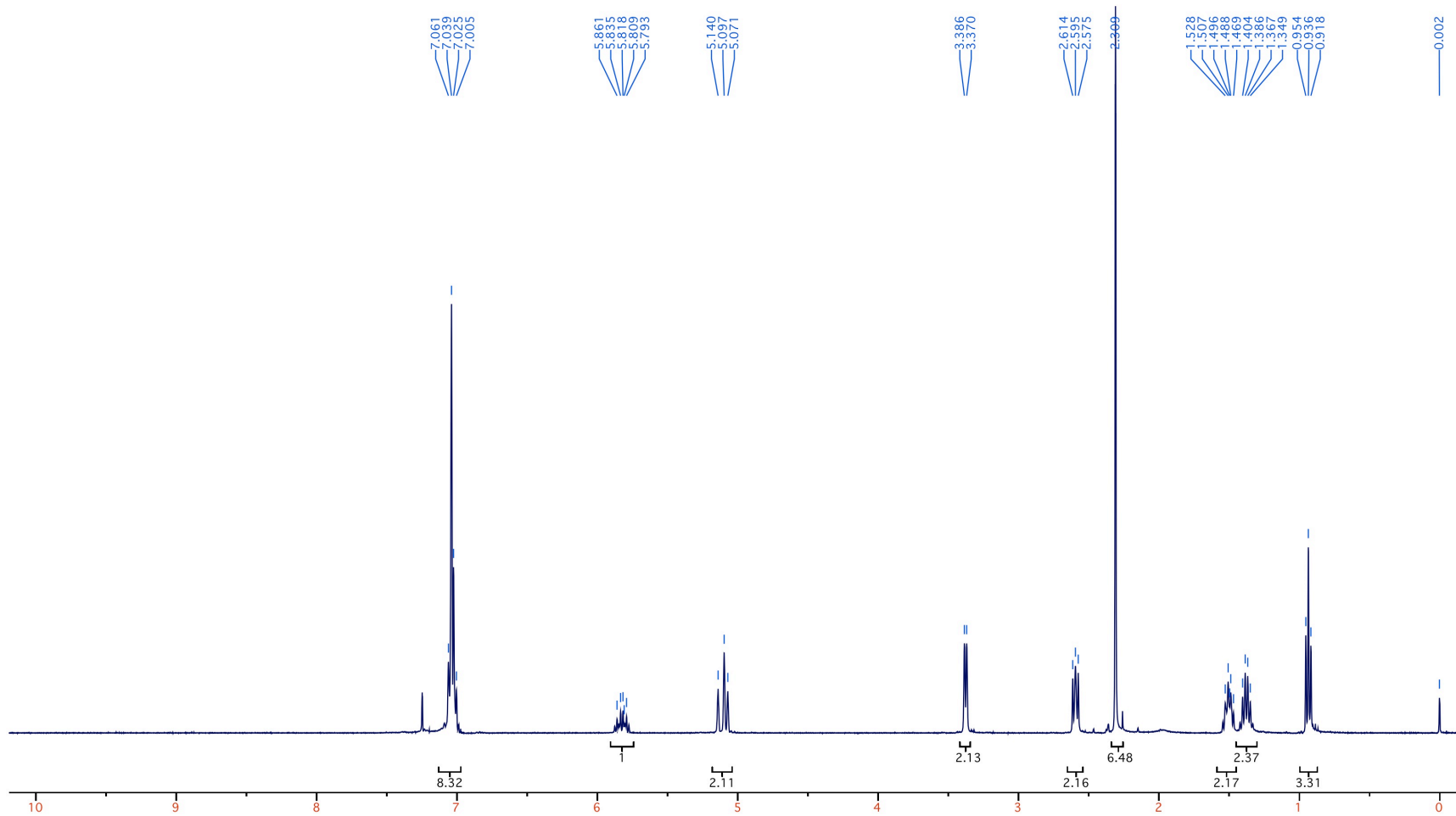
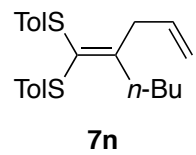


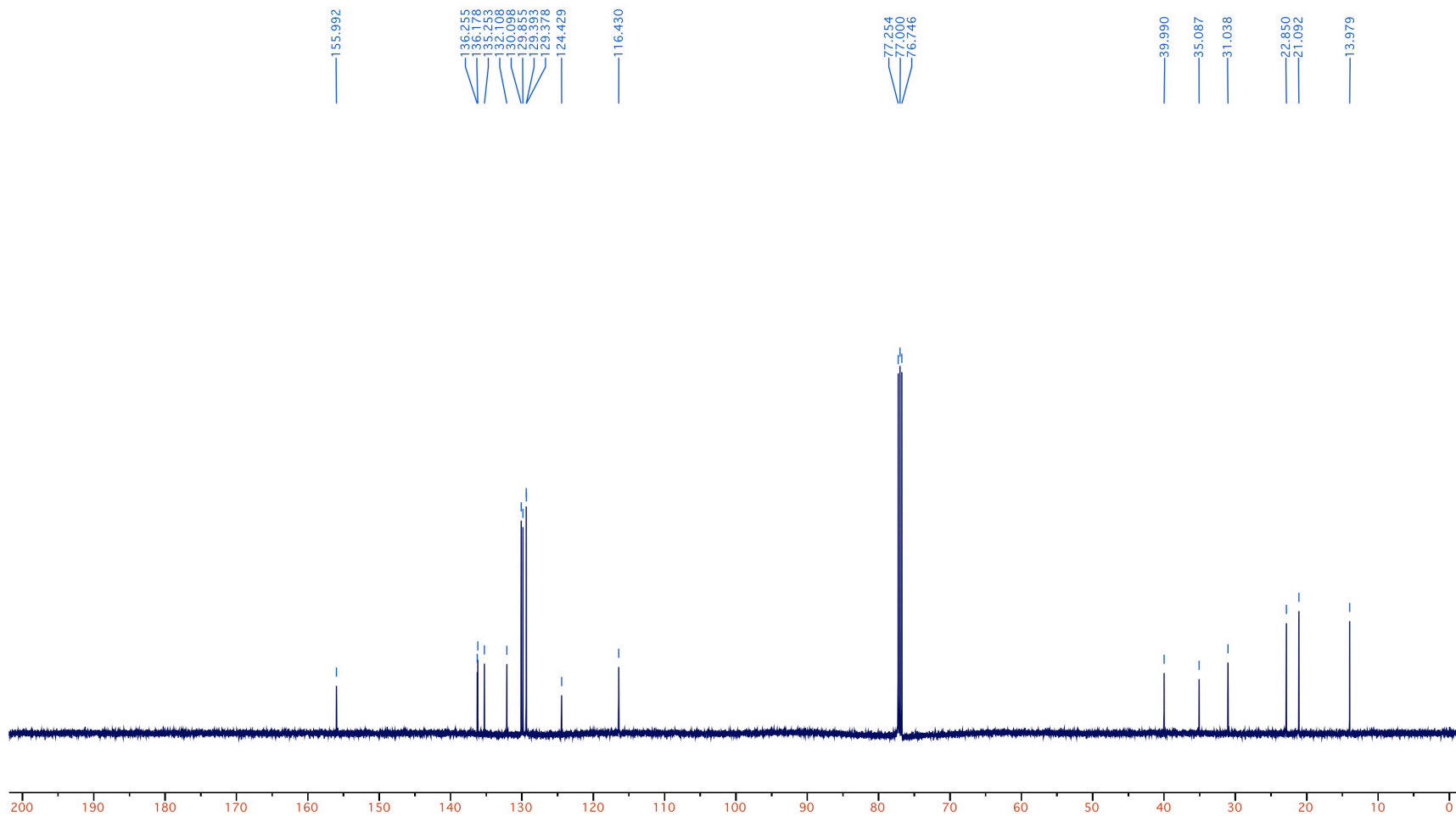
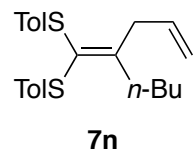


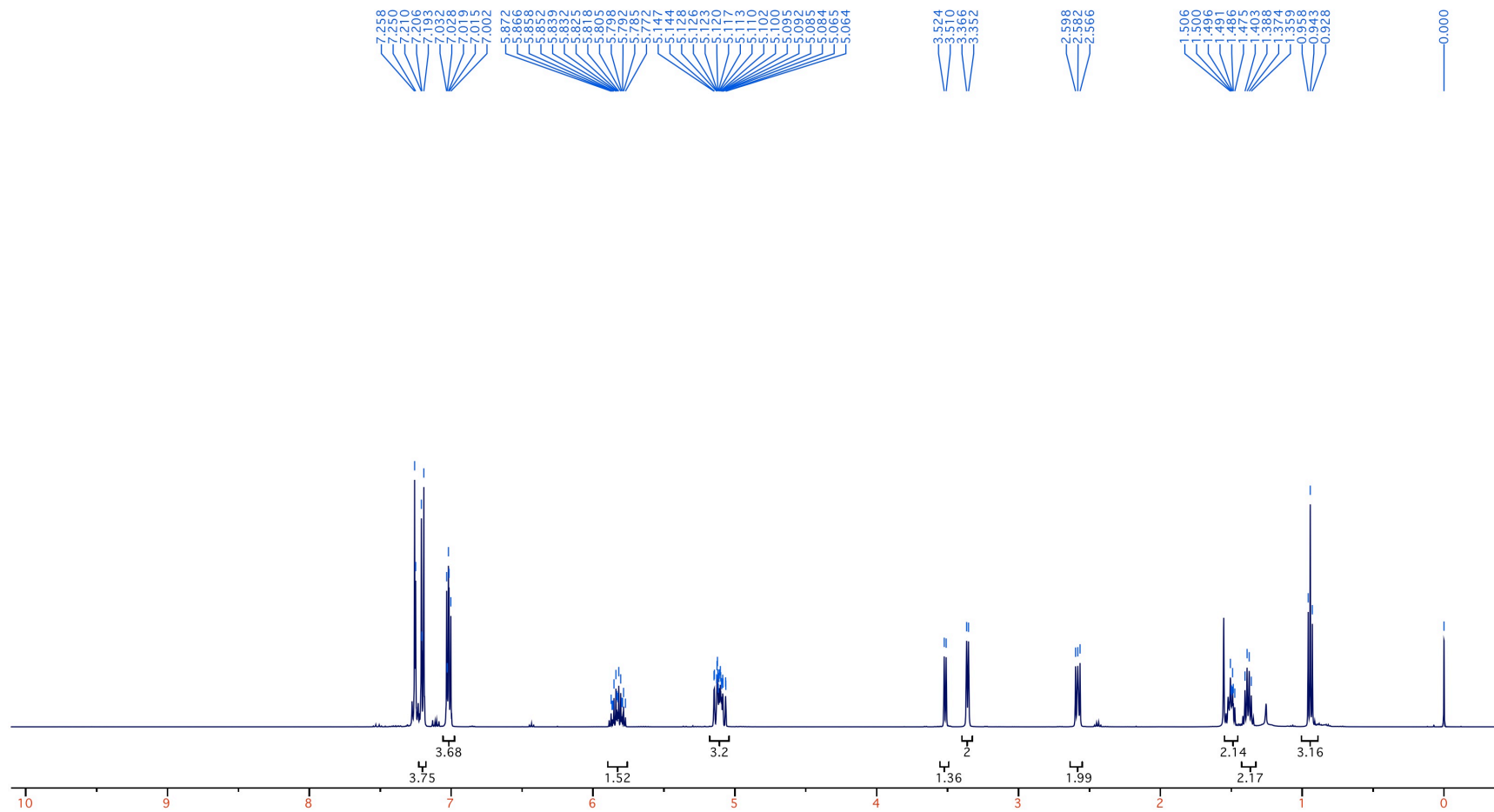
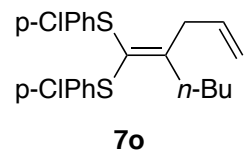


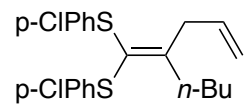
7I, Z/E= 1:1











7o

